NAPL Recovery and Treatment Using a Sequenced Remedial Approach with Surfactant Enhanced Technologies

Summary

EthicalChem Surfactant Enhanced Product Recovery (SEPR™) and Surfactant-enhanced In Situ Chemical Oxidation (S-ISCO®) technologies can be combined to provide an advanced and complete solution for non-aqueous phase liquid (NAPL) remediation including dense NAPL (DNPAL) such as creosote and light NAPL (LNAPL) such as fuel oil leaks. During the SEPR process a powerful surfactant/cosolvent and peroxide solution reacts with NAPL, allowing the product to flow to recovery wells. Once the SEPR process has removed the bulk NAPL contaminant mass, S-ISCO is implemented, which uses simultaneous injections of VeruSOL surfactants in combination with activated oxidants to solubilize and destroy residual contamination in place. Sequenced implementation of EthicalChem's SEPR and S-ISCO technologies eliminates or substantially reduces the need for excavation or long-term pump-and-treat remedies, resulting in significant cost savings and reduced treatment times.

The sequential SEPR/S-ISCO approach was implemented during a pilot test at a former wood treatment facility for remediation of creosote DNAPL. Due to the success observed during the pilot test, implementation immediately expanded to full-scale. The sequential treatment resulted in removal of approximately 81% DNAPL from the 6 – 15 ft depth interval, and eliminated visual free phase in groundwater samples.

Surfactant Enhanced Technologies

EthicalChem addresses NAPL with a sequenced approach that includes two innovative surfactant-enhanced technologies, SEPR and S-ISCO. EthicalChem surfactants are plant-based, non-ionic surfactant and cosolvent blends designed to desorb and emulsify organic contamination in subsurface soils. Surfactant molecules, are amphiphillic molecules composed of hydrophilic (water loving) heads and lipophilic (oil loving) tails. When the surfactants enter the subsurface in combination with oxidants, the lipophilic tails of the surfactant molecules are attracted to NAPL while the hydrophilic heads remain associated with the aqueous-phase. This creates micelles, micro-sized droplets of NAPL surrounded by surfactant molecules, which are incorporated into the aqueous solution (**Figure 1**). This allows the NAPL to enter aqueous phase oxidation reactions by sodium persulfate or hydrogen peroxide.

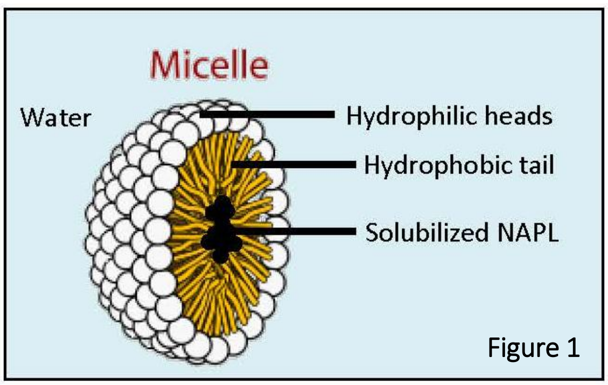

Figure 1

SEPR

SEPR involves the simultaneous injection of a surfactant/ cosolvent formulation with low doses of hydrogen peroxide, to mobilize NAPL free product for subsequent extraction. SEPR works through a combination of NAPL viscosity reduction, lowering of the interfacial tension between the NAPL phase and water, and physical action derived from the gas bubbles formed during the decomposition of hydrogen peroxide.

Unlike the surfactants used during the SISCO process, which form strong emulsions with contaminants, surfactants used in the SEPR process form a weak emulsion that separates readily once the product is recovered. This property allows separation of the product from the recovered water for potential reuse or disposal. **Figure 2** (panel 2) illustrates the SEPR process where the large NAPL plume is targeted by the SEPR chemicals (surfactant and peroxide solution). The NAPL, and NAPL emulsion is removed via extraction wells.

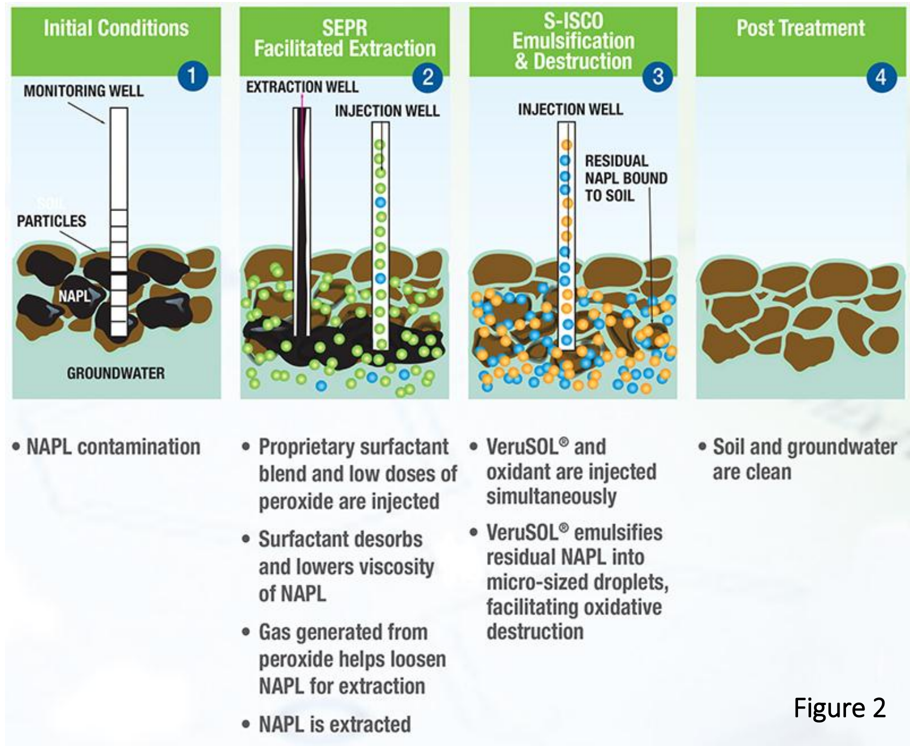

Figure 2

S-ISCO

Following SEPR extraction of the bulk contaminant mass, the S-ISCO process is implemented to address residual sorbed NAPL contamination. The S-ISCO chemicals work together by desorbing and emulsifying the residual contaminants (surfactants) and simultaneously oxidizing them once they become available in the aqueous phase (oxidants). **Figure 2** (panel 3) illustrates the injection of S-ISCO chemicals (surfactant and oxidant) to address residual contamination sorbed on the subsurface soil.

The S-ISCO emulsification process results in the formation of micelles. The formation of these tiny micelles, known as a micro-emulsion, substantially increases the surface area of NAPL exposed to the oxidant in the aqueous phase. As the diameter of the emulsion particles decreases, the surface area of NAPL exposed to oxidants is magnified (**Figure 3**). This increase in surface area allows the NAPL to enter aqueous phase oxidation reactions by sodium persulfate or hydrogen peroxide. Additionally, this increased exposure of contaminant to oxidant significantly improves the overall effectiveness and efficiency of the oxidant, where a higher degree of contamination is readily available in the aqueous phase to partake in the oxidation process.

Emulsions increase interface area between oxidant and contaminant by several orders of magnitude.

Figure 3

Field Case Study

Summary

A sequential treatment of EthicalChem patented Surfactant Enhanced Product Recovery (SEPR) and

Surfactant-enhanced In Situ Chemical Oxidation (S-ISCO®)[1] was completed at this former wood treatment facility for remediation of creosote DNAPL.

Implementation immediately expanded from a pilot test to full scale due to the successful results observed during the pilot test phase. The sequential SEPR and S-ISCO treatment resulted in removal of approximately 81% DNAPL impacts from the 6 – 15 ft depth interval, and elimination of visual free phase in post treatment groundwater samples.

Site Background

The Seaboard Lumber site, located southwest of the town of Bridgeville, in Sussex County Delaware, is a former wood treatment facility, where wood products were treated with creosote, an oil-based preservative, generating two types of hazardous wastes – creoste waste and condensate wastewater. The condensate wastewater from the plant was gravity-red to an unlined lagoon which was removed from service in 1985. Following termination of processing activities, the top five feet of the lagoon sediments were excavated; however additional contaminated soil was left at depth.

Site investigations and evaluations conducted by the U.S. EPA and its contractors, identified that the majority of the contamination was present as dense non-aqueous liquid (DNAPL). A supplemental soil and groundwater investigation was conducted in 2008, during which DNAPL was identified at locations not previously investigated. A feasibility study, conducted by TetraTech, evaluated and approved a sequential treatment using SEPR followed by S-ISCO for remediation of this site.

Implementation Design

The initial field implementation was designed as a pilot test, however due to the successfully high volume of DNAPL recovery within the first two weeks of the project, the treatment area was immediately expanded, progressing directly into full scale. The full scale operation was two phases of sequenced SEPR/S-ISCO injections, where the Phase I treatment area was an expansion of the pilot test area and the Phase II treatment area was a further expansion of the Phase I area. SEPR injections at the site consisted of a combination of SEPR surfactants with hydrogen peroxide. The S-ISCO treatment process involved simultaneous injections of VeruSOL combined with iron activated sodium persulfate.

Overall, approximately 13,900 gallons of SEPR chemistry (1-10% surfactant with 4-8% hydrogen peroxide) was injected into the Phase I and Phase II treatment areas, and approximately 8,000 gallons of total fluid were extracted. A total of 30,000 gallons of S-ISCO chemistry (5-10 g/L VeruSOL with 50-100 g/L sodium persulfate) were injected into the treatment areas following the completion of the SEPR phase.

Results

During the SEPR injections DNAPL is desorbed and mobilized to recovery wells. The photographs in **Figure 1** show fluid from extraction wells over time, where DNAPL extraction increase as the SEPR chemicals are introduced into the subsurface. On day 1 of injections, some emulsified product was recovered, as seen by the increased turbidity and dark color in the water sample. On day 2 product recovery increased, as seen by the distinguishable black layer in the sample. By day 3 onward, the extracted sample was dark black, indicating product flow.

[1] Ethical Solutions, LLC acquired the intellectual property developed by VeruTEK Technologies, in September 2014.

Following the subsequent S-ISCO treatment the residual DNAPL, which was emulsified during the SEPR process, is oxidized. **Figure 2** shows groundwater samples collected from extraction wells after the SEPR treatment (pre-S-ISCO) and post-S-ISCO treatment. The samples collected after the completion of the S-ISCO treatment appear clear and did not show any visual signs of DNAPL product.

Soil borings were collected upon completion of the treatment and were measured for the presence of DNAPL. Creosote volumes were estimated based on the thickness of the product measured during site characterization. Product was also measured on a daily basis at the beginning and end of each day at each injection well using a small diameter bailer. Comparison of pre- and post-treatment mass estimates for depth intervals of 6 to 15 ft. bgs. indicated that SEPR and S-ISCO treatment successfully removed more than 81% of the DNAPL impacts from the 6-15 ft. depth interval within the Phase I and Phase II treatment areas.

Figure 1. Fluid from extraction wells over time

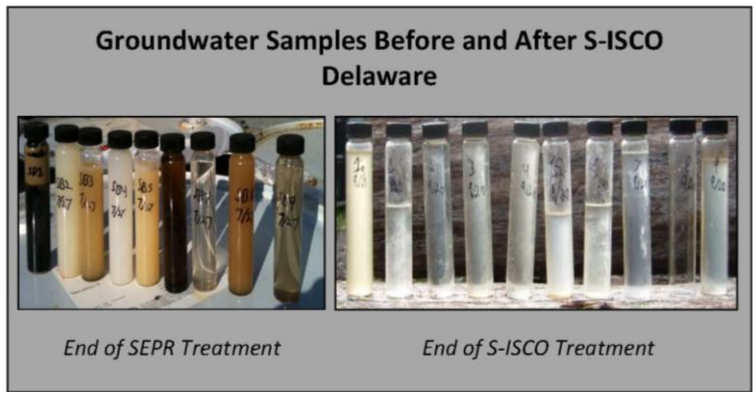

Figure 2. Fluid from extraction post SEPR and S-ISCO