



## Geo-Cleanse Remediation Summary Linden, New Jersey Grasselli Chemical Company Site Dense Non-Aqueous Phase Liquids (DNAPL)

### About the Site

An industrial brownfield site located in central New Jersey was impacted with dense non-aqueous phase liquid (DNAPL) following over 100 years of chemical manufacturing operations. The Grasselli Chemical Company owned and operated the site from 1885 until 1928. DuPont purchased the operations in 1928 and began production of acids, dyes, pesticides, salts and other products. Chemical production was terminated in 1990 and all of the manufacturing buildings were demolished. The site was impacted with a wide range of



contaminants of concern (COCs). Initial feasibility studies consisted of sheet piling, dewatering, and soil excavation to address a former lagoon; however, an alternative remedial approach was desired due to high remedial costs, sustainability implications, and the transport of thousands of truckloads of heavily contaminated soil through urban and residential communities.

### Site Conditions & Challenges

The site is underlain by fill deposits that range in thickness from approximately 5 to 12 ft and consists predominantly of fine to coarse sand and gravel. Underlying the fill deposits are marsh deposits (locally referred to as “Meadow Mat”) consisting of brown peat and organic clays. Soil and groundwater in an approximately 3.2-acre treatment area were impacted with a variety of COCs, including volatile organic contaminants (chlorobenzene, chloroform, methylene chloride, carbon tetrachloride [CT]) and pesticides, including a significant volume of DNAPL (measuring greater than 2 ft in thickness at some locations).

The main challenge regarding the use of in-situ chemical remediation was the selection of reagents that could address the full range of COCs, which required both chemical oxidation and reduction in order to be destroyed. Traditional reagents for chemical oxidation (e.g., permanganate, hydrogen peroxide, calcium peroxide, ozone/perozone, and persulfate) or reduction (e.g., zero valent iron) are not capable of producing both oxidants and reductants in sufficient quantities to destroy all of the COCs.

### An Innovative Remedial Approach

In response to this challenge, Geo-Cleanse International, Inc. (Geo-Cleanse) developed an innovative in-situ remediation treatment approach, combining in-situ chemical oxidation (ISCO) with in-situ chemical reduction (ISCR). The remediation program utilized catalyzed hydrogen peroxide (CHP) with a novel manganese-catalyzed technology to generate superoxide radicals. This novel approach would address the suite of COCs, destroy the DNAPL, reduce overall remedial costs and close the site for redevelopment.

Previous research demonstrated that the superoxide radical ( $O_2^{\bullet-}$ ), which is a chemical reductant and nucleophile capable of destroying reducible compounds such as chloromethanes, is produced by catalyzing hydrogen peroxide ( $H_2O_2$ ) with manganese ( $Mn^{+4}$ ) at a pH of about 6.8 or higher. However, applying this approach in the field would be a challenge because  $Mn^{+4}$  forms an insoluble precipitate ( $MnO_2$ ) at circumneutral pH; thus the application would require large pH shifts within an aquifer to maintain Mn in solution for distribution and subsequent precipitation of  $MnO_2$ . A method was needed to more efficiently distribute the  $MnO_2$  catalyst and then controllably react the catalyst with  $H_2O_2$  in order to produce  $O_2^{\bullet-}$  in-situ.

### **Bench- & Pilot-Scale Treatability Studies**

Geo-Cleanse performed several bench laboratory tests to optimize destruction of all of the COCs including the DNAPL phase. Obstacles overcome by the testing included delivery of a source of  $Mn^{+4}$ , pH buffering, and peroxide stabilization. The reductive reactions were key for the overall success. For the reductive reactions to occur, the  $Mn^{+4}$  needs to be easily distributed in order to come into contact with the peroxide. Permanganate was selected because of its wide use in ISCO, circumneutral pH, ability to oxidize certain contaminants, and preferential reduction in zones with highest contaminant mass. Manganese in the  $Mn^{+7}$  valence state in permanganate is reduced in-situ to  $Mn^{+4}$  and precipitated as solid  $MnO_2$ , thus generating the catalyst in-situ as a “fixed” solid in the target treatment zone.

Based on the positive results of the bench, a six-month field pilot-scale test was implemented to evaluate field-scale buffering effects, reagent requirements, radius of influence, injection rate, and overall treatment effectiveness. The primary COCs in the pilot-test area were reduced by 67-97% in groundwater and by 98-99.7% in soil.

### **Full-Scale Implementation**

The primary treatment objective was to eliminate the DNAPL to the extent practicable. The full-scale treatment program was designed utilizing results from the bench- and pilot-scale treatability studies. The full-scale treatment included the installation of 569 injection wells and 143 vent wells to target the 3.2-acre DNAPL-impacted area. Baseline sampling occurred at 143 continuously-cored boring locations. This sampling event confirmed soil lithology and depth to the meadow mat, DNAPL delineation, and analytical soil results, and allowed refinement and focusing of the overall treatment area architecture. The full-scale remediation design consisted of two injection phases to target the oxidizable (e.g., chlorobenzene) and reducible (e.g., CT) contaminants.



The first phase was ISCO utilizing CHP to address the contaminants that required oxidation. Approximately 1,055,600 gallons of 9.3% hydrogen peroxide was injected over a three injection phases. DNAPL volume estimates based upon measurements during injection were as much as five times greater than originally anticipated. Several wells yielded DNAPL thickness exceeding one foot. Geo-Cleanse’s process monitoring, which consists of daily groundwater and offgas sampling, provided the ability for day-to-day treatment modifications depending on the site-specific conditions as the treatment progressed. Following each injection phase, analytical sampling was

conducted in order to evaluate the destruction of the oxidizable compounds and evaluate the presence of DNAPL.

The second phase was ISCR utilizing manganese-catalyzed peroxide to address the contaminants that required reduction. Sampling following the CHP phase indicated the locations where the chloromethane contamination and DNAPL was still present. Approximately 10,025 gallons of 5% sodium permanganate was injected throughout the treatment area and allowed to reduce and precipitate the MnO<sub>2</sub> over a seven-week period. After process monitoring confirmed complete reduction of the permanganate, a phosphate buffer was injected to establish the geochemical conditions for the reductive treatment. Approximately 14,075 gallons of 34% CHP, diluted to an average concentration of approximately 9%, was injected throughout the treatment area.

#### **Treatment Results and Conclusion**

Post-treatment sampling included analysis of every monitoring, vent, and injection well at the site for the presence of DNAPL utilizing an interface probe, and soil borings for visual inspection and analysis with a hydrophobic dye (Sudan IV). All of the results were negative at the conclusion of the full-scale remediation, indicating complete DNAPL destruction across the approximately 3.2-acre site. This waterfront brownfield property site is now for sale and redevelopment

Geo-Cleanse was awarded U.S. patent 8,556,537, entitled, "Manganese-Meditated Redox Processes for Environmental Contaminant Remediation" in 2013 for this innovative, sustainable "combined oxidant" technology. Additional information regarding this patent, or how this technology may be applied to other sites, is available from Geo-Cleanse.

***This summary sheet is intended to provide a general overview of the referenced site. For more detailed information, please contact us at (732) 970-6696.***

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