TECHNICAL *Summary*

INDOT Research

Technology Transfer and Project Implementation Information

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Remediation of Soils and Ground Water Contaminated by Aromatic and Chlorinated Hydrocarbons and Metals

Introduction

Many of the Indiana Department of Transportation (INDOT) sites are contaminated with aromatic hydrocarbons and chlorinated solvents; these contaminants often occur in the form of light non-aqueous phase liquids (LNAPLs) or dense non-aqueous phase liquids (DNAPLs). Considerable effort has recently been focused on developing in-situ technologies for removing or destroying NAPL source zones, and several potentially viable methods have emerged, including in-situ chemical oxidation (ISCO). ISCO has become an attractive remediation option to managers at many contaminated sites. The three oxidants that are most often applied in-situ are hydrogen peroxide (H_2O_2) with iron catalysts, potassium permanganate ($KMnO_4$), and ozone (O_3). While each oxidant system has been field demonstrated to be effective in some instances, a clear understanding of these processes is important to the successful implementation of the technology.

A primary goal of the research project is to improve the *efficiency* and *effectiveness* of chemical oxidation systems during in-situ treatment of non-aqueous phase liquid (NAPL) source zones. Efficiency and effectiveness are defined in Table 1-1; other selection criteria include time required to achieve acceptable levels of treatment, oxidant selectivity, and oxidant delivery methods. Several novel approaches have been taken to reach the goals of the study. The first approach enhances the application of Fenton's reagent in soil slurry systems, resulting in a better understanding of the magnitude of non-specific oxidant losses relative to consumption by the target compounds. The second approach explores minimizing non-specific losses of the oxidant by introducing the oxidant ($KMnO_4$) in an encapsulated form. Finally, solubility enhancers are examined to enhance the aqueous NAPL concentrations. Significant enhancements in NAPL aqueous concentration will result in corresponding enhancements of the observed oxidation rate.

Findings

In order to enhance the rate and extent of in situ oxidation of BTEX compounds, Fenton-type treatment of BTEX-contaminated soil slurries was investigated. A characterized soil (Warsaw, IN) was spiked with BTEX compounds, and the performance of Fenton treatment was evaluated using a matrix of H_2O_2 concentrations and iron catalysts (Fe(II), Fe(III), and Fe(III)-organic ligand complexes) in the range of near-neutral pH. The results indicate that for initial concentrations of BTEX (20.3-36.1 mg/kg soil), 63.3-96.1 % mass reduction in 24 h was achieved by Fenton processes where H_2O_2 (150 and 300 mM) with combinations of Fe(II) or Fe(III) or Fe(III)-organic ligand complexes (2 and 5 mM) were utilized. The mass ratios of iron catalyst to hydrogen peroxide were 1:18, 1:37, and 1:92.

Soluble iron catalyst was a key parameter for effective performance of Fenton oxidation. In addition, Fenton treatment of toluene could be significantly enhanced in the presence of a chelating agent for Fe(III). It is anticipated that as long as a sufficient amount of soluble iron is augmented or effective chelating agents are employed, Fenton processes could be effectively utilized for remediation of gasoline-contaminated soils and groundwater within a fairly short clean-up time scale (hours to days).

It is possible minimize non-specific losses during ISCO by controlling the release of oxidant into the aqueous phase. Paraffin wax was applied as an environmentally benign and inert matrix for protecting solid $KMnO_4$ particles from rapid dissolution and undesirable reactions in moist conditions. The release of $KMnO_4$ from the encapsulated potassium permanganate—particles (EPPs) into reagent grade water was characterized by a relatively fast initial rate due to fast dissolution of partly coated $KMnO_4$ near the surface of the paraffin wax matrix, followed by a significantly slower rate in the later phase due probably to reduced mass of $KMnO_4$ that remained in the paraffin wax matrix. The wax coating completely dissolved almost immediately upon contact with a target contaminant (PCE). When transported with ground water flow, organic contaminants such as TCE and PCE dissolved in aqueous phase would preferentially partition into the paraffin wax coating due to their significant solubilities in the paraffin wax. Consequently, enhanced contact may occur between the contaminant and the locally high concentrations of $KMnO_4$ released into the interfacial region of EPPs and the aqueous phase. The $KMnO_4$ concentration in the vicinity of the EPPs will be close to its maximum aqueous solubility.

The time-efficiency of PCE oxidation by potassium permanganate is enhanced under solubility conditions that mimic a contaminant source zone. Both TBA and acetone are sufficiently recalcitrant to oxidation by $KMnO_4$ to be used individually as co-solvents. At specific volume fractions, TBA (20%) and acetone (<50%), increase the solubility of PCE significantly without mobilizing the DNAPL. The chloride production from PCE oxidation with $KMnO_4$ in a 20% acetone system was about twice as much as that in the absence of co-solvent, indicating the former system has a higher time-efficiency in utilizing $KMnO_4$.

Based on input from INDOT staff, selected sites have been assessed for amenability to remediation via in-situ oxidation. Site visits were also be made by research assistants to collect soil samples for laboratory experiments.

Implementation

INDOT should consider the use of ISCO when standard excavation of contaminated source soil would not be practical or cost-effective. This might be due to the depth of the source (especially with DNAPLs) or proximity to utilities, buildings, or a roadway. Ideally INDOT would have ownership or unlimited access rights to the prospective property. This would simplify investigation and implementation of the chosen remedial option.

Geologically, porous soil would help in dispersing oxidants and improving access to the contaminant plume. The “ideal” situation would consist of a small, concentrated source zone (especially if free-phase NAPL is present) that feeds a large, relatively dilute plume. Plumes composed of long-chain hydrocarbons or polyaromtics (diesel, fuel oil or waste oil) would be most useful for the study. They are less mobile (and therefore easier to gain regulatory approval for unconventional treatment methods) and traditionally more limited in treatment options compared to more volatile constituents such as BTEX. High molecular weight hydrocarbons will also show a higher affinity for the proposed paraffin wax encapsulated permanganate, improving selectivity.

The co-solvent approach would be most useful at sites where solubility is a limiting factor, such as at chlorinated hydrocarbon sites, including dry cleaner sites. Choice of solvent must take into account any neighboring receptors. Remote or industrial locations will be amenable to a more aggressive solvent than those in an urban or residential area. As with any of the techniques described in this report, regulatory approval at an early stage is critical to the success of such a remediation approach..

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