INNOVATIVE HEAVY OIL CONTAMINANT REMEDIATION AT TYPICAL MGP REMEDIATION SITES

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ABSTRACT

An innovative in-situ soil and groundwater treatment process has been developed to economically reduce total contaminant mass of viscous heavy oils and PAHs, which are typically encountered at MGP sites. This process uses a sequential treatment train, which is initiated by first dissolving the contaminants with a biodegradable co-solvent and then oxidizing the dissolved material with an aggressive oxidant, Fenton's Reagent, followed by accelerated aerobic bioremediation.

The innovative process presented is an enhancement of the Traditional Fenton's Reagent process, which has been demonstrated at numerous MGP contaminated sites throughout the United States. The unique basis of this process is to use a biodegradable co-solvent to dissolve the heavy-end organics into the aqueous phase in lieu of solely relying on the more expensive approach of using exothermic Fenton's Reagent to transfer the contaminants into the aqueous phase. Using this approach, the Fenton's Reagent oxidation properties are optimized, using low temperatures and pressures, wherein hydrogen peroxide efficiently reacts with ferrous ions to produce very reactive hydroxyl free radicals and superoxides rather than wasting the hydrogen peroxide to inefficiently generate heat and steam.

The exothermic Fenton's Reaction has previously been applied to thermally reduce viscosity and molecular weight of heavy oils and PAHs and increase it's solubility to enhance free-product recovery and enable oxidation of the dissolved heavy oils at MGP sites. This effective though inefficient peroxide based process has gained great acceptance in the treatment of inaccessible soils that are impacted with heavy-end oils. The authors have demonstrated that the application of a biodegradable co-solvent applied to the heavy oils effectively dissolves the mass without using the inefficient thermal desorption of the mass through the use of steam or catalyzed peroxide. Once the mass is transferred into the aqueous solution, the contaminants then can be recovered by groundwater hydraulic mounding (free-product push techniques) or total fluids recovery is employed. After mass recovery is applied, further treatment in the heavy oil contaminated source zones high concentration areas are then oxidized by selectively applying in-situ injection of low temperature/low pressure Fenton's Reagents techniques while continuing the enhanced recovery (free-product pull techniques). Even though this process is as effective as the traditional oxidation techniques, its low temperature application is much safer and more cost effective approach due to a more efficient use of oxidants.

This paper presents a case history from bench scale evaluation up to field demonstration. This recently developed sequential treatment train approach uses an innovative and environmentally friendly co-solvent/oxidation program which is designed to provide for effective and efficient biodegradable co-solvent dissolution of the heavy oil contaminants, enhanced free-product recovery and targeted oxidation of the dissolved mass source areas. This approach provides for an environmentally acceptable cost effective alternative to steam or oxidation treatments for heavy oil MGP Sites.

INTRODUCTION

Treatment of saturated soils impacted with heavy oils and petroleum aromatic hydrocarbons have always been a challenge due to the high viscosity and low aqueous solubility of the contaminants at ambient temperatures. Treatment of these sites has been impeded by the difficulty of dissolving and desorbing the contaminants for recovery or treatment by oxidants or biological technologies. Recent treatment successes have been achieved by using various thermal technologies (i.e., steam, six phase heating, Fenton's Reagent, etc.). All of the thermal approaches have proven to be effective in desorbing and dissolving the contaminants but they have proven to be very costly and have greatly impacted the use of the property during treatment. Of all these approaches only the oxidation process actually provides for the destruction of the contaminant in addition to its dissolution.

The goal of this program was to find a process which provides the benefits of the thermal and oxidation approaches while ensuring that the cost and site impacts are minimized. To achieve this goal, MEC^X LLC evaluated a sequential treatment train which consisted of a contaminant desorption and dissolution phase, a free product recovery phase, a source area oxidation phase, and a final polishing phase. The idea for the use of a sequential treatment train was to apply a series of cost effective and environmentally friendly processes has proven to meet the desired objectives without the negative impacts of high cost and restrictions of land use.

The sequential treatment train selection began with the evaluation of a solvent that would effectively dissolve the viscous organic contaminant while being both environmentally friendly and cost effective. The second step was the evaluation of the compatibility of the oxidant with the solvent to ensure that the solvent did not create an unacceptable adverse reaction (coagulants or participants). The third step was to evaluate the oxidant demand required to treatment of both the solvent and the dissolved contaminant. The fourth step is a laboratory permeability evaluation to determine the rate at which the solvent and the oxidants can be migrated through the soil at the site without fracturing the soil. (Note: fracturing of the soil will minimize the contact effectiveness of the solvent and oxidant and must be avoided to ensure treatment success) A fifth and final step is the field application to validate the application process and radius of influence of the solvent enhanced oxidation approach.

The following sections address the five steps essential in the design process and results for a MGP site in a silty sand aquifer. *(It should be noted that this approach can also be applied to unsaturated zone impacted soils if the area can be temporarily saturated during treatment periods of 72 hours or greater).*

STEP 1 – SOLVENT SELECTION PROCESS

A key parameter in ensuring the effectiveness of the oxidation system is to select a biodegradable solvent that will ensure that the sorbed organics are placed into solution to enable effective and efficient low temperature oxidation. The solvent was tested with soil from the actual site which will be mixed with or spiked with petroleum fluids from the site. The consultant provided soil samples from the site and heavy petroleum hydrocarbons (2 gallons) for this effort. Six (6) Shelby tube samples and (2) one-liter samples of petroleum hydrocarbon were collected for shipment to the testing facility at the Anachem Laboratory in Allen, TX (Anachem). The consultant recorded depth to water, pH, specific conductance, oxidation-reduction potential (ORP), and temperature conditions at the site.

The test was conducted by adding 1 ml of Solvent to 1 ml of Petroleum Hydrocarbon. The solution was mixed and then allowed to stand for 24 hours. Solvent that dissolved the petroleum hydrocarbon and remained in solution were identified as acceptable. All of these chemicals were evaluated from both a flammability and cost perspective. The optimum three (3) were selected for further oxidation testing.

Fourteen (14) solvent/surfactants were evaluated for their potential to dissolve the heavy Petroleum Hydrocarbons effectively from the soil. The chemicals that were evaluated are listed in Appendix A. Of these 14 chemicals, 5 chemicals (acetone, methanol, ethanol, propylene glycol, and “Orange Clean”) did not effectively dissolve the petroleum hydrocarbon. Of the remaining 9 chemicals, 4 were eliminated due to their very low ignition temperatures (<100 ^{O}F) and one was eliminated due to its expense (2-buthoxyethanol). The short list of remaining chemicals that were selected for further evaluation for the site was Isopropyl Alcohol (IPA), d-limonene, and d-limonene with surfactant.

STEP 2 – ADVERSE REACTION EVALUATION

The oxidants were first mixed with the Petroleum Hydrocarbons to ensure that no adverse reactions would occur with these chemicals. The samples that were treated with the selected solvent were then reacted with the acceptable oxidants. These reactions will be used for evaluation of the oxidation effectiveness in destruction of the dielectric fluid and to monitor reaction temperature ranges to ensure the maintenance of the temperature constraint. The oxidants that were evaluated was Low Temperature Fenton’s Reagent using peroxide in three concentrations (4%, 8%, 17%), and persulfate.

Results of the adverse reaction test indicated that surfactants are incompatible with all the oxidants and cause a coagulant precipitate. IPA and D-limonene had no adverse reactions.

STEP 3 – OXIDATION TEST

The Solvent and Soil oxidation tests were performed concurrently with each test being performed on three Fenton’s reagent concentrations listed as 1, 2, and 3 which corresponded to the addition of 12.5 g, 25 g, and 40 g of H_2O_2, respectively. The reaction samples were listed as A, B, & C for the respective solvents, A – d-limonene, B – Limonene with Surfactant, C- IPA.

The results of the test indicate that the most efficient combination of solvent and reactant is the IPA solution which had a 96% reduction in contaminant mass at 40g of H_2O_2 with no excessive heat generation. The d-limonene with surfactant created a precipitate that inhibited the reaction and was found to be generally non-reactive. The d-limonene was responsive at low concentrations of oxidant but became non-responsive to higher concentrations of oxidant. The total mass of oxidant required for treatment with IPA is significantly less than with the d-limonene; however if IPA is used the treatment area must remain well ventilated and screened to ensure that the vapor concentrations remain less than 10% of the LEL.

STEP 4 – LABORATORY PERMEABILITY EVALUATION

Undisturbed soil samples were evaluated under laboratory conditions to determine the system permeability and radius of design or influence parameters for the insitu application of the surfactant and oxidation chemicals using a geoprobe injection or gravity well system. This test was performed using a consolidation soil column of soil with 3 inches of deionized water applied to the water at three pressures, (minimal pressure of 3 inches of water, 5 psi, and 10 psi). The time for migration of the water through the soil column was measured to determine the optimum pressures for treatment at the site.

The pressure observations on the soil were 0 psi, 5 psi, and 10 psi. The optimum pressure that was observed for the site is 5 psi. Pressures above that range appear to over consolidate the soil and minimize the effectiveness of any injection treatment. In addition, a minimum of 5 psi is necessary to overcome the soil pressures at the site.

STEP 5 – FIELD APPLICATION DEMONSTRATION

At this time the field application has been delayed due to regulatory issues unassociated with the treatment technology. No problems with obtaining a UIC permit or other issues exist at the Site.

SUMMARY

The primary purpose of this evaluation was to determine if heavy-end oily materials associated with MGP could be cost effectively dissolved insitu with a biodegradable safe co-solvent and then recovered/oxidize with a low temperature low pressure oxidation approach to minimize environmental hazards and chemical costs. The results of the evaluation demonstrated that:

1- In permeable and moderately permeable sands, silts and silty clays, the solvents are very effective in dissolving the heavy petroleum hydrocarbons.
2- D-limonene was found to be a safe and effective biodegradable solvent for dissolving heavy petroleum hydrocarbons.
3- Use of d-limonene as a biodegradable co-solvent without surfactants had no adverse reactions with the tested oxidants Fenton's Reagent and Persulfate.
4- Both D-limonene and the oxidants could be distributed effectively at low pressure and temperature throughout the treatment zone.
5- Costs and time for treatment compare very favorably with alternative high temperature approaches. The estimated cost for treatment of the sample site which is 100' x 100' site with 15 vertical feet of treatment zone is roughly $75K USD, including application wells.