

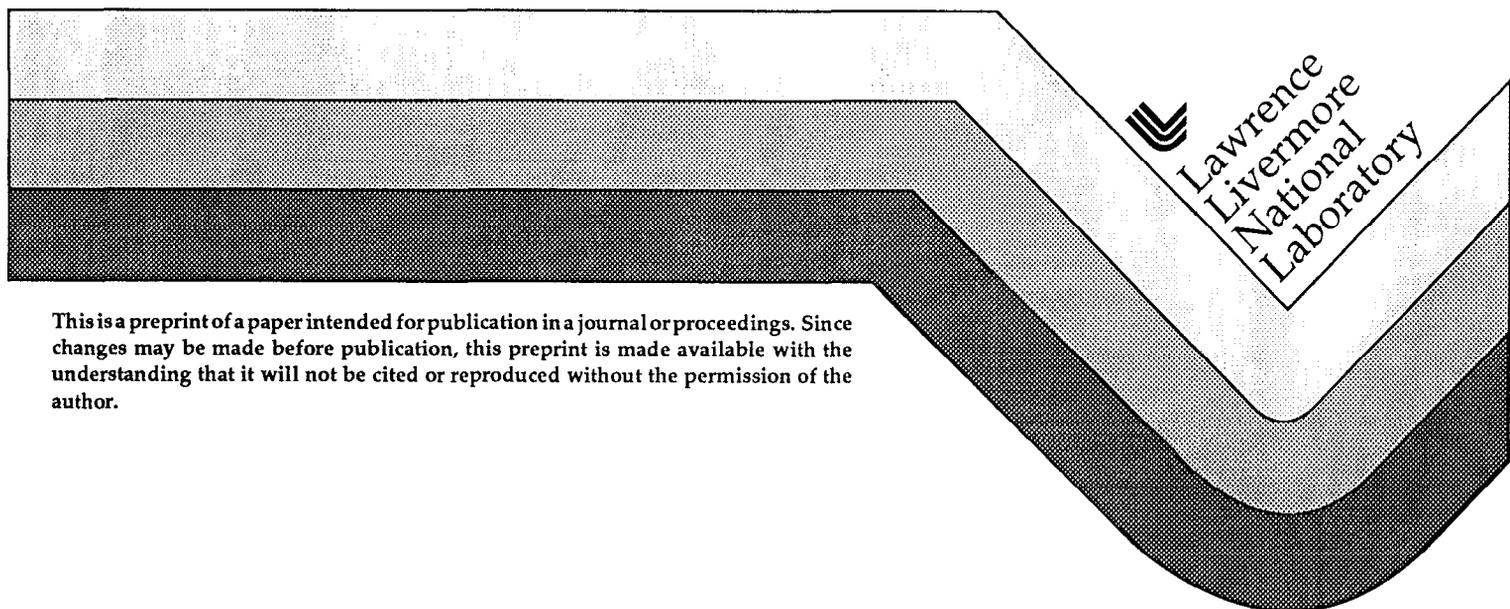
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IN SITU HYDROTHERMAL OXIDATIVE DESTRUCTION OF DNAPLS IN A CREOSOTE CONTAMINATED SITE

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ABSTRACT: Hydrous Pyrolysis / Oxidation (HPO) is an *in situ* thermal remediation technology that uses hot, oxygenated groundwater to completely mineralize a wide range of organic pollutants. A field demonstration of HPO was performed at a creosote contaminated site during the summer of 1997. The groundwater was heated by steam injections and oxygen was added by coinjection of compressed air. The remediation was monitored from multiple groundwater monitoring wells. Dissolved organic carbon levels increased in response to steam injections as a result of the enhanced dissolution and mobilization of the creosote into the heated groundwater. Elevated concentrations of partially oxidized organic compounds (i.e. phenols, benzoic acid, fluorenone, anthrone and 9,10-anthracenedione), decreased levels of dissolved oxygen and isotopic shifts in the dissolved inorganic pool were indicators of partial to complete oxidative destruction of the creosote in the heated aquifer as a result of the HPO process.

INTRODUCTION

The 4.3 acre Southern California Edison Pole Yard located in Visalia, California was in operation for 80 years as a wood preservation treatment facility. As a result of this operation, this site has become contaminated with a DNAPL mixture composed of pole-treating creosote and an oil-based carrier fluid containing pentachlorophenol. Placed on the EPA Superfund list in 1977, pump and treat technology was deployed to reduce and contain the contaminant plume. Over a period of nearly 20 years an estimated 10,000 lbs. of contaminant were removed from the soil and groundwater.

In the summer of 1997 Southern California Edison began the application of two thermally enhanced remediation technologies to accelerate the clean-up. The first method, Dynamic Underground Stripping (DUS), involves steam injection coupled with vacuum extraction to enhance the mobilization and removal of free product (Newmark and Aines, 1995). The second method, Hydrous Pyrolysis / Oxidation (HPO), is a novel *in situ* thermal remediation technology that uses hot, oxygenated groundwater to destroy organic contaminants by completely oxidizing the organic pollutants to carbon dioxide. The supplemental oxygen is delivered in the form of injected air. HPO is needed to destroy the residual DNAPL components not readily removed by the DUS process.

Initial laboratory-based feasibility experiments were conducted to investigate the HPO of actual DNAPL material with excess dissolved O_2 under conditions similar to those achievable during thermal remediation (Knauss et al., 1998; Leif et al., 1998). These experiments demonstrated that dissolved O_2 readily reacts with the compounds making up the DNAPL creosote mixture to form products ranging from partially oxidized intermediates, such as phenols and benzoic acid (Figure 1), to the fully oxidized product CO_2 (Figure 2).

Field implementation of HPO remediation at the Southern California Edison Pole Yard site was initiated in May, 1997 using 11 steam injection wells encircling the creosote DNAPL pool. An aquifer situated 75-102 ft. below ground surface was targeted for the HPO field demonstration.

Oxidative Destruction of Aqueous Creosote Components

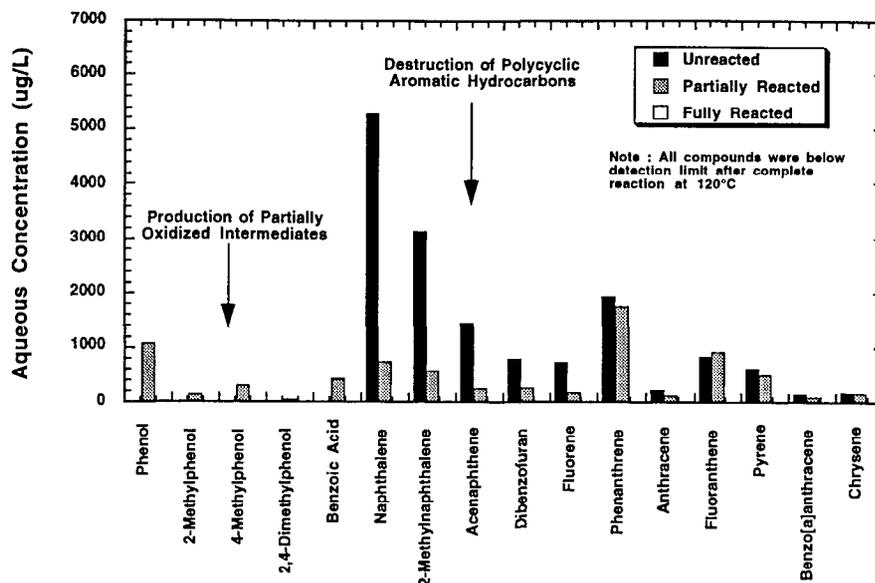


FIGURE 1. Histogram showing aqueous concentrations of organic compounds during a laboratory scale HPO experiment. Starting concentrations are shown in black and partially reacted are shown in gray. Complete destruction of creosote was achieved at 120°C.

O₂ Consumption and CO₂ Generation During HPO

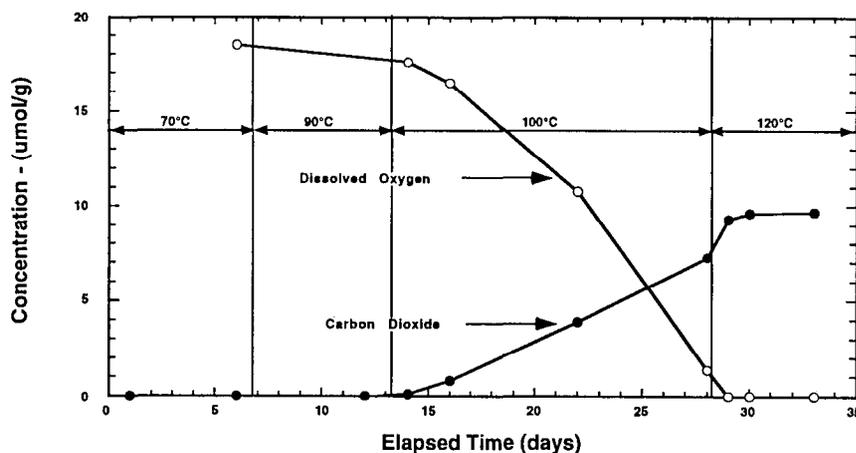


FIGURE 2. Oxygen consumption and carbon dioxide generation during a laboratory scale HPO experiment where the reaction temperature was increased from 70°C to 120°C over a duration of 33 days. Complete oxidation of creosote components is shown by the production of CO₂.

ANALYTICAL METHODS

Priority pollutants were extracted and concentrated by solid phase extraction (SPE) prior to analysis by gas chromatography - mass spectrometry (GC-MS). Typically a water sample ranging in volume from 1 to 4 liters was flowed by positive pressure through an SPE cartridge packed with 200 mg of ENV+ (International Sorbent Technology), a highly crosslinked styrene-divinylbenzene resin suitable for extraction of nonpolar and polar compounds from water. After sample extraction, the SPE tubes were dried and eluted with 4.5 mL of a dichloromethane / isopropanol eluent (1:1). The extracts were spiked with a six component internal standard mix and volumes adjusted to 5 mL. Bottles were extracted with a dichloromethane / isopropanol solvent mix (1:1) to extract organic compounds adsorbed to the glass. The extracts were spiked with a six component internal standard mix and the volumes adjusted to 5 mL. GC-MS analyses of the SPE extracts were performed on a Hewlett-Packard 6890 gas chromatograph equipped with a 30 m x 0.25 mm i.d. HP-5ms (5% phenyl methylsiloxane) capillary column (0.25 μ m film thickness) coupled to a Hewlett-Packard 6890 Series Mass Selective Detector operated in electron impact mode (70eV) over the mass range 35-450 dalton with a cycle time of 1.1 s. The GC oven temperature was programmed at isothermal for 2 min. at 50°C, ramped at 8°C/min. to 300°C, and isothermal for 6.75 min., with the injector at 250°C and helium as the carrier gas. The MS data were processed using Hewlett-Packard Chemstation software. Internal standard method, using a relative response factors, was used to quantitate the target compounds.

RESULTS AND DISCUSSION

The creosote-derived groundwater contaminants present in the intermediate aquifer of the Southern California Edison Poleyard exhibited large variations in both compound distributions and contaminant amounts depending on when and where the water samples were taken. Observations consistent with the process of DUS were the increased concentrations of dissolved organic compounds following increases in groundwater temperature as a result of the steam injections. This is represented by the elevated levels in the aqueous concentrations polycyclic aromatic hydrocarbons (PAH) following the injections of steam (Figure 3). The relative abundances of the higher molecular weight PAH (i.e. fluoranthene, pyrene and chrysene) were also observed to increase as a result of the steam injections.

One result from the HPO process was the rise in the groundwater concentrations of partially oxidized organic compounds. These oxygenated compounds (i.e. low molecular weight phenols, benzoic acid, fluorenone, anthrone and 9,10-anthracenedione) represent the partially oxidized intermediates formed during the HPO of a complex creosote mixture. Fig. 3 shows how the concentrations of these oxygenates changed in response to the steam injections. The levels of total oxygenates maximized following both steaming events and their presence is consistent with the aqueous phase oxidations expected under these conditions.

The measurement of dissolved oxygen also aided in the evaluation of the HPO process. A knowledge of the dissolved oxygen level in the groundwater was critical during the application of HPO because the fundamental principle of HPO is the ability of hot, oxygenated water to completely mineralize organic compounds to carbon dioxide. The aqueous phase oxidation will occur as long as sufficient dissolved oxygen is present. Figure 4 is a plot of the dissolved oxygen measurements in the aquifer as a function of time during the field test. A steady decrease in the level of dissolved oxygen was observed during the field test and is consistent with the HPO chemistry where the dissolved oxygen is the oxidant during the chemical oxidation of the aqueous organic species.

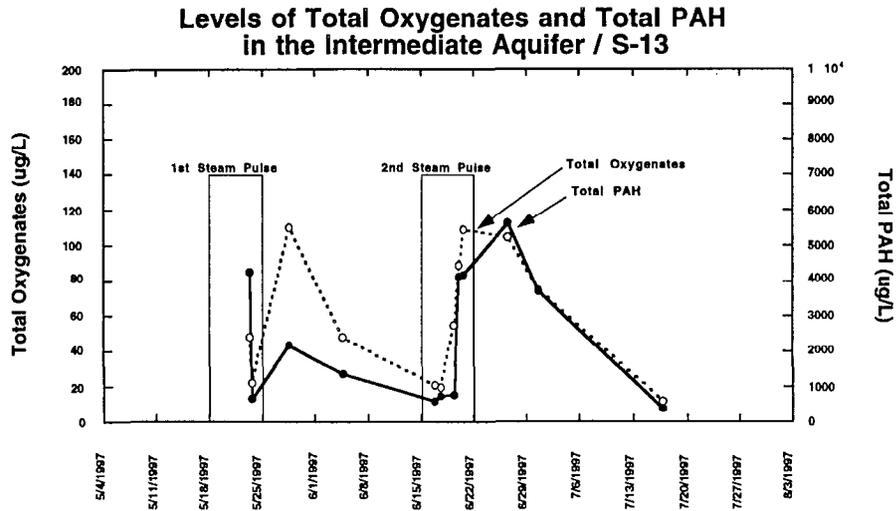


FIGURE 3. Concentrations of total oxygenates and total PAH (polycyclic aromatic hydrocarbons, EPA Method 8270C) in the aquifer during the HPO test period. Elevated PAH concentrations reflect enhanced mobilization due to DUS. Oxygenate increases are consistent with partial hydrocarbon oxidation by HPO.

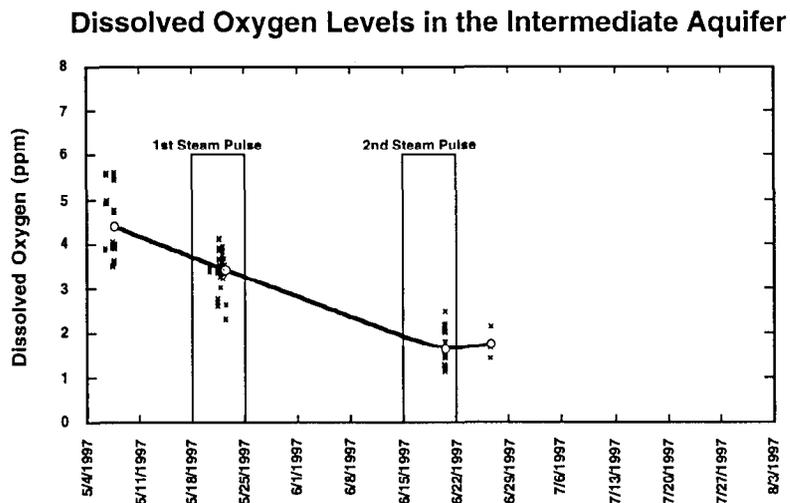


FIGURE 4. Concentration of dissolved oxygen as a function of time during the HPO demonstration. Average dissolved oxygen concentrations (open circles) were calculated using the combined values from three different analytical techniques. Dissolved oxygen levels dropped from 4.4 ppm to 1.7 ppm during the test period.

Another analytical tool used for evaluating the progress of the HPO remediation process was the measurement of carbon isotope abundances (^{12}C , ^{13}C and ^{14}C) of the dissolved inorganic carbon. Because both $^{13}\text{C}/^{12}\text{C}$ and $^{14}\text{C}/^{12}\text{C}$ values of the creosote are distinct relative to the groundwater, these measurements were used to trace carbon derived from the oxidation of the creosote compounds. Figure 5 shows the variations in ^{14}C versus $\delta^{13}\text{C}$ values of dissolved inorganic carbon in the groundwater. The groundwater end-member value was the isotopic signature prior to steaming. The dissolved inorganic carbon became "older" after steaming, consistent with the production of dissolved inorganic carbon by the oxidation of "dead" creosote carbon.

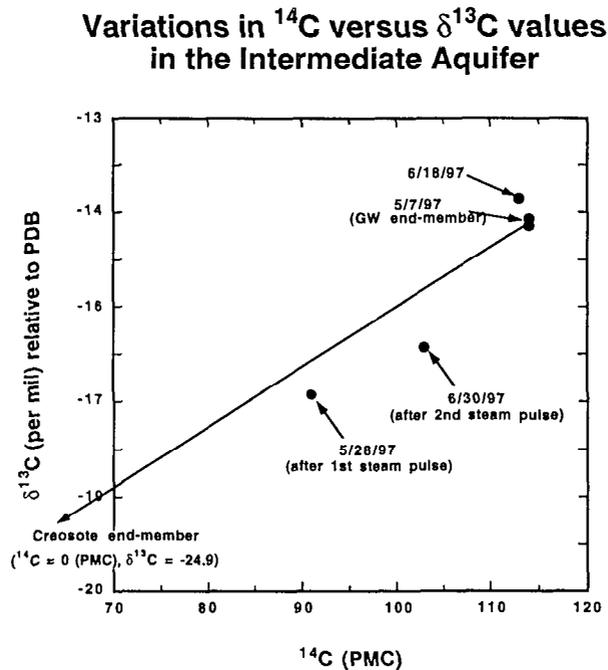


FIGURE 5. Variations in ^{14}C versus $\delta^{13}\text{C}$ values of dissolved inorganic carbon (DIC) in groundwater. The groundwater end-member value was the isotopic signature prior to steaming. The DIC became "older" after steaming, consistent with the production of DIC by the oxidation of "dead" creosote carbon.

CONCLUSIONS

It is clear from the Visalia Field Test at the Southern California Edison Pole Yard that the combined applications of two *in situ* thermal remediation technologies, Dynamic Underground Stripping and Hydrous Pyrolysis / Oxidation, have greatly accelerated the remediation of this creosote-contaminated site. The application of DUS to the site accelerated the mobilization and removal of creosote. The application of HPO to the Southern California Edison Pole Yard has accelerated the site remediation by oxidizing creosote components. Observations consistent with the process of HPO were increases in groundwater oxygenate concentrations, decreases in dissolved oxygen levels and shifts in carbon isotope abundances in the inorganic carbon pool.

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