

Persulfate Oxidation of a Gasoline Source Zone

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Summary

In situ chemical oxidation (ISCO) using persulfate is a potentially aggressive remediation technology remediation that can be used for the oxidation of petroleum hydrocarbons (PHCs) such as gasoline.

The current investigation was focused on evaluating the potential of persulfate for the treatment of a residual gasoline source zone. Concentration and mass flux of various gasoline compounds (e.g., benzene, toluene, trimethylbenzenes, naphthalene) were estimated post-oxidant injection and compared with background levels.

The experiment demonstrated significant decrease in concentration and mass flux of the target organics upon persulfate oxidation. Tools were employed for the estimation of persulfate oxidation performance and to distinguish between loss of target organics due to oxidation and due to dilution by injected solution. Overall, this investigation showed that persulfate was a viable oxidant for treatment of gasoline source zones. The system performance can be potentially enhanced by accurate estimation of persulfate dosing requirements.

Introduction

Petroleum hydrocarbons (PHCs) are among the most abundant organic contaminants and pose an imminent threat to aquifer systems around the world (Han et al. 2009). Among these PHCs, gasoline and diesel are used extensively and subsurface contamination by these organics is often caused by accidental release, spills and leakage from underground storage tanks (Shih et al., 2004). Gasoline consists of toxic organic compounds in the relatively lower carbon fraction composing of C₆ to C₁₆ compounds including benzene, toluene, ethylbenzenes and xylenes (BTEX) in addition to trimethylbenzenes and naphthalene. Health effects of BTEX include neurological impairment and hematological effects, and these compounds are often difficult to treat due to their low biodegradability and low volatility (Tsai and Kao, 2009). Efforts to remediate these components have led to the development and enhancement of various remediation technologies. During the past 5 years, *in situ* chemical oxidation (ISCO) employing persulfate has emerged as a potentially useful oxidant for the remediation of PHCs.

In order to establish remediation and site closure goals, it is important to understand the response of a source zone to persulfate-based ISCO remediation. In this investigation, we undertook the treatment of gasoline contaminated source zone, examining the evolution of contaminant concentrations and of residual inorganics resulting from persulfate injection.

Theory and/or Method

A 48 kg modern gasoline fuel source with 5% methyl *tert*-butyl ether (MTBE) and 5% *tert*-butyl alcohol (TBA) (collectively known as GMT) was emplaced below the water table at the research facility at CFB, Borden, Canada as a part of another study (Mocanu, 2006). Substantial concentration of gasoline compounds has historically existed in the monitoring suggesting a high residual mass in the source zone which, based on these historical mass fluxes, is anticipated to be ~40 kg. The soil is generally homogenous and is composed of well-sorted fine to medium grain sand with groundwater velocity of 10 cm/day. Based on preliminary bench-scale gasoline treatability studies, unactivated persulfate injection at 20 g/L concentration and ~2000 L volume was conducted for gasoline source zone treatment. The dissolved plume was monitored via a network of multilevel wells installed in a monitoring row perpendicular to groundwater flow and 3.5 m downstream of the residual source zone. Sampling was initiated prior to the oxidant injection to establish background conditions and post-injection samples were obtained weekly to biweekly over a 4 month period to examine the concentrations and mass fluxes of the target organics (BTEX, TMBs and Naph) and residual inorganics (persulfate, sulfate and sodium).

Concentrations of all the target organics were observed to decrease post-injection with the maximum decrease occurring after 2 to 3 months of injection. Mass flux through the monitoring row for all target organics was estimated from the concentration data for the experimental period and 45 to 85% decrease in mass flux was observed for the gasoline compounds analyzed (Figure 1). Further analysis of the experimental data demonstrated that the significant decrease in cumulative mass emanating from the monitoring row could be attributed to chemical oxidation by persulfate as opposed to decrease in flux due to dilution by injected solution. After 3 months, some rebound of organic compound concentrations was observed and was likely due to limited availability of persulfate within the reaction zone.

Significant breakthrough concentrations of sulfate and sodium were observed in the multilevel wells throughout the sampling duration denoting contact between organics and the oxidant and were also representative of persulfate degradation to sulfate. Residual persulfate breakthrough was generally <5% of the initial concentration implying that most of the persulfate degraded in the presence of organics and aquifer material constituents.

Examples

Mass fluxes of the toxic gasoline compounds such as benzene and ethylbenzene were reduced by up to 50 and 80% respectively (Figure 1). By the end of the experimental period, the mass flux had rebounded to within 80 and 40% of the background for these two compounds. Sulfate and sodium breakthrough was observed within 2 weeks of persulfate injection. Persulfate appeared much later during at the monitoring row (after 40 days) and appeared to be degrading to sulfate due to its reaction with organics and aquifer materials components.

Conclusions

This investigation establishes the use of persulfate as a viable ISCO technology for the destruction of gasoline source zone and significant suppression of organic concentration plume length and intensity. Tools were developed for the oxidant performance evaluation and demonstrated a significant impact of persulfate oxidation on dissolved phase concentrations of the target organics. For enhancement of oxidation efficiency, persulfate dosing requirements

should be accurately estimated and should include potential persulfate degradation in aquifer media apart from stoichiometric requirements of the target organics.

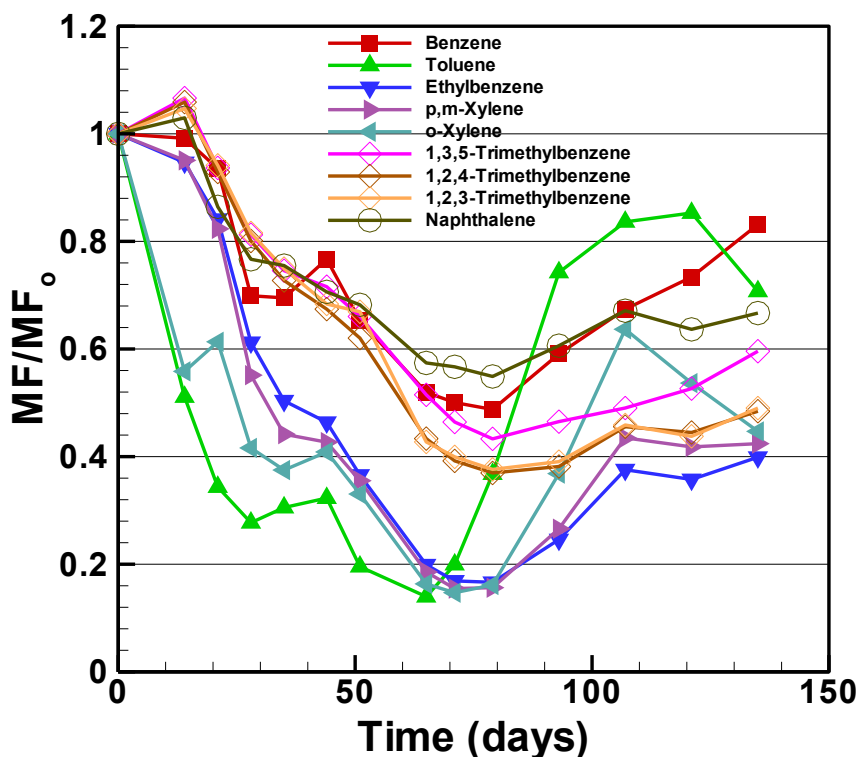


Figure 1: Normalized mass flux of target gasoline compounds emanating from the monitoring row during the 4-month post-persulfate injection observation.

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