Comparing Effectiveness of Activated vs. Un-activated Sodium Persulfate During In-Situ Remediation of Petroleum Hydrocarbons

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Background/Objectives: A retail petroleum site in southeast Alberta, Canada has been in operation since prior to 1929, with a history of widespread petroleum hydrocarbon (PHC) contamination in both soil and groundwater. Previous attempts to enhance biodegradation of the PHC contaminants using both oxidative and alternative electron acceptor approaches, by bioventing and hydrogen peroxide addition, have decreased the plume area; however, benzene concentrations remain high and are considered to be recalcitrant. The goal was to degrade the remaining PHC contaminants through in-situ remediation using sodium persulfate.

Approach: Persulfate is widely used to facilitate contaminant degradation during in-situ remediation through the generation of a sulfate radical, which is a strong oxidizer. Activated persulfate will promote rapid oxidation of PHCs through the production of these radicals. Un-activated persulfate also acts as an oxidizer, but it is anticipated that portions of non-activated persulfate may degrade into sulfuric acid over time, promoting the release of soil-bound phosphate and providing a sustained secondary anaerobic biological degradation of PHCs. Half of the research site was injected with alkaline activated persulfate, and we hypothesized that this would produce sulfate radicals that would stimulate the rapid, short-lived degradation of PHCs, particularly benzene. Furthermore, we hypothesized that the addition of non-activated persulfate to the other half of the site would, in addition to oxidative degradation, stimulate the slower and more sustainable anaerobic degradation of PHCs by producing sulfuric acid, which would liberate soil-bound phosphate. As the impacted soils in this site have low permeability, with near surface groundwater gradients measured at less than 0.02 m/m, distribution of the amendment was completed by hydraulic fracture propagation from injection boreholes.

Results: The research site was initially redox negative with naturally present sulfate functioning as the terminal electron acceptor. The addition of activated persulfate drove the site to become redox positive, which caused oxidation and an initial rapid decrease of the PHCs in wells that had detectable levels of persulfate. Five months post injection, the area treated with activated persulfate remained redox positive. The addition of non-activated persulfate also caused a positive shift of the oxidation reduction potential (ORP), with sustained redox positive values. In wells which had measureable persulfate, oxidative degradation of PHCs occurred to a similar extent as seen in the area treated with activated persulfate. Wells in the plume area that did not have measureable persulfate concentrations did not initially show a shift to redox positive conditions or a decrease in PHC concentrations. However, subsequent monitoring events indicate a slower shift to positive ORP in these wells, as well as slower PHC degradation. No significant changes in the nutrient profile have been noted for activated or non-activated persulfate treatment areas. Additional groundwater monitoring will be completed to assess redox conditions on-site, as well as confirm further PHC degradation.