

Comparative Study for ZVI/Peroxide versus Ferric Iron Oxide Persulfate Activation Followed by Intrinsic Facultative, Biologically-Mediated Processes

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Background/Objectives. An in situ chemical oxidation (ISCO) remedial process involves injecting an oxidizing agent, such as activated sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$), or other oxidant, into the subsurface to destroy organic compounds. The persulfate anion ($\text{S}_2\text{O}_8^{2-}$) has a high redox potential and can be chemically activated to form the sulfate radical ($\text{SO}_4^{2-\bullet}$), which is a stronger oxidant. The sulfate free radical is a very potent oxidizing agent roughly equivalent to the hydroxyl radical generated using ozone or peroxide.

Approach/Activities. Two activation methods are presented herein that have the advantage of utilizing both biotic and abiotic processes that include the use of free radical chemistry, oxidation chemistry and facultative biological attenuation. The potential combination of these processes extends oxidant and free radical residuals while enhancing the in situ environment for biologically based attenuation of the constituents of interest (COI).

The abiotic portion of the ZVI/Peroxide activated persulfate method uses a unique blend of peroxy, hydroxyl, evolved heat and sulfate free radicals which results in the oxidation of the COIs. This mixture allows Fenton-like reactions with long-lived sulfate free radical oxidation to occur, while the presence of zero valent iron acts as a catalyst for both reactions. The evolved heat is of value in situations where there is a high sorbed mass of the hydrophobic compounds of concern. Furthermore, the decomposition products of the oxidation process are utilized in the subsurface to stimulate facultative biological degradation of the targeted compounds.

The use of ferric iron to activate persulfate, for the purpose of degrading organic compounds, presents the additional advantage of quickly generating sulfate and ferrate radicals for ISCO treatment. Moreover, it supports long-term, sustained, secondary bioremediation processes to manage residuals and prevent contaminant rebound. Similar to the ZVI/Peroxide activation method, this process is achieved by enhancing the subsequent utilization of sulfate and iron as terminal electron acceptors for facultative redox reactions in order to improve biodegradation of any residual COIs. The ferric activated method, similar in its chemistry to the peroxide, ZVI persulfate, differs in that it is an endothermic process while still providing no extreme pH conditions that can mobilize heavy metals causing secondary impact issues, while the presence of iron will sequester sulfur liberation during sulfate reduction reactions to minimize H_2S formation. Moreover, the remedy combines treatment mechanisms thereby allowing for more cost-efficient dosing of the product.

Results/Lessons Learned. The available data from four sites, two more each described remedial approach demonstrates that both techniques have been found to be effective in case specific situations to address soil and groundwater contamination.