

Combining Persulfate, *In Situ* Ferrate Generation and Enhanced Bioremediation for Safer, More Effective Remedial Actions

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Background/Objectives: Ideally, ISCO rapidly oxidizes/mineralizes organic contaminants in a safe and effective manner (*i.e.*, materials easy to handle on site; no extreme activation chemistries such as heat or grossly elevated pH; no generation of secondary contaminants). And – importantly – remedial actions are completed via a one-time application event. However, with essentially all conventional ISCO technologies, the oxidation reactions are partially incomplete and contaminant desorption / rebound is a very common problem. Hence, ISCO that effectively combines multiple oxidation chemistries with enhanced, sustained secondary bioremediation would facilitate more effective application to persistent compounds/mixed contaminants with an improved ability to meet more stringent remedial action objectives.

Approach/Activities: When ferric oxide is used to activate persulfate the process quickly yields ferrate (tetraoxy iron or FeO_4^{2-} or Fe(VI)) in addition to the standard persulfate radicals (SO_4^\bullet ; $E^\circ = 2.600 \text{ V}$). Ferrate functions both as an oxidant and subsequent coagulant in the form of Fe(III) (hydro)oxides that can immobilize heavy metals. Ferrate also has one of the highest oxidation potentials of any chemical realistically usable in water and wastewater treatment; $E^\circ = 2.200 \text{ V}$ under acidic condition and $E^\circ = 0.72 \text{ V}$ under basic condition, making the protonated forms of ferrate the most reactive, but least stable and shorter lived. As such, it is beneficial to generate ferrate *in situ* for the treatment of groundwater contaminants. Ferric iron activation of persulfate also enhances subsequent utilization of sulfate and iron as terminal electron acceptors for facultative redox reactions that sustain bioremediation of residual contaminants and partially oxidized compounds. Alternative methods of stimulating secondary biodegradation processes using oxygen release compounds (such as calcium or magnesium oxyhydroxide) are limited in that they will remain active for only a few months, after which time their oxygen release potential is largely exhausted. Iron, on the other hand, remains in place and active for many years. Hence, the combination of chemical and biological treatment mechanisms allows for more cost-efficient treatment while supporting long-term, sustained, secondary bioremediation processes to manage residuals and prevent contaminant rebound.

Results/Lessons Learned: Provect-OX® is a pre-mixed, dry powder containing both sodium persulfate and ferric oxide that can be easily applied into a subsurface environment via direct mixing, hydraulic fracturing, pneumatic fracturing, and direct push injection of slurries. Ferrate will be continuously generated *in situ* to support extended oxidation of persistent compounds, provided that persulfate is maintained with iron as an activator. Thereafter, the residual iron and sulfate will support bioremediation processes to manage partially oxidized compounds and residual contaminants that continually desorb from the matrix over time (*ca.* 3 to 5 years but it is acknowledged that the rate and extent of these primary and secondary reactions are often unknown). This presentation will outline parameters considered for calculating material requirements, discuss field application considerations (material handling and implementation guidelines), and summarize performance data and costs from example projects.

Proposed Session:

Invited Paper - Cornuet / MacBeth

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