Reclamation of a TPH-Impacted Site via LNAPL Recovery and ISCO Treatment: Case Field, Italy

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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 ?; $E^\circ = 2.600 \text{ V}$). 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.

Results/Lessons Learned. The site in northwest Italy has been operating as a petroleum services station for several decades. Over that period, historical underground storage tank (UST) spills released total petroleum hydrocarbons (TPH) comprised of gasoline and diesel fuel into the soil and groundwater. These spills yielded groundwater impacts >100 mg TPH/L and free-phase LNAPL (light non-aqueous phase liquid) impacts. Surfactant flushing was used to remove LNAPL, and site reclamation was completed by ISCO treatment of the groundwater plume to remove TPH residuals. A total of 2,475 kg of Provect-OX® was applied via 10 points via direct-push technique (from 5 to 11 m bgs) throughout a 200 m² area. Reagent distribution was verified by performing a geophysical campaign that monitored the variation in electrical resistivity of soil due to ferric oxide present in the reagent, highlighting a total decrease of about 30% between pre- and post-injection. Groundwater monitoring campaigns carried out at the end of the first phase of chemical oxidation and those conducted in the second phase of enhanced bioremediation (six months later), highlighted the effectiveness of the technology by achieving recovery targets of 350 ug/l (Threshold Limit Value).