Technical Bulletin

Innovative Environmental Technologies, Inc.

"Zero Valent Iron Catalyzed Hydroxyl & Sulfate Free Radical Oxidation"

Technology Discussion:

Traditionally, oxidation processes utilize oxidizers, which require no activation; peroxide, permanganate. persulfate and ozone, or oxidants which require activation; Fenton's Process and activated persulfate. The advantage of activated processes is the evolution of free radicals, which offer higher oxidation capabilities and a broader spectrum of applicable targeted compounds. The disadvantages of activation processes and the evolution of free radicals typically focus on the limited half-lives of these species. The remedial approach utilizes both free radical chemistry and oxidation chemistry in such a way as to extend the oxidant and free radical residual.

Innovative Environmental Technologies, Inc. (IET), applies three remedial materials to the subsurface via a patented injection process and apparatus (United States Patent # 7,044,152) such that the activation processes occur in a controlled manner in-situ. In a unique application of zero-valent iron metal (2-4 microns in size), the process allows for activation of both the persulfate and the peroxide species in-situ.

Typically persulfates are activated via one of three mechanisms: heat, peroxide or soluble metal species. In the proposed approach there is limited activation via the evolved heat produced via the interaction of the peroxide and the iron particles. In addition to the limited heat production produced from the interaction of the iron and the peroxides, hydroxyl radicals are produced and iron oxides are formed on the surface of the particles. The peroxide, the heat and the metal ions at the iron surface all serve to activate the persulfate, forming sulfate radicals.

The advantages of the approach proposed are:

1) Management and containment of the activating iron species within the treatment area,
2) Evolution of multiple free radicals,
3) Extended residual of persulfate and the sulfate radical in-situ,
4) Attenuation following the exhaustion of the persulfate via Fe^{+2}/Fe^{+3} interactions,
5) In-situ management of sulfate via in-situ precipitation of sulfate iron salts as the in-situ conditions revert back to a less oxidizing environment.
6) Attenuation via SO_4^{+} and Fe^{+3} following the exhaustion of the persulfate as the conditions revert back to a less oxidizing state.

Oxidation Reactions:

$H_2O_2 + Fe^0 \rightarrow Fe^{+3} + OH^- + OH^-$
$Fe^{+3} + H_2O_2 \rightarrow Fe^{+2} + H^+ HO_2^-$
$S_2O_8 + Fe^0 \rightarrow Fe^{+3} + SO^{4-} + SO_4^{-}$
Direct oxidation of NaS_2O_8 and H_2O_2

Attenuation Process:

Sulfate Residual:
After dissolved oxygen has been depleted in the treatment area, sulfate (by-product of the persulfate oxidation) may be used as an electron acceptor for anaerobic biodegradation. This process is termed sufanogenesis and results in the production of sulfide. Sulfate concentrations may be used as an indicator of anaerobic degradation of fuel compounds. Stoichiometrically, each 1.0 mg/L of sulfate consumed by microbes results in the destruction of approximately 0.21 mg/L of BTEX. Sulfate can play an important role in bioremediation of petroleum products, acting as an electron acceptor in co-metabolic processes as well. As an example of benzene mineralization under sulfate reduction:

$$\mathbf{C_6H_6 + 3.754\ SO_4^{2-} + 3\ H_2O \rightarrow 2.25\ H^+ + 6HCO^{3-} + 3.75HS^-}$$

Ferrous Iron:
Ferric iron is also used as an electron acceptor during anaerobic biodegradation of petroleum hydrocarbons after sulfate depletion, or sometimes in conjunction with sulfate. During this process, ferric iron is reduced to ferrous iron, which is soluble in water. Ferrous iron may then be used as an indicator of anaerobic activity. Stoichiometrically, the degradation of 1 mg/L of BTEX results in the production of approximately 21.8 mg/L of ferrous iron.

Summary:
Oxidation and biological mineralization applied in a single injection process. The first phase, oxidation, oxidizes the majority of dissolved and sorbed targeted compounds. The second phase, biological attenuation, polishes and maintains the achieved treatment goals. Innovative Environmental Technologies, Inc. is proud to present this field proven alternative to our clients.

For more information go to **IET-INC.NET**.