

Provect-OX®

Self-Activating ISCO / Enhanced Bioremediation Reagent

TECHNOLOGY DESCRIPTION

Provect-OX is an *in situ* chemical oxidation (ISCO) / enhanced bioremediation reagent that uses ferric iron (Fe III) as a safe and effective means of activating persulfate (US Patent No. 9,126,245; patents pending). Provect-OX oxidizes a wide variety of organic compounds present in impacted soil, sediment and groundwater, including chlorinated solvents, petroleum hydrocarbons, and pesticides. Rodriguez *et al.*, (2014) recently reported that 2 mM Fe(III) and 6 mM persulfate was very effective in rapidly mineralizing even recalcitrant organic compounds such as the synthetic azo dye Orange G ($C_{16}H_{10}N_2Na_2O_7S_2$).

Provect-OX is the only ISCO technology designed to actively manage rebound. The advanced activation catalyst is further unique considering its ability to enhance bioremediation processes. This is accomplished via the subsequent utilization of sulfate and iron as terminal electron acceptors for facultative reductive processes. Degradation intermediates generated during pollutant oxidation may act as electron shuttles, allowing the reduction of Fe(III) to Fe(II) in the redox cycling of iron and continued activation of persulfate. This combined remedy provides supplemental treatment mechanisms thereby allowing for more cost-efficient dosing of the product.

Like all Provectus products, Provect-OX was developed by experienced practitioners who understand real-world field applications. For example, persulfate oxidant and its activator are conveniently packaged in a single, pre-mixed bag for ease of use and safe handling. Moreover, due to its safe and non-extreme activation chemistry, Provect-OX will not generate excessive heat / off-gases, nor will it mobilize heavy metals or lead to the generation of secondary impact issues, such as elevated arsenic, chromium, or pH.



TRADITIONAL ACTIVATION CHEMISTRIES

Heretofore, sodium persulfate has been activated via heat, chelated metals, hydrogen peroxide, ZVI/surface catalysis and/or pH extremes in order to generate sulfate radicals, hydroxyl radicals, etc. (Tsitonaki *et al.*, 2010). Not only do these systems require the addition of other products or energy, they tend to disregard the many biologically mediated processes possible as a consequence of the decomposition products of persulfate.

Divalent metal activation: The utilization of ferrous iron, usually as a chelated cation consumes the oxidant (persulfate) in a conversion of the ferrous iron to ferric iron. Additionally, the presence of the chelant inhibits biological utilization of the generated ferric species as a biological terminal electron acceptor and consumes oxidant. Over dosing of the chelated ferrous iron further consumes the oxidant.

Caustic Activation: The utilization of caustic (high pH) activation of persulfate presents inherent health and safety issues while creating an unsuitably high pH environment for biological attenuation. Further, within this activation mechanism is a self-limiting biological attenuation process once the pH returns to suitable levels. The sulfate, when used as a biological terminal electron acceptor, transitions to sulfite and finally sulfide. This final product forms hydrogen sulfide which inhibits further biological activity.

Heat Activation: The utilization of heat as an activation mechanism is generally difficult to implement, and it incurs high implementation costs while not addressing the hydrogen sulfide issue.

Hydrogen Peroxide Activation: The use of peroxide as an activating mechanism again does not address the hydrogen sulfide generation problem while having limited efficacy on many targeted compounds.

MODE OF ACTION

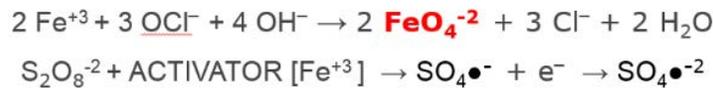
ISCO: Under the **Provectus** approach, persulfate is activated by Fe III (pre-mixed formulation) which requires a lower activation energy than alternative mechanisms while not consuming the persulfate oxidant. The mechanism is believed to elevate the oxidation state of the iron transiently to a supercharged iron ion which in itself may act as an oxidant. As this supercharged iron cation is consumed, the resulting ferric species can act as a terminal electron acceptor for biological attenuation. Coincidentally, the generated sulfate ion from the decomposition of the persulfate provides a terminal electron acceptor for sulfate reducers which may further remediate the targeted compounds in the groundwater and soils. The reactions that occur in the chemical oxidation include persulfate radicals and ferrate, as summarized below (Equation 1):



Provect-OX Oxidation Potentials

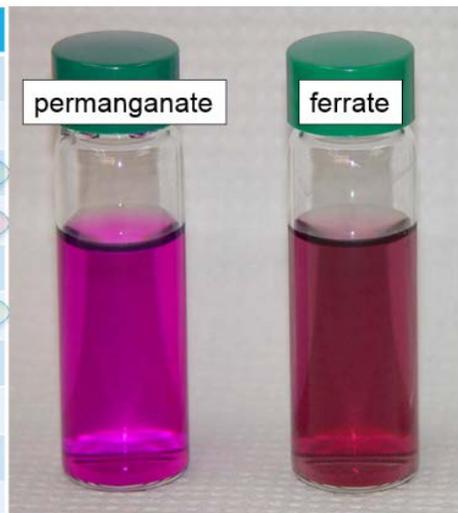


Ferrate salts can easily be prepared from iron salts, hypochlorite and a base:



Oxidation Potentials	Volts
Fluorine (F ₂)	2.87
Hydroxyl radical (OH●)	2.80
Persulfate radical (SO ₄ ●)	2.60
Ferrate (Fe ⁺⁶)	2.20
Ozone (O ₃)	2.08
Persulfate (S ₂ O ₈ ⁻²)	2.01
Hydrogen peroxide (H ₂ O ₂)	1.78
Permanganate (MnO ₄ ⁻)	1.68
Chlorine (Cl ₂)	1.49

<https://sites.google.com/site/ecpreparation/ferrate-vi>



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SECONDARY ATTENUATION PROCESS (Biologically Mediated)

1) Sulfate Residual

After dissolved oxygen has been depleted in the treatment area, sulfate (a by-product of the persulfate oxidation) may be used as an electron acceptor for anaerobic biodegradation by indigenous microbes. This process is termed sulfidogenesis and results in the production of sulfide. Stoichiometrically, each 1.0 mg/L of sulfate consumed by microbes results in the destruction of approximately 0.21 mg/L of BTEX compounds. Sulfate can play an important role in bioremediation of petroleum products, acting as an electron acceptor in co-metabolic processes as well. For example, the basic reactions for the mineralization of benzene and toluene under sulfate reducing conditions are presented in equations 2 and 3:



2) Ferric Iron:

Ferric iron is also used as an electron acceptor during anaerobic biodegradation of many contaminants, sometimes in conjunction with sulfate. During this process, ferric iron is reduced to ferrous iron, which is soluble in water. Hence, ferrous iron may be used as an indicator of anaerobic activity. As an example, Stoichiometrically, the degradation of 1 mg/L of BTEX results in the average consumption of approximately 22 mg/L of ferric iron (or “production” of ferrous iron) as shown below (equations 4-6).



3) Pyrite Formation:

While ferrous iron is formed as a result of the use of the ferric species as a terminal electron acceptor, residual sulfate is utilized as a terminal electron acceptor by facultative organisms thereby generating sulfide under these same conditions. Together, the ferrous iron and the sulfide promote the formation of pyrite as a remedial byproduct (equation 7). This reaction combats the toxic effects of sulfide and hydrogen sulfide accumulation on the facultative bacteria, while also providing a means of removing targeted organic and inorganic COIs via precipitation reactions. Moreover, pyrite possesses a high number of reactive sites that are directly proportional to both its reductive capacity and the rate of decay for the target organics.



PRIMARY FEATURES:

This technique maximizes the synergy between persulfate and iron for coupled oxidation and enhanced bioremediation: i) sulfate is generated from persulfate, i) Ferric iron (Fe III) is microbiologically reduced to ferrous iron (Fe II) readily supplying electrons to exchange and react with sulfide. Together, sulfide and iron form pyrite, an iron bearing soil mineral with a favorable reductive capacity.

- ◆ **Effective:** Promotes multiple free radical based *in situ* oxidation of a wide-range of organic contaminants. Also provides a unique microbiological component for multiple accelerated attenuation processes.
- ◆ **Efficient:** Significantly lower costs as a result of sub-stoichiometric dosing requirements.
- ◆ **Safe:** Fewer health and safety concerns as compared with use of traditional activation methods such as heat, chelated metals, hydrogen peroxide or pH extremes. Contains built-in activation which eliminates the need for additional and potentially hazardous chemicals required to achieve traditional persulfate activation.
- ◆ **Ease of Use:** Single component product with integrated activator results in simplified logistics and application. No additional containers or multi-step mixing ratios required prior to application. Fewer material compatibility issues.
- ◆ **Improved Performance:** Combined remedy prevents “rebound” which is often seen in other oxidation processes. Maximizes the inherent geochemistry of a “post-oxidation” environment for biologically based attenuation.
- ◆ **Patented Technology:** US Patent No. 9,126,245 (international filings in EU, Australia, Brazil, Canada, China, Colombia, Japan and Mexico) and others pending allow us to freely market this advanced persulfate-based ISCO technology globally, using our choice of suppliers.

LITERATURE CITED:

Rodriguez S, L. Vasquez, D. Costa D, A. Romero and A. Santos. 2014. Oxidation of Orange G by Persulfate activated by Fe(II), Fe(III) and zero valent iron (ZVI). *Chemosphere* 101:86-92.

Scalzi, M. and A. Karachalios. 2013. Chemical Oxidation and Biological Attenuation Process for the Treatment of Contaminated Media. US PTO 9,126,245.

Tsitonaki, A., B.Petri, M. Crimi, H.Mosbaek, R. Siegrist and P. Berg. 2010. *In Situ* Chemical Oxidation of Contaminated Soil and Groundwater using Persulfate: A Review. *Critical Rev. Environ. Sci and Technol.* 40: 55-91.

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