

**PROVTECT-OX™**

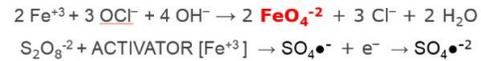
**Self-Activating ISCO / Enhanced Bioremediation Reagent**

Provect-OX™ (US Patent Approved) rapidly oxidizes a wide variety of organic COIs present in impacted soil, sediment and groundwater (including chlorinated solvents, petroleum hydrocarbons, and pesticides) and provides long-term, sustained secondary bioremediation to manage residuals and prevent contaminant rebound (COI rebound is a common problem encountered with conventional ISCO technologies). This is accomplished by using ferric iron (Fe III) as a safe and effective means of activating persulfate which quickly yields sulfate and ferrate radicals for more aggressive ISCO treatment (see inset).

**Provect-OX Oxidation Potentials**

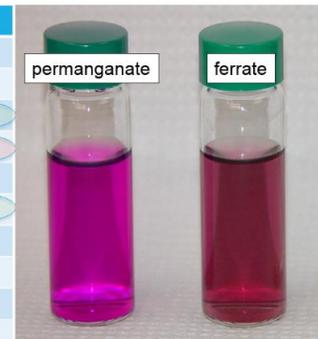


Ferrate salts can easily be prepared from iron salts, hypochlorite and a base:



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

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



The unique activation also enhances subsequent utilization of sulfate and iron as terminal electron acceptors for facultative anaerobic redox reactions to support secondary biodegradation of any residual COIs after the oxidation reactions are complete. This combined remedy combines treatment mechanisms thereby allowing for more cost-efficient dosing of the product.

**BASELINE SAMPLING AND PERFORMANCE MONITORING GUIDELINES**

Following the addition of Provect-OX to an aquifer environment, a number of physical, chemical and microbiological processes combine to yield effective removal of targeted COIs. As outlined below, a combination of field measurements and laboratory analyses can be used to determine effectiveness of the processes on petroleum hydrocarbons (BTEX/TPH) and/or halogenated aromatic / aliphatic compounds such as chlorinated solvents (CHC) or organochlorine pesticides (OCPs).

Standard operating procedures for sampling and analysis should always be followed, including purging at least three well volumes in order to ensure collection of formation water. Monitoring wells must be free of sediment or other deposits which may contain precipitated heavy metals, and were prescribed sample filtering may be required.

### Field Parameters: Sampled Frequently

When treating BTEX/TPH, CHC and/or OCPs, field parameters (**Table 1**) are comparatively inexpensive measurements and can be collected on a frequent basis to monitor general progress. They are also useful in assessing general zone of influence and longevity of the added reagents. Baseline data are needed to compare to those collected during an injection event to help determine that the groundwater is influenced by Provect-OX (zone of influence). For example, elevated levels of Fe are expected following Provect-OX emplacement.

**Table 1. Field Parameters for Routine Monitoring during Provect-OX™ Applications.**

Field Parameter	Analytical Method	Desired Range	Data Use
<b>pH</b>	Field probe	Short-term pH <4 to 6 Long-term pH = 6 to 8  Outside the immediate treatment zone, acid conditions can impede microbiological activity and yield secondary plumes	Production of sulfuric acid from persulfate (sulfate + water) will occur. With persulfate doses of around 5-10 g/kg in soils, the pH drop is usually <2 units due to soil buffering. However, in water with low alkalinity - or with poorly buffered or already acidic soils - local, transient pH decreases as low as pH<2 can occur. Buffers such as MgO, MgO <sub>2</sub> or lime can be applied, as needed. As biological reduction of sulfate occurs, hydrogen ions are consumed and the pH will increase.
<b>Turbidity (nephelometric)</b>	Field probe	Generally <1 NTU, or site specific standards	Excessive turbidity compromises data; indicates need for filtration; Gas bubbles (CH <sub>4</sub> /H <sub>2</sub> S) can cause high readings
<b>Water Level</b>	Field probe	+/- 50% baseline readings	Notable variations can indicate change in contaminant loading rates and are useful in interpreting COI data
<b>Water Temperature</b>	Field probe	+/- 50% baseline readings	Notable variations can indicate change in contaminant loading rates and are useful in interpreting COI data. Minimal temperature increases, if any, result from the application of Provect-Ox.
<b>DO/ORP or Eh (see equipment footnote below)</b>	Field probe (correct for SHE, if required; ORP + 200 mV = Eh)	Short-term > +200 mV Long-term < -50 mV	Rapid increase in redox should be observed in the zone influenced by the ISCR reagent; Field ORP values >+600 mV have been observed.
<b>Well head gases CH<sub>4</sub>, CO<sub>2</sub>, H<sub>2</sub>S, O<sub>2</sub>, [N<sub>2</sub>] (see equipment footnote below)</b>	GEM2000, GEM 5000, biogas5000, TVA2020 Total gas analyzers	< 5% H <sub>2</sub> S	Excessive gas production generates pressure which can exacerbate surfacing issues and represent potential health and safety problems. Generally only an issue at sites with high source area contaminant concentrations.
<b>Ferric Iron</b>	chemetrics.com/Iron	>200 mg/L for activating chemistry  >20 mg/L for sustained bioremediation	National Secondary Drinking Water Standard for iron is 0.3 mg/L, as iron concentrations in excess of 0.3 mg/L impart a foul taste and cause staining.
<b>Residual persulfate</b>	Test kits – contact us  Ferric thiocyanate based reactions are complicate but the presence of ferric oxide (red color) as the activating chemistry	Variable	Quantitative determination of persulfate concentration can be achieved by adding a known amount of Fe (II) to a sample. Persulfate anion will oxidize divalent iron Fe(II) to form trivalent iron Fe(III). Remaining Fe (II) is then titrated with either a known concentration of potassium permanganate (KMnO <sub>4</sub> ) to a pink end-point or ceric sulfate [Ce(SO <sub>4</sub> ) <sub>2</sub> ] to a Ferroin. indicator end-point, resulting in a color change from orange to clear or light blue

- <http://www.ysi.com/media/pdfs/T608-Measuring-ORP-on-YSI-6-Series-Sondes-Tips-Cautions-and-Limitations.pdf>
- Thermo/Foxboro TVA-1000B PID/FID Analyzer (PID sensitive to 2,000 ppm CH<sub>4</sub>; FID sensitive to 50,000 ppm CH<sub>4</sub>) and a LandTec GEM5000 Landfill Gas (LFG) Meter (infrared detector calibrated to 15% methane).
- Equipment purchase see <http://diamondsci.com> Equipment rental options see <http://www.fieldenvironmental.com>
- What about down-gradient ferrous iron and sulfide?

**Critical Parameters: Sampled Quarterly, or as Prescribed**

Critical parameters (**Table 2**) are initially used to assess the general applicability of an ISCO approach, and they establish an important baseline for subsequently measuring technology effectiveness. Groundwater samples should be collected according to standard protocols (trip blanks, field blanks) and shipped under proper conditions (preservatives, proper containers, chain-of-custody) to an analytical laboratory for timely analysis.

**Table 2. Critical Parameters for Monitoring Provect-OX™ Applications.**

Critical Parameter	Analytical Method	Data Use
<b>Anion Scan – chloride, sulfate, sulfide, sulfite, nitrate, nitrite</b>	US EPA 300	Indicates presence of potential ISCO reagents by-products and sustained microbiological activity
<b>Cation Scan - calcium, magnesium, potassium, sodium</b>	US EPA 200.7	Baseline values help determine reagent requirements.
<b>Total Organic Carbon, TOC</b>	SW846 9060 US EPA 415.1 / 415.2	Changes over time indicate presence of ISCO reagents, and are used to help document long-term effectiveness (biotransformations).
<b>RCRA Metals - DISSOLVED (include iron, calcium, magnesium, manganese. Hg optional)</b>	SW846 6010B 0.45 micron filtered, no preservatives	National Secondary Drinking Water Standards: <ul style="list-style-type: none"> <li>• Fe = 0.3 mg/L due to taste and staining</li> <li>• SO4 = 250 mg/L due to taste</li> <li>• Na is on the US EPA's Candidate Contaminant List (CCL)</li> </ul>
<b>RCRA Metals - TOTAL (include iron, calcium, magnesium, manganese. Hg optional)</b>	SW846 6010B	
<b>Total Iron</b>	US EPA 200.7	
<b>Other heavy metals – DISSOLVED AND TOTAL</b>	Arsenic 200.9/200.8 Cyanide 335.4/9010 Lead 200.9/200.8 Mercury 7470A Nickel 200.9/200.8 Cr	As determined necessary based on site-specific conditions
<b>ORGANIC CONTAMINANTS</b>		
<b>VOCs (if present) (chlorinated solvents, BTEX, MTBE, 1,2-DCA etc)</b>	SW846/ 8260B	Baseline values help determine reagent requirements.
<b>SVOCs (if present)</b>	SW846/ 8270B	Changes over time help document effectiveness (short term ISCO responses; sustained secondary bioremediation).
<b>TPH (if present) GRO, DRO, ORO</b>	SW846/ 8015B	Short-term increases in COIs is often observed immediately following subsurface injection events due to physical disruption of
<b>EDB (if present)</b>	SW846/ 8011	
<b>OCPs (if present)</b>	Method?	

**Non-Critical Parameters: Sampled Quarterly, or as Needed**

Various non-critical parameters are optional, but they provide general information about the soil and water chemistry that may be useful when analyzing and interpreting performance monitoring data. However, baseline measurements are needed in order to make best use of these complementary data.

**Table 3. Non-Critical Parameters for Monitoring Provect-OX™ Applications.**

Non-Critical Parameter	Analytical Method	Data Use
Microbial counts and activities	various	See <a href="http://www.microbe.com/">http://www.microbe.com/</a>
Biological Oxygen Demand, BOD 5 day	SW 846 5210B	Indicator of microbiological activity
Chemical Oxygen Demand, COD	US EPA 410.4	Indicator of redox and oxygen demand
Bicarbonate 2310B	Bicarbonate 2310B	Indicates microbiological activity – buffering capacity
Total Dissolved Solids (TDS)	SW846 2540C	Can indicates presence of reagents and microbiological activity
Hardness	US EPA 2340B	
Alkalinity	SW846 2310B US EPA 310.1	

**RESOURCES – DESIGN, MATERIAL HANDLING, COMPATIBILITY & SAFETY GUIDELINES**

General overviews of persulfate chemistry and other oxidants can be found at the links below:

- <http://www.chem.unep.ch/irptc/sids/OECD/SIDS/Persulfates.pdf>
- [https://clu-in.org/conf/itrc/advisco\\_092005/prez/ITRC\\_ISCO2\\_080305ibtbw.pdf](https://clu-in.org/conf/itrc/advisco_092005/prez/ITRC_ISCO2_080305ibtbw.pdf)

Design/application guidance documents can be found at the links below:

- [http://www.epa.gov/ada/gw/pdfs/insituchemicaloxidation\\_engineering\\_issue.pdf](http://www.epa.gov/ada/gw/pdfs/insituchemicaloxidation_engineering_issue.pdf)
- <http://www.itrcweb.org/Guidance/GetDocument?documentID=45>

An example of a very thorough, well-written, informative Work Plan for unactivated persulfate-based ISCO project can be found at the link below:

- [http://yosemite.epa.gov/R10/CLEANUP.NSF/6d62f9a16e249d7888256db4005fa293/25e3e8edb66bd9a688257142006a3860/\\$FILE/arkema%20Complete%20Final%20Persulfate%20IRM%20WP%20070705.pdf](http://yosemite.epa.gov/R10/CLEANUP.NSF/6d62f9a16e249d7888256db4005fa293/25e3e8edb66bd9a688257142006a3860/$FILE/arkema%20Complete%20Final%20Persulfate%20IRM%20WP%20070705.pdf)

**CONTACT US FOR A COMPLIMENTARY SITE EVALUATION**

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