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INTEGRATED TECHNOLOGIES

Provect-OX® is a dry powder containing 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 or liquids. Ferric iron can safely activate persulfate which quickly yields sulfate- and ferrate-radicals to effectively oxidize chlorinated solvents, petroleum hydrocarbons and other organic compounds such as pesticides in soil, sediment and groundwater. Importantly, the process also enhances subsequent utilization of sulfate and iron as terminal electron acceptors for facultative redox reactions for improved biodegradation of any residual COIs. This combination of chemical and biological treatment mechanisms allows for more cost-efficient dosing of the product while supporting long-term, sustained, secondary bioremediation processes to manage residuals and prevent contaminant rebound (COI rebound is a common problem encountered with conventional ISCO technologies).

Compared to other methods of stimulating secondary biodegradation processes using oxygen release compounds (such as calcium or magnesium oxyhydroxide), iron materials remains in place and active for many years. Additional benefits include:

- Does not generate excessive heat / off-gases
- Safe to Apply (no secondary containment)
- Easily Handled - All in one bag
- Enhances bioattenuation using Fe + SO₄
- Encourages the Formation of Pyrite which
 - Minimizes H₂S Formation
 - Minimizes Heavy metal mobilization
- No extreme activation chemistries (pH 12 base activation)
- Uses Fe⁺³ as activator = Conserves Oxidant compared to EDTA
- Formation of Reactive Ferrate Species increases reactivity*



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>

Fenton's

- Treats wide range of contaminants
- Short subsurface lifetime
- Difficult to apply in reactive soils

Persulfate

- Treats wide range of contaminants
- Sulfate radical forms slower than the hydroxyl radical, allowing a larger radius of influence

Provect-OX

- Generates Ferrate (Fe IV, V, VI possible)
- Treats wide range of contaminants
- Extended *in situ* lifetime w/ continual production
- Avoids Rebound

Ozone

- Treats wide range of contaminants
- Short subsurface lifetime
- Limited use in saturated zone

Permanganate –

- Treats limited range of contaminants
- Partial oxidation of TPHs, etc
- Long subsurface lifetime
- Potential effects on hydrogeology

CASE STUDIES

Shallow, unsaturated clayey soils at two sites in the Midwest USA were contaminated by organic contaminants. Site “A” (Mendota, a manufacturer of tractor components, specifically for the farming industry) had an estimated 500 tons of soil containing mixed petroleum and chlorinated solvents, exceeding soil saturation limits in many cases (PCE > 35,000 ppm, toluene > 4,000 ppm); the remedial goals were to reduce concentrations below soil saturation limits, calculated to be approximately 2,000 ppm for PCE and 1,000 ppm for toluene. Site “B” (LaSalle, a copper wire and cable manufacturer) had an estimated 250 tons of impacted soil representing a source of vinyl chloride in groundwater at about 1 mg/L (remedial goal was < 0.04 mg/L). Active facility operations were present at both sites, hence the remedial objectives were to rapidly reduced COI concentrations 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, and – importantly - a one-time application event to minimize disruptions to facility operations.

IMPLEMENTATION

Site A Mendota: November, 2015 Provect-OX was applied via direct soil mixing

- 12,100 lbs Provect-OX
- 15 g /kg soil
- 5 day application period
- RAO <Target Csat Soil
 - PCE < 2,420 (above 1m)
 - PCE <1,254 (below 1m)
 - Toluene < 1,654



Site B LaSalle: April 26, 2016 Provect-OX was applied via direct push injections



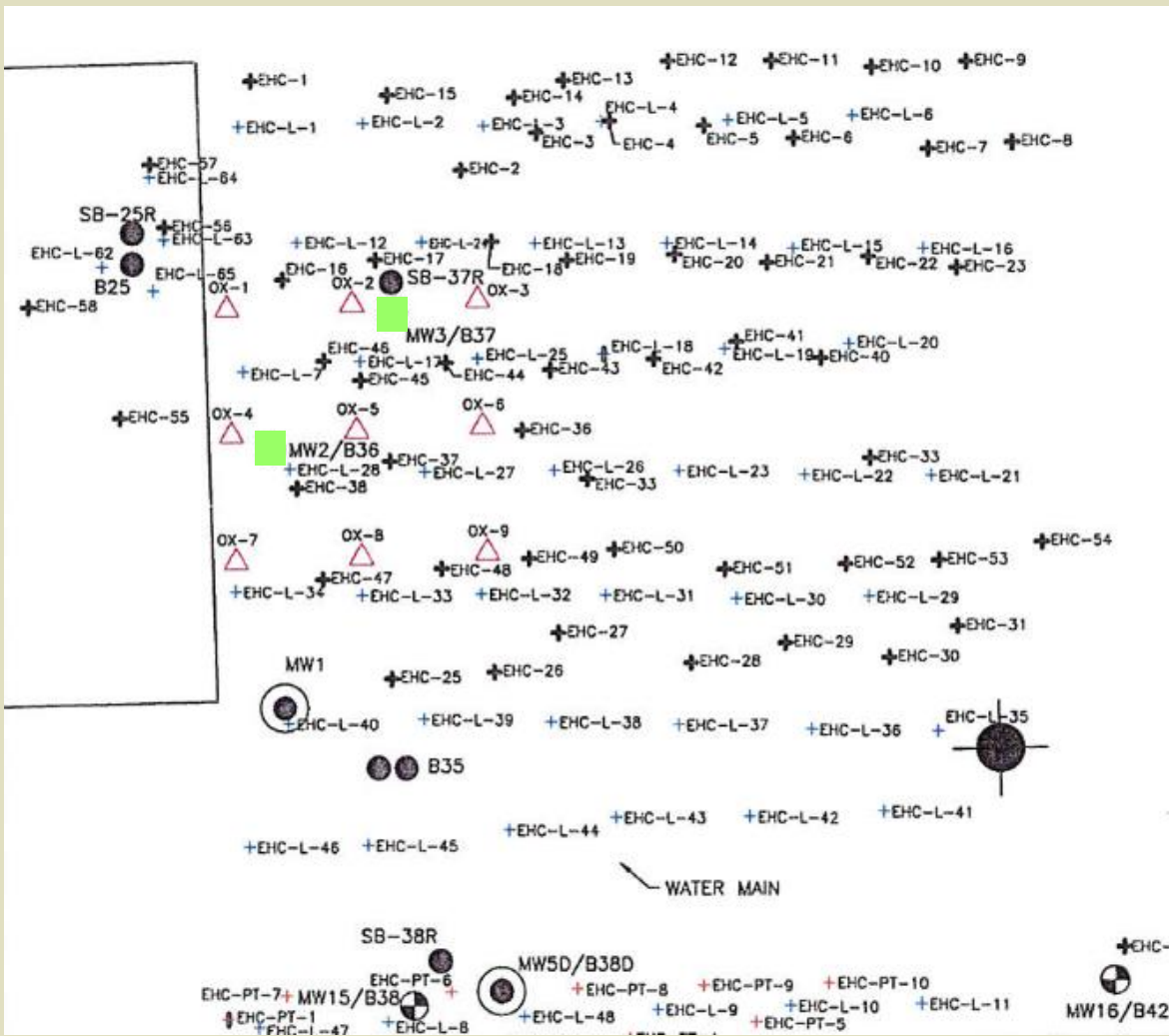
- 2,700 lbs Provect-OX
- 9 direct push points
- 10 ft apart
- Each point received 60 USG water containing 30 lbs Provect-OX (0.5 % slurry)
- Targeted interval 14 to 19 ft bgs
- Injection pressure <50 psi
- Flow rate estimated 1 to 3 gpm
- RAO = VC groundwater < 0.04 mg/L

RESULTS

Site A Mendota: Post-remedial monitoring showed sustained removal of mixed PCE and toluene constituents to levels well below soil saturation limits. For instance, illustrated in the table below are maximum locations in soil exceeding soil saturation limits. After application of Provect-OX, PCE concentrations declined by two orders of magnitude while toluene was non-detect.

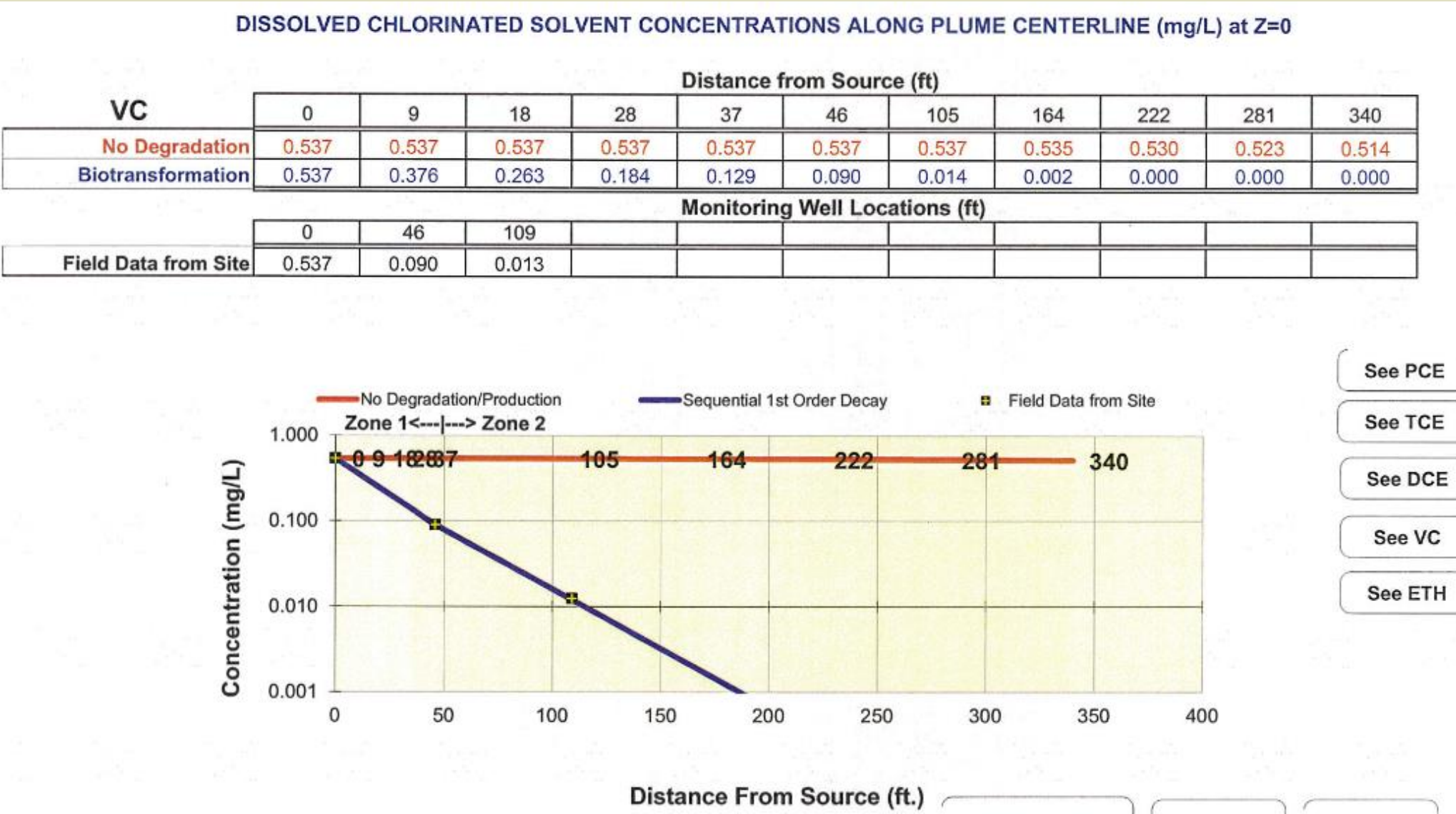
Site	Starting COI Concentration (ppm)	Ending COI Concentration (ppm)	Treatment Time
A	38,000 PCE 4,000 Toluene	< 900 PCE < 100 Toluene	1 week

Site B LaSalle: Initial remedial actions entailed 1,850 lbs EHC® (+) in 2008 followed by 17,200 lbs EHC (+) in 2010 then 550 USG of EHC-L (+) in October, 2011. By April 2016, the concentrations of VC and other site COIs were back to pre-treatment levels. Provect-OX (Δ) was applied proximal to MW-2 (■) and MW-3(■). Organic carbon present in the system from the previous remedial efforts minimized the effects of the oxidant. Nevertheless, 2,700 lbs Provect-OX rapidly reduced VC by >70% and established aquifer conditions that support natural attenuation.



Site	Starting COI Concentration (ppm)	Ending COI Concentration (ppm)	Treatment Time
B	0.7 mg/L VC	0.2 mg/L VC	< 2 days

Specifically, DO/ORP increased significantly (>5 ppm DO) at both MW-2 and MW-3. Coupled with vinyl chloride mass reduction, this induced aerobic zone quickly reduced modeled downgradient migration potential from >1,000 ft to *ca.* 130 feet. The migration potential increased slightly to 170 ft in 2017, but this remains below the site specific value of < 340 feet to support monitored RNA.



CONCLUSIONS

Amendment Costs: Site A: ~ \$60,000. Site B: ~\$30,000

No Rebound: A Single application of Provect-OX remained active with secondary bioremediation managing COI rebound at both sites