

LABORATORY EVALUATION OF Provect-OX™ SELF-ACTIVATING ISCO / ENHANCED BIOREMEDIATION REAGENT

Objective. Evaluate the performance of *in situ* chemical oxidation (ISCO) / Enhanced Bioremediation using Provect-OX reagent to reduce the concentration of volatile organic compounds (VOCs) in soil, sediment and/or groundwater, as noted in **Attachment 1**. Please contact us if an alternate analytical program is desired. The study can entail short-term or longer-term evaluation as summarized below.

Sample Requirements. The client will collect and ship a minimum of soil/sediment (3 kg per sample location) and/or groundwater (9 L per sample location) to the ReResolution Partners laboratory at:

967 Jonathon Drive

Madison, WI 53713

Attn: Kevin Baker, Laboratory Manager

Telephone: (608) 669-6949 / Email kbaker@resolutionpartnersllc.net

Please contact ReResolution Partners for assistance with sample containers and shipping details.

Baseline Characterization. The baseline characterization consists of the following tasks:

- Soil homogenization
- Compositional analysis of COIs (mg/kg)
- Analysis of COIs in groundwater (mg/L)
- Soil 48 hour Total Oxidant Demand (TOD) using the Provect-OX Reagent

Per **Attachments 2a/2b**, determine the TOD using either the back titration method and/or the rapid spectrophotometric method¹.

¹ Liang, Chenju, et. al. A Rapid Spectrophotometric Determination of Persulfate Anion in ISCO. Elsevier Ltd. Chemosphere 73 (2008). pp 1540-1543.

Short-Term ISCO Treatability Study. Provect-OX will be used as the oxidant reagent in all trials. Based on the results of the TOD analysis above, three dosage rates of Provect-OX will be tested (*i.e.*, 0.5x, 1x and 2x TOD) alongside an untreated control. Testing will be conducted in 125 mL glass VOA vials. Soil and groundwater from the site will be used to achieve a water:soil ratio of 1 part water to 1 part soil by weight (approximately 60 grams soil and 60 grams groundwater). A total of 40 VOA vials will be prepared for duplicate analysis of an unamended control and 3 treatments at Days 0, 2, 5, 10 and 15. The vials will be incubated in the dark at room temperature and inverted once per day. After each of the five designated reaction periods, 8 samples (duplicates of 3 treatments and 1 control) will be analyzed for the site-specific VOCs by headspace GC/PID using Henry's Law to estimate aqueous concentrations and measured for pH at each event. Residual persulfate assays will be completed once the VOC and pH analyses are completed on Days 0, 2, 5 and 10. Once the VOC samples have been collected on Day 15 the groundwater will be analyzed for pH, ORP, iron (ferrous and total), sulfate and residual persulfate.

At each sampling point, the Provect-OX Efficiency Number (PEN) can be calculated as follows: $PEN = \% \text{ contaminant destroyed} / \% \text{ Provect-OX consumed}$. PEN's > 1 indicate sufficient dosing; PEN's < 1 indicate under-dosing. Plotting the PEN versus time and dosage can aid in the selection of the most appropriate Provect-OX application rate.

OPTIONAL Longer-Term Combined Enhanced Bioremediation Treatability Study. In an effort to assess the enhanced bioremediation component of the Provect-OX process, the Short Term ISCO study above will be expanded by preparing 24 additional reaction vials on Day 0 to accommodate continued sampling². On the basis of the ISCO study Day 15 results, long-term reaction vials will be opened briefly to adjust the pH in the long-term reaction vials to near neutral pH with NaOH. The vials will be inverted once per day, sampled on Days 30, 45 and 60 and analyzed for COIs in groundwater to measure any COI loss over time. Once the COI samples have been collected on Days 30, 45 and 60, the groundwater will be analyzed for pH, ORP, iron (ferrous and total), sulfate and residual persulfate. PENs will again be determined for each reaction period.

The results of the baseline characterization and treatability study will be transmitted to the client for review prior to report finalization.

² This requires that the option be selected prior to the start of the treatability study.

Price.

The testing described in this proposal will be performed for a price ranging from \$10,300 for the short term study to \$15,800 for the long-term study.

Notices and Disclaimers

Any estimated dosage or recommended application methods are based on the site information provided by others, and they are not meant to constitute a guarantee of field performance. We recommend that a comprehensive remedial design take the precise nature of the COI impact and actual site conditions into consideration.

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Attachment 1

Screening-Level GC-PID/FID Analytes

Updated February 2015

Chlorinated Ethenes	Aromatic Hydrocarbons
Tetrachloroethene	Benzene
Trichloroethene	Ethylbenzene
cis-1,2-Dichloroethene	Toluene
trans-1,2-Dichloroethene	m-Xylene
1,1-Dichloroethene	o-Xylene
Chloroethene	p-Xylene
	Naphthalene
Chlorinated Ethanes	1,2,4-Trichlorobenzene
1,1,2-Trichloroethane	1,4-Dichlorobenzene
1,1,1-Trichloroethane	1,3-Dichlorobenzene
1,2-Dichloroethane	1,2-Dichlorobenzene
1,1-Dichloroethane	Chlorobenzene
Chloroethane	Isopropylbenzene
Gases	Ketones
Ethene	Acetone
Ethane	2-Butanone (MEK)
Methane	2-Hexanone
	2-Pentanone
Ethers	4-Methyl-2-pentanone
Methyl tert-butyl ether (MTBE)	

Additional volatile organic compounds can be analyzed upon request.

Attachment 2a - Ceric Sulfate Back Titration Method

1. Add 10 g homogenized, COI-IMPACTED soil sample to 50 ml conical graduated centrifuge tube (VWR)
2. Dissolve 3.5 g Provect-OX in 700 ml groundwater (or DI water)
3. Add 30 g of solution to each centrifuge tube containing 10 g soil to yield 15 g Provect-OX/kg soil
4. Cap the vials. Shake the samples until thoroughly mixed and allow them to stand at ambient temperature on a bench top. Shake each reaction centrifuge tube at least once/day.
5. Analyze replicate (n=3) samples at time zero and after 48 hours as follows:
 - a. Centrifuge the reaction tubes and transfer the aqueous layer to 400 ml glass beaker containing about 25 ml of dilute H₂SO₄ (4N).
 - b. Thoroughly wash the soil phase twice with DI water (20 mL each time), vigorously shake the reaction tubes and centrifuge: combine aqueous phases.
 - c. Analyze for unreacted Provect-Ox Reagent via titration of a 0.1N Ceric Sulfate (known normality with Ferroin indicator) with a standardized Ferrous Ammonium Sulfate (FAS) solution (known normality) by the back-titration method.
 - d. Add ca. 25 ml of 4N H₂SO₄ to the combined aqueous extracts in 400 ml glass beaker from step (B).
 - e. Add 10 ml 0.25 N (FAS) to the acidified extract.
 - f. Titrate the residual FAS with 0.1N Ceric Sulfate solution.
 - g. Record the volume of titrant used. Perform replicate (n=3) blank titrations of FAS (10 ml) from same stock with Ceric Sulfate solution and record the volume of titrant used.

$$\text{Residual Provect-OX Reagent} = \text{Vol. (ml) Blank} - \text{Vol. (ml) Sample} \times \text{Normality of Ceric Sulfate} \times 0.12$$

Attachment 2b - Rapid Spectrophotometric Method

Prepare the TOD extract following the steps 1 through 5 above. Also include an unamended (control) sample.

Each sample extract or standard will be analyzed by first placing 1 mL of KI/NaHCO₃ solution (KI =1g/mL, NaHCO₃ =50g/L) in an empty 10 mL cuvette. Then add 9 mL of the sample/standard. Gently swirl the cuvette. Allow the standard/sample to equilibrate for 15 minutes.

Perform a calibration of the spectrophotometer using a series of dilutions on a stock sodium persulfate standard solution to produce 7 standards between 0.05 and 60 mg/L sodium persulfate. Generate a standard curve for 352 nm and 400 nm wavelengths.

Since this is a colorimetric method, any background color may interfere with the analysis. If any sample extracts (amended or unamended) have any color (even slight), perform a background check to identify potential interferences for both wavelengths. Calculate a background correction within the range of the wavelength curve as appropriate or use the unamended extract to zero the instrument. Highly colored sample extracts may not allow the use of the spec method.

Read the samples on the spectrophotometer and use the calibration curve for the respective wavelength and any determined background correction to determine the residual persulfate in the sample. Calculate the residual persulfate in the reacted soil sample.

TOD (g/kg) = persulfate dose – residual (measured) persulfate in soil