

Advantages of a New Catalyzed Persulfate Technology in the Laboratory and at Field Scale

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Abstract

An improved persulfate-based *in situ* chemical oxidation (ISCO) process has been developed for the treatment of contaminated groundwater and soil. This catalytic oxidation process is based on a mixture of sodium persulfate (Na₂S₂O₈) with a silica-based catalyst that allows for pH-independent destruction of contaminants. In addition, the catalyst is not consumed in the oxidation process, and remains active for the life of the persulfate oxidant.

Fundamental laboratory studies demonstrated the catalyzed persulfate (commercially known as PersulfOx) is effective on a wide range of contaminants including petroleum hydrocarbons, chlorinated solvents, and oxygenates, such as 1,4-dioxane. All contaminants studied were degraded by 88% or more when treated with silicacatalyzed persulfate for a duration of 7 days (Table 1). Catalyzed persulfate can be applied as a single powder mixture, simplifying field application and reducing health and safety concerns.

PersulfOx Attributes

- Promotes rapid and sustained *in situ* oxidation of a wide-range of organic contaminants
- Provides a unique catalytic surface on which oxidants and contaminants react in a process known as "surface mediated oxidation"
- Contains built-in activation which eliminates complex and potentially hazardous chemical addition required to achieve traditional persulfate activation
- Fewer health and safety concerns than with use of traditional activation methods such as heat, chelated metals, hydrogen peroxide or base
- Single component product results in simplified logistics and application. No additional containers and/or multi-step mixing ratios required prior to application
- Contaminant oxidation performance equivalent to best alternative persulfate activation methods

Table 1. Chemical Oxidation Data, 7 Days

Contaminant	Starting Concentration (mg/L)	Final Concentration Control (mg/L)	Final Concentration PersulfOx (mg/L)	% Removed vs. Control
BTEX	232	204	7	96%
trichloroethene (TCE)	226	144	< 1	> 99%
1,4-dioxane	175	105	< 1	> 99%
1,2-dichloroethane (DCA)	101	87	< 10	> 88%

Lab Experiment Details and Procedures

For each contaminant test: A contaminant stock solution was prepared in distilled water to deliver between 100 mg/L and 250 mg/L of a given contaminant into the test vials. A stock mixture of PersulfOx (1.0 M as sodium persulfate) was also prepared in distilled water. A control condition and a PersulfOx-treated condition were run in parallel for each study, and these conditions were run in triplicate. For the test 10 mL of the contaminant stock solution and 10 mL of the PersulfOx mixture were added to each vial yielding a final persulfate concentration of 0.5 M. For each control vial, the 10 mL of the contaminant solution was combined with 10 mL of distilled water. The vials were then stored in the dark at room temperature. After 7 days, the contaminant concentrations in water were measured.

The data are reported in Table 1, as averages of the triplicate samples. The data demonstrates the efficacy of PersulfOx for oxidation of common classes of organic groundwater contaminants: hydrocarbons, chlorinated ethenes, chlorinated ethanes, and oxygenates. PersulfOx is widely applicable to treat a range of organic contaminants, and provides significant safety, convenience, and efficacy benefits in comparison with other persulfate activation technologies.

PersulfOx Catalysis

PersulfOx is an *in situ* chemical oxidation reagent that destroys organic contaminants found in groundwater and soil through powerful, yet controlled chemical reactions. PersulfOx is a sodium persulfate-based technology which employs a patented catalyst to enhance the oxidative destruction of both hydrocarbon and chlorinated contaminants in the subsurfaces. Traditionally, sodium persulfate is activated with the addition of heat, chelated metals, hydrogen peroxide or base in order to generate sulfate radicals (Table 2). These activation processes are inherently complex, costly and can pose additional health and safety risks. In comparison, PersulfOx is a relatively safe and easy-to-use ISCO agent.

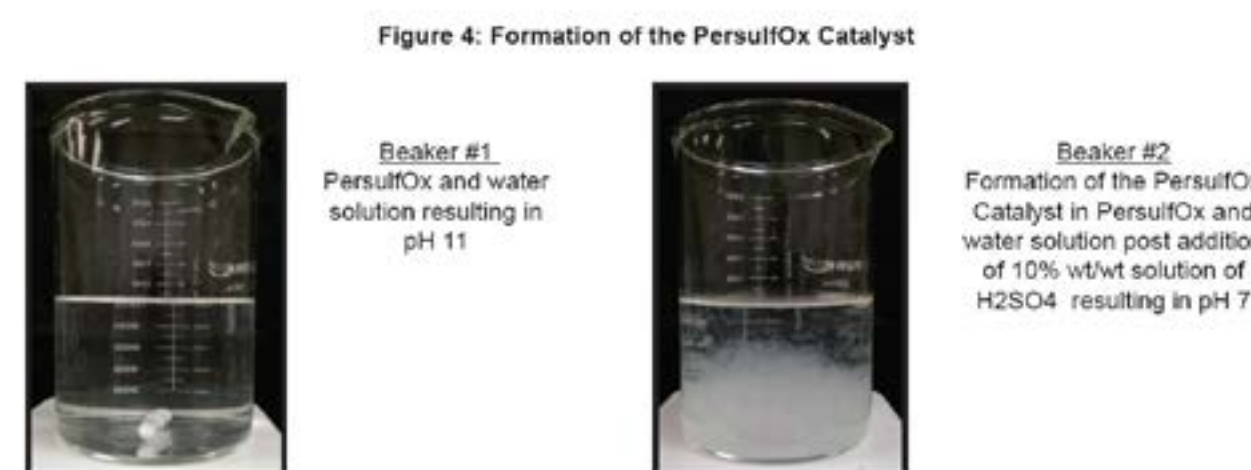
PersulfOx contains a built-in catalyst which activates the persulfate component and generates contaminant destroying free radicals without the need for the addition of a separate activator. The PersulfOx catalyst effectively facilitates oxidation of a wide range of groundwater and soil contaminants. Catalytic oxidation by PersulfOx is persistent over time, as the catalyst is reusable and not depleted in the subsurface over many oxidation cycles. In contrast, alkaline activation is subject to the limitations of stoichiometric activation. The combination of high buffering capacity in soils and the depletion of hydroxide activator over time can limit the ability to establish and maintain necessary pH conditions for contaminant oxidation. The table below summarizes some of the attributes discussed here for each ISCO persulfate activation technology.

Table 2. Comparison of Persulfate Activation Technologies

Activation Technology	Reactive Species				Contaminants Treated						
	Sulfate Radicals	Other Oxygen Radicals	Cost Prohibitive	Catalytic	Sacrificial	Aliphatic Hydrocarbons (TPH)	BTEX	Chlorinated Ethenes	Chlorinated Ethanes	Oxygenates	
PersulfOx	✓	✓		✓		✓	✓	✓	✓	✓	
Heat	✓	✓	✓			✓	✓	✓	✓	✓	
Alkaline	✓	✓			✓	✓	✓	✓	✓	✓	
Chelated Iron	✓	✓		✓		✓	✓			✓	
Hydrogen Peroxide	✓	✓			✓	✓	✓	✓	✓	✓	

Completely Soluble Alkaline Solution

PersulfOx is available as a pre-mixed single component product. Most applications of the product call for it to be mixed with water to a concentration range of 10% to 20% w/w. The mixture is completely soluble at standard temperature and pressure. In the field, mixing time may vary with water temperature and hardness, in some cases requiring several minutes of vigorous mixing to attain complete solution. The resulting mixture has a pH >11.



As mentioned above, if the pH of the system drops into the neutral range, alkaline activation will drop off and radical propagation slows. The PersulfOx product, once in this pH range forms a colloidal amorphous silica catalyst which serves to bind both the contaminant and other metal/metal oxide species upon its surface. This suspended colloidal silica complex can then serve as a heterogeneous catalyst mediating surface reactions between the target contaminants and persulfate.

Representative Field Studies

Former Printing Site, Georgia

The site housed a printing and lithography operation for approximately 10 years. Contaminants of concern included PCE and TCE with concentrations exceeding notification criteria at depths of 15 and 20 feet below ground surface. The estimated size of the contaminated area was 200 square feet. Product application included two injection events occurring approximately two months apart, with each application event delivering 165 lbs. of PersulfOx (100 gallons of 20% solution) into four direct-push injection points.

Results

- Overall total VOCs were reduced by 99% and 98% in the treatment zone area with PCE reduced from 325 µg/kg to 0.5 µg/kg and TCE from 1,130 µg/kg to 17 µg/kg
- Site closure is pending

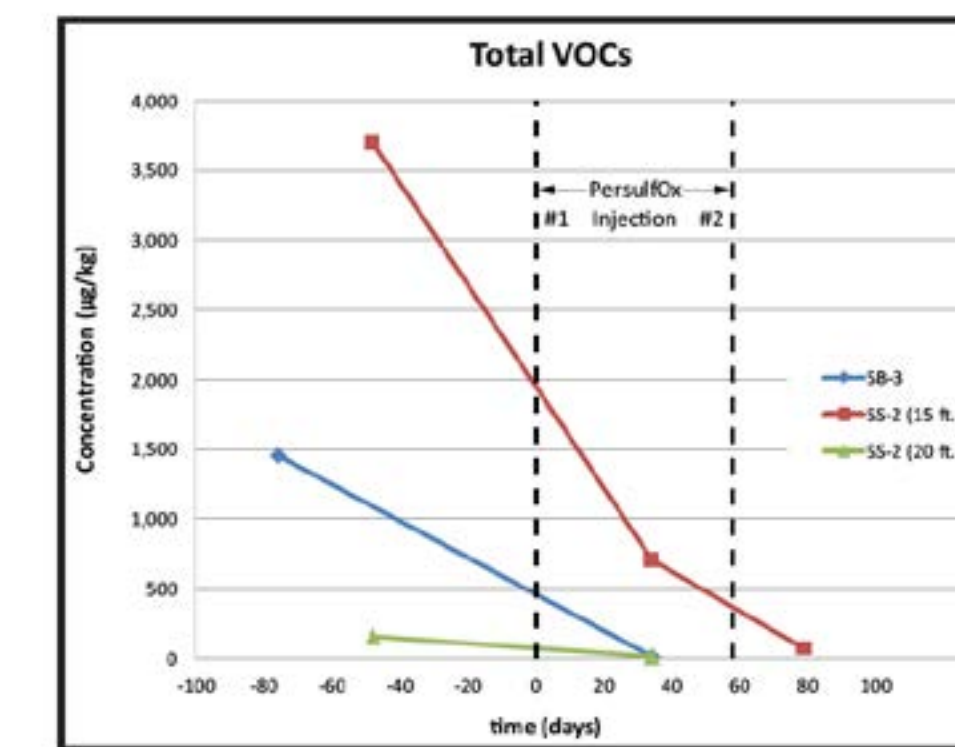


Figure 1. VOC Concentrations in Soil

Tanker Truck Rollover Gasoline Spill, Oklahoma

This site was contaminated as a result of a tanker truck rollover gasoline spill which impacted soil and groundwater. PersulfOx was delivered through five injection points within the treatment area.

Results

- After one month of treatment, reductions in the treatment zone ranged from 62-98% versus baseline concentrations
- The two month time point shows continued and effective treatment in MW-18 and OW-1 with slight increase in OW-2. This increase is likely attributed to influx of additional contaminant and/or desired desorption from soil

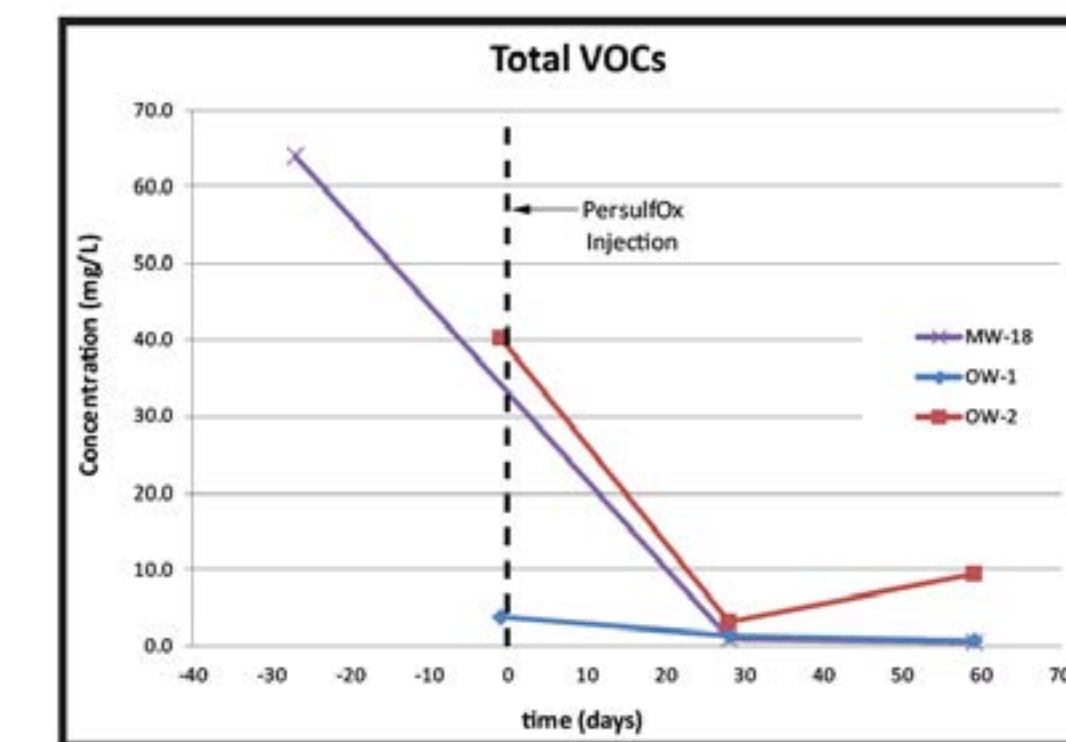


Figure 2. VOC Concentrations in Groundwater