



Advantages of the PersulfOx™ Catalyst

When combined with an appropriate activation or catalysis technology, sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$) is known to be an effective oxidant for organic contaminants in soil and groundwater. This *in situ* chemical oxidation (ISCO) process is chemically complex and can vary in effectiveness, ease of application, and safety profile depending on the activation technology selected. In addition, there are both catalytic and stoichiometric (sacrificial) methods of activating persulfate. This bulletin outlines the primary commercially-available activation technologies and distinguishes the advantages of using Regenesi's PersulfOx- a catalyzed sodium persulfate ISCO product.

PersulfOx™ Catalysis

PersulfOx is composed of the oxidant sodium persulfate, mixed with a patented silica-based heterogeneous catalyst for contaminant oxidation. The term "heterogeneous" refers to the fact that the catalyst is composed of microscopic solid particles rather than a dissolved species. Liquid-phase oxidation reactions are facilitated repeatedly on the surface of the catalyst. This catalyst is related to the RegenOx™ technology and has the ability to perform the following functions:

- Generates sulfate radical and other oxidizing species
- Adsorbs both contaminant molecules and oxidizing species on its surface to accelerate oxidation
- Catalyzes direct and free-radical-mediated oxidation of contaminants by sodium persulfate
- Is a true catalyst, and is therefore considered to be "green" under the USEPA Green Chemical definition

Alkaline Activation

The use of caustic sodium hydroxide is sometimes employed in field ISCO applications to activate sodium persulfate. Alkaline activation requires the pH of the aquifer to be maintained above pH 11, which can be challenging given the high buffering capacity of many soils and the generation of acids by persulfate oxidation. This method is a stoichiometric process by which hydroxide ions are consumed as sulfate radical and other oxidizing species are formed. Because of the sacrificial nature of alkaline activation, this process may deactivate as pH is lowered. There are also significant health and safety concerns surrounding on-site handling of 25% sodium hydroxide, a strongly caustic material.



Hydrogen Peroxide Activation

In this method of activation, hydrogen peroxide is mixed with sodium persulfate in water before injection into the subsurface. The mechanisms of this process are not well known, however it is postulated that soil minerals may play a part in hydrogen peroxide reactivity. In addition, the temperature increase associated with hydrogen peroxide decomposition may actually provide some thermal activation of the persulfate.

Hydrogen peroxide is an unstable and sacrificial activator which will be totally depleted in most sites within 1 to 2 days. In addition, the heat and gas pressure associated with hydrogen peroxide injection can present significant health and safety concerns as they have with traditional Fenton's ISCO applications.

Heat Activation

It is well known in the chemical and environmental literature that heating persulfate in water causes generation of sulfate radicals and aggressive promotes oxidation of most organics. However, in the remediation industry this has very little practicality due to the high costs of infrastructure and energy required to heat soil and groundwater in situ.

Chelated Iron Activation

Ferrous iron (Fe^{2+}) can react with sodium persulfate to generate sulfate radicals. This reaction is the basis for chelated iron activation – another commercially available method of persulfate activation for ISCO. The term “chelated” refers to the fact that the iron is stabilized by a ligand or “chelator”, usually an organic molecule like EDTA (ethylene diamine tetraacetate). The purpose of the chelation is to keep the iron in solution and allow continuous repeated activation of persulfate. Chelated iron is a catalytic activation technology.

There are a couple conceptual limitations to the chelated iron activation approach. Chelated iron has the ability to oxidize a limited range of contaminants. For example it is not effective for destruction of aliphatic hydrocarbons or chlorinated ethanes. In addition, the chelating agent is an organic compound that can be degraded by the activated persulfate. This can cause loss of efficacy over time.

Sacrificial Activation vs. Catalysis

There is an important distinction among persulfate activation technologies in that some are catalytic while others are stoichiometric (sacrificial). The following definitions are based in chemistry and the specific context of persulfate-based ISCO:



activation: *n.* the process of facilitating the oxidation of contaminants by persulfate. This is a general term that may refer to either catalytic or stoichiometric transformations.

catalysis: *n.* the process of facilitating the oxidation of contaminants by persulfate, specifically using a chemical (catalyst) that is conserved in the reactions. The catalyst is neither created or destroyed and can be recycled indefinitely. It is not depleted over time.

With these definitions in mind, one can see several advantages of a catalyst over a sacrificial activation technology. For example, regardless of how long the ISCO process takes in a given site, the PersulfOx catalyst will persist and be active toward contaminant and oxidant. In contrast, alkaline activation consumes hydroxide ions with each molecule of sodium persulfate activated. Over time the oxidation reactions can be inhibited by the absence of hydroxide ions and the corresponding drop in pH.

Conclusions

In summary, 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. Table 1 below summarizes some of the attributes discussed here for each ISCO persulfate activation technology.

Table 1. Comparison of Persulfate Activation Technologies										
Activation Technology	Reactive Species		Cost Prohibitive	Catalytic	Sacrificial	Contaminants Treated				
	Sulfate Radicals	Other Oxygen Radicals				Aliphatic Hydrocarbons (TPH)	BTEX	Chlorinated Ethenes	Chlorinated Ethanes	Oxygenates
PersulfOx™	✓	✓		✓		✓	✓	✓	✓	✓
Heat	✓	✓	✓			✓	✓	✓	✓	✓
Alkaline	✓	✓			✓	✓	✓	✓	✓	✓
Chelated Iron	✓	✓		✓			✓	✓		✓
Hydrogen Peroxide	✓	✓			✓	✓	✓	✓	✓	✓



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