

KLOZUR PERSULFATE OVERVIEW

Klozur[®] persulfate is a high purity environmental grade product used as an *in situ* chemical oxidation (ISCO) technology to treat a wide variety of contaminants of concern in soil and groundwater around the world. Klozur persulfate can be activated using PeroxyChem's patented technologies¹ to form the powerful oxidative and reductive radicals that aggressively treat targeted contaminants. This technology is well established having been successfully applied in thousands of field applications and scientifically validated in hundreds of independent peer-reviewed journal articles and conference presentations.

The Klozur persulfate portfolio includes several high purity products:

Klozur SP is based on sodium persulfate which is highly soluble and has been used for over a decade to treat contaminated source areas.

Klozur KP is based on potassium persulfate which has over an order of magnitude lower solubility than Klozur SP. This allows it to serve as an extended release oxidant to treat low permeable soils and in permeable reactive barriers.

Klozur CR provides a combined remedy of chemical oxidation and bioremediation. The product is a blend of Klozur SP and PermeOx[®] Ultra which is typically used to treat low to moderately contaminated site source zones and plumes.

CHEMICAL OXIDATION AND REDUCTION

Chemical oxidation is an abiotic process where thermodynamically powerful chemicals such as Klozur persulfate contact and oxidize, or take electrons from, other compounds. When completely oxidized by Klozur persulfate, organic contaminants of concern in soil and groundwater can be converted into end products such as carbon dioxide and water.

In contrast, a reductive process donates electrons to organic compounds. If enough electrons are donated to the organic compound, they will eventually become methane or ethane. While *In Situ* Chemical Oxidation (ISCO) is predominately an oxidative process, research has shown that properly activated Klozur persulfate can have both oxidative and reductive pathways², allowing Klozur activated persulfate to address compounds not normally treated by technologies that only employ an oxidative pathway.

TYPICAL COMPOUNDS TREATED WITH ACTIVATED PERSULFATE

Each Klozur product releases the persulfate anion (2.01 V) when placed in solution. The persulfate anion is a powerful oxidant that can be activated to form even more powerful oxidative radicals including the hydroxyl radical (OH•, 2.59 V), and sulfate radical (SO₄•-, 2.43 V) as well as the reductant superoxide (O₂•-, -0.33 V). With proper activation these different radical species allow for the creation of oxidative and reductive pathways in a single treatment system which gives activated Klozur persulfate the ability to treat virtually any organic contaminant of concern including:

- Petroleum hydrocarbons: benzene, toluene, ethylbenzenes, and xylenes (BTEX), polyaromatic hydrocarbons (PAHs), diesel range organics (DRO), and gasoline range organics (GRO)
- Energetics: Trinitrotoluene (TNT), RDX, etc
- Chlorinated solvents: trichloroethene (TCE), tetrachloroethene (PCE), carbon tetrachloride (CT), 1,1,1-trichloroethene (TCA), and others
- Chlorinated benzenes and phenols
- Pesticides: DDT, chlordane, heptachlor, lindane, etc



KLOZUR CR – COMBINED REMEDY OF CHEMICAL OXIDATION AND BIOREMEDIATION

Activated Klozur SP is a very effective technology for many recalcitrant compounds. However, contaminants may reside in low permeability zones or in down-gradient portions of plumes, where soil heterogeneity may make it difficult for any *in situ* technology to effectively and economically achieve remedial results. In addition, slow re-partitioning of contaminant from soils or bedrock may induce groundwater concentration re-bounding after the oxidant has been expended. As a result, multiple applications of the oxidant or soil blending may be required to improve contact with and treat the contaminant. Alternatively, aerobic bioremediation, enhanced through the slow release of oxygen via PermeOx Ultra, is effective for the treatment of BTEX, TPH, and other aerobically biodegradable contaminants. The slow release of oxygen from PermeOx Ultra allows for extended treatment longevity compared to typical chemical oxidation. This additional treatment time can help treat back diffusion of contaminants from difficult to contact areas or to achieve lower remedial goals. However, bioremediation of source zones and hot spots may be difficult; the high contaminant concentrations in these areas may be toxic to microbial populations. Moreover, treatment times are often lengthy due to the slow kinetics of mass transfer, making bioremediation unattractive for time sensitive remediation applications.

The combination of multiple technological approaches for challenging sites can take advantage of the strengths of each technology, thereby increasing the probability of success in meeting clean-up target goals. This has been accomplished with the blending of Klozur SP and PermeOx Ultra into a single product, Klozur CR, combining chemical oxidation and bioremediation remediation processes into a single product. This combines the strengths of chemical oxidation such as targeting hot spot and source zones, areas with significant contaminant mass, and the longevity of slow release PermeOx Ultra to stimulate aerobic bioremediation.. In addition Klozur CR can increase levels of natural organic matter by the partial oxidization of soil components and solubilization due to temporary elevation of the soil and ground water pH in excess of 10. It has been hypothesized^{3,4} that this increase in natural organic matter is beneficial to the nascent microbial population, increasing microbial density which can impact the rate of contaminant destruction.

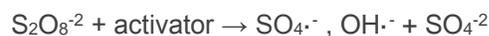
Klozur CR combines the speed and power of alkaline activated persulfate with the long-term efficiency of enhanced aerobic bioremediation. Initially designed for emplacement at the bottom of excavations to address residual contamination, Klozur CR is also injected as a slurry into subsurface formations. Klozur CR has been used for a variety of applications including treatment of BTEX and fuel oils contaminated soils and groundwater⁵ and for the destruction of pentachlorophenols and PAHs including naphthalene at a wood treating facility⁴.

KLOZUR CR MODES OF ACTION

Klozur CR attacks contaminants by promoting three modes of action: chemical oxidation, aerobic bioremediation, and anaerobic bioremediation.

1. Self-activating persulfate chemical oxidation

As with high pH - activated Klozur SP, Klozur CR will provide up to three months of chemical oxidation via persulfate chemistry.

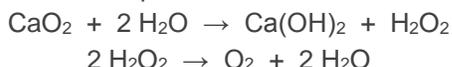


Klozur CR is self-activating, utilizing the alkalinity generated by the calcium peroxide to achieve a pH in the range of 11. In addition, calcium peroxide will slowly generate hydrogen peroxide (see the following section), allowing for peroxide activation of persulfate as well. High pH / peroxide activated persulfate can be used to treat BTEX, MTBE, polyaromatic hydrocarbons, petroleum hydrocarbons and chlorinated solvents, including PCE, TCE, DCE, TCA, DCA,

and vinyl chloride. As Klozur CR is self-activating, no additional activators or chemicals need to be added to the product for use in the field.

2. Enhanced aerobic bioremediation

Following the initial chemical oxidation phase, Klozur CR will continue to release oxygen for up to one year as a result of the slow hydration of the engineered calcium peroxide.



The resulting oxygen will provide electron acceptors for the bioremediation of BTEX, PAHs and petroleum hydrocarbons. Subsequent diffusion and transport of oxygen down-gradient will support contaminant reductions in plume zones, and will support biological polishing of low concentration contamination in the groundwater. Benefits of adding a slow-release oxygen source have long been demonstrated by the application of PermeOx Ultra at numerous sites.

3. Anaerobic bioremediation

The reaction of persulfate with organic compounds will generate sulfate ions. Sulfate reducing bacteria can utilize sulfate as an electron acceptor under anaerobic conditions to degrade BTEX, PAHs and petroleum hydrocarbons. As an example for benzene:



It is anticipated that sulfate-induced bioremediation may take place subsequent to the consumption of dissolved oxygen, and may support contaminant destruction in down-gradient contaminant plumes and polishing of low level contaminant residual.

KLOZUR CR PROPERTIES

As with PermeOx Ultra, Klozur CR is a sparingly soluble composition. As a result, the product needs to be applied in slurry form via emplacement (examples: bottom of tank pits and excavations and barrier walls), *ex situ* and *in situ* soil mixing or by direct push injection. No additional activation chemicals are required for this product. Only water is required to wet out contaminated soils and bring the oxidant in contact with the compounds of concern. Low concentration (1 wt%) slurries have had a pH of approximately 11, which will activate the persulfate. The typical active oxygen content of the Klozur CR is 11.3%.

CONCLUSIONS

Klozur CR is a treatment approach for contaminants of concern that combines the speed and power of chemical oxidation with the long-term performance of aerobic bioremediation. It can target both source zones and down-gradient plumes, capable of reducing high concentrations of contaminants and providing long-term polishing of low concentration residuals. It is easy to use, requiring no additional activation chemicals. Klozur CR can be utilized as a combined remedy for the treatment of BTEX, MTBE, PAHs and petroleum hydrocarbons, or as a high-pH activated persulfate system for the destruction of chlorinated solvents and pesticides. As a result, the Klozur CR can be readily applied to plumes with mixed petroleum and chlorinated solvents contamination.



1. A limited use license is included with the purchase of Klozur Persulfate for PeroxyChem's suite of national and international patents for the in situ activation of persulfate to remediate environmental contaminants of concern including, but not limited to US 6019548, US 6474908, US 7524141, US 7576254B2, and US 7785038.
2. Furman, O.S., Teel, A.L., and Watts, R.J. (2010) "Mechanism of Base Activation of Persulfate" Environ. Sci. Technol. 44, 6423-6428
3. M. Marley, et al. "A Case Study On Enhanced Reductive Dechlorination Resulting from a Chemical Oxidation Pilot Test". DNAPL-1 Conference, Sept 2006, Pittsburgh, PA.
4. J. Studer, et al. "An Innovative Couple Chem-Bio Treatability Study Leading to Large Scale Pilot Test at a Wood Treating Facility". Rem Tec 2007.
5. J. Studer, et al. "Design Considerations for Application of Klozur CR to Promote Sequential Chemical Oxidation and Oxidative Bioremediation". AEHS West Coast Soils Conference, March 2008, San Deigo, CA.

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