KLOZUR PERSULFATE

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 technologies[1] 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 pathways[2], allowing Klozur activated persulfate to address compounds not normally treated by technologies that only have the 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 (SO_4^{-}•, 2.43 V) as well as the reductant superoxide (O_2^{-}•, -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)
- 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
- Energetics: Trinitrotoluene (TNT), RDX, etc
- Emerging contaminants: 1,4-dioxane, PFOA, etc

ACTIVATION OF KLOZUR KP AND KLOZUR SP

Klozur KP and Klozur SP can be activated with one of PeroxyChem's patented[1] activation methods. These methods include heat, alkaline (high pH), iron-chelate, hydrogen peroxide, and zero valent iron (ZVI). To select the best activation method for your site, please contact your local PeroxyChem technical representative.

Heat, alkaline, and hydrogen peroxide activation methods are known to create both the oxidative and reductive pathways. Iron-chelate and ZVI activation of persulfate result in the oxidative pathway when activating persulfate; although ZVI could result in a reductive pathway independent of persulfate activation.

KLOZUR KP

Klozur KP is based upon the potassium persulfate (KP) molecule. Klozur KP dissolves in solution releasing the potassium (K^+) and persulfate anion. Klozur KP is different from Klozur SP in that it has relatively low solubility at typical aquifer temperatures and has potassium instead of sodium (Na^+) in its molecular structure. Klozur KP is an odorless dry white powder. The density of solid KP crystals is 2.48 g per cubic centimeter and the loose bulk density is approximately 1.30 g per cubic centimeter, as seen in Table 1.

The theoretical solubility of Klozur KP varies with temperature. In ranges typically found in the subsurface, the theoretical solubility of Klozur KP is approximately 17 g/L at 0°C (32°F), 29 g/L 10°C (50°F), and 47 g/L at 20°C (68°F). If Klozur KP is dosed above its theoretical solubility limit, it should dissolve over time to maintain concentrations close to its theoretical solubility limit. This creates an extended release potential, enabling Klozur KP to be used in permeable reactive barriers (PRBs); injected as a solid slurry to treat source zones, such as low permeable soils; used for *in situ* soil mixing; or at sites that have a limit on sodium concentrations in groundwater.

Klozur KP Physical Characteristics	
Formula	$K_2S_2O_8$
Molecular Weight	270.3
Crystal density (g/cc)	2.48
Color	White
Odor	None
Loose bulk density (g/cc)	1.30

Table 1. Physical characteristics of Klozur KP

Klozur KP Solubility		
Temperature °C (°F)	**Wt%**	**g/L**
0 (32)	1.6	17
10 (50)	2.6	29
20 (68)	4.5	47
30 (86)	7.2	74
40 (104)	9.9	109

Table 2. Solubility of Klozur KP as a function of temperature

EXTENDED RELEASE

Klozur KP can release the persulfate anion over an extended period of time when Klozur KP is dosed in quantities that exceed its theoretical solubility limit. In these situations the solid state Klozur KP will continue to dissolve into the system and can be expected to maintain a persulfate concentration near the theoretical solubility limit at the aquifer's temperature. A comparison of the extended release mechanism is shown below in Figure 1 for columns dosed with approximately 300 g of Klozur KP run at approximately 2°C and in Figure 2 at room temperature (20°C).

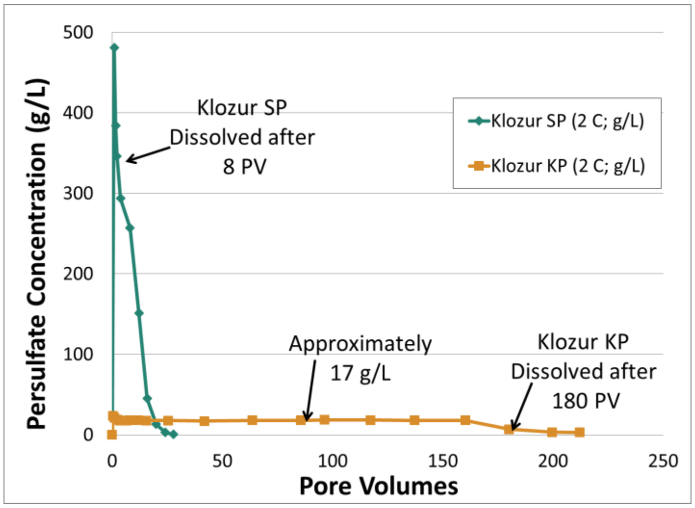

Figure 1. Klozur SP and Klozur KP sustained solubility as a function of number of pore volumes at 2°C

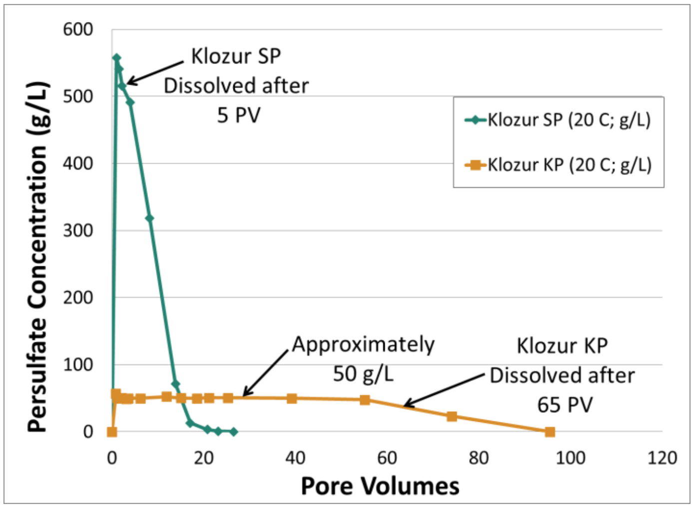

Figure 2. Klozur SP and Klozur KP sustained solubility as a function of number of pore volumes at 20°C

The data from the column studies show that the aqueous concentration of the persulfate anion from the Klozur SP systems is released quickly with the observed solid state Klozur SP disappearing after a few pore volumes of groundwater. In contrast, the systems dosed with Klozur KP steadily release persulfate at near the theoretical maximum of 17 g/L at 2°C and 50 g/L in the system held at room temperature (20°C). Because of the lower solubility, the Klozur KP persisted in the system for approximately 65 pore volumes at room temperature and approximately 180 pore volumes at 2°C.

In a controlled system shown above, the expected persistence of Klozur KP becomes a function of the initial mass of Klozur KP, ground water flux (cross sectional area times ground water velocity), and the solubility of Klozur KP which is a function of temperature.

Potential Persistence = (Initial Mass) / (Solubility x Groundwater Flux)

In actual field conditions it is expected that reactions with oxidant demand in groundwater and other non-target reactions could result in the actual persistence lower than projected by the above formula.

ESTIMATED PERSISTENCE OF KLOZUR KP IN A PERMEABLE REACTIVE BARRIER

When dosed above its theoretical solubility limit, solid state Klozur KP will persist and slowly dissolve maintaining aqueous phase concentrations at or near its solubility limit. Table 3 presents the potential persistence of Klozur KP for a unit area 1 foot (ft) high and 1 ft wide perpendicular to groundwater flow that is 3 ft deep, parallel to groundwater flow. Assuming that the PRB is filled with a 50 percent Klozur KP mixture with a dry bulk density of 90 lbs/ft^3 the 1 ft by 1 ft by 3 ft volume would contain approximately 135 lbs of Klozur KP.

This example shows that the Klozur KP could persist for several months to, potentially, up to several years depending on the groundwater flux and aquifer temperature. Assuming a groundwater velocity of 100 ft/yr at 10°C, the expected persistence of Klozur KP in this example would be 5 yrs, under theoretical conditions.

Bench scale tests and other methods to estimate the likely longevity of Klozur KP under specific site conditions are recommended. (See Appendix 1 for example in metric units of measure)

Conceptual Klozur KP Persistence (months)

	Temp (°C)	**5**	**10**	**15**	**20**	**25**
	Solubility (g/L)	**22**	**29**	**37**	**47**	**59**
Groundwater Seepage Velocity (ft/yr)	**10**	787	597	468	368	293
	25	315	239	187	147	117
	50	157	119	94	74	59
	75	105	80	62	49	39
	100	79	60	47	37	29
	500	16	12	9	7	6

Assuming: 1 ft by 1 ft unit area 3 ft deep; 135 lbs of Klozur KP; effective porosity of 15 percent, PRB filled with 50% Klozur KP and assumes fill at a dry bulk density of 90 lbs/ft^3.

Data represents potential longevity based on rate of dissolution only. Site specific factors such as reactions with target and non-target demand as well as persulfate decomposition are also expected to affect longevity.

Table 3. Conceptual persistence of Klozur KP as a function of temperature and groundwater flow

RECOMMENDED LOADING FOR KLOZUR KP

The extended release mechanism requires that Klozur KP be dosed above the solubility limit for the subsurface conditions that it will immediately contact. These conditions can vary depending on how Klozur KP was applied including emplaced (fractured) via injection, in a PRB, or through in situ soil mixing. For soil mixing and construction of PRBs, the maximum loading rate of Klozur KP is limited to approximately 80 lbs Klozur KP/ft^3, or 100 percent Klozur KP. For soil mixing and permeable reactive barriers, assuming a porosity within the soil matrix of 40%, PeroxyChem recommends a <u>minimum</u> loading of **<u>2 lbs Klozur KP/ft^3</u>**. Maximum and minimum loading for emplaced Klozur KP will be a function of site conditions. PeroxyChem recommends that you contact your local PeroxyChem technical representative to determine the appropriate loading rate of Klozur KP for your site. (See Appendix 1 for example in metric units of measure)

POTENTIAL APPLICATIONS

Klozur KP can be used under a variety of methods and manners. A few suggested by PeroxyChem include:

- As a permeable reactive barrier, as described above, can be activated with PermeOx Ultra blended along with the Klozur KP or zero valent iron (ZVI)* located in a separate permeable reactive barrier immediately down gradient of the Klozur KP. *NOTE: Klozur KP and ZVI should not be mixed together. Please contact PeroxyChem for more information.
- *In situ* soil mixing by itself or in combination with Klozur SP:
    - Blended with PermeOx Ultra, hydrated lime ($Ca(OH)_2$), quick lime (CaO), or Portland Cement.
    - Dropped through groundwater so that the lower soluble Klozur KP rests on top of a soil where it could be blended in or covered with fill material.
- Injected into lower permeable materials where the extended release could allow for longer contact time with contaminants.

Because of the lower solubility of Klozur KP, solid material should be expected with any application at injection concentrations above Klozur KP's solubility. In this situation, making sure that solid material can flow through the injection apparatus in critical.

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

APPENDIX 1: METRIC EXAMPLES

ESTIMATED PERSISTENCE OF KLOZUR KP IN A PERMEABLE REACTIVE BARRIER

When dosed above its theoretical solubility limit, solid state Klozur KP will persist and slowly dissolve maintaining aqueous phase concentrations at or near its solubility limit. Table 4 presents the potential persistence of Klozur KP for a unit area 1 meter (m) high and 1 m wide perpendicular to groundwater flow that is 1 m deep, parallel to groundwater flow. Assuming that the PRB is filled with a 50 percent Klozur KP mixture with a dry bulk density of 1,450 kg/m^3 the 1 m^3 volume would contain approximately 725 kgs of Klozur KP.

This example shows that the Klozur KP could persist for several months to, potentially, up to several years depending on the groundwater flux and aquifer temperature. Assuming a groundwater velocity of 30 m/yr and at 10°C, the expected persistence of Klozur KP in this example would be approximately 5 ½ years, under theoretical conditions. The overall duration of Klozur KP in the subsurface is expected to be less due to decomposition, and reactions with target and non-target demand.

Bench scale tests and other methods to estimate the likely longevity of Klozur KP under specific site conditions are recommended.

Conceptual Klozur KP Persistence (months)

	Temp (°C)	5	10	15	20	25
	Solubility (g/L)	22	29	37	47	59
Groundwater Seepage Velocity (m/yr)	3	879	667	523	411	328
	10	264	200	157	123	98
	20	132	100	78	62	49
	30	88	67	52	41	33
	60	44	33	26	21	16
	150	18	13	10	8	7

Assuming: 1 m by 1 m unit area 1 m deep; 725 kg of Klozur KP; effective porosity of 15 percent, PRB filled with 50% Klozur KP and assumes fill at a dry bulk density of 1,450 kg/m^3.

Data represents potential longevity based on rate of dissolution only. Site specific factors such as reactions with target and non-target demand as well as persulfate decomposition are also expected to affect longevity.

Table 4. Conceptual persistence of Klozur KP as a function of temperature and groundwater flow; metric units.

RECOMMENDED LOADING FOR KLOZUR KP

The extended release mechanism requires that Klozur KP be dosed above the solubility limit for the subsurface conditions that it will immediately contact. These conditions can vary depending on how Klozur KP was applied including emplaced (fractured) via injection, in a PRB, or through in situ soil mixing. For soil mixing and construction of PRBs, the maximum loading rate of Klozur KP is limited to approximately 130 kg Klozur KP/m^3, or 100 percent Klozur KP. For soil mixing and permeable reactive barriers, assuming a porosity within the soil matrix of 40%, PeroxyChem recommends a minimum loading of **32 kgs Klozur KP/m^3**. Maximum and minimum loading for emplaced Klozur KP will be a function of site conditions. PeroxyChem recommends that you contact your local PeroxyChem technical representative to determine the appropriate loading rate of Klozur KP for your site.