Klozur® Persulfate Oxidant Demand

Success in the remediation of a contaminated site with Klozur® activated persulfate is dependent upon several factors, including: good site characterization, proper activation of the Klozur persulfate, ensuring contact between the persulfate and the contaminant for an adequate period, and injecting sufficient persulfate to mineralize the contaminant to the target levels. Failure in any one of these areas may result in the inability to meet the site clean-up goals. In addition, the oxidant demand may impact the economics of the project. Determination of the oxidant demand for Klozur persulfate for a given site is therefore critical, and is the focus of this edition of Peroxygen Talk.

Persulfate oxidant demand for a site generally comes from three main sources: contaminant demand, soil oxidant demand and decomposition. Soil Oxidant Demand (SOD), sometimes referred to as Natural Oxidant Demand (NOD), combined with the loss of oxidant due to decomposition is often termed Total Oxidant Demand (TOD)[1].

Contaminant Demand

Determining the contaminant demand for radical-based oxidation is not straight forward and requires simplifying assumptions. Klozur persulfate is a strong oxidant and can transfer two electrons from the contaminant in a direct oxidation process.

$$S_2O_8^{-2} + 2H^+ + 2e^- \rightarrow 2HSO_4^-$$ **Equation 1**

However, in general the direct oxidation process is kinetically slow for most contaminants of concern. As a result, Klozur persulfate is "activated" to form sulfate radicals:

$$S_2O_8^{-2} + initiator \rightarrow SO_4^{\bullet-} + (SO_4^{\bullet-} \text{ or } SO_4^{-2})$$ **Equation 2**

Figure 1: Possible pathways for persulfate radical species
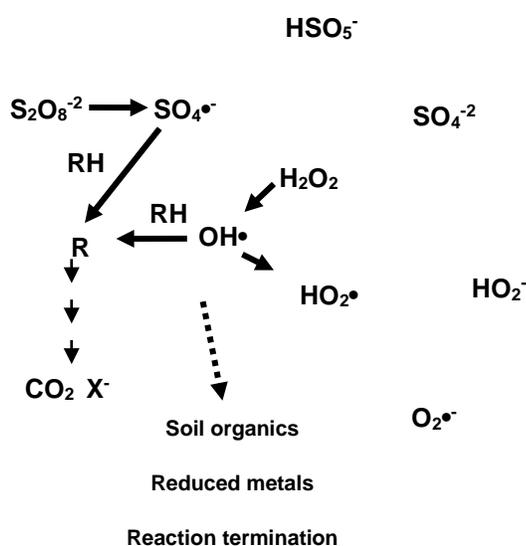
Radical chemistry is very rich, and in fact several oxidant species may be formed during the persulfate oxidation. Figure 1 shows some of the possible reaction pathways for the radical processes. Because of the potential of multiple pathways and chain reactions, it is near impossible to determine a stoichiometric relationship between the persulfate and the contaminant via a radical process without substantial laboratory investigation. As a result, initial oxidant demand calculations typically use only a first-level approximation, assuming the oxidation process proceeds via Equation 1 and a two electron transfer direct oxidation.

For example, the contaminant demand of one pound of trichloroethylene (TCE), with a molecular weight of 131.5 g / mol and 6 electrons / mol for full oxidation, requires 5.4 lbs of Klozur SP for mineralization, assuming persulfate transfers two electrons per mol.

Determination of the contaminant demand is dependent on a good understanding of the amount of contaminant present in the treatment zone. Ideally, a ground water and soil contaminant concentration measurement should be made. However, if only groundwater concentrations are available, an estimation of the soil contaminant concentration can be made by extrapolation from the ground water data in lieu of actual soil measurements by the use of a partitioning model (such as linear models employing K_{ow} partitioning coefficients or higher order models like the Freundlich or Langmuir models[2]).

Total Oxidant Demand (TOD)

Total oxidant demand is composed of the Soil Oxidant Demand (SOD) and the loss of persulfate due to decomposition. SOD (units of g oxidant per kg of soil) is a result of the interaction of the oxidant with soil organics (polyaromatic hydrocarbons and organic acids such as humic and fulvic acids) and reduced metals (such as iron and manganese) in the soils. As it is non-specific in its ability to react with organic species, activated persulfate will oxidize these non-target compounds, leading to an additional oxidant demand in and above the contaminant demand. Persulfate has a low SOD[3] versus other oxidants such as hydrogen peroxide or permanganate, with values typically ranging from 0.5 to 5 g / kg, depending on soil type and reduced metal concentration. The relatively low SOD for persulfate may be a result of the fact that persulfate oxidation of soil organic matter is an incomplete process[4-9], degrading the soil organics only 20 – 40%. The degradable soil organics tend to be soft, expanded organic matter, whereas the remaining un-oxidized organic matter exhibit higher organic carbon partitioning coefficients[10,11]. In essence, the persulfate can not penetrate into the high organic phase of the soil.

SOD can be a significant factor in the economics of a chemical oxidation field project. As an example, Table 1 depicts the impact of SOD on the total oxidant needed to remediate a hypothetical site. Under these conditions, the SOD has a greater impact on the total chemical demand, and hence chemical costs, than does the contaminant demand. This effect becomes more pronounced as the treatment zone area becomes greater.

Treatment Volume	Contaminant Conc	SOD	Oxidant Need For	Oxidant Need for Soil Demand
50 x 50 x 10	50	1	968	1,944
50 x 50 x 10	5	1	97	1,944
50 x 50 x 10	5	5	97	9,722
100 x 100 x 10	5	1	387	7,778
100 x 100 x 10	5	5	387	38,889

Table 1: Hypothetical Site Conditions Demonstrating Effect of Contaminant Demand and SOD on Klozur SP Usage

In addition to interactions with soils and metals, persulfate decomposition will contribute to the apparent TOD and impact the radius of influence. In an aqueous environment, ultimately persulfate will completely decompose. Factors that will impact persulfate lifetime include the temperature, pH, the presence of transition metals, and the persulfate concentration. The decomposition rate will also be a function of the activator system employed, and in general decomposition will be slower with iron activation as compared to hydrogen peroxide or high pH activation. In distilled water, the persulfate decomposition rate will be slow, even in the presence of activators. In the presence of soil, persulfate decomposition may be significantly faster. Field reports suggest that the persulfate lifetime under actual field conditions ranges from several weeks to several months. It has been reported that in some instances, persulfate is still residual up to five months after injection.

TOD and Treatability Testing

Due to the impact on the project costs, measuring the TOD is very important in determining the economic feasibility of using Klozur persulfate for site remediation. However there is not currently an industry-wide standard on measuring TOD. Several factors will impact the Klozur® persulfate TOD results, including:

- Activator. The activator system chosen may greatly impact TOD values, as it will affect the decomposition rate. Un-activated persulfate will indicate a very low TOD value, which may not be reflective of true field conditions. Always incorporate the activator system when measuring TOD.

- TOD measurement time. As persulfate decomposition is a component of TOD, the length of the TOD test will impact the TOD results. The longer the testing period, the high the TOD value will be obtained. There is not yet an accurate correlation between TOD value at a given time point and its relevance to actual field results.   However, over the past several years, anecdotal evidence would suggest that a 48 or 96 hour TOD test will generate results that have been successful for field implementation.

- Initial persulfate concentration. Initial persulfate dosage appears to impact the TOD value obtained, again most likely due to the decomposition component. Our laboratory work has demonstrated that most initial concentrations up to 25 g / kg generate equivalent TOD values for a given time period, and that concentrations above 25 g / kg show a significant increase in TOD value for the same time span. This is on-going work, so please keep an eye on up-coming *Peroxygen Talk* for updates.

- Other factors. Other factors such as the water to soil ratio, mixing time, and method of mixing, will all impact the measured TOD. Intra- and inter- lab variability in TOD result due to these factors has yet to be systematically measured. Please check back for future updates in this area.

Once TOD has been measured, a more refined economic assessment on the use of Klozur® persulfate may be made. However, the accuracy of the stoichiometric assumptions made for the contaminant demand has not yet been tested at this point. As a result, it is recommended that a treatability study be performed. A treatability study measures the destruction of contaminants in the presence of soil and oxidant, and combines the impact of contaminant demand and TOD. There are many variable and methods in performing a treatability study. We recommend a study time period of at least two weeks to allow time for the activated persulfate to perform the majority of the oxidation. It is then suggested that not only the concentrations of the contaminants of concern be measured, but also the residual persulfate concentrations. This will allow the "persulfate" efficiency to measured, and is defined as:

$$\text{Persulfate Efficiency} = \frac{\% \text{ Contaminant Reduction}}{\% \text{ Persulfate Used}} \qquad \textbf{Equation 3}$$

It is always recommended that TOD and lab treatability studies be conducted prior to employing Klozur persulfate in the field in order to increase the probability of success. Our recommended approach is;

First pass economic assessment → TOD testing → 2nd pass economic assessment → treatability study → field pilot demonstration → full scale application.

End Note

Use of Klozur activated persulfate can bring success to your remediation projects. However, as with all endeavors, the more data you have going into the field, the more likely your success will be. Measuring TOD and treatability efficiency can help gauge the economic impact the oxidant demand will have on your project as well as demonstrate the ability to meet your clean-up goals. Our team can support you in the use of Klozur activated persulfate by means of performing economic assessments and TOD testing.

[1] For a good general overview, see: Haselow, J., R. Siegrist, M. Crimi and T. Jarosch. **Remediation** 2003, 13, p. 5.

[2] Example see: Kunberger, T. "Temperature Effect On Desorption Kinetics of Benzene On Various Soils". pHD dissertation, NC State University, 2001.

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[11] Young, T. and W. Weber. **Environ Sci Technol** 1995, 29, p. 92.

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