Welcome to the first edition of Peroxygen Talk, a monthly forum to share experiences utilizing FMC’s chemistries. As you read Peroxygen Talk, if you have any topics that you would like to see discussed, please contact us at philip.block@fmc.com.

Common questions we receive regarding Klozur™ persulfate include: “Do I need to activate the persulfate?” and “What activation chemistry should I use?” The answer to the first question is that in almost every situation, it is recommended that an activator be added to the persulfate to increase reaction kinetics to help insure oxidation of the contaminant of concern. Persulfate is a remarkably stable oxidant given its high oxidation potential. Because of its stability, persulfate has a relatively long lifetime, lasting from weeks to months in most subsurface conditions. However, the consequence of its inherent stability is generally slow reaction kinetics with most contaminants. Addition of an activator converts the persulfate anion into sulfate radicals, which are even stronger oxidants (on the order of the hydroxyl radical) with kinetics that are significantly faster than the persulfate anion. This is analogous to “Fenton’s chemistry”, where iron (II) is added to hydrogen peroxide in order to form the stronger, kinetically faster hydroxyl radical.

Several activation chemistries are available that can be utilized to form the sulfate radical. These include three FMC patent pending chemistries: metal chelates, hydrogen peroxide and high pH. In addition other methods utilize transition metals or heat. While the underlying mechanisms of persulfate activation and contaminant destruction are not completely understood for every activator system, there are differences in the types and kinetics of radical formation depending on the activation approach chosen. As a result, the “aggressiveness” of the activated persulfate system towards a contaminant will be dependent upon the activator chemistry. This “aggressiveness” has two impacts. The first requires matching the activated persulfate system to a contaminant based on how recalcitrant the contaminant is. The second governs how long-lived the persulfate will be, and therefore how far the oxidant will transport and survive in the subsurface. Typically the more aggressive the activated persulfate system, the more recalcitrant contaminants can be addressed, but the shorter lived the persulfate will be in the subsurface. A qualitative assessment of the degree of activator – persulfate “aggressiveness” is as follows, from high to low: heat > high pH = H\textsubscript{2}O\textsubscript{2} > metal chelates > un-activated.

Metal chelates, such as Fe-EDTA which is a combination of iron (II or III) with the chelating molecule EDTA (ethylenediaminetetraacetic acid), in combination with Klozur™ persulfate, generate a moderately aggressive oxidation system. This system is capable of oxidizing contaminants such as: BTEX, most PAHs, MTBE, chlorinated ethenes, such as PCE, TCE and DCE, and 1,4-dioxane. This makes metal chelate – activated persulfate suitable for sites such as dry cleaners, gas stations, and manufactured gas plants (MGP). However, this activation approach is not recommended for more recalcitrant contaminants such as chlorinated ethanes, chlorinated methanes and long chain hydrocarbons.

FMC recommends an available iron concentration of at least 150 ppm to insure adequate radical formation kinetics, and thus effective contaminant destruction. It should not be assumed that iron measured in the soil and groundwater is sufficient to activate the persulfate, as the iron needs to be in a soluble, multi-valent form [Fe(II) or Fe(III)]. It is recommended that Fe-chelate additional should be considered even if iron is measured in the subsurface in order to insure sufficient activation. This should be verified through treatability testing. Several poor performances in the field have been recorded as a result of inadequate persulfate activation due to the assumption that there is enough available iron in the environment. On the other hand, it is recommended that iron not be added in excess of 600 ppm, as this will lead to rapid persulfate decomposition at the expense of contaminant destruction. Fe(II)-chelate will have faster sulfate radical formation kinetics than Fe(III)-chelate, but both will ultimately generate sulfate radicals. There is some evidence to suggest that Fe(II)-chelate rapidly converts to Fe(III)-chelate in the
presence of persulfate. Thus if one was following contaminant destruction rates using Fe(II)-chelate activated persulfate, one would observe an initial fast destruction rate, followed by a slower rate of destruction, primarily due to the conversion of Fe(II) to Fe(III).

As with all activator systems, it must be insured that the Fe-chelate and Klozur™ persulfate are delivered together to the location where the contaminant is. If adequate injection schemes that insure both oxidant and activator delivery to the contaminant location are not in place, then the chemical oxidation will fail. In addition, due to the slower kinetics of radical formation, there is greater potential with this activation scheme to generate observable intermediates and daughter products. While these daughter products and intermediates will be oxidized by activated persulfate as well, spikes in intermediate concentration may be measured.

Hydrogen peroxide is an aggressive activator system for Klozur™ persulfate, and can be used to treat most contaminants, including: BTEX, PAHs, TPH, chlorinated ethenes, chlorinated ethanes, chlorinated methanes, pesticides, 1,4-dioxane and others. Hydrogen peroxide activated persulfate is suitable for use in most sites, including MGP sites, gas stations, and drycleaners.

The recommended dosage of hydrogen peroxide is in the range of 1 to 10 moles of peroxide per mole of persulfate (this equates to 0.14 to 1.4 lbs peroxide [100% basis] to 1 lb persulfate). Laboratory experiments show that the higher the peroxide to persulfate ratio, the shorter the persulfate lifetime.

The advantages of using hydrogen peroxide activation include: the ability to treat a broad range of contaminants; and the relatively low cost of peroxide. In addition, there is field evidence that the use of peroxide aids in desorption of contaminants that are sorbed onto soils, thereby reducing the chance of subsequent rebound. However, several considerations must be taken into account when utilizing peroxide as the activator. Care in the use and handling of hydrogen peroxide (as well as any oxidant) must always be in the forefront of any project design and implementation. Also, hydrogen peroxide has a very high soil oxidant demand, which for certain lithologies, can significantly reduce the radius of influence of the peroxide. As a result, hydrogen peroxide may not be ideal for sites with high clay content or limited porosity. In addition, there is potential of volatilizing VOC and semi-VOC contaminants through heat generation and gas formation that may accompany peroxide injection; therefore care must be exercised in proximity to structures, where vapor intrusion may be of concern.

The high pH activation method also is an aggressive activator system, capable of treating a very broad range of contaminants, including BTEX, PAHs, TPH, chlorinated ethenes, chlorinated ethanes, chlorinated methanes, pesticides, 1,4-dioxane and others. Injection of a pH modifier, such as sodium or potassium hydroxide, or lime, is required to raise the pH of the soil and groundwater to a target 10.5 – 11. For less recalcitrant compounds such as BTEX and PAHs, the target pH may be somewhat lower, in the range of 9.5 – 10.5. As with the other activators, the pH modifier may be added to the persulfate solution prior to injection. The high pH may also help reduce the acidic corrosion of injection equipment due to the low pH's of around 2 associated with persulfate solutions.

This activation scheme can be utilized in most situations where the pH can be adjusted to the desired level, including under buildings where peroxide activation may be less desirable. Situations where alkaline activation may not be feasible include: lithologies with high levels of carbonates which may require significant loadings of the pH modifier to overcome the buffering capacity of the carbonate, sites with significant silica content may require special attention as silica can dissolve at pH's of 12 and above, and sites where significant pH change may trigger regulatory concerns. The pH modifier demand, or the amount of pH modifier that would need to be added, has two components. This first is the quantity needed to adjust the soil and groundwater pH to the desired level. This can be determined in the laboratory with simple titration methods. Secondly, additional pH modifier will need to be added to counteract the effect of persulfate decomposition. As persulfate decomposes, two moles of HSO₄⁻ are produced for every mole of persulfate. This will drive the pH down from the desired value, if not taken into account. As an example, if NaOH is used as the pH modifier, the amount of NaOH to be added equals the amount needed to raise the pH of the soil / groundwater to 11 plus two moles of NaOH per mole of persulfate injected (or 0.27 lbs NaOH per lb of persulfate).

Finally, heat can be utilized as an activator for Klozur™ persulfate. This is the basis for many TOC analyzers, which utilize heat to generate sulfate radicals, which in turn mineralize
organic carbon in the sample. Heat activated persulfate can be utilized to treat most organic contaminants. Persulfate can readily oxidize the compounds of concern at temperatures as low as 35 – 40 °C. Heat can be added to the sub-surface by several methods, including steam injection or with electrodes or radio waves. For smaller sites, such as half an acre or less, heat activated persulfate may prove to be an economically feasible approach. However, as the size of the site increases, the ability to raise the temperature of the soil and groundwater economically may diminish.

In summary Klozur™ persulfate can be activated to form sulfate radicals by a variety of methods. The key to successful remediation will depend on the proper choice of activation chemistry to treat your contaminant of concern within the constraints of the treatment site. We recommend running a well designed treatability study utilizing the one or two activation systems that match your treatment situation prior to field application. Please contact the FMC Environmental Solutions Team for technical support in choosing the appropriate activation chemistry.