Klozur® activated persulfate is a very robust technology that is capable of destroying a wide range of organic contaminants and is equally effective on highly reduced contaminants such as BTEX and polyaromatic hydrocarbons and highly oxidized species such as 1,1,1-TCA, carbon tetrachloride, methylene chloride and chloroform. Such versatility demonstrates a very rich and robust chemistry for persulfate in which well-known oxidative pathways and recently elucidated reductive mechanisms both play important roles. This edition of Peroxygen Talk explores the dual nature of activated persulfate systems, which can act as a strong, reactive oxidant and be a source of unique, reductive species. In addition, combinations of zero valent iron (ZVI) and persulfate will be explored in term of providing oxidizing and reducing conditions to a chlorinated solvent site.

**Persulfate Oxidation Chemistry**

The persulfate anion is a strong oxidant, with an oxidation potential of 2.12 V:

\[ \text{S}_2\text{O}_8^{2-} + 2 \text{H}^+ + 2 \text{e}^- \rightarrow 2 \text{HSO}_4^- \]

However, the persulfate anion typically has slow oxidative kinetics at ordinary temperatures for most contaminant species and really can only be applied to a limited number of contaminants, such as TCE or xylene, to be effective. As a result, persulfate is typically “activated” for use to oxidize most contaminants or concern. In the presence of certain activators, persulfate anion can be converted to the sulfate radical, an even stronger oxidant with an oxidation potential of 2.6 V:

\[ \text{S}_2\text{O}_8^{2-} + \text{activator} \rightarrow \text{SO}_4^{\cdot -} + (\text{SO}_4^{\cdot -} \text{or SO}_4^{2-}) \]

Under acidic conditions, persulfate anion can hydrolyze to form hydrogen peroxide:

\[ \text{S}_2\text{O}_8^{2-} + 2 \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + 2 \text{HSO}_4^- \]

Hydrogen peroxide itself has an oxidation potential of 1.77 V, and in the presence of various activators, can form the hydroxyl radical, with a potential of 2.8 V, making it the strongest oxidant available for remediation applications. In addition, sulfate radicals can react with water also to form hydroxyl radicals. Under stronger acidic conditions, persulfate can form peroxymonopersulfate anions, with an oxidation potential of 1.44V

\[ \text{S}_2\text{O}_8^{2-} + \text{H}_2\text{O} \rightarrow \text{HSO}_5^- + \text{HSO}_4^- \]

As a result, persulfate solutions may contain several different oxidant and radical species. One consequence of this mixture of oxidizing species is that multiple pathways for contaminant oxidation may exist, increasing the probability of reducing the target compound concentrations. However, such diversity of oxidant species makes the assessment of the “stoichiometric” amount of persulfate needed to destroy a given concentration of contaminant problematic, and thus it is common practice to revert back to the basic, two electron transfer associated with the persulfate anion (seen in first equation above) to determine the stoichiometric persulfate demand.
Formation of Superoxide: Reduction Chemistry Via Persulfate

In addition to reactive oxidizing species, it has recently been shown that persulfate can also generate the reductive specie, super oxide (O$_2^-$), under certain activation conditions. Watts, et al$^4$ demonstrated that under alkaline activation conditions through the addition of OH$^-$, persulfate generates both sulfate radicals and superoxide by the following combined reaction:

$$2 \text{S}_2\text{O}_8^{2-} + 2 \text{H}_2\text{O} \rightarrow 3\text{SO}_4^{2-} + \text{SO}_4^{.-} + \text{O}_2^- + 4 \text{H}^+$$

Watts explains this reaction as proceeding through an intermediate reaction between hydroperoxide (HOO$^-$) and persulfate anion. Furthermore, under these highly alkaline conditions, sulfate radical can react with hydroxide to form hydroxyl radicals

$$\text{SO}_4^{.-} + \text{OH}^- \rightarrow \text{SO}_4^{2-} + \text{OH}.$$ 

In this paper, Watts then demonstrates that the alkaline activated persulfate system can degrade contaminants such as hexachloroethane (HCA), a highly oxidized species which is used as a probe for reactions with superoxide. Alkaline activated persulfate has also been shown to react effectively with carbon tetrachloride$^5$, which contains fully oxidized carbon thought to only degrade through reductive pathways.

Watts also recently$^6$ proposed that hydrogen peroxide-activated persulfate can lead to the generation of superoxide radicals as well. This is mediated via the generation of hydroperoxide by iron-activated hydrogen peroxide, and then as in the high pH activation scenario, the hydroperoxide reacts with persulfate anion to form sulfate radical and superoxide species. Evidence of this has been observed with the activated persulfate destruction of carbon tetrachloride$^5$. Watts, et al, also demonstrated the formation of superoxide in mineral-activated persulfate systems$^7$, particularly in systems containing goethite (FeOOH).

The following table lists the potential reactive species potentially present in activated persulfate systems.

<table>
<thead>
<tr>
<th>Potential Reactive Species in an Activated Persulfate System</th>
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<tbody>
<tr>
<td>Species</td>
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<td>--------------------------</td>
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<tr>
<td>Persulfate anion</td>
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<tr>
<td>Sulfate radical</td>
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<tr>
<td>Hydrogen peroxide</td>
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<td>Hydroxyl radical</td>
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<td>Monopersulfate</td>
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<td>Hydroperoxide</td>
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<td>Superoxide</td>
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Combinations of Persulfate and Zero Valent Iron (ZVI)

Zero valent iron is a reductive technology that has been used over the years to treat chlorinated solvent contaminated sites. Recently, it has been demonstrated that persulfate can be activated using zero valent iron (ZVI), a well recognized reducing agent for chlorinated solvents, making for a combined oxidant – reductant remediation tool. While the use of hydrogen peroxide or permanganate with ZVI is detrimental to both the oxidant and the ZVI, ZVI – persulfate combinations have been shown to be effective on TCA, carbon tetrachloride, TCE and dinitrotoluene. It has been suggested that the mechanism of persulfate activation is by a two step process, whereas the ZVI is the source of divalent iron, which can be used to generate sulfate radicals from persulfate.

\[
\text{Fe}_0 + \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} \rightarrow 2 \text{Fe}^{2+} + 4 \text{OH}^{-}
\]

\[
\text{S}_2\text{O}_7^{2-} + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{SO}_4^{-} + \text{SO}_4^{2-}
\]

Of course, persulfate can react directly with the ZVI to form divalent iron and sulfate, a non-productive reaction. However, unlike permanganate and hydrogen peroxide, sulfate radical production appears to be significant as compared to the non-productive rusting of the ZVI or decomposition of persulfate. As a result, ZVI – persulfate combinations can provide a source of both oxidative and reductive destruction of chlorinated contaminants.

Application of ZVI and persulfate combinations has been demonstrated at the field scale. In both of these cases, ZVI, persulfate and hydrogen peroxide were applied to sites contaminated with BTEX and naphthalene, resulting in significant reductions of the contaminants. Application of persulfate and ZVI can occur through co-injection (sequentially or simultaneously). But it can also be imagined that a permeable reactive barrier (PRB) be emplaced with the ZVI, then the persulfate injected up-gradient of the barrier and allowed to flow through the ZVI in concert with the contaminants, activating as it passes through the PRB.

Conclusion

Activated persulfate provides a unique technology that can provide both oxidative and reductive processes to treat a wide range of contaminants that can be applied to soils and groundwater. As a result, persulfate is effective in destroying a wide range of organic contaminants and can address mixed contaminant plumes of petroleum products and chlorinated solvents. Persulfate can also be combined with zero valent iron, not only to provide activation for the persulfate, but as a source of combined oxidative and reductive chemistries.


6. R.J. Watts presentations at the 2nd Southeastern In Situ Soil and Groundwater Remediation Conference (2010, Raleigh, NC) and on the 2010 FMC Environmental Webinar Series


8. FMC Patent: US 7,785,038


