



## Treatment of MTBE and TBA using Activated Klozur<sup>®</sup> Persulfate

Methyl-tert-butyl ether (MTBE) and tert-butyl alcohol (TBA) are environmental contaminants of concern that have been widely added to gasoline as oxygenates or octane boosters. The environmental fate and transport of MTBE and TBA are different than other common gasoline components. MTBE and TBA are typically more mobile within the aqueous phase due to their high water solubility and low retardation coefficients. Aggressive investigation and treatment is often recommended due to the mobility of the compounds (ITRC, 2005).

Activated Klozur<sup>®</sup> persulfate is an aggressive treatment technology that has been used to successfully treat MTBE and TBA (Block, 2006).

### Laboratory Data

MTBE degradation has been shown to follow a classic oxidative pathway (Liang et al, 2010) resulting in the formation of carbon dioxide. Potential intermediate compounds formed during the oxidation of MTBE include TBA, methyl acetate (MA), tert-butyl formate (TBF), and acetone. The degradation products formed vary depending upon the stage of treatment and the specific location at which the oxidative reaction is initiated [Carver and Brown (2007); Liang et al (2010)]. Liang concluded the primary oxidation pathway with activated persulfate proceeded through TBF, TBA, and acetone before reaching the final product of carbon dioxide.

Several published articles have confirmed the treatment of MTBE and TBA using activated persulfate. The research showed that alkaline, hydrogen peroxide, and heat (greater than 40°C) activation degraded both MTBE, TBA and the other identified daughter products over the time period evaluated (Block et al, 2006; Deng et al, 2014; and Chen et al, 2009). Iron and iron-chelate activated persulfate, including pyrite [Fe (II) mineral], Fe (II), chelated Fe (II), and chelated Fe (III), was also observed to treat both MTBE and TBA (Block et al, 2006; Chen et al, 2009; Liang et al, 2010; and Deng et al, 2014) with the accumulation of acetone, which is known to biodegrade (ATSDR, 1994). The studies also evaluated the rate of degradation of MTBE and generally found that heat activation (40°C) was the most rapid followed by hydrogen peroxide, iron and iron-chelate activation. Huang et al (2002) found that the rate of MTBE treatment with heat activated persulfate increased with increasing temperature. The rate of reaction with alkaline activated persulfate was observed to be less aggressive compared to the other activation methods, but it was consistently among the most effective in treating MTBE, TBA and all observed daughter products within a timeframe typical of in situ remediation (Block et al, 2006 and Deng et al, 2014).

### Case Studies

Activated persulfate has been applied in the field to successfully treat MTBE. Block et al (2006) included case studies showing that a combination of heat and alkaline activated persulfate reduced the concentration of MTBE by 72 and 98 percent at two respective sites. A single application of hydrogen peroxide activated persulfate was used to reduce MTBE concentrations in a complex comingled plume by 77 percent (JAG, 2008). At separate sites, iron-chelate activated persulfate was used to reduce MTBE concentrations by 97 to 99.9 percent at a gas station (Rauch et al, 2014), to reduce elevated concentrations of MTBE in fractured bedrock





prior to transitioning over to bioremediation (Rees et al, 2011), and to treat a site to near detection levels (Cookson et al, 2004). The successful treatment of MTBE with Klozur® CR, which creates alkaline activated persulfate conditions followed by the slow release of oxygen, has also been reported (Exotech, 2012).

Both laboratory studies and field data data have shown that activate persulfate can be used to aggressively treat MTBE and TBA. PeroxyChem recommends a bench scale test be considered to develop site specific design parameters and to evaluate the potential rate of reaction with MTBE and daughter products with site specific soils and groundwater. Combined with the long history of successfully remediating petroleum hydrocarbons, activated persulfate is the “best choice for treating gasoline sites where MTBE is an issue. Activated persulfate provides a rapid, effective, and inexpensive remedial method for gasoline sites” (Carver and Brown, 2007).



## REFERENCES

- Agency for Toxic Substances and Disease Registry (ATSDR) (1994) "Toxicological Profile for Acetone," U.S. Department of Health and Human Services
- Block, P.A, Sethi, D., Yuan, S., and Huang, K. (2006) "In Situ and Ex Situ Treatment of MTBE Contaminated Groundwater," The Sixth International Conference on the Remediation of Chlorinated and Recalcitrant Compounds, Monterey, CA
- Carver, M., and Brown, R.A. (2007) "Chemical Oxidation of MTBE and TBA" Proceedings of the Ninth International In Situ and On-Site Bioremediation Symposium, Baltimore, MD
- Chen, K.F., Kao, C.M., Wu, L.C., Surampalli, R.Y., and Liang, S.H., (2009) "Methyl Tert-Butyl Ether (MTBE) Degradation by Ferrous Ion-Activated Persulfate Oxidation: Feasibility and Kinetics Studies," *Water Environ. Res.*, 81(7), 687-694
- Cookson, J. Kelly, K., Marley, M., and Sperry, K. (2004) "In Situ Chemical Oxidation of Oxygenates (MTBE)," NGWA-API Work Shop, Baltimore, MD
- Deng, D., Peng, L., Guan, M, and Kang, Y. (2014) "Impact of activation methods on persulfate oxidation of methyl-tert-butyl ether" *J. Hazard Mat.*, 264, 521-528
- ExoTech, Inc (2012) "Ft. McAllister Marina," Case Study-PeroxyChem Website, March 2014
- Huang, K.C, Couttenye, R.A., and Hoag, G.E., (2002) "Kinetics of heat-assisted persulfate oxidation of methyl tert-butyl ether (MTBE)," *Chemosphere*, 49, 413-420
- ITRC (Interstate Technology & Regulatory Council), (2005) "Overview of Groundwater Remediation Technologies for MTBE and TBA," Washington D.C. ITRC MTBE and Other Fuel Oxygenates Team, <http://www.itrcweb.org>
- JAG Consulting Group, Inc (2008) "ISCO Case Study: Use of Peroxide Activated Sodium Persulfate for Treatment of BTEX and MTBE, Lake Shasta, CA," Case Study-PeroxyChem website, March 2014
- Liang, C., Guo, Y.Y., Chien, Y.C., and Wu, Y.J. (2010) "Oxidative Degradation of MTBE by Pyrite-Activated Persulfate: Proposed Reaction Pathways," *Ind. Eng. Chem. Res.*, 49, 8858-8864
- Rauch, H., Haim, A., Lapid, Y., Kydar, G., and Rees, A. (2014) "The First Application of Full-Scale ISCO in Israel Using Activated Persulfate for Treating BTEX and MTBE," The Ninth International Conference on the Remediation of Chlorinated and Recalcitrant Compounds, Monterey, CA
- Rees, A., Rauch, H., Haim, A., and Lapid, Y. (2011) "Combined ISCO and ISB Approach Using Activated Persulfate and Propane-Butane Biosparging to treat MTBE and TBA in Groundwater," Poster, International Symposium on Bioremediation and Sustainable Environmental Technologies, Reno, NV

