



Klozur® Persulfate: The Impact of Sulfate Residual

Klozur® activated persulfate is a strong oxidant that can oxidize and destroy many organic contaminants, generating the by-product sulfate in the process. In this edition of *Peroxygen Talk*, the impact of sulfate on groundwater and on subsequent bioremediation processes is explored.

In general, one mole of the persulfate anion, $S_2O_8^{2-}$, will form two moles of sulfate, SO_4^{2-} , either through reaction with the contaminant or decomposition. As an example, one pound of sodium persulfate will generate 0.80 lb of sulfate. The injection of a Klozur SP solution to achieve an *in situ* persulfate concentration of 20 g / L may result in a peak sulfate concentration of 16 g / L. The maximum sulfate concentration and the longevity of augmented sulfate levels in the groundwater are dependent upon many factors, including: groundwater flow rate, lithology and the population density of sulfate reducing bacteria (SRB), to name a few. Treatment zones with slow to no groundwater flow rate may be impacted by elevated concentrations of sulfate for extended periods of time.

Sulfate – Groundwater Quality

Sulfate is ubiquitous in the environment because of the abundance of sulfur on earth. From the US Geological Survey's National Water Quality Assessment program, results indicate nearly 100% of all surface and ground water sites have sample analytical detections of sulfate.¹ Sulfate has also been detected in public water systems compliance monitoring samples, and occurrence estimates are very high by all measures (87% of samples show sulfate detections, with a median concentration of 24 mg / L).¹

The US EPA has recommended a secondary maximum contaminant level (SCML) for sulfate in drinking water of 250 mg/L.² This SCML is based on negative impacts on the aesthetic effects of a contaminant in drinking water, such as taste and smell, and is not a federally enforceable standard¹. It is estimated that humans can detect sulfate in water starting at concentrations between 250 and 350 mg / L.² The World Health Organization (WHO) recommends sulfate concentrations in drinking water not exceed 400 mg / L based on taste. In addition, the EPA states that the available toxicological data on sulfate indicate that sulfate may cause adverse health effects in humans and animals. This is a result of a laxative effect when sulfate is consumed in high doses (estimated in the range of > 500 mg / L to > 1000 mg / L), but the adverse health effects are temporary and recovery is rapid.¹ Also, there are no significant dose-response associations between sulfate exposure and reports of diarrhea in adults. High sulfate concentrations do not exert adverse reproductive or developmental effects.

How does this impact your use of Klozur activated persulfate? It is common for state and federal regulators to inquire about the generation of sulfate with respect to the SCML limitations. However, in the majority of instances, regulators have approved the use of Klozur activated persulfate in order to remove contaminants of concern; with the general philosophy that residual sulfate is more acceptable than the contaminant being treated. While this is highly dependent upon the regulator, and may be impacted by specific site conditions, the general acceptance of persulfate injection is evidenced in that Klozur activated persulfate has now been injected at over 300 sites in 35 different states. However, if Klozur activated persulfate is being injected into aquifers from which drinking water is being drawn or is in close proximity to drinking-water wells, the impact of residual sulfate on water quality may be of concern and should be taken into account during the feasibility analysis.

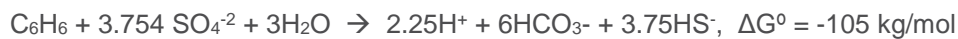
One possible approach to reduce potential sulfate groundwater concentration is the use of lime (CaO) as a high-pH activator for Klozur persulfate, especially when deploying Klozur persulfate in soil blending applications. The



calcium ions from the lime will react with the residual sulfate, forming gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), an insoluble mineral. This will result in a decrease in the soluble sulfate groundwater concentration.

Sulfate – A Role-player in Bioremediation

Sulfate can play an important role in the bioremediation of petroleum products, acting as an electron acceptor in a co-metabolic process. Several studies³⁻⁸ have investigated the application of sulfate for the reduction of BTEX and other species, and has been demonstrated to function in the anaerobic oxidation of these compounds. Roychoudhury⁵ collated redox reaction and thermodynamic data for reactions involving BTEX and sulfate. As an example for benzene:



As a result, sulfate injection into the aquifer has been used as a method to stimulate BTEX biodegradation⁹, especially in anoxic sediments. In addition, sulfate reduction via SRB has been suggested as a method to reduce metal contamination, through the production of hydrogen sulfide, and subsequent precipitation of the metal sulfide.¹⁰

In general, under aerobic conditions, oxygen is a very strong electron acceptor, and is thermodynamically favored over sulfate in this role. Nitrate in the soil also is thermodynamically favored over sulfate. However, in anaerobic zones, sulfate may be the primary electron acceptor in the bioremediation of petroleum contaminants. As a consequence, the use of activated persulfate may provide a two-fold remedial punch. This first is chemical oxidation of the contaminants of concern, especially in hot spot and / or source areas. Secondly, upon subsequent reaction / decomposition, a sulfate plume will extend from the injection zone, providing terminal electron acceptors for enhanced bioremediation of contaminants in the down-gradient areas. While this has yet to be demonstrated in the field, Klotz activated persulfate may be considered a “combined remedy”, combining ISCO of source zones coupled with bioremediation of plumes, all in one product. Several studies are now underway to investigate this “combined remedy” approach.

The impact of sulfate on the bioremediation of chlorinated solvents may be positive or negative, depending upon which bioremediation pathway is favored. In general, two pathways exist: 1) chlorinated solvents may undergo reductive dechlorination by acting as an electron acceptor; 2) certain solvents may be oxidized by acting as an electron donor. At a given site, both processes may be operating; but in many cases, the first pathway appears to be favored under natural conditions.¹¹

For the first pathway, the process will be electron- donor limited, as for the following example for PCE:



where H_2 is the electron donor in this case. Native organic carbon can be used as an electron donor, but often additional carbon source (electron donor) is added in the form of lactate, molasses, vegetable oil or other additive to provide an ample amount of electron donor to drive the above reaction forward. The impact of sulfate in these



circumstances may be negative, as sulfate will provide an additional source of electron acceptors (thermodynamically favored over chlorinated ethenes), burdening the electron donors that are present. As a consequence, treatment of a chlorinated solvent source via activated persulfate chemical oxidation may require additional carbon source be added to account for the increased sulfate concentration in down-gradient zones.

In the case where chlorinated solvents, such as vinyl chloride, dichlorinated ethenes and chlorinated ethanes, can act as an electron donor, the sulfate may play a role similar to that for the bioremediation of BTEX, and provide a beneficial outcome

Sulfate – A Role-player in Bioremediation

In general, the impact of sulfate on groundwater quality will be minimal; however, the SCML will most likely be exceeded. Sulfate may be an important remedial design consideration in cases where persulfate is injected into drinking-water aquifers or near wells. The presence of residual sulfate may provide significant benefits for down-gradient bioremediation / natural attenuation of petroleum contaminants. Benefits also may be observed for subsequent bioremediation of chlorinated solvents, but may negatively impact reductive biodechlorination efforts.

¹ USEPA-815-R-03-16; 2003; "Contaminant Candidate List – Regulatory Determination Support Document for Sulfate

² USEPA, 1979; 44 FR 42195

³ Anderson, R. and D. Lovley. *Environ. Sci. Technol* (34), 2000, p 2261.

⁴ Cunningham, J. , H. Rahme, G. Hopkins, C. Lebron and M. Reinhard. *Environ. Sci. Technol* (35), 2001, p 1663.

⁵ Roychoudhury, A. and G. Merrett. *Science of the Total Env.* (366), 2006, p. 262.

⁶ Lovely, D., J. Coates, J. Woodward and E. Phillips. *Appl and Env Micro* (61), 1995, p 953.

⁷ Weiner, J. and D. Lovley. *Appl and Env Micro* (64), 1998, p. 775.

⁸ Lovely, D. and E. Phillips. *Appl and Env Micro* (53), 1987, p 2636.

⁹ Krishnan, B. EPA Agreement Number R827015-01-0, "Enhancement of Microbial Sulfate Reduction for the Remediation of Hydrocarbon Contaminated Aquifers – a Laboratory and Field Scale Project", 2002.

¹⁰ Turick, C., P. McKinsey, M. Phifer, F. Sappington and M. Millings, Westinghouse Savannah River Company, WSRC-TR-2002-00346. "D-Area Sulfate Reduction Study Bacteria Population and Organic Selection Laboratory Testing", 2002.

¹¹ Pirkle, R. Microseeps Technical Bulletin: "A Summary of the US EPA Technical Protocol for Evaluation of Natural Attenuation of Chlorinated Solvents in Ground Water".

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