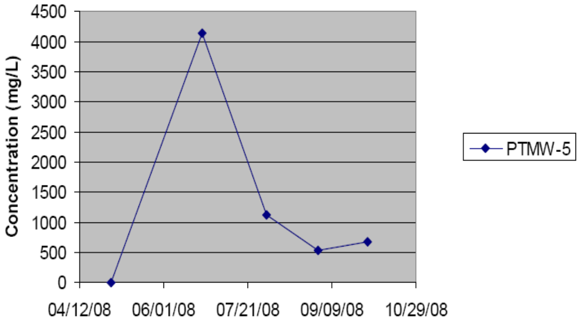
Sulfate Revisited: The Fate of Sulfate in the Groundwater

The main residual by-product of Klozur® Persulfate chemical oxidation of contaminants of concern is sulfate. In the February 2007 edition of *Peroxygen Talk*, the impact of sulfate residual was discussed. Sulfate will be produced upon the depletion of persulfate per the general equation:

$$S_2O_8^{-2} + 2\,H^+ + 2\,e^- \rightarrow 2\,HSO_4^-$$

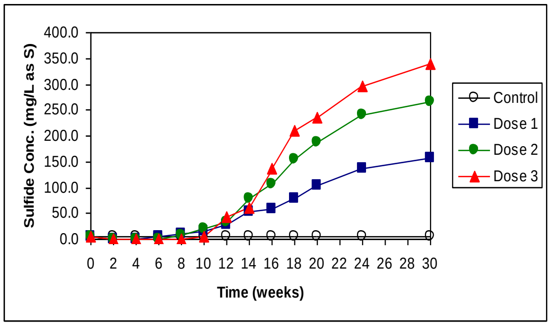
As a result, about 0.8 lbs of sulfate will be generated per every pound of persulfate applied. There is a secondary drinking water standard in the US for sulfate of 250 mg/L, based on taste and order quality issues. It is not uncommon that an *in situ* application of persulfate during a remediation event will impart enough residual sulfate to temporarily exceed the secondary sulfate standard. In this month's *Peroxygen Talk*, the impact of sulfate will be revisited as new information on its fate in groundwater is now available.

Figure 1: Sulfate field concentration post persulfate application at Site 1



Laboratory and field data indicate that sulfate concentrations do not remain elevated at persulfate injection sites for more than six months post the oxidant application. The reduction in sulfate can be attributed to two sources: 1) dilution by incoming groundwater and dispersion into the down-gradient aquifer, and 2) reduction to sulfide via metabolic processes by sulfate-reducing bacteria (SRBs). The conversion of sulfate to sulfide via SRB usage has been demonstrated in the laboratory[1]. These laboratory tests involved the treatment of PCB and PAH laden sediments with Klozur CR, a combined persulfate – calcium peroxide product. SRB microbial population concentrations were tracked, and the resulting conversion of sulfate to sulfide can be seen in Figure 1 for three different persulfate dosages (Klozur CR dosage increases from Dose 1 to Dose 3). Within twelve weeks, sulfate conversion to sulfide was observed.

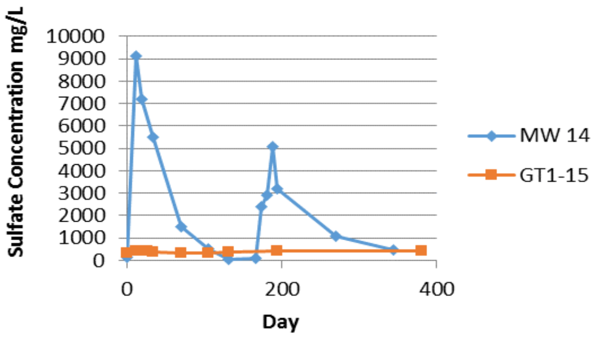
Figure 2: Formation of Sulfides from SRB Reduction of Sulfate



Coincidently, the formation of sulfate had the additional positive effect on the sediments in that mercury, which was a major contaminant of concern within the sediments, was precipitated as cinnabar (HgS), reducing the overall mercury groundwater concentration of the sediments.

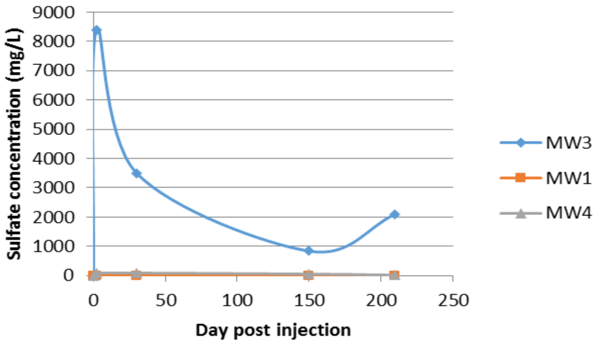
Similar effects have been observed in the field. As an example, the sulfate depletion following persulfate application at Site 1[2] is shown in figure 2. Site 1 lithology consists of sand and gravel, and has a relatively fast ground water flow rate of one foot per day. The concentration of carbon to support SRB metabolism and the availability of the carbon are important factors affecting the sulfate degradation rate. Carbon sources within in the area include the petroleum hydrocarbons from the contaminant source and naturally occurring soils within the soil. The decrease in sulfate concentration in well PTMW-5, which was located within the oxidant injection zone was rapid, and exhibited a rate of 37 mg sulfate reduced per day. The slowing in the sulfate reduction rate in September and October was attributed to the cold seasonal temperatures at this site (located in the very north of the United States). Down-gradient wells did not show any rise in sulfate concentration, indicating that the sulfate did not reach these wells.

Figure 3: Sulfate field concentration post persulfate application at Site 2



At a second site[3], sulfate reductions were seen within one hundred days post persulfate application, as seen in Figure 3. This site located in California consisted of interbedded layers of sands, silts and clay. Persulfate in combination with hydrogen peroxide and ferrous sulfate (a secondary source of sulfate), were injected at day zero, and re-injected at day 166. As can be seen in the data from well MW-14, located within the oxidant injection zone, sulfate groundwater concentrations significantly increased right after the persulfate application, but within one hundred days were back to levels observed prior to application. Well GTI-15 was located two hundred feet down gradient from the persulfate injection zone demonstrated no increase in sulfate concentration during or post the application of persulfate.

Figure 4: Sulfate Concentration post persulfate application at Site 3



Data from a third site[4] demonstrates similar behavior. This site is composed of silts and sands with a moderate groundwater flow rate. Immediately after persulfate application, sulfate groundwater concentrations rise rapidly in well MW-2, which is within the persuflate injection zone. However, within ninety days, the sulfate concentrations within this well are greatly reduced. Well MW-1, which is fifty feet upgradient, and MW-4, which is fifty feet down gradient, both did not show any increase in the sulfate groundwater concentration, indicating that sulfate did not reach these two wells within two hundred days. The slight increase in sulfate concentraiton within well MW-2 after ninety days was attributed to significant decreases in groundwater levels at that time, with several wells actually drying out during a portion of this time.

While every site is unique with respect to lithology and hydrogeology and evidence from one site is not a guarantee with respect to potential impacts at another site, several general conclusions can be made. Application of activated persulfate will lead to a transitory increase in sulfate groundwater concentrations within and near the oxidant injection zone, potentially above the secondary drinking water standard of 250 mg/L. However, either through reduction to sulfides via sulfate reducing bacteria or through dilution via dispersion and diffusion , it has been observed that typical sulfate concentrations do not stay elevated more than six months post the oxidant application event, and that sulfate residual does not travel significant distances within the aquifer under typical conditions.

1. D. Cassidy, Western Michigan U. “The Effect of Klozur®CR on Contaminant Oxidation, SRB, Sulfide Production and Cinnabar (HgS) Precipitation”, report to FMC, 2009.
2. Confidential site data. J. Dablow, ERM. 2009.
3. California site data. G. Cronk, JAG Consulting, 2010.
4. California site data. G. Cronk, JAG Consulting, 2010.

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