Klozur® ERH

Successful application of persulfate chemical oxidation of recalcitrant contaminants generally requires “activation” of the persulfate to form the sulfate radical. There a several typical methods of persulfate activation1, including heat, high pH, metals and hydrogen peroxide as the most common. Of these activation methods, the application of heat is very effective at forming energetic sulfate radicals

$$S_2O_8^{-2} + \Delta \rightarrow 2SO_4^{\bullet -}$$

through the hemolytic cleavage of the O – O bond. Given enough thermal input, these sulfate radicals can oxidize and mineralize virtually any organic compound. This (along with ultraviolet activation) forms the basis of the total organic carbon (TOC) analysis method2. Generally, in the laboratory, kinetic and mechanistic studies use thermal activation as the driving force for the sulfate radical formation (see references 3 – 7 as examples). The speed of the persulfate reaction in essence can be “dialed in” with selection of the activation temperature. On one extreme is the example of the TOC analyzer, where temperatures of 90 °C or higher can drive the full mineralization of all organic carbon in less than twenty minutes. However, for practical application, much lower temperatures are more suitable in order to reduce the rate of non-productive persulfate reactions, such as auto-decomposition and reactions with soil organic matter. For most contaminants of concern, a temperature range of 30 – 40 °C is sufficient to meet clean-up goals.

Over the past several years, it is more prevalent in field applications of activated persulfate to utilize high pH or metal activation as compared to the use of heat, with high pH activation representing approximately seventy five percent of all field scale projects. Thermal activation, while kinetically efficient, often suffers in practice due to the potentially high cost associated in raising the temperature of the soil and groundwater to the target range. Large sites or sites with fast moving groundwater may require significant thermal input, and as a result may incur a high economic cost to employ. Early applications of heat activated persulfate made use of steam to heat soil and groundwater, using either small, portable steam generators8,9 or available plant steam at the site10. In addition, use of hydrogen peroxide or lime as activators have a secondary (and perhaps as their primary) mode of action through the in situ generation of heat. Hydrogen peroxide upon injection into the subsurface decomposes and can liberate significant amounts of heat. The heat of decomposition can be controlled through the rate of peroxide application and can be utilized to deliver a source of heat input for persulfate activation. This method has been used to treat a wide range of contaminants, including petroleum NAPLs11. For soil blending applications, lime (either hydrated or quicklime) is often selected as the activator of choice. Upon hydration, lime can generate heat as well ($\Delta H_r = -63.7$ kJ/mol of CaO), providing a highly effective combination of both high pH and heat for activation of the persulfate.

The use of electrical resistive heating (ERH) to activate Klozur SP

In situ thermal desorption and thermal decomposition methods have been successfully utilized to treat volatile and non-volatile contaminants, by either volatilizing the contaminant out of the soil and groundwater for capture in a vapor extraction system or through the thermal decomposition of the contaminants in place. Generally, these techniques require significant energy input to raise the soil and groundwater temperatures to boiling (> 100 C for desorption or 100's C for decomposition). In addition, it often takes months for the subsurface to return back to pre-treatment temperatures. Klozur persulfate may be incorporated into this remediation scheme as the primary treatment chemistry, potentially reducing the required thermal input (reducing the required target temperatures from 100 C to the target range of 30 – 40 C), or one can take advantage of the "waste" heat during the cool down period at the site as a treatment polishing agent.

Recently, the largest heat-activated SP field implementation was conducted using electrical resistive heating (ERH) to provide the thermal input. The project was conducted in the Seattle area on soils contaminated with pentachlorophenol (PCP), the target contaminant of concern, in a petroleum hydrocarbon matrix. The site design and implementation was performed by Sound Earth Strategies12 with the ERH implementation provided by TRS13.

Figure 1 Electrode design by TRS

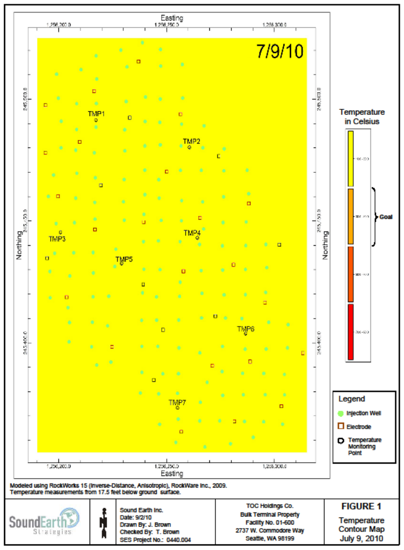

Figure 2 GW temperatures prior ERH

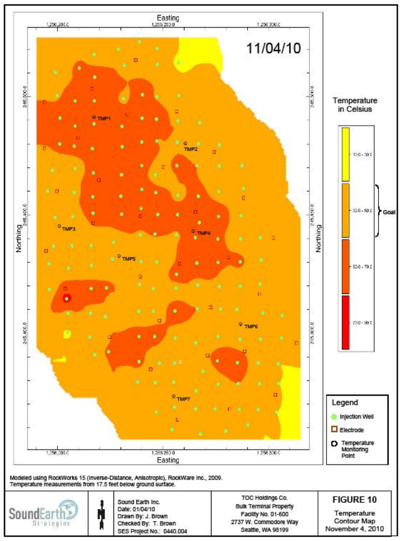

Figure 3 GW temperatures during Klozur SP application

ERH was applied for a couple of months prior to the Klozur SP injection. Groundwater temperatures were elevated between 35 and 50 C. Approximately 251,000 lbs of Klozur persulfate were applied to the site through a network of fixed wells. Figure 4 shows the impact of the ERH activated persulfate on the PCP concentrations in a selection of monitoring wells.

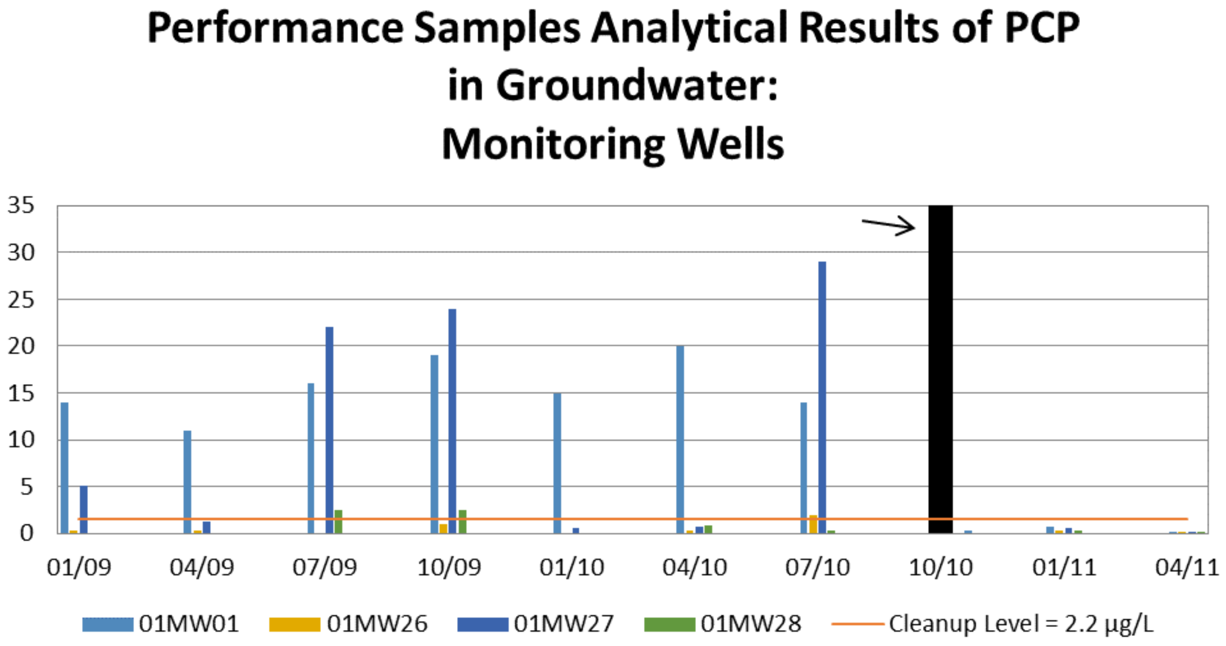

Figure 4 PCP concentrations before and after application of Klozur SP (data courtesy of Sound Earth Strategies).

From the figure, it can be observed that the PCP concentrations drop below the clean-up target level of 2.2 ug/L in all of the monitoring wells post persulfate application (actual values are all below 1 ug/L). No rebound of the PCP has been observed since the application has been done.

As a result, Klozur ERH can be an effective approach to remediate a contaminated site to clean-up levels. However, economics of the treatment process should be taken into account. The technology will be more feasible in parts of the country and around the world where energy costs are relatively low.

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