Treatment of NAPLs with Klozur® Activated Persulfate ISCO

Non-aqueous phase liquid (NAPL) contamination in the subsurface remains a challenging problem in the remediation of contaminated sites. Activated persulfate chemical oxidation can be used successfully to treat NAPLs, but there are many factors to be considered that may impact its effectiveness. In this month's Peroxygen Talk, NAPLs, and their removal via chemical oxidation with Klozur® activated persulfate will be explored.

NAPL Background

NAPLs are typically classified by their densities relative to water. Dense NAPLs (DNAPLs) have a density greater then 1 g/L and will sink in an aquifer until reaching an impermeable layer or become trapped in the pore structure of the soil due to hydrostatics. Examples of contaminants that form DNAPLs include chlorinated solvents, such as trichloroethylene (TCE) or perchloroethylene (PCE). Light NAPLs (LNAPLs) have densities less than 1 g / mL and can float in an aquifer until a confining layer is met, or likewise become trapped in the soil pore structure. These include contaminants such as BTEX or petroleum hydrocarbons. Neutral density ($\rho \sim 1$ g / mL) NAPLs may exist as well, and are often composed of a combination of contaminants of varying densities. NAPLs may exist as pools in the aquifer or as small, discrete droplets, fingers or thin layers dispersed in the soil or soil / groundwater matrix. In addition, NAPLs may absorb on to soil surfaces or penetrate into the soil structure.

Physical methods for removing NAPLs include excavation, pumping it out of a well, dual – phase extraction, or through volatilization via air sparging. However, as the volume and surface area of the NAPL decrease, the removal of NAPL through pumping or volatilization will reach a point of diminishing returns for which the energy and cost of pumping out the next gallon of NAPL may no longer be effective or economical. Heat can also be applied to the sub-surface in order to either increase the water solubility of the NAPL contaminant, increase the volatilization, or to thermally destroy the NAPL in place. Surfactants also can be used to flush the NAPL into capture wells. For details on these methods, please see Reference 1.

One of the major problems associated with NAPLs is that they often are poorly characterized either in location or extent, if they are known to exist at all. As a result, the NAPL can often be under-treated or missed altogether, resulting in residual NAPL after the remediation has taken place. NAPLs can provide a source of long-term contaminant rebound if not completely removed. If contaminant groundwater or soil concentrations are high, one can infer the presence of NAPLs at the site. Conservative estimates indicate that if the groundwater concentration is in excess of 1% of the contaminant solubility in water, then a NAPL is present (less conservative estimates indicate that 10% of the solubility indicates the presence of NAPLs). Table 1 shows several examples of contaminants and their solubilities and NAPL indicator groundwater concentrations.

Contaminant	Solubility (20 – 25 C) ppm	1% of solubility ppm	10% of solubility ppm
Benzene	1,790	17.9	179
Toluene	530	5.3	53
Naphthalene	30	0.3	3
TCE	1,000	10	100
PCE	150	1.5	15
Carbon Tetrachloride	8	0.08	0.8
Chlorobenzene	472	4.72	47.2

Table 1: Several chemical compounds and their solubilties in water, and the concentrations indicative of their presence of NAPLs.

Application of Klozur Activated Persulfate for NAPL Remediation

The application of an aqueous oxidant, such as Klozur activated persulfate, for the remediation of NAPLs presents several challenges. First, contact with the NAPL must be achieved. This requires a good understanding of the location and extent of the NAPL, and a well designed plan of delivery to insure maximum contact time between the oxidant and the NAPL. In addition, the density of the Klozur persulfate solution being injected can greatly influence the ability to contact the NAPL. Highly concentrated solutions of persulfate will have a relatively high density (ex: 30 wt% Klozur SP solution will have a density of 1.24 g / mL). For DNAPLs, a high density for the persulfate solution is an advantage, as it will bring the oxidant in contact with the DNAPL. However, for LNAPL's, a lower persulfate solution concentration should be used to insure the persulfate does not sink past the contaminant. Secondly, oxidizing pure phase contaminant can require a significant amount of oxidant to meet clean-up goals. As the pore space becomes filled with NAPL, the amount of Klozur persulfate needed to remediate the contaminant significantly increases. *As a result, it is recommended pumping out as much as the NAPL prior to chemical oxidation as feasible, to insure the Klozur persulfate application remains economically feasible.*

For residual or non-pump-able NAPL, Klozur persulfate can be successfully applied, as long as the oxidant is brought into contact with the contaminant. Klozur persulfate is highly hydrophilic, and will not significantly partition into oil-like phases or soils. As a result, oxidation will take place at the surface of NAPL only, resulting in a slow rate of NAPL destruction. If adequate contact and rapid NAPL destruction is to be achieved, the NAPL will need to be desorbed off of soils or solubilized into the aqueous phase. Enhancement of the contact between the persulfate and the NAPL can be achieved in several ways, as outlined below.

A. Heat activation of the Klozur persulfate.

Application of heat to the subsurface, via steam injection or other thermal technologies, will serve to increase the aqueous NAPL solubility and desorption rate from soil surfaces. As an example, for PAH NAPLs, the solubilities of pyrene increase four fold between 9 and 32 ºC and fourteen fold for anthracene over the same temperature range[2], although in general these solubilities still remain low until temperatures are significantly increased. In addition, heat application will increase persulfate reactivity, increasing the rate at which the NAPL is oxidized.

B. Activation By Hydrogen Peroxide

The use of hydrogen peroxide as an activator for Klozur persulfate will have several beneficial impacts on the treatment of NAPLs. Firstly, the decomposition of hydrogen peroxide in the sub-surface will generate localized heating, which as mentioned previously, can increase contaminant solubility.

In addition, there is evidence that hydrogen peroxide – activated persulfate may generate the superoxide radical, as evidenced by its ability to destroy carbon tetrachloride[3]. Watts, *et al*, have demonstrated that superoxide radicals can penetrate and enhance the degradation of sorbed PCE[4] and destroy carbon tetrachloride DNAPLs[5]. The advantage of Klozur activated persulfate over catalyzed hydrogen peroxide application is that the persulfate will remain in the subsurface for several weeks to months, as compared to hydrogen peroxide which is limited to a couple of days at most. Thus, persulfate will remain in contact with the NAPL a greater period of time.

C. High pH Activation

As with hydrogen peroxide activation, high pH activation of persulfate may generate the superoxide radical. This is evidenced by effectiveness of NaOH – activated persulfate on the destruction carbon tetrachloride[3]. Alkalinity is also known to provide detergency through solubilization of oils and saponification of fatty acid type compounds. As a result, addition of high pH modifiers, such as NaOH, lime, calcium peroxide and others will aid in the dissolution of NAPLs and enhance contact with the oxidant.

D. Surfactant Addition

Surfactants can support NAPL solubilization and enhance desorption by lowering the interfacial tension. Klozur persulfate in conjunction with surfactant systems can be a very powerful tool in the treatment of NAPLs. VeruTEK[8] has pioneered the combination of Klozur Persulfate with surfactants, coining the phrase "surfactant-enhance *in situ* chemical oxidation". An example of VeruTEK's surfactant enhanced Klozur persulfate for the treatment of coal tar and other manufactured gas plant residuals (MGP) can be found at the Klozur Persulfate Resource Center[6].

Conclusion

NAPLs are a technically challenging problem to address in the sub-surface, and represent one of the key targets for new methods to achieve site clean-up. In general, it is best to remove as much NAPL through extraction methods as possible before tackling the contaminant with chemical oxidation. However, Klozur activated persulfate have been used successfully to treat petroleum and chlorinated solvent NAPL sites. The breadth of activation methods, or the use of surfactants, coupled with persulfate provides the tools needed to remediate NAPL contaminated soil and groundwater. The keys to success are: identifying the location and amount of NAPL present; insuring adequate contact between the Klozur persulfate and the contaminant NAPL; adequately dosing the oxidant to achieve destruction of the entire NAPL; and increasing the NAPL solubility or desorption rate from the soil by the effective use of activator systems or surfactants.

1. Interstate Technology and Regulatory Cooperation Work Group. “Dense Non-Aqueous Phase Liquids (DNAPLs): Review of Emerging Characterization and Remediation Technologies”. June 2000.

2. Reza, J., A. Rejo and L. Vera-Avila. “Water Solubility and Solution Enthalpy of Polycyclic Aromatic Hydrocarbons”. 14th Symposium on Thermophysical Prperties, NIST, 2000.

3. Root, D., E. Lay, P. Block and W. Cutler. “Investigation of Chlorinated Methanes Treatability Using Activated Sodium Persulfate”. 1st Conference on Environmental Science and Technology. 2005 (see the Klozur Resource Center at www.klozur.com)

4. Watts, R**.** **Environ Sci and Tech** 33, p 3432, 1999.

5. Watts, R., J. Howsawkeng, A. Teel. “Destruction of Carbon Tetrachloride DNAPL by Modified Fenton’s Reagent”. **J. Environ Eng** 131, p

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