

Expectations for the Performance of In Situ Chemical Oxidation: Experimental and Numerical Investigations

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ABSTRACT: Only a limited set of data is available in the research literature describing the impacts of in situ chemical oxidation using permanganate on the long term reduction of contaminant concentrations in groundwater. In terms of both the removal of dense, non-aqueous phase liquids (DNAPL) and the reduction of contaminant concentrations in groundwater, three general outcomes which may be expected following an oxidant flush, along with the site-specific conditions which are likely to result in these outcomes, are presented.

At many sites, attempts to manage groundwater contamination associated with the presence of dense, non-aqueous phase liquids (DNAPLs) such as trichloroethene (TCE) and perchloroethene (PCE) have met with limited success. The depth and areal distribution of DNAPLs often precludes any attempts at excavation while the effectiveness of pump and treat is limited by the low solubility of these contaminants, the weakness of dispersive mixing processes, and kinetic limitations on the rates of mass transfer from the DNAPL into the dissolved phase. Increasingly, source removal technologies such as in situ chemical oxidation (ISCO) using permanganate are deployed to aggressively remove DNAPL mass and/or reduce the concentration of the target contaminants below regulatory criteria; however, only limited data is available in the research literature describing the effectiveness of this technology under varied site conditions. This abstract presents some conceptual outcomes that may be reasonably expected and the key factors that favor these outcomes. Examples of controlled laboratory and field studies evaluating the use of permanganate with TCE and PCE are used to demonstrate the specific factors; however, the discussion is generally applicable the use of Fenton's reagent.

The performance of chemical oxidation is dependent upon mixing between the oxidant and the contaminants, which in turn is controlled by site-specific conditions. Schnarr et al (1998) describe a macro-scale mechanism based on stagnant film mass transfer theory (Figure 1) in

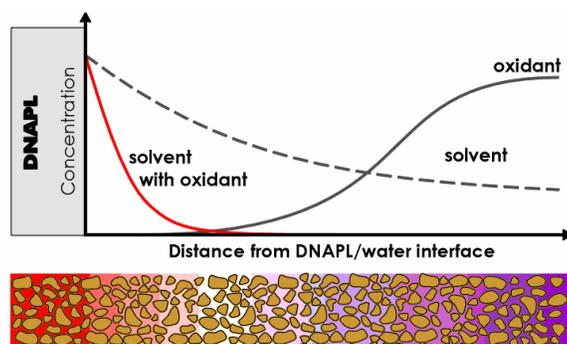


Figure 1 - Enhanced mass transfer mechanism

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which a rapid degradation reaction occurring in the aqueous phase sufficiently enhances the rate of mass transfer that significant DNAPL mass may be removed in a time scale that is short in comparison to pump-and-treat. The mass transfer enhancement results from an increase in the concentration gradient of the contaminant across the film at the interface between the DNAPL and water caused by oxidation of the contaminant in the bulk aqueous phase. In this model, advective oxidant transport to DNAPL interface is the most significant oxidant delivery process; however, Figure 1 suggests that dispersive mixing, a much weaker oxidant delivery process, may limit DNAPL mass removal. With this context, several conceptual outcomes of chemical oxidation are discussed in the following sections.

The most optimistic outcome of chemical oxidation is complete DNAPL removal which was observed in a field trial evaluating the impact of permanganate flushing on a residual PCE DNAPL source zone (Schnarr et al., 1998). Over the long term, since the large mass of DNAPL resulting in the formation of a groundwater plume is removed, the concentration of the contaminant in groundwater will drop to the background concentration. This outcome results when advective delivery of sufficient oxidant mass is possible throughout the source area and is favored under conditions including low volumetric DNAPL saturation, highly permeable and relatively homogeneous media, and high permanganate concentration.

However, the most likely outcome of a chemical oxidation treatment approach is partial removal of the DNAPL mass and a reduction in dissolved phase concentration. While the DNAPL mass present in regions of the aquifer where oxidant delivery is dominated by advection may be readily removed, the rate of mass transfer from the remaining DNAPL mass is limited by diffusion of the contaminant and oxidant through stagnant water surrounding the DNAPL. Oxidant delivery through diffusion is less likely to result in a significant mass transfer enhancement (Hood, 2000). Advective oxidant delivery is limited and diffusive oxidant delivery favored under conditions which include high volumetric DNAPL saturation, relatively impermeable and heterogeneous media, and low permanganate concentration. This outcome has been observed in a number of experimental investigations. For example, in a simulated remediation scheme in which a heterogeneous DNAPL containing very high volumetric DNAPL saturations was flushed with permanganate, removal of ~40% of the DNAPL mass resulted in a ~15% reduction of the contaminant mass within the dissolved phase plume (Hood and Thomson, 2000). Diffusion is also implicated as limiting DNAPL removal in an experimental evaluation of the effects of permanganate flushing on a PCE DNAPL pool (MacKinnon and Thomson, 2000). Partial DNAPL removal and concentration reduction may be expected to occur at the majority of sites, which suggests that an adequate understanding of the level of concentration reduction which may be reasonably expected will be critical to ensuring effective application of this technology.

Finally, the least desirable outcome of chemical oxidation is minimal DNAPL removal with only a temporary reduction in dissolved phase concentration. Factors favoring minimal DNAPL removal include the delivery of insufficient oxidant mass relative to mass of DNAPL (low oxidant concentration, poor mixing, short injection duration, etc.), and high DNAPL saturation. While the presence of the permanganate will rapidly degrade the dissolved phase concentration,

the duration of the concentration reduction will be dependent upon the persistence of the permanganate in the source area. Since oxidation of porous media can exert a significant oxidant demand in addition to that of the target contaminants (e.g., Barcelona and Holm, 1991; Hood, 2000), the persistence of permanganate is likely to be limited and once it is depleted, a dissolved phase plume will be generated by the remaining DNAPL resulting in an increase in contaminant concentration.

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