MEASURING EFFECTIVENESS OF IN-SITU CHEMICAL OXIDATION FOLLOWED BY BIOREMEDIATION

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Introduction

Evaluation of total contaminant mass destruction is required to measure the true effectiveness of in-situ chemical oxidation followed by bioremediation. At each site, the post-treatment question of this two stage treatment process should not be “has either technology worked?” but rather “how effective has the total treatment process been?” This question can only be answered by comprehensive pre-treatment and post-treatment total contaminant mass characterization including vapor, free-product, absorbed and dissolved phases.

In the past, in-situ total contaminant mass destruction technologies have too often been maligned for being ineffective at too many sites. This pre-assumed ineffectiveness bias is based on:

1. Apparent inadequate reductions or even possible increases in dissolved phase target constituents or reductive products,
2. Post-treatment dissolved phase concentration rebound.

Reality is that mass reduction has occurred but because these maligned sites were not properly characterized to evaluate the nature and extent of total contaminant mass, a fully effective application of these aggressive remediation approaches was too often not completed.

Benefit of Using Chemical Oxidation to Mass Transfer Adsorbed Phase Contaminants into the Dissolved Phase

There are some people that believe that chemical oxidation and bioremediation cannot co-exist as an effective primary and secondary treatment process. These same people believe that chemical oxidation actually completely sterilizes the natural environment to the extent that it would take decades to resume proactive bioremediation or even restore natural attenuation. The authors of this paper believe that this is belief is an incorrect assessment of what actually occurs when chemical oxidation is used as the primary treatment step and bioremediation is used as the secondary treatment step.

First, during the application of peroxide-based chemical oxidation technologies, the site is maintained in an oxygen rich environment, which facilitates aerobic bioremediation. Second, the mass transfer of difficult to treat recalcitrant compounds from the absorbed phase into the more readily accessible dissolved phase facilitates a second round of treatment, which could be another application of chemical oxidation reagents or the initiation of proactive bioremediation followed by natural attenuation. Third, the authors believe that aggressive total mass reduction initiated by chemical oxidation facilitates secondary treatment by bioremediation. This is particularly true when the contaminants are toxic towards naturally occurring facultative microbes.

Again, Total Mass Evaluation is Required; Dissolved Phase Evaluation alone is Inaccurate!

Regarding the issue of apparent ineffective dissolved phase contaminant reductions, a total mass evaluation is imperative when peroxide-based chemical oxidation technologies are applied because these treatments with exothermic and bubbling reactions affect the equilibrium conditions at the Site. These actions by themselves raise the dissolved concentrations but do not increase the mass. Through both physical and mechanical means, these technologies convert absorbed mass and phase-separated mass within and above the saturated zone into dissolved phase mass where it can be effectively oxidized.

In many cases, due to nature of the geochemistry, physical geology and technology application efficiencies; more mass is converted into the dissolved phase mass than is oxidized. The result is that immediately after treatment and for several months later, even though the total mass has been reduced by orders of magnitude, the dissolved constituents may have increased. However once the site returns to equilibrium, which could be many months, the actual reduction in concentrations will be reflected in the dissolved mass. In the event that a complete characterization of the nature and extent of the total mass in the treatment area had been evaluated, the realization of the success of the treatment would have been realized immediately.

For traditional mass transfer technologies, use of only dissolved phase mass characterization techniques to measure relative concentrations of contaminants at the Site has generally been effective because the equilibrium conditions for the system remain constant relying on relatively static partitioning characteristics of the organic contaminants. This is acceptable, if the most of the total mass resides in the saturated zone and the groundwater elevations are static. Unfortunately at most sites, the groundwater is not static, smear zones of LNAPL sorbed contamination and in some cases phase separated pockets of DNAPL also co-exist. In these cases, a mass evaluation even for a mass transfer technology is essential for an effective system design.

Rebound Impossibility, Poor Site Characterization the Reality!

The notion of isolated dissolved phase rebound being caused solely by an oxidation technology is absurd. Even if no treatment occurred, just the addition of the chemicals will cause the concentrations of the target contaminants to decrease through mere dilution. The only way that rebound can occur is if 1.) Contamination existing outside the treatment area migrates into the application area after treatment, 2.) Contamination exists as an undetected NAPL plug either within or outside the treatment area, and/or 3.) Leachable levels of sorbed contamination exist in the soils above the treatment area. All of these issues are associated with inadequate characterization of the Site and not an apparently ineffective application of the oxidation treatment.

Information Required for Characterizing Candidate Sites

To avoid the pitfalls described above and to ensure the success of any oxidation process application, three primary factors characterizing the true nature of the Site must be accurately identified and completed. These three factors are required for accurately evaluating a Site, designing an effective In-situ Fenton's Treatment, and evaluating the success of the application. These three factors are: 1.) Nature of the contamination – How is the Mass distributed throughout the saturated zone, dissolved, sorbed and does it exist as a NAPL above or below the treatment area? 2.) Extent of the contamination – Where are the limits of the various phases of contamination in the soil and saturated zone including smear zones and NAPL? and 3.) Is the Source Known? - Where are the unsaturated and saturated zone source areas?

If all of these factors are not well defined, in-situ Fenton's applications are likely to be regarded as a failure because the site will likely have unimpressive or misunderstood results with likely recontamination over time from plume migration. The following are recommendations for evaluating a site prior to designing and applying In-situ Fenton's Reagent and for post treatment evaluation.

Remember it's the Mass, Remember it's the <u>TOTAL MASS</u>!

Traditional intrusive soil boring and monitoring well investigations combined with soil gas surveys is typically acceptable for defining the source and extent of sorbed and dissolved contamination. They do not however, adequately define the mass distribution throughout the treatment area or the nature and extent of NAPL. Traditional sampling protocols rarely addressed the contaminant mass distribution throughout the entire saturated and unsaturated soil column. Since oxidation technologies address all phases of contaminants and convert sorbed and phase separated mass into the dissolved phase during treatment, an understanding of the total mass in both the saturated and unsaturated zone is essential. The most cost effective and accurate method for obtaining this information is through geoprobe sampling within the treatment area before and after treatment. It is important to try to locate post treatment sampling points within a reasonable proximity to the baseline direct push points to attempt to replicate as nearly as possible the baseline results. This geoprobe sampling must be performed throughout the entire unsaturated and saturated contaminated soil column to determine the entire mass to be treated.

NAPL characterization is very problematic. NAPL distribution in both the confined and unconfined condition is accurately estimated through geoprobe sampling. Use of monitoring well data for LNAPL thickness estimates in the unconfined condition can be also a good representation of actual NAPL mass. However in confined applications, monitoring well data for LNAPL thickness is usually over stated and should be confirmed through geoprobe or downhole geophysical methods. Monitoring well data for all DNAPL sites should be confirmed through direct push sampling or geophysical tools.

Summary and Conclusions

Full-scale field application of a chemical oxidant (such as Fenton's Reagent) followed by either proactive bioremediation and/or monitored natural attenuation is highly feasible. Use of exothermic chemical oxidation reactions for rapid source area contaminant reduction can have a positive impact upon subsequent aerobic and anaerobic biotreatment applications. The authors believe that bioremediation actually becomes more effective after source area contaminant reduction is completed.

Regarding the measurement of effectiveness of chemical oxidation technologies in combination with bioremediation, these are contaminant mass destruction processes and as such require an accurate and complete evaluation of the source location, nature and extent of the contaminant to successfully apply these technologies. Chemical oxidation technologies alter the equilibrium partitioning of total mass distribution by converting sorbed and phase separated mass to dissolved phase both during and for a period of time after the application of treatment reagents. For this reason, evaluation of the success of the treatment application cannot be based on dissolved phase concentrations alone.

Total mass destruction can be calculated between the chemical oxidation and proactive bioremediation steps, however, the authors believe it is more appropriate to delineate total mass destruction at the conclusion of both the chemical and proactive bioremediation steps. The bioremediation step in many cases can serve as an effective polishing step to clean up residual dissolved phase contamination after the more difficult to achieve absorbed phase contaminant mass reduction has been addressed.