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How Important is Oxidant Demand for In-Situ Chemical Oxidation?

Oxidant demand is a metric commonly evaluated in laboratory bench tests and utilized for in-situ chemical oxidation (ISCO) remedies. There are many terms applied to different forms of oxidant demand, including total oxidant demand, soil oxidant demand, and natural oxidant demand, with a variety of different methods for their assessment. We are often asked to develop ISCO proposals for sites based upon oxidant demand estimates prepared by other vendors. The problem that arises is that different methods of oxidant demand assessment often provide very different results, even for the same oxidant. Thus, comparing oxidant demand among different ISCO methods, and certainly among different oxidants, is like comparing apples and oranges.

Chemical oxidants such as hydrogen peroxide, permanganate, and persulfate injected into the subsurface react with many substances other than the target contaminants. Such reactants may include metals, natural organic compounds, and even the oxidants themselves or byproducts of the oxidation reactions. Several comprehensive studies have found that oxidant demand is highly variable and depends upon intrinsic, site-specific factors, with generally little or no correlation with easily measurable analytes such as total organic carbon or

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chemical oxygen demand. Ultimately, the oxidant demand consumes the oxidizing reagent with reactions that may not result in destruction of the target contaminant, which therefore will increase the amount of oxidant required at a site. Thus, a reliable estimate of oxidant demand is an important factor in ISCO project design.

The nature of the chemical oxidant utilized plays a commonly underestimated role in assessing oxidant demand. Chemical oxidation systems used in ISCO can be broadly differentiated into two groups: catalyzed and uncatalyzed systems. Catalyzed systems require a first reaction between an oxidant and a catalyst or an activator, resulting in formation of a stronger oxidant that is more effective at destroying the target contaminants. Catalyzed (or "activated") systems include hydrogen peroxide (Fenton's reagent, modified Fenton's reagent, or catalyzed hydrogen peroxide) and sodium persulfate. Uncatalyzed systems are those in which the injected reagent reacts directly with the contaminant and does not require a catalytic reaction to generate a stronger oxidant. Uncatalyzed systems are primarily permanganate (either potassium permanganate or sodium permanganate).

Persulfate is primarily catalyzed by heat, strongly basic conditions, and reaction with metals. Peroxide is primarily catalyzed by reaction with metals. However, the kinetics (reaction rate and efficiency) of formation of the more reactive oxidant (typically hydroxyl radicals or persulfate radicals) are highly dependent upon the catalytic system utilized. For example, while strongly basic conditions catalyze persulfate, the reaction kinetics are primarily determined by the precise pH at which the reaction occurs. Similarly, both pH and iron concentration exert a strong influence on the kinetics of hydroxyl radical production from hydrogen peroxide. Therefore, in the case of catalyzed systems, the specific catalytic approach is a primary determinant of oxidant demand, and intrinsic site factors are often secondary. In contrast, permanganate does not require catalyzation. Permanganate oxidant demand is therefore generally more straightforward to estimate, and an ASTM method (ASTM D-7262) has been developed for standardization. Permanganate oxidant demand is correlated with the concentration of permanganate applied; however overall, permanganate oxidant demand is much less dependent upon technology-dependent factors (such as pH or iron concentration) than on intrinsic site factors.

So how relevant are oxidant demand estimates for ISCO projects? Certainly they are very important. ISCO is not very efficient in terms of comparing stoichiometric oxidant demand and actual field demand, and many complex, site-specific factors (in addition to contaminant concentrations or mass) influence reagent requirements. Oxidant demand for an uncatalyzed system, such as permanganate, is much less dependent upon the exact reaction conditions and is therefore more comparable among different practitioners using different methods. However, for catalyzed systems such as persulfate or peroxide, the oxidant demand estimated by one practitioner using specific test conditions is at best a very poor predictor of how much oxidant may be required by a different practitioner utilizing different test conditions. It is an apples to oranges comparison because the precise conditions (such as pH, metal concentration, oxidant concentration, etc.) control the resulting oxidant demand, yet the test conditions nearly always vary among different application methods used by different practitioners. Thus, oxidant demand for catalyzed systems is best estimated by practitioners using the same methods they will utilize for a field application.

You can also find this article in last months [Pollution Engineering Magazine](#).

For additional information regarding this article, please contact Dr. Dan Bryant at dbryant@geocleanse.com.

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**Assessment, Remediation, Regulation and
the Energy Environmental Interface**
Oct. 20-23, 2014
Amherst, Massachusetts

Geo-Cleanse will be presenting the following abstracts:

Coupling Oxidative and Reductive Treatment Technologies for Integrated Site Remediation - Will Moody

Successful Implementation of Catalyzed Hydrogen Peroxide within a Sensitive and Active Brownfield Property - **Will Moody**

A Novel and Sustainable "Combined Oxidant" In-Situ Remediation Approach for Brownfield Redevelopment in New Jersey - **Dr. Dan Bryant**

Activated Sodium Persulfate or Catalyzed Hydrogen Peroxide? Outlining the Advantages of Each Oxidant for Remediating Two Petroleum Hydrocarbon Impacted Sites - **Stephanie Turkot**

Evaluating, Selecting, and Implementing Catalyzed Hydrogen Peroxide Applications - **Stephanie Turkot**



Railroad Environmental Conference

Oct. 28-29, 2014
Champaign, Illinois

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