Natural Oxidant Interaction (NOI): A Paradigm Shift

In this addition of Peroxygen Talk, guest author Professor Neil Thomson discusses the concept of Natural Oxidant Interaction as a tool for better understanding the oxidant demands of a given site. Dr. Neil Thomson is the Chair of the Department of Civil and Environmental Engineering, and a member of the Environmental Modelling and Analysis Group at the University of Waterloo. He has more than 20 years of research experience and expertise in the use of field investigations, laboratory experiments and numerical models to explore subsurface contaminant fate and remediation issues. Neil's research interests are focused on the environmental fate of contaminants in subsurface systems, including immiscible liquids, vapours and pathogens, the development and application of simulation tools, and the development and assessment of soil and groundwater remediation technologies. He can be reached at neil.thomson@uwaterloo.ca.

Introduction

A critical issue requiring careful consideration during the design of an *in situ* chemical oxidant treatment system is the interaction between the selected oxidant and the uncontaminated subsurface environment. It has purposely denoted this interaction here as the natural oxidant interaction (NOI) rather than the natural oxidant demand (NOD). The latter terminology has gained widespread misuse as will hopefully become apparent as you read on.

Naturally occurring reductants and catalysts at many contaminated sites can be reactive and, thus, influence oxidant persistence. Typically, the role of the dissolved groundwater species is overshadowed by the aquifer solids (Barcelona and Holm, 1991). Inorganic species containing iron (Fe), manganese (Mn), sulphur (S) and the natural organic matter (NOM) associated with the aquifer solids are usually of concern (Mumford et al., 2005). The possibility of multiple inorganic species, as well as a range of NOM, creates an extremely heterogeneous environment in which reactions may occur. NOM may be both refractory and labile towards oxidation, and therefore, the oxidation of NOM is highly dependent on the reactivity of the various functional organic groups that comprise the NOM.

The result of the interaction between the selected oxidant and aquifer material leads to either an increase in the consumption of the oxidant by the aquifer solids, or an enhancement in the oxidant decomposition rate. When an oxidant is consumed, the reactive species associated with the aquifer solids are finite, and hence there exists a finite consumption or NOD. Once the maximum NOD is satisfied there is minimal additional oxidant aquifer material interaction. Conversely, an enhancement in the oxidant decomposition rate implies that there is infinite interaction capacity available. The suggested paradigm shift from NOD to NOI is required to capture these behavioral differences and the associated underlying processes.

Regardless of the way in which NOI may manifest, it will decrease the mobility of the oxidant, the reaction rate with the target compound(s), and the mass of oxidant available thus creating an inefficient treatment system. Quantification of the NOI is a requirement for site-specific assessment and the design of cost-effective *in situ* chemical oxidant treatment systems.

A general kinetic expression that can be used to capture the behavior of most oxidants in the presence of uncontaminated aquifer solids is given by

[1]

$$\frac{\mathrm{d}[C_{ox}]}{\mathrm{dt}} = -k_o[C_{ox}] - \sum_{\text{cat}} k_{cat}[C_{ox}][C_{cat}] - \sum_{\text{NOM}} k_{\text{NOM}}[C_{ox}][C_{\text{NOM}}]$$

where C_{ox}, C_{cat}, and C_{NOM} is the concentration of the oxidant, catalyst and NOM respectively, and k_o, k_{cat}, and k_{NOM} is the reaction rate coefficient for a decomposition reaction, catalytic reaction(s), and NOM reaction(s) respectively. The first term on the right-hand side of Eq. [1] captures oxidant depletion due to auto or thermal decomposition processes, the second term represents oxidant reactions with catalyses (by definition the catalyses involved in these reactions are not consumed), and the third term represents reactions with the various forms of NOM.

Of interest here is a comparison of the behavior of peroxide, permanganate and persulfate under similar conditions. To aid in this effort, I will draw upon a study conducted at the University of Waterloo where we investigated the interaction of these oxidants with 10 different aquifer materials using primarily batch and column experiments, and some field tests. Specific details of the characteristics of these aquifer materials have been reported elsewhere; but in general the materials vary from sands to silty-sands (Xu and Thomson, 2009). The focus here is on aquifer materials which by their nature will have properties which are intrinsically different from surfacial soils or surface water sediments. A discussion of the attributes and limitations associated with the various bench-scale and field tests to estimate site-specific NOI is beyond the scope of this short note

Peroxide Behavior

The data generated from the batch experiments indicated that the decomposition of hydrogen peroxide (no ferrous Fe added) in the presence of the various aquifer solids followed a first-order rate law (Xu and Thomson, 2010). As expected these decomposition rate coefficients were higher in the column experiments relative to the batch experiments due to the larger solids mass to solution volume ratio. The peroxide half-life in the column experiments varied from 5 min to 7 hours. Repeated flushing of the same aquifer solids packed column with peroxide resulted in no change in the decomposition rate coefficients generated. The decomposition rate coefficients were strongly correlated to the content of amorphous transition metals, and only weakly correlated to the NOM content. The findings from this effort suggest that an appropriate form of Eq [1] for hydrogen peroxide is given by

$$\frac{\mathrm{d}[C_{\mathrm{H_2O_2}}]}{\mathrm{dt}} = -k_{Fe}[C_{\mathrm{H_2O_2}}][C_{Fe}] \qquad [2]$$

where $C_{\mathrm{H_2O_2}}$ and C_{Fe} is the concentration of the peroxide and amorphous iron respectively, and k_{Fe} is the reaction rate coefficient for the enhanced catalytic decomposition reaction. The following general attributes apply to peroxide NOI behavior:

- Enhanced first-order degradation rate
- Insignificant change in NOM
- Repeated decomposition behaviour
- Infinite interaction

Permanganate Behaviour

The permanganate concentration data collected from the batch experiments indicated that, as time progressed, the concentration of permanganate decreased and asymptotically approached a plateau (Xu and Thomson, 2009). The decrease in permanganate concentration and the initial mass of aquifer material were used to estimate the permanganate natural oxidant demand (NOD) (mass of $KMnO_4$ consumed per mass of dried aquifer material in g/kg). NOD is analogous to the biochemical oxygen demand (BOD) which results from a test used to measure the organic content of water. Figure 1 shows a typical permanganate NOD temporal profile.

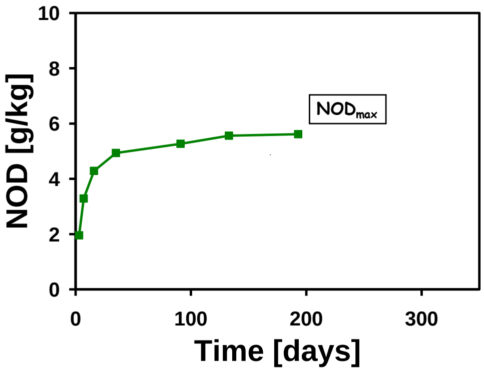

Figure 1. Typical permanganate NOD profile.

All NOD temporal profiles demonstrated an initial fast consumption rate followed by a slower consumption rate. Approximately 50% of the maximum NOD (NOD_{max}) was expressed within the first 7 days. The main factors controlling permanganate consumption rates are the mass loading ratio, the initial permanganate concentration, and the nature and quantity of reduced aquifer material species. For example, a higher initial permanganate concentration or a larger mass loading ratio yields a larger fast NOD consumption rate and generates a corresponding higher NOD_{max}. Both the NOD temporal profile and the NOD_{max} are not single-valued but are heavily dependent on the experimental conditions. A high degree of correlation was observed between NOD_{max} and the NOM content implying that organic carbon is the major reduced species contributing to permanganate consumption for the aquifer materials used in this investigation.

The following version of Eq. [1] was used to represent the consumption of permanganate in the presence of aquifer solids

[3] $$\frac{\mathrm{d}[C_{\mathrm{KMnO_4}}]}{\mathrm{dt}} = -k^{fast}_{\mathrm{KMnO_4}}[C^{fast}_{\mathrm{NOM}}][C_{\mathrm{KMnO_4}}] - k^{slow}_{\mathrm{KMnO_4}}[C^{slow}_{\mathrm{NOM}}][C_{\mathrm{KMnO_4}}] - k_{\mathrm{MnO_2}}[C_{\mathrm{KMnO_4}}]$$

where $C_{\mathrm{KMnO_4}}$ is the permanganate concentration, C^{fast}_{NOM} and C^{slow}_{NOM} are the concentrations of the fast and slow NOM fractions, $k^{fast}_{\mathrm{KMnO_4}}$ and $k^{slow}_{\mathrm{KMnO_4}}$ are the fast and slow reaction rate coefficients, and $k_{\mathrm{MnO_2}}$ is the reaction rate coefficient associated with the decomposition reaction catalyzed by MnO_2. The following general attributes apply to permanganate NOI behavior:

- Marked fast and slow consumption rates
- Significant change in NOM
- Passivation of reaction sites due to MnO_2 deposition
- MnO_2 catalyzed decomposition
- Finite interaction
- Definitive NOD

Persulfate Behavior

For all aquifer materials used, the decrease in persulfate concentration followed a first-order rate law (20° C, and no activator present) (Sra et al., 2010). This is consistent with the decomposition of persulfate in the presence of catalysts and other reductants in aqueous systems. Surprisingly, at a higher initial persulfate concentration (20 g/L) the reaction rate coefficients were significantly lower than the reaction rate coefficients observed at the lower concentration (1 g/L) indicating higher persulfate stability at higher concentrations. Column tests which are more representative of an *in situ* oxidant to solids mass ratio yielded reaction rate coefficients that were ~8 times higher than the corresponding batch test coefficients. Four of the aquifer materials showed a significant decrease in the NOM content following exposure to persulfate. The developed kinetic expression representing the interaction of unactivated persulfate with aquifer solids is

[4] $$\frac{d[C_{S_2O_8^{2-}}]}{dt} = -(k_1 + k_2[H^+])[C_{S_2O_8^{2-}}] - k_{cat}[C_{S_2O_8^{2-}}][C_{cat}]^{1.5} - k_{NOM}[C_{S_2O_8^{2-}}][C_{NOM}]^{1.5}$$

where $C_{S_2O_8^{2-}}$ is the persulfate concentration, C_{cat} is the catalyst concentration, C_{NOM} is the NOM concentration, k_1 is the reaction rate coefficient for uncatalyzed degradation, k_2 is the reaction rate coefficient for acid catalyzed degradation, k_{cat} is the reaction rate coefficient for mineral catalyzed reaction, and k_{NOM} is the NOM reaction rate coefficient. This kinetic expression was used to successfully model a series of persulfate push-pull tests performed at CFB Borden (Figure 2).

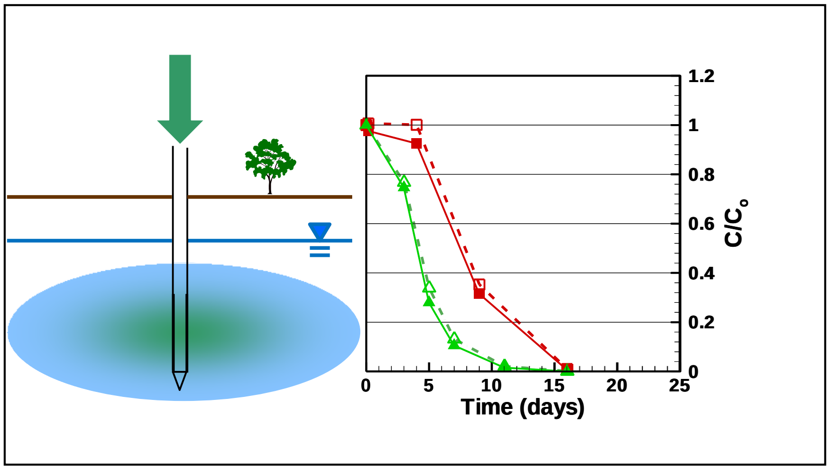

Figure 2. Observed (symbols) and theoretical (lines) persulfate concentration profiles from two push-pull tests conducted at CFB Borden with an initial persulfate concentration of 20 g/L.

The following general attributes apply to persulfate NOI behavior:

- Enhanced first-order degradation rate
- Higher stability at higher concentrations
- Slight to moderate decrease in NOM
- Repeated decomposition behaviour
- Infinite interaction, infinite NOD

Performance Comparison

To demonstrate the inherent differences between the persistence of peroxide, permanganate and persulfate in the presence of aquifer solids, consider the following injection scenario: (1) an uncontaminated aquifer is subject to the injection of an oxidant (peroxide, permanganate or persulfate) in two sequential episodes spaced 30 days apart; (2) following injection the oxidant solution remains immobile as it reacts with the aquifer material; (3) the controlling *in situ* kinetic parameters are taken from the bench-scale effort described above for the same aquifer material; and (4) the injection concentration is adjusted so that the "oxidation strength" is identical for each oxidant. Figure 3 illustrates the oxidant concentration profiles over 60 days.

The following observations are noteworthy:

- Peroxide concentration is rapidly reduced.
- The peroxide profiles following injection 1 and injection 2 are identical.
- The permanganate concentration profile following injection 1 decreases quickly and then slows down as it approaches an asymptote.
- The decrease in the permanganate concentration profile following injection 2 is much less than after injection 1 reflecting the consumption of much of the fast reacting NOM.
- The persulfate concentration profile is identical following injection 1 and injection 2.
- Since the persulfate reaction rate is substantially less than peroxide, an increase in persulfate persistence occurs.

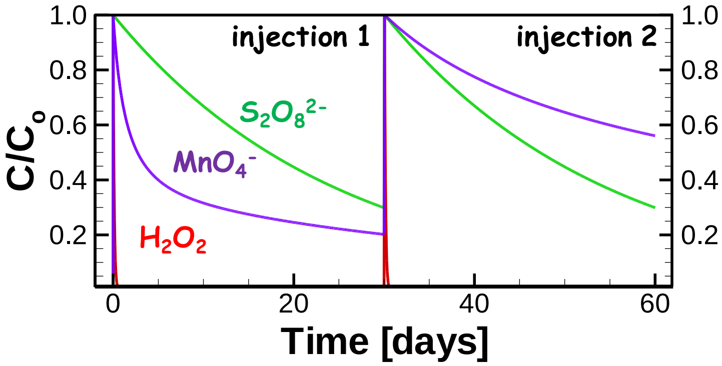

Figure 3. Concentration profiles following two sequential injection episodes into a synthetic aquifer for peroxide (red), permanganate (purple) and persulfate (green).

Summary and Warnings

- Peroxide NOI manifests as an enhanced decomposition rate without significant alteration to the NOM content of the aquifer solids. There is no finite peroxide NOD. Repeated addition of peroxide will lead to continual decomposition.
- Permanganate NOI manifests as a consumption by the NOM. Aquifer materials exhibit a finite demand for permanganate or NOD_{max}. Repeated addition of permanganate will lead to increased persistence.
- Persulfate NOI manifests as an enhanced decomposition rate with a slight decrease in the NOM content of the aquifer solids. There is no finite persulfate NOD. Repeated addition of persulfate will lead to continual decomposition.
- Ignoring NOI will overestimate treatment efficiency.
- Site geochemical heterogeneity should also be considered when assessing NOI variability for system design.
- Bench-scale data are hindered by experimental conditions and scale-up issues. NOI data estimated at this scale should be used with caution.

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