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Complexities of "New" Peroxide Stabilizers

In the April 2012 issue of our newsletter, we discussed how all experienced in-situ chemical oxidation practitioners use peroxide stabilizers of some type, and that there really is no difference between "catalyzed hydrogen peroxide" and "stabilized hydrogen peroxide" because peroxide must be catalyzed to effectively destroy contaminants and must be stabilized to allow safe and effective distribution in the subsurface. Today's newsletter focuses on the use of phytate as a stabilizer, which has been widely discussed recently in the literature and conferences. We show that the use of phytate is not straightforward and offers little benefit but much higher cost over more traditional stabilizers.

Phytate is a large organic molecule whose structure is basically an aromatic ring with six molecules of $H_2PO_4^-$ (a conjugate base of phosphoric acid) appended to the ring (Figure 1). Phytate is a naturally occurring compound that provides phosphate storage in many plants. Phytate is commercially available as the sodium salt, which has the formula $Na_{12}C_6H_6O_{24}P_6$ and has a molecular weight of about 924 grams per mole. When dissolved in solution, the sodium is swapped for certain cationic metals including iron. Phytate forms an unreactive

Figure 1.

complex with Fe(III), which terminates further redox cycling of iron and decomposition of peroxide to provide the stabilizing property (Graf et al., 1984, 1987). However, studies on the use of phytate for treatment of contaminated soil show that the impact of phytate on metal solubility is complex. In some cases phytate can increase metal solubility and in other cases decrease the solubility of the same metal, depending upon solution conditions, type and concentration of the metal, and the concentration of phytate (e.g., Seaman et al., 2003). This may be responsible for the variable efficacy of phytate in bench tests of peroxide stabilization with different soil types (e.g., Watts et al., 2007). Furthermore, the concentration of certain oxyanionic metals including arsenic, selenium, and
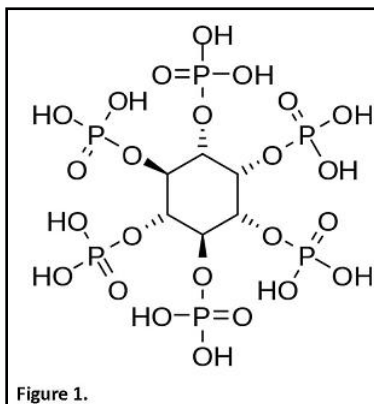
chromium has been observed to increase in solution (and thus have increased mobility) following phytate addition (Seaman et al., 2003).

Geo-Cleanse undertook an assessment of different peroxide stabilizers prior to field applications at a Superfund site in New Jersey, at which groundwater is characterized as acidic (with pH typically ranging from about 2.5 to about 6) with elevated iron concentrations (typically ranging from 300 to 900 mg/L). In our tests, hydrogen peroxide was added to groundwater with an initial concentration of 2,340 mg/L. Peroxide decomposition over time was analyzed at a range of phytate concentrations. The peroxide concentration in each experiment was plotted as a function of time. The log of peroxide concentration is a linear function of time (Figure 2), which indicates decomposition is first order with respect to peroxide concentration. The first order rate constants are plotted as a function of phytate concentration in Figure 3.

In the absence of phytate, peroxide was rapidly decomposed in groundwater from the site with a reaction rate constant 0.775 hr^{-1} (large blue circ les in Figure 2). Surprisingly, addition of phytate at low concentrations (0.3 to 0.7 mM phytate) resulted in an increase in the peroxide decomposition rate relative to the control; thus peroxide was destroyed more rapidly in the presence of low concentrations of phytate than in the absence of phytate (red symbols in Figure 2). Stabilization (i.e., a peroxide decomposition rate lower than in the control) was not observed until phytate concentrations reached approximately 1 mM (green symbols in Figure 2). At a phytate concentration of 2 mM, peroxide decomposition was completely inhibited; the experiment was allowed to run for over 44 hours (data past 2 hours are not shown in Figure 2) with negligible degradation after the first minute of reaction.
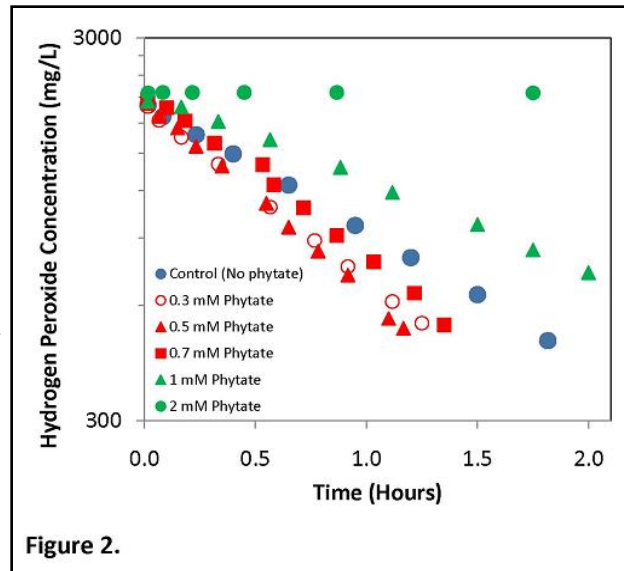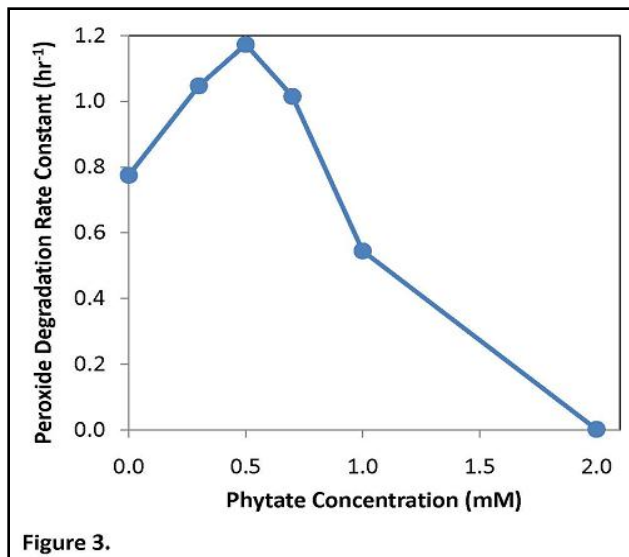
Figure 2.

The key conclusion drawn from these experiments and a review of the literature is that the stabilizing properties of phytate are complex. Maintaining a relatively constant phytate concentration within a narrow, but chemically optimal range in an aquifer is not feasible, which further complicates field application; thus at one end of a narrow range of concentrations phytate will actually enhance peroxide decomposition, while at the opposite end of the narrow range phyt ate reduces the peroxide decomposition rate to zero. Peroxide must be decomposed (catalyzed) in order to generate the hydroxyl radicals and other reactive species responsible for contaminant destruction, thus completely inhibiting peroxide degradation is not desired. An additional factor to consider is the cost of the reagent. Sodium phytate costs on the order of $20 per pound, and concentrations on the order of 1-2

mM are required for stabilization. In contrast, commonly-used phosphate stabilizers cost less than $3 per pound and require similar concentrations for effective stabilization, and thus are considerably less costly in addition to being easier to procure and apply. Although phytate has been utilized in the field (e.g., Cronk et al., 2012), there are equally (or more) effective stabilizers that are more readily available, less complex to apply in the field, and much less costly than phytate. Future issues of our newsletter will discuss the performance of other stabilizers.

Figure 3.

Article Notes

Figure 1. Phytic Acid- Chemical structure of phytic acid.

Figure 2. Hydrogen Peroxide Concentration (mg/L) Over Time (Hours)- Hydrogen peroxide degradation over time for a range of phytate concentrations. The 2 mM test was run for 44 hours (data not shown) but exhibited negligible peroxide degradation over that time period.

Figure 3. Peroxide Degradation Rate Constant (hr^{-1}) Over Phytate Concentration (mM)- Hydrogen peroxide degradation rate constants plotted as a function of phytate concentration.

References Cited

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