Chemosphere 74 (2009) 847–853

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Control of manganese dioxide particles resulting from in situ chemical oxidation using permanganate

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ARTICLE INFO

Article history:
Received 23 January 2008
Received in revised form 24 September 2008
Accepted 24 September 2008
Available online 25 November 2008

Keywords:
Sodium hexametaphosphate
Particle stability
Permanganate
Chemical oxidation
Manganese dioxide

ABSTRACT

In situ chemical oxidation using permanganate is an approach to organic contaminant site remediation. Manganese dioxide particles are products of permanganate reactions. These particles have the potential to deposit in the subsurface and impact the flow-regime in/around permanganate injection, including the well screen, filter pack, and the surrounding subsurface formation. Control of these particles can allow for improved oxidant injection and transport and contact between the oxidant and contaminants of concern.

The goals of this research were to determine if MnO_2 can be stabilized/controlled in an aqueous phase, and to determine the dependence of particle stabilization on groundwater characteristics. Bench-scale experiments were conducted to study the ability of four stabilization aids (sodium hexametaphosphate (HMP), Dowfax 8390, xanthan gum, and gum arabic) in maintaining particles suspended in solution under varied reaction conditions and time. Variations included particle and stabilization aid concentrations, ionic content, and pH.

HMP demonstrated the most promising results, as compared to xanthan gum, gum arabic, and Dowfax 8390 based on results of spectrophotometric studies of particle behavior, particle filtration, and optical measurements of particle size and zeta potential. HMP inhibited particle settling, provided for greater particle stability, and resulted in particles of a smaller average size over the range of experimental conditions evaluated compared to results for systems that did not include HMP. Additionally, HMP did not react unfavorably with permanganate. These results indicate that the inclusion of HMP in a permanganate oxidation system improves conditions that may facilitate particle transport.

1. Introduction

In situ chemical oxidation (ISCO) using permanganate is an approach to organic contaminant remediation increasingly being applied at hazardous waste sites throughout the United States and abroad. Manganese dioxide particles are products of the reaction of permanganate with organic contaminants and naturally reduced subsurface materials. For example, Eq. (1) demonstrates the reaction between permanganate and trichloroethylene (TCE) resulting in the generation of manganese dioxide solids

$$2KMnO_4 + C_2HCl_3 \rightarrow 2CO_2 + 2MnO_2 + 2K^+ + H^+ + 3Cl^- \quad (1)$$

The MnO_2 generated as per Eq. (1) are actually reactive semi-amorphous birnessite Mn oxides with a layered mineral structure (Li and Schwartz, 2004). The Mn oxides (hereafter referred to as MnO_2 for simplicity) can be soluble/colloidal or particulate in form depending on the reaction conditions. The amount of MnO_2 particles that develop, grow, and potentially deposit as a result of permanganate ISCO is a function of the particle size and concentration, the time allowed for particle development, and the impact of reaction conditions on the ability of the particles to agglomerate (Crimi and Siegrist, 2004b).

MnO_2 particles may deposit in the subsurface and impact the flow-regime in and around the zone of oxidant emplacement, thereby preventing effective oxidant distribution and contact with contaminants (e.g., Lee et al., 2003). Changes in hydraulic conductivity may result due to MnO_2 particle deposition, which has been observed in some laboratory and field evaluations (e.g., West et al., 1998, 2000; Li and Schwartz, 2000; Reitsma and Marshall, 2000; Schroth et al., 2001; Lowe et al., 2002; Reitsma and Randhawa, 2002; Lee et al., 2003), but not in others (e.g., Chambers et al., 2000a,b; Mott-Smith et al., 2000; Nelson et al., 2001; Struse et al., 2002). For example, Nelson et al. (2001) found that MnO_2 produced during oxidation of a tetrachloroethylene dense non-aqueous phase liquid present at approximately 4–7% saturation had a negligible effect on permeability; however Lee et al. (2003) found that permanganate oxidation of a TCE source zone at 8% saturation, where up to 4900 mg-MnO_2 per kg-porous media were generated, resulted in a six-fold decrease in velocity of the

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doi:10.1016/j.chemosphere.2008.09.074

oxidation front over a 2 month period. Heiderscheidt (2005) estimates, via calculation, that the MnO_2 generated in the experiments of Lee et al. (2003) results in 1.6% reduction in permeability. A much greater reduction, however, would be necessary to account for the changes observed in velocity according to Heiderscheidt (2005), who postulates that MnO_2 particles block pore throats in addition to filling pore spaces. In studies of his own in 2D tanks, Heiderscheidt (2005) found changes in permeability attributable to 100 mg-MnO_2 per kg-porous media. Reitsma and Randhawa (2002) found in 1-dimensional (1D) transport studies that MnO_2 filling as little as 1% of pore space resulted in 98% permeability reduction. Schroth et al. (2001) found in their 1D experiments a 96% permeability reduction under study conditions similar to those of Reitsma and Randhawa (2002), and suggest pore throat clogging, along with pore filling, as a mechanism for the permeability reduction.

The ability to control and inhibit particle deposition would provide distinct advantages to ISCO using permanganate. If reaction conditions can be manipulated to stabilize and control MnO_2 in groundwater to specifically allow for their facilitated transport through porous media, then issues associated with permeability changes and decreased contact between oxidant and contaminant can be avoided. Particle stability is defined here as the inhibition of the particle aggregation that leads to straining, settling, and/or deposition in the subsurface, and which is achieved through electrostatic repulsion, sequestration of ions that promote particle aggregation, and/or steric hindrance. Stabilized particles remain dissolved/suspended in solution (groundwater).

The stability of MnO_2 in solution, which is an indicator of their potential to be controlled and transported with groundwater flow, can be impacted by several reaction conditions. These include reactant/particle concentrations, pH, turbulence, the presence of anions/cations in solution, and the presence of stabilizing colloids (Morgan and Stumm, 1964; Perez-Benito et al., 1989, 1990; Perez-Benito and Arias, 1991,1992a,b; Insausti et al., 1992, 1993; Doona and Schneider, 1993; Chandrakanth and Amy, 1996; Crimi and Siegrist, 2004a,b). While the genesis and growth of these particles has been investigated at a fundamental level (e.g., Siegrist et al., 2002; Crimi and Siegrist, 2004b; Li and Schwartz, 2004), few efforts to specifically evaluate the ability to control the growth and transport of MnO_2 for favorable outcomes have been undertaken. Li and Schwartz (2005) describe studies the authors conducted to control particle growth using phosphate. Including phosphate in solution slowed the particle coagulation process, possibly via a pH buffering effect (maintaining near-neutral pH enhances electrostatic repulsion of the negatively charged MnO_2 particles), or via formation of a soluble phosphate-Mn(IV) complex, which eventually precipitates but at a rate slower than particle coagulation/precipitation without phosphate present (start of colloid growth was delayed by 35 min in their studies). The goals of the study described herein are to understand the genesis and control of MnO_2 particles under additional reaction conditions and to evaluate four particle stabilization aids with respect to their ability to inhibit coagulation and particle growth. The ideal particle stabilizer will (1) react minimally with permanganate, (2) interact minimally with groundwater components, (3) be acceptable to the regulatory community, and (4) be cost-effective.

2. Materials and methods

2.1. General materials

Potassium permanganate (Carus Chemical, technical grade) is the oxidant used to generate MnO_2. The primary reductant is the contaminant trichloroethylene (ACS grade). It is a highly prevalent contaminant at hazardous waste sites where permanganate oxidation is applied. A simulated groundwater was employed (Struse et al., 2002), with an ionic strength of 0.01 and adjusted to pH 3 or pH 7 with concentrated HCl or NaOH as appropriate. Ionic content was varied in calcium content ($CaCl_2$) or in phosphate (Na_3PO_4) content to examine anionic and cationic impacts on system properties. A review of the available literature with respect to particle stabilization was conducted to choose four (organic/inorganic, ionic/non-ionic) promising stabilization aids to meet the objectives of this study. This review focused on the food and pharmaceuticals industry in terms of non-toxic stabilizing additives, as well as the catalysis literature in terms of stabilizing reactive colloids and avoiding reaction inhibition (Perez-Benito et al., 1990; Perez-Benito and Arias, 1991; Stumm, 1992). Stabilization aids include sodium hexametaphosphate (HMP), an anionic inorganic polymer; Dowfax 8390, a di-anionic surfactant; and gum arabic and xanthan gum, which are water soluble food additives. Dowfax 8390 and HMP would be anticipated to affect particles through electrostatic interactions, whereas gum arabic and xanthan gum would be expected to impact particles via steric hindrance.

2.2. General analytical methods

Physical and chemical properties of aqueous phase samples and generated particles were characterized using standard methods for analysis, as follows: pH – wet chemistry with electrode (APHA, 1998); MnO_4^- – spectrophotometric measurement at 525 nm with Hach DR/4000 (APHA, 1998); MnO_2 quantification – sequential extraction and dissolution (Struse et al., 2002); MnO_2 behavior – spectrophotometry at 418 nm (Perez-Benito et al., 1989, 1990; Perez-Benito and Arias, 1991, 1992a,b; Crimi and Siegrist, 2004b); MnO_2 particle size and zeta potential – NICOMP 380 ZLS zeta potential/particle size measurements. Appropriate sample replication, sample controls, and corroboration of sample methods were applied.

2.3. General approach

Bench-scale, batch experimental systems were employed to assess the effects and interactions, using a full factorial experimental design, of (1) particle concentration (10 and 100 mg L^{-1}), (2) cations and anions in groundwater (excess Ca^{2+} or PO_4^{3-}), (3) pH, and (4) stabilization aid concentration and type (Dowfax 8390 at 3300 and 25540 mg L^{-1}; sodium HMP at 100 and 1000 mg L^{-1}; gum arabic at 100 and 1000 mg L^{-1}; and xanthan gum at 10 and 25 mg L^{-1}). Variation in particle concentration was provided by changing the initial concentrations of reactants in solution (permanganate and reductant), which were added in a 2:1 oxidant to reductant molar ratio (as per Eq. (1)). Ionic variations of calcium and phosphate (concentrations in excess of two times the K^+ or MnO_4^- charge attributable to the $KMnO_4$ concentration employed) were selected for their ability to promote Ca^{2+} and inhibit PO_4^{3-} coagulation of the negatively charged (in neutral pH) MnO_2 particles. The pH conditions of 7 and 3 were selected for the typical aquifer near-neutral condition (pH ~ 7) and for a near point of zero charge pH of MnO_2 (pH ~ 3) to compare resulting electrostatic impacts on particle aggregation. Two concentrations of each stabilization aid were evaluated based on their solubility (higher concentration = near maximum effective solubility) and/or ionic properties (i.e., provide negative charge in excess of K^+ from $KMnO_4$). The purpose of batch experimentation in aqueous systems was to gain a basic understanding of particle stability under varied conditions in systems where monitoring can be conducted in a straightforward manner with minimal disturbance.