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Permanganate diffusion and reaction in sedimentary rocks

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ABSTRACT

In situ chemical oxidation using permanganate has frequently been used to treat chlorinated solvents in fractured bedrock aquifers. However, in systems where matrix back-diffusion is an important process, the ability of the oxidant to migrate and treat target contaminants within the rock matrix will likely determine the overall effectiveness of this remedial approach. In this study, a series of diffusion experiments were performed to measure the permanganate diffusion and reaction in four different types of sedimentary rocks (dark gray mudstone, light gray mudstone, red sandstone, and tan sandstone). Results showed that, within the experimental time frame (~2 months), oxidant migration into the rock was limited to distances less than 500 μm. The observed diffusivities for permanganate into the rock matrices ranged from 5.3×10^{-13} to 1.3×10^{-11} cm^2/s. These values were reasonably predicted by accounting for both the rock oxidant demand and the effective diffusivity of the rock. Various Mn minerals formed as surface coatings from reduction of permanganate coupled with oxidation of total organic carbon (TOC), and the nature of the formed Mn minerals was dependent upon the rock type. Post-treatment tracer testing showed that these Mn mineral coatings had a negligible impact on diffusion through the rock. Overall, our results showed that the extent of permanganate diffusion and reaction depended on rock properties, including porosity, mineralogy, and organic carbon. These results have important implications for our understanding of long-term organic contaminant remediation in sedimentary rocks using permanganate.

1. Introduction

Remediation of chlorinated solvents in fractured bedrock aquifers has been a challenging task at several Department of Defense (DOD) and Department of Energy (DOE) sites. In situ chemical oxidation (ISCO) using strong oxidants (e.g., permanganate, persulfate, ozone, and hydrogen peroxide) has been effectively applied for treatment of chlorinated solvents (Conrad et al., 2002; Krembs et al., 2010; Schnarr et al., 1998; Siegrist et al., 2011). Several studies have demonstrated that uptake and back-diffusion of contaminants from the bedrock matrix can have a substantial impact on contaminant fate and treatment potential (Goldstein et al., 2004; Lipson et al., 2005; Sterling et al., 2005; West and Kueper, 2010). While there have been studies examining the effectiveness of chemical oxidants on the removal of dense non-aqueous phase liquids (DNAPLs) in fractured rocks (Schaefer et al., 2012; Smith et al., 1998; Tunnicliffe and Thomson, 2004), published peer-reviewed studies evaluating the ability of chemical oxidant to treat chlorinated solvents residing in the rock matrix are, to the best of our knowledge, not available except for one TCE treatability study in silty clay soil (Struse et al., 2002).

Permanganate has been applied to treat several contaminants, such as trichloroethylene (TCE), tetrachloroethylene (PCE), and styrene in the aqueous phase (Gates-Anderson et al., 2001; Tunnicliffe and Thomson, 2004; USEPA, 1998; Wu et al., 2012; Yan and Schwartz, 1999). For example, in a coupled reaction between permanganate and TCE, MnO_4^- is

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reduced to form a solid Mn oxide precipitate (birnessite, MnO_2), while chlorinated ethylenes break down to produce CO_2 (Li and Schwartz, 2004; Yan and Schwartz, 1999).

The success of this ISCO technology depends on a number of considerations, among which rock properties and naturally occurring reactive reductants are important ones. For example, porosity and permeability are important parameters affecting the susceptibility of contaminant to chemical oxidation in aquifer sediments (Bogan and Trbovic, 2003; Hønning et al., 2007a). Naturally present reactive reductants, such as total organic carbon (TOC) and reduced forms of iron, manganese, and sulfur, can also impact the effectiveness of the ISCO technology, because these reductants can influence the stability and mobility of strong oxidants such as permanganate (Mumford et al., 2005; Reynolds et al., 2008; Urynowicz, 2007; Xu and Thomson, 2009). Therefore, permanganate diffusion is likely to vary in different rock types due to the reactions between permanganate and different concentrations of naturally present reductants.

Permanganate oxidation of organic contaminants (e.g., TCE) typically results in the formation of MnO_2 solids (Crimi and Siegrist, 2004). A detailed mineralogical study of these solids further revealed semi-amorphous potassium-rich birnessite as a typical product (Li and Schwartz, 2004); however, the exact oxidation state of Mn in such material was not determined. In a field oxidation test with potassium permanganate, Scott et al. (2011) observed birnessite formation as well as an unidentified, poorly crystalline material that was believed to be a manganese oxide phase with a higher oxidation state of manganese. Loomer et al. (2010) studied the Mn oxidation state in manganese oxides formed by oxidation of TCE with permanganate using electron energy loss spectroscopy (EELS) and X-ray photoelectron spectroscopy (XPS). The authors found that the valence of Mn in such manganese oxides can vary from 2.2 to 3.6 depending on the amount of permanganate, pH, and aging (Loomer et al., 2010; Scott et al., 2011). This study raises the possibility that different Mn minerals can form depending on specific experimental conditions; however, the exact nature of such Mn solids remains unknown, especially in different rock types (e.g., mudstones vs. sandstones).

As described above, despite the importance of rock properties on the effectiveness of ISCO, a comprehensive understanding regarding the interaction between chemical oxidants and rock matrices is still lacking. It is currently unclear how implementation of ISCO impacts the bedrock matrix, as the reactions between oxidants and rock matrix at the fracture-rock interface and diffusion of oxidant into rock matrix could impact rock properties through Mn oxide precipitation and subsequently impact contaminant diffusive flux from the matrix to water-bearing fractures. Therefore, an improved understanding regarding diffusion of chemical oxidants into bedrock and oxidant reactions with naturally occurring reductants is needed to assess the potential benefits of in situ chemical remediation of chlorinated solvents in bedrock aquifers.

The objective of this study was to understand the mechanisms and controlling factors of permanganate diffusion and reaction in a variety of sedimentary rocks. Specifically, the distances and rates of permanganate diffusion into the rocks were measured, the factors controlling permanganate diffusion were assessed, the nature of the interaction between the oxidant and rock was evaluated (including identification of resulting manganese precipitates), and post-oxidation impact on the rocks (with respect to alteration of the effective diffusion coefficient due to Mn precipitate clogging) was assessed. Insights gained as part of this study provided information useful for assessing the feasibility of applying permanganate for treatment of chlorinated compounds within rock matrices.

2. Method and materials

2.1. Sample collection and rock characterization

Bedrock materials were collected from the former Naval Air Warfare Center (NAWC) in Trenton, New Jersey. The NAWC site is underlain by the Lockatong and Stockton formations on opposing sides of a geologic fault (Lewis-Brown et al., 2006). Water bearing fractures occur through each of these units, with some units more highly fractured than others. As summarized in Table 1, several different rock types, which were present at the NAWC site, were collected for this study. Four representative rock types were collected, including red sandstone (Stockton Formation), tan sandstone (Stockton Formation), dark gray mudstone (Lockatong Formation), and light gray mudstone (Lockatong Formation). Details of the collection process, which was performed to obtain minimally disturbed (chemically and physically) rock cores, were described previously (Schaefer et al., 2013). To limit oxygen exposure of the rocks, samples were stored in heat-sealed plastic bags under water-saturated and anoxic conditions. Once in the laboratory, samples were cut into 1 cm thick slices using a diamond blade electric saw and subsequently stored inside an anaerobic glove box. Initial

Table 1
Characterization of rock properties.

Rock type	TOC (g/kg)	1-Month oxidant demand (g/kg)	Ferrous iron (mmol/g)	Total iron (mmol/g)	Porosity
Dark gray mudstone	4.63	22.5	0.30	0.96	0.050 ± 0.006
Light gray mudstone	1.32	10.3	0.38	1.23	0.055 ± 0.009
Red sandstone	0.27	2.98	0.01	0.03	0.074 ± 0.004
Tan sandstone	0.17	2.58	0.005	0.09	0.068 ± 0.005