

In-Situ Oxidation Treatment of High Explosives in Groundwater Using Potassium Permanganate

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High Explosives (HE) compounds occur as a groundwater contaminant at a large number of U.S. Department of Energy (DOE) and Department of Defense (DOD) sites. However, in-situ technologies for the treatment of HE in groundwater have not been previously demonstrated, and as a result, most HE contaminated sites are forced to adopt large-scale groundwater pump and treat programs, that have indefinite durations.

In-situ oxidation is a technology that has developed over the past five to ten years for treatment of organic solvent contamination in groundwater. While oxidants have been used for HE treatment in ex-situ water treatment systems, in-situ oxidation of HE in groundwater has not been previously documented. Potassium permanganate (KMnO_4) is an oxidant that has been developed for in-situ application, largely under the direction of DOE and DOD funded research. KMnO_4 has relatively slow reaction rates that make it unsuitable for HE treatment in an ex-situ continuous flow reactor process. However, the slow reaction kinetics are favorable for subsurface transport and oxidant delivery, because KMnO_4 is more persistent in the subsurface than other oxidants. Lab and field testing and numerical modeling has been conducted to evaluate in-situ chemical oxidation using KMnO_4 for the treatment of HE compounds, including hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane (HMX), and 2,4,6-trinitrotoluene (TNT), and HE degradation byproducts including 2-amino-4,6-dinitrotoluene and 4 amino-2,6-dinitrotoluene (DNT). This testing was performed as part of an ongoing evaluation of alternatives for remediation of HE contaminated groundwater at the USDOE Pantex Plant in Amarillo, Texas.

Oxidation laboratory testing (Figure 1) showed that KMnO_4 effectively oxidizes RDX, TNT, DNT, HMX, and other HE compounds. The lab testing clearly showed the second-order nature of the oxidant-HE reactions, with measured RDX half-lives ranging from 0.5 to 35 days under a range of KMnO_4 concentrations from 48,000 mg/L to 400 mg/L, respectively (Table 1). Reaction kinetics second order with a rate constant k_2 , while during laboratory testing it is common to have an excess of permanganate, such that pseudo-first order half lives (k_1) can be observed, where $k_1 = k_2 [\text{KMnO}_4]$. Using these relationships, second order rate constants for RDX and HMX were estimated (Appendix B, Table B-2) from lab test data HE degradation by-products for treatment using KMnO_4 were also evaluated, and preliminary results indicate these by-products were transient, and not persistent in the presence of KMnO_4 .

In-situ chemical oxidation of HE using KMnO_4 was also evaluated in a field scale test consisting of a series of single-well push-pull tests. Each push-pull test involved the addition (push) of KMnO_4 and bromide tracer to the well, followed by a defined rest period, and then groundwater extraction (pull) to recover the KMnO_4 treated groundwater and tracer from this well. During extraction, groundwater sampling and analysis defined the recovery breakthrough curves for MnO_4 , tracer, contaminants, and selected potential reaction products. Additionally, a precursor (control) test was performed at each well that involved injection of treated groundwater and tracer only, without KMnO_4 . Comparison of the treatment push-pull test results to the control test results (Figure 2) allowed determination of the amount of HE treated, and other design parameters related to HE- KMnO_4 reaction kinetics.

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The reaction kinetics and stoichiometries determined from the lab and field tests were used as input to a 2-D numerical simulation of HE and KMnO_4 reactions and transport during large-scale treatment. The model code used was RT3D. This modeling accounted for second order kinetics of HE- KMnO_4 reactions and matrix- KMnO_4 reactions during in-situ treatment. The modeling results provided insight into the subsurface transport properties of the oxidant, such as the effects of matrix reactions on KMnO_4 transport. The model was also used to determine optimum injection parameters such as KMnO_4 solution concentration, flow rates, and injection durations. These parameters form the basis for design of planned large-scale field pilot tests.

Figure 1. RDX Treatment Time Series Data Measured in Lab Slurry Testing

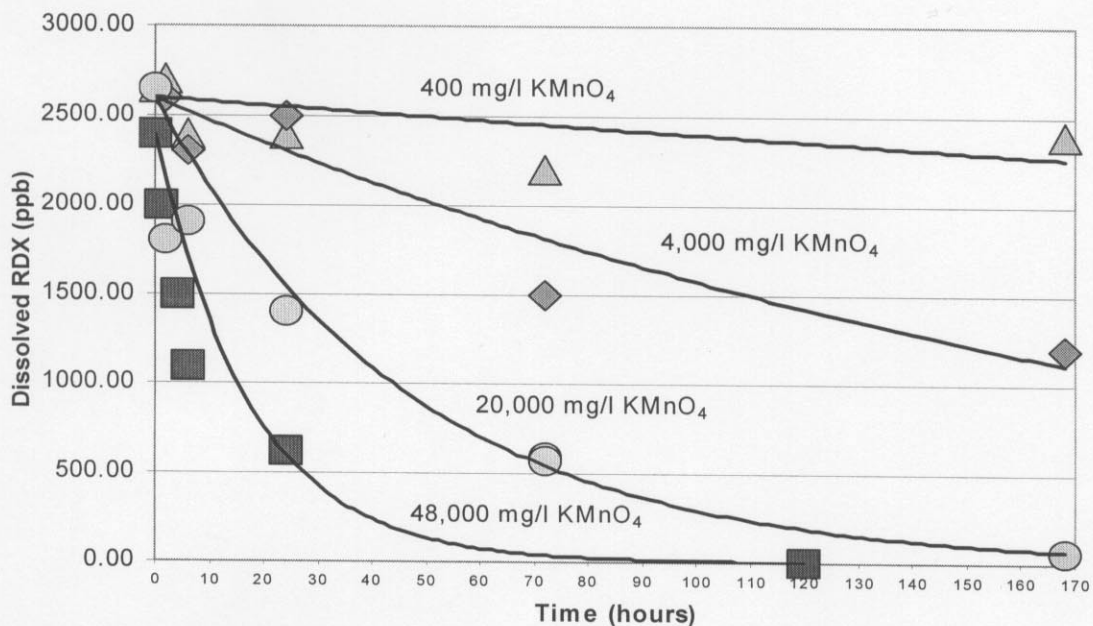


Table 1. First and Second Order Rate Constants for RDX and HMX

Initial [KMnO_4] (mg/L)	RDX k_1^a (1/hr)	RDX k_2 (L/mg \cdot hr)	HMX k_1 (1/hr)	HMX k_2 (L/mg \cdot hr)
48,000	0.0557	1.2×10^{-6}	0.0019	2.5×10^{-7}
20000	0.0206	1.0×10^{-6}	0.0006	2.8×10^{-7}
4000	0.0048	1.2×10^{-6}	0.0009	2.3×10^{-7}
400	0.0005	1.3×10^{-6}	0.0012	3.0×10^{-6}

^a k_1 values were obtained from graphs of c/c_0 versus time

Figure 2. Single Well Push Pull Test Results. Breakthrough Curves for RDX, Tracer and KMnO4 From Control and Treatment Tests

