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Dosing of ozone in oxidation of methyl *tert*-butyl ether while minimizing hexavalent chromium formation in groundwater

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ABSTRACT

Co-oxidation of trivalent chromium (Cr(III)) to hexavalent chromium (Cr(VI)) during ozonation of organic pollutants represents a common problem facing the implementation of in situ chemical oxidation (ISCO) for environmental remediation. A laboratory study was conducted by using groundwater and saturated soil samples from a field site in Sacramento, California, to determine optimal O_3 dosage to achieve satisfactory remediation of MTBE while minimizing co-oxidation of Cr(III) to Cr(VI). Total oxidant demand was determined (28.33 mg O_3 L^{-1}) and used as the benchmark to establish a range of ozone dosages for the study. Concentration changes in MTBE and chromium were monitored at O_3 dosages less than and greater than the benchmark. The results indicate that MTBE is preferentially oxidized by ozone at and below the indicated benchmark dosage prior to the oxidation of Cr(III) to Cr(VI). The resultant O_3 dosage of 28.33 mg L^{-1} was applied in the field implementation, verifying that the O_3 can be applied in a controlled manner to remediate MTBE while minimizing the formation of Cr(VI).

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1. Introduction

Methyl *tert*-butyl ether (MTBE) is a gasoline-additive that has contaminated groundwater from leaking underground storage tanks [1,2] and other sources. The water solubility of MTBE is 50,000 mg L^{-1} and it has an effective water solubility of 5000 mg L^{-1} when in a typical gasoline mixture [3]. MTBE also has a low tendency for adsorption to soil particles. As such, MTBE readily dissolves into groundwater and experiences little retardation resulting in migration nearly equal to the groundwater flow rate and the potential for widespread migration. MTBE also creates taste and odor problems in drinking water at relatively low concentrations. The California Department of Health Services adopted primary and secondary maximum contaminant levels (MCLs) for MTBE of 13 μg L^{-1} and 5 μg L^{-1}, respectively [4].

In-situ chemical oxidation (ISCO) using ozone (O_3) is a remediation technology that has been successfully applied at MTBE contaminated sites. Delivery approaches include fine-bubble sparging, gas injection, and aqueous injection technologies using O_3 and O_3/hydrogen peroxide [2,5–10]. Tertiary-butyl formate (TBF) and tertiary-butyl alcohol (TBA) are common intermediate by-products of MTBE oxidation with O_3 under the following predominant degradation pathway [6]:

$$O_3 + MTBE \rightarrow TBF \rightarrow TBA \rightarrow Acetone \rightarrow Acetic\ Acid \rightarrow CO_2 + H_2O$$

Ozone can also react with metals in groundwater and the soil matrix. In particular, trivalent chromium (Cr(III)), which is ubiquitous in soil, can be oxidized by oxidants such as O_3 to form the toxic hexavalent chromium (Cr(VI)) [8,11–13]. Research found that oxidation of Cr(III) to Cr(VI) was largely attributed to hydroxyl radicals in advanced oxidation process by ozone [14]. Few, if any, peer-reviewed studies have been done on Cr(VI) formation during or after ISCO implementation. The USEPA drinking water standard is 0.1 mg L^{-1} for total chromium, which includes all forms of chromium. Chromium form, Cr(VI) is much more soluble than Cr(III); therefore, proper dosing of O_3 oxidation is critical for achieving remedial goals while preventing Cr(VI) formation.

A field pilot test was conducted at a MTBE-contaminated site, where in situ injections of O_3 were conducted. Field monitoring

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indicated that MTBE was oxidized prior to Cr(VI) formation, and it was assumed that over dosing of O_3 might have caused the elevated Cr(VI). The following study was conducted to test this assumption and a series of ozone dosages was tested to determine the optimal dosage for oxidizing MTBE while limiting the co-oxidation of Cr(III). The optimal dosage was then applied during the remediation of MTBE-impacted groundwater.

2. Materials and methods

2.1. Field site history

A field pilot test was conducted at a leaking underground storage tank (LUST) site located in Sacramento, California. The MTBE released from the former gasoline service station migrated to and impacted a municipal water supply well. Ozone injection was tested as a potential remedial alternative for removing MTBE from groundwater. In the field pilot test, ozone was injected into the MTBE impacted groundwater at approximately 24.4 m below ground surface (bgs). Monitoring wells were located 4.6 m down-gradient (MW-4B) and 6.1 m cross-gradient (MW-13B) from injection well OZ-2, as shown in Fig. 1. An existing shallow interval monitoring well (MW-4A), screened from 10.7 to 15.2 m bgs and located 6.1 m down-gradient, was also included in the test.

Ozone injection was successful in reducing MTBE concentrations from approximately $10,000\,\mu g\,L^{-1}$ to approximately $300\,\mu g\,L^{-1}$ after 2 weeks and non-detect ($<0.5\,\mu g\,L^{-1}$) after 7 weeks. These results were complicated by Cr(VI) increasing from non-detect ($<1.0\,\mu g\,L^{-1}$) after 3 weeks to nearly $400\,\mu g\,L^{-1}$ after 10 weeks. The pilot test was shutdown after 5 weeks, and the Cr(VI) impacts were observed to be persistent. A temporary groundwater extraction system was used to remove the Cr(VI).

2.2. Field sampling

Groundwater and soil samples were collected from the field site in Sacramento, California, two weeks prior to conducting the laboratory experiments. Groundwater samples were collected from each using a bailer (purging groundwater equivalent to three times the well volume before collecting the sample). Groundwater samples (18.9 L) were collected from MW-4B, MW-3 (located up-gradient to MW-4B), and MW-4A (located adjacent to MW-4B) to establish a site baseline and assist in evaluating site heterogeneity. Field parameters of pH, dissolved oxygen (DO), oxidation-reduction potential (ORP), and electrical conductivity (EC) were measured at these locations during the sampling. During this sampling event, a new well (EW-1B) was completed using a sonic drill rig. Core samples taken during drilling were characterized in the field and a well log was produced. Soil samples were taken
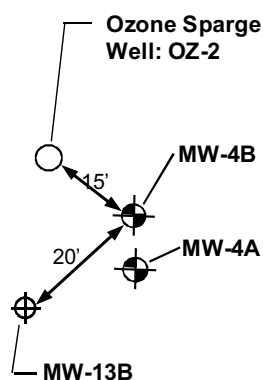
from the drilling core above the impacted interval, in the interval, and just below the interval at depths of 21.9 to 22.6 m, 24.4 to 25.0 m, and 25.3 to 25.9 m, respectively. The soil and groundwater samples were shipped at 4 °C to Western Research Institute (Laramie, WY) for analyses and laboratory experiments.

2.3. Sample characterization

Soil and groundwater were analyzed to establish baseline characteristics. Analytes included: pH, EC, DO, ORP, total organic carbon (TOC), dissolved organic carbon (DOC), anions including Fluoride (F^-), chloride (Cl^-), bromide (Br^-), nitrate (NO_3^-), phosphate (PO_4^{3-}), sulfate (SO_4^{2-}), total and dissolved metals including iron (Fe), manganese (Mn), copper (Cu), nickel (Ni), zinc (Zn), lead (Pb), chromium (Cr(III) and Cr(VI)), as well as MTBE and its intermediates.

The pH was measured by using an Orion 9106BNWP ion-selective probe (Thermo Electron Corp, Waltham, MA) attached to an Orion 720A+ meter (Thermo Electron Corp, Waltham, MA). Temperature was measured during the analyses for data correction. Oxidation-reduction potential (ORP) was measured by using an Orion 9678BN redox electrode connected to the Orion 720 A+ meter. Electrical conductivity (EC) was measured using an Orion 150A+ meter equipped with an Orion 013005D conductivity cell. Dissolved oxygen (DO) was measured using a YSI (Yellow Springs, OH) Model 58 DO meter. Anions were analyzed using a Dionex (Sunnyvale, CA) DX-100 ion chromatograph (IC) equipped with an IonPac AS14 Pack Column. Total and dissolved metals were analyzed by using inductively coupled plasma mass spectrometry (ICP-MS; PE SCIEX Model Elan 6000) with a method equivalent to EPA Method 200.8. Cr(VI) analysis was performed within 24-h of the sampling event using EPA method 7196A. Samples for MTBE were analyzed using EPA Method 8260 and a gas chromatograph-mass spectrometer (GC–MS; model 6890/5973, Agilent Technologies, Palo Alto, CA) equipped with a purge and trap system. The TOC and were analyzed using a Shimadzu TOC analyzer (Columbia, MD) by following standard methods.

2.4. Total oxidant demand

Total oxidant demand (TOD) was measured to estimate a benchmark based ozone dosage. Due to the difficulty in quantifying residual ozone, a TOD protocol was established using sodium percarbonate ($2Na_2CO_3\cdot3H_2O_2$) as a surrogate oxidant equivalent, due to its relative stability and simple measurability. The TOD was determined by reacting site groundwater and soil samples (10% w/v of soil) with a solution of $2Na_2CO_3\cdot3H_2O_2$ ($10,000\,mg\,L^{-1}$). Sodium percarbonate concentrations were evaluated by determining the residual H_2O_2 concentrations from reacting with titanium (IV) oxysulfate [15] and analyzing the solution on a Shimadzu UV min 1240, UV–vis spectrophotometer (Columbia, MD).

The O_3 demand was calculated based on an oxidizing potential of 2.1 V for O_3 and 1.8 V for H_2O_2 (1.8 V) from $2Na_2CO_3\cdot3H_2O_2$. The O_3 demand was then determined based on the stoichiometric relationship of 0.85 mol O_3 being equivalent to 1.0 mol H_2O_2. Since there are 3 mol H_2O_2 in 1 mol $2Na_2CO_3\cdot3H_2O_2$, the relationship in terms of $2Na_2CO_3\cdot3H_2O_2$ is 0.28 mol O_3 mol^{-1} $2Na_2CO_3\cdot3H_2O_2$.

2.5. Bench-scale study

Microcosm reactors were established in 500-ml amber glass bottles using composite groundwater and soil samples collected from the site. Soil was set at 10% (w/v) of the total volume in the reactors. A range of O_3 dosages were used corresponding to 0, 25, 50, 100, 200, and 400% of the benchmark dosage. Ozone was

Ozone Sparge Well: OZ-2

MW-4B

15'

MW-4A

20'

MW-13B

Fig. 1. Ozone Field Pilot Layout.