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Transport characteristics of gas phase ozone in unsaturated porous media for in-situ chemical oxidation

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Abstract

Laboratory column experiments were conducted by employing various porous media to delineate the characteristics of gaseous ozone transport in the unsaturated zone under various conditions. Water content, soil organic matter (SOM), and metal oxides (MOs) were found to be the factors most influential in the fate and transport of gaseous ozone in unsaturated porous media. The migration velocity of the gaseous ozone front was inversely proportional to the MO content of the porous media. Increased water content at fixed gas flux decreased the ozone breakthrough time proportionally as a result of reduced gas pore volume (PV) in the column, and increased pore water interfered with reactions of gaseous ozone with SOM and MOs on the surface of porous media. The feasibility of in-situ ozone injection for the remediation of unsaturated soils contaminated with either phenanthrene or diesel-range organics (DROs) was investigated under various conditions. The maximum removal after 1 h of ozone injection was achieved in columns packed with baked sand, followed, in descending order, by glass beads and by sand, indicating that catalytic ozone decomposition with MOs in columns packed with baked sand enhanced hydroxyl radical formation and resulted in increased contaminant removal. Overall removal efficiency of multicomponent C_{10} -

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 C_{24} DROs after 14 h of ozonation was 78.7%. Ozone transport was retarded considerably because of the high ozone demand of DROs, requiring more than 6 h for the gaseous ozone to initially break through the soil column under the experimental conditions tested in this study. Overall, gaseous ozone was readily delivered and transported to remediate unsaturated soils contaminated with phenanthrene and DROs. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Ozone transport; Unsaturated porous media; In-situ chemical oxidation; Metal oxides; Soil organic matter; Diesel-range organics

1. Introduction

The contamination of the subsurface by petroleum hydrocarbons (PHs) resulting from leaky fuel storage tanks, refineries, factories, oil spills, and improper waste disposal has been of concern for many decades. Considerable effort has been made to understand the consequences of the contamination and to develop proper technologies for remediating subsurface areas contaminated with various PHs. Recently, in-situ chemical oxidation (ISCO) technologies have been viewed as promising alternatives to physical/biological remediation technologies for removing certain recalcitrant PHs such as polycyclic aromatic hydrocarbons (PAHs) and chlorinated organic compounds that cannot be removed effectively by other technologies (i.e., pump and treat, soil venting, and bioremediation) because they are generally semivolatile or nonvolatile and/or because they are not easily biodegradable. The chemical oxidants commonly used are ozone, hydrogen peroxide, chlorine dioxide, and potassium permanganate (Yin and Allen, 1999).

Ozone ($E^\circ = 2.07$ V) has been used for the in-situ oxidation and enhanced bioremediation of chlorinated solvents, PAHs, and petroleum products (e.g., Nelson and Brown, 1994; Nelson et al., 1997; Michael et al., 2000). The basic concepts of ozonation, its technology status, and pilot and field application cases were recently reviewed (U.S. EPA, 1998; Yin and Allen, 1999; ESTCP, 1999). Ozonation offers several advantages for site remediation over other ISCO technologies. Ozone is a gas, and therefore it can be applied for treating both the vadose zone and the saturated zone. Moreover, ozone can be delivered readily to the contamination zone (Masten and Davies, 1997) by injection through both vertical and horizontal wells.

Ozone oxidizes organic contaminants in two ways: by direct oxidation with ozone molecules and by the generation of free-radical intermediates, such as hydroxyl radical (OH·, $E^\circ = 3.06$ V), a powerful, effective, nonspecific oxidizing agent (Glaze and Kang, 1988). Faster reaction rates promoted by OH· oxidation can often shorten the time required to achieve the destruction of the contaminants of concern and can also expand the range of contaminants to be treated. Metal oxides such as goethite (α -Fe₂O₃), MnO, and Al₂O₃ on the surface of sand and soil are known to accelerate ozone decomposition to generate OH· via heterogeneous catalytic reactions of ozone with the metal oxides (MOs) (e.g., Masten, 1991; Choi et al., 2001).

The application of ozone in the vadose zone has recently been studied (Hsu, 1995; Hsu and Masten, 1997; Masten and Davies, 1997; Kim and Choi, 2002). Hsu and Masten (1997) estimated reaction constants for soil organic matter (SOM) and phenanthrene

sorbed onto soils during the ozonation of unsaturated soils. Masten and Davies (1997) presented a brief summary of some field experience and experimental results on the efficacy of in-situ ozonation for the remediation of PAH-contaminated soils without much experimental detail. Kim and Choi (2002) developed mathematical models to investigate the characteristics of gaseous ozone transport under various soil conditions and the feasibility of in-situ ozone venting for the remediation of unsaturated soils contaminated with nonvolatile PAHs. Assumptions about the mass transfer and reactions of ozone led to consideration of equilibrium, kinetic, and lump models. Hsu (1995) also developed a mathematical model similar to the lump model of Kim and Choi (2002). The effective removal from contaminated air-dried soil of commercial diesel fuel containing PAHs was reported (Yoo, 1999). PAHs represent approximately 1.1 wt.% (weight-percent) of the more than 200 compounds in diesel fuel (U.S. EPA, 1982).

Although the transport and reactions of ozone in unsaturated soils have been studied to some extent, no attempts have been made to systematically investigate the effects of parameters expected to affect the performance of innovative in-situ ozone injection technology. In particular, the effects of MOs on the fate of ozone and on contaminant removal by ozonation have been studied only in soil slurry systems. Thus, the objectives of this research were (1) to delineate the characteristics of gaseous ozone transport under various soil conditions (e.g., water content and SOM) in different porous media containing various MO contents and (2) to investigate the feasibility of in-situ ozone injection for ISCO of unsaturated soils contaminated with either phenanthrene or diesel-range organics (DROs).

2. Materials and methods

2.1. Materials and chemicals

Phenanthrene (Wako, 99.9%), methylene chloride (Fisher Scientific, HPLC grade), diesel fuel (commercial product), and other chemicals were used as obtained from the respective sources without further purification. For simplicity, diesel fuel concentration was calculated on the basis of the summation of DROs, including carbon numbers C_{10} – C_{24} . DROs were quantified on the basis of calibration of the DRO standard (UST Modified DRO Mix, Supelco). The composition of DRO standard solution is presented elsewhere (Yoo, 1999).

In this study, three different types of porous media (glass beads, sands, and soils) were employed. Sands were obtained in Jumunjin, South Korea, and soils (weathered feldspar) were excavated from the northern part of Kyungki province, South Korea, at a depth of approximately 1 m below ground surface. Tables 1 and 2 show the characteristics of the three porous media and the results of X-ray fluorescence analysis of sand and soil, respectively. Glass beads were washed with water, baked at 500 °C for 24 h, and stored at room temperature. Before use, the glass beads were soaked in hydrogen peroxide solution for 10 h and washed with deionized water. Sands were sieved through a 400- to $600-\mu m$ sieve (sieve number) to provide a consistent surface, then washed with water. The excavated soil samples were air-dried at room temperature for at least a week, sieved

| Characteristics of glass beaus, said (Juniunjin, South Korea) and son (Kyunggi, South Korea) | | | | | | |
|----------------------------------------------------------------------------------------------|------------------------|---------------|-------------|--|--|--|
| Soil property | Soil | Jumunjin sand | Glass beads | | | |
| Organic matter content (%) | 4.37 | 0.12 | _ | | | |
| Porosity | 0.46 | 0.41 | 0.40 | | | |
| Bulk density (g/cm ³) | 1.34 | 1.48 | 1.56 | | | |
| Specific weight | 2.66 | 2.5 | _ | | | |
| Water content (wt.%) | 1.47 - 14.41 | 0-26 | _ | | | |
| Particle size (µm) | Silt sand ^a | 600-800 | 800 | | | |

Table 1

Characteristics of glass beads, sand (Jumunjin, South Korea) and soil (Kyunggi, South Korea)

^a Coarse sand (4.75-0.25 mm)=50%, fine sand (0.25-0.05 mm)=25%, silt (0.05-0.005 mm)=21%, clay (<0.005 mm)=4%.

through nos. 50 and 16 screens (0.3-1.2 mm), and washed with water. Sands and soils were prepared by baking them at 500 °C for 24 h to eliminate SOM sorbed to the surface. To study hydrocarbon removal by ozone, samples were prepared by spiking the porous media with phenanthrene (dissolved in methyl chloride) or diesel fuel, followed by a 1-week aging period. The methyl chloride that delivered phenanthrene was allowed to volatilize during the aging period. The initial concentrations of phenanthrene and diesel fuel were 100 and 1400 mg/kg, respectively.

Ozone was generated from dried oxygen (99.99%) by electric discharge by using an ozone generator (PCI Ozone and Control System, model GL 1). Ozone gas generated was moisturized to prevent the soil columns from drying out by passing the gas stream through a gas washing bottle containing deionized water acidified to pH 2 with phosphoric acid. The gaseous ozone was monitored by placing a PCI® ozone monitor with temperature and pressure compensation (PCI Ozone and Control system, model HC 400) before the soil column. Off gas ozone was trapped in the potassium iodide (KI) solution to calculate the amount of ozone consumed in the reactor.

2.2. Experimental methods

Pyrex glass columns 20 or 30 cm long and 2.5 cm wide (internal diameter, id) were used for the experiments. A porous glass diffuser plate placed on each end cap provided an

| Contents | Analysis data (wt.%) | | Contents | Analysis data (wt.%) | |
|---------------------------------------------|----------------------|-------|-------------------|----------------------|-------|
| | Jumunjin sand | Soil | | Jumunjin sand | Soil |
| SiO ₂ | 90.41 | 66.25 | CaO | 0.07 | 0.47 |
| Al_2O_3 | 5.48 | 15.26 | MgO | <85 ppm | 1.90 |
| Fe ₂ O ₃ ^a | 0.12 | 6.96 | K ₂ O | 3.45 | 2.76 |
| TiO ₂ | 0.02 | 0.97 | Na ₂ O | 0.36 | 0.19 |
| MnO ₂ | <74 ppm | 0.08 | P_2O_5 | 0.01 | 0.09 |
| L.O.I. ^b | 0.09 | 5.03 | TOTAL | 100 | 99.95 |

Table 2

Result of X-ray Fluorescence (XRF) analysis of Jumunjin sand (South Korea) and natural Soil (Kyunggi, South Korea)

^a Fe₂O₃ : Total iron.

^b L.O.I.: Loss on Ignition.

even distribution of gaseous ozone in the soil column. The end caps, column body, and fittings of the columns were made of Teflon, Pyrex glass, and stainless steel, respectively, to prevent ozone demand. The columns were initially filled with water, and small increments of sand were added successively. Care was taken to prevent layer formation during packing. A nylon membrane capillary barrier (air entry pressure of 30 mbar) was sealed at the bottom of each column. Two layers of a glass fiber filter paper were placed at the top of the packed soil to distribute water evenly across the inlet boundary. A small orifice at the top plate maintained atmospheric pressure in the upper region of each column during the development of a target water content. The required degree of saturation in the soil column was achieved by maintaining a steady flux boundary condition at the inlet and a constant negative pressure at the bottom of the column. A homogeneous distribution of water content throughout the column was obtained by installing Teflon tubing (0.16 cm id; length equal to the column length) at the outlet end to maintain a constant negative pressure at the bottom of the column. The target level of water saturation was achieved primarily by controlling the influent flow rate of the solution for each experiment. Volumetric water content was measured gravimetrically after steady state water flow conditions were established, both before and after the displacement experiments.

As Fig. 1 shows, gaseous ozone was passed through a mass flow controller (Masterfield, Inc.) to regulate the flow rate at the desired value. The gas phase ozone that passed through a soil column flowed through a UV spectrophotometer (Smart Plus SP 1900/2700,



Fig. 1. Schematic of soil column experiment.

Young Woo Inst., South Korea) equipped with a flow cell for continuous monitoring of the gaseous ozone concentration. During all experiments, the gaseous ozone was measured at a wavelength of 254 nm, and the results were recorded by a PC-based data acquisition system. This system allowed ozone breakthrough curves (BTCs) to be plotted continuously. Once an equilibrium ozone concentration was reached, a three-way valve was switched to direct the ozone flow to the column. The off-gas ozone was trapped in a KI solution scrubber to quench ozone.

2.3. Chemical analysis

Phenanthrene and diesel fuel were extracted from the soil by sonication in either methylene chloride or acetone. The recovery rate for both phenanthrene and diesel fuel was $83 \pm 3\%$. The quantitation of phenanthrene was carried out by using a WATERSTM HPLC system equipped with an autosampler (WATERSTM 717) and a Young-In UV absorbance detector (wavelength = 254 nm) with a Nova-Pak C₁₈ column (3.9×150 mm, WATERSTM) at a flow rate of 1.0 ml/min. The temperature of the column box was 40 °C. The eluent consisted of a 65:35 (water/acetonitrile) isocratic mixture. A GC-FID (Model # HP-5890) was used to analyze diesel fuel components. Operational conditions for the diesel fuel analysis are described elsewhere (Yoo, 1999).

3. Results and discussion

Because soil media contain various kinds of ozone-demanding matter such as catalytic metal oxides (e.g., goethite) and SOM on their surfaces, ozone molecules migrating in pore spaces are believed to undergo enhanced decomposition. Therefore, a series of experiments was conducted to investigate (1) the fate and transport and (2) the enhanced reactive decomposition of ozone under various conditions in unsaturated porous media. Phenanthrene and commercial diesel fuel were used to further delineate characteristics of ozone-enhanced remediation of unsaturated soils contaminated by low-soluble and non-volatile organic carbons.

3.1. Transport and decomposition characteristics of ozone

3.1.1. Effects of soil types on ozone transport

Gaseous ozone was injected into a total of 16 columns packed with dry sand (eight columns) or glass beads (eight columns) to investigate the characteristics of ozone decay and to confirm the enhanced decomposition of ozone by MO in the presence of SOM under ozone-demanding contaminant-free conditions. This set of experiments was conducted in a cycling batch column system. Ozone was pumped into the column for several pore volumes (PVs), until the ozone concentration reached a constant value. Then the columns were closed on both sides, and the ozone decay rates in the two different porous media were evaluated by sacrificing the columns to measure the ozone mass concentration at selected times. Fig. 2 presents the decomposition of ozone in both columns. As shown in Fig. 2a for normalized ozone concentration versus time, the ozone decay rate was



Fig. 2. Decomposition of ozone in sand and glass beads packed columns: (a) Ozone disappearance, (b) Pseudo-first-order plot.

considerably faster in the columns packed with sand than in the columns packed with glass beads. The half-lives of ozone decomposition were approximately 40 and 1000 min, respectively, for sand versus glass beads, which means that the ozone decay rate was 25 times greater in the columns packed with sand than in the columns packed with glass beads. Fig. 2b shows pseudo-first-order plots of the same data, from which ozone decay rate constants of 2.89×10^{-4} and 1.15×10^{-5} s⁻¹, respectively, were estimated for the columns packed with sand versus glass beads.

Fig. 3 presents BTCs of gaseous ozone in various porous media with the water content of 16 wt.%. Four different materials—glass beads, sand, baked sand, and baked soil (see Tables 1 and 2 for physical and chemical characteristics)—were used to investigate the effect of porous-medium type on gaseous ozone transport in a dynamic flow system.

The BTCs for gas phase ozone differ considerably with the type and condition of the material tested. The gaseous ozone in the columns packed with glass beads broke through first because the inert glass beads allowed the gaseous ozone to migrate with no surface reaction. The BTCs front at $C/C_0=0.5$ was approximately 2.3 times greater than the theoretical value of 1 PV for inert glass beads. Along with unknown factors such as self-decomposition of gaseous ozone, sorption of ozone molecules onto the surfaces of the glass beads presumably caused this unexpected retardation. Ozone transport was approximately caused the glass beads presumably caused the surface of the glass beads presumably caused the surface of the glass beads.



Fig. 3. Breakthrough curves (BTCs) of gaseous ozone in various soils: influent concentration of ozone was 2.42 wt.%, particle size was 0.85 ± 0.05 mm (baked soil: 0.85 - 1.14 mm) at the flow rate of 200 ml/min. The water content was kept at 16 wt.%.

imately twice as fast in the baked sand as in the sand containing 0.12% SOM, which exerted ozone demand. However, despite the difference in retardation, the final normalized ozone concentrations, as measured at 30 PVs, were identical at 0.96. This value (smaller than unity) indicates that gaseous ozone was destroyed continuously by the catalytic reaction with MOs on the sand surface. Ozone transport was most retarded in the column packed with baked soil, followed by columns packed with sand, baked sand, and glass beads. Approximately 100 PVs were required for complete ozone breakthrough in the column packed with baked sand after the initial appearance at 7.7 PVs. Ozone transport was approximately five times slower in the column with baked soil than in columns packed with baked sand. Retardation increased and the final ozone concentration decreased in the columns containing baked soil because the MO content was higher on the surface of the baked soil than on the sand surface (see Table 2). For example, the soil content of goethite (Fe_2O_3), known to be an effective catalyst, is 6.96%, whereas it is only 0.12% in the sand tested. Apparently, MOs such as goethite (α -Fe₂O₃), MnO, and Al₂O₃ on the surface of sand and soil (Table 2) accelerated the decomposition of ozone. The migration velocity (i.e., soil < sand < glass bead) of the ozone front was inversely proportional to the content of MOs. Based on equal volume, Imamura et al. (1991) reported the following order of the reactivity of gaseous ozone decomposition by unsupported oxides catalysts: Ag₂O>NiO>Fe₂O₃>Co₃O₄>CeO₂>Mn₂O₃>CuO>Pb₂O₃>Bi₂O₃>SnO₂>MoO₃> V_2O_5 >SiO₂. Heisig et al. (1997) found that MnO₂-Fe₂O₃ system showed the highest ozone decomposition from the investigation of binary oxide combinations formed from MnO₂, Co₃O₄, Fe₂O₃, NiO, the most active transition-metal single oxides for the reaction. Dhandapani and Oyama (1997) present a through review on gas phase ozone decomposition by metal oxide catalysts.

3.1.2. Effects of water content on ozone transport

Soil moisture content is one of the most important factors to consider in characterizing the fate and transport of gaseous ozone in unsaturated porous media. Thus, a 20-cm long column was tested at different water contents to determine the influence of water content on ozone migration. Fig. 4 shows ozone BTCs for various water contents as a function of pore volume. As the water content increased, the ozone breakthrough time at $C/C_0 = 0.5$ decreased proportionally, because the average linear gas velocity at a fixed gas flux increases proportionally as a result of reduced gas PV in the column. The ozone breakthrough time at $C/C_0 = 0.5$ was about 6 PVs for 0% water content, whereas the ozone breakthrough times were 3.6, 2.5, and 2.0 PVs for water contents of 6%, 16%, and 26%, respectively.

The BTC was more retarded in the dry column than in the other cases. This phenomenon is again due to the interactions of ozone with SOM and MOs on the sand surface. Water molecules cover the sand surface even at lower moisture contents, and the wetting fluid interferes with the reactions; in other words, the pore water blocks the reactive sites of the surface of the sand, thus subduing catalytic reactions with ozone. With fewer opportunities to react with MO and SOM, the ozone breaks through the surface faster. Although dissolved ozone in pore water may undergo similar reactions, the reaction rate is much faster in the gas phase than in the aqueous phase. This argument is also justified by the similarity of the BTCs.



Fig. 4. Effects of water content on the ozone breakthrough in sand column: ozone concentration was 2.42 wt.%, soil organic matter content was 0%, and flow rate was 200 ml/min.

3.1.3. Effects of flow rate

In applying gas phase ozone as an in-situ remediation technology, the flow rate is also an important parameter. Hsu (1995) used two different flow rates for removing VOCs in unsaturated zone. A high flow rate was used in preliminary air stripping using air to volatilize contaminants, followed by a low flow rate using either air or ozone to remove the residual contaminants. In this study, gas phase ozone transport in a column of dry sand was tested for flow rates of 100, 200, and 300 ml/min. For negligible gas phase compressibility, the estimated gas velocities at flow rates of 100, 200, and 300 ml/min are 0.74, 1.49, and 2.23 cm/s, respectively, and the times required for 1 PV are 26.8, 13.4, and 8.9 s, respectively. In fact, the flow rates are related linearly to gas velocity and inversely to breakthrough time. Fig. 5 presents the ozone BTCs for the three flow rates versus time. As Fig. 5 shows, less time was required for the ozone gas to break through as the gas flow rate increased. However, the PVs required at $C/C_0 = 0.5$ were 6.0, 6.5, and 3.3 for flow rates of 100, 200, and 300 ml/min, respectively, as obtained by dividing the breakthrough time by the time required for 1 PV. Theoretically, the PVs required at C/ $C_0 = 0.5$ must be identical regardless of the magnitude of flow rates. This discrepancy, especially at 300 ml/min, might be attributed to different trends for the reaction of ozone with either SOM or MOs on the sand surface at this high flow rate. However, in general, the linear velocity of ozone and the total ozone injection rate could be controlled easily, depending on the site conditions.

90



Fig. 5. Effect of flow rate on ozone breakthrough in sand column: influent ozone concentration was 4.0 wt.%, particle size was 0.85 mm, SOM content was 0.12 wt.%.

3.2. Hydrocarbon removal by ozone

3.2.1. Ozone transport and phenanthrene removal

To investigate the effects of hydrocarbon contaminant on the characteristics of ozone transport, experiments were conducted with a column packed with dry sand. Phenanthrene was used as a model PAH because of its low solubility and volatility. A column of sand contaminated with phenanthrene was prepared. The ozone flow rate, the initial phenanthrene concentration, and the water content used in this study were 200 ml/min, 100 mg/kg, and 0 wt.%, respectively. The organic matter content of the sand was 0 wt.% (baked sand). Fig. 6 shows the BTCs of the gas phase ozone versus PV in a column packed with clean sand and another packed with phenanthrene-spiked sand ("PAH-Contaminated Sand"). Ozone BTCs show significantly different patterns, depending on the presence of phenanthrene. Although the gas phase ozone at the outlet eluted at a similar PV of 2.0, more than 150 PVs were required for complete breakthrough in the column with phenanthrene-contaminated sand, while only 27 PVs were needed in the column with clean sand.

Retardation factors were determined by employing the first-time moment analysis (Nkedi-Kizza et al., 1987) as follows:

$$R = \int_0^{T_{\text{max}}} (1 - C/C_0) \mathrm{d}T \tag{1}$$



Fig. 6. Ozone breakthrough in clean sand and phenanthrene contaminated sand column: ozone concentration was 2.42 wt.%, soil organic matter content was 0%, and flow rate was 200 ml/min at dried condition.

where *C* is the outlet ozone concentration, C_0 is the inlet ozone concentration, *T* is the PV, and T_{max} is the total PVs displaced when $C = C_0$. The integrated area above the BTC up to $C/C_0 = 1.0$ provides a measure of retardation. In this calculation, the retardation factor R for the nonreactive gas (such as nitrogen gas) is assumed to be 1. The ozone BTCs indicate that ozone transport is significantly more retarded (more than five times) in the columns packed with PAH-contaminated sand than in the columns with clean sand, as confirmed by the *R* values for clean sand (3) and PAH-contaminated sand (16). The BTC for the PAH-contaminated sand revealed an asymmetry with relatively rapid breakthrough before 5 PVs. There also appeared to be an ozone fraction that eluted more slowly. However, ozone consumption gradually diminished as the contaminant was removed from the column.

Fig. 7 compares the phenanthrene mass removal after 1 h of ozone injection in columns packed with glass beads, sand, and baked sand. The phenanthrene mass removal ranged was 5080 mg/kg soil h. The maximum removal (>80 mg/kg soil h) was achieved in the columns packed with baked sand; lower rates were achieved, in descending order, with glass beads and with sand. This finding indicates that catalytic ozone decomposition with MOs in columns packed with baked sand enhanced OH· formation, resulting in increased contaminant removal. In columns packed with sand, however, some portion of the ozone was consumed by direct reaction with SOM, resulting in a decreased rate of contaminant removal. The rate of contaminant removal was also higher in the columns packed with glass beads than in columns packed with sand because of SOM on the sand surface. However, the removal rates for glass beads and sand are within experimental error limits estimated at a 95% confidence interval. The removal in columns packed with glass beads



Fig. 7. Phenanthrene removal by gaseous ozone in various soils ($d=425-600 \mu m$), after 1-h ozone injection: the ozone concentration was 2.42 wt.%, and the flow rate was 200 ml/min at dried condition. (GB: glass bead, S: sand, BS: baked sand).

is attributed to the direct reaction of ozone with phenanthrene. Comparison of the removal rates for columns packed with baked sand or with glass beads shows that more than 20% of enhanced phenanthrene removal was due to catalytic ozone decomposition and the



Fig. 8. Breakthrough curve of gaseous ozone and diesel removal rate (as diesel range organics): flow rate was 50 ml/min, ozone concentration was 119 mg/l, initial diesel concentration was 1485 mg/kg soil (as DRO), organic matter content was 0.12 wt.% and moisture content was 8.4 wt.% at 25 °C.



Fig. 9. Residual concentration of eight diesel-range organics in the outlet of Kyunggi soil column: flow rate was 50 ml/min, ozone concentration was 119 mg/l, initial diesel concentration was 1485 mg/kg soil (as DRO), organic matter content was 0.12 wt.% and moisture content was 8.4 wt.% at 25 °C.

subsequent reaction of OH· with phenanthrene. The effects that MOs on soil surfaces have on the enhanced decomposition of hydrocarbons in water have been investigated (e.g., Masten, 1991; Choi et al., 2001). Through experimental investigations on ozonation of VOCs in the presence of humic acid and soils, Masten (1991) suggested that the free radicals generated during the decomposition of ozone influenced the oxidation of VOSs significantly and that contaminated soils and waters containing high concentrations of naturally occurring organic matter can be treated by ozone. Choi et al. (2001) also reported that in a soil slurry system, OH· formation enhanced phenanthrene removal by 25% via catalytic ozone decomposition with MOs. The reduced phenanthrene removal in the presence of SOM in the sand columns indicates that ozone demand may be substantial during the ozone-enhanced remediation of PAH contamination in the vadose zone. Ohlenbusch et al. (1998) carried out experiments to investigate the effects of ozonation of soil organic matter in groundwater. After ozonation of an aqueous soil extract in a stirred tank reactor, the humic acid fraction and its average molecular size decreased, resulting in an increase of the building block fraction and the low molecular acid fraction.

Fig. 10. Breakthrough curves (BTCs) of ozone (a) and diesel removal rate in inlet (b) and outlet (c) of soil column under various water contents: flow rate was 50 ml/min, concentration of ozone was 119 mg/l, initial concentration of diesel was 1432 \pm 50 mg/kg soil (as DRO), and organic matter content was 4.37% at 25 °C: (a) Ozone BTCs, and DRO removal in (b) Inlet, (c) Outlet.



3.2.2. Ozone transport and DRO removal

The feasibility of using gaseous ozone for the remediation of DRO-contaminated soils was investigated by using a cyclic batch reactor that consisted of columns containing field soil spiked with DROs. Gas phase ozone was injected continuously. The initial SOM content and water content were 0.12 and 8.4 wt.%, respectively. Ozone flow rate, inlet ozone concentration, and initial DRO concentration in soil were 50 ml/min, 119 mg/l, and 1485 mg/kg, respectively. The total removal of DROs was measured for 14 h by sacrificing columns once every 2 h. In addition, a number of experiments were conducted by using various water contents to investigate the effects of water content on DRO removal and the characteristics of subsequent ozone transport.

Fig. 8 shows the ozone BTCs and rates of DRO removal. Ozone transport was retarded considerably, with more than 6 h required for the gaseous ozone to break through the soil column initially. The initial rapid rate of DRO removal in the inlet was attributed to the volatilization of relatively volatile smaller compounds having carbon numbers of C_{10} – C_{18} . Detailed analysis of compound groups in the column outlet confirmed this conclusion, as shown in Fig. 9, which presents the residual concentrations of DROs, ranging from decane (C_{10}) to tetracosane (C_{24}), versus the ozonation time in the column outlet. The oxidation of higher-carbon-number DROs (> C_{18}) to lower ones (i.e., C_{10} – C_{18}) and the subsequent volatilization of these lower-carbon-number DROs in the inlet region resulted, at early reaction times, in increased effluent concentrations of the smaller-carbon-number DROs over the initial concentrations, as shown in Fig. 9. The overall DRO removal efficiency after 14-h ozonation was 78.7%.

Fig. 10a presents the ozone BTCs at various water contents as a function of ozonation time. As Fig. 10a shows, water content significantly affected the ozone BTCs. Gaseous ozone began to elute at 1100, 600, and 300 PVs, and the relative gas phase ozone concentrations after 6 h of ozonation (1400 PVs) were 0.03, 0.22, and 0.44 for the columns at 1.47, 8.39, and 14.41 wt.% water contents, respectively. This result clearly indicates that water content also strongly influenced the fate and transport of gaseous ozone through the unsaturated soils contaminated with DROs. Fig. 10b and c, respectively, show the DRO removal rates at the inlet and outlet boundaries of natural soil columns, at various water contents. In general, for the water contents tested in this study, higher water contents were associated with higher DRO removals in both boundaries. Although DRO removals over 97% were obtained at 14 h (1600 PVs) at all water contents tested in the inlet boundary, the water contents significantly affected the DRO removals in the outlet. At 14 h, for example, approximately 63%, 88%, and 90% of DRO removals were achieved at 1.47, 8.39, and 14.41 wt.% water contents, respectively. The increased pore water is believed to have blocked the reactive sites of soil surfaces to some extent, thus enhancing gaseous ozone transport. Hsu (1995) also found that the presence of water (wet sand) increased the removal of residual trichloroethylene as compared to contaminated dry sands because the pore water (wetting fluid) blocked small pores, keeping residual trichloroethylene (nonwetting fluid) from entering small pores. The effect of water content on the removal rates of DROs and other contaminants should be investigated further in terms of the reactions of ozone with reactive sites (such as SOM and MOs). This is particularly important because the DROs, which consist of saturated alkanes, are more readily oxidized by the OH.

produced by the reaction of ozone with MOs on the soil surface than by the ozone molecule itself.

4. Summary and conclusions

Water content, SOM, and MOs were found to be the factors most influential in the fate and transport of gaseous ozone in unsaturated porous media. Overall, gaseous ozone was readily delivered and transported to remediate unsaturated soils contaminated with phenanthrene and DROs. The maximum removal of phenanthrene was achieved in the columns packed with baked sand, followed, in descending order, by glass beads and by sand, indicating that catalytic ozone decomposition with MOs in columns packed with baked sand enhanced OH· formation and resulted in increased contaminant removal. Cyclic batch experiments using columns containing field soil spiked with multicomponent DROs ranging from C_{10} to C_{24} indicated that ozone transport was retarded considerably, as more than 6 h were required for the gaseous ozone to initially break through the soil column under the experimental conditions tested.

The reaction kinetics and reaction stoichiometries between ozone and SOM, MO, and contaminants (which might be site specific because of the local SOM and MO contents of heterogeneous soils) must be determined so that they can be used to assess the application of ozone-enhanced remediation technology. Continued studies should also involve mathematical models being developed for use in field remediation applications of the technology.

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