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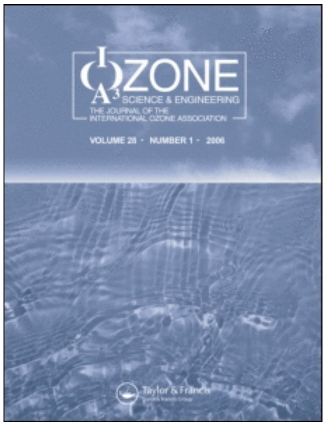

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# Efficient Decomposition of Trichloroethylene (TCE) in Groundwater by Ozone-Hydrogen Peroxide Treatment

**N. Yasunaga and J. Hirotsuji**

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*It was verified that the ozone-hydrogen peroxide treatment ($O_3/H_2O_2$) was very effective for decomposing trichloroethylene (TCE) in groundwater. The reaction efficiency of $O_3/H_2O_2$ was 40% better than that of ozone treatment by using a diffuser type reactor and the optimum operating conditions were also revealed by laboratory-scale experiments and computer simulations. Taking these results into consideration, the 2-port ozone injection method using an ejector-type reactor was investigated to decompose TCE more rapidly and efficiently, and it was revealed that the ozone dose necessary for satisfying the Japanese water quality standard for drinking water (0.03mg/L) by the 2-port ozone injection method was 13% less than that by the conventional 1-port ozone injection method under the condition of the same amount of ozone injected. Also, the effectiveness of the 2-port injection method was proved by a sequential plant-scale experiment for about 40 days.*

**Keywords** Ozone, Hydrogen Peroxide, Hydroxyl Radical, Groundwater, Trichloroethylene (TCE), 2-Port Ozone Injection Method

## INTRODUCTION

Recently, the impacts of industrial development on environmental pollution have become of great concern. Indeed, many sites in groundwater polluted by a high concentration of Volatile Organic Compounds (VOCs) such as trichloroethylene (TCE) were revealed (Clancy, 1996). In response to the presence of TCE in groundwater and concern about potential health effects, the concentration of TCE was regulated to under 0.03 mg/L in the Japanese water quality standard for drinking water. As a result of this regulation, many groundwater suppliers have installed treatment facilities at wells polluted by TCE. The most frequently used treatment techniques include packed tower air stripping followed by granular activated carbon (GAC) adsorption (Linek et al., 1998). Using the packed tower and GAC methods involves just transferring TCE from the water to the GAC, and the TCE is not decomposed. The use of GAC has been expensive because of the need to replace it on a very frequent basis. Because of such limitations, alternative treatment technologies have been investigated for TCE removal from groundwater.

Ozone-hydrogen peroxide treatment ($O_3/H_2O_2$) is one advanced oxidation process (AOP) that promotes the OH radical, a powerful oxidant. The OH radical decomposes almost all organic compounds to $H_2O$, $CO_2$ and others, and its reaction rate is so fast that the reaction with pollutants is finished in a very short time. Since the rate constant of the OH radical with TCE is $4.0*10^9\ M^{-1}s^{-1}$ and much larger than that of ozone with TCE ($17\ M^{-1}s^{-1}$) (Masten and Hoigne, 1992; Sunder and Hempel, 1997), TCE is supposed to be decomposed by $O_3/H_2O_2$ in a very short time. Moreover, it is supposed that TCE will be volatilized by gas injection including ozone; therefore it is necessary to grasp the rate of decomposition and volatilization of TCE in $O_3/H_2O_2$.

On the other hand, improvement of the reaction efficiency in $O_3/H_2O_2$ is also expected. The OH radical, with its high potential energy, reacts with not only organic compounds but also with various substances such as inorganic carbon, ozone, and radicals. Therefore, the concentration of the target substances does not decline so much, in spite of a large amount of ozone consumed.

Yasunaga et al. (2001) reported that the 2-port ozone injection method for decomposition of sodium acetate was more advantageous for reaction efficiency in $O_3/H_2O_2$ than the conventional 1-port ozone injection method. They also revealed that by injecting ozone in two ports the amount of ozone consumed for OH radical formation

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was increased and that consumed by radical chain reactions was decreased more remarkably than that by injecting ozone in one port.

The present study focuses on the decomposition of TCE with the OH radical in $O_3/H_2O_2$ and the relationship between decomposition and volatilization of TCE by injecting ozone gas in experiments and simulations. Moreover, we applied the 2-port ozone injection method in decomposition of TCE by $O_3/H_2O_2$ in the laboratory and on-site in order to verify the effectiveness of this method.

## MATERIALS AND METHODS

### TCE Decomposition and Volatilization by Experiment

In these studies a solution of TCE in ion-exchanged water was used. Figure 1 shows the schematic diagram of the laboratory-scale apparatus for TCE decomposition and the comparison of reaction efficiency of ozone treatment with that of $O_3/H_2O_2$. Ozone gas was generated by an ozone generator from oxygen and injected to the reactor. NaOH solution was added into the reactor in order not to lower the pH by HCl generation by decomposition of TCE and the pH in the reactor was maintained at 6–8. In $O_3/H_2O_2$ hydrogen peroxide was added into the reservoir tank in advance. The concentration of dissolved ozone, TCE, hydrogen peroxide and chloride ion ($Cl^-$) was measured at the reservoir tank and sampling port. Inlet and outlet ozone gas concentration were monitored and measured by absorption to KI solution. Experimental conditions are summarized in Table 1.

Since TCE is volatile, the amount of TCE reduced is not considered to be the amount of TCE decomposed. Therefore, the amount of TCE decomposed and volatilized was calculated by the following equations:

$$\begin{aligned}&(\text{The amount of TCE decomposed})\\&\quad = (\text{The amount of } Cl^-\text{generated}) * 131.5/(35.5 * 3);\end{aligned}$$

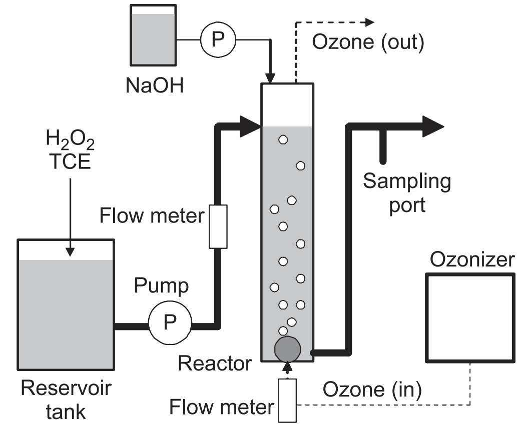

**FIGURE 1.** Schematic diagram of TCE decomposition by ozone and $O_3/H_2O_2$.

**TABLE 1.** Experimental Conditions of TCE Decomposition by Ozone and $O_3/H_2O_2$

| | |
|---|---|
| Feed ozone concentration ($g/m^3$) | 0–150 |
| Gas flow rate (L/min) | 0.11 |
| Liquid flow rate (L/min) | 0.25 |
| Initial TCE (mg/L) | 60–90 |
| Initial hydrogen peroxide (mg/L) | 11 |
| Water temperature (degrees C) | 14 |
| pH (-) | 7 |
| Effective reactor volume (L) | 1.0 |
| Effective reactor height (m) | 0.35 |
| Cross-section area ($m^2$) | $2.8*10^{-3}$ |
| Retention time (min) | 4 |

$$\begin{aligned}&(\text{The amount of TCE volatilized})\\&\quad = (\text{the amount of TCE reduced})\\&\qquad - (\text{the amount of TCE decomposed}).\end{aligned}$$

Figure 2 shows the schematic diagram of the laboratory-scale apparatus to measure the rate for TCE transfer from the liquid to gas phase. The change in TCE concentration in the liquid phase by injecting oxygen was traced and the bubble size was measured. These experimental conditions are summarized in Table 2.

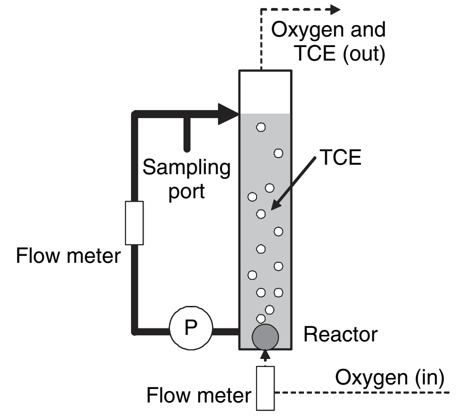

**FIGURE 2.** Schematic diagram of TCE volatilization.

**TABLE 2.** Experimental Conditions of TCE Volatilization

| | |
|---|---|
| Oxygen gas flow rate (L/min) | 0.3–1.1 |
| Initial TCE (mg/L) | 5–6 |
| Liquid circulation flow (L/min) | 2.3 |
| Water temperature (degrees C) | 17 |
| pH (-) | 6 |
| Effective reactor volume (L) | 4.8 |
| Effective reactor height (m) | 1.7 |
| Cross-section area ($m^2$) | $2.8*10^{-3}$ |

## TCE Decomposition and Volatilization by Simulation

A computer simulation was studied on the preceding experiments in order to grasp the condition where TCE was decomposed completely, not volatilized. The reaction model and its rate constants of the ozone-hydrogen peroxide system reported by Kawaai et al. (1995) and Yasunaga et al. (2006) were modified and applied to this simulation study. In this model it was assumed that the byproducts from TCE decomposition did not react with anything. In addition to the reaction of TCE with ozone and the OH radical, the volatilization of TCE by injecting ozone gas was integrated into this model. Also, the values of some coefficients such as the distribution coefficient of TCE ($H_{TCE}$: 3.29) were cited in the literature (Linek et al., 1998). The experiments and simulations were performed in accordance with Table 1. The obtained results by the above experiments and simulations were compared in terms of the concentration of residual TCE, ozone gas (outlet) and residual hydrogen peroxide, and the appropriateness of the simulation model was investigated. Then, the simulations were performed minutely in order to grasp the conditions where TCE was decomposed completely. These simulation conditions are summarized in Table 3.

These simulations were performed in two conditions as follows. One was the condition where the G/L was constant (0.5) while changing the feed ozone concentration from 0 to 100 g/m$^3$. The other was the condition where the ozone dose was constant (2.5 mg/L) while changing the gas flow rate and feed ozone concentration from 0.025 to 1.0 L/min and from 2.5 to 100 g/m$^3$, respectively.

In these simulation the value of $K_L$ of TCE from the liquid to gas phase was quoted from TCE volatilization experiments and the contact area between the gas and liquid phases, a, was calculated from the $K_La$ of ozone and the above $K_L$ of TCE.

## Highly Effective TCE Decomposition

Since TCE was considered to be decomposed in a short time by $O_3/H_2O_2$, an ejector type reactor was applied. Figure 3 shows the schematic diagram of the apparatus of the 2-port ozone injection method. The 1-port ozone injection method was carried out as a reference by removing the ejector (2). The gas flow rate was divided equally in the 2-port injection method. The inside structures of these ejectors were different in order to be able to suck ozone gas at each ejector.

In the laboratory-scale study, a set amount of TCE was injected into the underground water where volatile organic compounds where removed previously by air bubbling overnight. The optimum ratio of ozone and hydrogen peroxide dose was determined before comparing with the 1-port and 2-port injection methods. Continuously, the underground water contaminated by TCE and cis1,2-dichloroethylene (DCE) was used for the 2-port ozone injection method in the on-site study. This study lasted for about 40 days (from late August to early October). The quality of this underground water is summarized in Table 4. The experimental conditions in the laboratory and on-site are summarized in Table 5. The concentration of TOC and IC in this underground water was 2–5 mg/L and 10–20 mg/L, respectively.

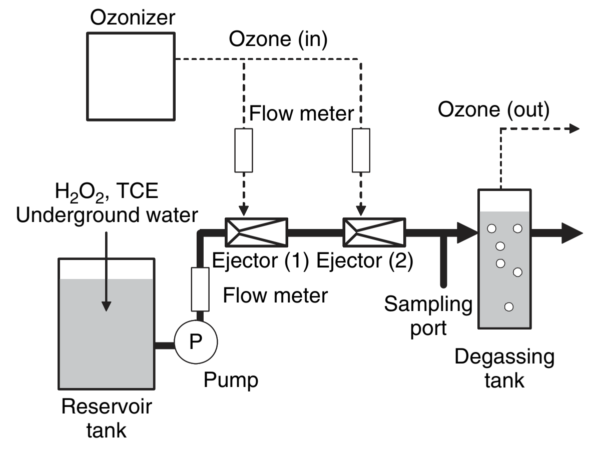

**FIGURE 3.** Schematic diagram of 2-port injection method.

**TABLE 3.** Conditions of Simulations

| | |
|---|---|
| Feed ozone concentration (g/m$^3$) | 0–100 |
| Gas flow rate (L/min) | 0.01–0.4 |
| Liquid flow rate (L/min) | 0.40 |
| G/L (-) | 0.025–1.0 |
| Initial TCE (mg/L) | 10 |
| Initial hydrogen peroxide (mg/L) | 1.25–2.5 |
| Water temperature (degrees C) | 15 |
| pH (-) | 7 |
| Effective reactor volume (L) | 4.0 |
| Effective reactor height (m) | 0.51 |
| Cross-section area (m$^2$) | 7.8*10$^{-3}$ |
| Retention time (min) | 10 |

**TABLE 4.** Quality of underground Water Used in On-Site Experiments

| Items | Concentration (mg/L) |
|---|---|
| Fe | 0.67 |
| Mn | 0.20 |
| $NO_2$-N | < 0.01 |
| $NO_3$-N | 0.16 |
| $NH_4$-N | 0.25 |
| Ca | 13 |
| Mg | 6.0 |
| Cl | 36 |
| Br | 0.07 |

**TABLE 5.** Experimental Conditions of 2-port Injection Method

| Scale | Laboratory | On-site |
|---|---|---|
| Substance to be decomposed | TCE | TCE, cis1, 2-DCE |
| Feed ozone concentration (g/$m^3$) | 75–120 | 70–80 |
| Total gas flow rate (L/min) | 3.0 (1.5*2) | 2.5 (1.25*2) |
| Liquid flow rate (L/min) | 10 | 2.5 |
| Initial TCE (mg/L) | 9–21 | 5–12 |
| Initial cis1, 2-DCE (mg/L) | – | 5–8 |
| Initial hydrogen peroxide (mg/L) | 0–10 | 2–5 |
| Water temperature (degree C) | 9–11 | 26–27 |
| pH (-) | 6–7 | 6–7 |

## ANALYTICAL METHODS

Chemical analysis in this study was conducted regarding TCE, cis1, 2-DCE, $Cl^-$, TOC, IC, hydrogen peroxide and ozone. Methods utilized include the following;

- TCE and cis1, 2-DCE: Purged and trapped gas chromatograph analyzer;
- $Cl^-$: Ion chromatograph analyzer;
- TOC and IC: Catalytic combustion method using a Shimadzu TOC-5000 analyzer;
- Hydrogen peroxide: Purge by nitrogen gas and decomposition by catalase method (Hunt and Sitar, 1998);
- Ozone: Absorption to KI solution and titration by $Na_2S_2O_3$ (0.01mol/L).

## RESULTS AND DISCUSSION

### TCE Decomposition by using Diffuser-Type Reactor

*Comparison of ozone treatment and $O_3/H_2O_2$.* The comparison of the reaction efficiency ($\Delta O_3/\Delta TCE$, $\Delta O_3$: the amount of ozone consumed; $\Delta TCE$: the amount of TCE decomposed) of ozone treatment and $O_3/H_2O_2$ is shown in Figure 4. It was revealed that the reaction efficiency in ozone treatment and $O_3/H_2O_2$ was 1.24 g-$O_3$/g-TCE and 0.77 g-$O_3$/g-TCE, respectively. That is to say, the reaction efficiency of $O_3/H_2O_2$ was 40% better than that of ozone treatment, and this indicated that TCE decomposition by the OH radical was more effective than ozone.

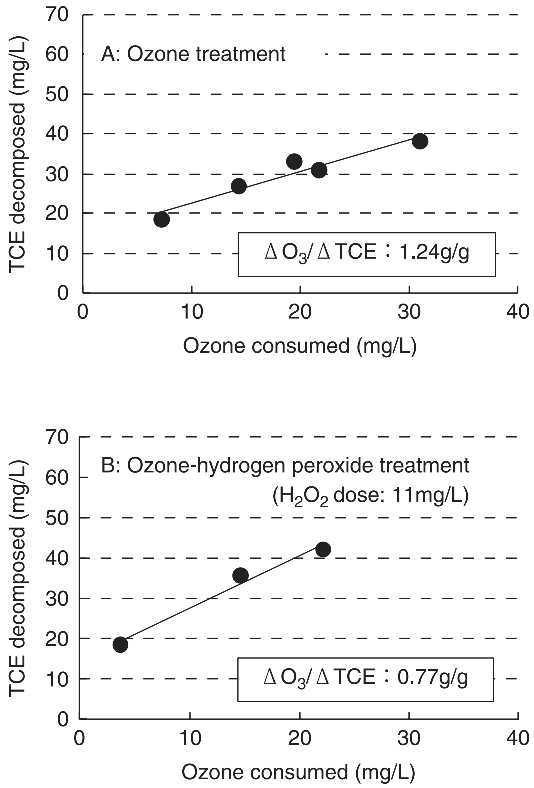

**FIGURE 4.** Reaction efficiency of ozone treatment and $O_3/H_2O_2$ (A: ozone treatment, B: $O_3/H_2O_2$).

*Transfer rate of TCE from liquid to gas phase.* The relationship between gas linear velocity ($V_a$: $m^3/m^2$/min) and $K_La$ (1/min) acquired by the oxygen bubbling experiments was shown in Figure 5 and the expression is as follows:

$$K_La = 0.16 \times V_a^{0.45}$$

Since the shape of bubbles was an ellipse, the average volume ($V_b$: $m^3$) and the average surface area ($S_b$: $m^2$) of one bubble were calculated by the following expressions:

$$V_b = (4/3) * \pi * D_1^2 * D_2$$

$$S_b = 2 * \pi * (D_1^2 + D_1 * D_2 * \log\{(D_1^2/D_2^2 - 1)^{1/2} + D_1/D_2\}/(D_1^2/D_2^2 - 1)^{1/2})$$

where $D_1$is a major axis, and $D_2$ is a minor axis.

Gas holdup ($H_{gas}$: -) was acquired by a rise of the liquid surface and contact area between the gas and liquid

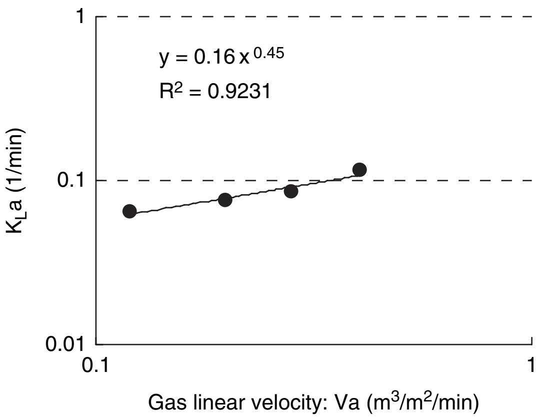

**FIGURE 5.** Relationship between gas linear velocity and $K_La$.

phases and (a: 1/m) was calculated by the following expressions:

$$a = H_{gas} * V_b / V_a$$

The transfer rate of TCE from the liquid to gas phase ($K_L$) was calculated by the above values and to be 0.005–0.007 cm/sec (0.003–0.004 m/min). This was about a quarter of the $K_L$ of ozone 0.020-0.030 cm/sec (0.01–0.02 m/min).

### Comparison of Experimental and Simulated Results

Comparison of experimental and simulated results is shown in Figure 6. As shown in these figures, these simulated results were in the good agreement with the experimental results where the feed ozone gas concentration was under 90 g/m$^3$. The simulated results were indicated as smaller than the experimental results where feed ozone concentration was over 90 g/m$^3$. The reason is considered to be as follows. When the ozone dose increased, the amount of TCE decomposed and by-products such as Cl$^-$ increased. Then the reactions involving the OH radical with these by-products were promoted and the efficiency of TCE decomposed decreased. The difference between the experimental and simulated results is considered to have occurred because in the simulation model these by-products couldn't react with anything.

### Investigation of the amount of TCE Decomposed and Volatilized by Simulation

The relationship between the rate of TCE decomposed and volatilized was investigated by computer simulation. The amount of TCE decomposed and volatilized and the residual TCE concentration is shown in Figure 7. In Figure 7(A) G/L (ratio of gas and liquid flow rate) was fixed at 0.5. The concentration of TCE in untreated water was 10 mg/L and about 2 mg/L of TCE was volatilized by oxygen injection as shown at the point of an ozone dose of 0 mg/L. In Figure 7(B) the ozone dose was fixed at 2.5 mg/L and the feed ozone concentration increased when G/L decreased.

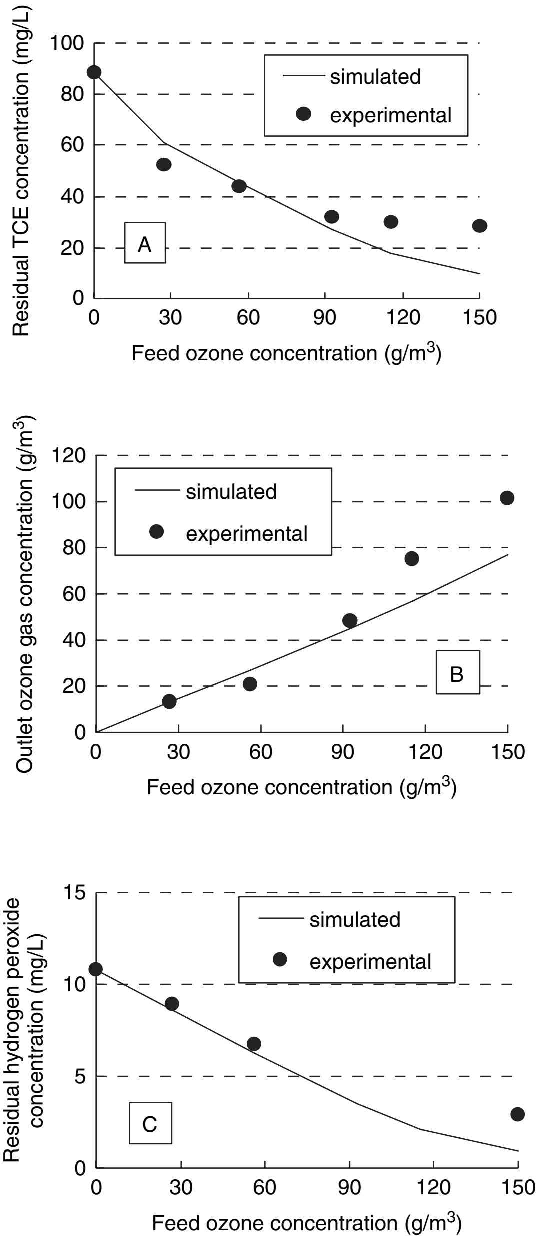

**FIGURE 6.** Comparison of experimental and simulated results of the concentration of residual TCE (A), outlet ozone gas (B) and residual hydrogen peroxide (C).

As shown in Figure 7(A), it was suggested that the amount of TCE decomposed increased and the amount of TCE volatilized decreased by increasing the ozone dose. TCE was completely decomposed and the amount of TCE volatilized was almost nothing under the condition of an ozone dose of 10 mg/L (feed ozone concentration 20 g/m$^3$). That is, the rate of TCE decomposed was much larger than that of TCE volatilized by increasing

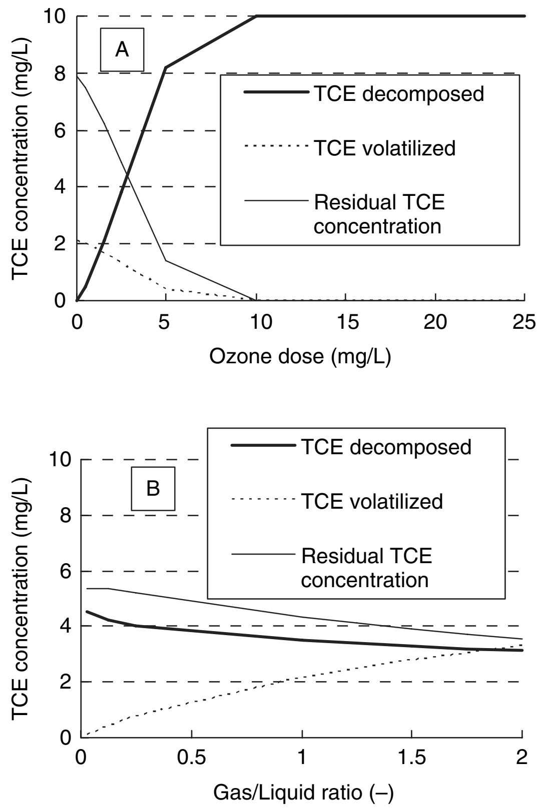

**FIGURE 7.** Relationship between amount of TCE decomposed and volatilized (A: G/L was constant: 0.5, B: ozone dose was constant: 2.5 mg/L).

the feed ozone concentration though G/L was 0.5. In another words, it is considered that the amount of TCE volatilized was nothing where the residual TCE concentration was nothing in $O_3/H_2O_2$.

As shown in Figure 7(B), it was revealed that the amount of TCE volatilized increased and the amount of TCE decomposed did not increase when the ozone dose was not enough for complete decomposition of TCE. The reason was that the volatilization of TCE was promoted by an increase in G/L where the ozone dose was not enough for complete TCE decomposition. Consequently, it was concluded that the decomposition of TCE was promoted efficiently and the volatilization of TCE was restrained by making G/L low and the feed ozone concentration high.

## Highly Effective TCE Decomposition by using Ejector-Type Reactor

*Laboratory-scale experiments.* From the above results and discussion, it was concluded that $O_3/H_2O_2$ was very effective for decomposing TCE and that the optimum condition where TCE could be completely decomposed, not volatilized, was acquired. At the first step, the optimum ratio of hydrogen peroxide to ozone dose where ΔTCE was the maximum was obtained by the 1-port injection method and the result is shown in Figure 8. Figure 8(A) and (B) indicate residual TCE concentration and the difference of hydrogen peroxide between inlet and outlet ($\Delta H_2O_2$). In these experiments TCE concentration of untreated groundwater was 21 mg/L and G/L was 0.3.

It was revealed that with a hydrogen peroxide dose over 2 mg/L, residual TCE concentration was almost settled as shown in Figure 8(A). Therefore, the optimum hydrogen peroxide dose was 2 mg/L and the optimum $H_2O_2/O_3$ ratio (ratio of ozone to hydrogen peroxide dose) was 0.062 (= 2/32) g-$H_2O_2$/g-$O_3$. This indicated that the hydrogen peroxide dose was much lower than the ozone dose in $O_3/H_2O_2$ for TCE decomposition. It was reported that the optimum $H_2O_2/O_3$ ratio exists where ΔTOC (reduction of TOC, TOC: acetic acid, 10 mg/L) was the maximum and ΔTOC was reduced where the $H_2O_2/O_3$ ratio was larger than the optimum one (Shishida et al., 1997). On the other hand, as mentioned, residual TCE

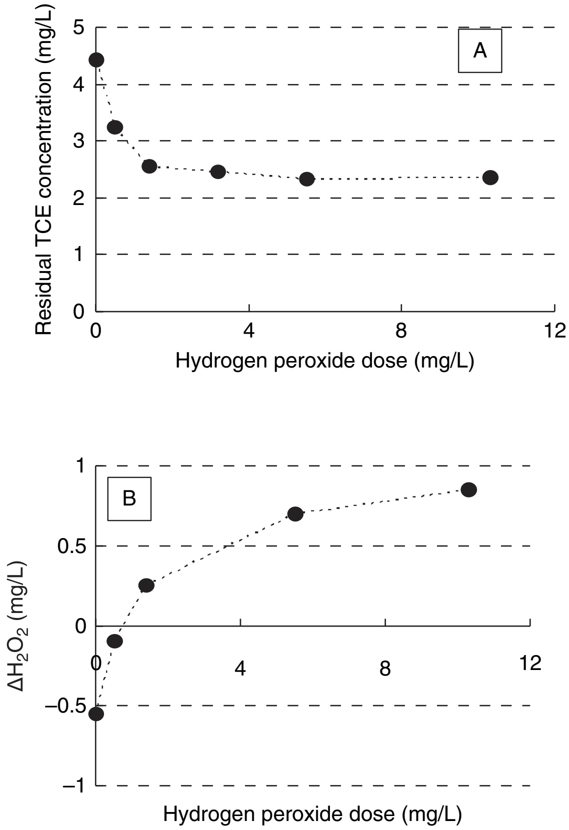

**FIGURE 8.** Experimental results of residual TCE concentration (A) and $\Delta H_2O_2$ (B) by 1-port injection method (ozone dose: 32 mg/L, hydrogen peroxide dose: 0–10 mg/L).

concentration was almost settled over the optimum $H_2O_2/O_3$ ratio. The reasoning is considered as follows:

1. Hydrogen peroxide is involved in reactions of both OH radical formation and OH radical consumption. In another words, hydrogen peroxide plays the roles of a promoter or a scavenger of the OH radical.
2. The rate constants involving the OH radical between TOC (acetic acid) and TCE are widely different.

The reaction rates of the OH radical with TCE, acetic acid and hydrogen peroxide are summarized in Table 6. The reaction rate of the OH radical with TCE: $k_{TCE} * [OH] * [TCE]$ ([ ] shows the concentration of the substance) was much more than that with hydrogen peroxide $k_{H2O2} * [OH] * [H_2O_2]$ in these experimental conditions ($k_{TCE} * [OH] * [TCE]$ / $k_{H2O2} * [OH] * [H_2O_2] > 100$); and then the reaction of the OH radical with TCE and hydrogen peroxide was in progress according to the ratio of this reaction rate. Since the reaction rate of the OH radical with TCE was much faster than that with hydrogen peroxide, residual TCE concentration was almost settled as shown in Figure 8(A).

In other words, an excess hydrogen peroxide dose did not disturb TCE decomposition by the OH radical in the range of these experimental conditions. On the other hand, since the $k_{TOC}$ is almost the same as that of $k_{H2O2}$, the reaction rate of the OH radical with TOC: $k_{TOC} * [OH] * [TOC]$ was almost the same as that of OH radical with hydrogen peroxide: $k_{H2O2} * [OH] * [H_2O_2]$ in the range of these experimental conditions. The reactions involving the OH radical were competitive with TOC and hydrogen peroxide. Therefore, in the range of conditions of cited in the literature (Kawaai et al., 1995), the point where $k_{TOC} * [OH] * [TOC] > k_{H2O2} * [OH] * [H_2O_2]$ -> $k_{TOC} * [OH] * [TOC] < k_{H2O2} * [OH] * [H_2O_2]$ is the optimum hydrogen peroxide dose. An excess hydrogen peroxide dose is considered to make TOC reduction efficiency worse.

As shown in Figure 8(B), $\Delta H_2O_2$ showed minus values. This was considered to be because in the conditions under a hydrogen peroxide dose of 1 mg/L, the TCE decomposition by the OH radical was not promoted, and that the amount of hydrogen peroxide produced by the decomposition of TCE by ozone was larger than that consumed by radical reactions.

The following experiments were conducted and compared with 1-port and 2-port injection methods under the condition of the optimum $H_2O_2/O_3$ ratio. The results of these experiments are shown in Figure 9. It was revealed that ΔTCE was improved by the 2-port injection method in the condition of the same ozone dose as shown in Figure 9(A) and that the ozone dose satisfying the Japanese water quality standard for drinking water (0.03 mg/L) was reduced from 32 mg/L to 28 mg/L by the 2-port injection method. Namely, the improved efficiency of the ozone dose was 13%.

**TABLE 6.** Reaction Rate of OH Radical with TCE, Acetic Acid and Hydrogen Peroxide

| | |
|---|---|
| TCE | $4.0*10^9$ $M^{-1}s^{-1}$ |
| Acetic acid | $8.5*10^7$ $M^{-1}s^{-1}$ |
| Hydrogen peroxide | $2.7*10^7$ $M^{-1}s^{-1}$ |

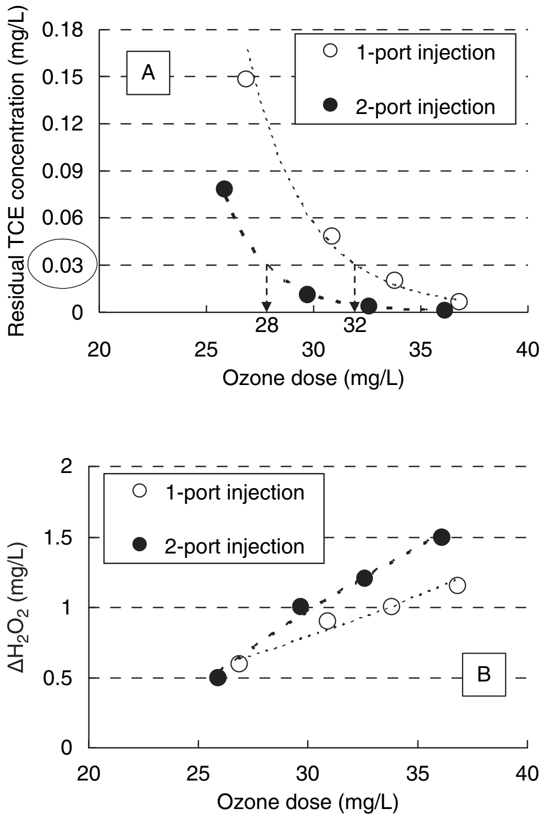

**FIGURE 9.** Experimental results in comparison with 1-port and 2-port injection methods in laboratory scale (A: residual TCE concentration, B: $\Delta H_2O_2$, ozone dose: 26–37mg/L, hydrogen peroxide dose: 4.1mg/L, $H_2O_2/O_3$ ratio: 0.11–0.16 g-$H_2O_2$/g-$O_3$, TCE concentration of untreated water: 10.9 mg/L).

As shown in Figure 9(B), the amount of hydrogen peroxide consumed in the 2-port injection method was slightly larger than that in the 1-port injection method. This indicated that the amount of OH radical produced by the reaction of hydrogen peroxide with ozone was increased, and that the reaction of TCE decomposition by the OH radical was promoted more efficiently by the 2-port injection method.

## Experiments On-Site

The results of the experiments on-site for about 40 days comparing the 1-port and 2-port injection methods is shown in Figure 10.

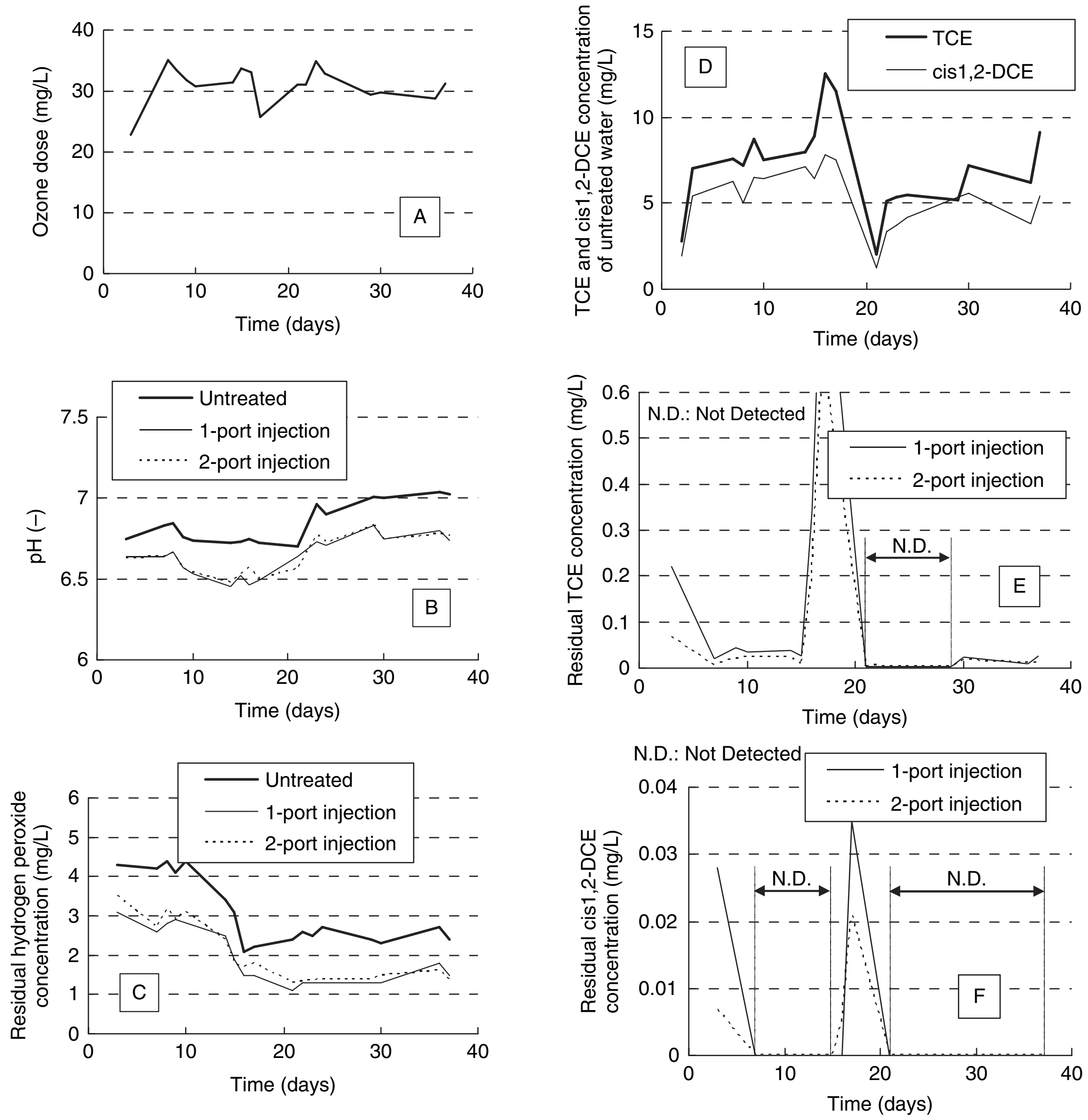

**FIGURE 10.** Experimental results comparing 1-port and 2-port injection methods on-site (A: ozone dose, B: pH, C: residual hydrogen peroxide concentration, D: residual TCE and cis1,2-DCE concentration, E: residual TCE concentration, F: residual cis1,2-DCE concentration, ozone dose: 70–80 mg/L, hydrogen peroxide dose: 2–5 mg/L, $H_2O_2/O_3$ ratio: 0.03-0.07 g-$H_2O_2$/g-$O_3$).

- Ozone dose: As shown in Figure 10 (A) the ozone dose was maintained over 30 mg/L except in the early stage of these experiments on-site. The ozone dose of the 16th day was decreased due to ozone generator operating problems.
- pH: As shown in Figure 10(B) the pH of untreated water changed from 6.7 to 7.0 and that of treated water decreased by 0.2–0.3 on account of the generation of HCl by decomposition of TCE and cis1,2-DCE.
- Hydrogen peroxide: As shown in Figure 10(C) from the beginning to the 10th day the hydrogen peroxide dose was 4 mg/L and was 2.0–2.5 mg/L after the 16th day. The $H_2O_2/O_3$ ratio was maintained at 0.07–0.18 g-$H_2O_2$/g-$O_3$ in the period of these experiments on-site and it was the optimum ratio for TCE decomposition by $O_3/H_2O_2$. $\Delta H_2O_2$ was almost the same in the 1-port and 2-port injection methods through the period of these experiments on-site.

- TCE and cis1,2-DCE: As shown in Figure 10(D) the underground water was contaminated by TCE 5–9 mg/L and cis1,2-DCE 1–7 mg/L and the concentrations of these substances have sharp fluctuations in the period of this experiment on-site.

As shown in Figure 10(E) and (F), it was revealed that $O_3/H_2O_2$ was very effective for decomposition of TCE and cis1,2-DCE, and that the 2-port injection method was more efficient than the 1-port injection method for about 40 days. TCE and cis1,2-DCE were not detected between the 21–29th days and the 7–16th and 21–37th days, respectively, although at the 16th day the TCE concentration of treated water was over 0.03 mg/L because of the lowering ozone dose as a result of ozonizer trouble as mentioned. The cis1,2-DCE concentration of treated water was always below the Japanese water quality standard for drinking water (0.04 mg/L).

## CONCLUSIONS

$O_3/H_2O_2$ treatment of underground water was investigated for TCE decomposition. The findings of this study can be summarized as follows.

1. The reaction efficiency of $O_3/H_2O_2$ was 40% better than that of ozone treatment and this indicated that TCE decomposition by the OH radical was more effective than ozone treatment.
2. Decomposition of TCE was promoted efficiently and volatilization of TCE was restrained by making G/L low and the feed ozone concentration high.
3. The ozone dose satisfying the Japanese water quality standard for drinking water (0.03mg/L) was reduced from 32 mg/L to 28 mg/L by the 2-port injection method. Namely the improved efficiency of the ozone dose was 13%.
4. It was revealed that $O_3/H_2O_2$ was very effective for decomposition of TCE and cis1,2-DCE, and that the 2-port injection method was more efficient than the 1-port injection method for about 40 days.

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