(사)한국지하수토양환경학회
00년춘계학술발표회 5.26~27

Ozone kinetics and Diesel decomposition by Ozonation in Groundwater

Choong-Il Kwon · Sung-Ho Kong · Moo-Hoon Kim*

Dept. of Chemical Eng., Hanyang University, Seoul 133-791, Korea
**Samsung Engineering R&D center, Suwon 449-910 , Korea*
[Tel]+82-2-2290-0489 [Fax]+82-2-2293-8551 [e-mail] shkong@email.hanyang.ac.kr

Abstract

본 연구에서는 지하수내에서의 오존의 거동과 오존산화공정에 의한 디젤의 분해를 조사하였다. 오존의 초순수와 지하수내에서의 반응은 모두 2차 분해반응속도식을 나타냈고, 초순수와 지하수내에서의 반감기는 각각 평균 37.5분, 14.7분으로 계산되었다. 지하수내에서 오존의 자가분해반응속도가 더 빠른 것으로 나타났는데 이는 오존이 지하수내에 존재하는 각종 유기·무기물질들과의 빠른 반응때문이라고 생각된다.

오존의 TCE, PCE 그리고 디젤의 빠른 제거효율을 통하여 디젤로 오염된 지하수를 처리하는데 있어서 오존산화공정은 효과적으로 적용될 수 있을 것이라 판단된다.

Key words : ozone oxidation, ozone kinetics, groundwater, diesel

1. Introduction

The problems of soil and groundwater contamination have been evoked around the world while the remediation processes and applications have been developed for some decades. The US EPA reported that many volatile compounds (VOCs) were existed in many groundwater wells. In Korea, numerous subsurface contamination by leakage from underground storage tanks (UST) was also reported, recently. To remediate contaminated soils and groundwater various advanced oxidation processes (AOPs) have been developed. Especially ozone is considered to be an attractive method in chemical oxidation processes due to its high oxidant capacity (E^0=2.08V) and electrophilic character. Hydroxyl radicals were also produced during ozonation process that has even higher oxidation potential (E^0=3.06V). However, little studies have been performed regarding ozone behavior and decomposition in groundwater since it consists of complex components and has site specific characteristics.

In this study, ozone kinetics and diesel decomposition in groundwater by ozonation process were investigated for further pilot-scale application at site.

2. Experiment

2.1 Experiment apparatus and method

Figure 1 is a schematic of the apparatus used for ozone oxidation experiments in this study. The reactor vessel is a cylindrical, approximately 0.2 m in diameter by 1m in height. The reactor has an effective volume of 25L.

Ozone gas was provided by an ozone generator (model OZAT^{R} CFS-2A, Ozonia Co.) Gas-phase ozone measurements were made by an in-line ozone monitor (Afx series H1-S bench, IN-USA Co.). The concentration of residual dissolved ozone concentration was followed by indigo procedure.

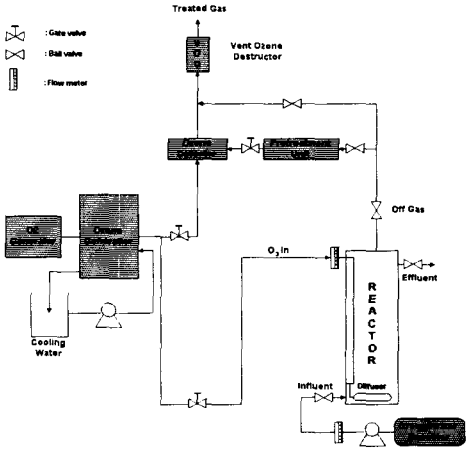

Figure.1 Schematic of experimental system

To determine changes of diesel decomposition in aqueous phase, TOC (Sievers.Co) were measured with varying ozone gas dosage.

Analytical measurement for PCE and TCE (Junsei. Co) was made with a GC-ECD (HP 6890) after liquid-liquid extraction with n-hexane.

Deionized water was prepared with ultrapure water(Maxima Ultra Pure Water, Elga, $\geq 18.2M\Omega$), and simulated groundwater (SG) was prepared based on the major components of J site groundwater. Ozone kinetics experiments were performed with deionized water and actual diesel-contaminated groundwater and TCE, PCE and diesel decomposition experiments were performed with deionized water and SG.

2.2 Groundwater analysis

Groundwater for this experiments was collected from wells in J site where it was contaminated with diesel. Table 1 shows the analysis results of groundwater.

Table.1 Properties of groundwater in J site

	pH	Temp (℃)	Alkalinity ($CaCO_3$ mg/L)	Hardness ($CaCO_3$ mg/L)	TCE (μg/L)	PCE (μg/L)	COD (mg/L)	TOC (mg/L)
Ground -water	6.5-7.5	12-15	312	99.6	188	79	32	42

3. Result and discussion

Figure 2 is the result of ozone auto-decomposition in deionized water and Figure 3 is the result in groundwater. Two reactions showed the high resolution (r^2>0.95) with second-order. In deionized water, second-order reaction rate constant (k) was $5.0*10^{3}$, $2.9*10^{3}$, $1.7*10^{-3}$ L/mg·min in each reaction, and half-life of ozone was 37.5 min. However, in groundwater k was $4.9*10^{-2}$, $1.4*10^{-2}$, $0.65*10^{2}$ L/mg·min with 14.7 min of half-life of ozone. The results shown Figures 2 and 3 demonstrated that the ozone decomposition rate in groundwater was much higher than that in deionized water. Considering those results, it is expected that ozone could have been decomposed rapidly in proportion as introduced ozone reacted with varieties of organic species.

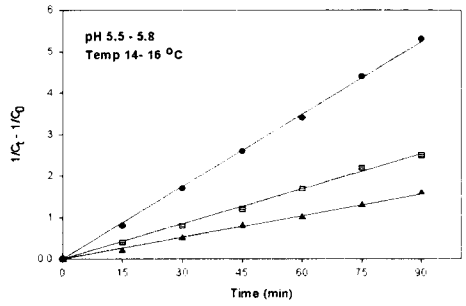

Figure.2 Ozone auto-decomposition reaction rates with second order in deionized water (●: 10mg/L,▩: 20mg/L,▲: 30mg/l in feed gas)

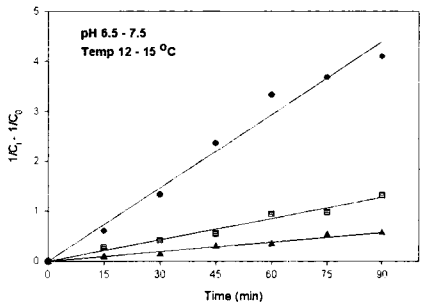

Figure.3 Ozone auto-decomposition reaction rates with second order in groundwater (●: 10mg/L,▩: 20mg/L,▲: 30mg/l in feed gas)

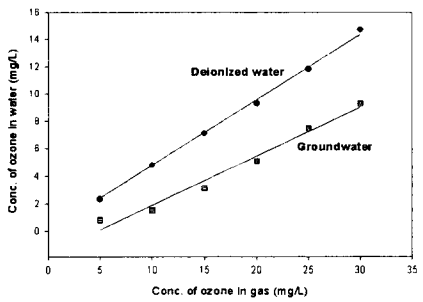

Figure. 4 Residual ozone concentration in water

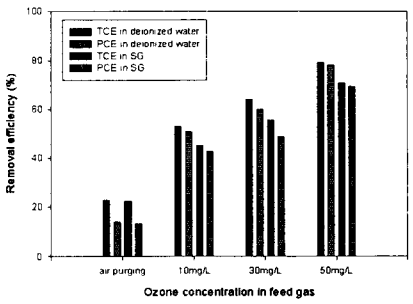

Figure. 5 Removal efficiency of TCE & PCE after ozone reaction 3hr

In Figure 4, the residual ozone concentration in deionized water was higher than in groundwater, indicating that ozone was decomposed quickly by reacting with organic matters in groundwater.

Figure 5 shows the removal efficiencies of TCE and PCE in deionized water and SG. Compared to gas purging, the removal efficiency by ozonation was much

higher at low ozone concentration. Therefore, ozone oxidation could be used to eliminate TCE and PCE from groundwater efficiently. However removal efficiency in deionized water was higher than in SG by 10% indicating hydroxyl radicals were quenched by scavengers, such as carbonate & bicarbonate in groundwater.

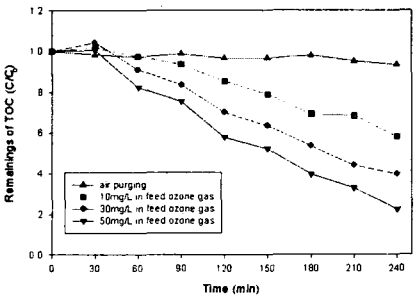

Figure. 6 Diesel decomposition in deionized water with variance ozone feed gas

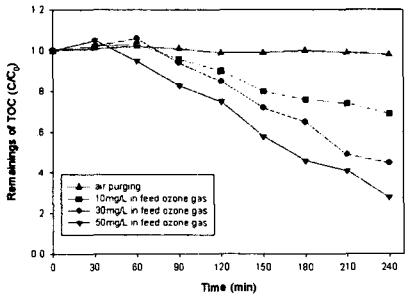

Figure. 7 Diesel decomposition in SG with variance ozone feed gas

Figures 6 and 7 show the remainings of TOC in diesel saturated-deionized water and SG after ozone oxidation. Air purging itself could not lower TOC values. TOC values were only lowered by ozonation process and higher ozone concentration showed higher removal of TOC. The removal of TOC was greater in deionized water than in SG coinciding with results of Figure 5.

4. Conclusion

In groundwater, the ozone auto-decomposition rate showed second-order reaction and residual ozone concentration in groundwater was lower than in deionized water indicating scavenging effects of ozone by inorganics in SG.

Ozone oxidation showed the good removal efficiencies of TCE and PCE, and diesel in aqueous phase. Therefore, ozone oxidation process could be applied to diesel-contaminated groundwater site remediation.

5. References

1) Langlais, B., D.A.Reckhow and D.R.Brink, Eds, "Ozone in Water Treatment: Application and Engineering", Lewis, Chelsea, MI, 1991
2) Staehelin, J. and J. Hoigne , "Decomposition of ozone in water: rate of initiation by hydroxide ions and hydrogen peroxide", *Environ. Sci & Techol,* vol 16, 10, 1982.
3) R.A.Freeze and J.A.Chery, "Groundwater", Prentice-Hall Inc., New Jersey, 1979
4) J.Hoigne, and H.Bader, "Rate Constants of rections of ozone with organic and inorganic compounds in water I : non-dissociating organic compounds", *Wat. Res*, 17, 1983
5) Standard methods for the Examination of Water and Wastewater.", 20th Ed., Am. Public Health Assoc., Washington, D.C.(1998)