

# DESTRUCTION OF HUMIC MATTERS AND AMMONIA IN THE LANDFILL LEACHATE BY SUPERCRITICAL WATER OXIDATION

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**Abstract** : Feasibility of destroying synthetic and actual leachate containing humic acids and ammonia compounds by supercritical water oxidation (SCWO) was evaluated. In this study, destruction efficiencies of humic acids and ammonia respectively were investigated at various reaction temperatures and residence times under pressure a supercritical pressure (280 atm). To lower reaction temperature, chemical oxidants were used. The experiment was carried out in a cylindrical batch reactor made of Hastelloy C-276 that can withstand high temperature and pressure. Concentrations of humic acids and ammonia were measured using a COD<sub>Cr</sub> method and an ammonia selective electrode, respectively. The optimal destructive condition of humic acids in the presence of stoichiometric oxygen (air) was 3 min at 380°C, but the temperature could be lowered to subcritical region (360°C) along with H<sub>2</sub>O<sub>2</sub> as an oxidant. For ammonia, the optimal destructive condition with air was 5 min at 600°C, but it was possible to operate the process for 3 minutes at 550°C or 2 min at 600°C along with H<sub>2</sub>O<sub>2</sub> as an oxidant. At 2 min and 550°C along with H<sub>2</sub>O<sub>2</sub> as an oxidant, humic and ammonia compounds in the actual leachate were easily destructed and the effluent quality met the Korea Standard Leachate Quality.

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**Key Words** : Humic acid, Ammonia, Leachate, Subcritical and Supercritical Water Oxidation, Oxidants.

## INTRODUCTION

Characteristics of landfill leachate are highly affected by waste properties, climatic conditions, soil properties and the design and age of landfill. Landfill leachate is known to include organic carbon (biodegradable and non-biodegradable organic matter), ammonia nitrogen, halogenated organics, inorganic salts, and toxic metals, but the characteristics of these pollutants are changing with age of landfill<sup>9,16)</sup>. The longer the landfill age, smaller the BOD<sub>u</sub>/COD<sub>Cr</sub> ratio, and the ratio in old landfill leachates is usually less than

0.2<sup>3)</sup>. It means that the leachate in the old landfill contains a high portion of non-biodegradable (NBD) organics. Since most biodegradable (BD) organics can be decomposed by aerobic microbes, the portion of NBD organics is relatively greater than BD organics.

Treatment of leachate in the old landfill aims at the removal of two major NBD materials: they are humic or fulvic substances and nitrogen compounds. Humic substances in the leachate contain macro-molecules NBD organics<sup>1,7)</sup>. These humic substances have a negative influence on the biological/ chemical processes. For example, Fenton's oxidation process has been used to treat these refractory species in the leachate. However, this process is inefficient in the acidic environment and the costs for the pH adjustment

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and iron salts are high; the resulting iron sludge also creates a disposal concern. In addition, the oxidation efficiency by  $\bullet\text{OH}$  radicals is reduced because the scavenging effect given by humic substances and the interreactions between humic substances and ferrous ions interfere the production of  $\bullet\text{OH}$ . All these reasons raise the operating cost for the treatment of the leachate by Fenton's oxidation process<sup>8)</sup>.

The presence of a large amount of nitrogen compounds in the food-waste landfilling often causes nitrification and results in accumulation of nitrite, so it requires external carbon sources for denitrification<sup>2,17)</sup>. There are many techniques for the ammonia removal: air stripping, ion exchange, and chemical/biological oxidation. These methods can reduce ammonia concentration to very low level but they require high capital costs and operating expenses<sup>12)</sup>.

Economically, there is a strong interest to remove both NBD organics (humics) and ammonia in leachate by one unit process. For the purpose, supercritical water oxidation (SCWO) technology can be offered as a good alternative for the treatment. The SCWO is applicable to a broad range of organic compounds as well as easily oxidizing inorganics such as ammonia and cyanide<sup>11,15)</sup>. The key reason why the process is so effective is that gases including oxygen and organic substances are completely soluble in supercritical water, whereas inorganic salts exhibit greatly reduced solubility under the process conditions<sup>6,19,20)</sup>. Above the critical temperature and pressure (218 atm and 374°C), properties of water are quite different from those of normal liquid water or steam. Typically, organic substances are completely soluble while salts are insoluble in water above its supercritical temperature. Effluent from the process is of near potable quality and contains no  $\text{NO}_x$ , no acid gases ( $\text{SO}_2$ ,  $\text{HCl}$ ), no particulates, and less than 10 ppm of carbon monoxide. The SCWO has many advantages over other unit operations, such as residence time of less than one minute, achievable destruction efficiencies of 99.99% to 99.9999%, minimum discharge of by-products

that require no additional treatment facilities. But SCWO also has several weaknesses that include high installation costs, production of char as a by-product, and scaling under subcritical region<sup>4,10)</sup>. Nevertheless, the SCWO process is an excellent technology to decompose NBD compounds.

The overall objective of this study was to assess the leachate effluent quality with regard to humic substances and ammonia nitrogen after the treatment by SCWO. The first objective was to study the optimal conditions of SCWO for the destruction of synthetic wastewaters containing humic substances and ammonia respectively. The second objective was to study the feasibility using the aforementioned optimal conditions from the first approach on actual leachate. Results of the study are expected to be used to assist to formulate guidelines for upgrading the Korea Standard Leachate Quality (KSLQ) (Table 1).

## METHODOLOGY

### Sample Collection and Site Characteristics

Both landfill leachate and synthetic wastewater were used in this work. For preparing synthetic wastewater of humic acids and ammonia were made by dissolving 5 g of humic acids (Aldrich Chemical Co. Germany) or 2 g of  $\text{NH}_3$  (ammonia acetate) in 100 mL of 0.1 N NaOH solution, and then diluted to desired concentrations. Recalcitrant properties of humic acids are known to be due to the inclusion of aromatic compounds with double bonds such as benzene, naphthalene, pyridine and anthracene via polycondensation<sup>7)</sup>. Because of the nonbiodegradability of humic acids, only humic acids were investigated in this study.

Leachate samples were collected from a sanitary landfill site in Gyeonggi Province, South Korea. This site is going to be closed in 2012 and the landfill area is about 30,000 m<sup>2</sup>. Wastes collected in the site are mainly household and food wastes. Leachate has been collected up to 50 tons a day and the facilities for the leachate

treatment consist of an aerobic digestion by Hanging Bio Contactor (HBC) and nitrogen removal process. Characteristics of the landfill leachate is presented in Table 2. Samples for the study were pretreated to remove solids by filtrating through a 0.45  $\mu\text{m}$  pore diameter membrane filter (Membrane filter, 0.45  $\mu\text{m}$ , MFS).

Table 1. The Korea Standard Leachate Quality.

BOD <sub>5</sub> , mg/ℓ	≤ 70
COD <sub>Cr</sub> , mg/ℓ	≤ 800
Ammonia nitrogen, mg/ℓ	≤ 100

Table 2. Landfill leachate characteristics.

pH	6.5 - 7.5
BOD <sub>5</sub> , mg/ℓ	450 - 520
COD <sub>Cr</sub> , mg/ℓ	6,200 - 8,800
TOC, mg/ℓ	4,900 - 7,500
Organic nitrogen, mg/ℓ	80 - 210
Ammonia nitrogen, mg/ℓ	70 - 125
Nitrate nitrogen, mg/ℓ	50 - 95
Total solid, mg/ℓ	320 - 760

### Experimental Methods

Figure 1 shows the SCWO reactor employed in this study, consisting of a reactor, heating, and thermal controller. The reactor was made of non-corrosive Hastelloy C-276 that can withstand high temperature and pressure. The experiment was carried out in a cylindrical batch reactor. Temperature at the inner part of the reactor was controlled by a Proportional Integral & Derivative (PID) device. Wastewater was pumped into the reactor using a high pressure peristaltic pump. Liquid effluent samples were cooled by a heat exchanger (as condenser), and depressurized to ambient pressure. As the effluent was cooled and depressurized, resulting products such as carbon dioxide, oxygen, and excess reacting compounds were condensed and collected from the outlet line. However, in recovery tests, the residual samples in the outlet line were less than 1% of total volume, which was negligible quantity.

Total effective volume of the reactor was 500 ml and the reactor was heated up to the

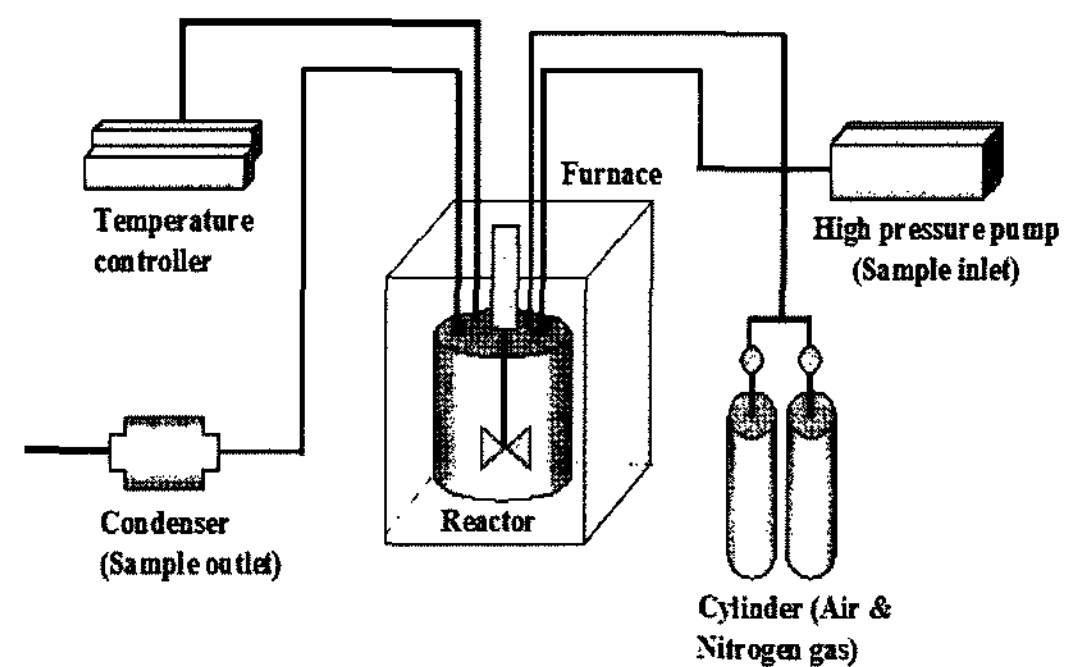


Figure 1. Schematic diagram of SCWO equipment

desired temperature, after the initial injection of deionized water (300 mL) and gases such as air or nitrogen in order to maintain the constant pressure in the reactor. The operating pressure in all experiments was fixed at 280 atm because pressure variations were reported to have insignificant effects on the decomposition of organic materials after reaching the critical pressure<sup>15</sup>. When the reactor was heated to preset temperature, samples (surrogate leachates) were fed into the reactor by peristaltic pump and it took 30 sec. Approximately 15 ml of sample volume was collected for analysis, the destruction efficiency of organic compounds was determined by a COD<sub>Cr</sub> method and the concentration of ammonia was determined by ammonia selective electrode (pHoenix Electrode Co., P/N NH<sub>4</sub>1502-003B).

Initial concentrations of humic acids and ammonia were set at 1,000 and 10,000 mg/ℓ, respectively, which are within the range of concentrations in a landfill of which ages are 5 to 10 yr. Theoretically, SCWO reactions are self-sustaining provided the waste stream has a COD of approximately 5,000 mg/ℓ or higher<sup>4</sup>). In this study, air and H<sub>2</sub>O<sub>2</sub> (35% purity) were used for the complete oxidation of target materials, and temperatures lower than critical temperature were tested. The amounts of oxidants required were calculated based on the equivalence of stoichiometric oxygen requirement for the initial concentration of sample and injected into the reactor by the peristaltic pump or pressurized air. Under the oxygen deficit condition which is

less than 80% of the stoichiometric oxygen amount, pyrolytic char can be procuded<sup>13)</sup>. This char would cause undesirable clogging problems. Therefore, stoichiometric amount of oxygen (air) and/or H<sub>2</sub>O<sub>2</sub> were supplied in all experiments. All chemicals used were analytical grade and water was double deionized. The experimental conditions are summarized in Table 3.

Table 3. Experimental conditions.

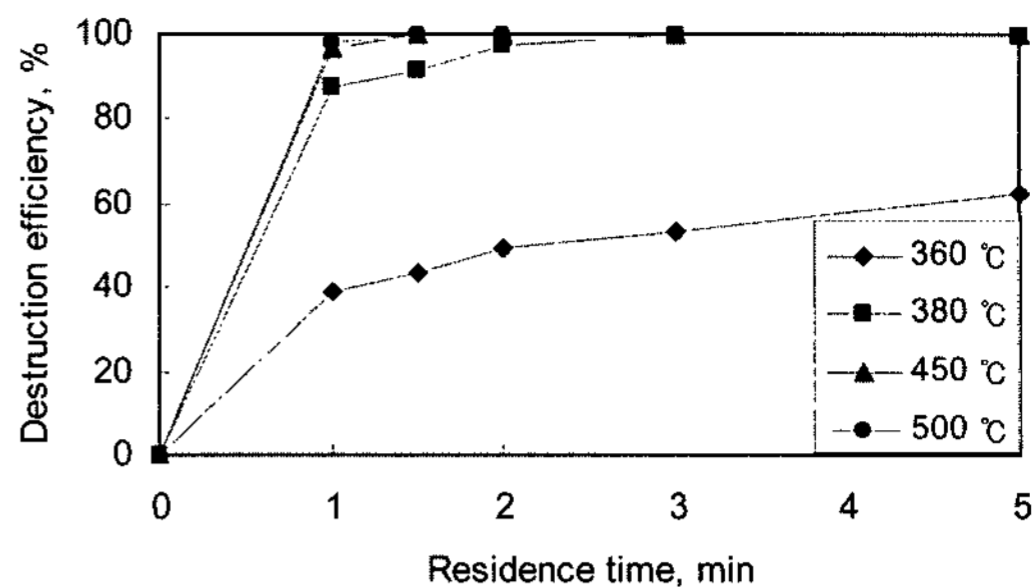
Experiment	Conditions
Organic destruction	Concentration (mg/ℓ) : 10,000 as humic acid
	Temperature (°C) : 360 ~ 550
	Residence time (minute) : 1, 1.5, 2, 3, 5
	Oxidant (Air : H <sub>2</sub> O <sub>2</sub> ) : 1:0, 1:1, 0:1
NH <sub>3</sub> -N destruction	Concentration (mg/ℓ) : 1,000 as NH <sub>3</sub> -N
	Temperature (°C) : 450 ~ 600
	Residence time (minute) : 1, 1.5, 2, 3, 5
	Oxidant (Air : H <sub>2</sub> O <sub>2</sub> ) : 1:0, 1:1, 0:1

## RESULTS AND DISCUSSION

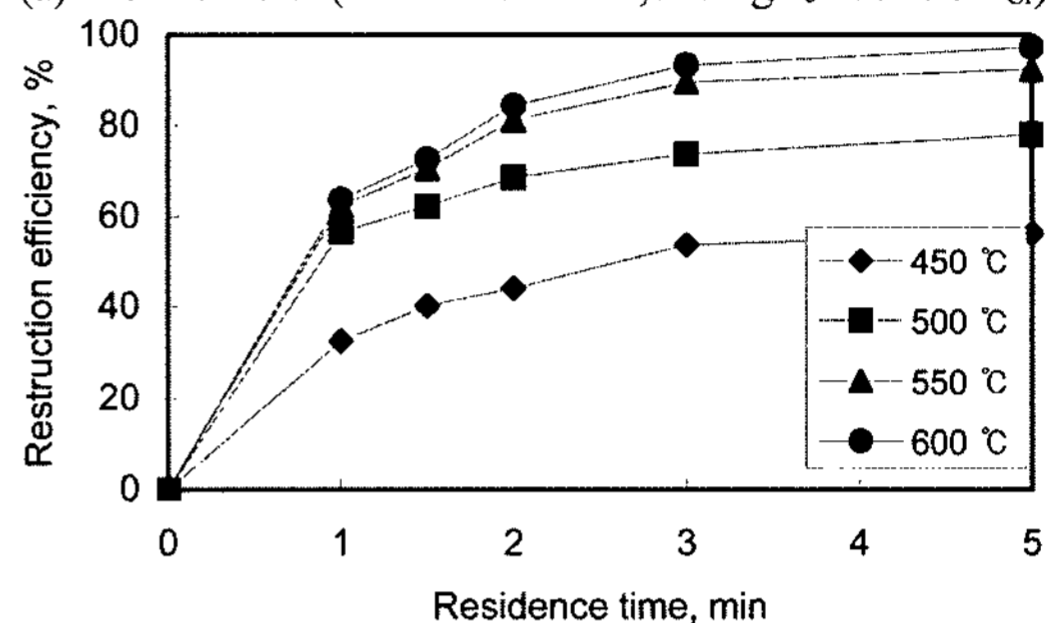
### Effect of Temperature and Residence Time.

Figure 2 presents the effects of temperature and residence time on the destruction efficiency (DE) for humic acids and ammonia, respectively. The DEs for humic acids in case of temperature (Figure 2a) reached a level greater than 99.9% within 1.5 minute of residence time except in cause of 380°C, the qualities of the effluent at these conditions exceeded the KSLQ. At least 3 minutes were required to satisfy the KSLQ which was longer than twice of residence time required for the higher temperatures. But DE was less than 65% under the subcritical condition at 360°C. Overall, recalcitrant organic compounds in the leachate was observed to be at near critical temperature (380°C) in about 3 minutes.

As shown in Figure 2b, the DE for ammonia compound was 97.3% at 600°C and 5 min resident time, this was the only condition that meets the KSLQ (50 mg/L residual ammonia). Therefore, operating conditions for the treatment of both organics and ammonia in the leachate was determined to be 5 min at 600°C. But this



(a) Humic acid (Initial conc.=10,000mg/ℓ as COD<sub>Cr</sub>)



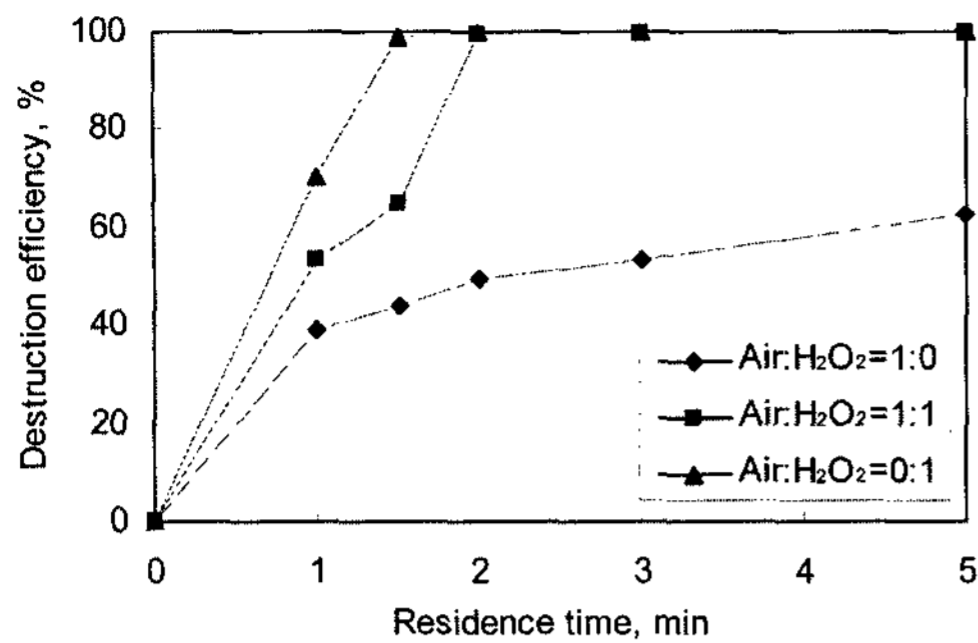
(a) Ammonia (Initial conc.=1,000mg/ℓ as NH<sub>3</sub>)

Figure 2. Destruction efficiency of humic acids and ammonia nitrogen at various temperatures and residence times.

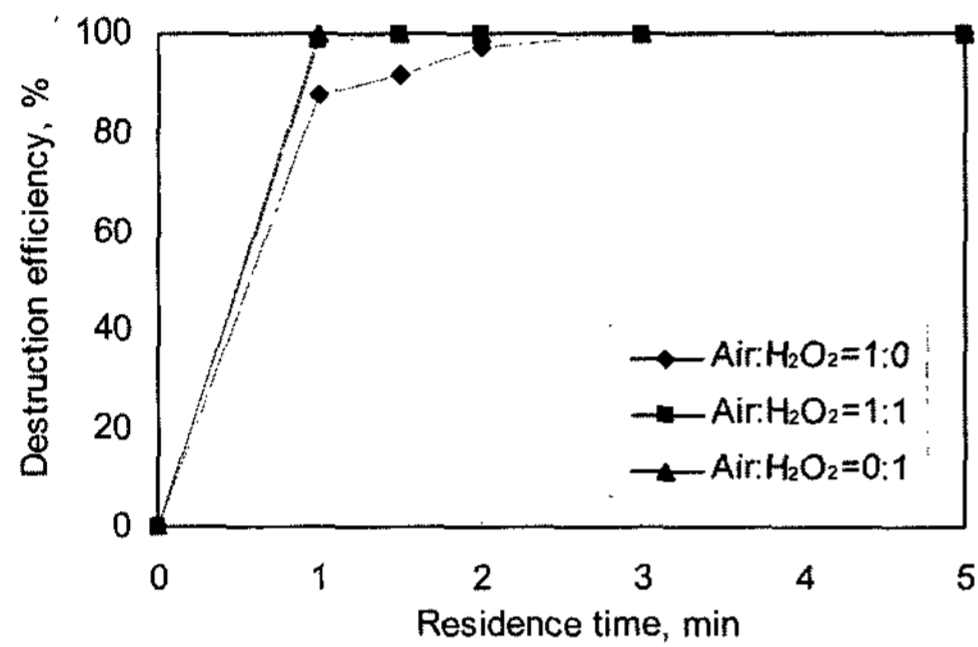
condition would be in danger of reactor operating and then be resulted in high cost. In order to above such problems, oxidant more powerful than air (H<sub>2</sub>O<sub>2</sub>) was injected into the reactor to enhance oxidation and to evaluate if less stringent operating conditions were possible.

### Effect of Oxidants

The DEs for humic acid along with oxidants (air and H<sub>2</sub>O<sub>2</sub>) are shown in Figure 3. At the subcritical temperature of 360°C (Figure 3a), the DEs for humic acids along with air only (Air: H<sub>2</sub>O<sub>2</sub> =1:0) at 360°C were less than 65% and the residence time of 5 min. After oxidant mixture (Air:H<sub>2</sub>O<sub>2</sub> =1:1) was injected into the reactor, 99.5% of humic acids were removed at 2 minutes and 98.7% of humic acids were removed at 1.5 min using H<sub>2</sub>O<sub>2</sub> only (Air: H<sub>2</sub>O<sub>2</sub> =0:1). There were great differences in humic acids DEs when results were compared between using H<sub>2</sub>O<sub>2</sub> versus not at 360°C, but the results without H<sub>2</sub>O<sub>2</sub> at 380°C (Figure 3b) were not as significant. The results in Figure 3 demonstrate



(a) Humic acid (360°C)

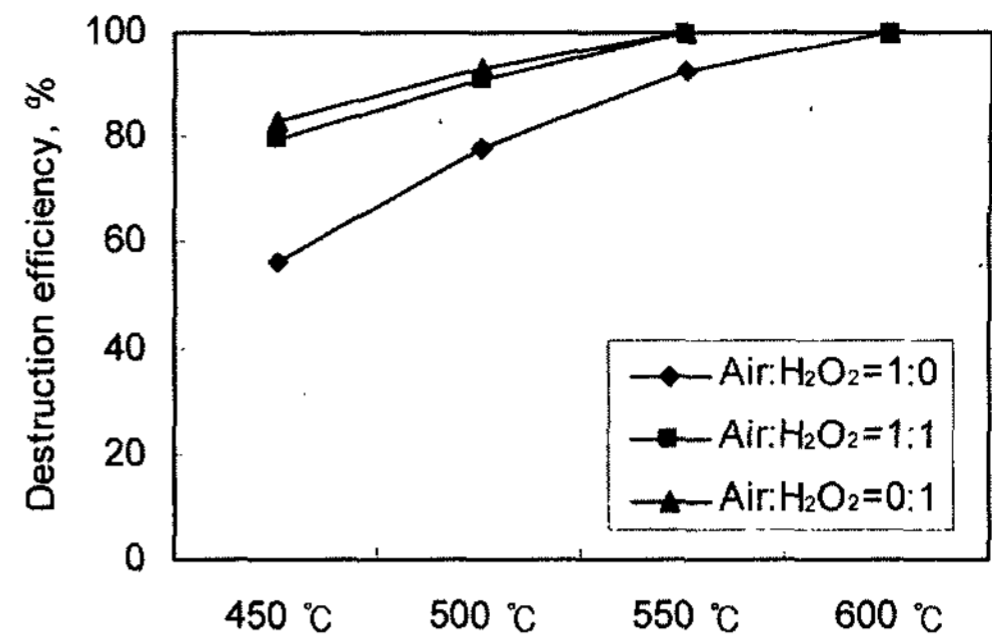


(b) Humic acid (380°C)

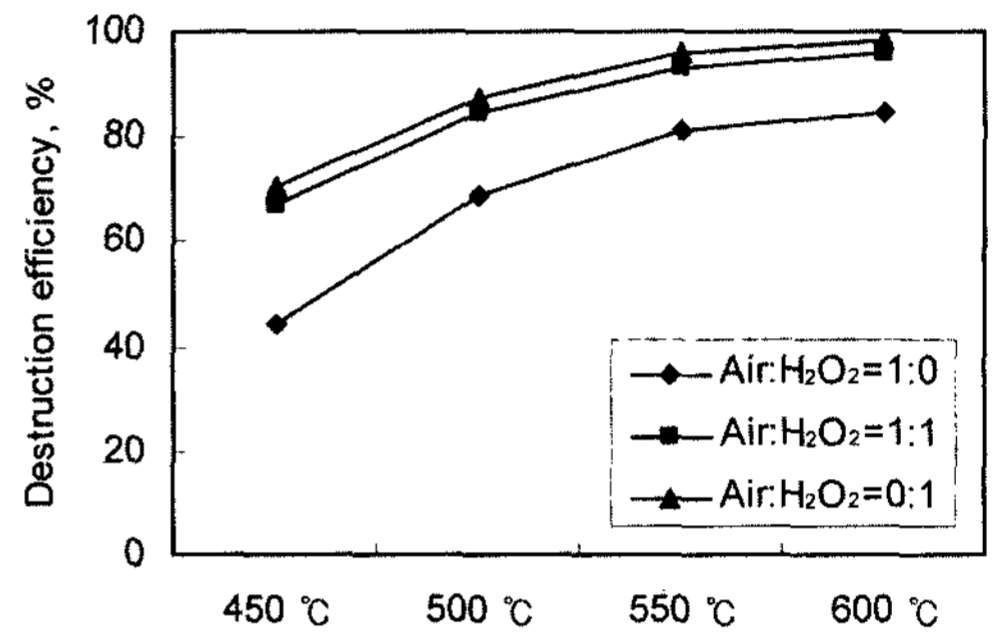
Figure 3. Effect of oxidants for humic acids.

that results indicated two facts: First, at subcritical temperature of 360°C, organic decomposition was more dominant by chemical oxidation than thermal oxidation, and second, thermal oxidation at supercritical temperature (380°C) was more dominant than chemical oxidation. However, addition of H<sub>2</sub>O<sub>2</sub> still enhanced the oxidation process.

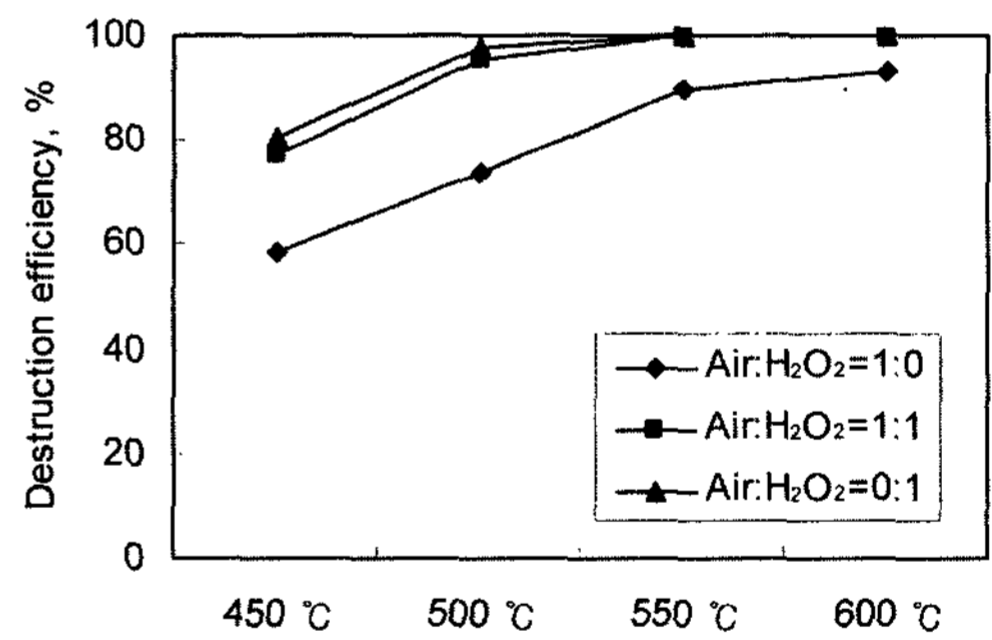
Figure 4 shows the effect of oxidants for the ammonia removal at different resident times (RT). When air was used the only oxidant, the DEs for ammonia at 5 min resident time did not meet the KSLQ limit at temperatures between 450 to 550°C except at 600°C (Figure 4a). But if oxidant mixtures (Air:H<sub>2</sub>O<sub>2</sub>=1:1 or 0:1) were used, DEs for ammonia varied from 99.9% to 99.99% at 550 and 600°C with 5 min resident time. There was a significant difference of DEs between with H<sub>2</sub>O<sub>2</sub> and without H<sub>2</sub>O<sub>2</sub> at various reaction temperatures, but there was insignificant difference of DEs with or without air addition to the H<sub>2</sub>O<sub>2</sub> oxidant when operating with increasing temperatures. These results suggested that reaction temperature is more important to



(a) Destruction efficiency at RT 5 min



(b) Destruction efficiency at RT 2 min



(c) Destruction efficiency at RT 3 min

Figure 4. Destruction efficiency for ammonia at various oxidant mixtures (Air and H<sub>2</sub>O<sub>2</sub>).

decompose the ammonia than additional oxygen (air) when H<sub>2</sub>O<sub>2</sub> was used as oxidant. Figure 4b and 4c show similar trends at various resident times. Therefore, the optimal condition for ammonia destruction could be determined that, with mixture of air and H<sub>2</sub>O<sub>2</sub> (1:1) additions, reaction temperature and residence time were 550°C with 3 min resident time or 600°C with 2 min resident. Shanableh and Gloyna<sup>18)</sup> and Gloyna and Johnston<sup>5)</sup> reported that ammonia in the SCWO system decomposed at a significant rate above 425°C and the primary products below 650°C were N<sub>2</sub> and N<sub>2</sub>O that further decom-



posed to  $N_2$  and  $O_2$ . If a water oxidation system is to be operated at or below  $400^\circ\text{C}$ , the ammonia may be removed by steam stripping or other methods.

### Treatment of Actual Leachate

Experiments with actual leachate were carried out with the addition of mixture of oxidant (air: $H_2O_2$ =1:1) at  $550^\circ\text{C}$  and  $600^\circ\text{C}$  (Figure 5). DEs for organic materials (determined by  $COD_{Cr}$ ) were above 99.99% at 1.5 minute resident time at  $550^\circ\text{C}$  and  $600^\circ\text{C}$ . At 2 minute of resident time, DEs for ammonia were 95% at  $550^\circ\text{C}$  and 98.6% at  $600^\circ\text{C}$ , respectively. Levels of organic materials and the ammonia in the effluents produced under by all these conditions were sufficient low to meet the KSLQ. Therefore, the optimal operation condition for the treatment of both organics and ammonia compounds was 2 minute of resident time and  $550^\circ\text{C}$  of reaction temperature along with mixtures at the ratio of 1:1 of air and  $H_2O_2$ .

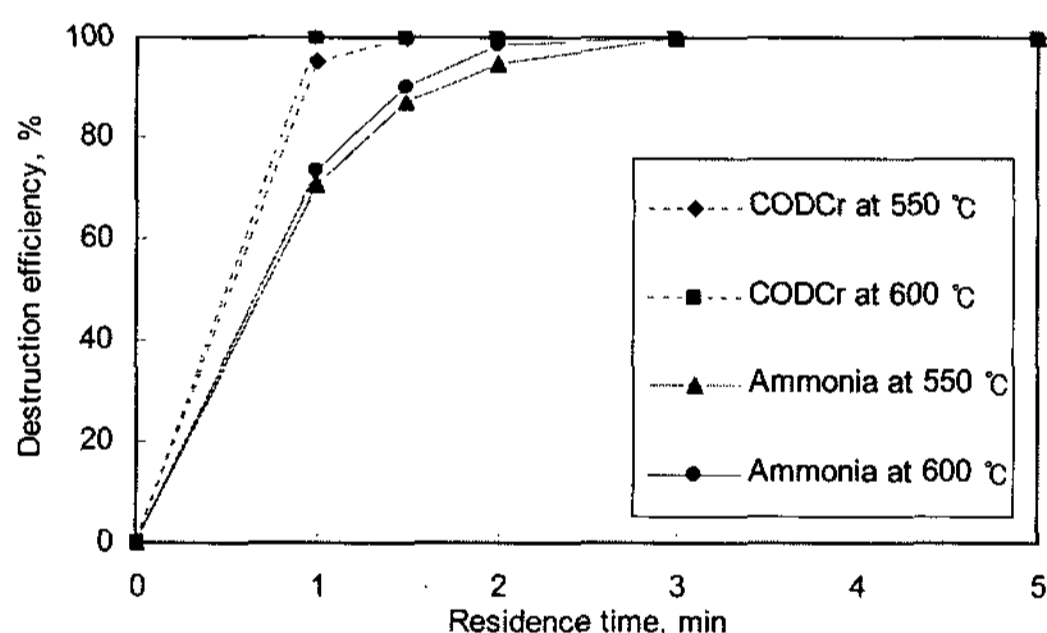


Figure 5. Destruction efficiencies for actual leachate at various temperatures and residence times.

### CONCLUSIONS

This study for the degradation of NBD compounds and ammonia in the leachate by SCWO provides us with the basic information to establish guidance for the application of such treatment system. The results can be summarized as follows.

NBD compounds such as humic acids were removed easily by the SCWO and its optimal condition was 3 min of resident time at  $380^\circ\text{C}$

along with air as an oxidant. If an oxidant mixture of air and  $H_2O_2$  (1:1) was used, this temperature could be decreased to subcritical temperature of  $360^\circ\text{C}$ . The optimal condition for the ammonia removal without  $H_2O_2$  oxidant was 5 min of resident time at  $600^\circ\text{C}$ . If  $H_2O_2$  was injected, it was possible to obtain a similar removal efficiency with 3 min resident time at  $550^\circ\text{C}$  or 2 min of resident time at  $600^\circ\text{C}$ . Both thermal and chemical destruction occurred in the oxidation of NBD and ammonia compounds. Chemical oxidation was more important than thermal oxidation at subcritical temperature, but the role of chemical oxidation and thermal oxidation reversed when operated at above critical conditions ( $380^\circ\text{C}$ ). The optimal condition for the actual landfill leachates was found to be 2 minute of resident time at  $550^\circ\text{C}$  along with equivalent oxidant mixture (air:  $H_2O_2$ ) at a ratio of 1 to 1.

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### REFERENCES

1. Bae, W. K., Ko, G. B., Hong, S. H., and Lee, Y. W. Leachate Treatment Using Shortcut Biological Nitrogen Removal Process, *J. Korean Society of Waste Management*, **19**(2), 192-198 (2002).
2. Bum, B. S., Bae, J. H., and Cho, K. M. Nitrogen Removal of Leachate Using the Landfill, *J. Korean Society of Environmental Engineerings*, **25**(3), 370-378 (2003).
3. Chian S. K. and Dewalle F. B. Sanitary Landfill Leachate and Their Treatment, *J. Environmental Engineering Division*, Proceeding of the American Society of the Civil Engineers, **102** (EE2), 411-431 (1976).
4. US EPA, Engineering Bulletin for Supercritical Water Oxidation, EPA/540/ S-92/006, U.S.

- Environmental Protection Agency, Washington, DC (1992).
5. Gloyna, E.F., and K. Johnston Supercritical Water Oxidation. Presented at the 11<sup>th</sup> Industrial Symposium on Wastewater Treatment, Montreal, Quebec, Canada, November 21-22 (1988).
  6. Helling R. K. and Tester J. W. Oxidation of Simple Compounds and Mixtures in Supercritical Water; Carbon Monoxide, Ammonia, and Ethanol, *Environ. Sci. Tech.*, **22**(11), 1319-1324 (1988).
  7. Jeon, E. J., Kim, Y. J., Lee, D. H., and Yang, T. S. Fundamental Study on the Behavior of POP's in Landfill Comparison of Leachate Humic Matters and Commercial Humic Acid in terms of Characteristics and Binding Coefficients of Pyrene and Phenanthrene, *J. Korean Society of Waste Management*, **18**(8), 737-745 (2001).
  8. Kim, H. Y., Kim, J. S., and Won, C. H. Treatment of Landfill Leachate by Coagulation and Fenton's Oxidation Process, *J. Korean Society of Environmental Engineers*, **23**(6), 979-987 (2001).
  9. Kim, J. K., Kim, S. K., and Park, N. B. A Study on the Chemical Characteristics of Waste and Leachate on Landfill Site, *J. Korean Society of Waste Management*, **21**(6), 607-617 (2004).
  10. Kim, Y. K. and Cho, S. H. Suppression of Char Formation and Treatment Anti-Freezing Solution by Sub and Supercritical Water Oxidation, *J. Korean Society of Environmental Engineerings*, **18**(8), 939-951 (1996).
  11. Koo, C. and Lee, D. S. Destruction of Aqueous Cyanides at Elevated Temperatures and Pressures (II); Behavior of Complex Metal Cyanides, *J. Korean Society of Environmental Engineerings*, **16**(3) 333-341 (1994).
  12. Lee, B. J. and Cho, S. H. Removal of Nitrogen Contained in Wastewater from Wafer Cleaning Process by Ammonia Stripping, *J. Korean Society of Waste Management*, **19**(1), 58-69 (2002).
  13. Lee, D. S. Supercritical Water Oxidation of Hazardous Organic Substance, *J. Korean Society of Environmental Engineerings*, **14**(1), 31-40 (1992).
  14. Lee, D. S. and Gloyna, E. F. Supercritical Water Oxidation of Acetic Acid, *J. Korean Society of Environmental Engineerings*, **15**(1), 377-386 (1993).
  15. Lee, G. S., Lee, D. S., and Nam, Y. W. Destruction of Aqueous Cyanides at Elevated Temperatures and Pressures ( I ); Behavior of Free Cyanide Ion, *J. Korean Society of Environmental Engineerings*, **16**(2), 227-237 (1994).
  16. Ragle N., Kissel J., Ongerth JE., and DeWalle FB. Composition and Variability of Leachate from Recent and Aged Areas within a Municipal Landfill, *Water Environment Research* **67**(2), 238-243 (1995).
  17. Ryu, H. D., minutes, K. K., and Lee, S. L. Reuse of Structive Obtained from Treatment of Nitrogen Contained in Landfill Leachate, *J. Korean Society of Environmental Engineerings*, **25**(6), 747-752 (2003).
  18. Shanableh, A. and Gloyna, E. F. Supercritical Water Oxidation-Wastewater and Sludges. Presented at International Association for Water Pollution Research and Control Conference, Kyoto, Japan. August (1990).
  19. Thomason, T. B., Hong, G. T., Swallow, K. C., and Killilea, W. R. The MODAR Supercritical Water Oxidation Process, Thermal Processes Innovative Hazardous Waste Treatment Technology Series, **1**, 31-41 (1990).
  20. Timberlake S. H., et al., Supercritical Water Oxidation for Wastewater Treatment; Preliminary Study of Urea Destruction, SAE Tech. Pap. Ser. No. 820872 (1982).