

**Anti-Corrosive SCWO 반응기에서의 2,4-Dichlorophenol 의 분해**이창하\*, 황경엽<sup>1</sup>, 이현철, 인정현

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**Decomposition of 2,4-Dichlorophenol in Anti-Corrosive SCWO Reactor**Chang-Ha Lee\*, Kyung-Yub Hwang<sup>1</sup>, Hyeon-Cheol Lee, Jung-Hyun In

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**Introduction**

The use of supercritical water (374 °C, 221 bar) oxidation (SCWO) process for wastewater treatment has increased since mid 1970's after the works performed by Modell and Amin [1]. The SCWO systems were found to most appropriate for the treatment of refractory/hazardous compounds like as PCB [2] and Dioxins[3] and among other feasible technologies including wet air oxidation. Some researchers focused on their attention on the variables for the process design through experimental works with various industrial wastewaters [4]. However, the applicability of this process hinges not just on its capability to remove the pollutant to the desired degree, but more importantly on its cost competitiveness with other feasible alternatives. A major obstacle to successful application of chlorinated organic compounds to SCWO process may be significant corrosion of equipment including tubing due to formation of acidic byproduct [5]. For removal of these problems, adding agents or transpiring wall being used as internal of SCWO reactor can be aging when exposed to an acidic condition. Neutralizing acids with alkaline solution can be one viable option. However, the salt formation still remains a problem since the reactor and tubing can be partially or completely blocked by these salts, ultimately leading to increase maintenance costs significantly. Therefore, it is of critical to overcome those problems for practical use of the underlying system in such wastes treatment. The aim of the present study is to develop an anti-corrosion/anti-fouling reactor system, named as the floating type SCWO system.

**Experimental Section**

The floating type SCWO system portrayed in Fig. 1 was developed and used in this study. The system consists of three different units. The reactor, all valves and connecting parts were made of stainless

steel (SS 316). Firstly, the feed was heated to 80°C in a preheating unit and subsequently added to the reactor by a high pressure pump. In the vessel, the feed flowing upward was instantly heated up to reaction temperature by an electronic heating element (max. 1,300 °C) and subjected to oxidation. The feed further proceeded to upper end of the vessel and neutralized with NaOH solution fed through a separate pipeline prior to discharge in the effluent storage tank.

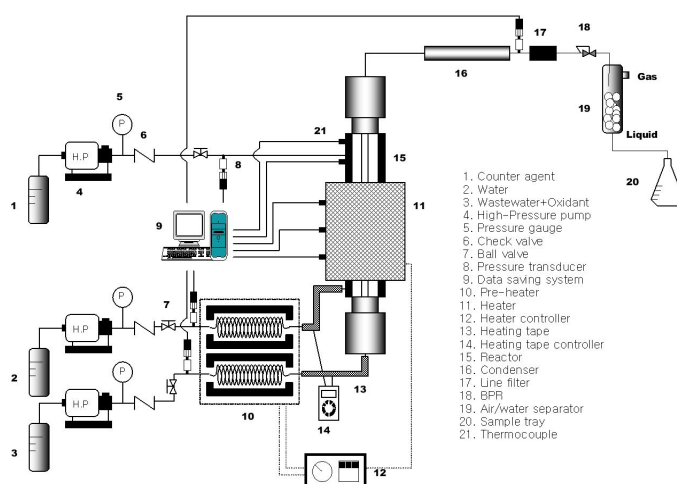


Fig. 1. Schematic diagram of anti-corrosive SCWO reactor

## Results and Discussion

**Performance of Anti-corrosive reactor.** To study optimum dose of  $H_2O_2$ , experiments were

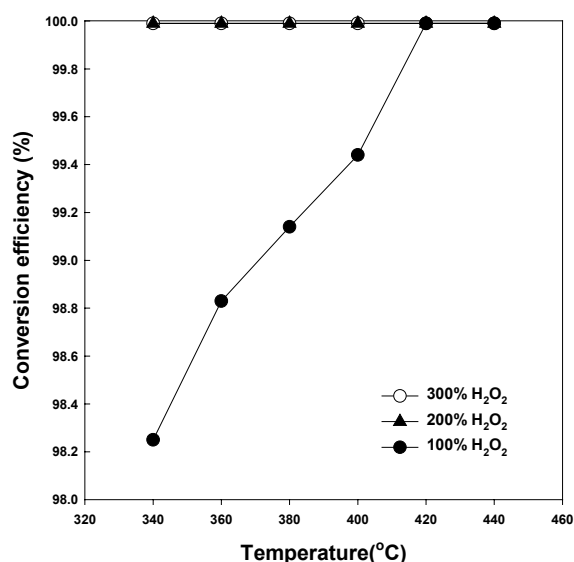


Fig. 2. Effects of operating variables on conversion of 2,4-DCP with  $H_2O_2$  supply (100–300%) at 300mg/L of 2,4-DCP, feed flow rate of 1ml/min and 250bar.

conducted in the reactor, where the applied pressure was set at 250 bar. To convert of the 2,4 DCP (300 and 3,000 mg/L) completely,  $H_2O_2$  was required equal to or more than 200 % of stoichiometric demands. Higher conversion efficiency was observed at higher temperature, higher pressure, lower flow rate and lower feed concentration due to the increase in residence time and reactivity as shown in Fig 2. However, it is difficult to say which parameter actually influenced the conversion efficiency most because all parameters influence residence time.

**Corrosion and fouling control.** The product liquid in the anti corrosive reactor was compared for oxidized impurities in solid form with that in a

reference reactor generally used for SCWO reaction. No observable particles were found in the effluent of the anti-corrosive reactor, while in the effluent of the reference reactor, noticeable amount of impurities was found. No considerable corrosion or fouling problems were observed at any parts of the anti-corrosive reactor as shown in Fig. 3. In summary, it is distinctly possible that the anti-corrosive reactor system can be used for conversion of chlorinated compounds over a long period of operation without any significant corrosion or fouling problems.

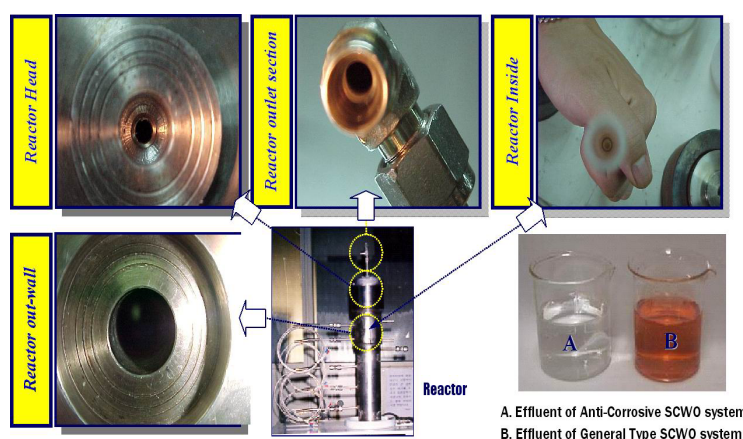


Fig. 3. Photographs of anti-corrosive SCWO reactor after operation

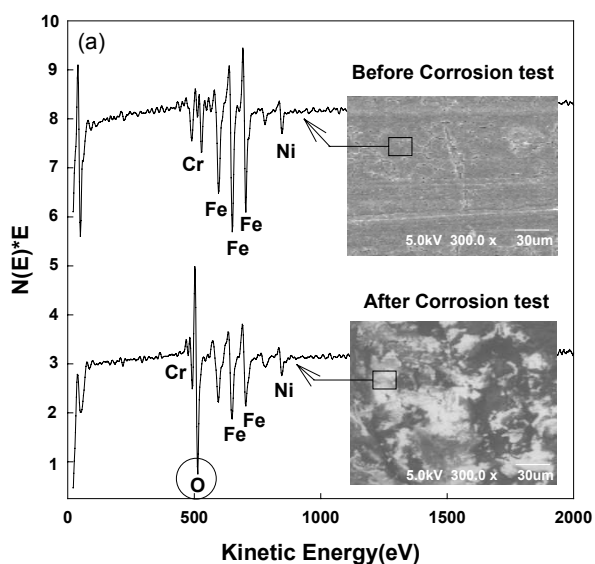


Fig. 4. Depth profiles of Stainless steel using AES/SAM

Corrosion test was to investigate corrosion phenomena on surface of alloys in the condition of SCWO of halogenated hydrocarbon.

To test corrosion, several alloy were exposed in SCW condition using 2,4-DCP of 4,000mg/L,  $H_2O_2$  of 700% at 250bar, 400°C. As a result of investigating of thermal decomposition and corrosion test, intermediate like as acid in SCWO of halogenated hydrocarbon occur corrosion problem. And Fig. 4 shows the survey scan of Stainless steel 316. After-corrosion test, the intensity of O appeared greater than those in before-test. By analyzing the AES survey scan, we found that oxide layer was formed on surface of the every alloy by decomposition of 2,4-DCP in SCW condition.

**Kinetics study.** 2,4-Dichlorophenol (2,4-DCP), a model pollutant, was oxidized by supercritical water (SCW) at 380–420 °C and 230–280 bar with 50–200 % hydrogen peroxide as the oxidant in a batch reactor. The effects of the temperature, pressure and supply amount of hydrogen peroxide on the decomposition rates of 2,4-DCP were correlated by using kinetic model in power-law rate expressions. The kinetic model was established with the reaction rate constants and orders found by fitting the experimental data. Good oxidation efficiencies for 2,4-DCP at SCW condition were obtained. The process is well described by simple first-order kinetics and supercritical water oxidation using hydrogen peroxide as an oxidant enhances the decomposition efficiency.

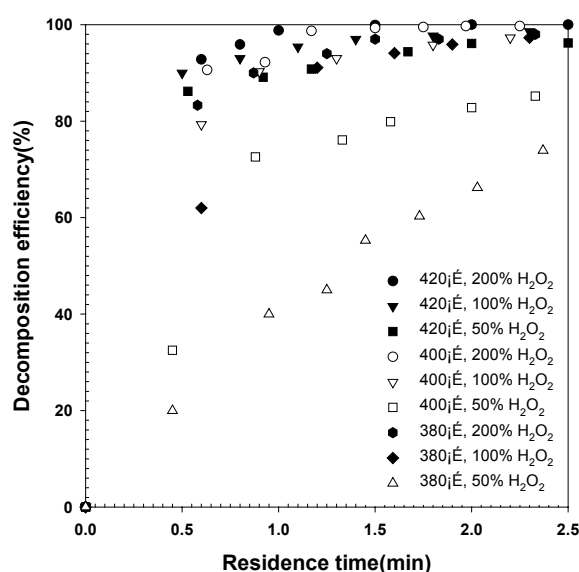


Fig. 5. Effects of H<sub>2</sub>O<sub>2</sub> supply(50, 100 and 200%), temperature(380, 400 and 420°C) on 2,4-DCP decomposition(1,000 mg/L) at

### Conclusion

To decompose halogenated organic compounds without corrosion and fouling problems, an anticorrosive supercritical water oxidation system using nonporous ceramic tube was developed. No corrosion and fouling problems were observed during the test period in a floating type SCWO system. And the process is well described by simple first-order kinetics and supercritical water oxidation using hydrogen peroxide as an oxidant enhances the decomposition efficiency.

### Reference

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