초임계수산화반응에서의 금속부식에 따른 2-chlorophenol의 분해 효율 향상에 대한 연구

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Catalytic Effect of Corroded Metal Alloys on the Decomposition Efficiency of 2-chlorophenol in the Supercritical Water Oxidation Process

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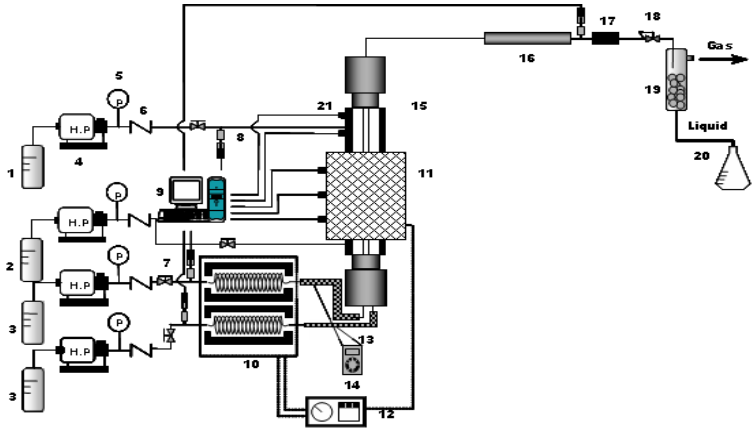
Introduction

Use of supercritical water (374℃ and 221 bar) oxidation (SCWO) for wastewater treatment has been increasing since the mid 1970's. SCWO systems are known as a very efficient way to treat refractory/hazardous compounds such as PCB and Dioxins. However, major obstacles to the successful application of halogenated chlorinated organic compounds in the SCWO process are the significant corrosion due to acidic byproduct and fouling problem by low solubility of inorganic salts when alkaline solution is added to neutralize the acid.[1-3]. Therefore, it is critical to overcome both corrosion and fouling for the SCWO system to have practical use in treating halogenated wastes[4,5]. In this study, corrosion phenomena of various metal alloys were investigated when 2,-chlorophenol was oxidized in continuous type anti-corrosive SCWO reactor. Corrosion tests were conducted at both sub critical region and supercritical region. comparing with decomposition efficiency of 2-chlorophenol without metal coupons, corrosion of metal coupons contributes to the elevation of decomposition efficiency of 2-chlorophenol, even though the degree of contribution is different from each alloys.

Experiments and results

1. Experimental Apparatus

2-chlorophenol with 99.9 % purity was mixed with primary distilled water as a feed solution of 1000 ppm. As oxidizing and neutralizing agents, H_2O_2 and NaOH were used, respectively. The corrosion test was conducted using continuous anti-corrosive SCWO reactor as shown in Fig. 1. For the corrosion test of alloys under SCWO conditions, Stainless steel 316, Inconel 625, Hastelloy C-276, Monel 400, Titanium Gr2 and Zirconium 702 were selected. each metal coupons were exposed to both subcritical conditions (360 ℃, 220 atm) and supercritical conditions (400 ℃, 250 atm). The effluent samples were collected every five minutes for one hour. Corrosion phenomena of various alloys were investigated using microscopy and AES-SAM (Auger Electron Spectroscopy / Scanning Auger Microscopy). Decomposition efficiencies of effluent samples were analyzed with TOC (Total Organic Carbon) analyzer.



1. Counteragent(NaOH) 2. Water 3. Wastewater + Oxidant 4. Highpressure pump
5. Pressure gauge 6. Check valve 7. Ball valve 8. Pressure transducer
9. Data saving system 10. Pre - heater 11. Heater 12. Heater controller
13. Heating tape 14. Heating tape controller 15. Reactor 16. Condenser (cooling zone)
17. Line filter 18.Back pressure regulator 19. Air/water separator 20. Sample tray 21. Thermocouple

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

2. Corrosion Analysis

The corrosion phenomena on the surface of the alloys were studied under halogenated hydrocarbon oxidation conditions in the SCW. The six alloys were exposed to SCW conditions of 250 atm and 400 ℃ with 2-CP of 1,000 mg/L, and 100% H_2O_2. Fig. 2 shows microscopic images of surface of Hastelloy C-276 and Inconel 625. After the exposure to the subcritical and supercritical conditions respectively, each surfaces of metal alloys changed their colors and morphology even though the degree of change is differed. The surface color seems to be differed according to the constituent element of each metal alloys.

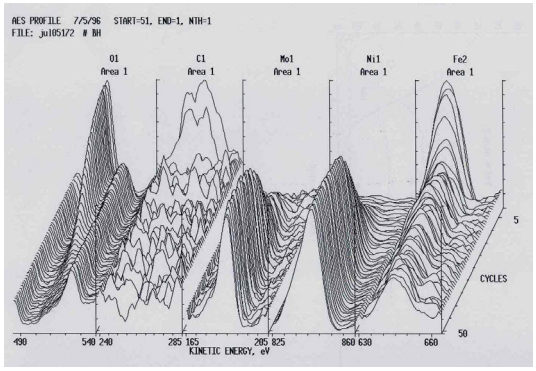
(a) Hatelloy C-276

(b) Inconel 625

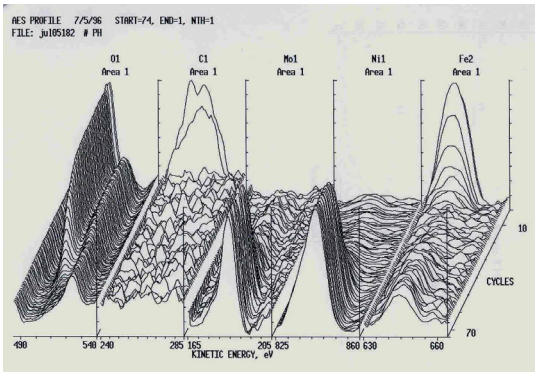
before corrosion subcritical condition supercritical condition

Fig. 2. Microscopy images of alloys of Hastelloy C-276 and Inconel 625

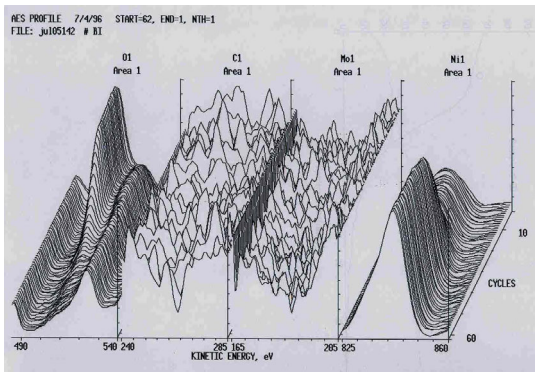
AES montage was helpful to understand quantitatively the atomic % percentage (at. %) of the chemical on the surface according to the depth of the alloy. Fig. 3 shows the AES montage display of the corroded Hastelloy C-276 and Inconel 625 in the subcritical and supercritical region respectively. As shown in Fig. 3, there were no severe carbon contaminations on the surface of metal alloys and the penetrations of oxygen were observed in each surface of metal alloys. At the top of the surface, major constituents of each metal alloys loses their portions because of domination of oxygen but their at. % were completely restored after certain amount of sputtering time. The depth of oxygen penetration was deeper in supercritical condition than subcritical condition of Hastelloy C-276 but reverse was observed in Inconel 625.



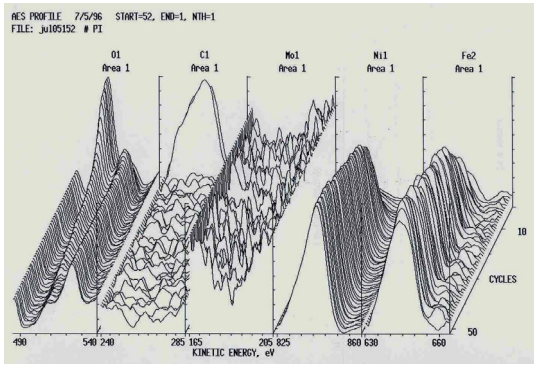
(a) Hastelloy C-276 in subcritical region



(b) Hastelloy C-276 in supercritical region



(c) Inconel 625 in subcritical region



(d) Inconel 625 in supercritical region

Fig. 3. AES mantage displays Hastelloy C-276 and Inconel 625 with SCOW of 2-CP

3. Comparison of decomposition efficiency

Fig. 4. shows decomposition efficiencies of 2-CP. As shown in Fig. 4(a), the decomposition efficiency was elevated when temperature and pressure got higher. the decomposition efficiencies were 95.200 % and 95.916 % in the subcritical region and supercritical region respectively. It was observed that the decomposition efficiencies were elevated when metal coupons were installed in the reactor even though the amount of elevation differed alloys to alloys. It seems that metal oxides which were formed by the penetration of oxygen in to the metal coupons or metal ions depleted from the metal coupons would function as catalysts to elevate the decomposition efficiency in the SCWO of 2-CP. It was also observed that the decomposition efficiencies of 2-CP at supercritical region were generally higher than those at subcritical region.

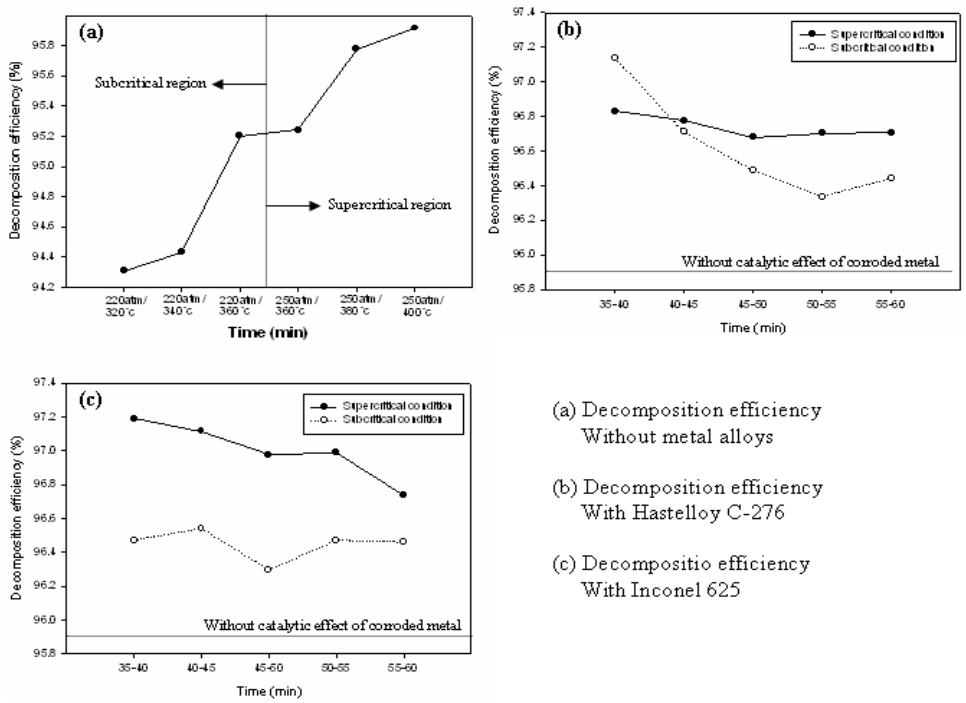


Fig. 4. Decomposition efficiency of 2-chlorophenol at various conditions

Conclusion

corrosion phenomena of various metal alloys were investigated when 2,-chlorophenol was oxidized at subcritical region and supercritical region using continuous type anti-corrosive SCWO reactor. The metal alloys changed their surface colors and morphology at both subcritical region and supercritical region but the degree of change differed. In both metal alloys, oxygen penetration was observed and the portion of constituents of metal alloys were rehabilitated after certain amount of sputtering time. Two metal alloys showed reverse aspects of oxygen penetration depth in subcritical and supercritical region. Decomposition of 2-CP with metal alloys were higher than that without metal alloys, which means that the corroded metal alloys function as catalyst to elevate the decomposition efficiency.

References

1. Kritzer, P. Corrosion in high-temperature and supercritical water and aquaous solutions: a review. J. of Supercritical Fluids. 29, 1-29(2004)
2. Mitton, D.B., Yoon, J. H., Cline, J. A., Kim, H. S., Eliaz, N., and Latanision, R.M. Corrosion behavior of nickel-based alloys in supercritical water oxidation systems, Ind. Eng. Chem. Res. 39, 4689-4696(2000)
3. Son, S. H., Kim, J. H., Lee, H. C. and Lee, C. H., Effect of NaOH Neutralization on the Decomposition of Halogenated Hydrocarbon by Supercritical Water Oxidation, Korean J. Chem. Eng., 23(3), 385-390(2006)
4. Lee, H. C., In, J. H., Lee, S. Y., Kim, J. H., and Lee, C. H., An Anti-corrosive Reactor for the Decomposition of Halogenated Hydrocarbons with Supercritical Water Oxidation, J. of Supercrit. Fluids, 36, 59-69(2005)
5. Lee, H. C., Son, S. H., Hwang, K. Y., and Lee, C. H., Surface Chemical Analysis on the Corrosion of Alloys in the Supercritical Water Oxidation of Halogenated Hydrocarbon, Ind. Eng. Chem. Res., 45(10) 3412-3419(2006)