금속의 부식이 2-chlorophenol의 초임계산화에서 미치는 영향

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Effect of high concentration and long time reaction on the metal corrosion in decomposition of 2-chlorophenol by Supercritical Water Oxidation

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1. Introduction

Supercritical water oxidation (SCWO) is one of effective techniques for the treatment of toxic and refractory compounds, it needs to take into account both corrosion due to acid and fouling due to the low solubility of inorganic salts before it can be successfully applied to halogenated compounds[1]. Many researchers have focused on solving the problems of corrosion and fouling using a variety of methods and reactor designs[2-4]. Recently, we reported on the continuous anti-corrosive SCWO reactor system, which installed a ceramic tube into a reactor[4]. In this study, the SCWO decomposition efficiency of 2-chlorophenol with zirconium 702 metal coupon and the metal corrosion phenomena were investigate.

2. Experimental and Analytical Conditions

2.1. Chemicals

2-chlorophenol with 99.9 % purity (2-CP, WAKO Pure Chemical Industries, Ltd.) was mixed with primary distilled water as a feed solution of 3000 ppm. As oxidizing and neutralizing agents, a 100% stoichiometric amount of hydrogen peroxide (H_2O_2, 30 wt. %, Junsei Chemical. Co., Ltd.) and 200% stoichiometric amount of sodium hydroxide (NaOH, Yakuri Pure Chemicals Co., Ltd.) were used, respectively. The theoretical amount of H_2O_2 and NaOH for the complete neutralization was calculated under the assumption of thecomplete decomposition of 2-chlorophenol in the SCWO as follows:

$$C_6H_5ClO + 13H_2O_2 \rightarrow 6CO_2 + HCl + 15H_2O \qquad (1)$$

2.2. Experimental apparatus and procedure

The corrosion test was conducted using a continuous anti-corrosive SCWO reactor system, made of Stainless steel 316, as shown in Fig. 1. [4]. The waste water and oxidant were heated to less than 100C in a preheating unit and added to the reactor via a high pressure pump, separately. Since these two influent were mixed inside the ceramic tube after passing the ceramic partition in the reactor, the inlet lines and bottom part of reactor could be

protected from corrosion. In the reactor, the feed was heated up to reaction temperature by an electronic heating element (max. 1,300C). The neutralizing NaOH solution was fed into the top of the reactor. Therefore, an oxidized solution was mixed with a neutralizer at the top of the reactor. Since NaOH solution was supplied at room temperature, it also acted as a cooling device and this helped to prevent fouling problems.

For the corrosion test of alloys under supercritical conditions (400 ^{o}C, 250 atm), Zirconium 702 were selected as test alloy. The metal coupons with the total surface area of about 250 mm^{2}were located in the middle of the reactor. After reaching the desired temperature and pressure with water, the feed was switched to 2-CP solution. Effluent samples were collected every five minutes after the first 30 minutes [5]. In 2 hours reaction, effluent samples were collected every ten minutes after the first 30minutes.
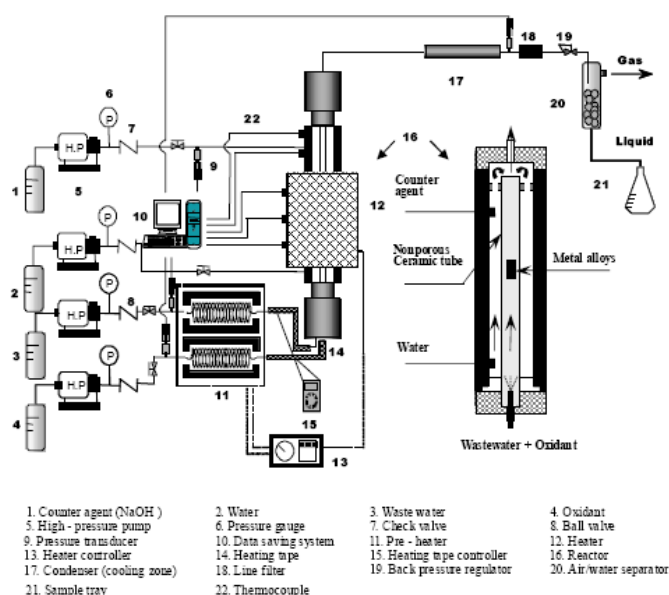

1. Counter agent (NaOH)	2. Water	3. Waste water	4. Oxidant
5. High - pressure pump	6. Pressure gauge	7. Check valve	8. Ball valve
9. Pressure transducer	10. Data saving system	11. Pre - heater	12. Heater
13. Heater controller	14. Heating tape	15. Heating tape controller	16. Reactor
17. Condenser (cooling zone)	18. Line filter	19. Back pressure regulator	20. Air/water separator
21. Sample tray	22. Thermocouple		

Fig 1. Schematic diagram of continuous type anticorrosive reactor

2.3. Analytical methods

ICP-MS spectroscopy (Inductively Coupled Plasma Mass Spectrometry, Perkin-Elmer Sciex, ELAN 6100) was applied to the effluent solutions to verify the corrosiveness of the reactor and to understand the metal depletion from the sample coupons during the oxidation reaction. Surface chemical analysis of corroded metal alloys was conducted by using AES/SAM (Auger Electron Spectroscopy-Scanning Auger electron Microscopy, Perkin Elmer, PHI model 670). The conditions of the survey scan and sputter depth profile of the AES were recorded as the following: Primary beam energy Ep = 5 keV, primary beam current Ip = 0.01 μA, and beam diameter 0.4 μm. The resolution of the cylindrical mirror analyzer was set to 0.6 %. The argon ion beam, with an ion energy level of 3keV and current density of 0.6 μAm^2, was produced by a differently pumped ion gun. The sputter profiles were analyzed using the PC PHI-MATLAB software package. Morphology analysis of the surface of the alloys was done by Scanning Auger-electron Microscopy (SAM). Decomposition efficiencies were measured

using Total Organic Carbon (Total Organic Carbon, SHIMADZU) analysis.

3. Results and Discussion

Figure 2 shows the AES depth profiles of Zirconium 702 metal alloy exposed to supercritical conditions at different oprating condition. In the results, the oxygen peak coexists with the two Zr peaks at the supercritical conditions as shown in Fig. 2 (a) and (b). However, the left side Zr peak disappears simultaneously whenthe oxygen peak disappears. This implies that the Zr peak on the left side indicates an oxide form of Zr. In addition, Fig. 2 shows that the oxygen penetration depth is much deeper at the reaction time 2hours. The results indicate that oxygen dominates at the surface of metal alloys. The sputter rate was a depth of 199 Å/min, based on the SiO2 in the AES. Therefore, with the sputter rate, oxygen penetration depth could be calculated [5]. Oxygen penetration depth was 7761 Å at the 1hour condition and 10547 Å at 2 hours. Fig. 2(c) shows that the oxygen penetration depth is much deeper at high concentration than at low concentration. The oxygen penetration depth in high concentration condition was almost 4.5 times greater than that in low concentration condition (31044Å).
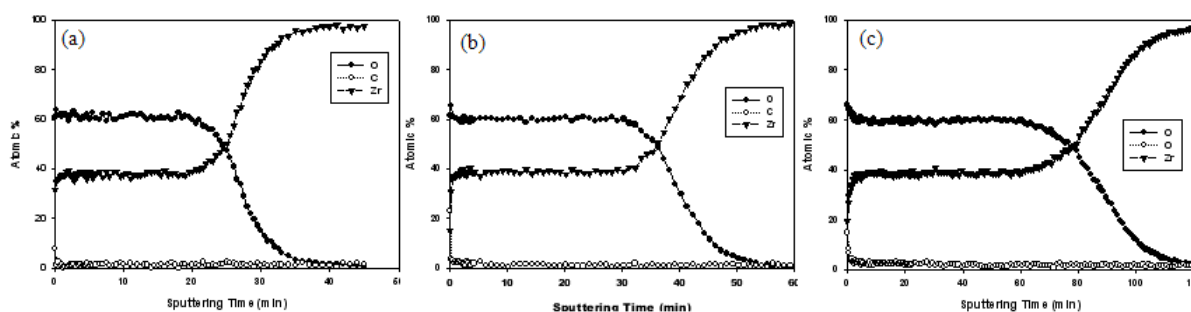

Fig. 2. AES depth profile of zirconium 702 at the supercritical conditions at different reaction time and feed concentration (a)1000 ppm 1hr, (b) 1000ppm 2hr, (c) 3000ppm 1hr

Fig. 3 shows decomposition efficiencies of 2-chlorophenol for reaction time with corrosion of Zirconium at the supercritical conditions. Compare (A) with (B), 2hr reaction result not different from 1hr reaction result. By the way, A 60- 70 minute point of figure (b) is analytical error. Fig. 3(c) shows, high concentration experiment (90~92%) decomposition of 2-chlorophenol lower than low concentration experiment (97%). We need a more oxidant for high decomposition efficiency. In sum corrosion phenomena is influenced by feed concentration and reaction time.
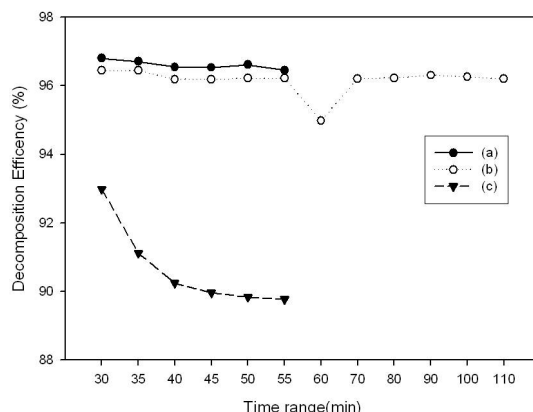
Fig. 3 Decomposition efficiencies of 2-chlorophenol at different reaction condition with corrosion of Zirconium (a) 1000ppm 1hr, 1000ppm 2hr, 3000ppm 1hr

4. Conclusion

   Using anti-corrosive continuous SCWO reactor system, the decomposition efficiency of 2-CP in supercritical water oxidation was studied at different concentrations and reaction times. In addition, corrosion phenomena of various metal alloys and the effect of corrosion on the decomposition efficiency of 2-chlorophenol at supercritical condition were examined. In the AES-SAM analysis, oxygen penetration was severe at high 2-CP concentration than at low concentration or long time reaction condition.

   The decomposition efficiency was 97% at low concentration, while it was 90~92% at high concentration. These decomposition efficiency can easily reach high than 99.99% with an increase in oxidant concentration or temperature. In addition, since the added metal coupon worked as a catalysis in the SCWO, the decomposition efficiency could be higher than the case without the metal coupon. It suggested that metal oxide could improve the decomposition efficiency without any additional energy in the SCWO.

5. Reference

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