

Dissolved Oxygen Removal in a Column Packed with Catalyst

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(Received February 19, 1996)

Abstract

The dissolved oxygen removal by H_2-O_2 reaction in column packed with various catalysts was examined. The catalysts employed were the prepared polymeric catalyst, platinum on activated carbon, and Lewatit OC-1045 which is available commercially. The column experiments with the prepared polymeric catalyst showed the dissolved oxygen reduced to 35 ppb which is below the limit in feed water of power plants. This implies the likely application of the prepared catalyst for practical use. The activated carbon required the pre-treatment for the removal of dissolved oxygen, since the surface of activated carbon contains much oxygen adsorbed initially. The Lewatit catalyst exposed the best performance, however, the aged one showed the gradual loss of catalytic activity due to degradation of resin catalyst.

1. Introduction

The corrosion of steam generator in PWR(Pressurized Water Reactor) is attributed to the pH, dissolved oxygen, electrochemical potential, and chemical impurities included in the feed water[1-5]. The dissolved oxygen relates to the metal corrosion as one of major causes. Relatively high concentration of dissolved oxygen induces the stress corrosion in sensitized stainless steels and sensitized Inconel 600[6]. Thus the dissolved oxygen concentration in coolant is controlled rigorously by power plants[7].

One of major sources of oxygen intrusion into secondary side of power plant is makeup water. The makeup water is treated by ion exchange resin to remove the impurities. Then the demineralized water is stored in the makeup water tank, where the water contacts with the oxygen coming through the small

openings between the ceiling cover and tank wall. The oxygen concentration may become a few ppm which is over the limit of allowed concentration.

The dissolved oxygen in secondary side has been removed by combined use of mechanical deaeration coupled with chemical scavenging using hydrazine[8]. If the dissolved oxygen concentration tends to exceed the limit, the hydrazine is added through the chemical injection system. However the hydrazine reacts with oxygen ineffectually at low temperature. Moreover the hydrazine dissociates at high temperature, yielding ammonia which influences the pH of the system remarkably. Recently the catalytic reaction of oxygen and hydrogen has been of interests, since the reaction yields pure water which has no impact on the system[9].

This study represents the catalytic reaction of dissolved oxygen and hydrogen. The polymeric catalyst

was prepared and characterized. The column reaction was conducted employing the prepared catalyst. This catalyst was compared with the commercial catalysts in respect to the reaction efficiency.

2. Theoretical Approach

If the hydrogen is saturated excessively in feed water, the reaction of dissolved oxygen and hydrogen is assumed to depend only on the oxygen concentration. This means that the reaction is in first order. Neglecting the axial dispersion in the column for the simple analysis, the material balance of the oxygen is given by

$$-\nu \cdot (dC_l/dV) = k\eta_l C_s \quad (1)$$

where ν refers to water flow rate, C_l to dissolved oxygen concentration in bulk liquid, V to reactor volume, k_l to reaction constant, η_l to effectiveness factor, C_s to oxygen concentration at the catalyst surface, respectively.

As the mass transfer rate at the catalyst surface equals to the rate of reaction under the steady state, the following relation is established.

$$k\eta_l C_s = K_s a (C_l - C_s) \quad (2)$$

where $K_s a$ is the overall mass transfer coefficient. Rearranging equation (2), the following equation can be achieved.

$$C_s = K_s a \cdot C_l / (K_s a + k\eta_l) \quad (3)$$

Substituting the equation (3) into equation (1), then the result is

$$-\nu \cdot (dC_l/dV) = C_l \{1/(k\eta_l) + (1/K_s a)\} \quad (4)$$

The boundary conditions for the equation (4) are

$$\begin{aligned} C_l &= C_i & \text{at } V &= 0 \\ C_l &= C_o & \text{at } V &= V \end{aligned} \quad (5)$$

The solution of equation (4) with the boundary conditions (5) can be readily obtained.

$$(\nu/V \ln(C_i/C_o))^{-1} = 1/(k\eta_l) + 1/K_s a \quad (6)$$

Generally the mass transfer coefficient $K_s a$ relates to the fluid velocity. The relation is expressed as the following[10]:

$$K_s a = K U_l^n \quad (7)$$

where U_l^n denotes the superficial velocity of liquid in column, and K is the proportional constant. Combining the equation (7) and (6) gives final equation (8),

$$(\nu/V \ln(C_i/C_o))^{-1} = 1/(k\eta_l) + 1/(K U_l^n) \quad (8)$$

The values of $1/K$ and $1/(k\eta_l)$ can be obtained by plotting the value of LHS in equation (8) with $1/U_l^n$. If the water velocity is fixed, then RHS in the equation (8) can be calculated using the parameters determined previously by plotting, resulting in the design value, i. e., ν/V for the desired concentration ratio, C_i/C_o .

3. Experimental

The polymeric catalyst support was prepared by suspension polymerization of styrene and divinyl benzene. The detailed procedures are described in elsewhere[11,12]. A metal favorable in hydrogenation reaction, e. g., Pt was impregnated on the prepared polymer support. Then reduction by hydrogen flow was followed. The product is characterized by high surface area, greater than 400m², and by about 0.6 wt% of metal loading. The specification of prepared catalyst and the column information were described in Table 1. The commercial catalysts such as Pt on activated carbon or Lewatit OC-1045 were also tested for the comparison of catalyst behaviors. The specifications of the catalysts were summarized in Table 2.

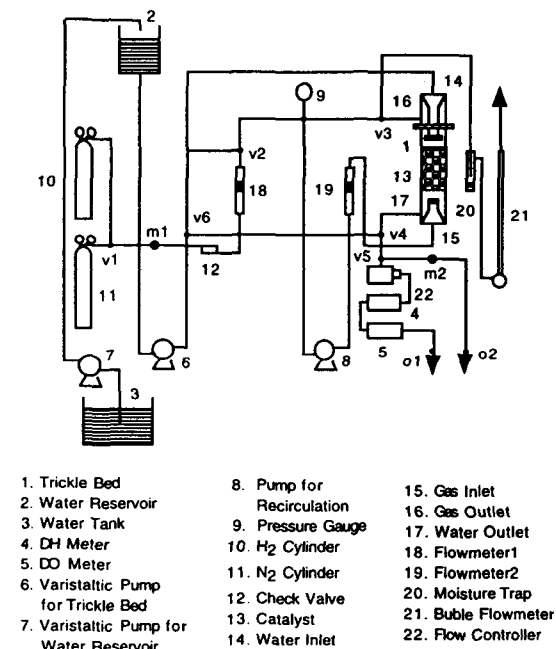
The experimental apparatus consists of a pre-saturator where the hydrogen is saturated excessively, and a catalyst column for the reaction as depicted in Fig. 1. The hydrogen is fed into the pre-saturator upward, whereas the feed water flows downward.

Table 1. Specification of prepared catalyst and column

| | | |
|----------|----------------------------------|--------------------------|
| Catalyst | material | styrene, divinyl benzene |
| | crosslinkage | 40% |
| | specific surface area | 459m ² /g |
| | shape & type | sphere, macroporous |
| | size | 2~5mm ϕ |
| Column | Pt content | 0.6wt% |
| | catalyst packed | 45g |
| | Length of catalytic bed | 41 cm |
| | apparent volume of catalytic bed | 160 ml |
| | water flow rate | 100 ml/min. |

Table 2. Specification of commercial catalysts

| Catalyst | Description |
|------------------|--|
| Activated carbon | Engelhard 0. 5% Pt-Carbon 1/16" pellet |
| Lewatit OC-1045 | polystyrene matrix gelular bead, 0.25~0.5 mm Cl/dopped with palladium, 0.3 wt% quatamary amine functional group |



/1 - v6: Threeway Valve, m1-m2: Metering Valve, o1-o2: On-Off Valve

Fig. 1. Apparatus for the removal of oxygen

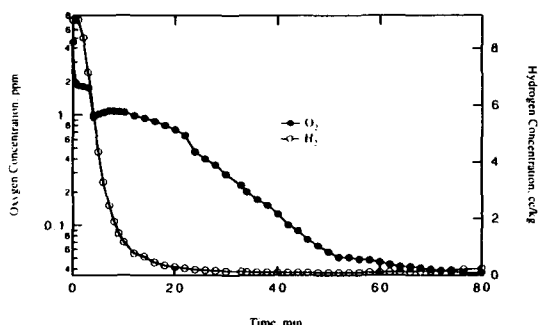
The pre-saturator is filled with ceramic packing material for enhancement of pertinent mixing of hydrogen and water. The concentrations of dissolved oxygen and hydrogen at saturator outlet were measured by DO-30A and Hydran 202N respectively. To prevent the diffusion of oxygen from the atmosphere, stainless steel is used for the connection lines, and glass for the catalytic column.

Prior to the experiment, the line was purged by nitrogen to remove the oxygen remaining in the system. The column and the line were then filled with water to remove the air or nitrogen pocket. The hydrogen saturated water was introduced to the column packed with catalyst. The dissolved oxygen and hydrogen concentration at the column outlet were measured by DO-30A and Hydran 202N.

4. Results and Discussion

The dissolved oxygen concentration of feed water was dramatically reduced in Fig. 2 from about 4.5 ppm to 35 ppb which is below the control limit of oxygen concentration, 100 ppb in Power Plant. This result showed that the polymeric catalyst prepared is also likely for the removal of dissolved oxygen in practical point of view. The dissolved hydrogen concentration also reduced, which ensures the reaction of oxygen and hydrogen over the catalyst.

The activated carbon was employed for the reac-

**Fig. 2. Oxygen and hydrogen concentration change in a column packed with prepared polymeric catalyst**

tion instead of the prepared polymeric catalyst. The behavior of each catalysts was compared and shown in Fig. 3. The oxygen concentration decreased slowly when the activated carbon was used. Even the column packed with activated carbon was purged and filled with water before the reaction experiment, the air still adsorbed on the activated carbon surface strongly. The hydrogen dissolved in feed water reacted with the dissolved oxygen as well as with the oxygen adsorbed on the catalyst surface. This led to the decrease of oxygen removal rate. This activated carbon has been left in the column for 6 months to test of aging effect. After 6 months a gas pocket was generated at the top of the column. After removing this gas pocket, the reaction experiment was conducted again, of which result was shown in Fig. 4. The aged activated carbon showed better performance for the removal of dissolved oxygen in feed water, which

indicates that the oxygen adsorbed on the activated carbon has dissolved in the water or degassed from the catalyst yielding the gas pocket. This also indicates that the activated carbon is also likely for the removal of dissolved oxygen even its efficiency is not in satisfaction in the beginning of column operation.

The commercial catalyst, Lewatit OC-1045, was replaced in the column to investigate the performance. The results shown in Fig. 5 illustrate the dissolved oxygen removal to desired extent. The open circles in Fig. 5 represent the behavior of Lewatit that has been aged with contacting the air for one year, whereas the solid circles refer to fresh Lewatit catalyst. The fresh catalyst is superior to the aged one. As described in Table 2, Lewatit OC-1045 is characterized by gelular resin bead with ammine functional group. Palladium is dopped on the catalyst. This resin catalyst undergo slow degradation in general due

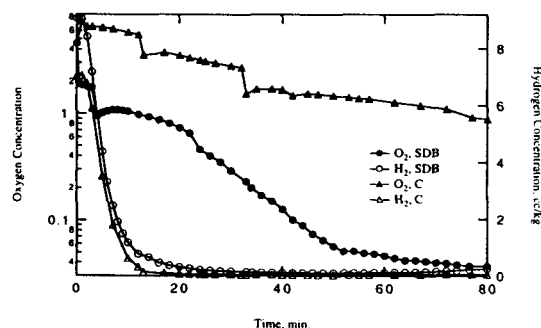


Fig. 3. Comparison of results by SDB catalyst and by activated carbon catalyst

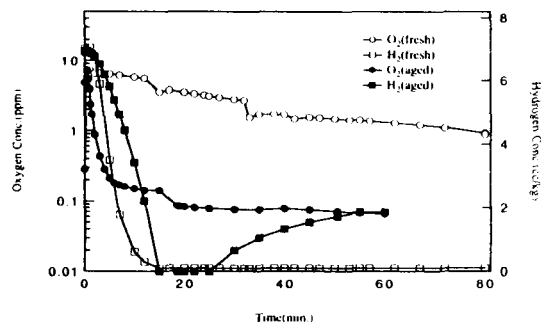


Fig. 4. Oxygen removal by activated carbon catalyst and by aged activated carbon catalyst

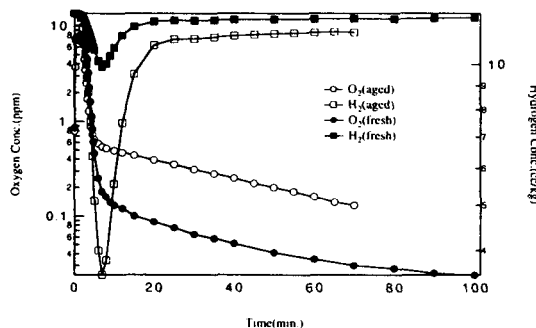


Fig. 5. Comparison of fresh Lewatit and aged one

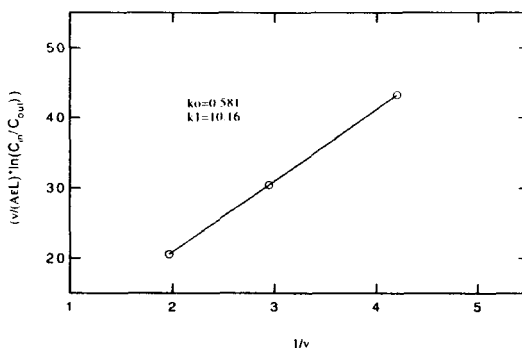


Fig. 6. Correlation of experimental data with the model equation

to irreversible chemical sorption, fouling, or deformation of metal or functional group[13,14]. The degradation of resin catalyst implies that the aged Lewatit shows the worse performance for the reaction of oxygen with hydrogen. This also implies one of the causes restraining catalyst life.

The column packed with Lewatit-OC 1045 was employed under variable water flow rates for testing the model. The results of correlation of equation (8) with the experimental data were shown in Fig. 6. The experimental data were correlated well with the proposed model equation. From these correlation results, i. e., slope and intercepts, the design parameters can be estimated. Then the height of catalytic column under the given flow rate and desired eluted oxygen concentration can be calculated.

5. Conclusions

The polymer bound platinum catalyst was prepared and tested for the removal of dissolved oxygen in the makeup water. As the experimental results employing the prepared catalyst showed that the dissolved oxygen reduced to 35 ppb which is below the limit of dissolved oxygen concentration, the catalyst was likely for the practical application.

The platinum on activated carbon catalyst was also tested for the oxygen-hydrogen reaction. The fresh activated carbon catalyst showed slow oxygen removal rate, since the air adsorbed so much on the activated carbon surface that the most hydrogen dissolved in the feed water was consumed for scavenging the adsorbed oxygen. The aged activated carbon, however, behaved better, since the adsorbed oxygen seemed to be removed from the surface by degassing or dissolving.

The Lewatit OC-1045 that is available commercially was employed for testing the performance, aging effect, and model application. The performance of Lewatit OC-1045 was the best in the viewpoint of dissolved oxygen removal rate. However aged Lewatit

showed slower reaction rate due to degradation of resin catalyst, causing the catalytic activity reduction.

The model described the catalyst performance well, from which the design parameters could be estimated. The required catalytic column length could be calculated under desired oxygen outlet concentration and water flow rate.

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