Estimation of Hydrazine Decomposition on Measuring the High-Temperature pH in Hydrazine/ETA Solutions at 553 K

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1. Introduction

Hydrazine is one of the most excellent oxygen scavengers used in the secondary circuit of nuclear power plants. Furthermore, in some pants, the hydrazine is used as a source of hydrogen required to suppress radiolysis of the coolant water in the primary loop [1]. When hydrazine was exposed in the high temperature and high pressure water, it can be decomposed into the various products such as NH_3, N_2, H_2, and NO_3 ions. As the result, the pH of solution containing hydrazine in the condition of the high temperature and high pressure can be changed by those decomposed products.

In the present work, we investigated the decomposition behavior of hydrazine in ETA (ethanol amine) solution. In addition, we measured the high temperature pH at 553 K on the various hydrazine/ETA solutions for confirming the applicability of the yttria stabilized zirconia (YSZ)-based pH electrode in secondary circuit of the nuclear power plants,

2. Methods and Results

A high temperature pH electrode was established by using Ni/NiO mixed powder as an electrode material and YSZ (8.5 wt% Y_2O_3, Friatec AG, Germany) tube as an oxygen-ion-conducting membrane. A typical Ag/AgCl external electrode with 0.1M KCl was used as a high temperature reference electrode [2,3]. A Pt electrode was used to monitor the redox potential of the test solution. A high pressure once-through loop system equipped with the three electrodes was used for measuring a high temperature pH.

2.1 High temperature pH and decomposition of hydrazine in hydrazine/ETA solutions

Fig. 1 shows the change of pH value upon addition of hydrazine to ETA solution and the decomposition behavior of hydrazine at 553 K and 10 MPa. We added the 5ppm ETA considering the operating condition in secondary circuit of nuclear power plant, and measured the high-temperature pH by adding the hydrazine concentration in the range 0 - 6 ppm. Hydrazine is decomposed into nitrogen gas and ammonia at the high temperature water as shown in below equation (1).

$$3N_2H_4 \rightarrow N_2 + 4NH_3 \qquad (1)$$

If the test solution contains dissolved oxygen, hydrazine slowly can be oxidized according to the equation (2).

$$N_2H_4 + O_2 \rightarrow N_2 + 2H_2O \qquad (2)$$

For prevent the hydrazine oxidation, the test solution was purged with 4% hydrogen gas (Ar gas based).

The high temperature pH slightly increased with increase of the concentration of hydrazine. And the decomposed product, ammonia, was produced gradually with increase of the concentration of hydrazine.

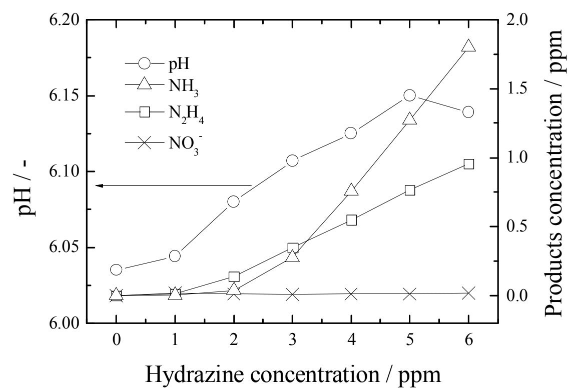

Fig. 1. The change of pH value upon addition of hydrazine to ETA solution and the behavior of decomposition of hydrazine at 553 K and 10 MPa.

From the literature [4], ammonia retards the rate of hydrazine decomposition and the rate was most affected by initial ammonia concentrations below 2%. The relationship of the concentration of ammonia and the rate of hydrazine decomposition is shown in Fig. 2. As the concentration of ammonia increased, up to 1.82 ppm, the rate decreased to 2.65% per added hydrazine concentration. The observed rates for decomposition of hydrazine were inversely related to the ammonia concentration.

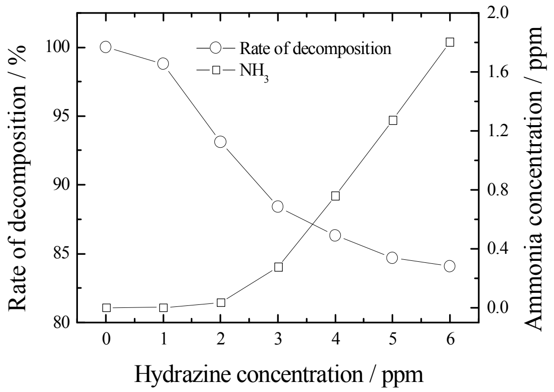

Fig. 2. Effect of ammonia concentration on the rate of decomposition of hydrazine at 553 K and 10 MPa.

2-2. Comparison of the measured pH with the calculated pH

As shown in Fig. 3, we compared the difference between the pH value measured by using YSZ-based pH electrode on the high temperature pH measurement and the calculated pH value upon addition of hydrazine to 3 ppm-ETA solution at 553 K and 10 MPa. The concentration of Hydrazine only considered, the calculated pH value increased with increasing the concentration of hydrazine. However, in case of addition of products, the calculated pH was similar to the measured pH by YSZ-based pH electrode. This result indicated that the pH electrode was acceptable and applicable for the hydrazine/ETA solutions in the secondary circuit of nuclear power plants.

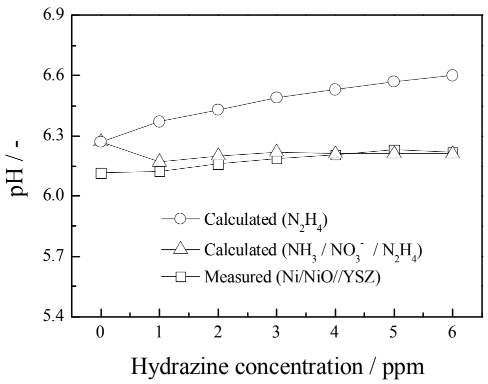

Fig. 3. Comparison of the measured pH and the calculated pH in various Hydrazine/ETA solution at 553 K and 10 MPa.

3. Conclusions

We investigated the pH change caused by the decomposition of hydrazine at a high temperature and a high pressure by using YSZ-based pH electrode. The pH values increased slightly as the concentration of hydrazine increased, and the decomposition rate of the hydrazine decreased with an increase of the ammonia concentration. The pH values we measured were almost identical with those from calculation. We confirmed that the pH measurement with the YSZ-based pH electrode would provide a reasonable pH value under secondary circuit condition of nuclear power plants.

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