Solubilities of iron and nickel oxides under high temperature and high pressure conditions

Ke-Chon Choi, Yongju Jung, Jei-Won Yeon and Kwang Yong Jee
Nuclear Chemistry Research Division, Korea Atomic Energy Research Institute,
150 Deokjin-dong, Youseong-gu, Daejeon, 305-353
nkcchoi@kaeri.re.kr

1. Introduction

The purposes of primary coolant chemistry are to assure fuel and material integrity and to minimize out of core radiation fields. During the PWR operation, crud deposits are expected on the cladding, leading to cladding failure and raising the radioactivity[1]. Such deposits come from the corrosion products of system surface[2]. To achieve optimal conditions for primary coolant, basic researches on mass transfer, deposition and solubility of corrosion products are needed[3]. The initial stage of crud formation could be the studies on the solubility of a structural material. It has been known that the solubility of metal oxides in boric acid under high temperature and high pressure condition depends on the pH and dissolved hydrogen. Thus, the effect of various pH on the solubility of metal oxide in boric acid solution was investigated in this work.

2. Experiments and Results

2.1 Instrumental

The experiments for the solubility measurements of structural material in a primary coolant system were carried out in a flow-through autoclave. The experimental setup is not shown. It consists of tubular autoclave, sample introduction part, gas injection part, hydrogen detector, and sampling loop. Pyrex glass was used for the reservoir of sample solution connected to a HPLC pump to introduce the sample solution. Ti and Zr alloy was used to resist high temperature and high pressure, and on line controller was used for BPR regulator[3].

2.2 Experiments

To prepare simulated coolant, 2.0 g metal oxide (Fe_2O_3, NiO) was added to 500 mL of 0.01 M H_3BO_3 in a 1.0 L glass bottle. Then hydrogen gas was purged for 30 minutes in order to remove dissolved oxygen. Sampling was done periodically by a 5mL syringe connected to a section of Tygon tubing. The concentration of dissolved iron and nickel ion in a sample solution was analyzed by ICP-AES, and that of hydrogen in an autoclave was measured by hydrogen detector (Methrom, Co.).

2.3. The solubility of Fe_2O_3 and NiO as a function of time

The solubility of Fe ion and Ni ion in 0.01 M boric acid was measured as a function of time using Fe_2O_3 and NiO, respectively. *Figure* 1 shows the solubility of Fe ion in 0.01 M boric acid at different chemical equilibrium concentrations static and dynamic method.
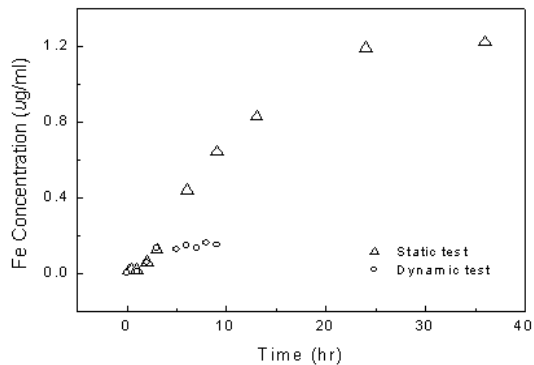

Fig. 1. Time dependence of Fe_2O_3 solubilities in 0.01 M boric acid solution at pH 3.0, 70℃. △: Static method, ○: Dynamic(FTA) method.
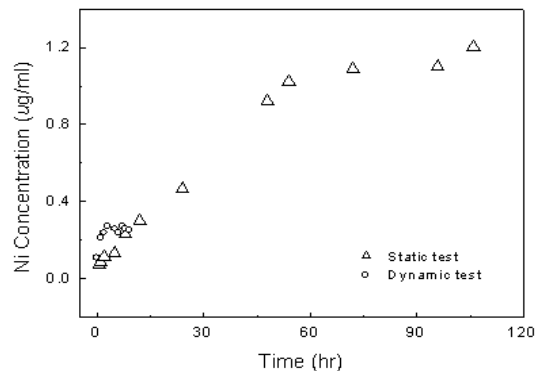

Fig. 2. Time dependence of NiO solubilities in 0.01 M boric acid solution at pH 3.0, 70℃ △: Static method, ○: Dynamic(FTA) method.

As shown in *Figure* 1, the solubility of Fe increased significantly with time and then reached equilibrium after about 24 hrs at pH 3.0 by static method. On the other side, the static state concentration of Fe reached equilibrium after about three hours at the same conditions by FTA method. *Figure* 2 shows that the solubility of nickel oxide increased significantly with time and reached equilibrium after about 50 hrs. On the other side, the static state concentration of Ni reached equilibrium after about 3~4 hours under the same conditions by FTA method. From this result, we concluded that the dissolution rate of nickel oxide is lower than that of iron oxide.

2.4. Solubility of metal oxide as a function of pH

The results of the iron and nickel oxide solubility measurements in boric acid at high temperature (280 ~ 320℃) are shown as a function of pH in *Figure* 3-4, respectively. In case of Fe_2O_3(*Figure* 3), at acidic pH (pH <7.0) , the solubility(280℃) decreases as the pH increases, which is similar to the results with magnetite solubility (Tremaine P.R.,(1980)) in the reducing environment at a temperature of 373 K [3]. However, the solubility (320℃) of nickel oxide at alkaline region (pH > 7.3) were higher than acidic region.
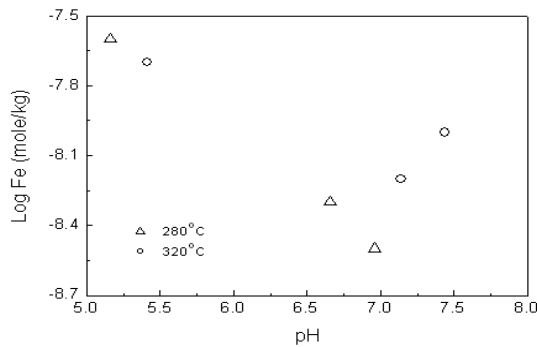
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Fig. 3. The pH dependence of the iron oxide solubility in 1000 μg/㎖ H_3BO_3(as B) under reducing conditions(saturated hydrogen concentration). △: 280℃ , ○: 320℃, respectively.

The solubility of nickel oxide also shows the same phenomenon as that of iron oxide. In case of NiO(*Figure* 4), at the solubility (280℃) of acidic pH (pH <6.7) were lower than acidic region but it increased with the pH. The solubility (320℃) did not change much with increasing pH (<7.2), but it increased with the pH.
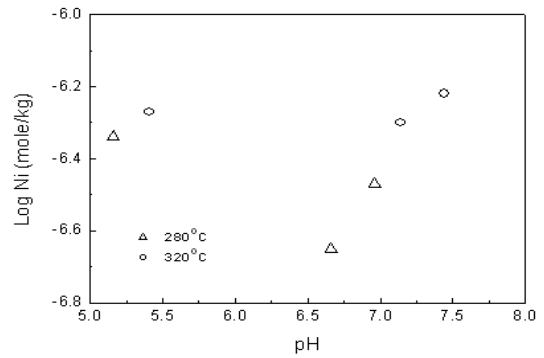

Fig. 4. The pH dependence of the nickel oxide solubility in 1000 μg/㎖ H_3BO_3 (as B) under reducing conditions (saturated hydrogen concentration) at △: 280℃ , ○: 320℃, respectively.

3. Conclusion

The effects of pH and time on the solubility of metal oxide in boric acid solution were investigated in this work. The chemical equilibriums of Fe_2O_3 and NiO at high temperature in H_3BO_3 were reached after about 24 and 50 hrs, respectively. The nickel oxide needed longer equilibrium time than iron oxide. In both Fe_2O_3 and NiO, at a acidic pH (pH <6.7), the solubility is decreased as the pH increased. The solubility of alkaline region (pH > 7.3) was higher than acidic region and did not change much with increasing pH.

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