Solubility of metal oxide under simulated primary water chemistry

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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. To achieve optimal conditions for primary coolant, basic researches on mass transfer, deposition, and solubility of corrosion products are needed. 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 concentration of dissolved hydrogen and lithium hydroxide. Thus, the effect of hydrogen on the solubility of metal oxide in boric acid solution was investigated in this work.
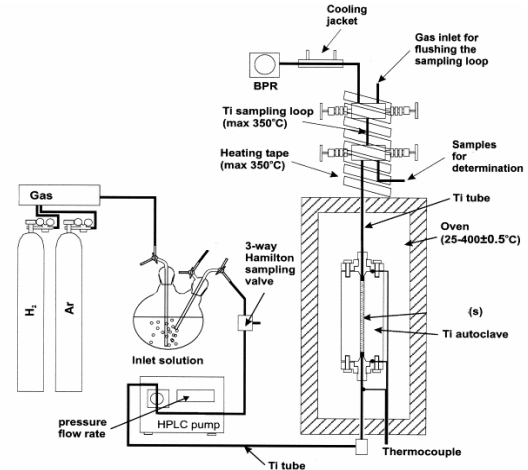

Fig. 1. Configuration of the experimental setup used in the present study. BPR=back-pressure regulator, HPLC=high-performance liquid chromatography.

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 shown in Fig. 1. 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[2].

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. Fig.2 shows the solubility of Fe ion in 0.01 M boric acid.
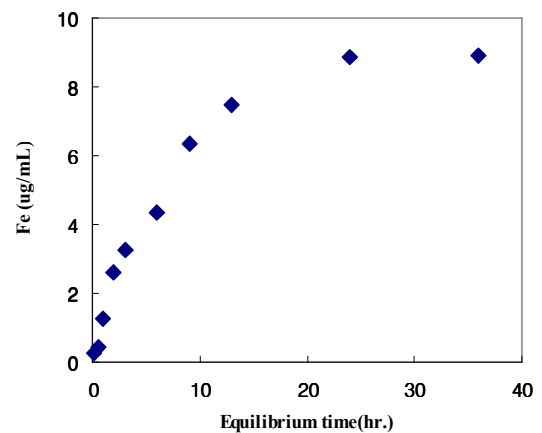

Fig. 2. Solubilities of Fe_2O_3 in 0.01 M boric acid at pH 3.0, 343 K, filtered through 0.02 um pore size teflon membrane
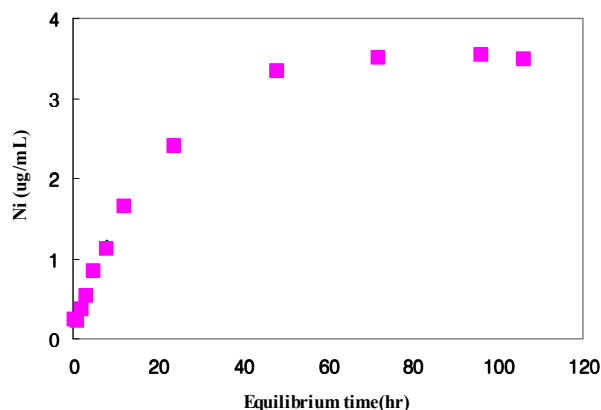
Fig. 3. Solubilities of NiO in 0.01 M boric acid at pH 3.0, 343 K, filtered through 0.02 um pore size teflon membrane

Fig. 4. Solubility of Fe_2O_3 in 0.01 M boric acid as a function of pH at 343 K, filtering with 0.02 um pore size teflon membrane

As shown in this figure, the solubility of Fe increased significantly with time and then reached equilibrium after 24hrs at pH3.0. Fig. 3 shows that the solubility of nickel oxide Fe increased significantly with time and reached equilibrium after 50 hrs. 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 343 K are shown as a function of pH in Fig. 4-5, respectively. In case of Fe_2O_3, at a acidic pH (pH < 7), the solubility is decreased as increasing the pH, which is similar results with magnetite solubility (Tremaine P.R.,(1980)) in the reducing environment at temperature of 373 K [3]. At alkaline region (pH > 8), the solubility was lower than acidic region and did not change much as increasing pH. The solubility of nickel oxide also show the same phenomenon as that of iron oxide.

Fig. 5. Solubility of NiO in 0.01 M boric acid as a function of pH at 343 K

3. Conclusion

The effect of pH and time on the solubility of metal oxide in boric acid solution was investigated in this work. The chemical equilibrium of Fe_2O_3 and NiO in H_3BO_3 was reached after 24 and 48 hrs, respectively. The nickel oxide needed longer equilibrium time than iron oxide. Both of Fe_2O_3 and NiO, at a acidic pH (pH < 7), the solubility is decreased as increasing pH. At alkaline region (pH > 8), the solubility was lower than acidic region and did not change much as increasing pH.

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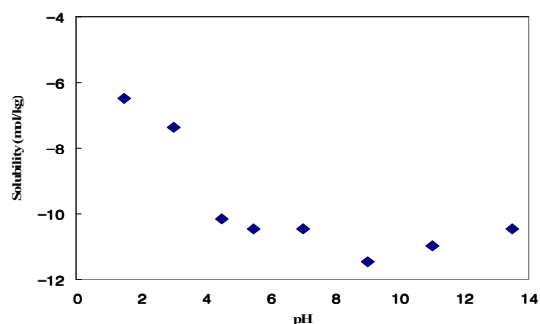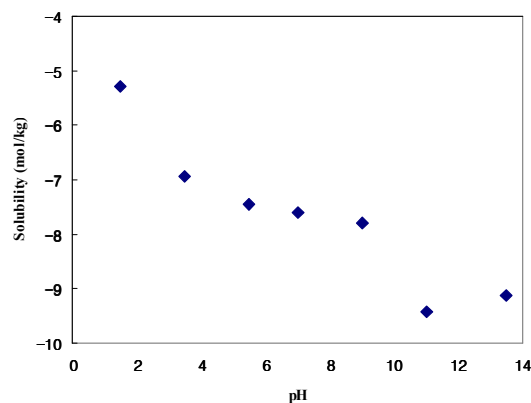
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