



Original Article

Solubility Study of Nickel Ferrite in Boric Acid Using a Flow-Through Autoclave System under High Temperature and High Pressure

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ABSTRACT

The solubility of nickel ferrite in an aqueous solution of boric acid was studied by varying the pH at the temperatures ranging from 25°C to 320°C. A flow-through autoclave system was specially designed and fabricated to measure the solubility of Fe in hydrothermal solutions under high temperature and pressure. The performance of this flow-through system was directly compared with the conventional static state technique using a batch-type autoclave system. The stability of fluid velocity for the flow-through autoclave system was verified prior to the solubility measurement. The influence of chemical additives, such as boric acid and H₂, on the solubility of nickel ferrite was also evaluated.

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1. Introduction

The stable operation of reactor coolant systems is strongly dependent on various processes, including the corrosion process in the cooling system, mass transport, deposition of corrosion products, as well as numerous physicochemical processes (e.g., propagation of radioactivity) [1]. These processes of the cooling system are mainly influenced by physicochemical factors such as temperature as well as chemical composition of the fluid mechanics or coolant, owing to the current trend of long-term period operation of the nuclear power plant [2,3]. For these reasons, water

chemistry control must be improved for the operational reliability and stability of nuclear power plants. In order to achieve optimal performance of the power plant cooling system, detailed experimental data such as mass transport and solubility of various corrosion products are necessary [4].

Moreover, the relationship between the effects of corrosion products, temperature, pH, and dissolved gases must be experimentally illustrated, for instance, as models that quantitatively evaluate the effect of water control on the nuclear power plant lifetime [5,6]. The solubility of the materials may vary according to temperature, amount of dissolved oxygen in the coolant, concentration of chemical additives, and the

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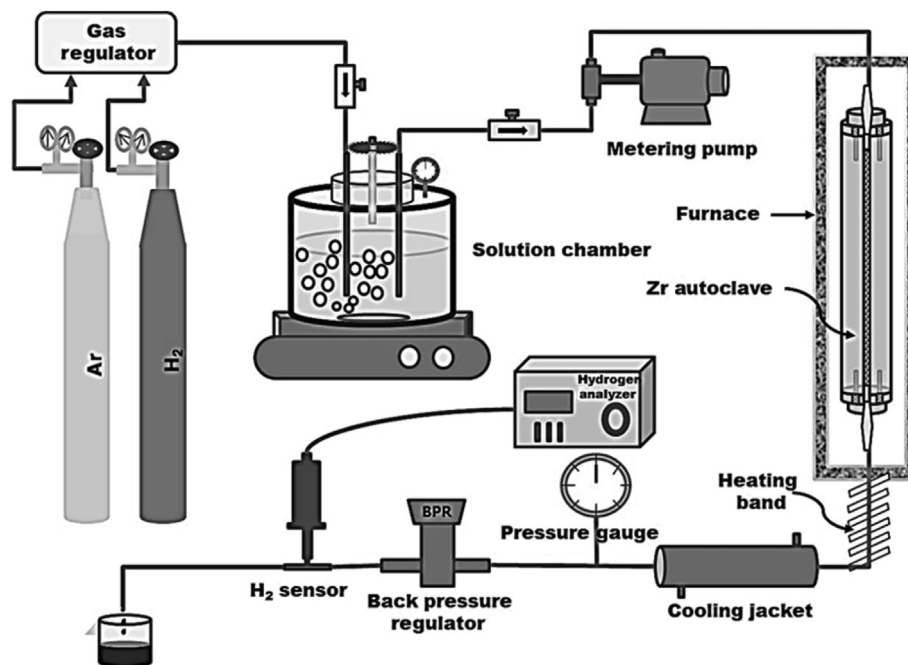


Fig. 1 – Schematic layout of the experimental setup for the flow-through autoclave system.

operating conditions of the nuclear reactor; however, there are many other factors that influence corrosion of the primary coolant system materials. The pH control of the coolant is known as a fundamental water control method that can be used to understand the corrosion behavior and transport route of the corrosion products, because it is closely related to the solubility of various corrosion products [7].

The primary coolant of the pressurized water reactor (PWR) is composed mainly of water with some chemical additives. H_3BO_3 , in particular, is added for the control of the nuclear reaction [8–11]. H_3BO_3 content at room temperature does not strongly influence the pH or conductivity of the coolant solutions, because it is a weak electrolyte and its conductivity decreases with the coolant temperature [12]. However, with the high operating temperatures of nuclear power plants (280–320°C), H_3BO_3 may influence the corrosion of manufactured materials because of the high pH, which drastically increases by the dissociation reaction of water. This corrosion phenomenon can cause significant problems for the safety of the operating system in nuclear power plants.

Corrosion products originate from the internal surface of piping and steam generator tubing. Nickel ferrite (NiFe_2O_4) is known as a main corrosion product in the primary coolant system, and its solubility becomes important to optimize water chemistry control for a long-term fuel cycle [13,14].

To determine the solubility under high pressure and high temperature conditions, conventional static state and fluid dynamic state methods can be used. The conventional static state method has advantages of simplicity and low cost. However, the conventional static state method is a slower measurement technique because a relatively long time is required to reach equilibrium. Experimentally, more than 10 days are required for equilibrium when measuring the solubility of magnetite (Fe_3O_4) at 423 K using this method [15]. By

contrast, equilibrium is achieved quicker when using the fluid dynamic state method because of the relatively high surface area of the sample.

In this study, a flow-through autoclave system for the measurement of NiFe_2O_4 solubility in an aqueous H_3BO_3 solution was specially designed and fabricated to simulate the flow circulation system of a nuclear power reactor. The time for Fe to reach chemical equilibrium was measured with the flow-through system, and the results were compared with those obtained using the conventional static system. Solubility measurements were carried out in aqueous solutions of primary coolant at temperatures of 25–320°C with pH values of 4.5–8.0. The solubility of NiFe_2O_4 in H_3BO_3 solutions under high pressure and high temperature is discussed considering parameters such as H_2 gas content and pH.

2. Materials and methods

Solubility measurements were performed in a flow-through autoclave system at temperatures and pressures up to 400°C and 1,500 bar, respectively. The experimental setup is illustrated in Fig. 1. The main structure of the flow-through autoclave system is composed of the solution chamber with a gas regulating system for Ar and H_2 , a high temperature and pressure autoclave system located inside a furnace, and a sampling unit with a cooling jacket, H_2 sensor, and back-pressure regulator.

A stainless steel solution chamber with a capacity of 4.5 L at 8 bar was used to contain the aqueous H_3BO_3 solution (various concentrations were used). Prior to the solubility measurement, the H_3BO_3 solution was carefully degassed by repeatedly pressurizing with Ar and decompressing, then flushing with H_2 gas at a constant pressure. This procedure

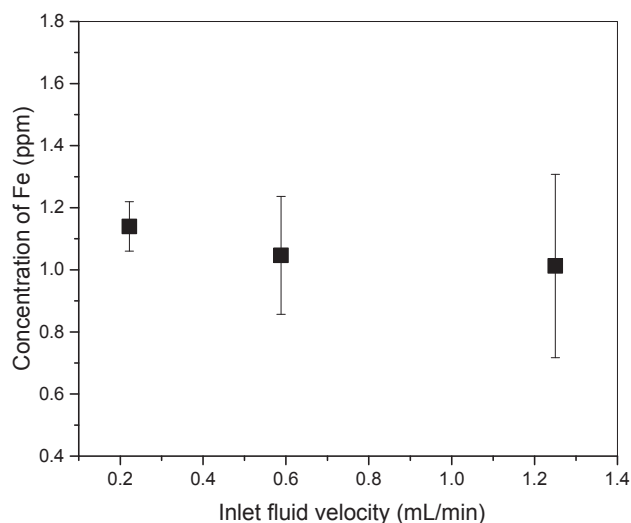


Fig. 2 – Fe concentrations at different inlet fluid velocities (H_3BO_3 solution of 800 $\mu\text{g}/\text{mL}$) using the flow-through autoclave system.

was continued beyond no O_2 by the oxygen sensor. The solution was then pressurized and supplied continuously to the mainstream line by a metering pump. The pressure was regulated by a back-pressure regulator with 6,000 lb/in² capacity. In addition, the flow rate of the solution was maintained constant, typically at 0.22 mL/min.

The cylindrical autoclave reactor with a size of 250 mm and a diameter of 6.5 mm was placed in an electric furnace, in which the temperature was controlled to within $\pm 2^\circ\text{C}$ using two thermocouples attached to different positions on the reactor. The autoclave reactor was fabricated with Zr alloy (99.5% purity). The autoclave reactor port was built with Ti fitting (Grade II) tubing where the ceramic filter (0.2 μm pore size) was installed.

NiFe_2O_4 (99.9% purity) was used for the solubility measurement. Twenty grams of NiFe_2O_4 was packed into the autoclave reactor. The H_3BO_3 solution was added into the solution chamber and then pressurized with a fluid velocity of 0.22 mL/min. The pH of the solution was adjusted with HCl or NaOH. Samples (100 mL) were taken hourly to measure the Fe concentration using inductively coupled plasma-atomic emission spectroscopy, after filtering with a disk filter (pore size of 0.22 μm , syringe type). Five replicates of the data set were obtained to provide a mean value and relative standard deviation (RSD).

Classical static experiments were carried out at $70 \pm 0.5^\circ\text{C}$. A solution of H_3BO_3 (0.01M, pH 3.0) was stirred in a glass vial after adding 5.0 g of NiFe_2O_4 into the solution. Samples were then taken hourly to measure the Fe concentration using inductively coupled plasma-atomic emission spectroscopy, after filtering with a disk filter (pore size of 0.22 μm , syringe type) in order to remove any NiFe_2O_4 particles in the solution.

3. Results

3.1. Optimization of the flow-through autoclave system

Prior to measuring the solubility, background Fe concentrations were measured by analyzing the flow-through autoclave

system effluent using a blank H_3BO_3 solution (800 ppm, pH 5.4) without NiFe_2O_4 . The blank values were obtained at three temperatures (25°C , 150°C , and 320°C) for 12 hours. The blank results were unaffected by temperature changes; therefore, the mean Fe concentration of the blank solutions was $0.012 \pm 0.0098 \mu\text{g}/\text{mL}$.

In order to optimize the flow rate of the H_3BO_3 solution in the flow-through autoclave system, the Fe concentration was measured while the H_3BO_3 solution (800 ppm) flow rate of boric acid solution was maintained at 0.22 mL/min, 0.58 mL/min, and 1.20 mL/min. At each flow rate, the RSDs from four replicate measurements are 7.9%, 18.9%, and 29.1%, respectively, as shown in Fig. 2. The RSD increases with the flow rate of the sample solution. This phenomenon may be attributable to the shorter retention time when the flow rate increases. A flow rate of 0.22 mL/min was used throughout this study.

As shown in Fig. 3, the Fe concentration reaches equilibrium at 3–4 hours for our system. When using the classical static state method, as shown in Fig. 4, 70–80 hours are required to reach equilibrium under the same condition of pH 3.0 and 70°C . It seems that this is due to the higher surface area of the sample in contact with the eluent solution for the dynamic flow technique.

3.2. Solubility study of NiFe_2O_4

It is well known that reducing environment is effective for increasing the resistance of steam generator tubing to intergranular attack and pitting. Fig. 5 shows the influence of the dissolved H_2 content on the solubility of NiFe_2O_4 under thermohydraulic conditions (200°C and 320°C). Prior to flushing H_2 , the sample solution was degassed by repeated pressurizing with Ar in order to minimize residual traces of O_2 , which is known as a radiolysis product of water in the reactor core. The increased content of dissolved H_2 , which was controlled by increasing H_2 pressure, leads to higher NiFe_2O_4 solubility.

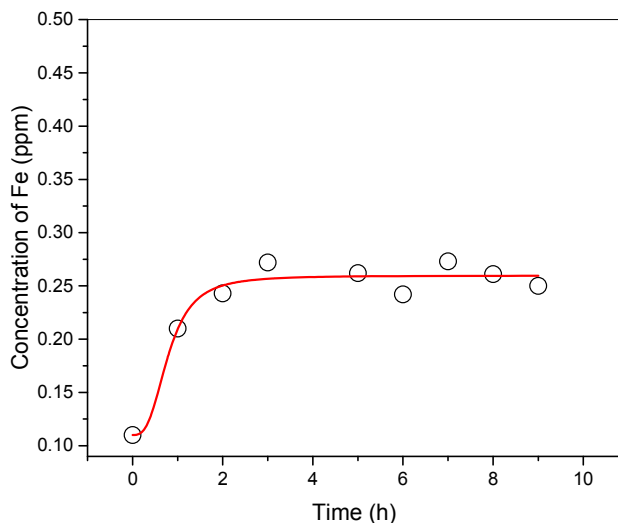


Fig. 3 – Time dependence of NiFe_2O_4 solubility in the flow-through autoclave system under the following conditions: 0.01M H_3BO_3 , pH 3, and 70°C .

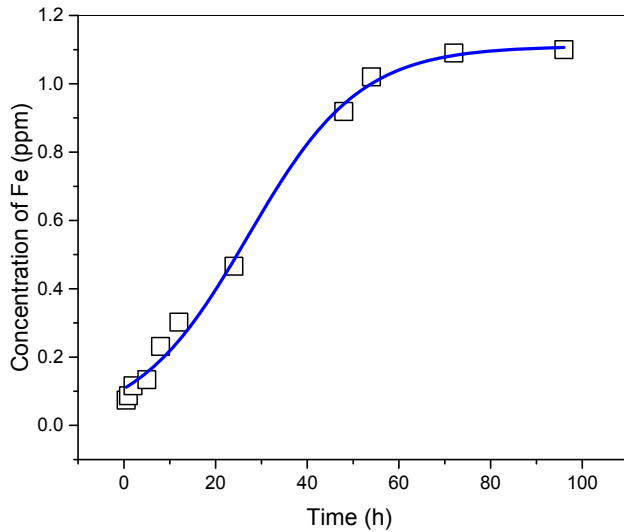


Fig. 4 – Time dependence of NiFe₂O₄ solubility using the classical static state technique under the following conditions: 0.01M H₃BO₃, pH 3.0, and 200°C.

Therefore, the dissolved H₂ content must be optimized for the effective control of corrosion products in an actual operating nuclear power plant.

An increase in the primary coolant pH is known to reduce the primary circuit corrosion. Under the normal operating conditions of PWR, long-term control of the reactivity in the reactor is achieved by varying the H₃BO₃ concentration in the reactor coolant. A higher pH of the primary coolant containing H₃BO₃ can be achieved by increasing the LiOH content.

The solubility of NiFe₂O₄ was measured in the samples with three different H₃BO₃ concentrations (800, 1,200, and 2,000 µg/mL). As shown in Fig. 6, at pH 5.15, the NiFe₂O₄ solubility increases with the concentration of H₃BO₃. However, the influence of the H₃BO₃ content is insignificant at pH values of 7.0 and 7.4.

Fig. 7 shows the solubility dependence of NiFe₂O₄ on the pH of the H₃BO₃ solution (800 µg/mL) at 320°C. The NiFe₂O₄

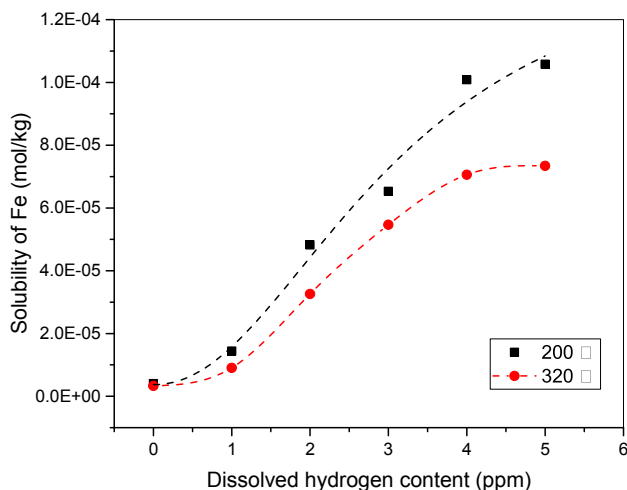


Fig. 5 – Solubility dependence of NiFe₂O₄ on dissolved H₂ content at 200°C and 320°C (pH 5.1, 800 µg/mL H₃BO₃).

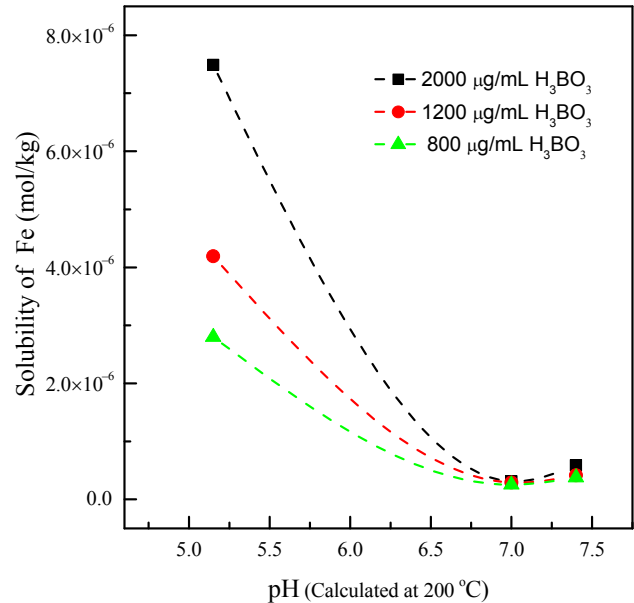


Fig. 6 – Solubility of Fe as a function of pH at 200°C.

solubility decreases in pH, as reported elsewhere. The minimum NiFe₂O₄ solubility at 320°C is 1.0×10^{-7} mol/kg in the pH range of 7.0–7.4. The result of this study shows similar trend to the solubility data of magnetite at 300°C reported by Tremaine and LeBlanc [15] and Anthoni [8].

4. Discussion

The study of Fe solubility in the primary coolant of the PWR in terms of temperature, dissolved H₂ content, and pH provides essential data for better operational reliability and stability of

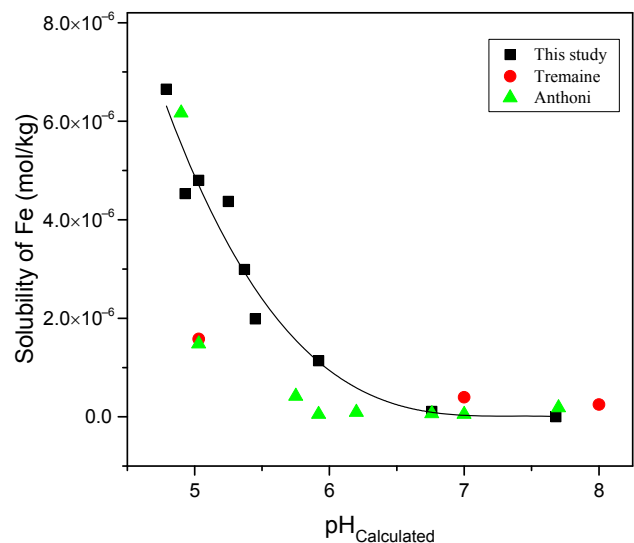


Fig. 7 – Comparison of Fe solubility data from this study (NiFe₂O₄, 320°C), with those from the studies by Tremaine and LeBlanc [15] (magnetite, 300°C) and Anthoni [8] (Fe₃O₄, 300°C).

nuclear power reactors. The solubility dependence of NiFe_2O_4 in an aqueous solution of H_3BO_3 was studied by varying the pH at the temperature range of 25°C to 320°C. A flow-through autoclave system was fabricated and used to measure the solubility of NiFe_2O_4 in hydrothermal solutions. This system has an advantage of fast equilibrium compared to the conventional static state method. The increase of dissolved H_2 content controlled by increasing H_2 pressure led to higher NiFe_2O_4 solubility. NiFe_2O_4 solubility increased with the concentration of H_3BO_3 at pH 5.15, whereas the influence of H_3BO_3 content was insignificant at neutral pH. The minimum solubility of NiFe_2O_4 at 320°C was found to occur within the pH range of 7.0–7.4.

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