Effect of Temperature on Particulate Behavior of Nickel Ferrite

IN HYOUNG RHEE, BYUNG GI PARK, HYUN KYOUNG AHN
Department of Energy and Environmental Engineering
Soonchunhyang University
646 Eupnae-ri Shinchang-myeon Asan-si Chungcheongnam-do 336-745
KOREA
ihrhee@sch.ac.kr

Abstract: The particulate behaviors of nickel ferrite were investigated under the simulated PWR shutdown chemistry conditions. Temperature of the simulated water with concentration of 0.1 ppm Li and 2,000 ppm B was dropped from 300 °C to 150 °C with a rate of 0.625 °C/min and then constantly maintained at 150 °C under the pressure of 2,500 psi. The on-line particle counting and the concentration measurement of nickel dissolved were performed under 5, 15 and 25 cc/kg H2O dissolved hydrogen. Experimental results showed that total particle count in the simulated water was not greatly changed for three hydrogen concentrations as temperature was decreased. However, particles were smaller as temperature was decreased and then maintained constantly when temperature was constant. The degree of variation in particle size distribution was greater at 15 cc/kg H2O dissolved hydrogen than any other dissolved hydrogen concentrations. Concentration of nickel ion was increased as temperature was decreased and was higher at 15 cc/kg H2O dissolved hydrogen than any other dissolved hydrogen concentrations. Theses results show that nickel ferrite is unstable with temperature variation and at dissolved hydrogen concentration of 15 cc/kg H2O.

Key-Words: nickel ferrite, aqueous equilibria, corrosion product, hideout, oxide solubility, oxide adsorption

1 Introduction
The reduction of radioactivity in a reactor coolant system of PWR is important to decrease the radiation exposure dosage of workers and to enhance the efficiency of maintenance during the periodic overhaul. The radiation exposure dose is directly affected by the shutdown chemistry which is the main process to dissolve the radioactive nuclides deposited on the fuel cladding and to remove the activated corrosion products attached on the components in the reactor coolant system. The effect of shutdown chemistry on radiation exposure can be improved by the effective elimination of cobalt and other corrosion products which account for the activity in the reactor coolant system.[1] Therefore, PWR shutdown chemistry has to be controlled to achieve the most favorable conditions to crud decomposition and to avoid re-precipitation of metals in the reactor coolant system.

In shutdown procedure, most of PWRs utilize two step processes that are known as an acid-reducing step and then an acid-oxidizing step. The acid-reducing condition is maintained by keeping some amount of hydrogen in RCS and boration. EPRI guidelines [1] indicates that the acid-reducing condition enhance the nickel ferrite decomposition. Under acid-reducing condition, nickel ferrite is reductively decomposed into nickel metal and magnetite and then magnetite is dissolved with ionic species. According to EPRI guidelines [1], the best conditions for nickel ferrite decomposition are the hydrogen concentration of higher than 10 cc/kg H2O and the temperature between 120 °C and 150 °C. Theses conditions should be maintained at least for 16 hours. After acid-reducing condition, hydrogen is degassed from the RCS achieve the acid-oxidizing condition in coolant water chemistry. Under acid-oxidizing condition, nickel metal from nickel ferrite is dissolved into nickel ion.

During shutdown of reactor, water chemistry of reactor coolant system is steeply changed. Especially, the great change of water temperature and hydrogen concentration in reactor coolant system affects the property of the crud which is mainly composed of nickel ferrite. Decomposition of crud will produce ionic species and particulates that are removed by cleanup system in PWR. Particle size distribution was observed at French PWR.[2] The observation of particle size distribution before and during shutdown exhibited that particle is larger at hot shutdown and then smaller during shutdown. Understanding this behavior of particles will be helpful to remove crud in the reactor coolant system.
2 Experimental
An experimental loop, as shown in Figure 1, was developed to investigate particulate behavior of nickel ferrite under PWR shutdown condition. The loop consisted of a mixing tank, a high pressure pump, an autoclave, a particle counter, a cooler, a pressure regulator, and a water chemistry measuring unit. The loop has a capability of controlling temperature with a rate of 0.625 °C/min under high pressure condition. In the loop, particle size distribution was measured under high temperature with the on-line particle counter. In the water chemistry measuring unit, sensors for measurement of pH and conductivity were installed. Pressure in the loop was controlled with automatic pressure regulator.

In the experiment nickel ferrite particles were injected into the mixing tank and then were transferred to autoclave by high pressure pump. The mixing tank was pressurized with hydrogen. Hydrogen pressure was adjusted to meet the required hydrogen concentration.

To examine the effect of hydrogen concentration on nickel ferrite under PWR shutdown condition, experiments were conducted with three hydrogen concentration of 5, 15, and 25 cc/kg H₂O. During each experiment, temperature was maintained at 300 °C for 4 hours, decreased to 150 °C for 4 hours, maintained at 150 °C for 12 hours, and then decreased to 80 °C for 4 hours. Solution with 2,000 ppm boron, 0.1 ppm Li, and 0.00625 ppm nickel ferrite particle was injected into autoclave via high pressure pump. During experiment, temperature, pressure, particle size distribution, pH and conductivity were recorded. Solution was sampled at prescribed time. Solution sample was analyzed with inductively coupled plasma (ICP) to obtain concentration of nickel and iron in solution.

3 Results and Discussion
Research was focused on the particulate behavior of nickel ferrite depending on dissolved hydrogen concentration under temperature profile of PWR shutdown chemistry. Size distribution, concentration of nickel and iron, elemental composition of particulates, and water conductivity were measured.

Figure 2 shows pH behavior during each experiment. Each experiment showed pH of about 6, regardless of hydrogen concentration. Figure 3 shows conductivity behavior during each experiment. As
shown in Figure 3, experiment with hydrogen concentration of 25 cc/kg H₂O exhibited lower conductivity among other hydrogen concentrations. Conductivity was increased during decreasing temperature from 300 °C to 150 °C, regardless of hydrogen concentration. However, conductivity was not altered during maintaining temperature at 150 °C.

Figure 4 shows a particle size distribution at 5 cc/kg H₂O hydrogen. The range of particle size was 8-63 μm in diameter at the constant temperature of 300 °C. But the particle size distribution was moved to 8-16 μm during the decreasing step in temperature from 300 °C to 150 °C. Figure 5 shows a particle size distribution of 15 cc/kg H₂O hydrogen concentration at which the particle size was smaller than under 5 cc/kg H₂O hydrogen. During the decreasing step temperature from 300 °C to 150 °C, a similar trend was observed with 5 cc/kg H₂O hydrogen. Figure 6 shows a particle size distribution at a condition of 25 cc/kg H₂O hydrogen. Under this condition, particle size distribution was not altered regardless of temperature change.

Figure 2. pH behavior under each condition of hydrogen concentration

Figure 3. Conductivity behavior under each condition of hydrogen concentration
Figure 4. Particle size distribution under 5 cc/kg H₂O

Figure 5. Particle size distribution under 15 cc/kg H₂O

Figure 6. Particle size distribution under 25 cc/kg H₂O
Experimental results showed that particle size distribution was affected by temperature and hydrogen concentration. The effect of temperature on particle size distribution might be induced by pH that depends on temperature. While temperature was decreased from 300 °C to 150 °C, pH was decreased from 5.6 to 4.7. Solubility of nickel ferrite, magnetite, and nickel is dependent upon pH. Particle in solution is composed of nickel ferrite, magnetite, and nickel because nickel ferrite is decomposed under acid-reducing condition. The different rate of solubility change of each chemical species can induce stress on particle and disrupt into the smaller particle size. Particle size distribution was also affected on hydrogen concentration that changes the water chemistry of reducing or oxidizing environment.

Figure 7 and Figure 8 shows concentrations of iron and nickel, respectively. As shown in Figure 7 and Figure 8, iron concentration was greatly changed at a condition of 5 cc/kg H₂O hydrogen and was not changed at conditions of 15 cc/kg H₂O hydrogen and 25 cc/kg H₂O hydrogen. But nickel concentration was
increased at all experimental conditions. The increase of nickel concentration was induced by decrease of pH according to temperature decrease. According to fast reaction of nickel ferrite decomposition, nickel product is increased as hydrogen concentration is increased. Oxidation of nickel is increased as hydrogen concentration is decreased. Therefore, at the condition of 25 cc/kg H₂O hydrogen, production rate of nickel metal is high but production rate of nickel ion is low. In contrary, at the condition of 5 cc/kg H₂O hydrogen, production rate of nickel metal is low but production rate of nickel is high. At intermediate condition of 15 cc/kg H₂O hydrogen, nickel concentration in solution is the higher because produced nickel metal is oxidized into nickel ion.

4 Conclusions
Experimental results showed that total particle count in the simulated water was not greatly changed for three hydrogen concentrations as temperature was decreased. However, the particle size was smaller as temperature was decreased and then maintained constantly when temperature was constant. The degree of variation in particle size distribution was greater at 15 cc/kg H₂O dissolved hydrogen than any other dissolved hydrogen concentrations. Concentration of nickel ion was increased as temperature was decreased and was higher at 15 cc/kg H₂O hydrogen concentration than any other hydrogen concentration. Theses results show that nickel ferrite is unstable in the condition of temperature variation and 15 cc/kg H₂O hydrogen concentration.

References: