Hydrogen as a New Chemical Factor on the Deposition of Fe Ions

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1. Introduction

Corrosion Products released from PWR primary circuit surfaces are transported to the reactor core, where they deposit and are activated to form radioactive corrosion products, which can be released to re-deposit on out-of-core surfaces. It has been well known that the deposition phenomena depend greatly on the type of nuclear reactor. In BWRs, the corrosion products are principally deposited on the fuel cladding. In the PWRs of a short-term fuel cycle, on the contrary, most of them are deposited on the steam generator. For these reasons, a study of the fuel CRUD has not been considered as an important issue in the PWRs, while it has been intensively carried out for a long time in the BWRs [1,2]. Recently, however, the operation programs of many PWR plants have been changed to use a long-term fuel cycles and higher thermal duties. In result, the trend the amount of fuel CRUD has increased in the some PWRs, has been observed. It has been reported that the fuel CRUD contributes to the occurrence of axial offset anomaly (AOA) and an increase of dose rate. The impact of the fuel CRUD could be reduced by various filtering systems installed in the chemistry and volume control system (CVCS) and the ultrasonic fuel cleaning system which has been recently developed [3]. Nevertheless, it is generally accepted that the most effective solution is to find out an optimal chemistry condition to mitigate the deposition process of the corrosion products on the fuel cladding [4]. In this study, the deposition tests of various iron species were carried out on the Zr heat transfer surface using a once-through loop system and a HT-HP (high-temperature and high-pressure) loop system, as a part of a goal to elucidate the formation process of fuel CRUD.

2. Methods and Results

2.1 Apparatus and Chemical Condition for Deposition Tests

Ferric ions (Fe^{3+}) and ferrous ions (Fe^{2+}) were chosen as the simulated corrosion products. The sources of the ferric ions and ferrous ions were ferric nitrate and ferrous acetate, respectively. Test solutions were supplied to the bottom of the autoclave of a once-through loop system and a HT-HP loop system (Fig. 1).

Zirconium rods (Zircadyne-702, Wah Chang, USA) with an electrically insulated heater as the simulated fuel rods were installed in the autoclave. The Zircadyne-702 has a chemical composition similar to that of Zircaloy-4 as a kind of zirconium alloy.

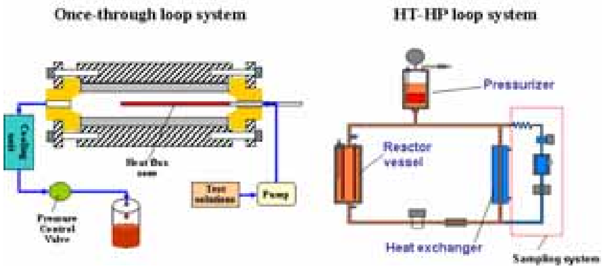

Figure 1. Schematic of a once-through loop system and a HT-HP loop system for deposition tests.

Table 1 shows the comparison of the operating conditions between the two systems and the PWR primary system. After the pressure, flow rates, and the iron concentration were maintained at room temperature, the solution temperature was controlled with the electric heater within the Zr rods.

Table 1. Comparison of operating environments of the PWR primary system, the once-through loop system and the HT-HP loop system.

Operating Conditions	PWR	Once-through Loop	HT-HP Loop
Temperature (°C)	287 ~ 326	200	280
Pressure (MPa)	10 ~ 16	2.5	11
Heat Flux (J/cm^2s)	≈ 60	1 ~ 10	1 ~ 10
pH	6.9 ~ 7.4	4.5 ~ 6.5	4.5 ~ 6.5
Concentration of Corrosion Product (ppm)	0.01 ~ 0.1	10 ~ 50	10 ~ 50

The temperature profile with the time which was applied to the test solutions consisted of the following three periods: (1) the first stage: the temperature increases to reach a desired value (*e.g.*, 200°C, 280°C); (2) the second stage: the temperature is fixed for 10 hours; (3) the third stage: the electric heater is turned off. The iron oxide deposits were removed from the Zr surface basically by an ultrasonic cleaning. The iron concentration was determined by ICP-AES, after dissolving the resulting solutions in hot hydrochloric acid.

2.2 Deposition in a Once-through Loop System

To evaluate the influence of the hydrogen on the formation of fuel crud, deposition tests were carried out in the following two solutions: (i) a deaerated ferric nitrate solution and (ii) a hydrogen-dissolved ferric nitrate solution. Figure 2 shows the fuel CRUD generated on the surface of Zr rods. It is noteworthy that a relatively dark CRUD was observed in the hydrogen-dissolved solution and the color of deposits became dark with solution temperature in the two solutions. When considering that ferric oxides have brighter color than ferrous oxides, we think that the dark CRUD was caused by the reduction of ferric ions. However, ICP-AES results showed that there was little difference in the deposits amounts between the two solutions. The deposit amounts were examined qualitatively without a removal from the Zr surface by LIPS (laser induced plasma spectroscopy) analysis. The concentration of the iron gradually decreased along the flow direction of the coolant, that is, from the bottom to the top of the heat flux zone.

Figure 2. Zr rod surfaces after the deposition tests at 200°C in the deaerated ferric nitrate solution (A) and the hydrogen-dissolved ferric nitrate solution (B).

2.3 Deposition in a HT-HP Loop System

To evaluate the influence of hydrogen under the conditions similar to those of the PWRs cores, deposition tests was carried out using the HT-HP loop system under severe conditions in some respects, compared to those of the once-through system. First, a ferrous acetate solution was used as corrosion products instead of the ferric nitrate solution, since most of Fe ions exist as ferrous ions state in the primary system of PWRs. Second, temperature of reactor was increased from 200 to 280°C. Third, pressure of system was increased from 25 to 110 bar. Deposition behaviors in the HT-HP loop system were different greatly from ones in the once-through loop system. In the hydrogen-dissolved conditions, deposits amount considerably increased. However, the reason has not been proved yet.

3. Conclusion

Deposition tests performed in the HT-HP loop system offering conditions similar to those of the PWR cores, showed that dissolved-hydrogen considerably affect the generation amount of fuel CURD on the Zr surface. To elucidate the detailed pathway of hydrogen effect on the formation of the fuel CRUD, more extensive studies is needed.

REFERENCES

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