

## Considerations for Dissolved Hydrogen in Primary Water of a PWR

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### 1. Introduction

In water cooled nuclear power plants, water molecules can decompose by ionizing radiation in the core, producing several chemical species including oxygen, hydrogen peroxide, and hydrogen [1,2]. The oxidizing species such as oxygen and hydrogen peroxide have been known to accelerate corrosion of the structural materials. Therefore, excess hydrogen is intentionally added to the primary cooling water to suppress water radiolysis and thus maintain a reducing condition in pressurized water reactors (PWRs).

The dissolved hydrogen (DH) content is currently recommended to be controlled in a range of 25~50 cm<sup>3</sup>/kg H<sub>2</sub>O (STP) in the EPRI Guidelines [3]. There are several factors that should be considered in determining the optimal DH content. The main factors are as follows: The effect of DH on primary water stress corrosion crack initiation and growth, general corrosion, and fuel crud deposition. In this paper, the effect of DH on each factor is reviewed through literature data and our experimental results, and based on these data the optimal DH content is recommended.

### 2. Effects of Dissolved Hydrogen

In this section, we discuss how these factors are affected by DH content in operation conditions.

#### 2.1 Primary Water Stress Corrosion Crack Initiation and Growth

Hydrogen related researches have mainly been focused on the stress corrosion cracking of structural materials in the primary water (PWSCC). Many experimental studies have consistently reported that the crack growth rate (CGR) of Ni-based alloys at a given temperature varies with DH concentration, as shown in Fig. 1 [4]. That is, the CGR shows a maximum peak at a DH concentration approximately corresponding to the Ni/NiO phase transition [5-9], and decreases as DH concentrations deviate from the peak point. In addition, the CGR peak shifts to the higher DH concentration with increasing temperature [4]. However, the effect of DH on crack initiation time seems a little inconsistent or relatively small [10-13].

Up to now, the optimal range of DH concentration in PWRs has been determined in the view point of PWSCC of Ni-based alloys.

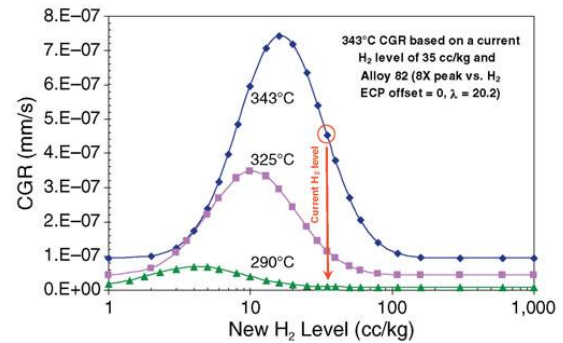


Fig. 1. Predicted effect of H<sub>2</sub> on the crack growth rate of nickel based alloys with an assumed “8X peak” at 290, 325, or 343°C. The noted circle and line represent a hypothetical case where the current H<sub>2</sub> level is 35 cc/kg.

#### 2.2 General Corrosion

Alloy 600 has been replaced with Alloy 690TT and no corrosion damage of Alloy 690TT including SCC has been reported since its application to PWRs. Therefore, we believe that the focus regarding DH concentration should be shifted from PWSCC to general corrosion. This is because the released corrosion products through general corrosion are the sources of radiation field and crud induced power shift.

Therefore, we investigated the effect of DH content (in the range of 5 to 100 cm<sup>3</sup>/kg H<sub>2</sub>O) on the general corrosion behavior and oxide films of Alloy 690TT in simulated primary water at 330°C [14]. With increasing DH, the structure of oxide film significantly changed and the corrosion rate decreased. At DH = 5 cm<sup>3</sup>/kg H<sub>2</sub>O, the oxide layer was thick, and consisted of outer Ni oxide layer and inner Cr<sub>2</sub>O<sub>3</sub> layer. Under the conditions of DH = 35 and 100 cm<sup>3</sup>/kg H<sub>2</sub>O, the oxide films grew thinner and composed of outer polyhedral spinel oxide particles such as NiCr<sub>2</sub>O<sub>4</sub> or NiCrFeO<sub>4</sub> and an intermediate metallic Ni-rich layer, with inner Cr<sub>2</sub>O<sub>3</sub> layer.

As shown in Fig. 2, the general corrosion rate significantly decreased by about 72% as DH concentration increased from 5 to 35 cm<sup>3</sup>/kg H<sub>2</sub>O. In the range of 35-65 cm<sup>3</sup>/kg H<sub>2</sub>O, the corrosion rate slightly decreased with increasing DH concentration. However, no further changes were observed in the range of 65-100 cm<sup>3</sup>/kg H<sub>2</sub>O. The calculated  $E_{corr}$  values of Alloy 690TT were also superimposed in Fig. 2. The  $E_{corr}$  of Alloy 690TT decreased with increasing DH concentration. The variation trend of  $E_{corr}$  is very similar to that of the general corrosion rate as a function of the DH concentration. In addition, the calculated potential-pH diagram of Ni in pure water at 330°C indicates that

under the condition of  $DH = 5$  and  $10 \text{ cm}^3/\text{kg H}_2\text{O}$ , Alloy 690TT locates in the NiO stable region, whereas at  $DH = 35$ - $100 \text{ cm}^3/\text{kg H}_2\text{O}$ , Alloy 690TT is in the Ni stable region. This result means that the control of dissolved hydrogen in the upper part of the  $25$ - $50 \text{ cm}^3/\text{kg}$  range or beyond the upper limit of  $50 \text{ cm}^3/\text{kg}$  is beneficial for mitigation of general corrosion.

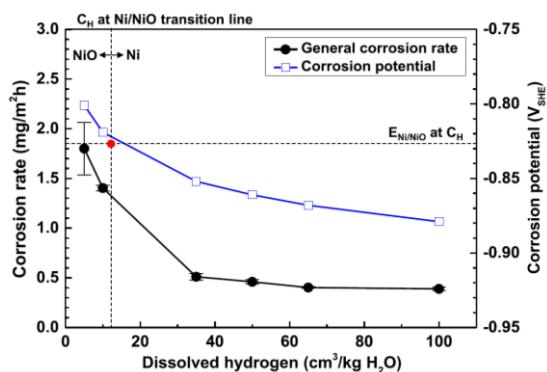


Fig. 2. General corrosion rates and corrosion potentials of Alloy 690TT in simulated primary water with various dissolved hydrogen concentrations at  $330^\circ\text{C}$ .

### 2.3 Crud Deposition

We investigated the effect of DH content (in the range of  $0$  to  $70 \text{ cm}^3/\text{kg H}_2\text{O}$ ) on the crud deposition behavior on ZIRLO™ fuel cladding under sub-cooled nucleate boiling conditions in simulated primary water at  $328^\circ\text{C}$ . Fig. 3 shows the amount of crud deposited on the fuel claddings with the three different DH contents. It is clear that DH has no meaningful effect on the amount of crud in the range of  $0$ - $70 \text{ cm}^3/\text{kg H}_2\text{O}$ .

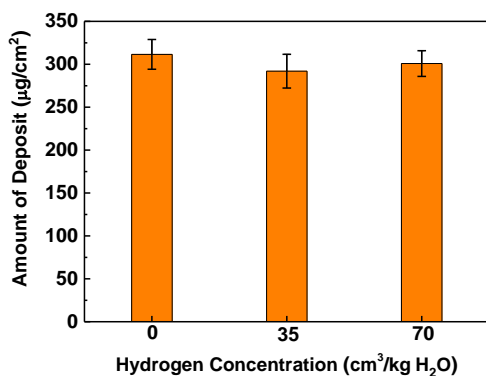


Fig. 3. Effect of dissolved hydrogen on the crud deposition behavior in simulated primary water at  $328^\circ\text{C}$ .

### 2.4 Integrated Effects of Dissolved Hydrogen on PWSCC, General Corrosion and Crud Deposition

We have briefly reviewed the effects of DH concentrations on PWSCC susceptibility, general corrosion, and crud deposition. All these effects can schematically be shown in Fig. 4. This indicates that the option of dissolved hydrogen in the upper part of the

$25$ - $50 \text{ cm}^3/\text{kg}$  range or beyond the upper limit of  $50 \text{ cm}^3/\text{kg}$  is beneficial for not only mitigation of PWSCC but also general corrosion and crud deposition.

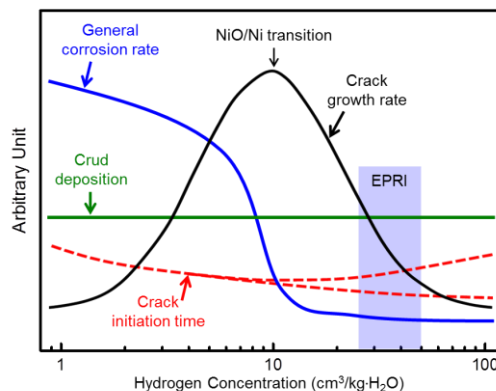


Fig. 4. Schematic of the effect of dissolved hydrogen concentrations on the PWSCC crack growth rate, crack initiation time, general corrosion rate of Ni-based alloys, and crud deposition on fuel cladding in primary water of PWRs.

## 3. Conclusions

To optimize the dissolved hydrogen content in primary water, the following factors should be considered: the effects of DH concentrations on PWSCC growth rate, initiation time, general corrosion of Ni-based alloys, and crud deposition on fuel assemblies. It is recommended that shifting to the upper limit of the  $25$ - $50 \text{ cm}^3/\text{kg}$  range or beyond the upper limit of  $50 \text{ cm}^3/\text{kg}$  is best option for not only PWSCC mitigation but also general corrosion and crud deposition.

## ACKNOWLEDGEMENTS

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