Prediction of coupled behavior of CRUD deposition and boron precipitation on the upper span fuel of pressurized water reactors

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1. Introduction

AOA (Axial Offset Anomaly) has been observed during the long-term and high-power operation of nuclear power plants, with a significant reduction of power in the upper span of the fuel assembly [1]. The distribution of AOA shows similarity to the distribution of CRUD (Corrosion-Related Unidentified deposit), which is a porous layer composed of several corrosion products in the PWR conditions[2]. The source of power shift is regarded as a boron hideout, which is boron precipitation within the CRUD deposits in the upper span of a fuel rod. It is necessary to predict the boron hideout by coupling into the CRUD deposition, so in this study, a new CRUD deposition and chemistry model was developed, by discussing the long-term behavior of CRUD and boron hideout for the assumed simulation case during 3 cycles of operation.

2. Method

The multi-physics within the CRUD deposits on the surface of the fuel rod in PWR conditions were developed in MATLAB conditions, as shown in Figure 1. The wick-boiling structure of the CRUD which leads to the different physical mechanisms of heat and mass conservation was implemented and coupled with each other. The chemistry within the CRUD deposits was divided into two sub-models. The first model includes the chemistry to determine the pH distribution within the CRUD by coupling into the mass transfer mechanism through the wick-boiling structure, such as water radiolysis and ionization as well as boron and lithium chemistry. The main characteristic of the chemistry is that the reactions were considered through the reaction kinetics, with corresponding kinetics data. The second sub-model predicted the solubility of the species within the CRUD deposits based on the simulated temperature and pH distribution, by being separated from the mass transfer mechanism, with the fact that almost reactions in the second sub-model are not sensitive to the pH distribution. The list of the chemical reactions is summarized as shown in Figure 2 and Figure 3.



Figure 1. Summary of the model developed in this study.

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Chemsitry in the first sub-model	
Water ionization	$e^- + H_2 O \rightarrow H^+ O H^-$
$H^+ + OH^- \leftrightarrow H_2O$	$e^- + HO_2^- \rightarrow O^- + OH^-$
Water radiolysis	$e^- + H^+ \rightarrow H$
$OH+OH\rightarrow H_2O_2$	$H + H \rightarrow H_2$
$OH+e^- \rightarrow OH^-$	$H^+ O_2^- \rightarrow HO_2^-$
$OH + H \rightarrow H_2O$	$H + HO_2 \rightarrow H_2O_2$
$OH + HO_2 \rightarrow O_2 + H_2O$	$H^+ H_2O_2 \rightarrow OH^+ H_2O$
$OH + O_2^- \rightarrow O_2 + OH^-$	$H+OH\rightarrow HO_2$
$OH + H_2O_2 \rightarrow HO_2 + H_2O$	$H+OH^- \rightarrow e^- + HO_2$
$OH+H_2 \rightarrow H+H_2O$	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$
$OH + OH^- \rightarrow H_2O + O^-$	$HO_2 + O_2^- \rightarrow HO_2^- + O_2$
$OH + HO_2^- \rightarrow HO_2 + OH^-$	$HO_2 \rightarrow H^+ + O_2^-$
$OH+O^- \rightarrow HO_2^-$	$H_2O_2 + OH^- \rightarrow HO_2^- + H_2O$
$O^- + H_2 O \rightarrow OH + OH^-$	$HO_2^- + H_2O \rightarrow H_2O_2 + OH^-$
$2\epsilon^- + 2H_2O \rightarrow H_2 + 2OH^-$	$H_2O_2 \rightarrow H_2O + O$
$e^- + H^+ H_2 O \rightarrow H_2 + OH^-$	$O + O \rightarrow O_2$
$e^- + O_2^- + H_2 O \rightarrow HO_2^- + OH^-$	$O_2^- + O_2^- + H^+ \rightarrow HO_2^- + O_2$
$e^- + HO_2 \rightarrow HO_2^-$	Boron-lithium reactions
$e^- + H_2O_2 \rightarrow OH + OH^-$	$B(OH)_3 + OH^- \rightarrow B(OH)_4^-$
$e^- + O_2 \rightarrow O_2^-$	$Li OH + H^+ \rightarrow Li^+ + H_2O$

Figure 2. List of chemical reactions used in the first sub-model to estimate the pH distribution within the CRUD deposits.

Chemistry in second sub-me	odel: for iron-nickel solubility
Precipitation of iron-nickel oxides	Soluble iron-nickel reaction
$Fe_3O_4 + 6H^+ + H^2 \leftrightarrow 3Fe^{2+} + 4H_2O$	$Fe^{2+} + H_2 O \rightarrow Fe(OH)^+ + H^+$
$NiO + 2H^+ \leftrightarrow Ni^{2+} + H_2O$	$Fe^{2+} + 2H_2O \leftrightarrow Fe(OH)_2 + 2H^+$
$Ni + 2H^+ \leftrightarrow Ni^{2+} + H_2$	$Fe^{2+} + 3H_2O \leftrightarrow Fe(OH)_3^- + 3H^+$
$NiFe_2O_4 + 6H^+ + H^2 \leftrightarrow Ni^{2+} + 2Fe^{2+} + 4H_2O$	$N_{\tilde{\iota}}^{2+} + H_2 O \mapsto N_{\tilde{\iota}} (OH)^+ + H^+$
	$Ni^{2+} + 2H_2O \leftrightarrow Ni(OH)_2 + 2H^+$
	$N_{\tilde{t}}^{2+} + H_2 O \leftrightarrow N_{\tilde{t}} (OH)^+ + H^+$
Chemistry in second sub-mod	lel: for boron-lithium solubility
Precipitation of boron-lithium	Soluble boron-lithium reaction
$LiBO_2 + H^+ + H_2O \rightarrow B(OH)_3 + Li^+$	$B(OH)_3 + OH^- \leftrightarrow B(OH)_4^-$
$Li_2B_1O_7 + 2H^+ + 5H_2O \mapsto 4B(OH)_3 + 2Li^+$	$2B(OH)_3 + OH^- \leftrightarrow B_2O(OH)_5^- + H_2O$
	$3B(OH)_3 + OH^- \leftrightarrow B_3O_3(OH)_4^- + 3H_2O$
	$3B(OH)_3 \leftrightarrow B_3O_3(OH)_3 + 3H_2O$
	$Li OH + H^+ \leftrightarrow Li^+ + H_2O$

Figure 3. List of chemical reactions used in the second sub-model to estimate the solubility of nickel, iron, boron, and lithium within the CRUD deposits.

The operation conditions such as cladding heat flux, bulk coolant temperature, the turbulent kinetic energy of the coolant, and bulk concentration of boron and lithium were selected from the Seabrook plants for Assembly G70 of Unit 1 during Cycle 5, at the fuel height of 3 m [3-5]. The history of the bulk boron and lithium concentration was shown in Figure 4 [4]. The simulation was conducted during 3 cycles with the assumption that the operation conditions above are repeated for each cycle.



Figure 4. History of boron and lithium concentration in the bulk coolant of Seabrook plant Unit 1 during Cycle 5 [4].

3. Results and discussion

Figure 5 shows the mass of CRUD deposits and mass of precipitated boron within the CRUD on the surface of the fuel rod at the height of 3 m, where the maximum CRUD deposits occur for the used case of the Seabrook plant. It is predicted that with the used CRUD conditions, the CRUD was deposited about 46.60 µm at the end of the first cycle, 59.42 µm at the end of the second cycle, and 64.45 μm at the end of the third cycle. The mass of CRUD deposits leads to the increase of concentrating tendency of soluble species within the wick-boiling structure, so higher thickness means easier boron precipitation. The model predicted that boron precipitation was not occurred during the first cycle, due to an insufficient amount of CRUD deposits. After the first cycle, however, boron started to be precipitated inside CRUD deposits, and at the end of the second cycle, all of the boron existed in the soluble phase. In the third cycle, otherwise, a significant amount of boron existed as a precipitated phase during the entire third cycle. Also, the figure shows that the CRUD thickness below 40 µm was not sufficient for boron precipitation in the first cycle.

4. Summary

The amount of CRUD deposits is strongly dependent on the operation conditions such as cladding heat flux and bulk coolant temperature, as well as the concentration of corrosion products. This leads to various ranges of CRUD deposition along with each condition. Change of the CRUD deposits is sensitive to the start point of boron precipitation, so additional study is necessary for validating the boron hideout.



Figure 5. Mass of CRUD deposit and precipitated boron within the CRUD during 3 cycles operation.

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