Applicability of Waterside Corrosion Models in Range of IFPE Database

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Abstract: Fuel rod cladding waterside corrosion is one of the phenomena that limit the life time of nuclear fuel. Corrosion performance depends on the cladding material properties as well as operating conditions during the irradiation of the fuel. As a function of temperature, power history, water chemistry, time, etc., waterside corrosion is of great concern in fuel performance evaluation, especially for high burnup fuels. This paper is dedicated to the study of the waterside corrosion phenomenon using the IFPE database by COPENIC, which is developed for the analysis of fuel rod behaviors in normal operation and transient conditions. Different models, MATPRO, FRAMATOME and EPRI models, for example, are adopted in the simulations. The results derived from the models are compared and the unconformities are analyzed. Based on the comparative analysis, reasonable models are chosen to simulate certain irradiated fuel rods. Our analyses indicate that potential affecting factors which are not considered in COPENIC code, such as water chemistry and alloy composition, should be responsible for discrepancies of certain rod predictions.

Key words: Waterside corrosion, model comparison, influencing factors, IFPE database.

1. Introduction

The corrosion rate of Zircaloy is one of the major controlling parameters for the in-core components of water reactor fuel elements [1]. This is a result of the evolution of PWRs to extend the average fuel rod discharge burnups, obtain higher coolant inlet temperatures to increase the nuclear plant thermal efficiency, and increase coolant pH and lithium concentration to reduce plant radiation levels due to corrosion products. Extension of the utilization period of reactor fuel, i.e., burnup extension, is being promoted worldwide for efficient use of natural resources, etc.. The tendency for higher discharge burn up of the fuel has therefore raised a large amount of analytical or global R & D work in this area [2]. To get a

better knowledge of corrosion mechanism, quite a few experiments have been performed recently, aiming at a variety of Zr alloys in different test conditions [3-5].

With the help of such experiments, the physical mechanisms controlling the corrosion rate of unirradiated Zircaloy become more and more understood, however, a large number of individual steps and their interactions remain unclear [6]. For in-reactor corrosion, even though the corrosion mechanism of Zircaloy is still not fully understood as yet, the factors determining its corrosion rate are the metal-oxide interface temperature, heat flux, metallurgical characteristics [7] of the cladding, alloy composition [8], fast neutron flux, water chemistry [9, 10] and the thermo-hydraulic condition of the coolant.

In this paper, four mature waterside corrosion models incorporated in COPENIC code are investigated. In view of the complexity of in-reactor corrosion phenomenon, dominant affecting factors are

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analyzed including metal-oxide interface temperature and fast neutron flux. Based on implemented post irradiation examination, the measurement data of oxide thickness from SuperRamp and US-PWR Project is employed to validate the capability of these models in predicting axial oxide distribution and average oxide thickness over the rods. Finally, selected models are applied to predict the measured thickness. The results indicate good agreements while significant discrepancies show up when it comes to several SuperRamp rods.

2. Experimental Details

2.1 US-PWR Project

The samples of this program were fabricated of Zircaloy-4 alloy with the purpose to demonstrate improved nuclear fuel utilization through more efficient fuel management and increased discharge burnup. The use of the 16×16 LTAs with Zircaloy-4 cladding in this program demonstrated the capability to achieve peak fuel rod average burnups of ~ 60 GWd/MTU. Both poolside (nondestructive) and hot cell (destructive) PIE (post irradiation examinations) of selected rods from the two LTAs were conducted. These examinations included rods irradiated for 3 and 5 cycles. In subsequent poolside examinations, items such as visual inspection, dimensional measurements, ECT (eddy current testing), and waterside corrosion thickness measurement were conducted, especially cladding examinations which included metallography, hydrogen concentration measurement and mechanical property testing.

The irradiation of two 16×16 LTAs was completed in a US commercial PWR. The irradiation of LTA D040 (including fuel rods TSQ002, TSQ022, TSQ053 and TSQ064) was extended through reactor cycle 6 to achieve a lead rod, axial average burnup of 58 GWd/MTU. Assembly D040 was irradiated during three irradiation cycles for a total exposure of 1,641 EFPD (effective full power days). At discharge, LTA D040 had achieved assembly average and lead-rod average

burnups of 52 and 58 GWd/MTU, respectively.

2.2 SuperRamp Project

The Project power ramped 28 individual PWR test fuel rods in a PWR subprogram. The PWR test fuel rods were all tested using a high ramp rate. All the rods underwent a thorough examination program, comprising characterization prior to the base irradiation, examinations interim to base and ramp irradiations and examinations after the ramp irradiation.

The PWR subprogram consisted of 6 groups of rods with variations in design and material parameters. The rods were base irradiated in a power reactor environment (the Kernkraftwerk Obrigheim or the reactor BR-3) at time average heat ratings mainly in the range of 14 kW/m to 26 kW/m to peak burnups in the range of 33 MWd/kgU to 45 MWd/kgU, and were subsequently ramp tested in the research reactor R2 at Studsvik, Sweden. The power history of PWR subprogram can be summarized as follows:

- Group PK1 and PK2: The rods all sustained the power ramping to power levels in the range of 410 W/cm to 490 W/cm and power changes in the range of 160 W/cm to 240 W/cm;
- Group PK4: The rods all sustained the power ramping to power levels in the range of 390 W/cm to 505 W/cm and power changes in the range of 140 W/cm to 250 W/cm;
- Group PK6: a failure threshold of RTL 440 W/cm, delta power 185W/cm, was established for these rods.

3. Corrosion Models

3.1 Zircaloy Corrosion Mechanism

Amongst several phenomena interfering with the corrosion of zircaloy, the corrosion rate has been considered to be controlled by the transport of oxygen through the zirconia scale, meaning that the velocity with which the reaction proceeds depends on the rate at which the atoms or ions can diffuse through the ZrO_2 -zircaloy matrix [11]. In general, the corrosion process starts at the waterside surface of Zircaloy

cladding with appearance of a lustrous, black oxide film. The film is very compact and protective and grows according to a simple cubic rate equation. This period is then followed by a transition to a friable gray or white oxide with a linear rate equation [12]. The first stage is called the pre-transition growth regime. Once the oxide reaches a critical thickness, the second period begins, which is called the post-transition growth regime. During the second stage, the corrosion rate sharply increases due to the formation of pores and cracks in the oxide film structure, allowing easier access of oxygen to the metal-oxide interface. The change from the first stage to second stage is called the first transition or breakaway in the oxidation rate.

The precise mechanism for this transition is not yet well understood. However, it has been argued that since zirconium has a rather high Pilling-Bedworth ratio (the ratio of the molar volumes of ZrO_2 and Zr) of about 1.56, stresses caused by volume change can lead to oxide scale cracks, which forms pathways for the oxidant. In addition, it has been found that a second transition in the oxidation rate of zircaloy takes place where an enhancement in the reaction rate occurs after a certain irradiation exposure. It can be argued that the presence of a fast neutron flux creates additional defects in the oxide layer which, after reaching a certain concentration, open up new diffusion pathways for oxygen and enhance the oxidation rate.

In fact, the corrosion process is a rather complex issue including several interfering phenomena, such as dissolution and precipitation of ZrO_2 [13], radiation-induced corrosion acceleration [14], thermal or radiation-induced transformations of ZrO_2 [15], acceleration of corrosion by hydrides precipitates and lithium addition in the water coolant [16].

3.2 Model Description

The oxidation process of Zircaloy-4 cladding can be estimated using semi-empirical correlations divided into pre-transition and post-transition kinetics. The corrosion rate equation in the pre-transition regime

is generally given by:

$$dX^3/dt = C_{pre} \cdot \exp(-E_{pre}/(R \cdot T)) \quad (1)$$

While the oxidation rate in the post-transition regime is given by:

$$dX/dt = C_{post} \cdot \exp(-E_{post}/(R \cdot T)) \quad (2)$$

where,

X = the oxide thickness (μm);

t = the time (day);

R = the universal gas constant (J/mol-K);

T = the metal-oxide interface temperature (K);

C_{pre} = the frequency factor for pre-transition regime ($\mu\text{m}^3/\text{day}$);

C_{post} = the frequency factor for the post-transition regime ($\mu\text{m}/\text{day}$);

E_{pre}, E_{post} = the activation energy for pre-transition and post-transition (J/mol).

Cladding oxidation during normal PWR operation occurs in two stages, depending on the oxide thickness and to some extent on the temperature of the oxide. For thin oxide, the rate of oxidation is controlled by the entire oxide layer. When the oxide layer becomes thicker, a change of the outer portion occurs; and further oxidation is controlled by the intact inner layer. The transition between stages is described in terms of thickness of the oxide layer at transition.

For the MATPRO corrosion model, the thickness of the oxide layer at transition is:

$$X_{tran} = 7.749 \times 10^{-6} \exp(-790/T) \quad (3)$$

In this paper, two FRAMATOME models are considered and the main distinction between them is the different values assigned to C_{pre} , C_{post} , E_{pre} and E_{post} . For convenience, we named one model F-1 and the other F-2. Take F-2 for example, it employs a transition thickness which expresses in a similar way:

$$X_{tran} = 280 \times 10^{-6} \exp(-2005/T) \quad (4)$$

Several PWR fuel rod corrosion models have been developed for interpreting Zircaloy-4 cladding oxide data and predicting cladding oxide thickness for fuel reload design applications. The EPRI/KWU/CE model developed by Garzarolli et al. [17] took a simple approach by attributing the entire in-reactor corrosion

enhancement to an effect of fast neutron flux on the protectiveness of the zirconium oxide. This approach has provided a useful tool for interpreting some fuel rod oxide data, but failed to produce enough accuracy in many high burnup cases, particularly in interpreting the axial oxide profiles [18].

The EPRI/KWU/CE model takes into account the influence of the fast neutron flux variation. The fast neutron flux, ϕ , imposed on PWR cladding is on the order 10^{13} to 10^{14} neutron/cm²-s. Garzarolli [17] reviewed evidence that high neutron flux affects either or both (a) the crystal structure of the oxide films on Zircaloy cladding or (b) the chemistry within pores in the oxide. Either change in the oxide was argued to be expected to accelerate the Zircaloy corrosion by an amount depending on the intensity of the neutron flux. Based on correlation of available, largely lower burnup data, Garzarolli proposed a corrosion predictor in which the frequency factor included a term dependent on fast neutron flux taken to the 0.24 power.

4. Results and Discussions

The MATPRO, FRAMATOME and EPRI/KWU/CE models are incorporated in the COPENIC code. To investigate their prediction creditability, simulations are implemented to test these models in two dominant aspects mentioned in Section 3, i.e., influences of metal-oxide interface temperature and fast neutron flux. Finally, corresponding prediction and measurement results, such as axial oxide distribution and average oxide thickness, are compared and appropriate model is selected for specific rod group.

4.1 Analyses of Separate Effects

4.1.1 Effect of Interface Temperature

The in-reactor corrosion model simulates the oxidation of Zircaloy in PWR environments and conditions with numbers of factors used to accelerate the oxidation rate. Factors such as the heat flux and its associated temperature gradient and the influence of fast neutron irradiation are included.

In power reactors, the heat flux through the oxide affects the temperature gradient and specifically the temperature of the metal-oxide interface. The interface temperature rises from the bulk fluid temperature not only across the fluid film thickness but also in the oxide, which causes the metal-oxide interface temperature to be significantly larger than the bulk fluid temperature. For this reason, the metal-oxide interface temperature may not be the same as the bulk fluid one. To investigate the influence of interface temperature on waterside corrosion, the developing trends of the four models mentioned above are presented in Figs. 1 and 2 with metal-oxide interface temperature set to 300 °C and 360 °C respectively (average fast neutron flux set to 0.84×10^{14} n/cm²-s).

As can be seen in Fig. 1, when the metal-oxide interface temperature is 300 °C, there is a significant transition between pre- and post-transition regimes for F-1 and EPRI/KWU/CE models. The oxide layer increases smoothly at initial stage and then develops in a linear relationship with time while the transition of MATPRO model is not obvious. However, prediction of F-2 model does not obey the same law. Noting the clues observed in Fig. 2, we can conjecture that the oxide thickness of MATPRO prediction may not exceed the transition thickness at 300 °C.

Fig. 2 shows the 360 °C condition, prediction of MATPRO model is not as conservative as the other three models. F-1, F-2 and EPRI/KWU/CE models predict that the oxide thickness increases rapidly

Fig. 1 Prediction of corrosion models with the metal-oxide interface temperature set to 300 °C.

Fig. 2 Prediction of corrosion models with the metal-oxide interface temperature set to 360 °C.

during their post-transition regimes, and stabilizes at 150 μm which is set as the maximum oxide layer thickness. Relatively, EPRI/KWU/CE model is the most conservative one as shown in Fig. 2. Descending from the same company, the transition of F-1 model begins earlier than that of F-2.

4.1.2 Effect of Fast Neutron Flux

As described in Section 3, fast neutron flux is another affecting factor which is recommended to take into consideration in corrosion model development. In this section the effect of fast neutron flux is investigated by introducing two flux levels, i.e., $5 \times 10^{13} \text{ n/cm}^2\text{-s}$ and $1 \times 10^{14} \text{ n/cm}^2\text{-s}$ respectively (Figs. 3 and 4).

Comparing Fig. 3 with Fig. 4, MATPRO, F-1 and F-2 models have no response to the variation of fast neutron flux while the oxide layer prediction of EPRI/KWU/CE model is slightly thicker under higher flux level with the maximum increment of less than 40 μm . Comparison between Figs. 2 and 4 indicate that the corrosion developing trend changes a little. A flux dependence is believed to contribute to acceleration of Zircaloy cladding corrosion, but not to be the only effect responsible for the acceleration. At least for EPRI/KWU/CE model, the influence of fast neutron flux still lags behind metal-oxide interface temperature.

4.2 Model Verification

4.2.1 Axial Oxide Distribution

It is well known that a large variability in zircaloy oxide layer thickness is obtained not only from one

Fig. 3 Prediction of corrosion models with the fast neutron flux set to $5 \times 10^{13} \text{ n/cm}^2\text{-s}$.

Fig. 4 Prediction of corrosion models with the fast neutron flux set to $1 \times 10^{14} \text{ n/cm}^2\text{-s}$.

reactor to another but also even within the same reactor with rods manufactured by the same process and experiencing similar irradiation histories [1, 19-22]. Part of the variability can be attributed to fabrication variations; the rest is due to thermal-hydraulic conditions or water chemistry differences.

In present analyses, US-PWR rods are used to validate the prediction capability of selected corrosion models because the SuperRamp rods are too short (less than 400 mm) to fully exhibit axial distribution of the oxide layer thickness.

The cladding materials were standard zircaloy-4 and no other detailed information was provided from the project documents. During poolside and hot cell examinations, eddy current and metallographic tests are employed to measure the cladding oxide thickness. The results of the oxide layer thickness measurements as a function of axial rod position at a given end of operation

cycle are compared with those of simulations. In these simulations the fuel rod has been divided into 25 axial segments and the results are shown in Figs. 5 and 6.

Taking TSQ002 and TSQ064 for instance, the oxide layer thickness increases along the elevation and reaches maximum at about 3,400 mm. Note that the corrosion rate-controlling temperature of the metal-oxide interface varies along the length of a PWR cladding tube. And the temperature at every axial point generally increases (depending on power history) with hot operating time because of the relatively high heat flux acting on the increases of the insulating oxide thickness.

Both of the figures indicate that F-1 model predicts the metallography result well while the F-2 model prediction is consistent with the ECT one. EPRI/KWU/CE model is a little bit over-predicted, namely more conservative. By comparing the model predictions with measurement results, we find that the

Fig. 5 Measurements versus model predictions: axial oxide layer thickness distribution of fuel rod TSQ002.

Fig. 6 Measurements versus model predictions: axial oxide layer thickness distribution of fuel rod TSQ064.

MATPRO model failed to track the changes of axial oxide layer thickness at least in these simulations.

4.2.2 Model Prediction Validity

Every model has its own focus on specific aspects, as for waterside corrosion models, mechanisms of different effects are considered and multifarious databases are used to calibrate the developed model. Using these databases, changes in oxidation due to in-pile effects are incorporated into the present model with an enhancement factor or empirical constants. Thus it is very essential to test these models with as much experimental data as possible.

Four sets of model prediction results are plotted against the measurement data as a scatter diagram (Fig. 7). All these models under-predict the oxide thickness. Perhaps this is because the other affecting factors, such as water chemistry and metallurgical characteristics of the cladding, become indispensable in simulations under specific operating conditions of PK rods.

As shown in Fig. 8, the oxide thickness is measured by two disparate techniques. The ECT measurement results are thicker than that of metallography. It is hard to tell what the accurate oxide thickness is and thus we regard the average as a standard of reference. Among the results, the prediction of F-1 model fits the measurement data best and then follows the F-2 model.

4.3 Application of COPENIC to Waterside Corrosion

Based on the investigation mentioned above, detailed fabrication data and power history are adopted as parameters prepared in input files. As a result of model selections, reasonable corrosion models are applied for SuperRamp and US-PWR Project. The results illustrated in Fig. 9 show a good agreement with the measurement data. It should be noted that there is only three ECT measurement data, this is because the data for fuel rod TSQ053 is unavailable in corresponding project documents.

Distinct from US-PWR project, the measurement data from SuperRamp Project is not well predicted by all four models (Fig. 7). Thus we selected a comparatively accurate model during the process of

Fig. 7 A comparison of the model predictions with measurement data from SuperRamp project.

Fig. 8 A comparison of the model predictions with measurement data from US-PWR project.

Fig. 9 F-1 model predicted versus measured waterside corrosion for fuel rods from US-PWR project.

simulation, and the comparison between predicted and measured data is shown in Fig. 10. Three deviating data points indicate there is a considerable discrepancy and

Fig. 10 EPRI/KWU/CE model predicted versus measured waterside corrosion for fuel rods from SuperRamp project.

the extent of the under-prediction is unacceptable. This is probably caused by neglecting other uncertain influences which includes operating conditions (water chemistry for instance), corrosion hydrogen radial thermal redistribution, metallurgical characteristics of the cladding, alloy composition, etc. in the code. However, it is excusable to focus on the dominant affecting factors with proper consideration of other ones. Models developed in this way sometimes show good anticipation but not always succeed in certain prediction.

5. Conclusions

Four waterside corrosion models are investigated in this paper under the framework of COPENIC code. The corrosion mechanism is reviewed and crucial equations are described. By comparing the models, two affecting factors, namely metal-oxide interface temperature and fast neutron flux, are believed to be dominant and different developing trends of corrosion oxide layer thickness versus time are analyzed. Based on the investigation, we reconfirmed that only the EPRI/KWU/CE model considers the influence of fast neutron flux variation.

Subsequently, axial oxide layer thickness distribution and average oxide layer thickness of the fuel rods from SuperRamp and US-PWR project are employed to validate these four corrosion models. During the validation of axial oxide layer thickness distribution

which refers to US-PWR data, F-1 model predicts the metallography measurement results well and the prediction of F-2 model is consistent with the ECT measurement results. As for the prediction of average oxide layer thickness, the US-PWR results are well predicted by F-1 model while all of the models failed to predict certain SuperRamp rods. This is probably caused by neglecting potential affecting factors in the code, such as water chemistry and alloy composition.

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