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MODELING THE WATER SIDE CORROSION AND HYDROGEN PICKUP OF THE VVER 1000 FUEL CLAD

by

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Zirconium alloys, are usually used as fuel cladding materials in VVER (water-cooled, water-moderated energy reactor) type reactors, mainly, due to their low neutron absorption cross-section, desirable mechanical properties, and good corrosion resistance under reactor operating conditions. During exposure to water at high temperature, water reacts with zirconium alloys, which results in the production of an oxide layer. The entire area of corrosion along with the accompanying absorption of hydrogen in the zirconium metal matrix has attracted a lot of attention when the performance of the core components as well as the operation of the reactor is emphasized. The growth of the zirconium oxide layer plays a destructive role in decreasing thermal efficiency of the reactor by restricting the inlet temperature and chemical properties of the coolant. The present study aimed to develop a computer code to predict long-term water side corrosion weight gain, oxide thickness and determine the concentration of absorbed hydrogen in VVER-1000 reactors during normal operating conditions. The proposed model can be utilized to estimate the pre-transition and post-transition corrosion weight gain and the oxide thickness in operating conditions.

Key words: fuel cladding, corrosion, zirconium oxide, hydrogen pickup

INTRODUCTION

Corrosion is strictly the process that results in the deterioration of the performance of a material, the result of which is corrosion damage. Corrosion may be defined as: a physicochemical interaction leading to a significant deterioration of the functional properties of either a material, or the environment with which it has interacted, or both of these [1]. The production of almost all metals (and engineering components made of metals) involves adding energy to the system. As a result of this uphill thermodynamic struggle, the metal has a strong driving force to return to its native, low energy oxide state. This return process to the native oxide state is what we call corrosion and it is inevitable [2]. Based on this explanation, metal can never be completely protected from corrosion as long as it is regarded as corrosion to an acceptable level. Zirconium alloys are widely used for fuel cladding, pressure tubes, fuel channels (boxes), and fuel spacer grids in almost all water-cooled reactors, including light water reactors such as the pressurized water reactor (PWR), VVER-1000 and the boiling water reactor (BWR). The corrosion of Zircaloy cladding in VVER-1000 has been more emphasized because of high fuel discharge

burnup to reduce fuel cycle costs, high coolant inlet temperature to increase plant thermal efficiency, and increase of the coolant pH and lithium concentration in order to reduce plant radiation levels. Nuclear fuels are not directly inserted into the coolant while they are always used as covered. The fuel cladding keeps the coolant isolated from the fuel, which protects fuel and prevents the expansion of fission products into the surrounding environment. In addition, this cladding is considered as a structural support of fuel which contributes to heat transfer. Like the fuel, the cladding material should possess good thermal and mechanical properties and it should be chemically stable over the interaction with the fuel and material of the environment. The zirconium alloy is oxidized on contact with primary coolant circuit water. Zirconium alloys corrode in high temperature water to form zirconium dioxide. The corrosion rate of zirconium alloys is one of the major controlling parameters for the design of in-core components of water reactor fuel elements [3].

Therefore, oxidation is very important in reactor operation so it is desirable to be able to understand and predict the oxidation process and, if possible, to slow it down or prevent it. Further, zirconium has a low absorption neutron cross-section, high melting point, good mechanical properties, and high corrosion resis-

tance to water. These properties make zirconium a superior material as a fuel cladding for reactors. The mechanical properties of zirconium and its corrosion resistance can be improved by alloying it with a small amount of tin, iron, chromium and nickel. The zirconium alloy E110 (Zr + 1 % Nb) has been used in the construction of fuel rods cladding in the Bushehr nuclear power plant [4]. The use of this type of alloy in the fuel cladding has increased fuel burnup, as well as the life cycle of fuel efficiency. Due to the significance of zirconium oxidation, many attempts have been made to examine the oxide layer in order to decrease its growth, and calculate its thickness in the operating conditions of a reactor. To this aim different models have been presented to design and evaluate fuel cladding operating. As in the developed codes of the Nuclear Regulatory Commission, the EPRI Model (developed by the Electric Power Research Institute) is used as the most famous model in order to calculate the growth rate of the oxide layer, the aforementioned model is used in the present research, which has exhibited desirable results [5]. The formation of the oxide layer on zirconium metal does not have any consequences on the behavior of the fuel rod although it may increase hydrogen diffusion into the zirconium metal which has a negative impact on the fuel rod. Zirconium metal has a very low solubility for hydrogen and once the solubility limit is exceeded, the hydrogen precipitates as a zirconium hydride phase. As a result, the following effects have been reported (although not all confirmed) to occur in the cladding: hydrogen embrittlement due to excess hydrogen or its localization into a blister or rim [6, 7] loss of fracture toughness; delayed hydride cracking (DHC), and acceleration of corrosion and of irradiation growth. Hydrogen embrittlement impacts the mechanical resistance of the zircaloy cladding to failure. The ductility reduction due to hydrogen embrittlement is dependent on the volume fraction of hydride precipitates in the cladding and their degree of agglomeration [8, 9].

$$Zr(H.sln^1) + H_2 \rightarrow ZrH_{1.6} \text{ or } ZrH_2 \qquad (1)$$

ZIRCALOY OXIDATION MECHANISM

In general, the corrosion process of Zircaloy starts with the formation of an adherent, thin, black oxide film and grows according to a simple cubic rate equation [10]. It is then followed by a transition to a gray or white oxide with a linear rate eq. [10]. The first period is called the pre-transition growth regime. Once the oxide reaches a critical thickness (transition or breakaway), the second period begins, which is called the post-transition growth regime, where 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 oxide-metal interface [10]. A
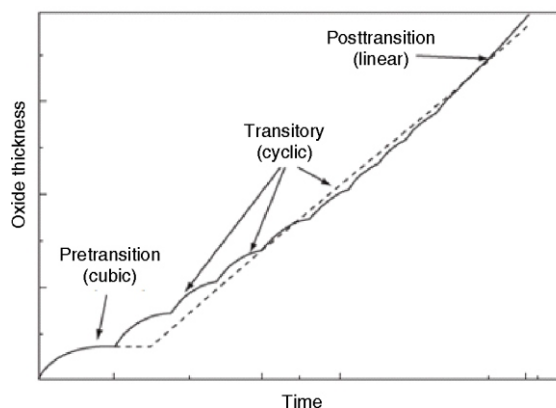
Figure 1. Schematic representation of the zirconium alloy corrosion showing the pre-transition, transitory, and post-transition regions [7]

close inspection of the oxide shows a variety of structures, depending upon the temperature attained and the oxygen concentration [10]. A schematic representation of this pre-transition and post-transition kinetics is shown in fig. 1 as the dashed lines. Also shown in this graph is the more recent view that three stages can be discriminated for zirconium alloy corrosion processes [7].

(1) The early pre-transition regime, characterized by the formation of a thin, black, tightly adherent corrosion film that grows thicker in accordance with a nearly cubic rate law,

(2) The intermediate stage that lies between the pre-and post-transition stages. As initially shown by Bryner [11] this region appears to comprise a series of successive cubic curves, similar to the initial cubic kinetic curve. This linear rate results from the superposition of various regions of the oxide layer following the pre-transition growth rate but slightly out of phase with each other, and

(3) The linear post-transition kinetic regime.

CORROSION AND HYDROGEN PICKUP MODEL

The VVER-1000 reactor is a 1000 MW PWR type reactor, with uranium dioxide fuel with light water as a coolant and moderator and consists of 163 fuel assemblies with 311 fuel rods. The fuel clad was manufactured of zirconium alloy E110 (Zr + 1 % Nb). Some main characteristics of this reactor are presented in tab. 1 [4]. The fuel rods in a VVER assembly are arranged on a triangular lattice and it differs from other PWR with a square lattice which affects the thermohydraulics and ultimately corrosion calculations. To address this issue, we have developed a code that specifically describes the Bushehr reactor during the working cycles

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[1] The designator (sln) is used for the substance in the solution without specifying the actual equilibrium composition of the substance in the solution

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Table 1. Main characteristics of the VVER-1000 reactor

No.	Characteristic	Value
1	Reactor nominal thermal power [MW]	3000
2	Coolant pressure at the core outlet [MPa]	15.7
3	Coolant temperature at the reactor outlet [°C]	321
4	Coolant heating in the reactor [°C]	30
5	Pressure differential in the reactor [MPa]	0.381
6	Number of loops [pcs.]	4
7	Fuel assembly geometry	Hexahedral prism
8	Helium pressure under fuel rod cladding [MPa]	2.0 0.25
9	Outside diameter of cladding, mm, nominal	9.1
10	Inside diameter of cladding [mm], nominal	7.73
11	Outside diameter of pellet [mm], nominal	7.57
12	Diameter of pellet central hole [mm], nominal	1.5

of the thermohydraulics and corrosion calculations which yields a more accurate modelling.

The single-channel thermohydraulic model assumes a closed sub-channel and calculates the coolant temperature and clad surface temperature at the axial mid-plane of each chosen axial segment of a fuel rod. Sub-channel geometry, coolant inlet temperature, coolant inlet mass flow and rod power as a function of burn-up (or time) are regarded as the inputs for the proposed model. Coolant flow is from the bottom to the top at an axial position of the rod. The fuel rod with maximum power generation is called the *hot fuel rod* and the sub-channel related to the hot fuel rod is characterized as a *hot sub-channel* in the hot channel. Maximum enthalpy rise does not exceed the specified values and

analysis is extended to the hot rod in the hot channel of the reactor core in order to demonstrate the thermohydraulic limits in the reactor core such as maximum cladding and fuel temperatures. Then, the hot channel is assumed in the analysis for calculating the oxidation layer. A schematic process of corrosion modeling of the VVER-1000 fuel clad is shown in fig. 2.

In addition, the EPRI Model is selected to calculate the corrosion rate in the VVER-1000 fuel clad. In this model, the cubic rate law for corrosion-layer thickness as a function of time is utilized to achieve a transition thickness of 2.0 μm [12].

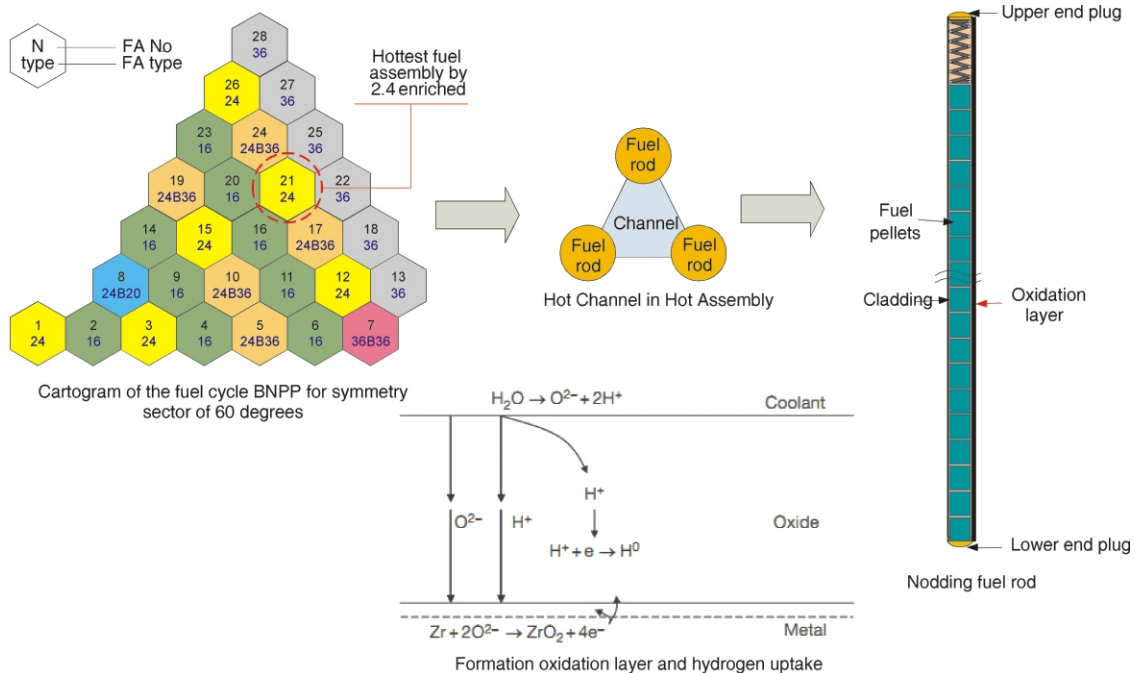$$\frac{d(s^2)}{dt} \quad \frac{A}{s^2} \exp \quad \frac{Q_1}{RT_1} \tag{2}$$

where S [m] is the oxide thickness, t [day] – the time, A [m^{3}d^{-1}] – the constant value 6.3 10^9, Q_1 – the activation energy with constant value 32289 [cal mol^{-1}], R [cal mol^{-1} K^{-1}] – the gas constant value 1.98, T [K] – the metal-oxide interface temperature.

This equation is integrated in order to obtain the following equation, regardless of the feedback between the oxide layer thickness and oxide metal interface temperature

$$s_{i\,1} \quad 3A \exp \quad \frac{Q_1}{RT_1} \ (t_{i\,1} \quad t_i) \quad s_i^3 \quad {}^{\frac{1}{3}} \tag{3}$$

After attaining the transition thickness, a flux-dependent linear rate law is applied, with the constant rate, which is considered as an Arrhenius function of the oxide-metal interface temperature

$$\frac{ds}{dt} \quad \{C_0 \quad U(M\phi)^P\} \exp \quad \frac{Q_2}{RT_1} \tag{4}$$

Figure 2. Schematic presentation of the corrosion modeling of the VVER-1000 clad
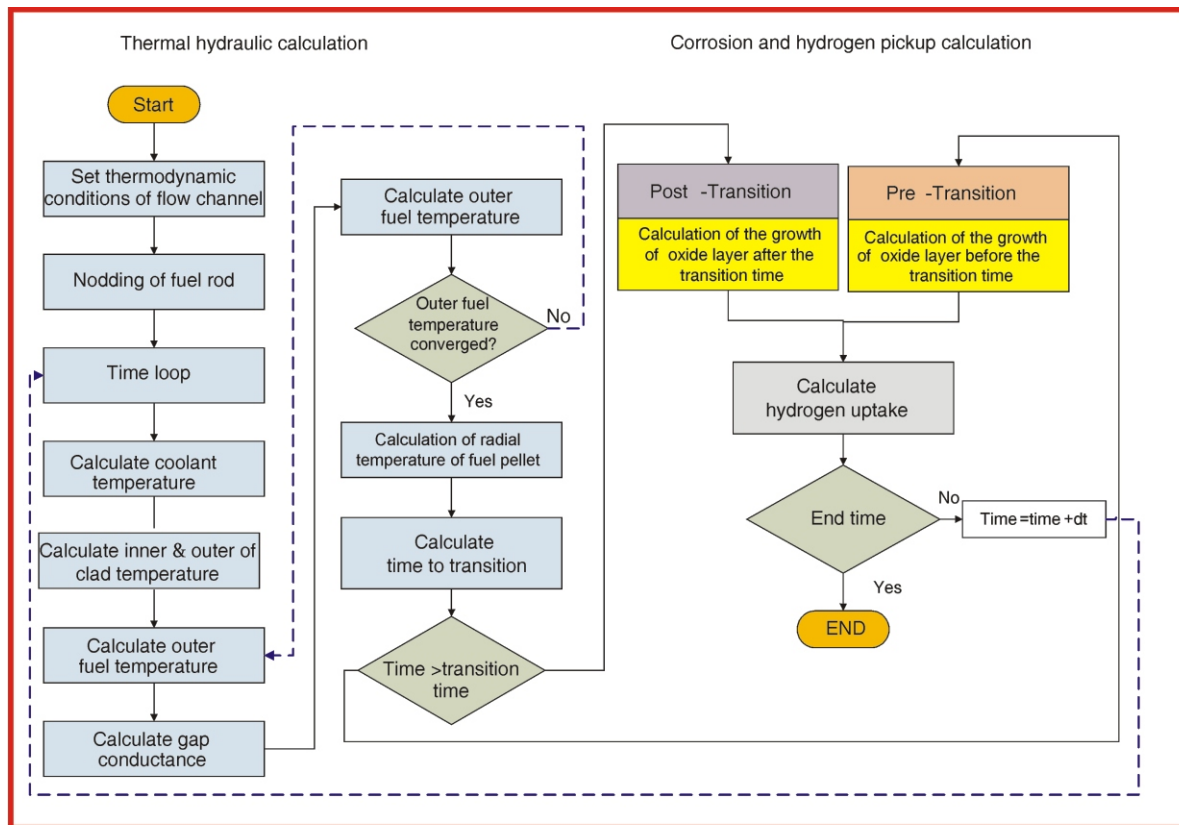
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Figure 3. Computer simulation flowchart

$$\{C_0 \quad U(M\Phi)^{0.24}\} \quad k_0$$
$$11863 \quad 3.5 \; 10^4 \, (1.91 \; 10^{-15} \Phi)^{0.24} \; [\mathrm{g(cm^2 d)}^{-1}] \quad (5)$$

Because there is significant feedback between the oxide-layer thickness and oxide-metal interface temperature, the oxide thickness is converted to weight gain, and the approximate integral solution from Garzarolli, *et al.* [12] is used. This solution has the form [13]

$$\Delta w_{i+1} \quad \Delta w_i \quad \frac{R\lambda T_0^2}{\gamma Q_2 q}$$

$$\ln \; 1 \quad \frac{\gamma Q_2 q}{R\lambda T_0^2} \, k_0 \exp \; \frac{Q_2}{RT_0}$$

$$\exp \; \frac{\gamma Q_2 q}{R\lambda T_0^2} (\Delta w_i) \; (t_{i\,1} \quad t_i) \qquad (6)$$

where i, $i + 1$ refers to (ends of) previous and current time step, $\gamma = 0.6789$ [cm^{3}g^{-1}], s is the oxide thickness [m], λ – the oxide thermal conductivity [Wcm^{-1}K], Δw – the weight gain [gcm^{-2}], $Q_2 = 27354$ [calmol^{-1}], $R =$ = 1.98 [cal mol^{-1} K], q'' – heat flux [Wcm^{-2}], T_o – the oxide-to-water interface temperature [K], – the fast neutron flux ($E > 1$ MeV) (1 cm^{-2}s^{-1}), k_0 – the 11863 + + 3.5 10^4(1.91 $10^{-15}\varphi$)$^{0.24}$ [gcm^{-2} d^{-1}], t – the time [d]

The fraction of the hydrogen liberated by the metal-water corrosion reaction that is absorbed locally by the cladding is called the pickup fraction. For PWR conditions, a constant hydrogen pickup fraction has been found to be applicable [13].

As for the Zr + 1 % Nb (E110) cladding material used in VVER fuel rods, the hydrogen pick up mass is calculated by

$$m_{\mathrm{H}} \quad \rho_{\mathrm{ZrO_2}} \quad V_{\mathrm{ZrO_2}} \quad F \quad \frac{1\,\mathrm{molZrO_2}}{123\,\mathrm{grZrO_2}} \; \frac{4\,\mathrm{molH}}{1\,\mathrm{molZrO_2}} \; \frac{1\,\mathrm{grH}}{1\,\mathrm{molH}}$$
$$(7)$$

then
$$H_{\mathrm{conc}}(\mathrm{ppm}) \quad \frac{m_{\mathrm{H}}}{m_{\mathrm{Zr}}} \; 10^6 \quad 6.5 \frac{F \; 5.8 \; D_{\mathrm{co}} \; t}{6.5 \; (D_{co}^2 \quad D_{ci}^1)} \; \frac{16}{123} \; 10^6$$
$$(8)$$

where H_{conc} [ppm] is the hydrogen concentration, D_{co} [m] – the outside cladding diameter, D_{ci} [m] – the inside cladding diameter, t [m] – the oxide layer thickness, and F – the hydrogen pickup fraction.

The pickup fraction of 0.175 is used. The computer simulation flowchart is illustrated in fig. 3.

RESULTS AND DISCUSSION

The following curves (see fig. 4 and fig. 5) indicate the temperature changes of the inlet fluid of the reactor core and the power of the reactor during the first cycle.

In this section, the modeling results by code are presented. The distributions introduced in the FSAR (Final Safety Analysis Report) are used to apply for the axial power distribution in the hottest fuel rod. Fig-
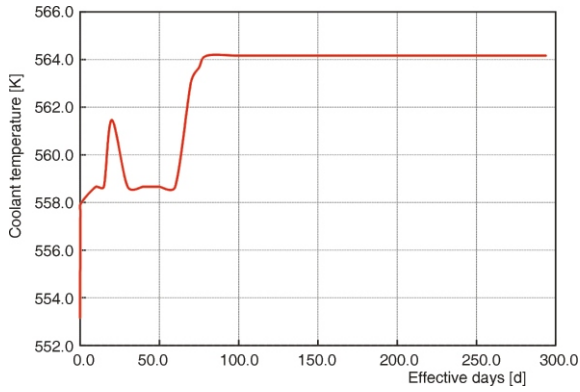
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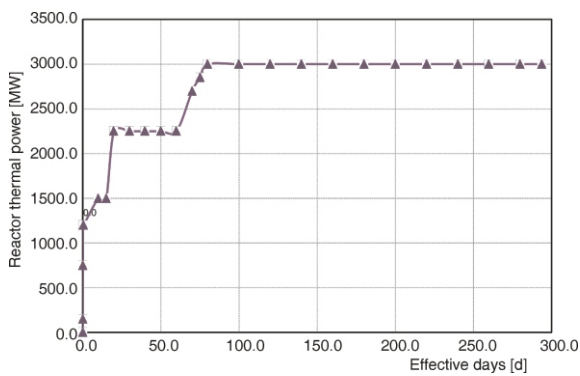**Figure 4. Coolant temperature in the first cycle of BNPP [4]**

Figure 5. Thermal power in the first cycle of BNPP [4]

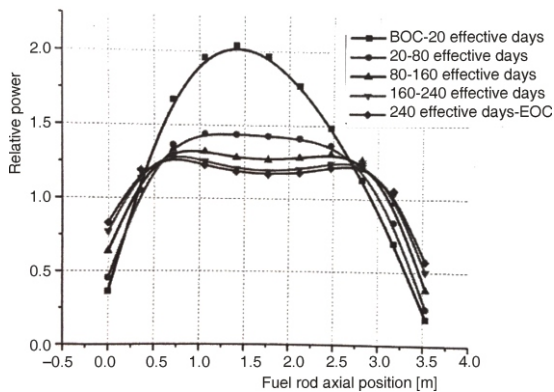**Figure 6. Relative power distributions by the hot fuel rod in the first cycle of BNPP**

Figure 7. Coolant temperature in the different effective days
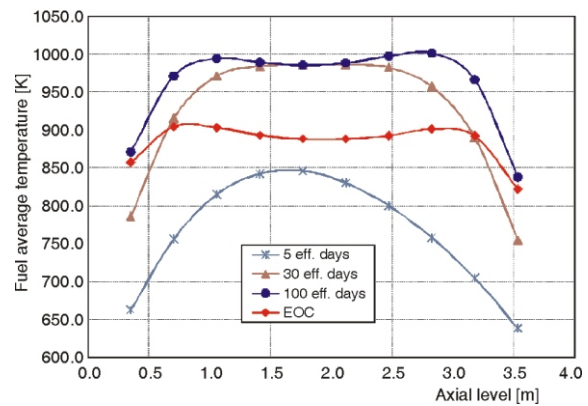
Figure 8. Average hot fuel rod temperature in the different effective days

Figure 9. Average fuel cladding temperature in the different effective days

ure 6 illustrates the curve of the axial power distribution in the hottest fuel rod at different time periods of the reactor operation, upon which the amount of fuel cladding oxidation is calculated [4]. Due to the fuel burnup at the core of the reactor, the cosine curve of relative power turns into the flat form after 20 days, along with a gradual fall at the edges. The inlet coolant temperature versus the axial level in the different effective days is shown fig. 7.

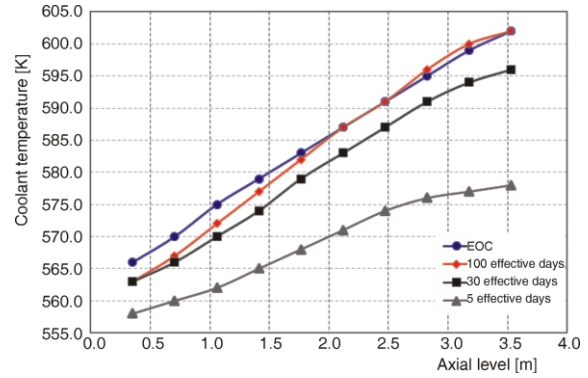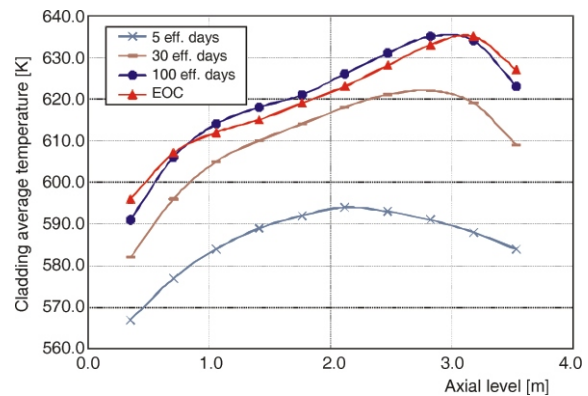In addition, as show in fig. 8 and fig. 9, maximum relative power is transferred from the middle

area of the core to the lower heights of the core. Due to some changes in the power level during the cycle, the average fuel temperature and cladding are affected by these changes in a similar manner in order to produce thermal power. In this regard, a lot of attempts have been made to include all the data corresponding to the FSAR reference. Further, an increase in the power of the reactor core and the temperature of inlet water to the core, results in changing the temperature of the fuel rod during the operation of this reactor until the hun-
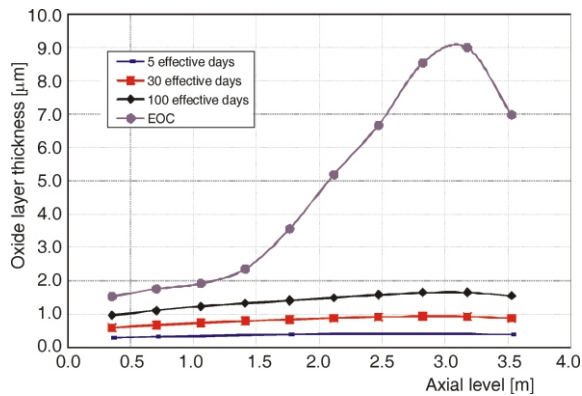
Figure 10. Axial oxidation layer in the different effective days
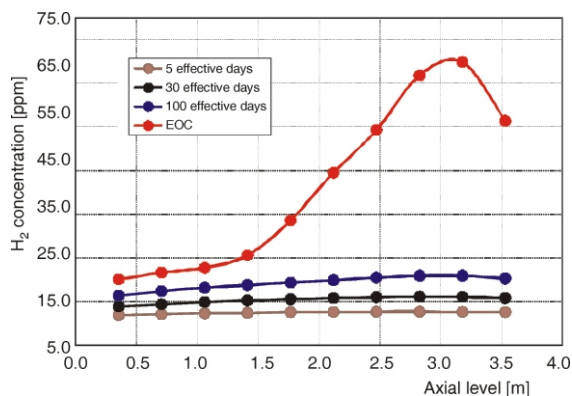
Figure 11. Axial hydrogen concentration in the different effective days

dredth day. Then, the power and the temperature of the inlet fluid to the core as two important factors in changing the axial curve of the fluid temperature are stable over the fuel rod until the end of the cycle. Generally, the oxide layer on the cladding surface grows due to the temperature and time required for the oxidation reaction. Therefore, the growth of the oxide layer thickness increases at the higher end of the length of the fuel rod (fig. 10). As illustrated in fig. 9, the growth of the oxide layer on the cladding surface results in increasing the average temperature. In addition, the growth of the oxide layer becomes parabolic before 2 μm while it changes linearly. The maximum thickness of the oxide layer in the fuel rod cladding during the reactor operation cycle is about 9 μm, which is less than 60 μm in the modeled value mentioned in the FSAR. Figure 11 illustrates the amount of absorbed hydrogen in the cladding by the reaction of zirconium with water and its variation with the operating time. Further, the amount of hydrogen concentration in the fuel rod cladding increases by increasing the oxide layer thickness on the cladding. As shown, the concentration of 25 ppm^2 (mgL^{-1}) in growth has a parabolic curve, which increased linearly. This type of alloy (E119), used in the fuel cladding in the Bushehr reactor, has a high resistance to oxidation in high burnup along with a low hydrogen absorption.

CONCLUSION

In the VVER reactor due to the use of the Zr + 1 % Nb alloy (E110) and different coolant chemistry, which results in low hydrogen pick up, there is normally no acceleration of the corrosion process. The maximum oxide thickness criterion used today by most regulators including the NRC for most PWR applications is 100 μm [14]. The hydrogen content of zirconium alloys must be limited to prevent brittle mechanical failures [14]. The present study aimed to develop a code for oxidation and hydrogen uptake of the fuel rod in the Bushehr nuclear power plant based on the power distribution of the fuel rod. Based on the results, hydrogen uptake is similar to the power distribution according to the manner of oxidation power distribution. Hence a good agreement has been observed and this confirms that the correct modeling of the reactor is accomplished using the code anticipated expectations are realized. Finally, the oxidation value is 9 μm, (about 0.013 % of the thickness in the fuel rod cladding), which is considerably lower than the maximum limit of the model, (18 % of the thickness in the fuel rod cladding).

AUTHORS' CONTRIBUTIONS

The manuscript was written by L. Ramezani, and scientific supervision was done by M. Mansouri and M. Rahgoshay.

REFERENCES

[1] ***, ISO 8044-1986, Corrosion of Metals and Alloys – Basic Terms and Definitions
[2] Shaw, B. A., Kelly, R. G., What is Corrosion?, *Interface-Electrochemical Society 15* (2006), 1, pp. 24-27
[3] Lefebvre, F., Lemaignan, C., Irradiation Effects on Corrosion of Zirconium Alloy Claddings, *J. Nucl Mater, 248* (1997), pp. 268-274
[4] ***, NPP Bushehr Unit 1, Final Safety Analysis Report Chapter 4, October, 2003
[5] ***, PNNL-19418, Vol. 1 Rev. 2 FRAPCON-4.0: A Computer Code for the Calculation of Steady-State, Thermal-Mechanical Behavior of Oxide Fuel Rods for High Burnup, September 2015
[6] Pierron, O. N., *et al.*, The Influence of Hydride Blisters on the Fracture of Zircaloy-4, *J Nuc Mater, 322* (2003), 1, pp. 21-35
[7] Allen, T. R., *et al.*, 5.03 Corrosion of Zirconium Alloys, *Comprehensive Nuclear Materials, 5* (2012), pp. 49-68
[8] Raynaud, P., *et al.*, Fracture Toughness of Hydrided Zircaloy-4 Sheet Under Through-Thickness Crack Growth Conditions, In Zirconium in the Nuclear Industry, *Journal of ASTM International, 5* (2008), 1, pp. 1-15
[9] Daum, R. S., *et al.*, On the Embrittlement of Zircaloy-4 under RIA-relevant Conditions, In Zirconium in the Nuclear Industry: Thirteenth International Symposium, ASTM International, 2002
[10] Almarshad, A. I. A., Klein, A. C., A model for water-side Oxidation of Zircaloy Fuel Cladding in pressur-

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L. Ramezani, *et al*.: Modeling the Water Side Corrosion and Hydrogen Pickup of ...
Nuclear Technology & Radiation Protection: Year 2018, Vol. 33, No. 4, pp. 334-340

ized Water Reactors, *J Nuc Mater, 183* (1991), 3, pp.186-194

[11] Bryner, J. S., The Cyclic Nature of Corrosion of Zircaloy-4 in 633 K Water, *J Nuc Mater, 82* (1979), 1, pp. 84-101

[12] Garzarolli, F., *et al*., Review of PWR Fuel Rod Water-side Corrosion Behavior. EPRI NP-2789, Project 1250 Final Report, Electric Power Research Institute, Palo Alto, Cal., USA

[13] Berna, G.A., *et al*., FRAPCON-3: A Computer Code for the Calculation of Steady-State, Thermal-Mechanical Behavior of Oxide Fuel Rods for High Burnup (No. NUREG/CR--6534-Vol. 2; PNNL--11513-Vol. 2), Nuclear Regulatory Commission, Washington, DC (United States). Div. of Systems Technology; Pacific Northwest Lab., Richland, WA (United States); (1997), Idaho National Engineering Lab., Idaho Falls, ID (United States).

[14] Rudling, P., Adamson, R., Cox, B., Zr Alloy Corrosion and Hydrogen Pickup ANT International, Mölnlycke, Sweden December (2013)

Лејла РАМЕЗАНИ, Масуд МАНСОУРИ, Мохамад РАХГОШАЈ

МОДЕЛОВАЊЕ КОРОЗИЈЕ КОНТАКТНЕ СТРАНЕ СА ВОДОМ И НАКУПЉАЊА ВОДОНИКА У КОШУЉИЦИ ГОРИВНОГ ЕЛЕМЕНТА VVER-1000 РЕАКТОРА

Легуре циркконијума обично се користе као кошуљице горивних елемената у водено хлађеном и водено модерисаном енергетском реактору (VVER реактору), углавном услед ниског ефикасног пресека за апсорпцију неутрона, пожељних механичких особина и добре отпорности на корозију у условима рада реактора. Током излагања води на високој температури, у реакцији воде и легура циркконијума настаје слој оксида. Целокупна област корозије заједно са пратећом апсорпцијом водоника у матрицу метала циркконијума привлачи доста пажње када се говори о перформанасама компоненти језгра и целокупног рада реактора. Раст слоја оксида циркконијума има деструктивну улогу у смањењу термичке ефиканости реактора ограничавањем улазне температуре и хемијских особина система за хлађење. У овом раду приказан је развој програмског пакета за предвиђање дуготрајног нарастања корозије кошуљице горивног елемента на контактној страни са водом, дебљине оксида и одређивање концентрације апсорбованог водоника у нормалним условима рада VVER-1000 реактора. Предложени модел може се применити за процену пораста корозије пре и после транзиције и дебљине оксида у радним условима.

Кључне речи: горивна кошуљица, корозија, цирконијум оксид, прикупљање водоника