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Division I

VIBRATION CRACK CORROSION – A PHENOMEN THAT COULD PROMOTE THE OCCURRENCE OF INCREASED OXIDE LAYER THICKNESSES IN THE UPPER REGION OF FUEL RODS MADE OF M5 CLADDING TUBES

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ABSTRACT

In the observation of increased corrosion on fuel assemblies (FA) in German pressurized water reactors in the area between the 8th and 9th spacer grid (SG) - this corresponds to the transition from the active fuel rod column to the fuel rod plenum - many contributing factors to the formation of oxide layers were considered and analysed. The compilation of the data shows that, in addition to the material influence and the thermohydraulic operating conditions, at least one additional operating condition should be relevant that promotes the occurrence of increased corrosion in the upper area of fuel rods (FR) made of M5 cladding tubes (CT).

The FR- and FA-structures are exposed to dynamic stresses in a corrosive environment due to coolant flow and hydrostatic buoyancy. Thermo hydraulics and neutron irradiation change the FR-stiffness and FR-mounting conditions over the operating time. This combination can result in favourable conditions particularly regarding vibration crack corrosion. In the following root cause analysis, it is deduced that the increased corrosion found on M5 CT is essentially due to the factors as

- thermohydraulic operating conditions,
- material properties as well as,
- a dynamic load acting at the metal-oxide interface during oxide growth.

NATURAL FREQUENCY DISPLACEMENT OF A SINGLE FR

The FA-structure consists of the top end piece, which houses the hold-down devices, the bottom end piece, the guide tubes as the connecting elements between top and bottom end piece, and the SG for firmly connecting to the guide tubes and clamping the FR. The lower part of the guide tube is designed as a shock absorber (Figure 1).

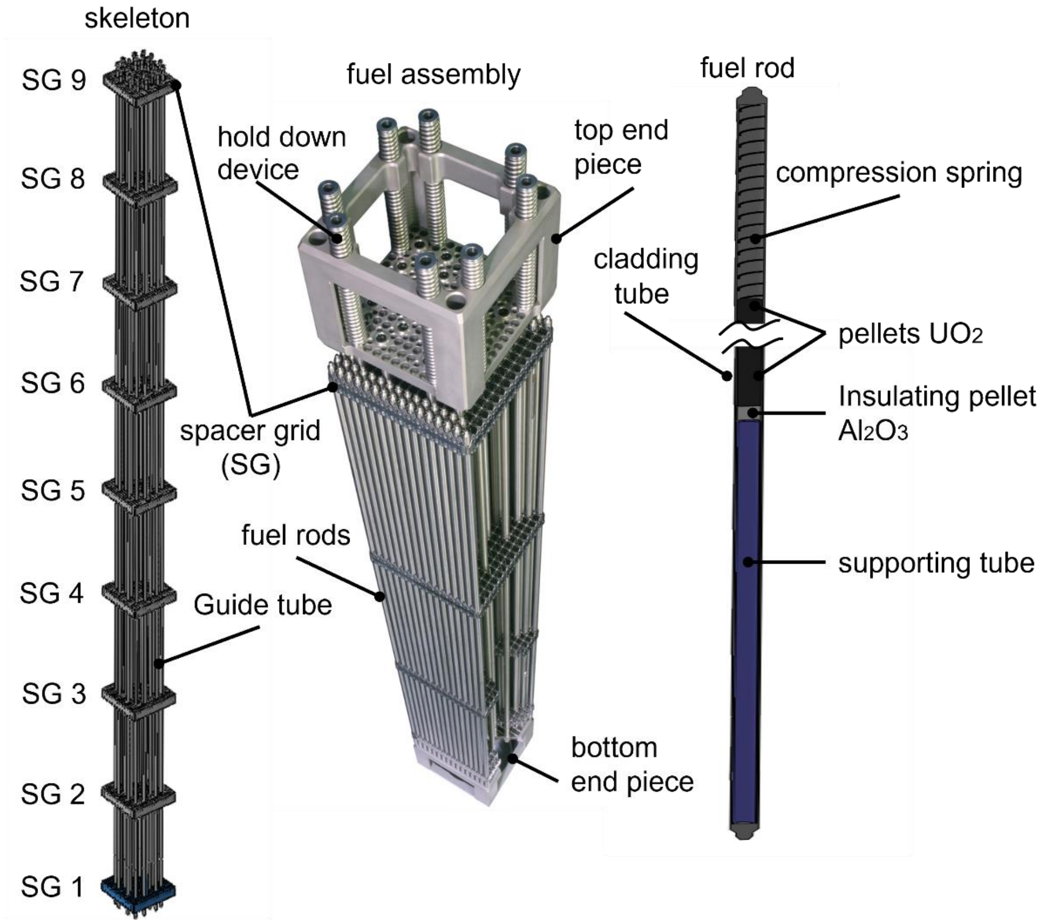

Figure 1. Schematic representation of the FA-structure (skeleton, without top and bottom end piece) and the FR

The FRs are held in the SG-cells by friction via SG-spring elements. During operation, lateral forces act on the FR- and the FA-structure due to coolant flow. In the course of the operating time, the FR-mounting conditions change due to various physical influences, which partly influence each other in their effect.

The SG spring force decreases with increasing temperature with the ratio of the E-modulus. Due to the different thermal expansion of the SG-cells and the FR-cladding tube, the effective spring deflection and spring force are changing, respectively. As a result of the pressure difference between coolant pressure and FR internal pressure, the cladding tube is elastically compressed and thus the FR holding force is reduced.

During operation, the outer diameter of the cladding tube and thus the holding force on the FR is changing. The evolution of the diameter change essentially depends on the cladding material, the filling clearance between pellet and cladding tube, the fuel behaviour (recompression, swelling) and on the local accumulated neutron fluence, i.e., the considered axial position in the fuel assembly (e.g., 1st, 2nd, ... 5th SG level).

As a result of the neutron irradiation, the SG spring elements relax as a function of the fluence resulting in a fluence-dependent loss of spring force and associated spring deflection. The struts of the SG grow because of the neutron irradiation. This increases the size of the SG cells, which results in a reduction of the effective spring deflection.

Even after short operating times in the reactor, the spring forces on the FR in the SG are decreasing noticeably because of the decrease in diameter of the fuel rods and the relaxation of the spacer spring forces.

In all operating conditions according to the design, the fuel assembly structure is predominantly subjected to compressive stress by axial forces (self-weight, hydrostatic buoyancy force, flow force, hold-down force). Tensile stress occurs when the fuel rods expand axially more than the guide tubes during power operation. Thus, due to the different material conditions and operating conditions of the FR cladding tube and the guide tube, the radiation-induced longitudinal growth and thermal expansion of the fuel rods is larger than that of the guide tubes. Eventually, the fuel rods slip through the SG meshes and transmit the maximum possible frictional forces to the guide tubes.

The vibration amplitudes are limited by the neighbouring FAs and the FAs at the edge of the core.

In sum, due to

- fluid flow and
- hydrostatic buoyancy

the FA- and FR-structures are exposed to dynamic stresses (superposition effects due to pressure fluctuations such as standing pressure waves; fluid resonances with hydraulic oscillation of water masses) in a corrosive environment, Stegemann D. and Runkel J. (1996).

Especially thermo hydraulics and neutron irradiation change the:

- **FR-stiffness**
    - Filling clearance between pellet and cladding tube
    - Fuel behaviour (recompression, swelling)
    - Locally accumulated neutron fluence (i.e. the considered axial position in the fuel assembly e.g. 1st, 2nd, ... 5th SG-level)
    - Stiffness changes of the compression spring with the ratio temperature - E-modulus
    - Irradiation-induced growth in length of the FR
    - The complex fluid-structure interactions of the resonating water mass, Capanna et al. (2021).
- **FR-mounting conditions**
    - Decreases of the SG-spring force with increasing temperature with the ratio of the E-Modulus
    - Change of the effective spring deflection due to the difference in thermal expansion of the SG cell and FR cladding tube
    - Elastically compression of the FR due to the difference between coolant pressure and internal pressure of the FR thus reducing the FR holding force
    - Change of the outer diameter of the cladding tube and thus of the FR holding force.

Due to different material and operating conditions, natural frequencies change for individual FR. Excitation of a specific mode and reaching a specific amplitude threshold result in particularly favourable conditions with regard to vibration crack corrosion, Vichytil C. (2012).

OXIDATION OF ZIRCONIUM ALLOY FR-SURFACES

The zirconium oxide formed on the surface of FRs made of Zr alloys has a passivating effect on the further oxidation behaviour. After the formation of the oxide layer, there is no direct contact between the metal/alloy and the oxidative medium (coolant/water), so that the corrosion reaction is inhibited. The species involved in the reaction must now diffuse through the oxide layer. As a result of the thermodynamics of the zirconium oxidation system and the environmental conditions to which the material is exposed, different potentials are established at the two interfaces of the oxide layer (oxide/water and oxide/metal interfaces). The resulting potential difference is the primary driving force for the transport of species through the oxide layer. The formation of new oxide takes place at the metal/oxide interface. The overall reaction can be described by the following equations from 1 to 5 below, Couet A. (2014):

$$2H_2O \xrightarrow{dissotiation} 4H^+ + 2O^{2-}_{ads.} \quad (1)$$

$$O^{2-}_{ads.} + \blacksquare \xrightarrow{absorption} O^{2-}_{abs.} \quad (2)$$

$$Zr \xrightarrow{oxidation} Zr^{4+} + 4e^- \quad (3)$$

$$Zr^{4+} + 2O^{2-}_{abs.} \xrightarrow{oxide\ formation} ZrO_2 \quad (4)$$

$$4H^+ + 4e^- \xrightarrow{reduktion} 2H_2 \quad (5)$$

Under these conditions, zirconium alloys tend to exhibit cyclic corrosion kinetics, with "transition zones" separating the cycles. These transitions are associated with some breakdown of the protective properties of the oxide. The oxidation kinetics of zirconium alloys can be represented as a four-stage model, Figure 2, Couet A (2014), Platt P. (2014):

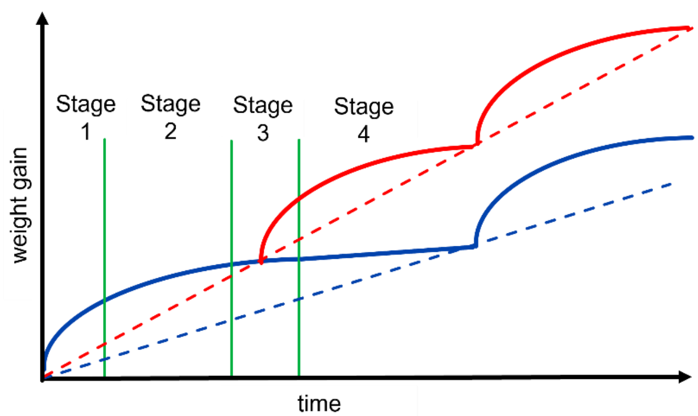

Figure 2. Schematic representation of the transformation points in the oxidation kinetics of zirconium alloys, Platt P. (2014)

Stage 1 - Initial Oxidation

Initial oxidation involves the formation of an oxide layer up to about 500 nm thickness, which consists of the monoclinic and metastable tetragonal phases of zirconia. Thin oxide layers have a higher proportion of the tetragonal phase compared to thicker oxides and exhibit a strong compressive stress. The phase transformation from tetragonal to monoclinic during oxide layer growth can cause cracking and pore formation in the early oxide. This damages the oxide layer and accelerates the early corrosion kinetics.

Stage 2 - Reduced Oxidation Rate

From about 500 nm to about 1.5 µm, the oxidation rate decreases as forming a protective, highly textured barrier layer that determines the corrosion kinetics through oxygen diffusion and electron transport. Therefore, the thicker the barrier layer becomes, the slower the oxidation rate. The transition from stage 2 to stage 3 is characterized by an increase in compressive stress in the oxide.

Stage 3 - Transition Region

In the stage known as the "transition region", corrosion accelerates. A network of circumferentially oriented cracks forms near the metal-oxide interface. These cracks have a destabilising effect on the tetragonal phase near the metal-oxide interface, which in turn negatively affects the protective nature of the barrier layer.

Stage 4 - Post Transition Region & „Breakaway"

During oxidation, zirconium alloys show a repetition of the behaviour described above, forming a series of similar oxide layers. Eventually the corrosion kinetics appear approximately linear. A possible explanation for this behaviour is that the transition in different regions on the sample surface are no longer synchronous. Different parts of the sample are undergoing the transition from protective to non-protective at different times.

Under pressurized water reactor oxidation conditions, the most stable phase is the monoclinic ZrO_2 (α-ZrO_2). The tetragonal phase of ZrO_2 (β-ZrO_2) is especially observed near the oxide/metal interface. This metastable phase can be stabilised by compressive stresses and alloying elements (especially iron), Couet A (2014), Yilmazbayhan A. et al. (2004), Pêcheur D.et al. (1992). The phase transformation from tetragonal β-ZrO_2 to monoclinic α-ZrO_2 during oxide layer formation near the oxide/metal interface may play a key role in controlling the oxidation kinetic of zirconium alloys, Figure 3. Characteristic of the stress-induced (martensitic) transformation of metastable tetragonal β-ZrO_2 to stable monoclinic α-ZrO_2 is an increase in volume by about 4 %. Due to the larger volume of the monoclinic crystal form, the transformation of the tetragonal to the monoclinic phase creates higher tensile stresses in the oxide and fine microcracks form, Couet A (2014), Platt P. (2014).

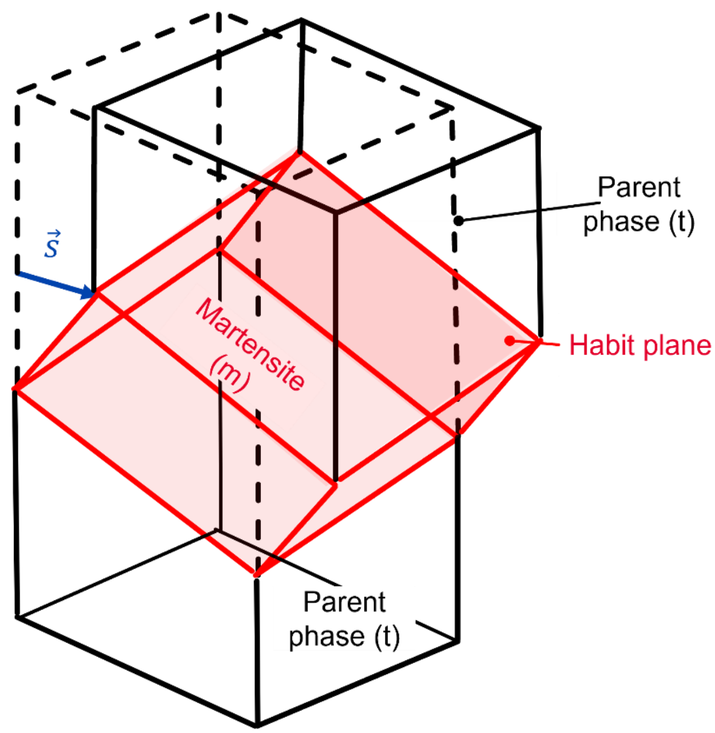

Figure 3. The tetragonal to monoclinic - martensitic phase transformation, Couet A (2014)

VIBRATION CRACK CORROSION

System conditions of vibration crack corrosion are the medium (water chemistry, thermohydraulic operating conditions), the material (composition, content of alloying elements, microstructure) and the mechanical stresses (mechanical vibrations and residual stresses). The dependence of the stress intensity on the frequency has not yet been clearly defined. In general, with a decrease in frequency, there is a larger decrease in fatigue strength, Vichytil C. (2012).

The observation of increased corrosion at FAs in German pressurised water reactors in the region between the 8th and 9th SG, the transition from the active fuel rod column to the fuel rod plenum, in the majority of cases developed at Pre-Convoy type reactor. With the aim of estimating the distribution of von Mises stress in the frequency domain in terms of the statistical properties of the applied forces and overall frequency behaviour, to determine the differences between the Pre-Convoy and Convoy type reactors, random vibration study of FR-mounting at room temperature without thermohydraulic operating conditions was performed for the two types of plants.

The calculation provides the modal analysis and contour overview of the root mean square (RMS) of von Mises stress for the frequency range from the 1st to the 9th mode shape of the entire FR-structure, Segalman et al. (2000). The following assumptions were made for the simulation: The SG are rigid. The spring force of the first SG is 50 N at room temperature. All other springs in the SG 2 to 9 have a spring force of 35 N at room temperature (design specifications). The calculations were carried out at 100 % and 50 % of the initial FR-mounting stiffness for the two types of reactors to determine the influence of the changing FR-mounting conditions caused by the various effects described above. A uniform power spectral density (PSD function) of acceleration was defined in only one lateral direction to act as the basic excitation on the FR-structure.

The simulation revealed one maximum of the RMS von Mises stress over the entire FR structure and for the entire frequency range. This maximum is located between the 8th and the 9th SG in the transition region from the UO_2 pellets to the compression spring in the FR plenum (Figure 4).

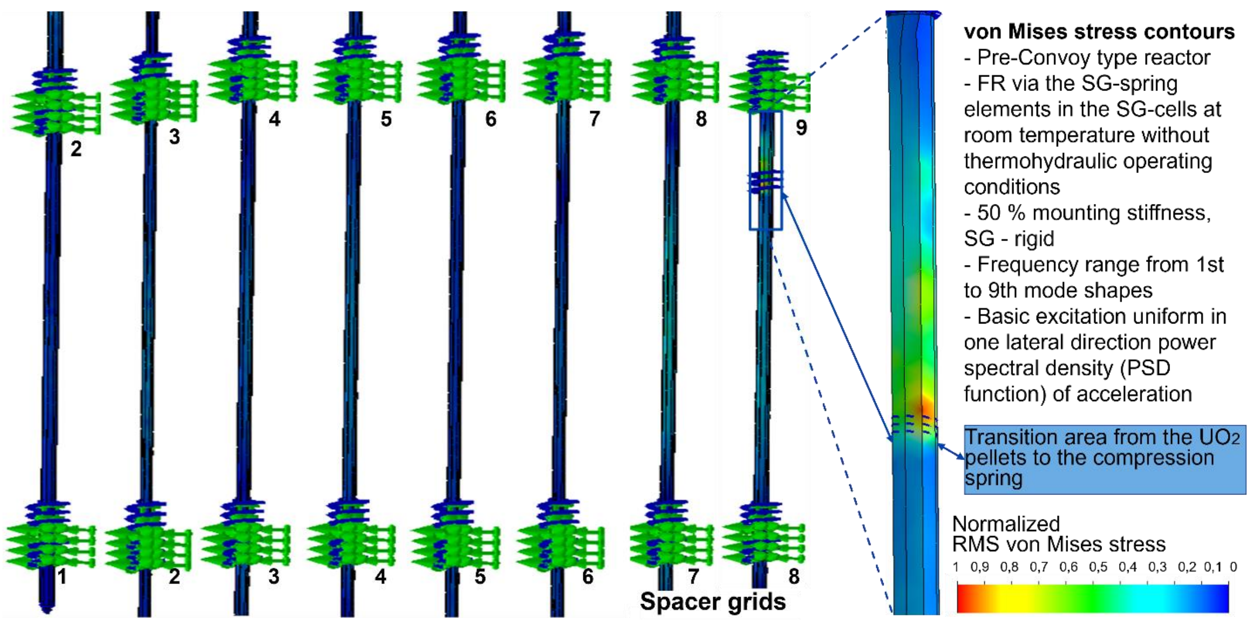

Figure 4. Random vibration study - the contours of the RMS von Mises stress of the FR for the frequency range from 1st to 9th modes

For comparison the frequency range was normalized to the 1st mode of the Pre-Convoy type reactor. The reduction of the FR-mounting stiffness (up to 50 % in the simulation) leads to a shift of the natural frequencies into the lower frequency range (Figure 5). The Convoy type reactor is characterised by a higher FR stiffness compared to the Pre- Convoy type reactor. Even with a reduction of the FR mounting stiffness by up to 50 %, the 1st mode of the Convoy type reactors is only approx. 15 % lower in the frequency range than the 1st mode of the Pre- Convoy type reactor in the initial state with 100 % FR mounting stiffness.

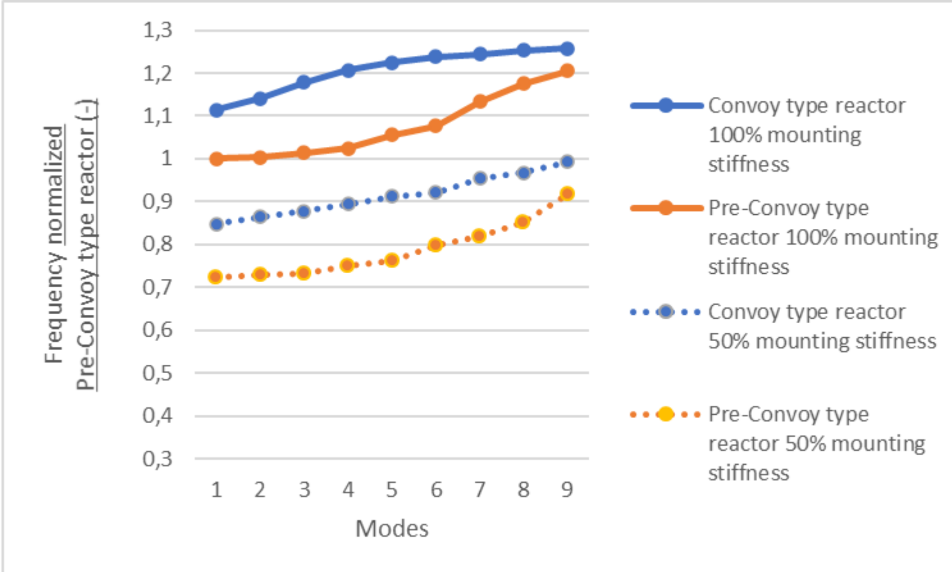

Figure 5. Modal analysis of the FR-mounting at room temperature for the Pre-Convoy and Convoy type reactors

If the stiffness and/or mounting conditions of the FR change, its natural frequencies shift downwards. If a particular FR natural frequency is excited due to the actual operation conditions, and the system response is dominated by a single mode, Stegemann D. and Runkel J. (1996), then also the dynamic loads increase in the respective spot, here in the transition region from the UO_2 pellets to the compression spring. This increased dynamic load accelerates the transformation of the tetragonal phase of zirconia oxide into the monoclinic phase, which in turn leads to an increased fatigue damage of the oxide layer. In fact, a higher proportion of the monoclinic phase of zirconia oxide can be found at the metal/oxide interface of fuel rods exhibiting aforesaid anomalously increased corrosion, which can now be attributed to the transformation of the tetragonal phase into the monoclinic phase by the vibrations. Due to the larger volume of the monoclinic crystal form, the transformation of the tetragonal to the monoclinic phase generates higher tensile stresses and fine microcracks in the oxide layer, which can expose unprotected metal surface in microscopic areas. This type of phase transformation can in turn have a negative effect on fatigue strength in the operating environment due to the induced stresses and act as an additional driving force for the zirconium oxidation.

SUMMARY

It was shown that a change in the vibration behaviour of individual FRs can contribute to the appearance and the different expression of corrosion observed at the end of the active column and in the plenum area on different sides of the FA and on individual FRs. In addition to the material influence and the thermohydraulic operating conditions, the shift of the vibration modes into an "unfavourable" frequency range with excitation coincidence can be an additional operation-related factor, which favours the occurrence of increased corrosion in the upper area of individual FRs on M5 cladding tubes.

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