Production

POROSIMETRY OF ZIRCONIA SCALES FORMED DURING OXIDATION OF ZR-BASED FUEL CLADDINGS IN STEAM AND AIR-STEAM MIX AT HIGH TEMPERATURES

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CONTEXT AND OBJECTIVES

In **Severe Accident** (SA) conditions, the residual power leads to water vaporization and to corrosion of **Zr-based fuel claddings**, which constitute the first containment barrier:

$$Zr(s) + 2\,H_2O(g) \xrightarrow{\Delta H = -600\ kJ.mol^{-1}} ZrO_2(s) + 2\,H_2(g)$$

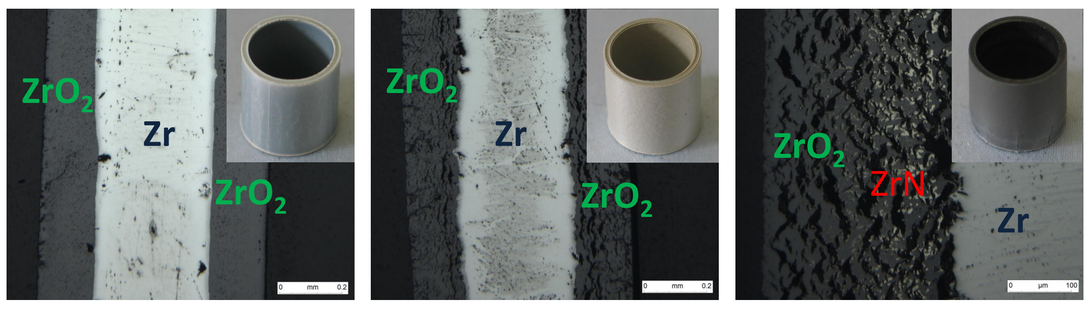
Many experimental studies about corrosion of Zr-based claddings in SA conditions were conducted so far [1,2]. In particular, semi-integral experiments, such as several QUENCH tests led at KIT, pointed out that:

- Before cooling down the reactor core, a **reflooding with water** may temporarily enhance the oxidation of Zr and so the **generation of H_2**, a combustible gas;
- Most of SA codes **underestimate this enhanced H_2 release**, which is experimentally observed in these semi-integral tests. However, it could be attenuated in reactor cases due to different temperatures, atmospheres or reflooding flow rates.

Consequently, **EDF R&D** aims at identifying, understanding and **modeling in MAAP** the phenomena which induce these enhanced H_2 releases, in particular the **degradation of the oxide layers**.

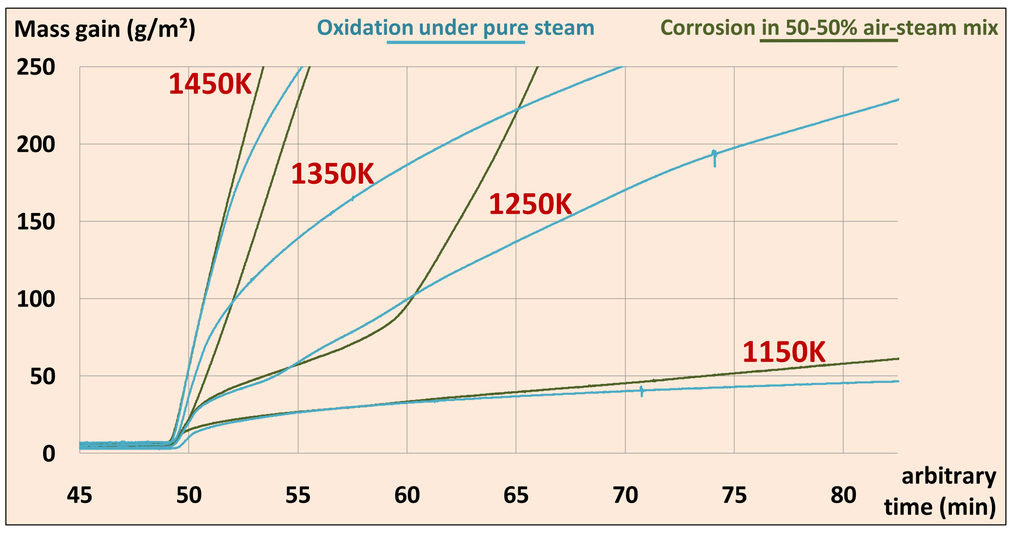
DEGRADATION OF ZR-BASED CLADDINGS

The oxidation rate is exponentially **temperature-dependent**. Moreover, at specific temperatures, a ZrO_2 allotropic phase change facilitates the **cracking of this oxide** layer which becomes **porous** and not protective anymore. Moreover, in case of a melt quenching in the reactor pit inducing **air ingress** into the vessel, $O_2(g)$ and $N_2(g)$ react with Zr-based claddings through a **self-sustained process** (formation and re-oxidation of nitrides ZrN) which leads to more **degraded and porous zirconia layers**.



*Micro- and macro-graphs of **Zirlo cladding samples** oxidized in pure steam at 1350K (left) and 1250K (middle), and in 50-50% air-steam mix at 1450K (right) [3]*

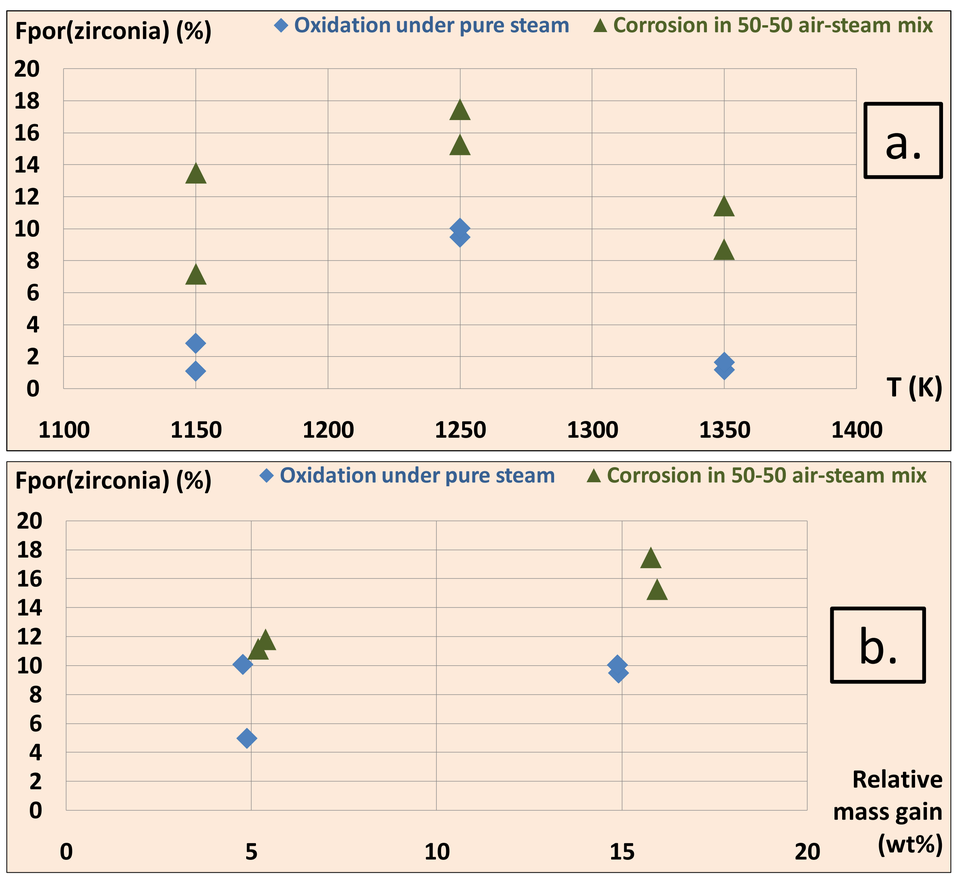
Mass gain curves highlight the influence of both the **temperature** and the **atmosphere composition** on the reaction rate.



***Mass gain** curves of 8 **Zirlo samples** reacting in various SA conditions [3]*

POROSIMETRY OF ZIRCONIA SCALES

Porosimetries by Hg intrusion were performed for the first time on such **Zirlo samples corroded in SA conditions.**



***Volume percentage of accessible porosity** in zirconia layers formed: [3]*
a.** Until mass gain ≈ **285 g.m^{-2}** (≈15wt%), depending on the **temperature
b.** At temperature = **1250K**, as a function of their relative **mass gains

These **innovative** measurements:

- Not only **confirmed** qualitatively the influence on the cladding degradation of the **experimental conditions**: temperature, presence of air, reaction duration;
- But also quantified the **accessible porosity of ZrO_2 layers**.

CONCLUSIONS AND PERSPECTIVES

Since these first **porosimetries by Hg intrusion** provided quantified and coherent data, a larger experimental test matrix will be achieved in 2015, in order to:

- **Identify correlations** between experimental **conditions** and **porosity** increase rates, and between the **zirconia porosity** and its impact on the **corrosion rate**;
- **Implement** these correlations in the **MAAP code** through a **new corrosion model**;
- **Validate** this new model by comparisons with **semi-integral experiments**, such as QUENCH-16 for instance.

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REFERENCES

[1] M. Steinbrück et al., "Synopsis and outcome of the QUENCH experimental program", *Nuclear Engineering and Design 240 (1714–1727)*, 2010.
[2] M. Steinbrück, M. Böttcher, "Air oxidation of Zircaloy-4, M5 and ZIRLO cladding alloys at high temperatures", *Journal of Nuclear Materials 414 (276-285)*, 2011.
[3] F. Haurais, "Degradation mechanism of Zr-based fuel claddings in steam and air-steam atmospheres at high temperatures", presented at the 20th IQW, ISBN 978-3-923704-88-0, 2014.

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