Corrosion of M5® in PWRs: Quantification of Li, B, H and Nb in the oxide layers formed under different conditions

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Introduction (1)

In PWRs, in the last two decades, major trends:

- Achieve higher BU with increasing the corrosion resistance:
  
  → Introduction of new alloys containing Nb (M5 in this study)

- Modification of the primary circuit conditions to:
  
  - Mitigate InterGranular Stress Corrosion Cracking (IGSCC) of primary loop components in SS and Ni alloys
  - Reduce the radiation field (exposition of workers) by reducing the release of activated corrosion products in the primary loop
  - Reduce Crud deposits on the surface of fuel claddings: Axial Offset Anomaly, Corrosion of Zr alloys
  - Reduce costs: longer fuel cycles, shorter outages

  → Increase in Li content and temperature, ... among other modifications (cycle length, Zn,...)
Objective of this study:

- Impact of more demanding conditions (Li, T°) on the corrosion behaviour of M5

And in particular, to state on:

- The Nb content in the oxide layers formed on M5 / possibility of $^{94}$Nb release in the primary coolant

- The Li and B content in the oxide layers formed on M5 / possible corrosion enhancement due to the Li increase

- The impact on hydrogen pick-up of M5
Outline

- Materials & operating conditions
- Characterization of oxide layers
- Hydriding and Hydrogen Pick-Up
- Quantification of Nb
- Quantification of Li and B
- Conclusion
M5 (from different ingots) in three different operating conditions:
- Standard
- Increased Li
- Elevated T°

<table>
<thead>
<tr>
<th>Operating conditions</th>
<th>Nb content wt%</th>
<th>No of cycles</th>
<th>Burn-up Gwd/t</th>
<th>Mean Temp. °C</th>
<th>Local Temp.</th>
<th>Li wt ppm</th>
<th>B wt ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard</td>
<td>0.91</td>
<td>7</td>
<td>77.8</td>
<td>313</td>
<td>Medium</td>
<td>2.2→0.5</td>
<td>1800→0</td>
</tr>
<tr>
<td>Increased Li</td>
<td>1.01</td>
<td>5</td>
<td>68.6</td>
<td>315</td>
<td>Highest</td>
<td>3.5→0.5</td>
<td>1800→0</td>
</tr>
<tr>
<td>Elevated T°</td>
<td>0.99</td>
<td>1</td>
<td>16.8</td>
<td>335</td>
<td>Highest</td>
<td>2.0→0.5</td>
<td>900→0*</td>
</tr>
</tbody>
</table>

* EBA (enriched boric acid) chemistry
Modified Li chemistry:

[Provost, ANS LWR, 2006]
Characterization of oxide layers (1)

- Optical microscopy

Standard, 7 cycles

- Very regular and stable oxide
- Absence of spalling
- Thickness in accordance with respective burn-ups and T°
- No impact of increased Li on thickness

Increased Li, 5 cycles

Oxide = 19.0 µm

Elevated T°, 1 cycle

Oxide = 4.9 µm
Characterization of oxide layers (2)

No impact of increased Li on oxide thickness → in accordance with plant feedback:

M5 corrosion behavior in increased Li chemistry

[Kaczoroswki, ANS WRPFM, 2008]
Characterization of oxide layers (3)

- *SEM characterization*

**Standard, 7 cycles**

- Very regular and stable oxide, and stable metal/oxide interface
- Stable periodicity: no variation or loss of periodicity with high BU or increased Li
  → in accordance with the absence of any acceleration of corrosion kinetics
- $T^o$ standard medium temp. $< T^o$ increased Li highest temp. $< T^o$ elevated $T^o$ highest temp. :
  → increased periodicity with increasing $T^o$, in accordance with previous results on M5
  [Bossis, ASTM STP, 2005] or Zy4 [Bouineau, ASTM STP, 2009]

**Increased Li, 5 cycles**

- Periodicity = 2.3 µm

**Elevated $T^o$, 1 cycle**

- Periodicity = 2.6 µm
Hydriding of M5 (1)

- Hydrogen content: Effect of $T^\circ$ in standard conditions

Measurement of hydrogen content at 5 different elevations of a single M5 7 cycles’ rod:

- Globally, H pick-up is mostly dependent on the oxide thickness formed
Hydriding of M5 (2)

- *Hydrides distribution: impact of Li*

**Standard, 7 cycles**

**Increased Li, 5 cycles**

- Low hydrides content → below the solubility limit at irradiation $T^\circ$
- Circumferential hydrides
- No impact of Li
Hydriding of M5 (3)

- **Effect of Li and $T^\circ$: comparison of hydrogen content**

- **No impact of increased Li chemistry on the H pick-up and HPUF of M5**
- **Within ± 20 ppm, no impact of both Li and $T^\circ$ on the H pick-up of M5**
Nb content in oxide layers (1)

- Qualification of the EPMA measurement

Nb distribution profile on non-irradiated standard (0.91 wt% Nb), after oxidation in air at 500°C up to 8 µm:

Comparison of the Nb quantification results in the metallic matrix of two irradiated M5 alloys with different nominal Nb content.

- Correction factor is necessary in oxide

An accuracy of the quantification of Nb vs. Zr of ± 0.05 at% is achieved.
**Nb content in oxide layers (2)**

- **Quantification of Nb in standard, increased Li, and elevated T° conditions**

<table>
<thead>
<tr>
<th>Operating conditions</th>
<th>Nominal Nb wt%</th>
<th>Nb/(Nb+Zr) at%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Nom.</td>
<td>Met.</td>
</tr>
<tr>
<td>Standard 7 cycles</td>
<td>0.91</td>
<td>0.89</td>
</tr>
<tr>
<td>Increased Li 5 cycles</td>
<td>1.01</td>
<td>0.99</td>
</tr>
<tr>
<td>Elevated T° 1 cycle</td>
<td>0.99</td>
<td>0.97</td>
</tr>
</tbody>
</table>

- Nb content in oxide = Nb content in metal (± 0.05 at%)
- Absence of Nb gradient across the oxide films
- No significant release of Nb from the oxide layers to the primary coolant, whatever the operating conditions
Li and B content in oxide layers (1)

- NRA Analysis - Methodology

- The NRA analysis is performed on the hotline (named CASIMIR) of Laboratoire Pierre Süe (LPS) at CEA-Saclay.
- The absence of fuel is required
- Beam size : from 5 x 5 µm²

- Incident particle : Proton H⁺ at 3 MeV
  - X-ray emission by desexcitation : PIXE (for Z > 17)
  - Rutherford Backscattering of protons : RBS (majoritary)
  - Nuclear Reaction (p,α) emitting ⁴He (minoritary) :
    - $^{11}$B + p $\rightarrow$ ⁸Be + α, α emission with a 6.221 MeV energy
    - $^{7}$Li + p $\rightarrow$ 2α, α emission with a 7.709 MeV energy

- Double detector, to discriminate protons from RBS and α from NRA :
  - Thin ΔE detector : slowing down proportional to Z (=1 for p, =4 for α)
  - Thick E_res detector : p or α loose the rest of their energy
Li and B content in oxide layers (2)

- NRA Analysis - Methodology

Analysis chamber in CASIMIR hotcell
Li and B content in oxide layers (3)

- NRA Analysis - Methodology

\[ \Delta E = f(E_{\text{res}}) \]

\( \Delta E \) allows to filter only the \( \alpha \) particles, and then to work on the \( E_{\text{res}} = f(\text{Energy}) \) spectrum.
Li and B content in oxide layers (4)

- NRA Analysis – Methodology : Spectra

B$_4$C, pure B, and Li$_2$B$_4$O$_7$ reference spectra normalized to charge, stopping power and number of atoms.

Reference B and Li spectra used in this study for fitting and quantification

Experimental spectrum obtained on NIST SRM 610 standard

Good agreement with a reference material containing low content of Li (460 wt ppm) and B (350 wt ppm)
Li and B content in oxide layers (5)

- NRA Analysis - Results

Spectrum obtained in the oxide layer of an irradiated M5 sample:

![Graph showing alpha counts vs. energy (channel)]

- experimental spectrum
- B contribution
- Li contribution
- fitted spectrum
Li and B content in oxide layers (6)

- NRA Analysis – Results: Localization of the analyses (5x20 μm²)

Standard, 7 cycles

Increased Li, 5 cycles

Elevated T°, 1 cycle

ZrO₂

Alloy
- NRA Analysis – Results: Spectra obtained on the 1 cycle elevated $T^\circ$ sample

ZrO$_2$

Alloy

Li and B content in oxide layers (7)
## Li and B content in oxide layers (8)

### NRA Analysis – quantitative results

<table>
<thead>
<tr>
<th>Operating conditions</th>
<th>Oxide layer thickness (µm)</th>
<th>Location</th>
<th>Distance from metal/oxide interface (µm)</th>
<th>$^{11}$B content (wt ppm)</th>
<th>$^7$Li content (wt ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard (7 cycles)</td>
<td>12.5</td>
<td>a</td>
<td>8</td>
<td>97</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td></td>
<td>b</td>
<td>4</td>
<td>51</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td></td>
<td>c</td>
<td>3</td>
<td>55</td>
<td>8</td>
</tr>
<tr>
<td>Increased Li (5 cycles)</td>
<td>19.0</td>
<td>a</td>
<td>16</td>
<td>79</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td></td>
<td>b</td>
<td>12</td>
<td>105</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td></td>
<td>c</td>
<td>12</td>
<td>83</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td></td>
<td>d</td>
<td>8</td>
<td>73</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td></td>
<td>e</td>
<td>2.5</td>
<td>24</td>
<td>4</td>
</tr>
<tr>
<td>Elevated $T^\circ$ (1 cycle)</td>
<td>4.9</td>
<td>a</td>
<td>2.5</td>
<td>132</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td></td>
<td>b</td>
<td>2.5</td>
<td>143</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td></td>
<td>c</td>
<td>2.5</td>
<td>145</td>
<td>19</td>
</tr>
</tbody>
</table>
NRA Analysis – quantitative results

- We do not observe any significant effect of the increased Li or elevated $T^\circ$ on the Li content in the oxide layers formed on M5
- The Li content in oxide layers in the three investigated conditions is low, below 25 ppm, and B is significantly present: the conditions for Li enhanced corrosion are not present
- Comparison with previous results on irradiated samples:

<table>
<thead>
<tr>
<th>Reference</th>
<th>Reactor type</th>
<th>Alloy</th>
<th>oxide thickness ($\mu$m)</th>
<th>Li content (ppm)</th>
<th>B content (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ramasubramanian-91</td>
<td>CANDU</td>
<td>Zr-2.5Nb</td>
<td>8-13</td>
<td>3-50</td>
<td>-</td>
</tr>
<tr>
<td>Warr-96</td>
<td>CANDU</td>
<td>Zr-2.5Nb</td>
<td>up to 15</td>
<td>10</td>
<td>-</td>
</tr>
<tr>
<td>Kido-00</td>
<td>PWR</td>
<td>Zircaloy-4</td>
<td>4-16</td>
<td>10-30</td>
<td>100-250</td>
</tr>
<tr>
<td>Gebardht-99</td>
<td>PWR</td>
<td>Zircaloy-4</td>
<td>11</td>
<td>12.5</td>
<td>99</td>
</tr>
<tr>
<td>Gebardht-99</td>
<td>PWR</td>
<td>Zr-1Nb</td>
<td>75</td>
<td>7</td>
<td>135</td>
</tr>
<tr>
<td>Gavillet-02</td>
<td>PWR</td>
<td>Zircaloy-4</td>
<td>75</td>
<td>7</td>
<td>135</td>
</tr>
<tr>
<td>Gavillet-02</td>
<td>PWR</td>
<td>Zr-1Nb</td>
<td>6.5</td>
<td>7.8</td>
<td>60</td>
</tr>
<tr>
<td>Gavillet-02</td>
<td>PWR</td>
<td>Zr-1Nb</td>
<td>18</td>
<td>12</td>
<td>24</td>
</tr>
</tbody>
</table>

- Our results obtained on M5 in the present study, with mean Li concentrations ranging from 13 to 18 ppm, and mean B concentrations ranging from 70 to 140 ppm, are in the range of these previously acquired data, with an additional margin regarding the B content in the oxide previously obtained on Zr-1Nb.
Conclusion

The oxide layers formed on M5 in three different operational conditions were studied:
- Standard
- Increased Li
- Elevated T°

1. The stability of the corrosion behaviour of M5 is not affected by increased Li or T°.

2. The hydrogen pick-up fraction of M5 is not affected by increased Li or T°.

3. The Nb content was precisely measured by EPMA: there is no significant release of Nb in the primary coolant, whatever the operating conditions.

4. The Li and B contents were measured by NRA: the respective Li and B contents obtained are of the same order in all three conditions, and in a range where no enhanced corrosion is expected (nor observed).