Supplement of

Safety of Nuclear Waste Disposal

The anaerobic corrosion of the carbon steel overpack under anoxic alkaline conditions representing the Belgian supercontainer concept

Roberto Gaggiano

Correspondence to: Roberto Gaggiano (r.gaggiano@nirond.be)

The copyright of individual parts of the supplement might differ from the article licence.
The anaerobic corrosion of the carbon steel overpack under anoxic alkaline conditions representing the Belgian supercontainer concept

R. Gaggiano

12/09/2023
Geological disposal concept
The ‘Supercontainer’ design

Reference disposal concept in Belgium

- Carbon steel overpack containing either vitrified HLW canisters or spent fuel assemblies
- The overpack is surrounded by a OPC-based concrete buffer
- The cylindrical cavity between the overpack and the concrete buffer is filled with a cementitious filler
- The concrete buffer is entirely encased in a stainless steel envelope.
Corrosion programme: RD&D methodology and research activities
**Contained Environment Concept**

- **Aim**: to fix and preserve a favourable chemical environment in the immediate vicinity of the overpack for a long time, at least for the duration of the thermal phase.

- The main goal of the ongoing RD&D corrosion studies is to **provide confidence that the integrity of the carbon steel overpack will not be jeopardized at least for the duration of the thermal phase.**

**Long-term safety function C-steel overpack**
Integrated 3-step approach

1. Development of the Corrosion Evolutionary Path
   - before backfilling: aerobic phase \( t_{oa} \)
   - after backfilling: anaerobic phase \( t_{an} \)

   - Fabrication of SC
   - Closure of disposal gallery
   - Depletion of oxygen
   - End of thermal phase \( t_{th} \)
   - Perforation of overpack

   - Hot oxic relatively dry
   - Cool anoxic fully saturated

2. Determining reliable uniform corrosion rate data
   - Reliable estimate of the uniform corrosion rate for the different phases of the CEP
   - Lifetime predictions (i.e., the reduction in wall thickness in µm/year)
   \[
   d_{overpack} = \sum v_i \cdot t_i
   \]
   - Evolution of the passive film with time

3. Proving the validity of the ‘exclusion principle’
   - Any other form of corrosion cannot occur
     - Pitting corrosion
     - Stress corrosion cracking
Research activities

- **Measurement of H₂ generated during the anoxic corrosion of carbon steel**
  \[ \text{3Fe} + \text{4H₂O} \rightarrow \text{Fe₃O₄} + \text{4H₂} \]
- **4 independent techniques:**
  - Barometric glass gas cells
  - Autoclaves equipped with pressure transducers
  - Solid-state hydrogen sensor
  - Electrochemical measurements

- **Study of chloride pitting of carbon steel**
  - Potentiodynamic polarization measurements
  - Modelling of the results and long-term prediction by means of the Point Defect Model and the Mixed Potential Model.

- **Passive oxide film**
  - Study of the characteristics and evolution of the passive film
    - electrochemical techniques and surface analysis

- **Stress corrosion cracking**
  - Study the SCC susceptibility of plain and welded C-steel exposed to alkaline media (YCW, pH ~13.5) under anoxic conditions
    - Slow Strain Rate Tests

- **Uniform corrosion**
  - Modelling of the radiolysis of water in the concrete buffer
    - Equilibria in solution
    - Hydrogen produced by radiolysis

- **Radiolysis of the buffer**
  - Electrochemical screening of possible construction materials exposed to highly alkaline media.
Current status
Belgian RD&D corrosion programme
Uniform corrosion

Results - volumetric method  (Limit of detection: ~100 nm/y)

25°C

Increase in gas generation steeper in irradiated cells over initial period

80°C

Boundary conditions:

- $[\text{Cl}^-]: 100 \text{ mg/L}$
- $[\text{S}_2\text{O}_3^{2-}]: 100 \text{ mg/L}$
- $T = 25^\circ\text{C}, 50^\circ\text{C}, 80^\circ\text{C}$
- $\gamma = 25 \text{ Gy/h}$

unirradiated

no radiolysis or other degassing process

irradiated

radiolysis
Uniform corrosion

Results - volumetric method

- Irradiated YCW corrosion rate past 5 years = 0.045 µm/year
- Unirradiated YCW corrosion rate past 5 years = 0.025 µm/year
- For all unirradiated cells the total gas generation is immeasurably small
- Irradiated YCW +S\textsuperscript{2-} +S\textsubscript{2}O\textsubscript{3}\textsuperscript{2-}+Cl\textsuperscript{-} corrosion rate over all 4 years = 0.013 µm/year
- Irradiated YCW +S\textsuperscript{2-} corrosion rate over all 4 years < 0.01 µm/year

Boundary conditions:
- [Cl\textsuperscript{-}]: 100 mg/L
- [S\textsuperscript{2-}]: 500 mg/L
- [S\textsubscript{2}O\textsubscript{3}\textsuperscript{2-}]: 100 mg/L
- T = 25°C, 50°C, 80°C
- γ = 25 Gy/h
Uniform corrosion

Results: autoclaves with pressure transducer

(YCW + 500 mg/l S2−, pre-corroded, 25 °C)

After approximately one year’s exposure the corrosion rate had dropped to less than 0.03 µm/year (still decreasing)

Currently transferring all glass cell experiments (operating >10 years) to autoclaves.

Boundary conditions:
[Cl−]: 100 mg/L
[S2−]: 500 mg/L
[S2O32−]: 100 mg/L
T = 25°C, 50°C, 80°C
γ = 25 Gy/h
Uniform corrosion

Results – hydrogen sensor  
(Detection limit: ~0.01 nm/y)

- Effect of the steel composition/form
- **Wire** corrodes at **10 nm/year**
- **Plate** corrodes at **0.03 nm/year**

- **Temperature change to 80°C → lower LT corrosion rate**

- **Effect of temperature on passivation?**
- 50°C → unexpectedly high corrosion rate
- Exactly same conditions as a previous cell at 80 °C, corroding at 10 nm/yr.
In the long-term corrosion products predominantly composed of magnetite

- Thickness corrosion product layer ~ 2-3 µm (after ~ 5 years)

The outer surface of the film changed from mixed maghemite/magnetite to pure magnetite from 100 to 1000 hours exposure
Oxide film characterization
Exposure to cementitious solutions

- **Bi-layer structure**
- **More complex composition than the corrosion products in YCW:** outer and inner layer are composed of calcium, silicon, iron and oxygen (and traces of aluminum).

TEM measurements
Pitting corrosion
Experimental details

- Experiments

**EIS data:**

- Cell

**Optimization process**

- Igor Pro Software

Extrapolation of the long-term behavior by means of the MPM

\[
\begin{align*}
\text{Metal} & \rightarrow \text{Barrier Layer} & \rightarrow \text{Electrolyte} \\
(1) \quad m + V_f^e & \rightarrow M_{M} + V_{Fe} + \chi e^+ \\
(2) \quad m & \rightarrow M_{Fe}^+ + V_{Fe} + \chi e^+ \\
(3) \quad m & \rightarrow M_{M} + \frac{\chi}{2} V_{O} + \chi e^+ \\
(4) \quad M_{M} & \rightarrow M_{Fe}^+ + V_{Fe}^e + (\delta - \chi)e^+ \\
(5) \quad M_{Fe}^+ & \rightarrow M_{Fe}^+ + (\delta - \chi)e^+ \\
(6) \quad V_{Fe} + H_{2}O & \rightarrow O_{2} + 2H^+ \\
(7) \quad MO_{2} & + \chi H^+ \rightarrow M_{M}^+ + \frac{\chi}{2} H_{2}O + (\delta - \chi)e^+ \\
\end{align*}
\]

For example: Optimization parameters

**Butler-Volmer Equation**

- Hydrogen electrode reaction:

\[
H_2 + 2OH^- = 2H_2O + 2e^- \\
\text{current density: } i_{\text{HER}} = \frac{e^{2.303y/B_a}}{i_0} + \frac{e^{2.303y/B_a}}{i_f} - \frac{e^{2.303y/B_c}}{i_{l_r}}
\]

- Cathodic impedance:

\[
Y_{\text{HER}} = \frac{d_i_{\text{HER}}}{dE} = \frac{DN^l - ND^l}{D^2}
\]

Focus on chloride pitting
No other aggressive species are taken into account
Pitting corrosion

Effect of chloride

- The breakdown potential ($E_b$) decreases with increasing chloride concentration.
- $\text{Cl}^- < 1\text{M}$, no passivity breakdown occurs on carbon steel in SCPS.
- $\text{Cl}^- > 2\text{M}$, pitting corrosion occurs. The $E_b$ decreases with increasing chloride concentration.
- When the Cl- of SCPS is 1.5M, passivity breakdown occurs at random, indicating that 1.5M is the Cl- concentration for the transition of carbon steel from passivity to passivity breakdown in simplified concrete pore solution.
**Pitting corrosion**

**Artificial pit experiment**

- Experimental confirmation that, even if pits nucleate in the oxic period, they cannot maintain differential aeration during the anoxic period → no further pit activation

- The pit cavity becomes polarity inverted, → hydrogen evolution occurs within the cavity → (metal oxidation) occurs on the external surface

- The solution within the cavity is expected to become more alkaline than the external environment and

- Cations (e.g., Na⁺) are preferentially transported into the pit and chloride ejected from the pit.
Long-Term modelling approach

- **Deterministic Monte Carlo Simulation**: keep track of each stable pit that nucleates, propagates, and repassivates on the metal surface.
  - Simulation of the following processes
    - Pit nucleation rate
    - Pit propagation rate
    - Probability of pit repassivation

Assumption:
Pit nucleation occurs immediately after metal exposure, during the high temperature, oxic period.

Average depth of the deepest pit as a function of time

- Pitting represents no threat to the integrity of the overpack (if corrosion allowance = 15 mm)
SSRT tests were conducted on base and welded samples:
- Base and welded samples (SAW, MIG/MAG, RPEB)
- Anoxic conditions
- $T = 140^\circ C$
- Open circuit potential/applied potential
- YCW (pH 13.5) (in the presence or absence of aggressive species)

SSRT tests at OCP and at applied potential:
- **OCP**: no increased SCC susceptibility, typical stress-strain behaviour of a ductile material.
- **Applied potential**: so far, the potential does not seem to have a significant effect on the SCC susceptibility and the stress-strain behaviour of carbon steel in high pH solutions.

Stress corrosion cracking (welds)
### Stress corrosion cracking (welds)

#### Typical results

**WELD-L**

**Longitudinal**

<table>
<thead>
<tr>
<th>Condition</th>
<th>YS (MPa)</th>
<th>UTS (MPa)</th>
<th>EaF (%)</th>
<th>TTF (hours)</th>
<th>RA (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>587.0</td>
<td>798.0</td>
<td>22.1</td>
<td>124.7</td>
<td>47.3</td>
</tr>
<tr>
<td>YCW</td>
<td>605.0</td>
<td>816.0</td>
<td>20.5</td>
<td>116.0</td>
<td>37.8</td>
</tr>
<tr>
<td>YCW + 100 mg/L Cl</td>
<td>522.2</td>
<td>740.3</td>
<td>20.2</td>
<td>113.3</td>
<td>32.3</td>
</tr>
<tr>
<td>YCW + 35000 mg/L Cl</td>
<td>605.7</td>
<td>717.7</td>
<td>22.0</td>
<td>122.2</td>
<td>33.9</td>
</tr>
</tbody>
</table>

**HAZ-L**

**Heat-affected zone - Longitudinal**

<table>
<thead>
<tr>
<th>Condition</th>
<th>YS (MPa)</th>
<th>UTS (MPa)</th>
<th>EaF (%)</th>
<th>TTF (hours)</th>
<th>RA (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>403.0</td>
<td>592.0</td>
<td>29.1</td>
<td>163.4</td>
<td>82.6</td>
</tr>
<tr>
<td>YCW</td>
<td>424.0</td>
<td>603.0</td>
<td>27.5</td>
<td>154.6</td>
<td>67.5</td>
</tr>
<tr>
<td>YCW + 100 mg/L Cl</td>
<td>437.0</td>
<td>514.5</td>
<td>25.5</td>
<td>147.4</td>
<td>60.6</td>
</tr>
<tr>
<td>YCW + 35000 mg/L Cl</td>
<td>406.3</td>
<td>583.8</td>
<td>23.7</td>
<td>131.4</td>
<td>50.7</td>
</tr>
</tbody>
</table>

**WELD-T**

**Transversal**

<table>
<thead>
<tr>
<th>Condition</th>
<th>YS (MPa)</th>
<th>UTS (MPa)</th>
<th>EaF (%)</th>
<th>TTF (hours)</th>
<th>RA (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>503.0</td>
<td>690.0</td>
<td>23.5</td>
<td>133.8</td>
<td>64.1</td>
</tr>
<tr>
<td>YCW</td>
<td>507.0</td>
<td>719.3</td>
<td>21.0</td>
<td>116.6</td>
<td>87.6</td>
</tr>
<tr>
<td>YCW + 100 mg/L Cl</td>
<td>490.3</td>
<td>709.8</td>
<td>19.7</td>
<td>109.6</td>
<td>62.0</td>
</tr>
<tr>
<td>YCW + 35000 mg/L Cl</td>
<td>487.8</td>
<td>720.9</td>
<td>25.8</td>
<td>143.2</td>
<td>61.5</td>
</tr>
</tbody>
</table>

**MIG/MAG welding**
Stress corrosion cracking (welds)

Typical results

SAW welding longitudinal 1,000 mg/L
Selection of candidate materials

- List of candidate materials was studied (pitting and uniform corrosion behaviour)

<table>
<thead>
<tr>
<th>Material Type</th>
<th>Material</th>
<th>UNS</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>C</th>
<th>N</th>
<th>Cu</th>
<th>Other</th>
<th>PREN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Austenitic</td>
<td>316L</td>
<td>S31603</td>
<td>16.18</td>
<td>10.14</td>
<td>2.3</td>
<td>0.03</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
<td>23</td>
</tr>
<tr>
<td>Nickel-based</td>
<td>Alloy 625</td>
<td>N08825</td>
<td>19.5-23.5</td>
<td>36-46</td>
<td>2.5-3.5</td>
<td>0.05</td>
<td>-</td>
<td>1.5-3.5</td>
<td>Ti: 0.6-1.2</td>
<td>28</td>
</tr>
<tr>
<td>Nickel-based</td>
<td>G04L</td>
<td>N08904</td>
<td>19-23</td>
<td>23-28</td>
<td>4.5</td>
<td>0.02</td>
<td>-</td>
<td>1.2</td>
<td>-</td>
<td>32</td>
</tr>
<tr>
<td>Super Austenitic</td>
<td>254 SMO</td>
<td>S31254</td>
<td>19.5-20.5</td>
<td>17.5-18.5</td>
<td>6.65</td>
<td>0.02</td>
<td>0.180.22</td>
<td>0.5-1</td>
<td>-</td>
<td>42</td>
</tr>
<tr>
<td>Nickel-based</td>
<td>Al-60N</td>
<td>N08367</td>
<td>20-22</td>
<td>23.5-25.5</td>
<td>6.7</td>
<td>0.03</td>
<td>0.180.25</td>
<td>0.75</td>
<td>-</td>
<td>43</td>
</tr>
<tr>
<td>Nickel-based</td>
<td>Alloy 31</td>
<td>N08031</td>
<td>26-28</td>
<td>30-32</td>
<td>6.7</td>
<td>0.02</td>
<td>0.15-0.25</td>
<td>1-1.4</td>
<td>-</td>
<td>48</td>
</tr>
<tr>
<td>Lean Duplex</td>
<td>LDX2004</td>
<td>S32304</td>
<td>21.5-24.5</td>
<td>3.5-5</td>
<td>0.05-0.6</td>
<td>0.03</td>
<td>0.05-0.2</td>
<td>-</td>
<td>-</td>
<td>22</td>
</tr>
<tr>
<td>Duplex</td>
<td>DX2205</td>
<td>S31603</td>
<td>21.23</td>
<td>4.5-6.5</td>
<td>2.5-3.5</td>
<td>0.03</td>
<td>0.08-0.2</td>
<td>-</td>
<td>-</td>
<td>31</td>
</tr>
<tr>
<td>Super Duplex</td>
<td>SDX2507</td>
<td>S32750</td>
<td>24.26</td>
<td>6.6</td>
<td>3.5</td>
<td>0.03</td>
<td>0.24-0.32</td>
<td>0.5</td>
<td>-</td>
<td>38</td>
</tr>
<tr>
<td>Super Duplex - Mo</td>
<td>SDX100</td>
<td>S32760</td>
<td>24.26</td>
<td>6-8</td>
<td>3-4</td>
<td>0.03</td>
<td>0.2-0.3</td>
<td>0.5-1</td>
<td>W 0.5-1</td>
<td>37</td>
</tr>
<tr>
<td>Nickel-based + Mo</td>
<td>C-276</td>
<td>N10276</td>
<td>15.5-16.5</td>
<td>Ca: 57</td>
<td>15-17</td>
<td>0.01</td>
<td>-</td>
<td>-</td>
<td>W 3.5-4.5 Fe: 4.7</td>
<td>-</td>
</tr>
<tr>
<td>Nickel-based + Mo</td>
<td>C-4</td>
<td>N06455</td>
<td>16</td>
<td>Ca: 65</td>
<td>16</td>
<td>0.01</td>
<td>-</td>
<td>-</td>
<td>Fe: 2</td>
<td>-</td>
</tr>
<tr>
<td>Nickel-based + Mo</td>
<td>C-22</td>
<td>N06922</td>
<td>20-22.5</td>
<td>Ca: 56</td>
<td>12.5-14.5</td>
<td>0.01</td>
<td>-</td>
<td>-</td>
<td>W 2.5-3.5 Fe: 2-6</td>
<td>-</td>
</tr>
<tr>
<td>Nickel-based + Mo</td>
<td>C-2000</td>
<td>N06200</td>
<td>22-24</td>
<td>Ca: 67</td>
<td>15-17</td>
<td>0.01</td>
<td>-</td>
<td>1.3-1.9</td>
<td>Fe: 3</td>
<td>-</td>
</tr>
<tr>
<td>Zirconium</td>
<td>Zr/Ti2</td>
<td>R60702</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Ti: 2</td>
<td>Zr: 86</td>
</tr>
</tbody>
</table>

- **Super austenitic 254 SMO = best candidate for pitting corrosion**
- **Corrosion rate of stainless steel in cement (CEM I): very low, not measurable. (< 0.01 nm/year)**
Conclusions and open questions
Conclusions and open questions

- **Uniform corrosion:**
  - $v_{\text{CORR}}$, volumetric method: 10 - 48 nm/year
  - $v_{\text{CORR}}$, pressure transducer = 20 – 30 nm/year
  - $v_{\text{CORR}}$, hydrogen sensor = 0.03 - 10 nm/year

- **Pitting corrosion:**
  - Pits (due to chloride) cannot propagate under the expected conditions in the supercontainer
  - Pits cannot reactivate during the anoxic period

- **Stress corrosion cracking**
  - Currently no indication of increased susceptibility

Open questions:
- Initial surface finish?
- C-steel composition?
- Microstructure
- Pre-existing oxides?
- Effect of S-species?
- Effect of potential?
- H-embrittlement possible?
Alternative solutions?

- ONDRAF/NIRAS currently keeps a technological eye on alternative canister material solutions

  - Ceramic Materials and Coatings
    - Bulk materials: $\text{SiO}_2/\text{Al}_2\text{O}_3$ & SiC-Cr
    - Coatings: $\text{TiO}_2$ & CrN

  - Metallic materials and coatings
    - Bulk materials: Cu alloys
    - Coatings: Cu, Ti, Cr, Cu/Al$_2$O$_3$