

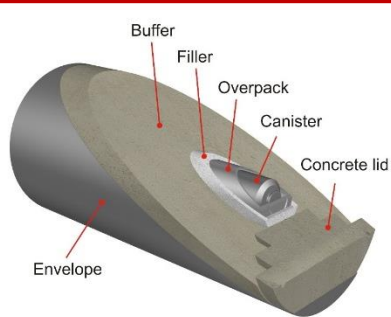
# Corrosion behavior of iron in cementitious solution at 80°C in anoxic condition

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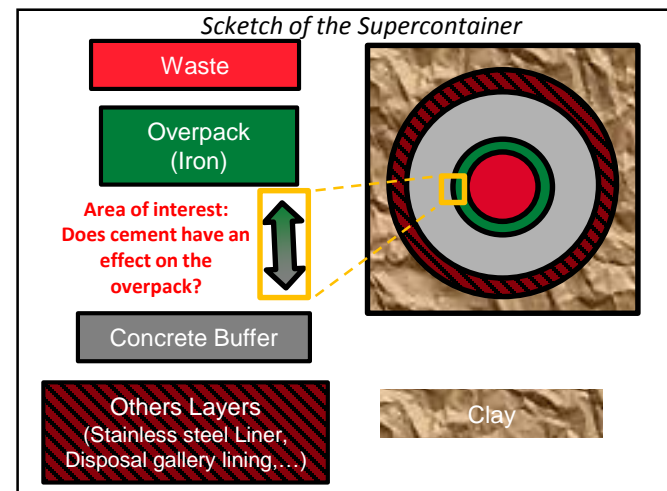
## Context



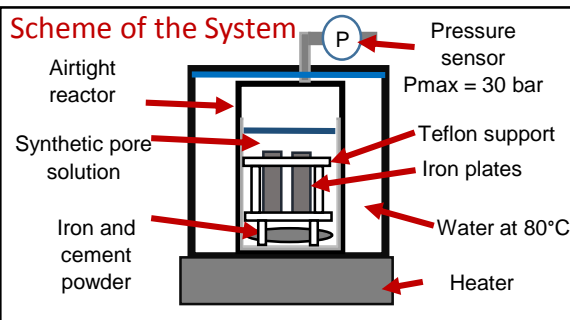
The Belgian reference concept for high-level radioactive waste packaging proposed by ONDRAF/NIRAS is called « Supercontainer ».

Inside the container, a concrete buffer allows to maintain high alkaline conditions at the surface of the overpack. → a passive film should form on the iron surface (in anoxic condition and 80°C),.

→ Aim of this study : Characterize the passive layer and its stability over time



## Experimental device



N°	Cementitious material	Corrosion days	Temperature (°C)
Fe D+4 days	CEMI	4	80
Fe D+20 days	CEM I	20	80
Fe D+160 days	CEM I	160	80

## Corrosion parameters

Solution :  
NaOH = 63 mmol/l + KOH = 139 mmol/l  
(Alkaline solution pH 13.2)  
+ Cementitious material  
(CEM I powder hydrated)

**Anoxic condition, 80°C**

## Results / Characterization

**SEM**

**D+4**

Neoformation  
Iron + thin layer of oxide

**D+20**

Neoformation  
Iron + thin layer of oxide

**D+160**

Neoformation

**XPS**

**D+4**

D+4 : Presence of Fe<sup>2+</sup> and Fe<sup>3+</sup> = magnetite.  
Fe<sup>0</sup> = the layer is fine.

**D+20**

D+20 : Fe<sup>2+</sup> and Fe<sup>3+</sup> = magnetite  
Peak Fe<sup>3+</sup> in contact with Silicate = hydrogarnet.

**D+160**

D+160 : Only the peak Fe<sup>3+</sup> in contact with Silicate proves that the layer is thick.

**XRD**

Microstructural analyses

D+4 : Only Fe peak, the corrosion layer is so thin  
D+20 and D+160 : hydrogarnet Ca<sub>3</sub>(Fe<sub>x</sub>Al<sub>1-x</sub>)<sub>2</sub>(SiO<sub>4</sub>)(OH)<sub>8</sub> contributions (0 < x < 1).

■ = Iron  
● = Magnetite  
▲ = Hydrogarnet

**μ-Raman**

D+4 : Peak of magnetite (Fe<sub>3</sub>O<sub>4</sub>) only (546 and 666 cm<sup>-1</sup>)  
D+20 and D+160 : the signal corresponds to a mixture between magnetite and one other compound (peak at 503/863/972 cm<sup>-1</sup>) (Hydrogarnet).

**FIB lamina and EDS**

Outer Layer : 1000 nm  
Border : 4nm  
Inner Layer : 200 nm (Fe inclusion)

The inner and outer layers appear to be composed of Fe / Ca / Si and O (hydrogarnet)  
Border appears to be composed of Fe and O (magnetite)

## Conclusions – Proposition of a scenario

In our conditions (Alkaline solution with cement powder/80°C/anoxic conditions):

- First days : Formation of magnetite
- After several days : Formation of Hydrogarnet Ca<sub>3</sub>(Fe<sub>x</sub>Al<sub>1-x</sub>)<sub>2</sub>(SiO<sub>4</sub>)(OH)<sub>8</sub>
- Presence of Inner and outer layer composed of Hydrogarnet
- Presence of central layer composed of magnetite

## Perspectives

- 1° Determination of the formation condition of the hydrogarnet layer
  - Influence of chemical conditions (effect of aluminum and silicon)
    - Influence of pre-corroded surfaces
- 2° Ability of neoformations to inhibit pitting corrosion
  - Chlorides influence