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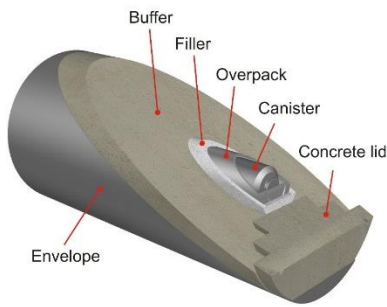
Corrosion behavior of iron in cementitious solution at 80°C in anoxic condition

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Context

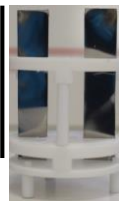
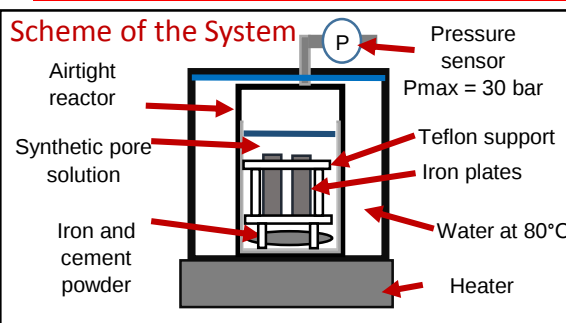


The Belgian reference concept for high-level radioactive waste packaging proposed by ONDRAF/NIRAS is called « Supercontainer ».

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

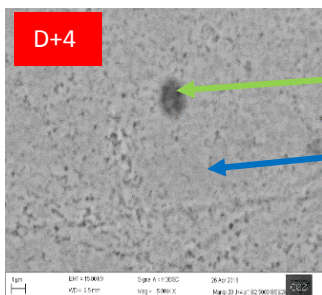
Solution :
NaOH = 63 mmol/l + KOH = 139 mmol/l
(Alkaline solution pH 13.2)
+ Cementitious material
(CEM I powder hydrated)

Anoxic condition, 80°C

Results / Characterization

Time

SEM

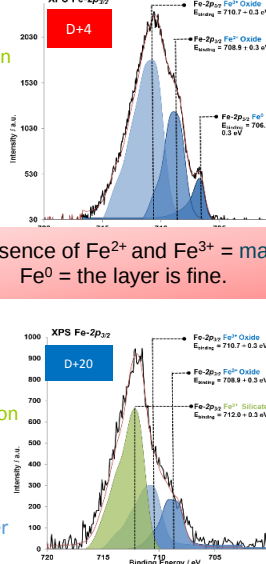


Neoformation

Iron + thin layer of oxide

D+4 : Presence of Fe²⁺ and Fe³⁺ = magnetite. Fe⁰ = the layer is fine.

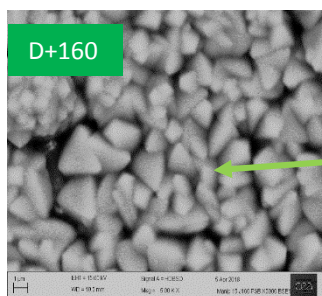
XPS



Neoformation

Iron + thin layer of oxide

D+20 : Fe²⁺ and Fe³⁺ = magnetite
Peak Fe³⁺ in contact with Silicate = hydrogarnet.

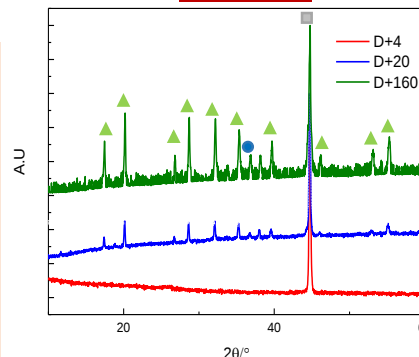


Neoformation

D+160 : Only the peak Fe³⁺ in contact with Silicate proves that the layer is thick.

XRD

Microstructural analyses



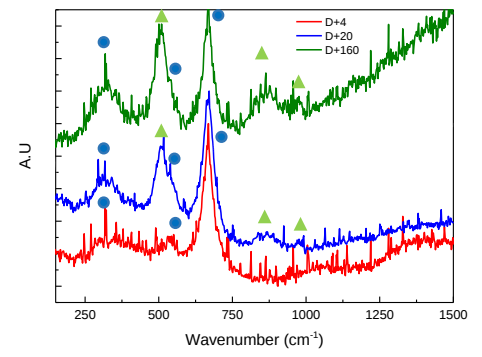
D+4 : Only Fe peak, the corrosion layer is too thin
D+20 and D+160 : hydrogarnet Ca₃(Fe_xAl_{1-x})₂(SiO₄)(OH)₈ contributions (0 < x < 1).

■ = Iron

● = Magnetite

▲ = Hydrogarnet

μ-Raman



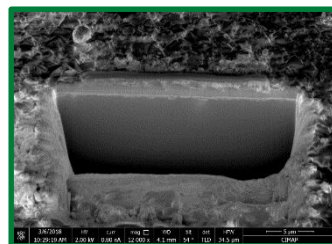
D+4 : Peak of magnetite (Fe₃O₄) only (546 and 666 cm⁻¹)

D+20 and D+160 : the signal corresponds to a mixture between magnetite and one other compound (peak at 503/863/972 cm⁻¹) (Hydrogarnet).

FIB lamina and EDS

20μm

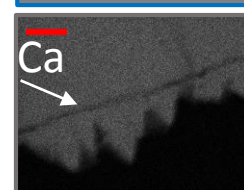
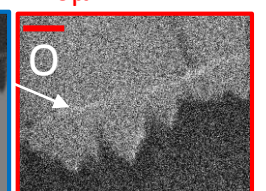
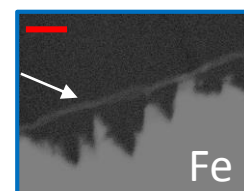
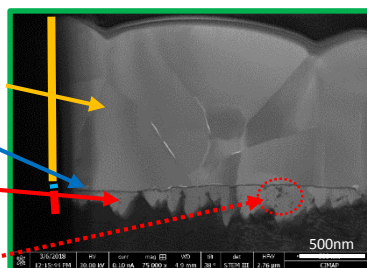
D+160



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 Ca₃(Fe_xAl_{1-x})₂(SiO₄)(OH)₈
- Presence of Inner and outer layer composed of Hydrogarnet
- Presence of central layer composed of magnetite

Perspectives

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