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

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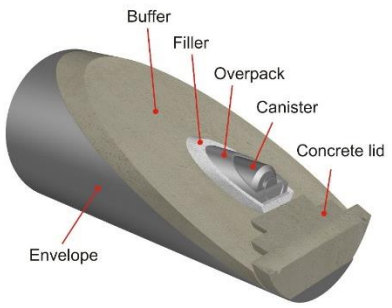
Context

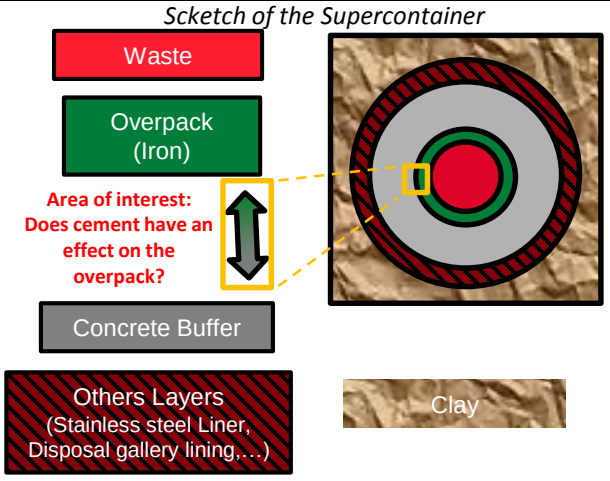


The Belgian reference concept for high-level radioactive waste packaging proposed by ONDRAF/NIRAS is called « Supercontainer ».

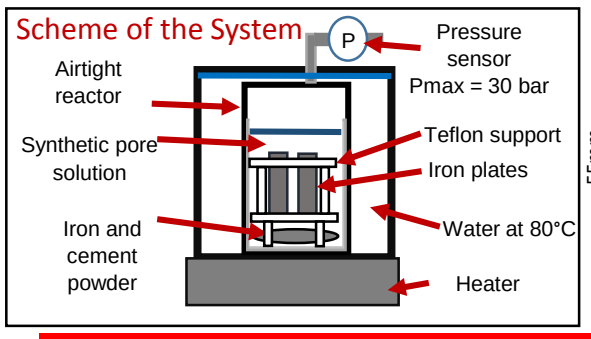
Inside the container, a concrete buffer allows to maintain high alkaline conditions at the surface of the overpack. → a passive film should form on the iron surface (in anoxic condition and 80°C),.

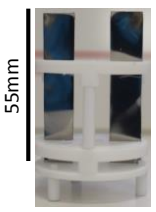
→ Aim of this study : Characterize the passive layer and its stability over time

Scketch of the Supercontainer



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

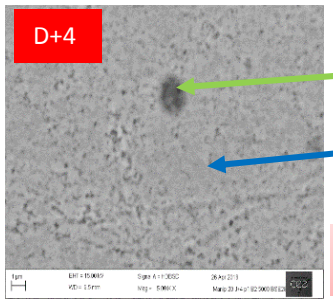
Solution :
NaOH = 63 mmol/l + KOH = 139 mmol/l
(Alkaline solution pH 13.2)
+ Cementitious material
(CEM I powder hydrated)

Anoxic condition, 80°C

Results / Characterization

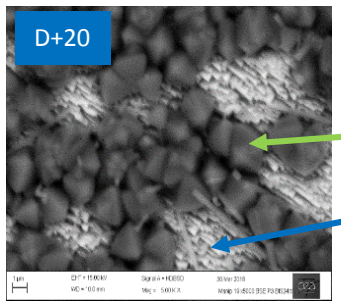
Time ↓

SEM



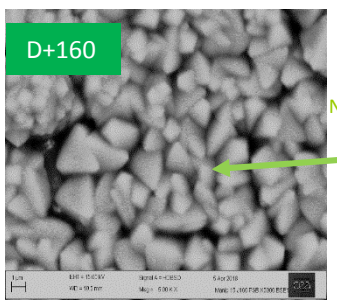
Neoformation

Iron + thin layer of oxide



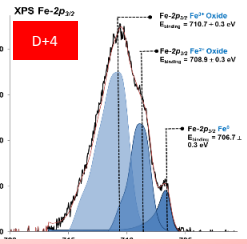
Neoformation

Iron + thin layer of oxyde

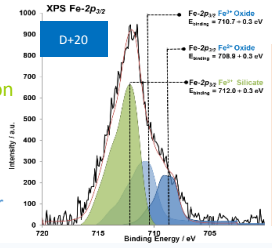


Neoformation

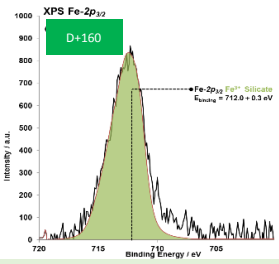
XPS



D+4 : Presence of Fe^{2+} and Fe^{3+} = magnetite.
Fe^0 = the layer is fine.

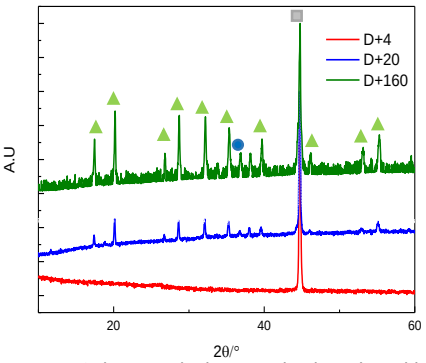


D+20 : Fe^{2+} and Fe^{3+} = magnetite
Peak Fe^{3+} in contact with Silicate = hydrogarnet.



D+160 : Only the peak Fe^{3+} in contact with Silicate proves that the layer is thick.

XRD

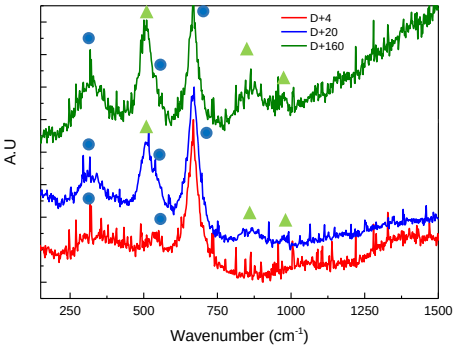


Microstructural analyses

D+4 : Only Fe peak, the corrosion layer is to thin
D+20 and D+160 : hydrogarnet $Ca_3(Fe_xAl_{1-x})_2(SiO_4)(OH)_8$ contributions (0<x<1).

■ = Iron ● = Magnetite ▲ = Hydogarnet

µ-Raman



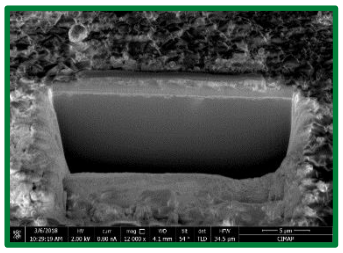
D+4 : Peak of magnetite (Fe_3O_4) only (546 and 666 cm^{-1})

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).

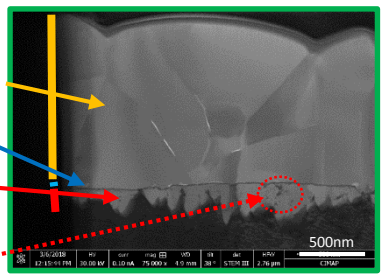
Elementary analyses

FIB lamina and EDS

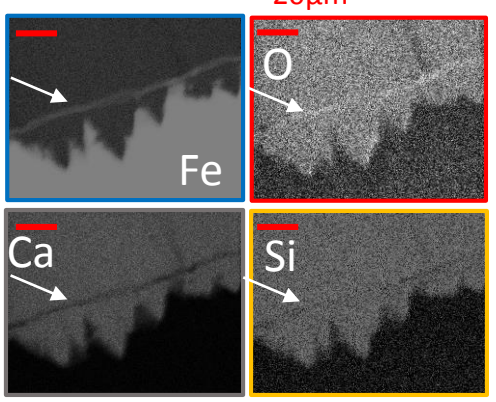
D+160



FIB lamina of this sample

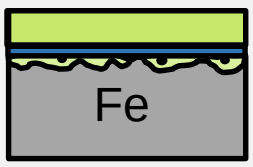


Outer Layer : 1000 nm
Border : 4nm
Inner Layer : 200 nm (Fe inclusion)



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 $Ca_3(Fe_xAl_{1-x})_2(SiO_4)(OH)_8$
- 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