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Corrosion processes at the GGG40 steel–bentonite interface

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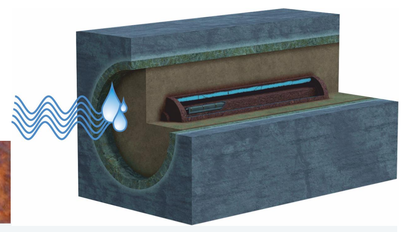
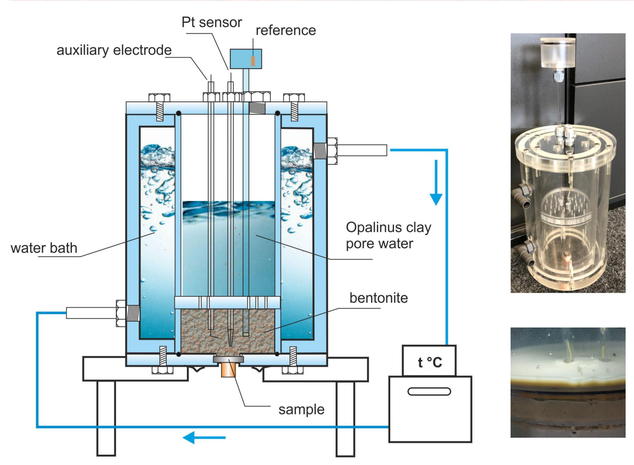


Motivation

Spheroidal graphite cast iron (GGG40/0.7040) is a classical material, the outer wall containers for granite disposal concepts are made of. This work aims to provide a deeper insight into the corrosion mechanism acting at the interface steel-bentonite after saturation with aerated Opalinus clay water. The steel degradation was monitored by polarization and electrochemical impedance in middle-term experiments performed in an special bentonite three-electrodes electrochemical cell.

Experimental

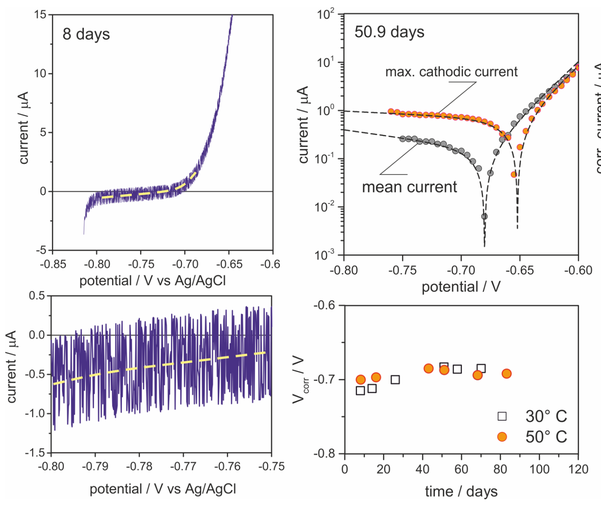


- Three-electrodes bentonite cell
- Slurry of Wyoming bentonite with Opalinus clay water (1:10)
- Initial oxygen content: 8.6 mg l^{-1}
- Duration of experiment: 3 months
- Samples mirror polished: emery paper + diamond suspension 6 µm and 1 µm

Electrochemical studies

The polarization curves are characterized by random oscillations showing an upper and a lower current limit. This is probably due to a coupling of the cathodic activity of the graphite nodules with the corroding steel matrix. The oxygen reduction is attenuated by diffusion-control and water reduction on the steel matrix dominates the dissolution process.

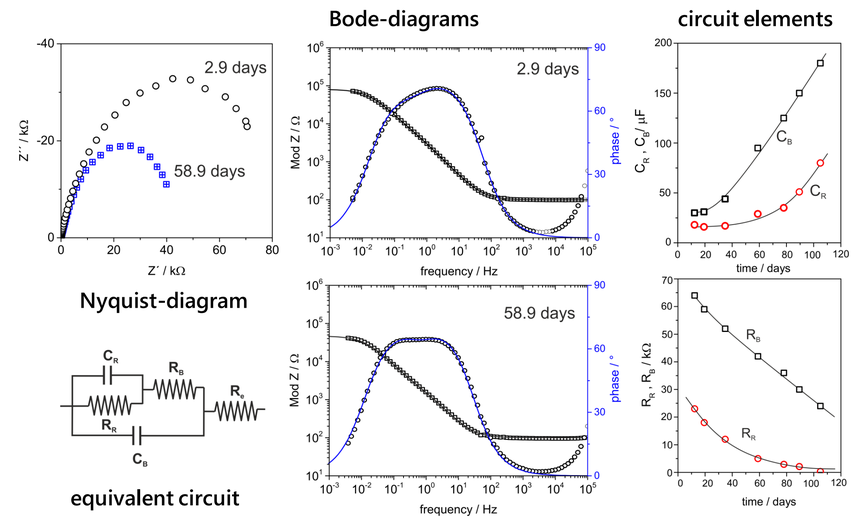
Polarizations



anodic
$Fe(m) \rightarrow Fe^{2+} + 2\ e^-$ (m: matrix)
$Fe^{2+} + H_2O \rightarrow Fe(OH)_2 + 2\ H^+$
$3\ Fe(OH)_2 \rightarrow Fe_3O_4 + H_2 + 2\ H_2O$
$Si(m) + 2\ H_2O \rightarrow SiO_2 + 4\ H^+ + 4\ e^-$

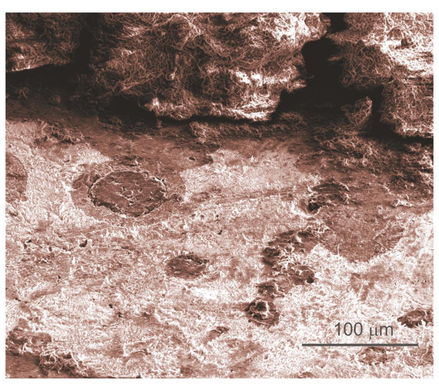
cathodic
$O_2 + 4\ e^- + 2\ H_2O \rightarrow 4\ OH^-$
$2\ H_2O + 2\ e^- \rightarrow H_2 + 2\ OH^-$

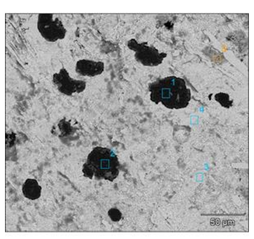
Electrochem. Impedance



Surface morphology and chemistry

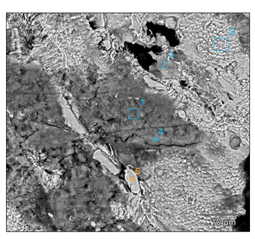
SEM - EDX





element	% at 1	3	4	5
C	99.4	5.0	6.5	6.4
O		5.6	6.8	48.2
Na		1.4	2.1	1.6
Mg		1.4	1.5	0.3
Al				1.0
Si	0.2	5.3	6.0	4.5
P			0.2	
S	0.1	0.6	0.7	0.2
Cl	0.3	0.2	0.5	4.4
Fe		80.5	75.5	33.5

graphite spheres | Ferrite ? | oxide-silicate



element	% at 1	4	3	2	5
C	6.1		3.5	4.9	5.7
O	52.3	38.2	29.6	4.4	2.3
Na			2.1	2.0	
Mg		0.1	2.1	1.2	
Al	0.3	0.3	3.2		
Si	2.9	3.1	9.6	4.6	0.6
S	0.2		0.8	0.6	
Cl	5.8	29.4	0.4	0.4	
Cr					2.0
Mn					0.6
Fe	32.4	28.9	48.7	81.9	88.9

Iron oxide | Iron oxide-chloride | Iron oxide-silicate | Steel phases

Interpretations

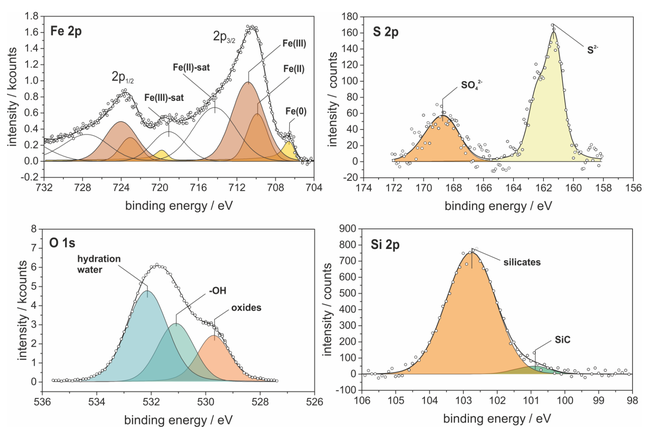
The initial corrosion phase of GGG40 is characterized by the formation of local elements. Graphite nodules, specially reactive for the oxygen reduction, act as cathodic elements. They are coupled with the corroding matrix, accelerating the material degradation.

There is an accumulation of non-passivating corrosion products at the interface steel-bentonite. It consists of hydrated Fe(II)/Fe(III) oxy-hydroxides, silicates, and alkaline earth sulfates.

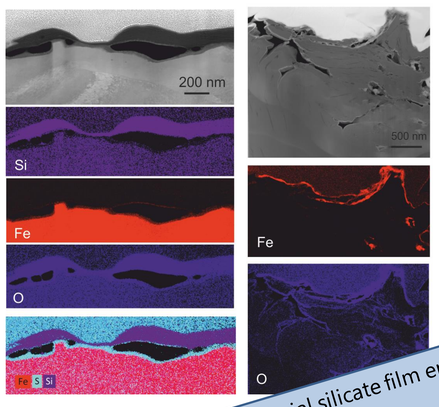
The formation of local elements accelerates the dissolution of ferrite around the graphite nodules which are exfoliated by hydrogen intercalation.

Surface spectroscopy

LOCAL XPS

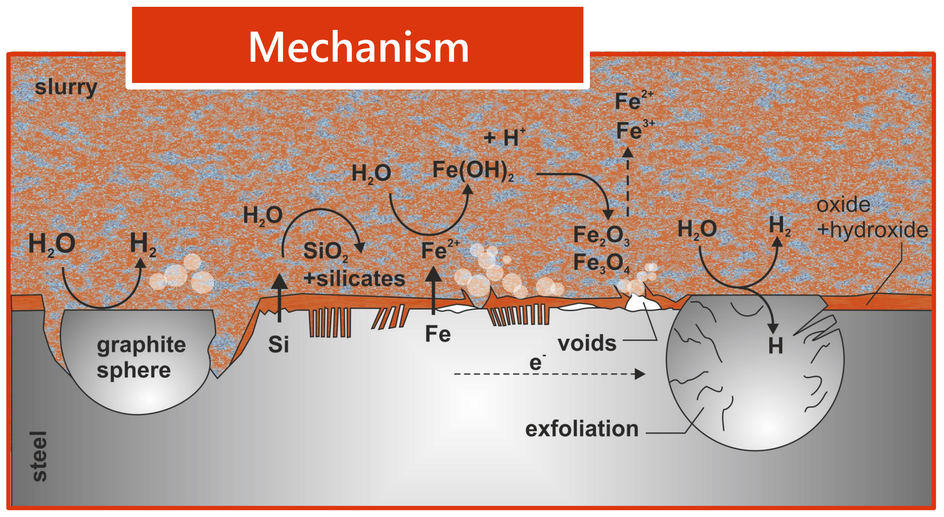


TEM - EDX



Deposition of an interfacial silicate film enclosing voids containing hydrogen.

Mechanism



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