Corrosion mechanism of spheroidal graphite cast iron GGG40 in Opalinus Clay water

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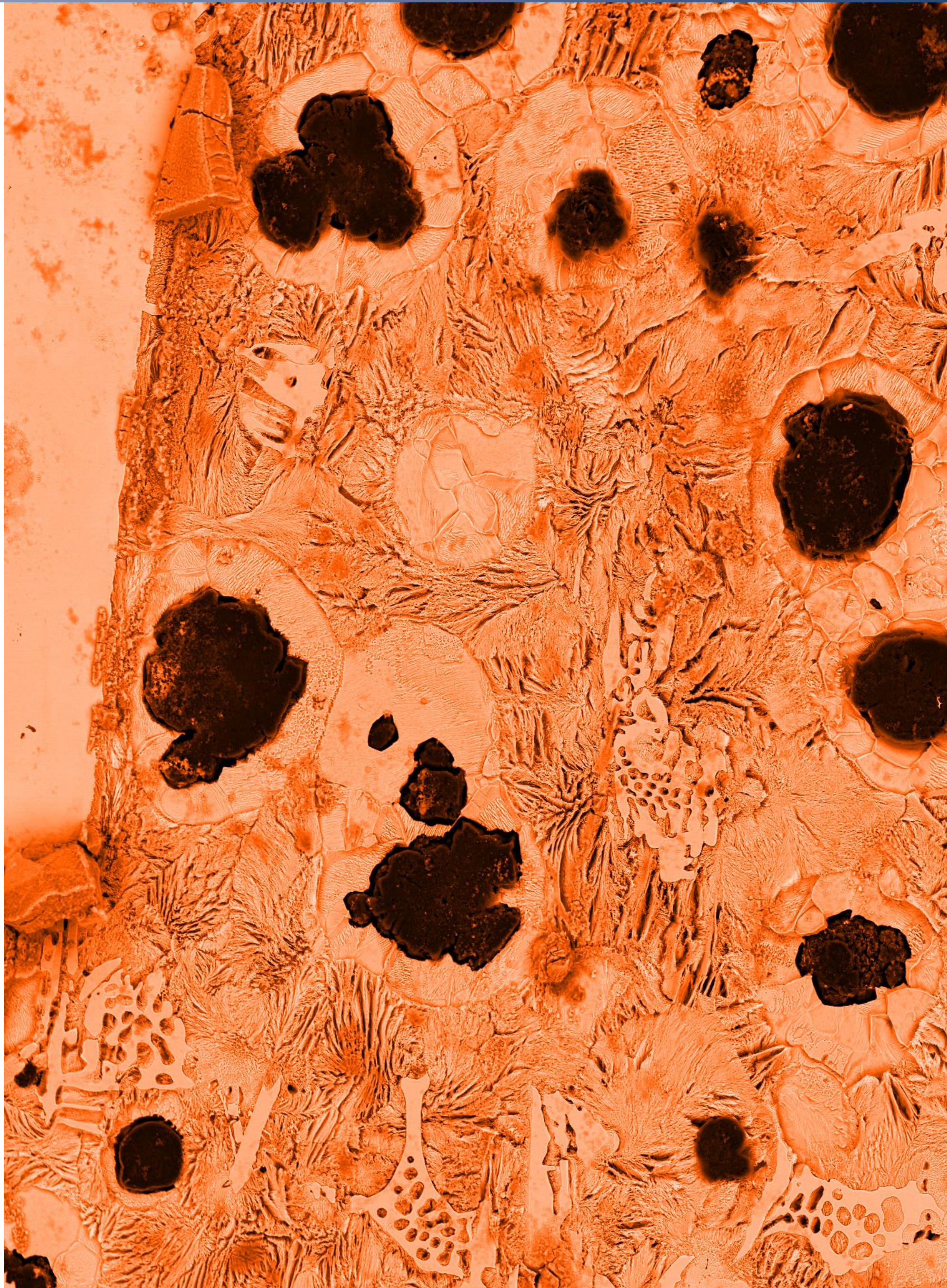

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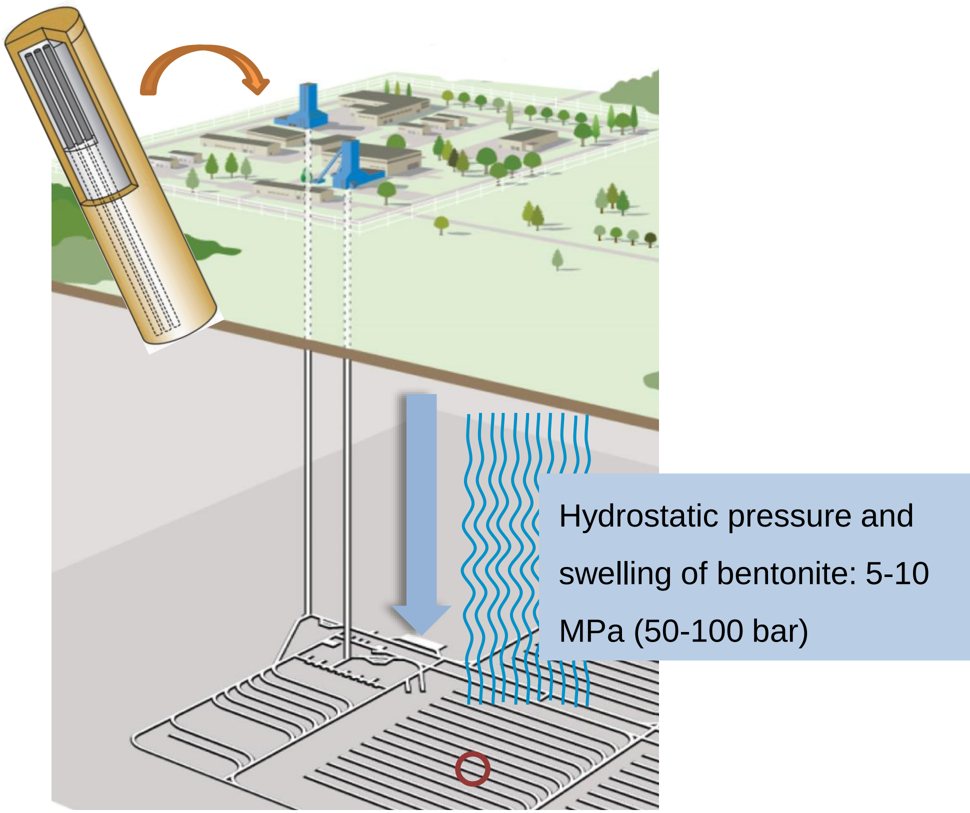

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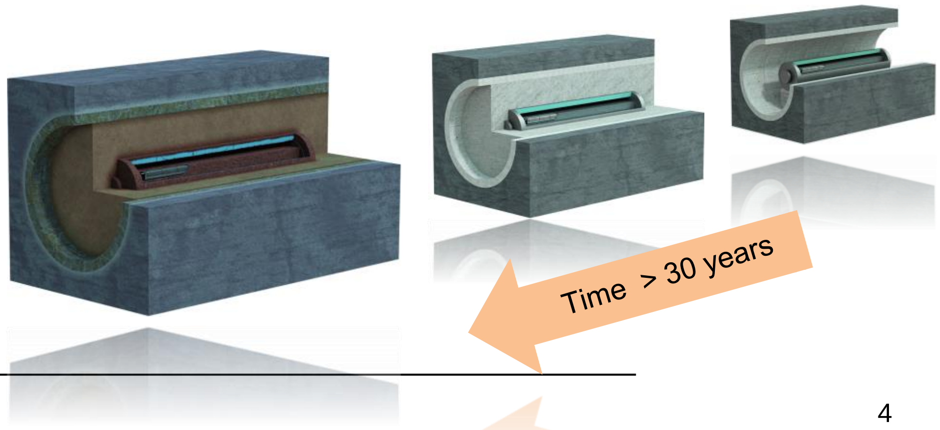

W. Bollingerfehr et al, Technical report TEC-20-2008-AP, DBE-Technology, Peine, 2008.
GNS Gesellschaft für Nuklear-Service mbH, www.gns.de

F. King, Waste Containers in Comprehensive Nuclear Materials (2012).

(*) Pictures: courtesy from Olivier Leupin / NAGRA

- motivation
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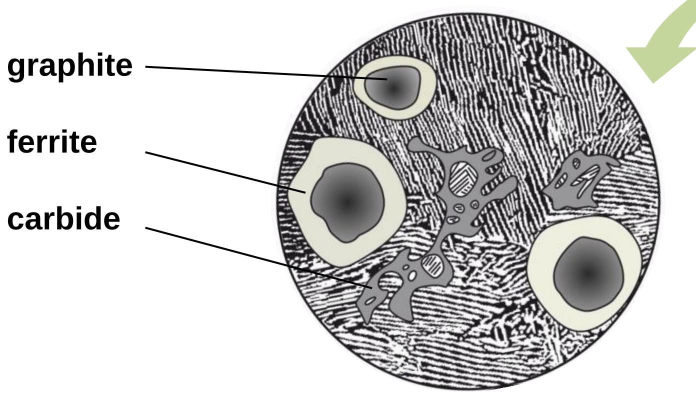
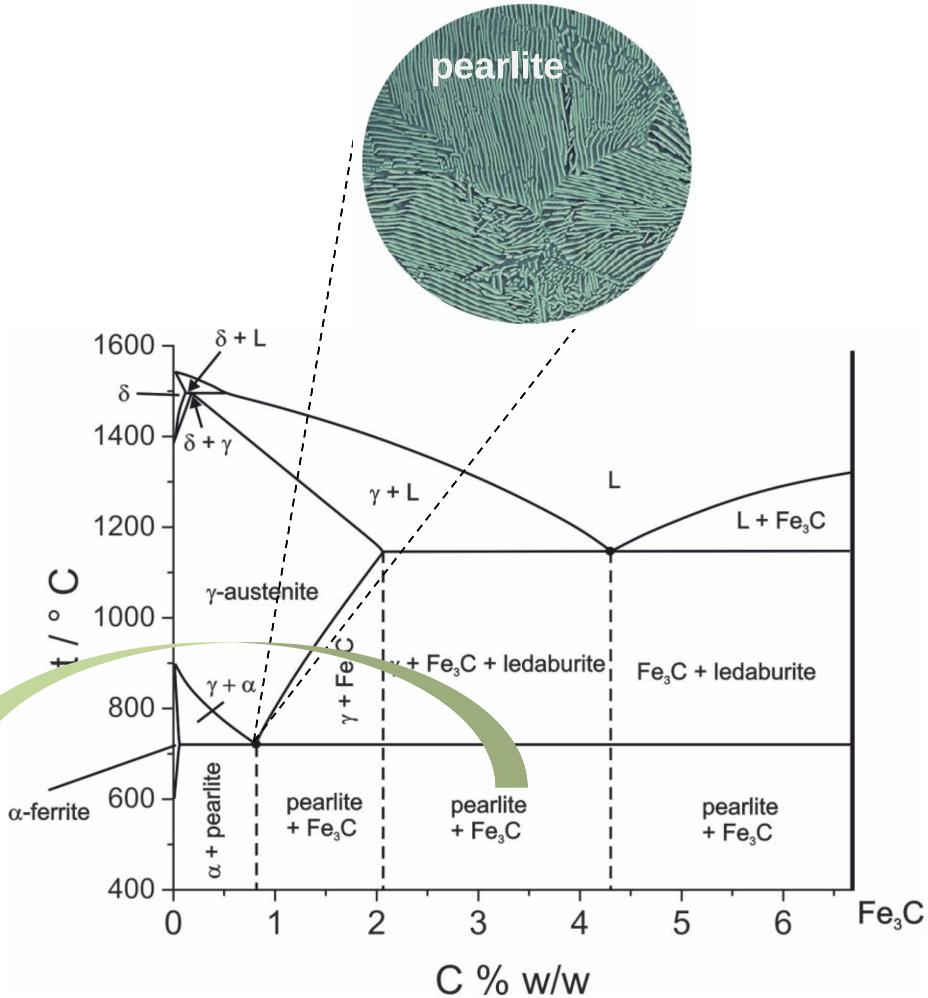
Experimental setup / Material

Spheroidal graphitic steel GGG 40

element	% at
C	13.85
Si	5.80
Mn	0.25
P	0.14
S	0.004
Mg	0.10
Cr	0.039
Cu	0.028
Fe	79.86

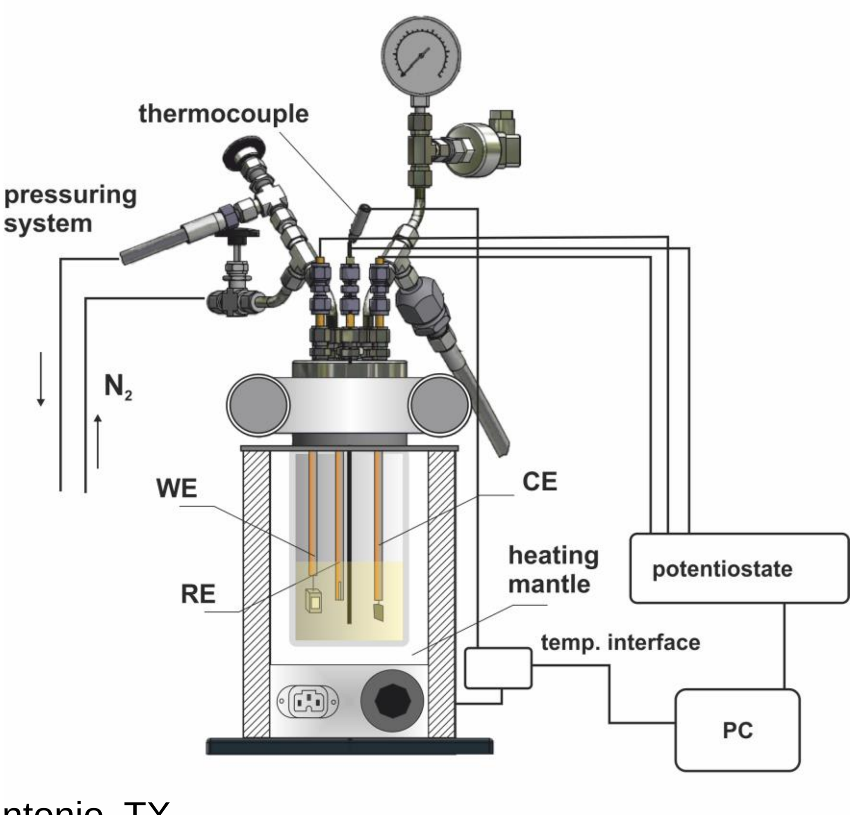




Opalinus-clay water / type A

Ion	m / mol kg^{-1}
Na	0.24
Cl	0.30
K	0.0016
Mg	0.017
Ca	0.026
Sr	0.00065
SO_4	0.014
HCO_3	0.00048

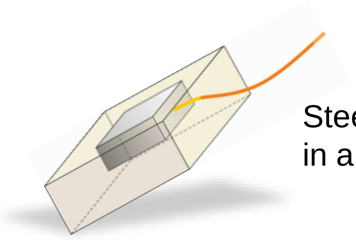
High-pressure electrochemical cell



- polarizations v: 0.166 mV s
- impedance spectroscopy: open circuit potential
- HP- HAT-electrodes from Corr Instruments, San Antonio TX

- t 30 °C and 50°C
- 5 bar and 100 bar

- samples polished until mirror grade: 1 μm diamond paste



Steel pieces embedded in araldite ®

- motivation
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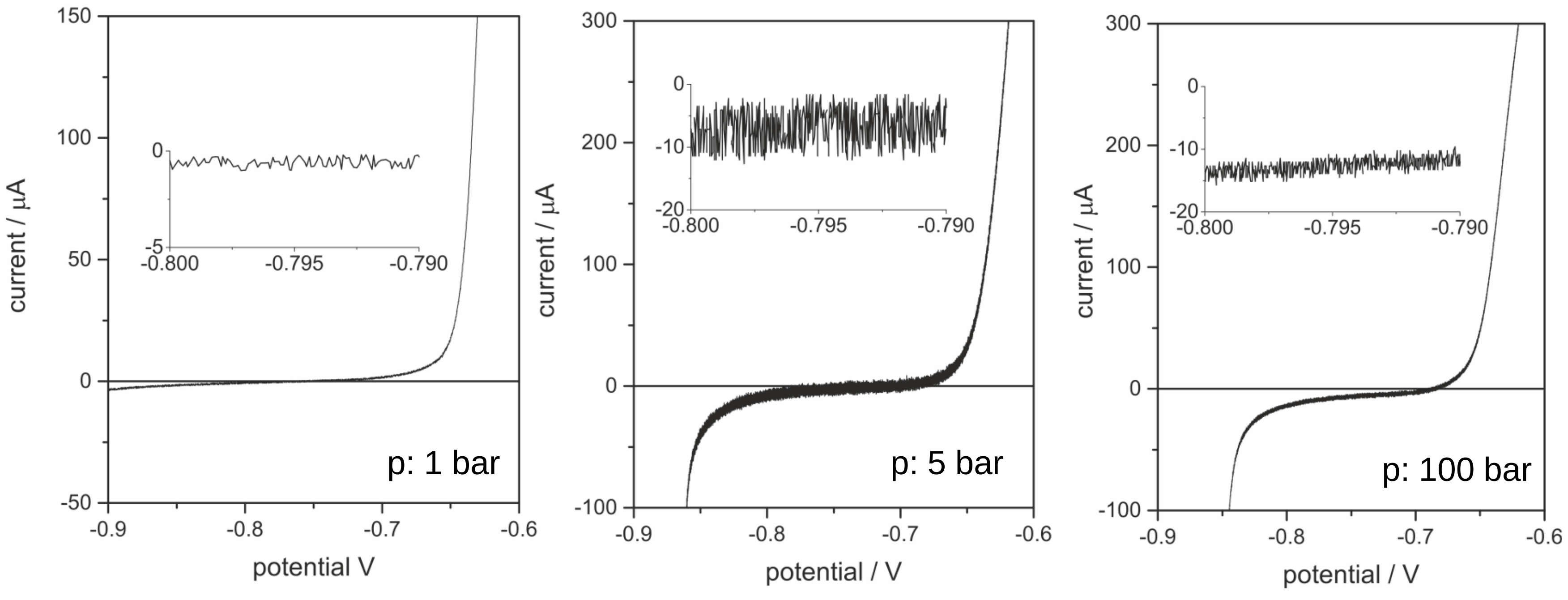
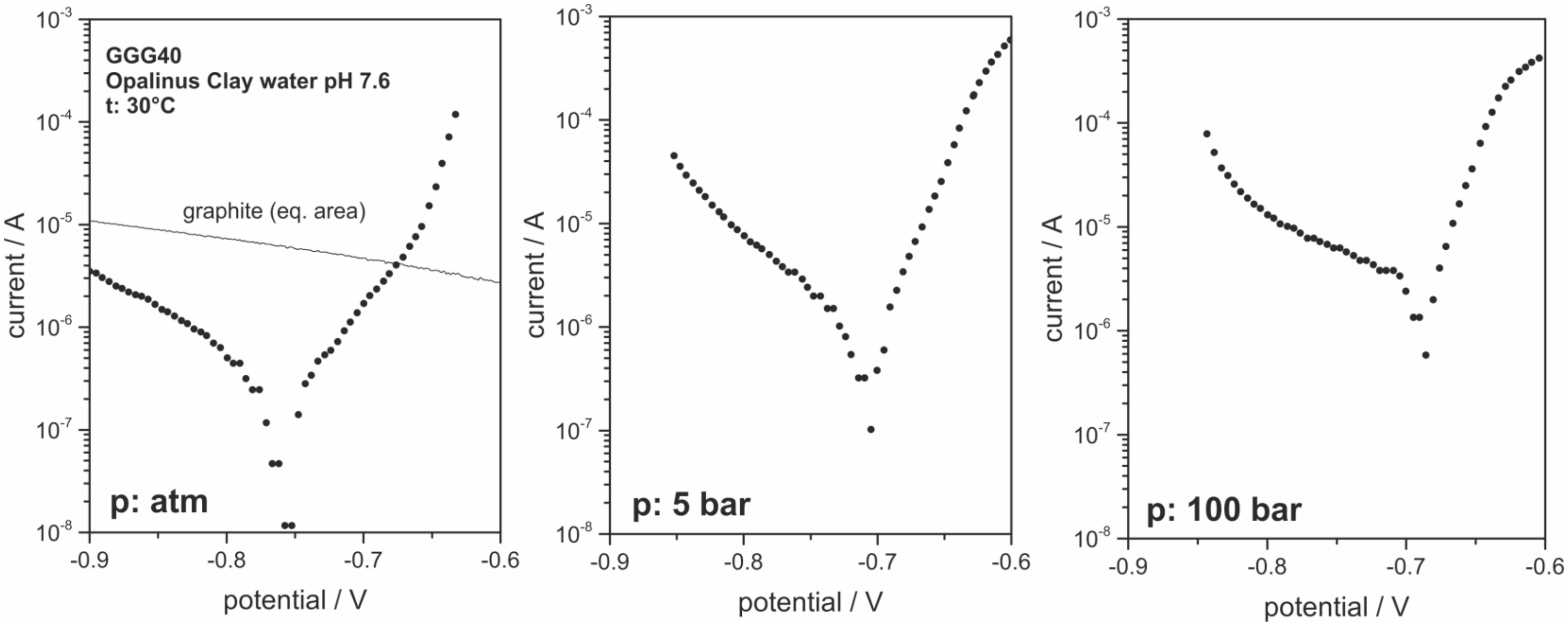
Electrochemical measurements / Polarization curves



Polarization curves of GGG40 in Opalinus Clay water (pH 7.6) at 30°C at different pressures

Scan rate: 0.166 mV s^{-1}

The cathodic current shows a random oscillation denoting some perturbation effect.



Polarization curves of GGG40 in Opalinus Clay water (pH 7.6) at 30°C at different pressures

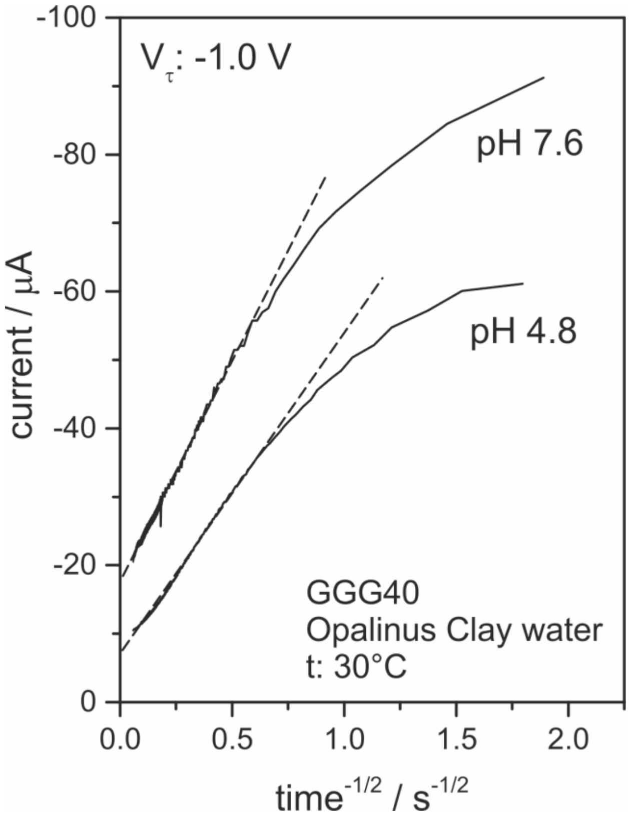
Scan rate: 0.166 mV s^{-1}

X.L. Xiong et al, Electrochim. Acta 283 (2018) 1534

The pressurizing of the cell brings about an increase of the corrosion rate. An enhancement of both cathodic and anodic reaction is observed.

Possible causes:

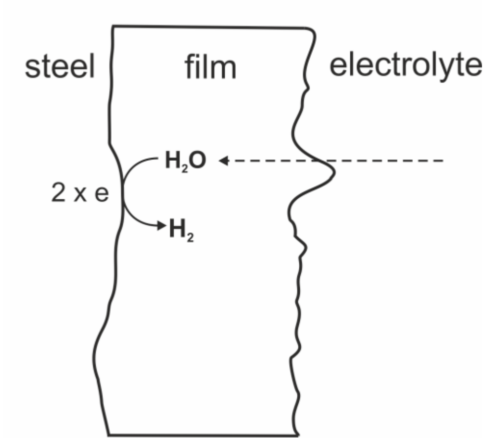
- acceleration of the Heyrovsky reaction step
  $H_2O + H_{ads} + e^- \rightarrow H_2 + OH^-$
- Reduction of surface oxide and inward diffusion of H

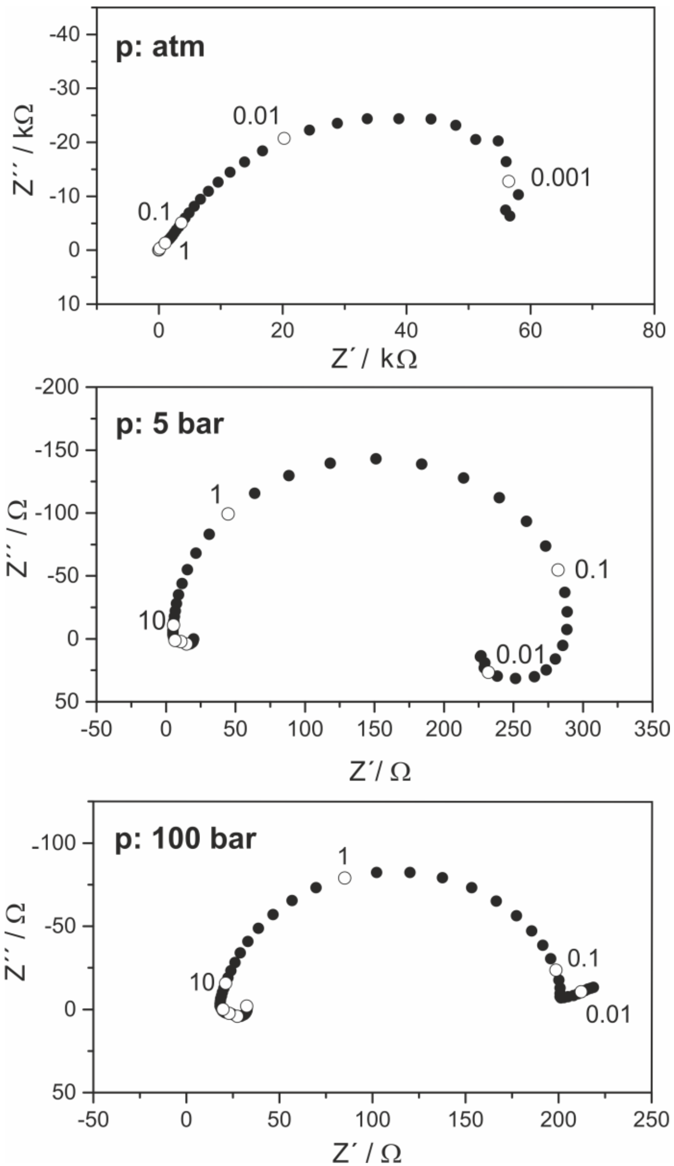


$$I = \frac{n\,\mathrm{F}\,A\,\sqrt{D}\,C}{\sqrt{\pi}}\frac{1}{\sqrt{t}} + I_{\mathrm{kin}}$$

C_{H2O} : 55.5 × 10^{-3} mol cm^{-3}

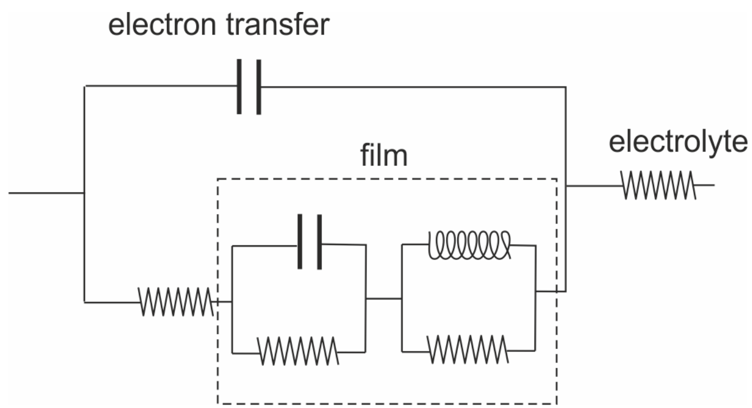
D: 3.5 × 10^{-15} cm^2 s^{-1}





Nyquist impedance diagrams of GGG40 Opalinus Clay water (pH 7.6) at 30°C at different pressures.

Spectra in pressure cells taken after 48 h at the OPC



The impedance diagrams indicate that the corrosion occurs under the formation of a non passivating film. The decreasing resistance of the Faraday process with pressure determines the shape of the diagram.

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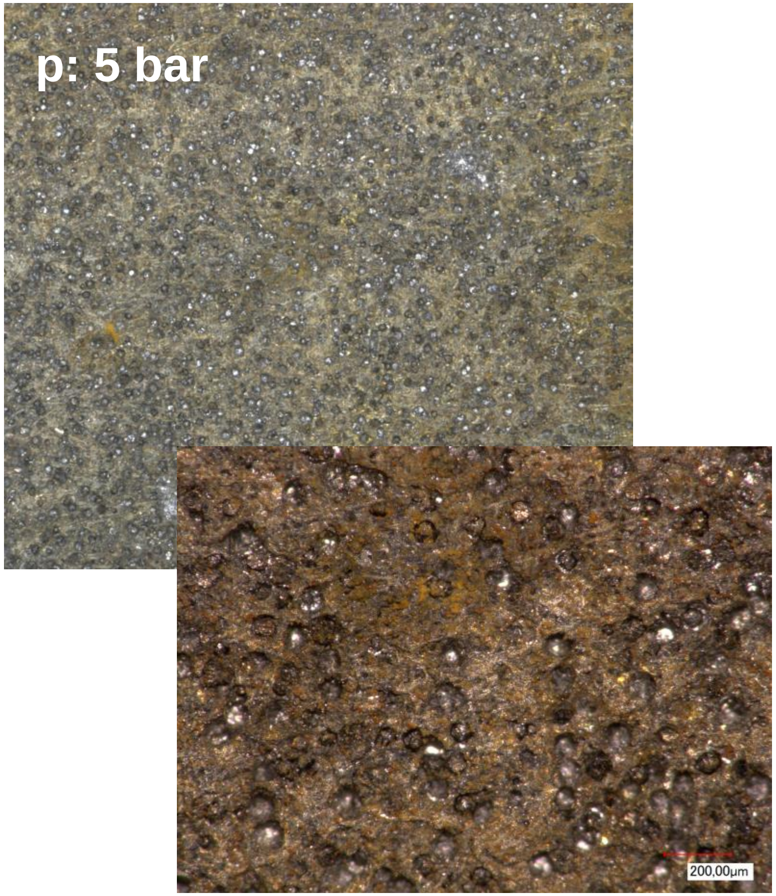
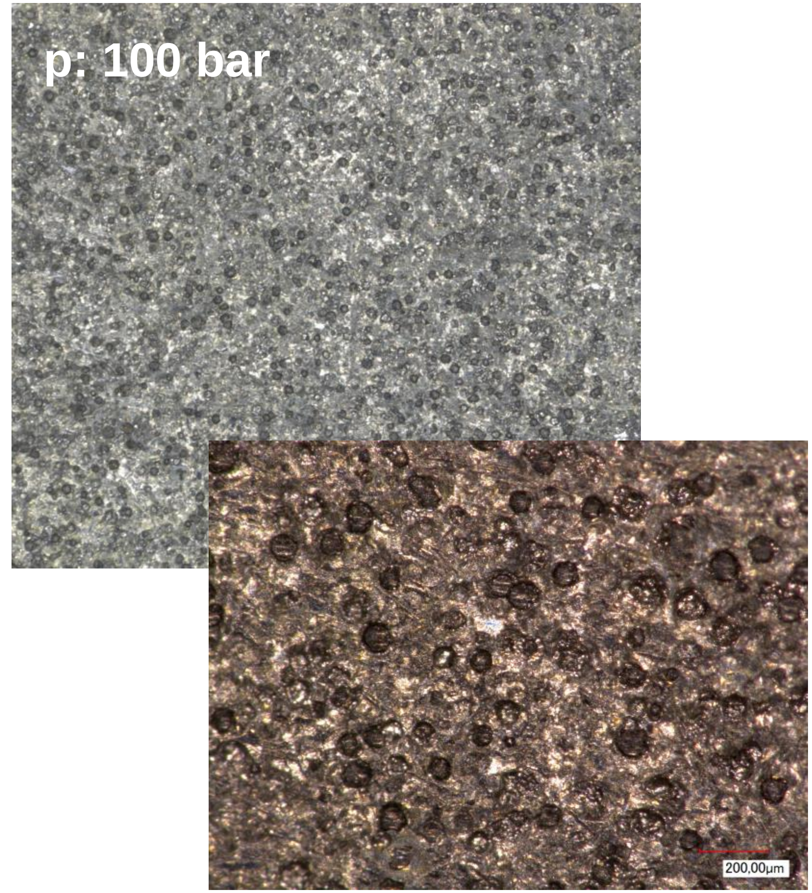
Surface analysis / Optical aspects



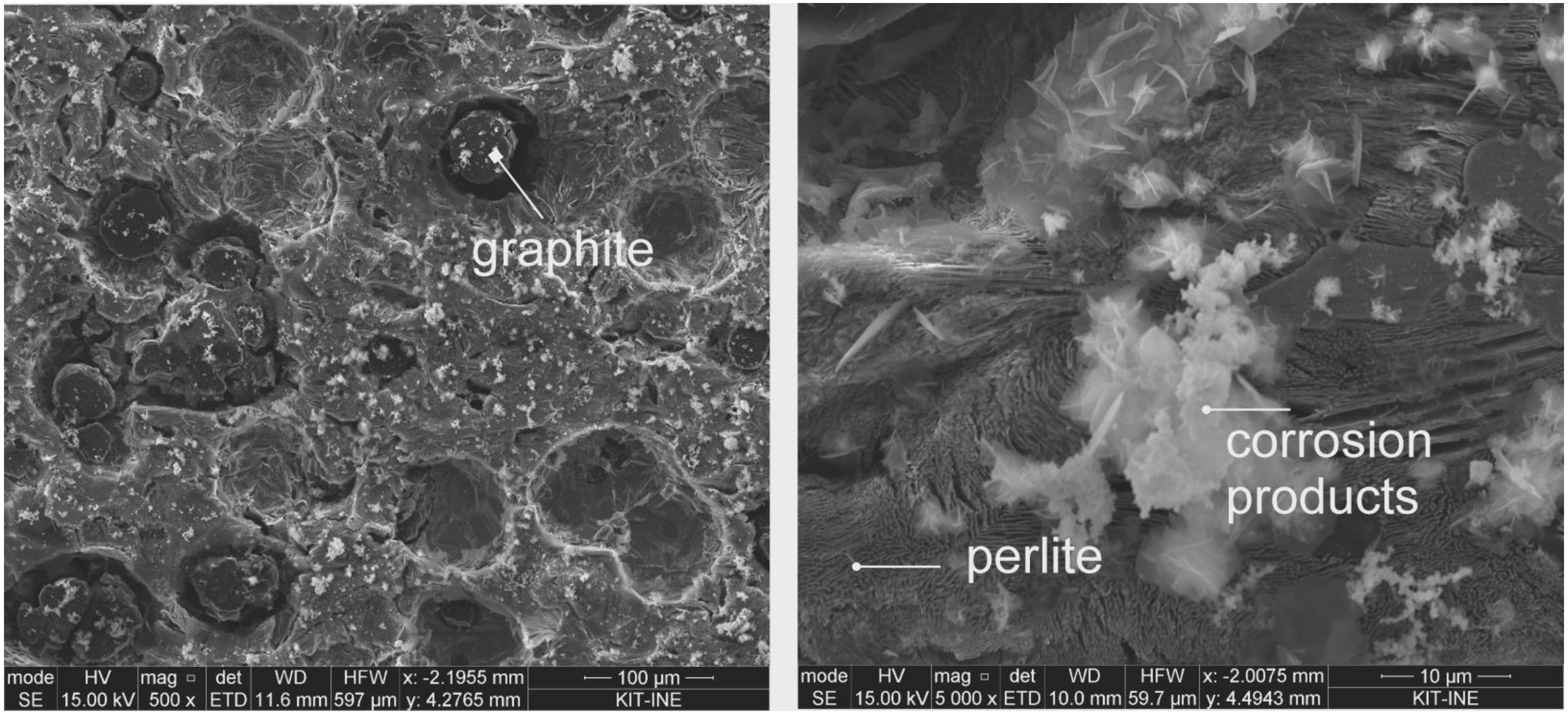


Optical microscopy of GGG40 surface after 48 corrosion in

Opalinus Clay water pH 7.6 at different pressures

t: 30°C

Surface analysis / SEM-EDX



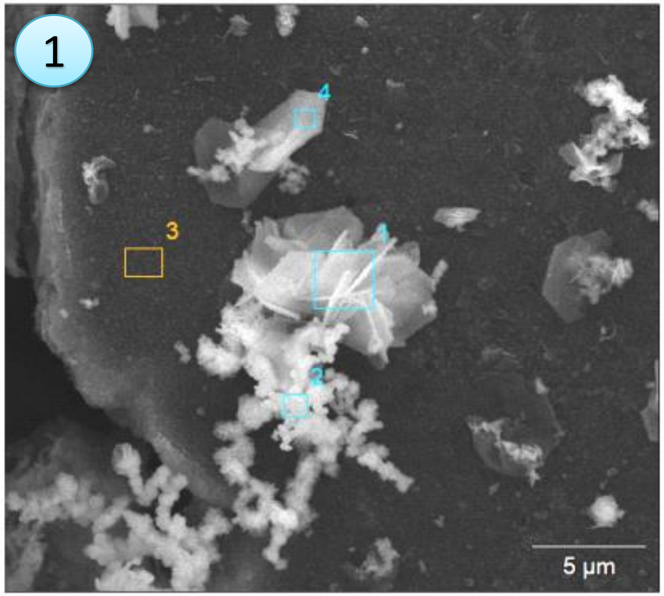
SEM Micrographs of GGG40 surface after 48 corrosion in Opalinus Clay water

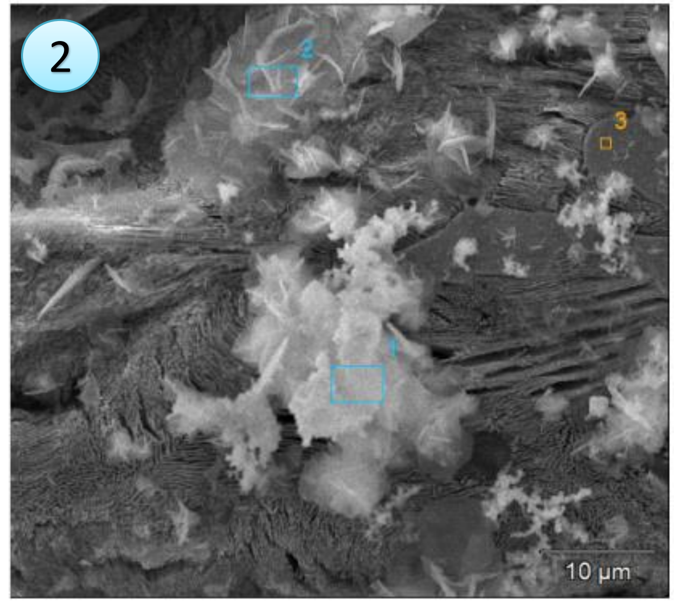
p: 5 bar

t: 30°C

pH 7.6

Surface analysis / SEM-EDX





Atom %	C	O	Mg	Al	Si	P	Cl	Cr	Fe	Cu
pt1	**45.6**	**39.8**	0.2	0.5	**3.7**		0.1	0.4	**9.7**	
pt2	**30.7**	**45.1**	0.2	0.5	**2.4**	0.1		0.2	**20.8**	0.0
pt3	**100.0**									
pt4	**61.8**	**27.8**	0.1	0.5	**2.2**	0.1		0.2	**7.2**	

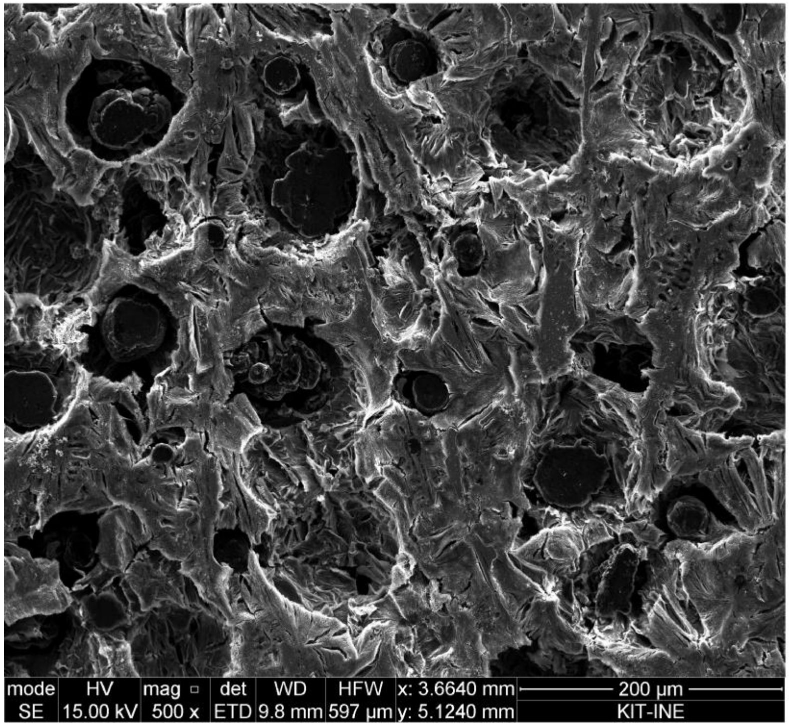
1

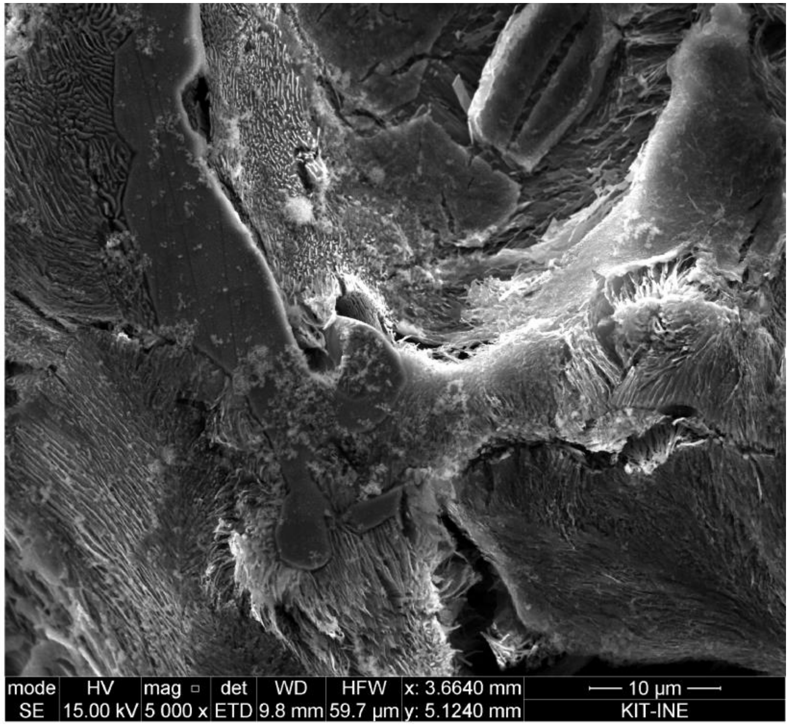
Atom %	C	O	Na	Mg	Al	Si	P	S	Cr	Mn	Fe
pt1	**8.6**	**57.2**	0.4	0.4	0.3	**3.1**		1.1			**28.8**
pt2	**14.9**	**39.2**			2.6	**5.1**	0.3		0.3		**37.6**
pt3	**11.6**					**0.6**			0.5	1.2	**86.1**

2

EDX analysis of GGG40 surface after 48 corrosion in Opalinus Clay water pH 7.6

t: 30°C, p: 5 bar



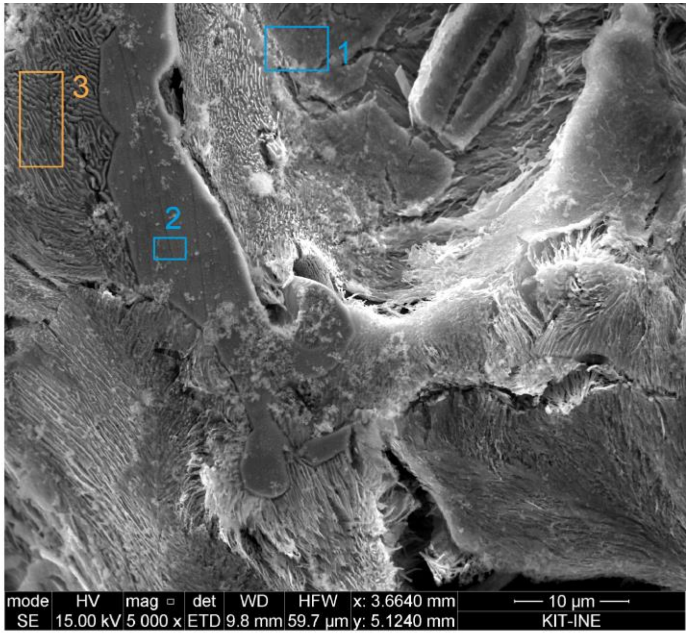


SEM Micrographs of GGG40 surface after 48 corrosion in Opalinus Clay water

p: 5 bar

t: 30°C

pH 9

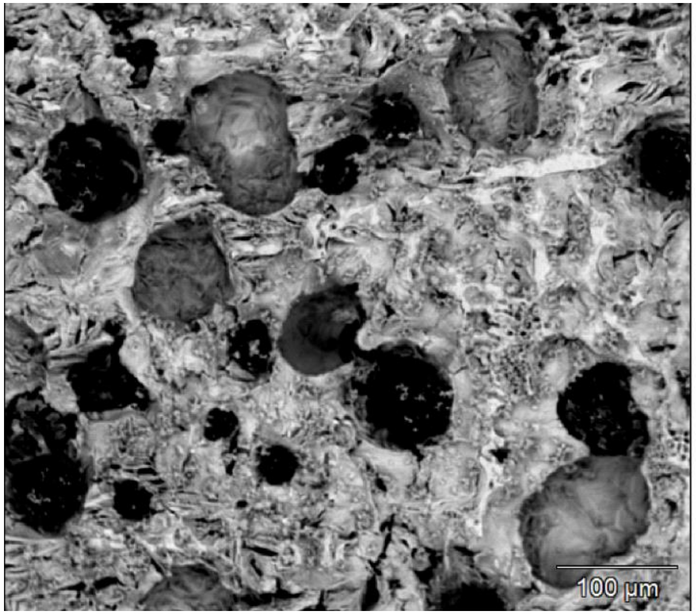


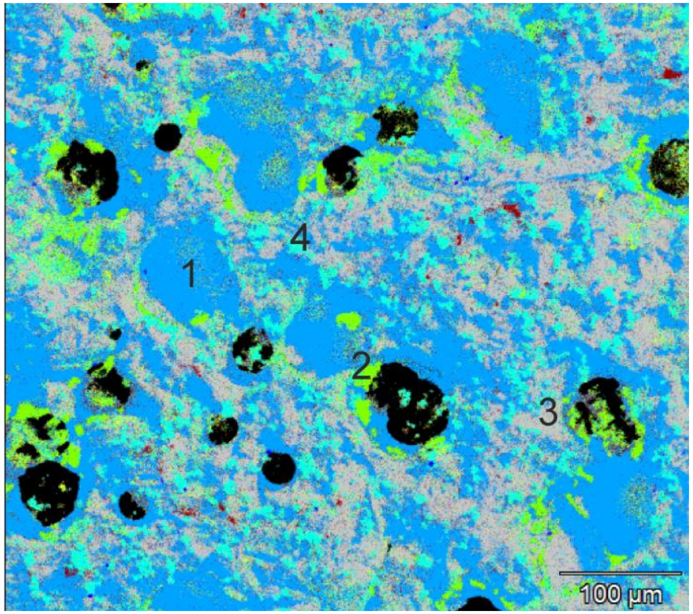
Atom %	C	O	Mg	Al	Si	P	S	Cl	Ca	Cr	Mn	Fe	Ni
pt1	**19.9**	**32.8**	1.7	1.3	**6.2**	0.6	0.5	0.3	0.2	0.2	0.3	**34.9**	1.0
Pt2	**10.0**											**90.0**	
pt3	**11.1**	**9.3**	1.0	0.7	**1.0**	0.6	0.4			0.5	1.1	**73.2**	1.2

EDX – Analysis of GGG40 surface after 48 corrosion in Opalinus Clay water pH 9

t: 30°C, p: 5 bar

Surface analysis / SEM-EDX





Identification composition phases on GGG40 surface after 48 corrosion in Opalinus Clay water

p: 5 bar
T: 30°C
pH 7.6

1

Element	Atom %
C	**8.8**
O	**13.1**
Mg	0.2
Al	0.6
Si	2.4
P	0.2
S	0.2
Cr	0.4
Mn	0.8
Fe	**72.4**
Ni	0.4
Cu	0.5

2

Element	Atom %
C	**21.4**
O	**38.0**
Mg	0.4
Al	1.9
Si	**12.9**
P	0.4
Cl	0.2
Ca	0.1
Cr	0.3
Mn	0.2
Fe	**22.3**
Ni	0.5
Cu	1.1
Mo	0.2

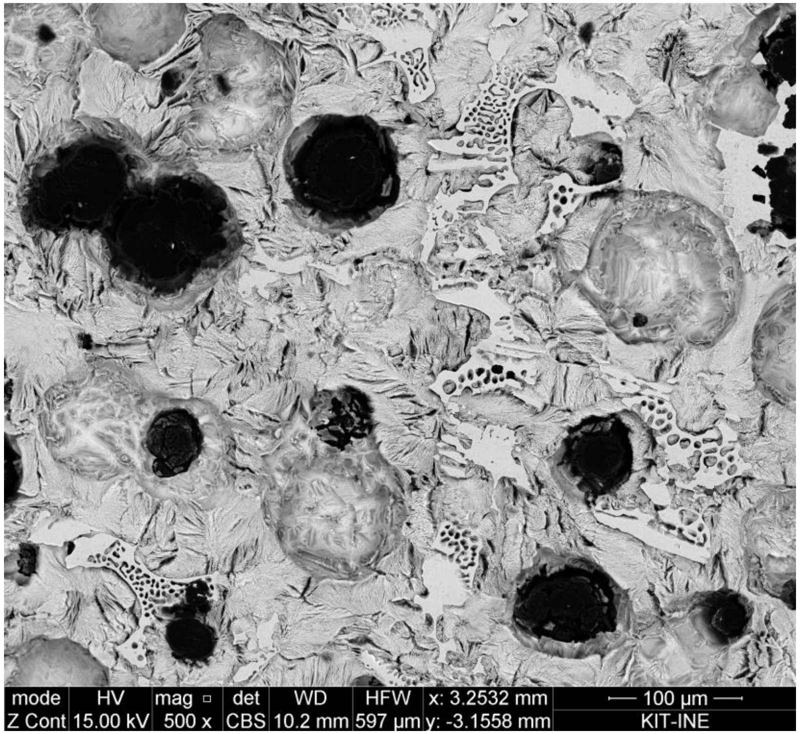
3

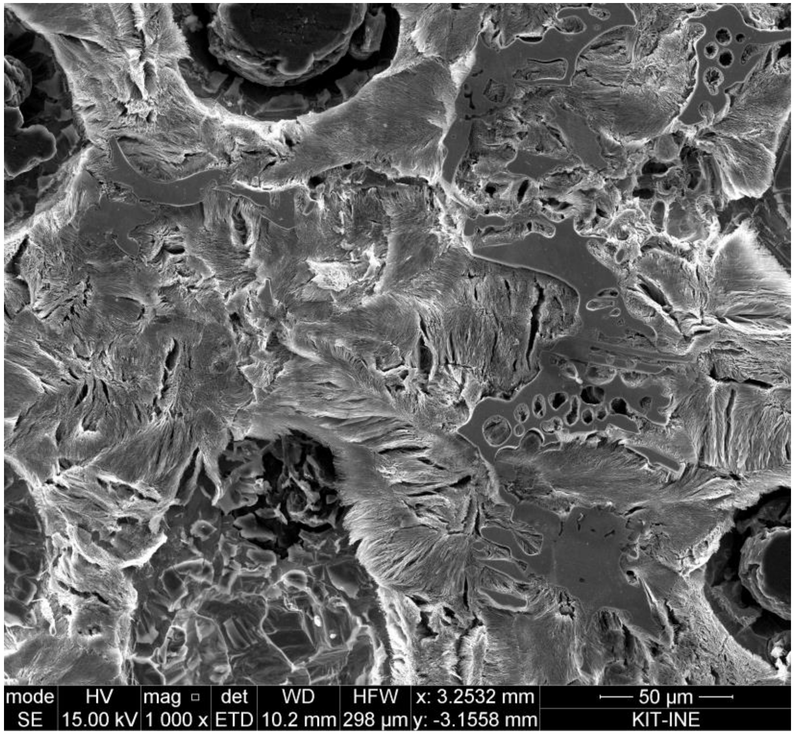
Element	Atom %
C	**14.0**
O	**17.2**
Mg	0.3
Al	0.6
Si	**2.6**
P	0.3
S	0.1
Cl	0.1
Ca	0.1
V	0.1
Cr	0.3
Mn	0.8
Fe	**63.2**
Ni	0.2
Cu	0.2

4

Element	Atom %
C	**11.2**
O	**47.1**
Mg	0.4
Al	0.4
Si	**3.0**
P	0.2
S	0.2
Cl	0.1
Ca	0.1
V	0.1
Mn	0.4
Fe	**36.6**
Ni	0.1

Influence of pressure



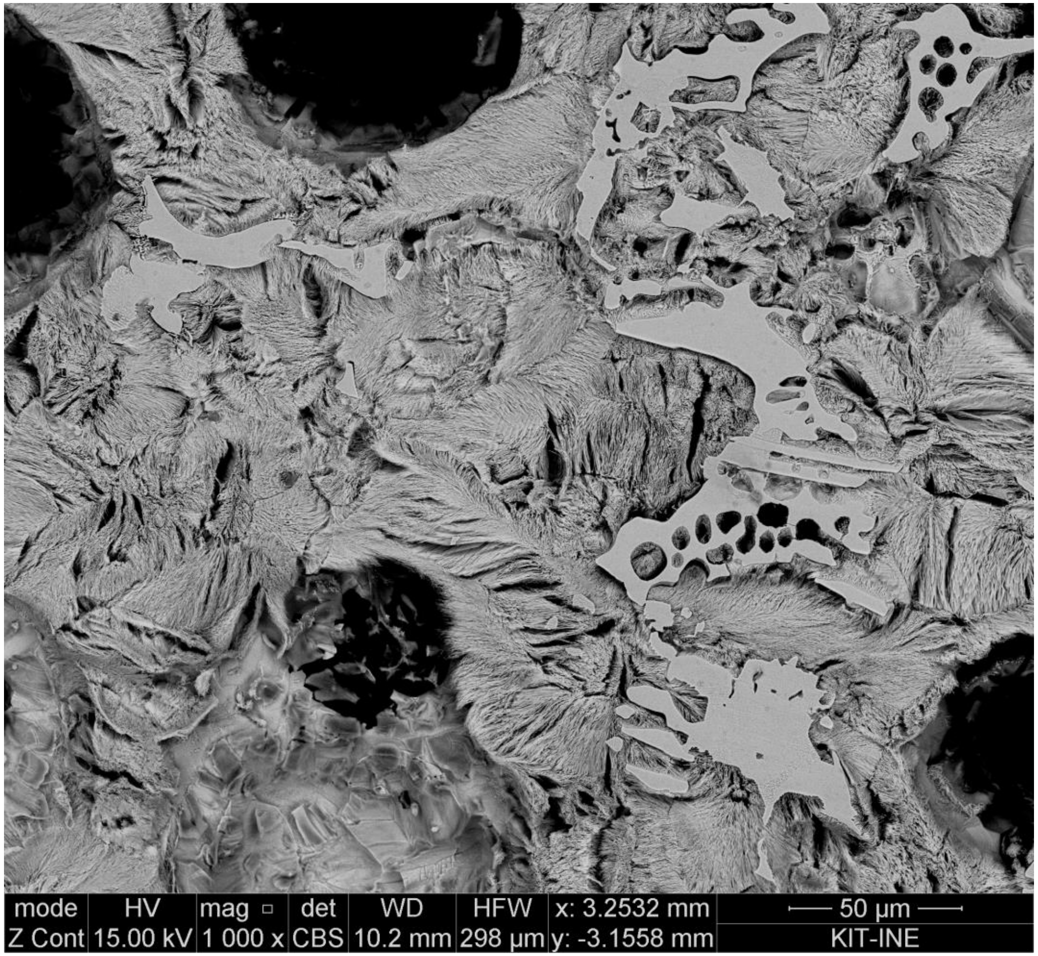


GGG40 after 48 corrosion in Opalinus Clay water

p: 100 bar

T: 30°C

pH 7.6

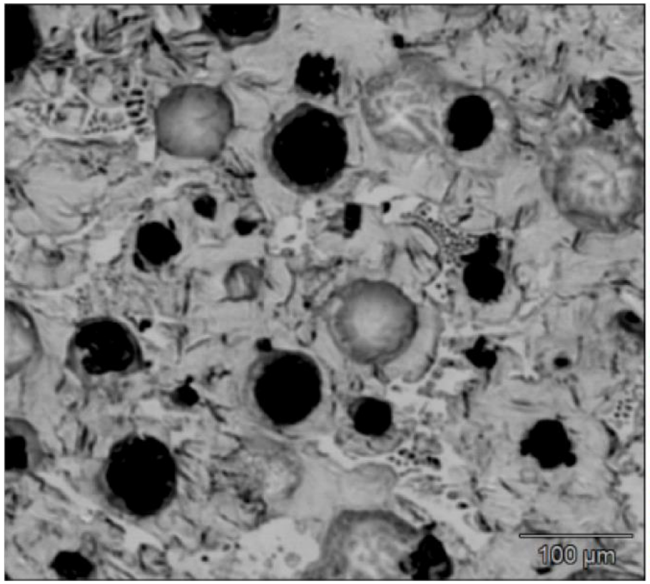


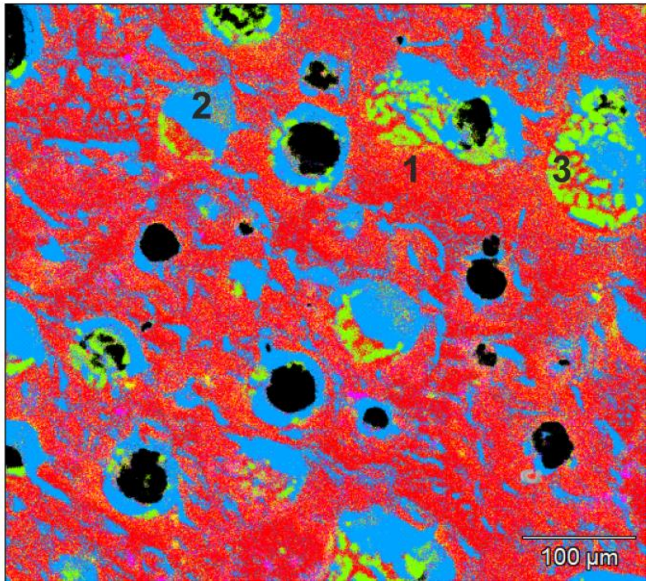
Influence of pressure

SEM micrograph of the GGG40 surface after 48 corrosion in Opalinus Clay water pH 7.6

t: 30°C

p: 100 bar





Identification of composition pahses on GGG40 surface after 48 corrosion in Opalinus Clay water

p: 100 bar

T: 30°C

pH 7.6

1

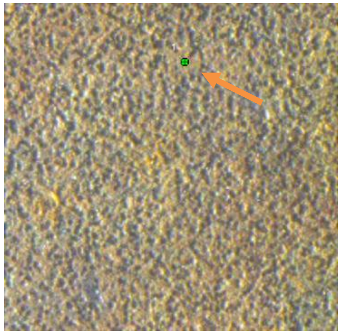
Element	Atom %
C	**13.9**
Mg	0.4
Al	0.2
Si	**1.7**
S	0.1
Cr	0.2
Mn	0.7
Fe	**82.6**
Cu	0.1
Zr	0.1
Total	100.0

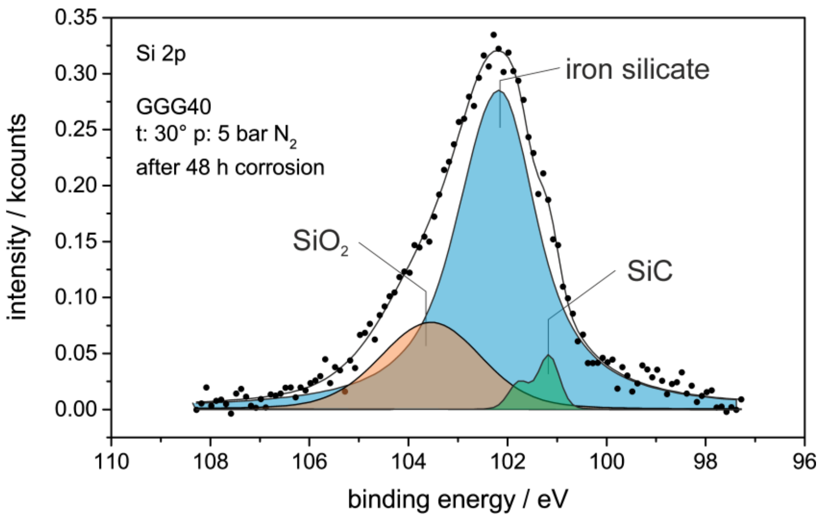
2

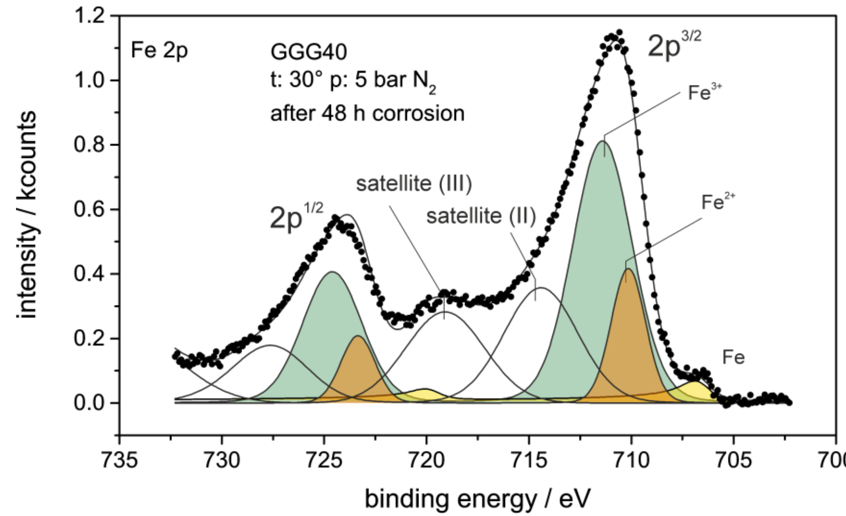
Element	Atom %
C	**8.1**
O	**5.3**
Mg	0.1
Al	0.2
Si	**1.6**
P	0.3
Cl	0.2
V	0.1
Mn	0.8
Fe	**82.5**
Ni	0.3
Cu	0.3
Total	100.0

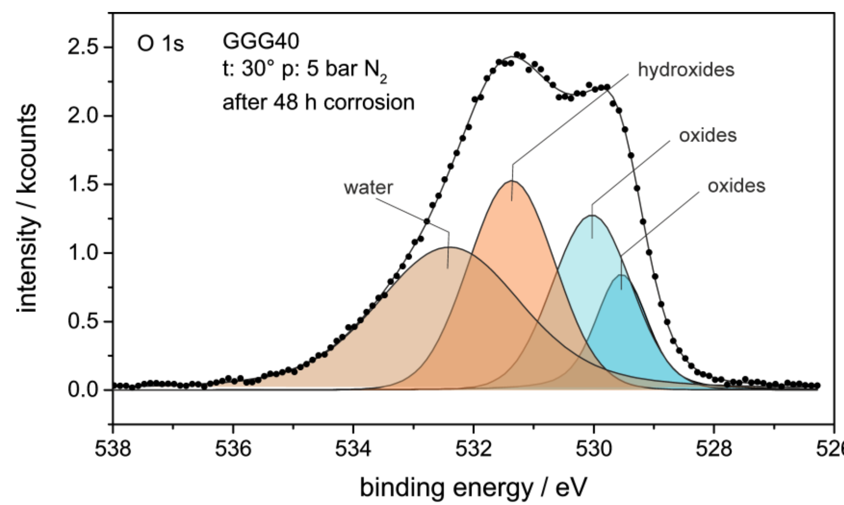
3

Element	Atom %
C	**18.4**
O	**29.6**
Mg	0.2
Al	**1.8**
Si	**12.0**
S	0.3
Cl	0.1
Cr	0.3
Mn	0.1
Fe	**34.7**
Ni	0.3
Cu	1.2
Zr	1.0
Total	100.0









XPS core level spectra of GGG40 after 48 h

of corrosion in Opalinus Clay water pH 7.6

t: 30°C

p: 5 bar

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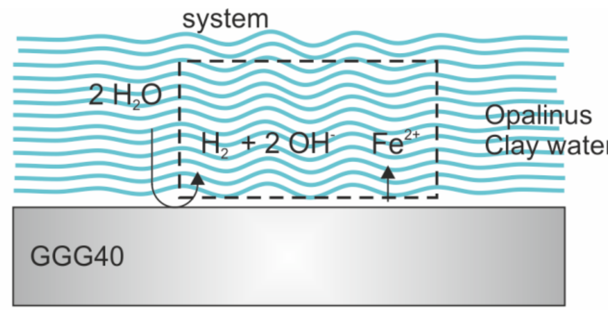
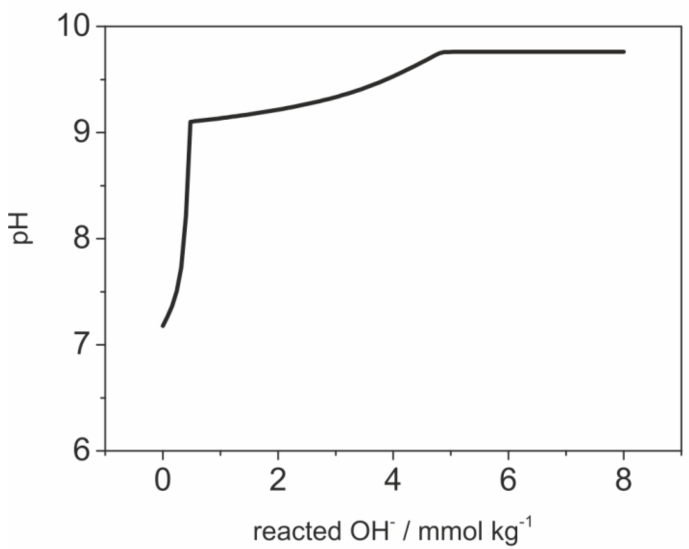
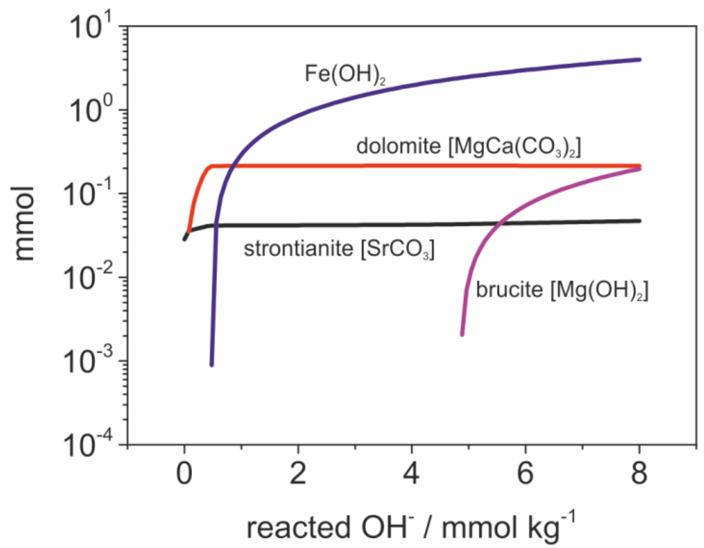
Thermodynamic calculations made using the Geochemist´s Workbench® and Yucca Mountain Project dataset data0.ypf.R2 (Jove-Colon et al. 2007)

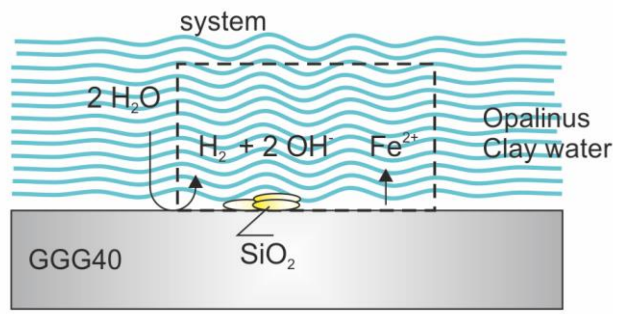


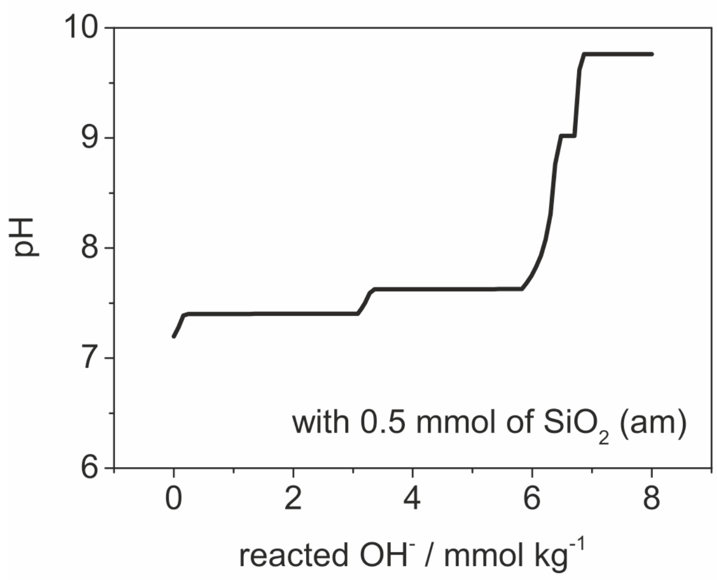


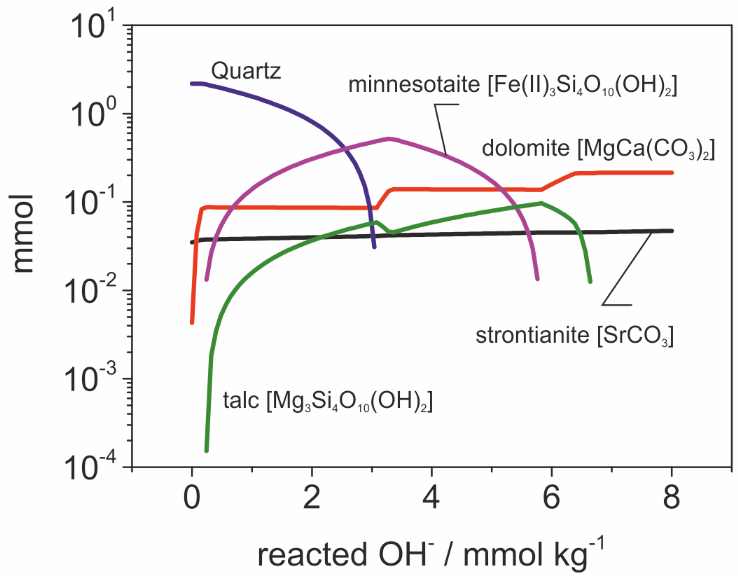


C. Jove-Colon, et al. (2007) In-Drift Precipitates/Salts Model, ANL-EBS-MD000045 REV 03, DOC.20070306.0037 Sandia National Laboratories.
http://www.lsnnet.gov/

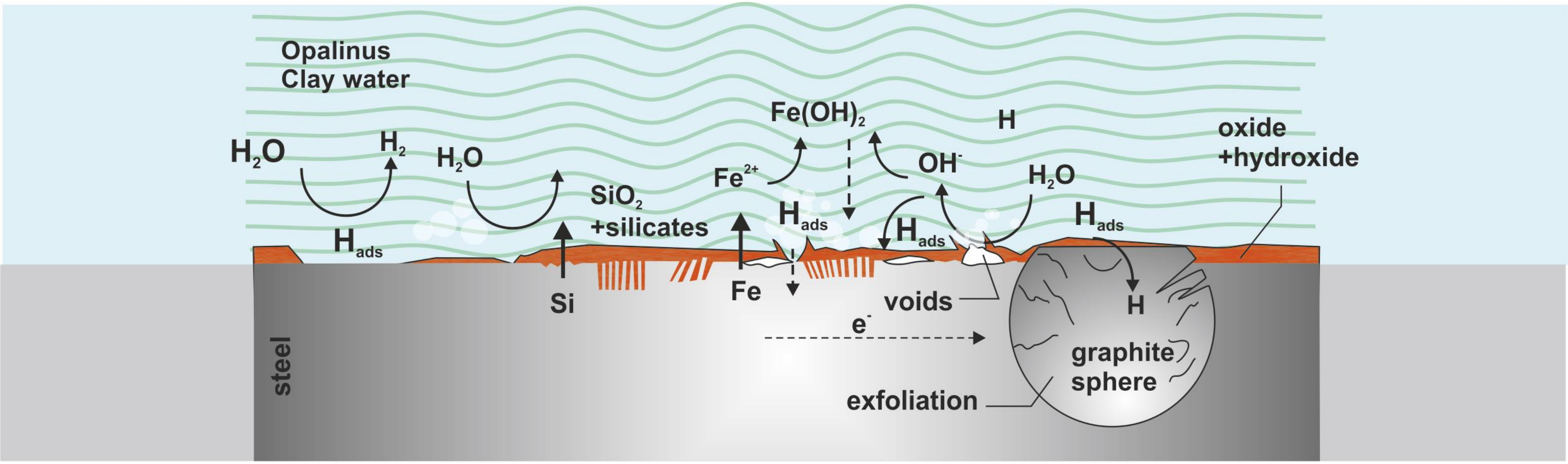
The formation of amorphous silica is expected by oxidation of free released Si from the alloy. This react with iron and magnesium from the system to generate complex silicates.







Model



- The anodic dissolution of iron and steel alloying elements is coupled with the reduction of water
- The strong surface alkalization leads to the deposition of an inhomogeneous film constituted by iron (II) hydroxide and silicates arising from reaction with the simultaneous formation of silica
- The hydrostatic pressure increase the corrosion rate by a simultaneous enhancement of the cathodic water reduction and the anodic iron dissolution rate

Thank you for your attention

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- Project ConCorD Nr. 847593 / Work package 15 EURAD