Corrosion Study in Geothermal Wells - Soultz Study

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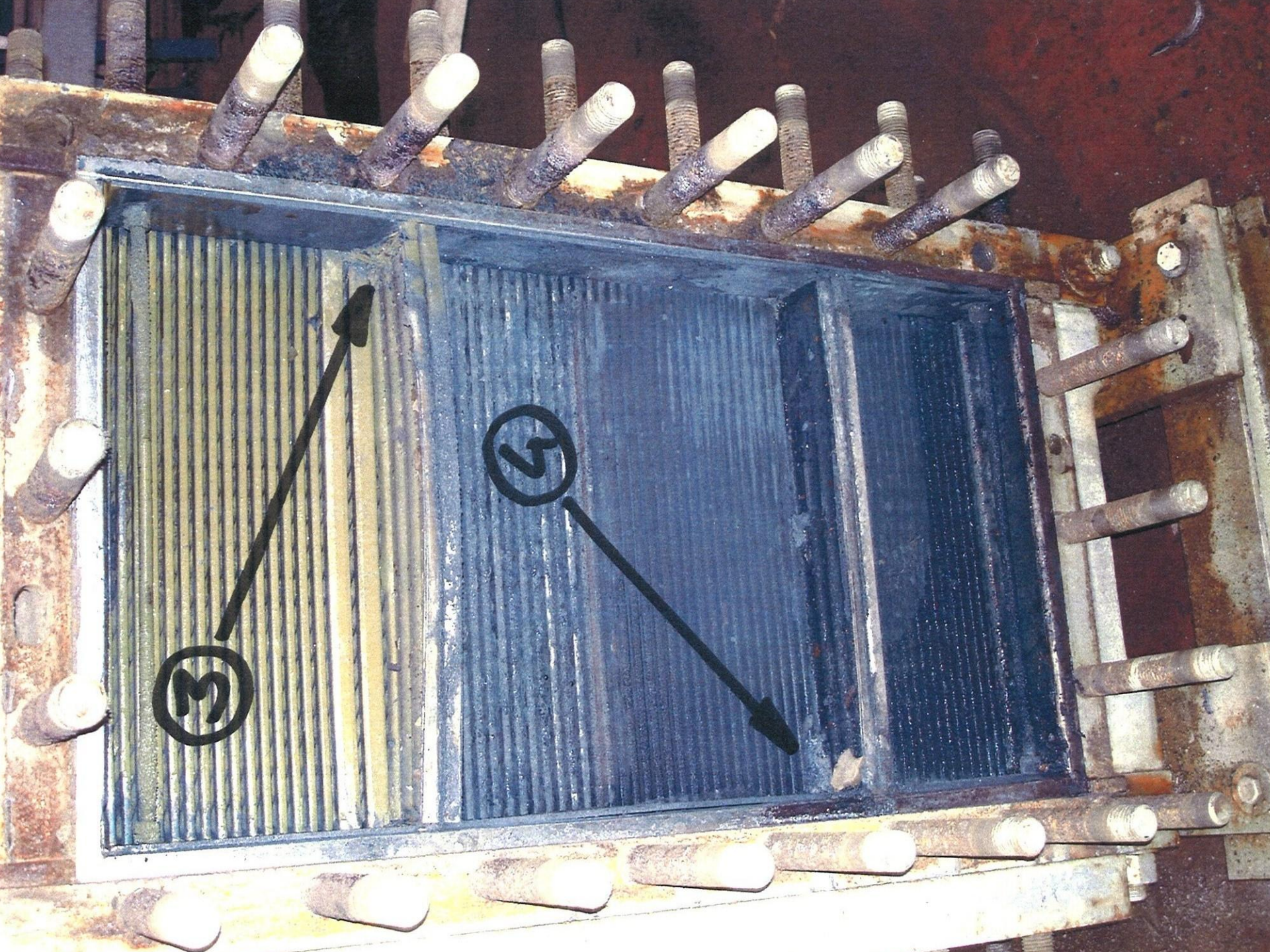
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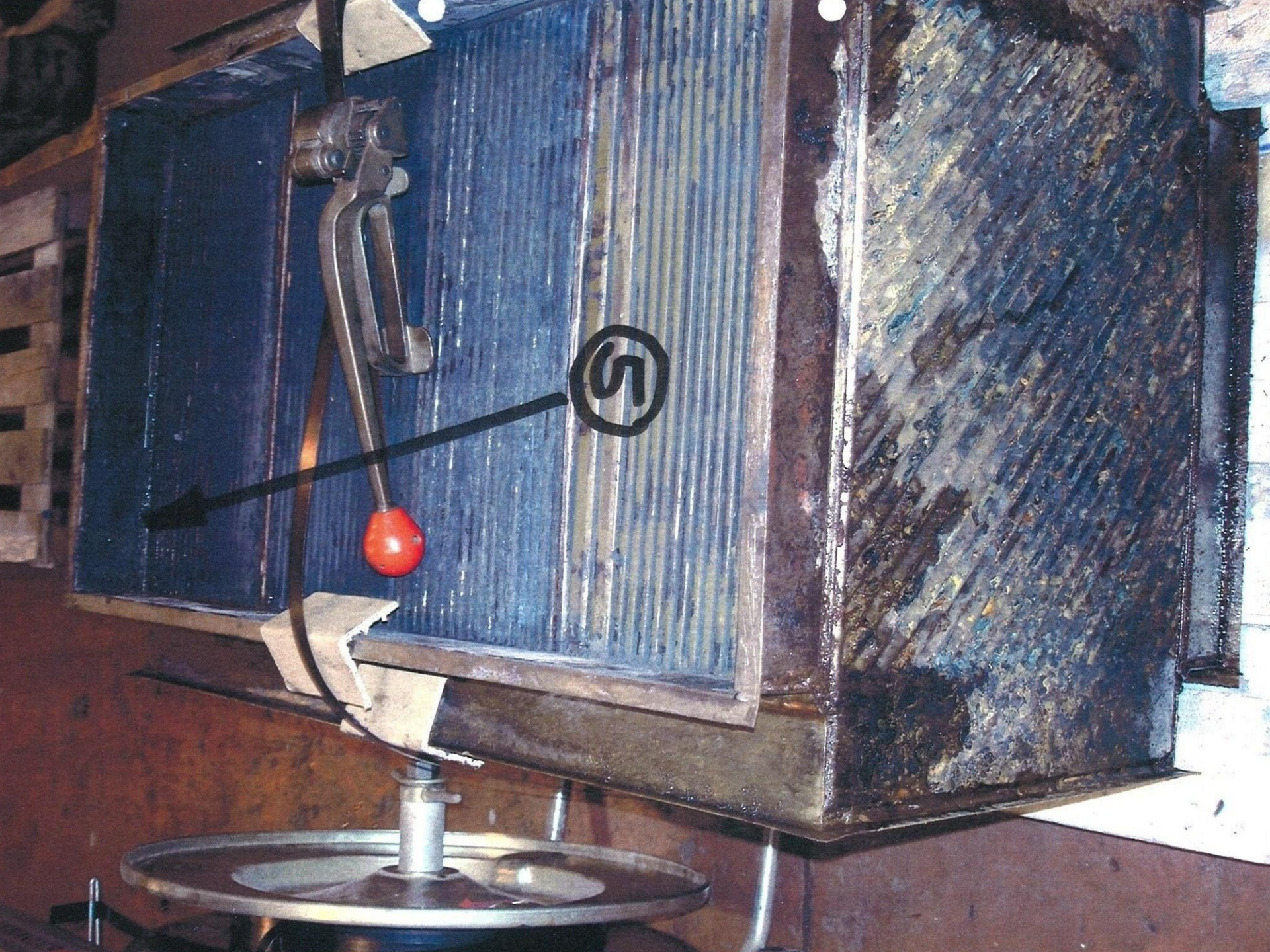


Carbon steel exposed for 10 days in non-alkaline brine with 0.02 m CO2 at 200 °C

Abstract

- Corrosion risk for some materials proposed for Soultz project at 200 C was evaluated for different steels with and without protective coating. The preliminary experiments were performed at autoclave which could house specimen of various geometries and which allowed electrochemical measurements. In some cases the testing was performed using a corrosion inhibitor. For uncoated steels the corrosion tests showed erosion at 2 mm/y at 200 °C. The corrosion products formed on the surface did not provide any corrosion protection. All the tested coatings performed very well. They effectively reduced the corrosion and they did not deteriorate during the test. The chosen inhibitor did not give any significant inhibitor effect.

CO_2 corrosion mechanism

- CO_2 is the main corrosive specie in the production wells

- CO_2 forms H_2CO_3 in aqueous solutions

$$CO_2 + H_2O \leftrightarrow H_2CO_3$$

- Corrosion: Cathodic reactions

$$H_2CO_3 \rightarrow H^+ + HCO_3^-$$

$$HCO_3^- \rightarrow H^+ + CO_3^{2-}$$

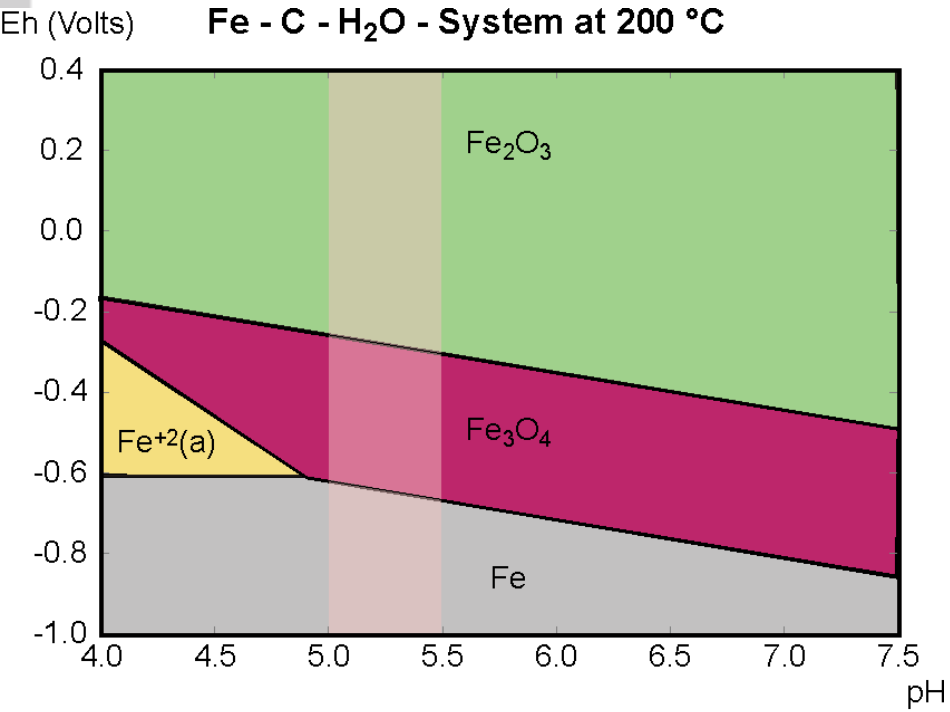
$$2H^+ + 2e^- \rightarrow H_2(g)$$

Anodic reaction and possible precipitation

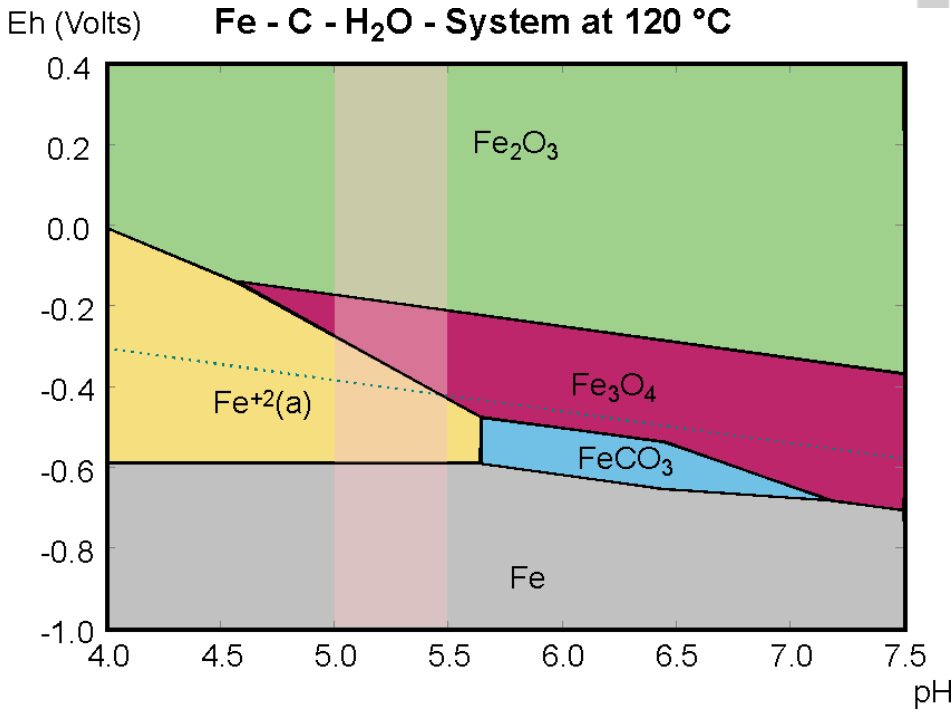
$$Fe \rightarrow Fe^{2+} + 2e^- \rightarrow FeCO_3$$

$$\rightarrow Fe_3O_4$$

Fe stability diagram gives the stability of the iron phases at the Soults-sous-Forêts conditions.



ELEMENTS	Molality	Pressure
Fe	1E-3m	20 bara
C	0.02m	20 bara



ELEMENTS	Molality	Pressure
Fe	1E-3m	20 bara
C	0.02m	20 bara

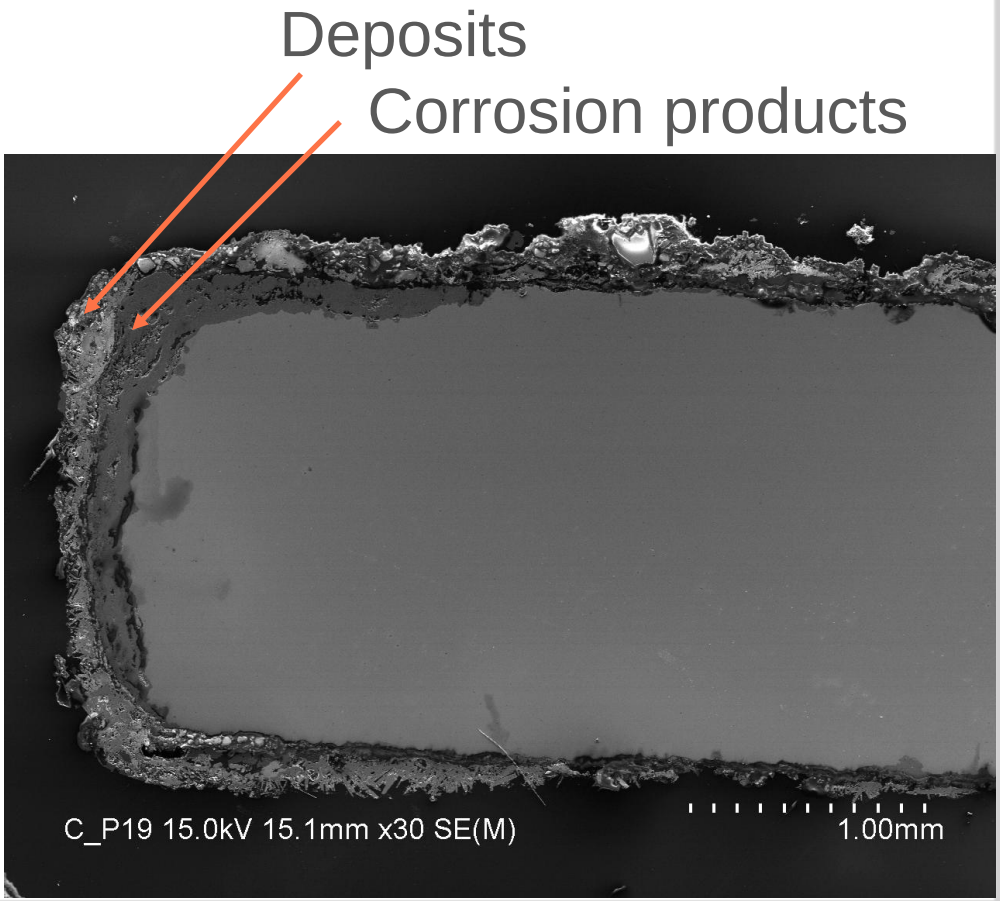
Solid Fe_3O_4 phase could form at 200 C, while dissolved iron is expected at 120 C at the pH in the production wells.

Methods for corrosion rate monitoring

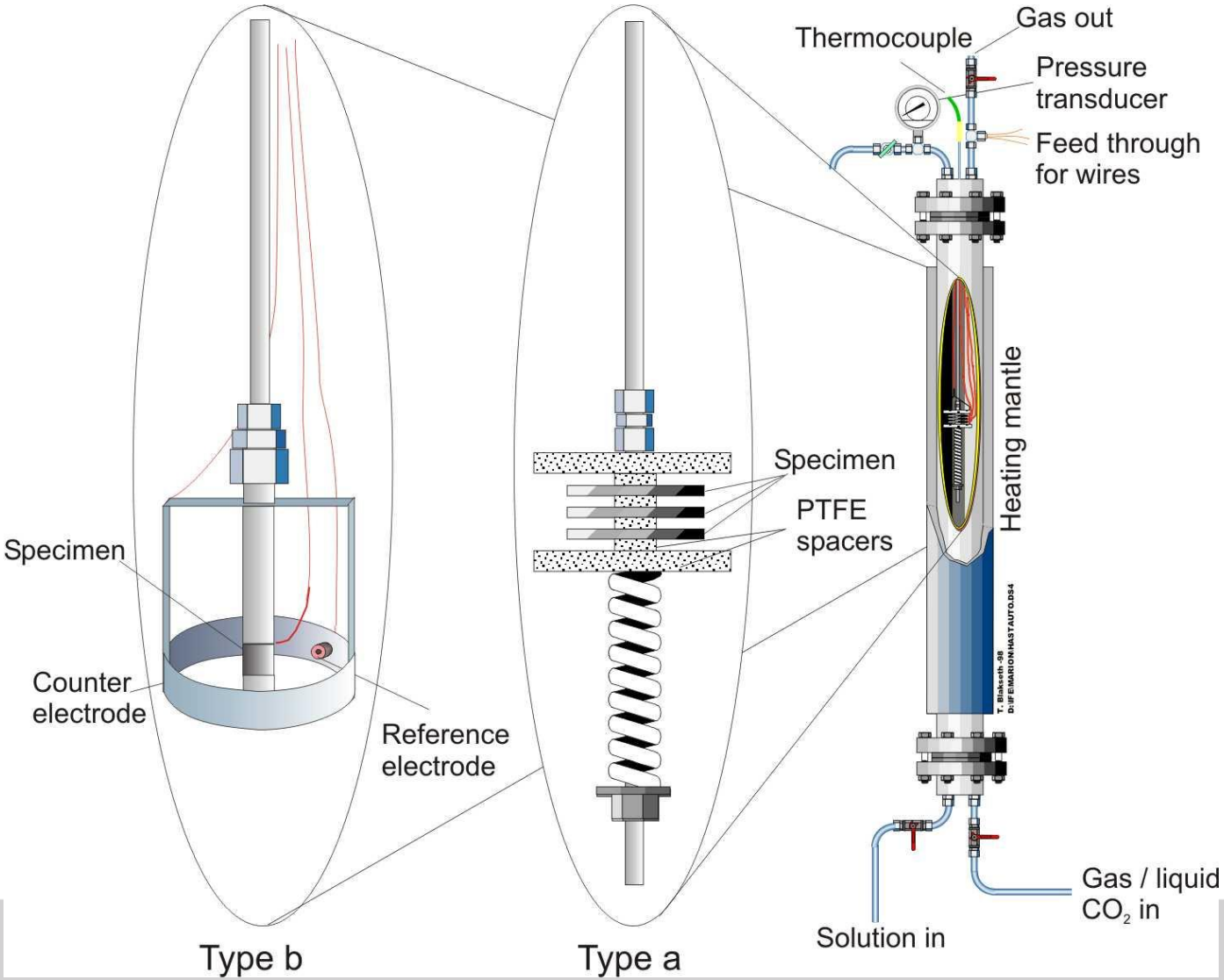
- Measurement of iron concentration in liquid samples
  - Monitors only dissolved Fe^{2+}, precipitated corrosion products not monitored
- Mass loss coupons
  - Determines corrosion rate as a weight difference of the coupon before and after exposure
- Electrical resistance method
  - Measures changes in the electrical resistance of a corroding sensor relative to a shielded reference sensor
- Field Signature Method
  - Non-intrusive technique used to measure corrosion damage over a relatively large section of a structure
  - Measures the potential response to an induced current
- Linear Resistance Polarization method
  - Mainly laboratory method (requires 3 electrode set-up)
  - Measures the polarization resistance of a corroding material

Nature of corrosion attack on GPK4 P19

- Cross-sectioned coupon, SEM image
- Corrosion product: $FeCO_3$
- Deposits: $(Ba,Sr)SO_4$, PbS, + +



The tests were carried out in an autoclave which can house specimens of various geometries.



Experimental Procedure

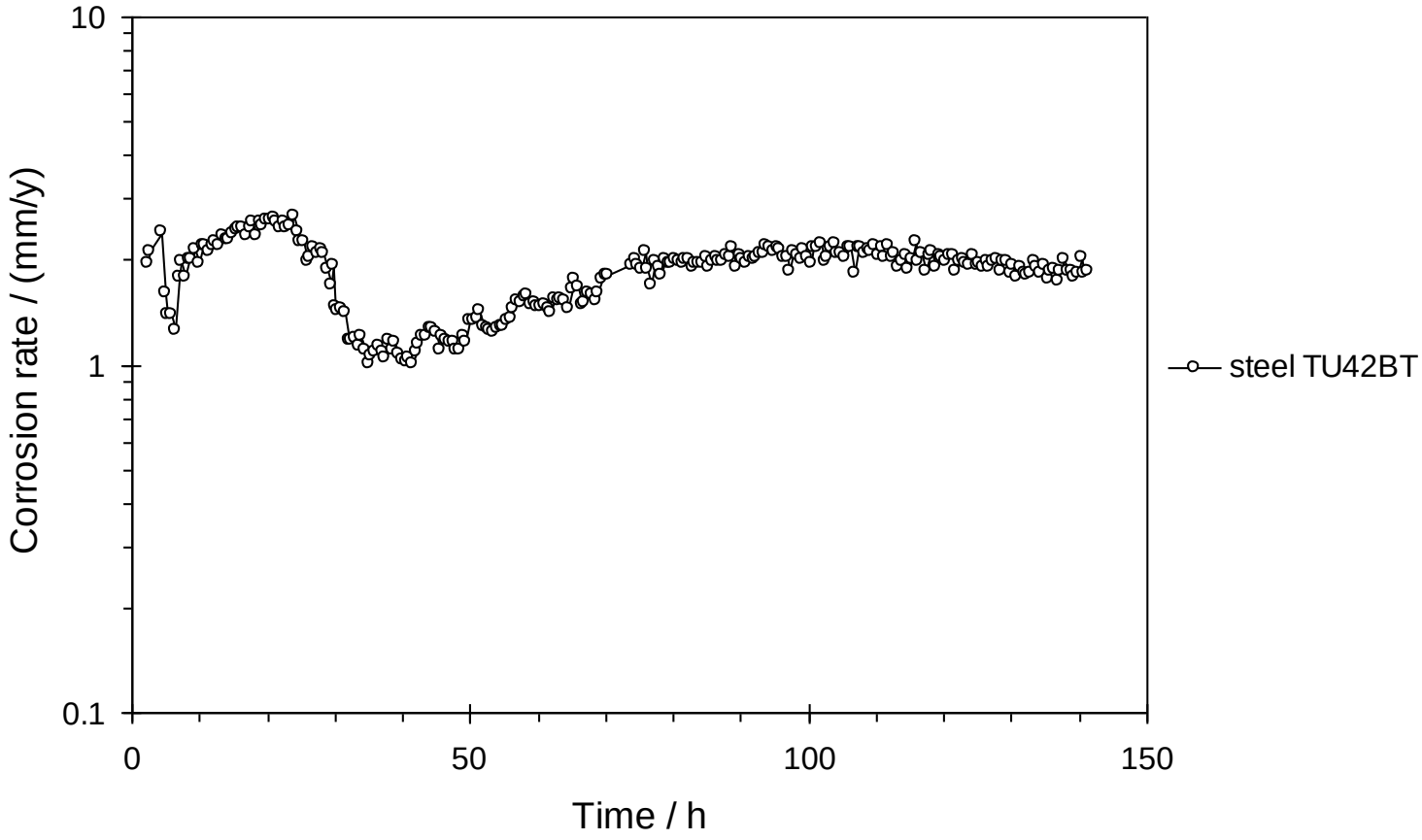
- Temperature: 200 C
- Materials tested:
  - Carbon steel TU42BT
  - Steel coated with Saskaphen synthetic coating
  - Steel coated with two types of Teflon coating (red Teflon coating and green Teflon coating)
  - Steel P110
  - Steel N80
- Solution:

Ion	Concentration	
	mmol/l	mg/l
Na^+	1225.5	28174
K^+	73.7	2880
Mg^{2+}	3.1	75
Ca^{2+}	165.9	6650
Cl^-	1630.5	57800
SO_4^{2-}	1.8	171

Methods and measurements

- Corrosion rate
  - Mass loss method for all the materials
  - Linear Polarization Resistance method (LPR) in 30 min interval during the entire test for the non-coated steel specimens
- Inspection of the specimens after the test
  - Analysis of the corrosion products (SEM, EDS, XRD)
  - Evaluation of the corrosion attack (optical microscopy, SEM)

The corrosion rate for the carbon steel stabilized about 2 mm/y for the test without the inhibitor.



Mass loss corrosion rates for the materials in the test without the inhibitor

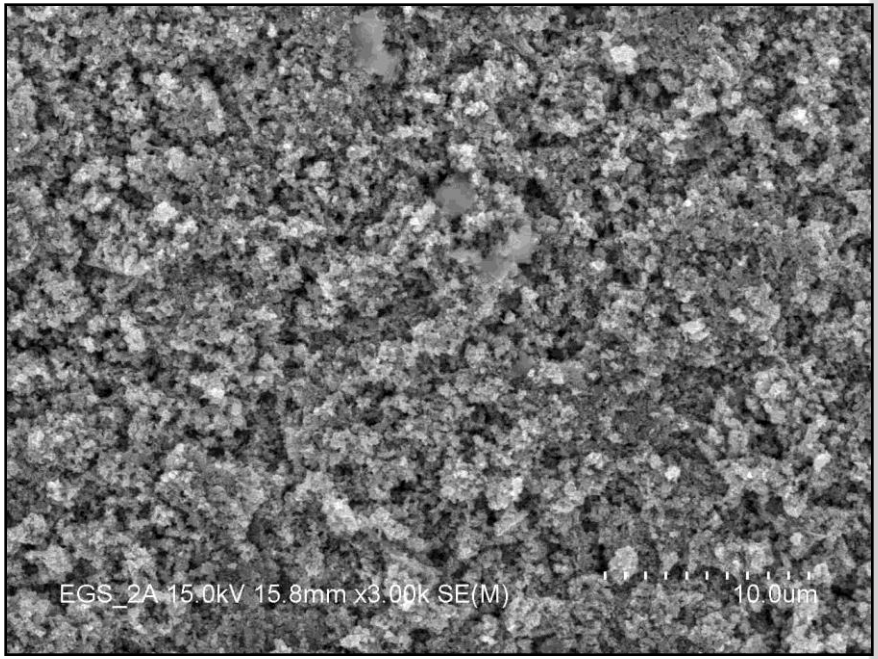
Specimen	Mass loss C.R. [mm/y]	Mass of the corrosion products [mg/cm^2]
Non-coated TU42BT steel	1.8	4
Saskaphen coating	0.03	n/a
Red Teflon coating	Not detectable	n/a
Green Teflon coating	Not detectable	n/a

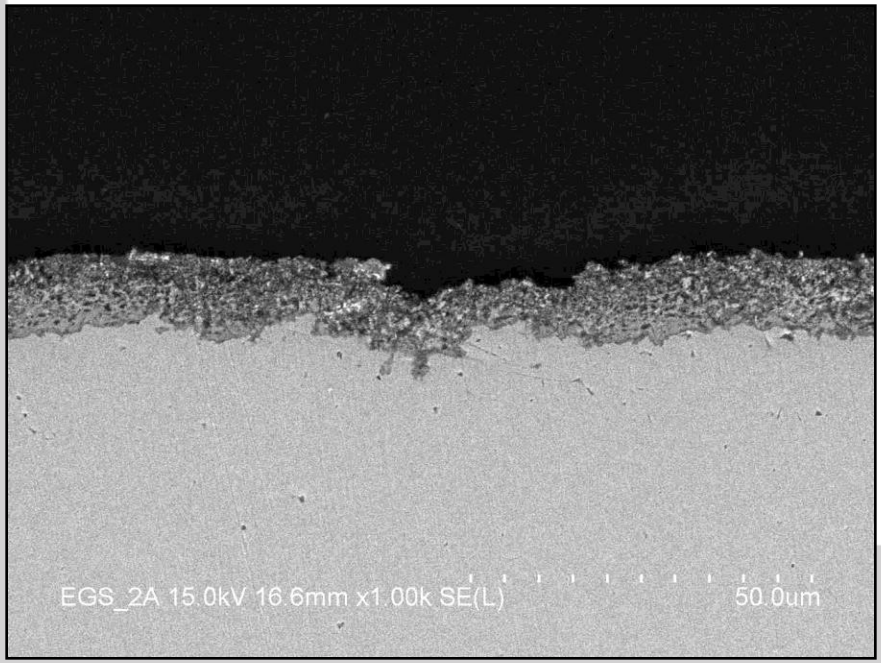
The C.R. for the non-coated steel was quite high, 1.8 mm/y. All the coatings provided very good protection against corrosion.

The carbon steel specimen was covered with black corrosion products after the test.

The corrosion product layer was crystalline, quite porous and from 6 to 35 μm thick.

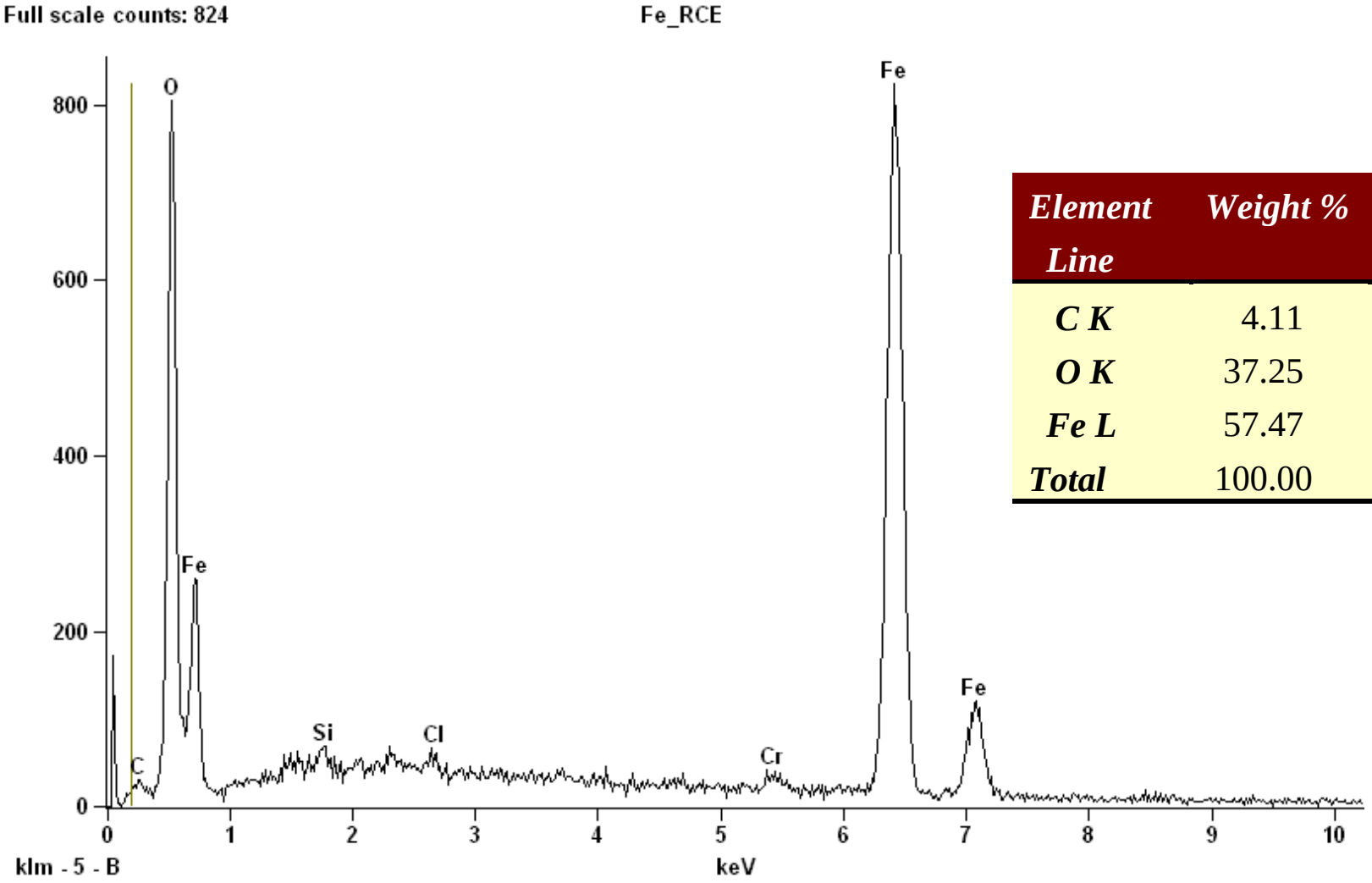
SEM image of the surface of the non-coated steel specimen





SEM image of a cross section of the non-coated steel specimen

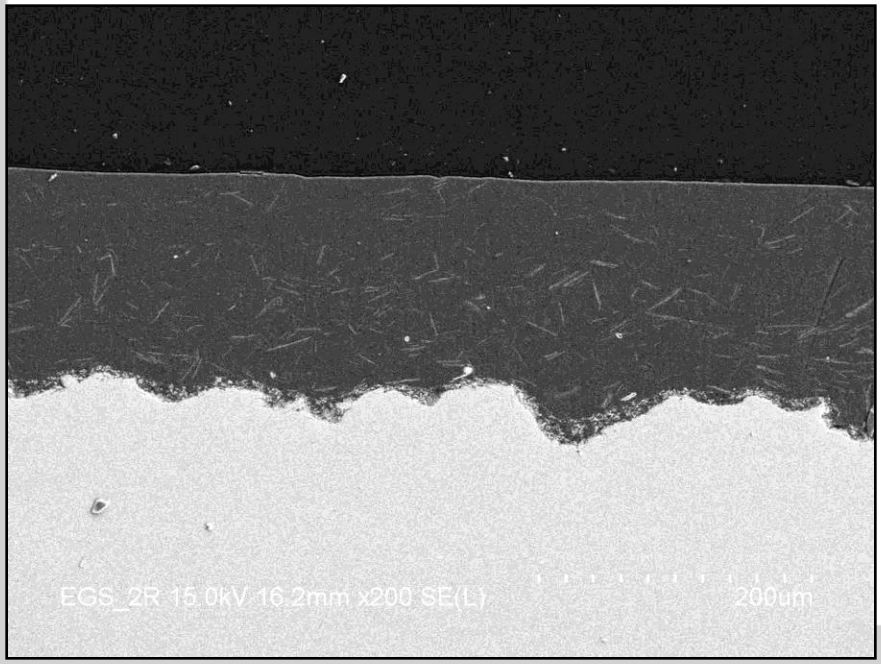
EDS analysis indicated that corrosion product layer was probably a hydrated iron oxide.



Element Line	*Weight %*	*Atom %*
C K	4.11	9.19
O K	37.25	62.47
Fe L	57.47	27.61
Total	100.00	100.00

The red Teflon coating did not deteriorate during the test.

Photograph of the specimen with the red Teflon coating



SEM image of a cross section of the specimen with the red Teflon coating

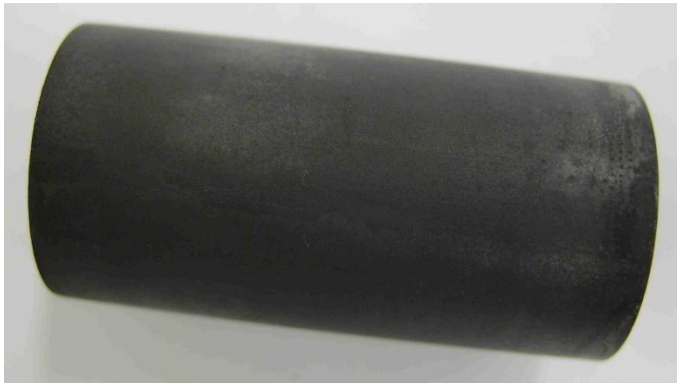
Mass loss corrosion rates for the materials (only non-coated steels) with 10 ppm MEXEL inhibitor

Specimen	Mass loss C.R. [mm/y]	Mass of the corrosion products [mg/cm^2]
TU42BT steel	1.4	9
P110	2.5	17
N80	2.5	14

The C.R. for the all the tested steel was quite high. The inhibitor did not have any significant inhibitor effect.

Surface of all the tested steels was covered with a corrosion product film.

TU42BT steel ⟶

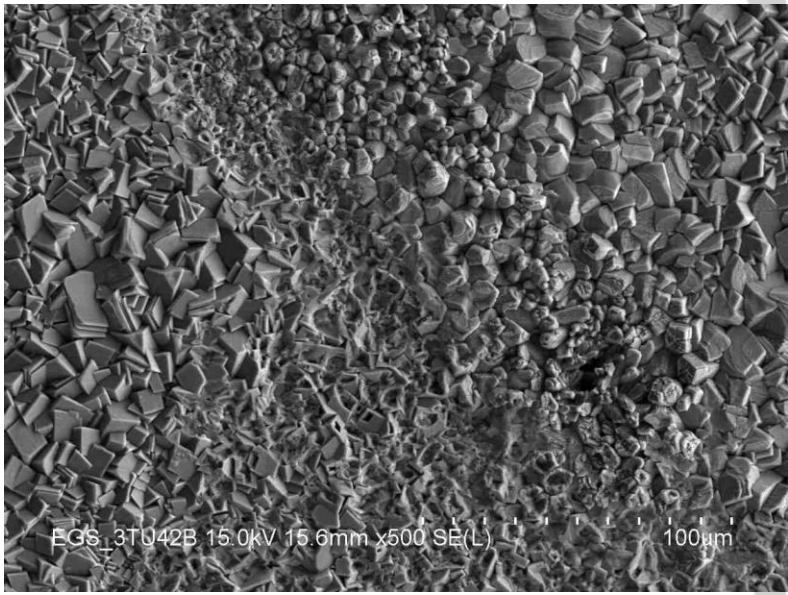


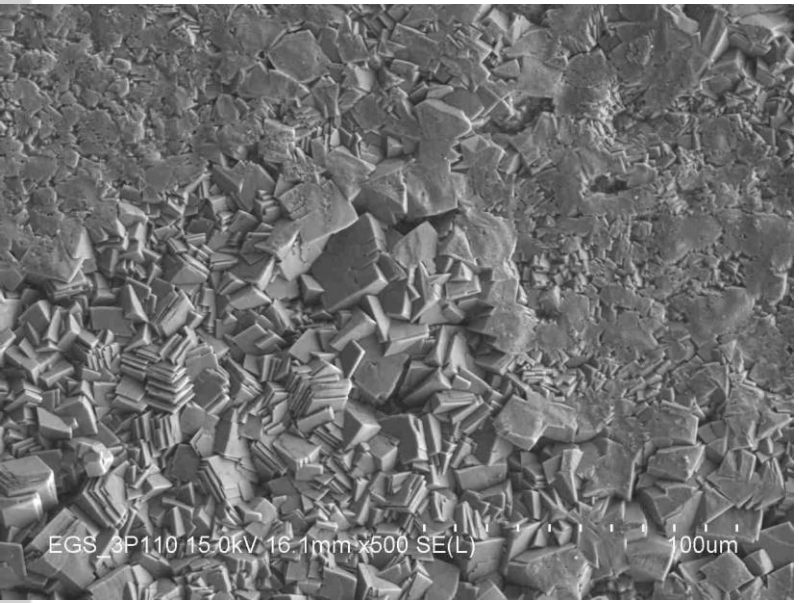
⟵ P110 steel

N80 steel ⟶

Crystalline corrosion product layers formed on all the steels.

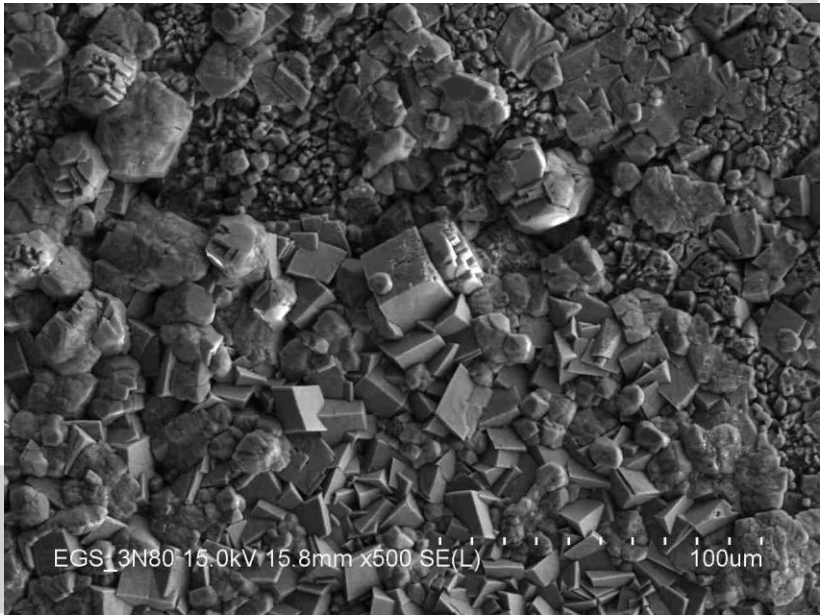
TU42BT steel ⟶





⟵ P110 steel

N80 steel ⟶



Conclusions

- Theoretical prediction of worst case corrosion rate indicated that pH and CO_2 content control the corrosion in production wells.
- The corrosion tests showed that carbon steel corroded at 2 mm/y at 200 C. The corrosion products formed on the surface did not provide any corrosion protection.
- All the tested coatings performed very well. They effectively reduced the corrosion and they did not deteriorate during the test.
- Mexel inhibitor did not give any significant inhibitor effect. The corrosion rate for TU42BT steel was nearly the same with and without the inhibitor.

Tracing of geothermal fluid flow

Tor Bjørnstad and Jiri Muller

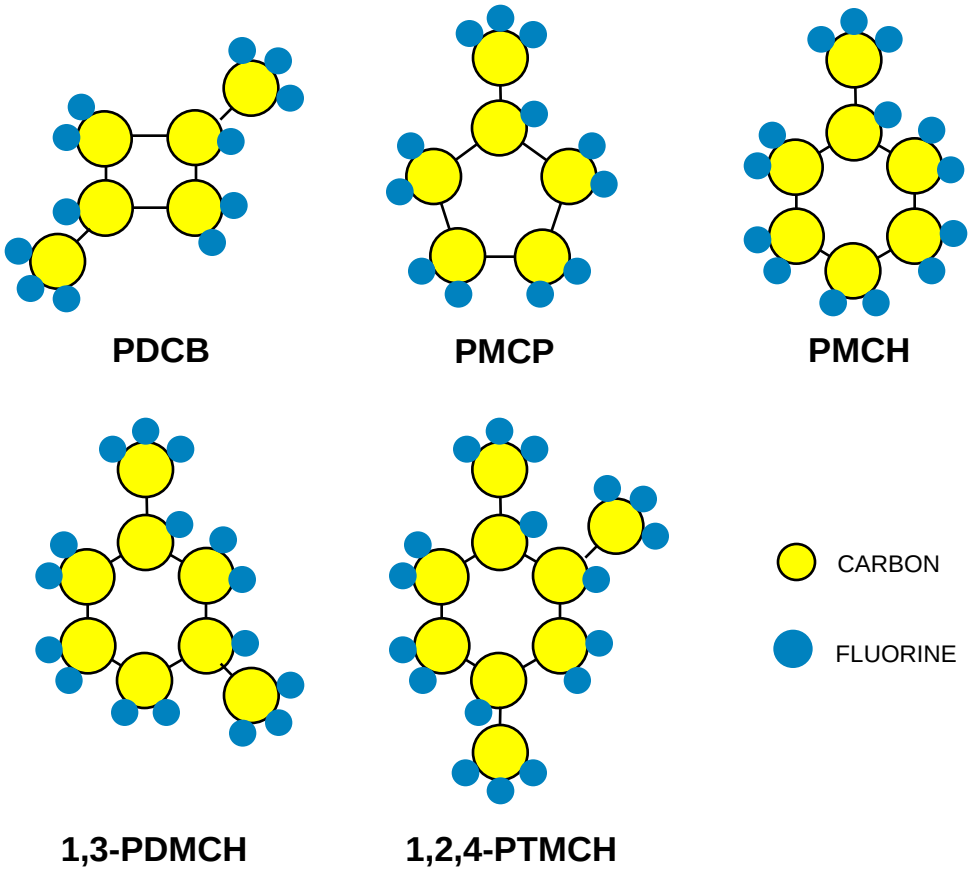
Abbreviations:

SF_6 : Sulphur hexafluoride
PDMCB: Perfluorodimethyl cyclobuthane
PMCP: Perfluoromethyl cyclopentane
PMCH: Perfluoromethyl cyclohexane
PDMCH: Perfluorodimethyl cyclohexane
PTMCH: Perfluorotrimethyl cyclohexane
HTO: Tritiated water
1-NS: 1-Naphtalene sulphonic acid
2-NS: 2-Naphtalene sulphonic acid
1,5-NDS: 1,5-Naphtalene disulphonic acid
2,6-NDS: 2,6-Naphtalene disulphonic acid
2,7-NDS: 2,7-Naphtalene disulphonic acid
1,3,6-NTS: 1,3,6-Naphtalene trisulphonic acid
2-FBA: 2-Fluorobenzoic acid
3-FBA: 3-Fluorobenzoic acid
4-FBA: 4-Fluorobenzoic acid

GC/ECD: Gas chromatography with electron capture detector
GC/MS: GC with mass spectroscopy detector.
GC-MS/MS: GC with tro mass spectrometers (two-dimentional mass spectrometer)
HPLC: High-performance liquid chromatography
LSC: Liquid scintillation counting

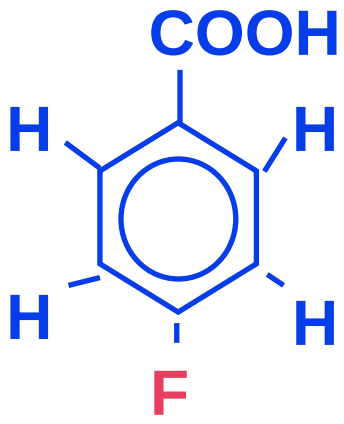
Non-radioactive gas tracers

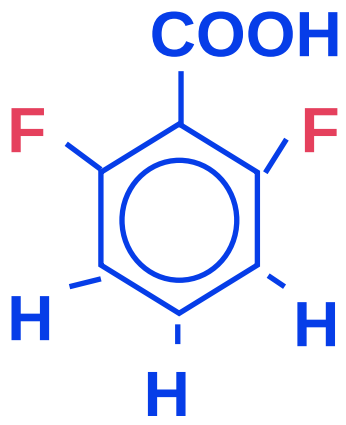
Perfluorinated cyclic hydro-carbons with coordinated light hydro-carbon (methyl) groups

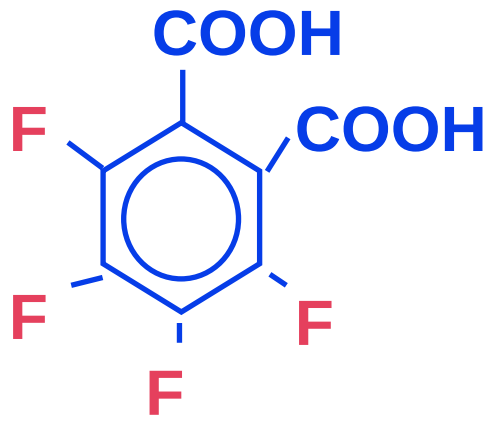
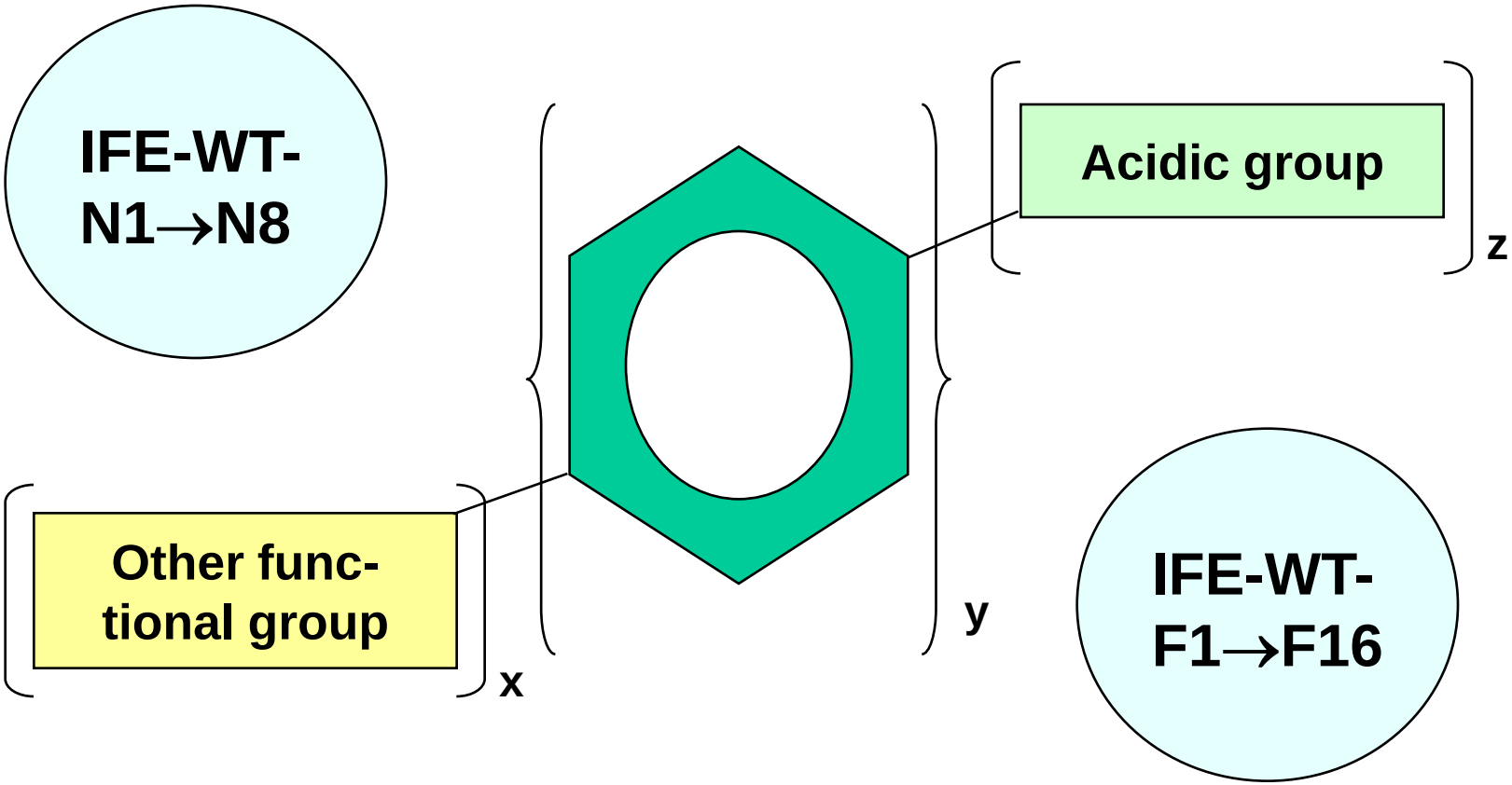


Passive Water Tracers

Non-radiolabel-led passive water tracers are polyfluorin-ated benzoic acids. These can also be made radio-active by tritium or ^{14}C labeling







Other water tracers