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High performance coatings for the geothermal industry

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MATChING
MATERIALS & TECHNOLOGIES FOR PERFORMANCE IMPROVEMENT OF COOLING SYSTEMS IN POWER PLANTS

THE FRAMEWORK PROGRAMME FOR RESEARCH AND INNOVATION
HORIZON 2020

The H2020 MATChING project

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MATChING is the acronym of *"**Materials & technologies for performance improvement of cooling systems in power plants**"*

MATChING aims to **reduce the water demand and improve energy efficiency for cooling systems in the energy sector** through the use of advanced and nano-technology based materials and innovative configurations

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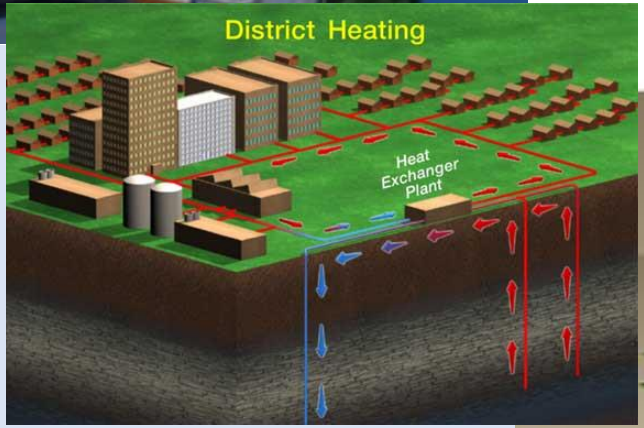
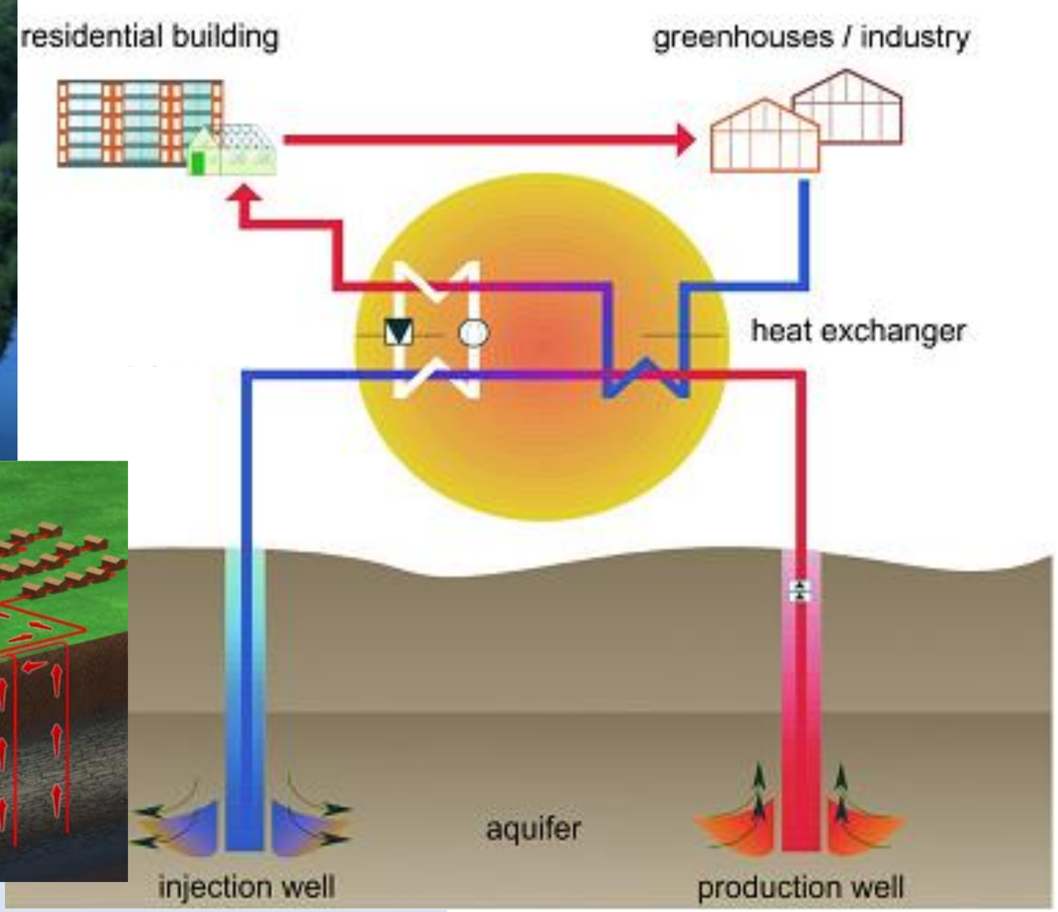
Users group:
>10 additional global partners

14 Partners from 6 EU Countries: 4 from Italy, 4 from Belgium,3 from Spain, 2 from Netherlands and 1 from Denmark

The geothermal site of Balmatt (Be)





Balmatt Brines*

Production T **125-128 C**
P: **40 bars**
Brine type **Na-(Ca)-Cl**
Salinity: **165 g/l**
Gas brine volume ratio is 2.5
CO_2: 75 vol.%, other CH_4
pH unseparated fluid (with the CO_2) is **5.4**

**S Bos, B Laenen. Development of the first deep geothermal doublet in the Campine Basin of Belgium. European Geologist 43, May 2017*

Technological Issues of Geothermal Energy

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- Material solutions have to be adapted for the particular characteristics of the geothermal site
- Exotic expensive materials perform very well, but economic aspects have to be taken into account

To reduce the installation costs, we investigate the **application of coatings for upgrading the corrosion resistance of carbon steel** in place of expensive, corrosion resistant alloys.

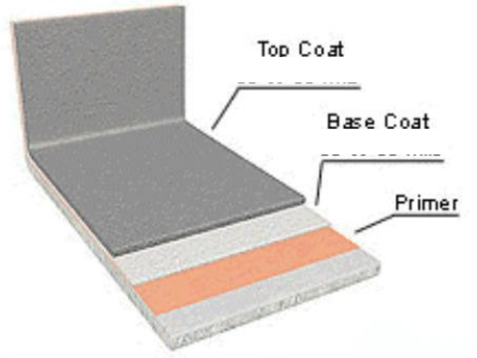
Material Group	Tested Metals	PRE %	Cost (relative to steel)
Carbon steel	**P265G, P235G, P110, L80, N80**	-	**1**
Stainless steels & Alloys	316L	27	8.3
	318LN	34	7.1
	904L (Super austenitic)	36	**19.4**
	2507 (Duplex)	41	**12.6**
	Alloy 31 (Super-Duplex)	52	**33**
Titanium	Grade 2: 99.9%Ti	-	16.2

High performance coatings

- For **cost-effectiveness**, we considered existing commercial coatings and combinations of commercial and newly developed coatings.

- We tested different families of coatings that were selected based on having a range of different formulations and track record in related fields (oil & gas, etc)

Coating	Description	Dry film thickness	Surface Energy (mN/m)	Comments
A	Phenolic based heat cured coating	250-270 microns	30	Commercial
B	Epoxy coating and a sol-gel top coat	250-300 microns	<24	DTI modified
C	Epoxy coating	~ 500 microns	30	Commercial
D	Fluoropolymer based coating	~ 1000 microns	<24	Commercial



Except the fluoropolymer the other coatings are multilayer systems

Testing Strategy

- To the best of our knowledge, there are no established standard laboratory procedures to test anti-corrosion coatings in geothermal fluids.
- The test designed at DTI, is based on the NACE TM0185, ASTM G111-97 and ASTM E 1068-85, and simulate the operational conditions at the Balmatt site (test duration 540 h).

Lab Characterization of coatings (adhesion, rusting, blistering) → **Mock up (540 h)** → Lab characterization (adhesion, rusting, blistering) →

Sucess criteria:
ISO 2409:2007 (adhesion) Rating 1 or less
ASTM D714-02 (blistering) Rating 8F or no blisters
ISO 4628-3 (rusting) Rating Ri 0 (no rust)

Failed → Discarded

Pass ↓

Electrochemcial Impedance Spectroscopy

- Electrolyte permeation
- Coating deffectivenes
- Substrate corrosion

	LOTU (mock-up)	In situ Balmatt	
Temperature	130 °C	125-130 °C	
Pressure	30-40 bars	~ 40 bars	
Media	Synthetic brine	Balmatt brine	
Partial pressure of CO_2	-	CO_2 in the gas mixture	76,5 Vol. %
pH	5.55	~ 5.50	
Stirring	600 rpm	Flow rate	100-200 m^3 h^{-1}
Exposure time	~ 24 days (570h)	Flow velocity	1 m s^{-1}

Laboratory Characterization

- Samples are **P265G** coupons (5 x 3 x 0.5 cm) coated with the correspondent coatings

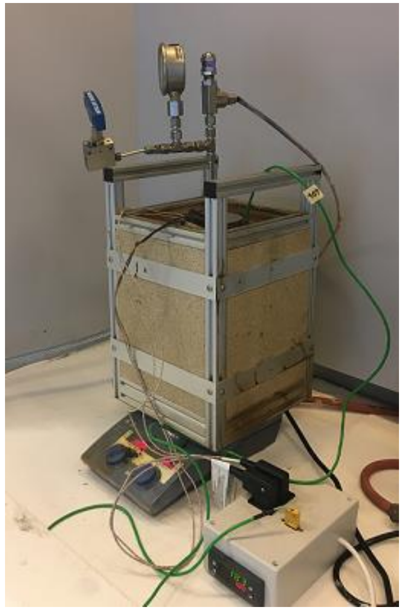
Coating A

Coating B

Coating C

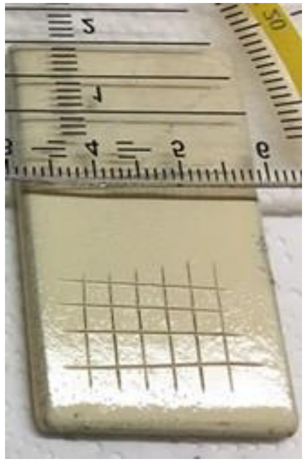
Coating D


LOTU

After LOTU test

Coating A

Coating B

Coating C

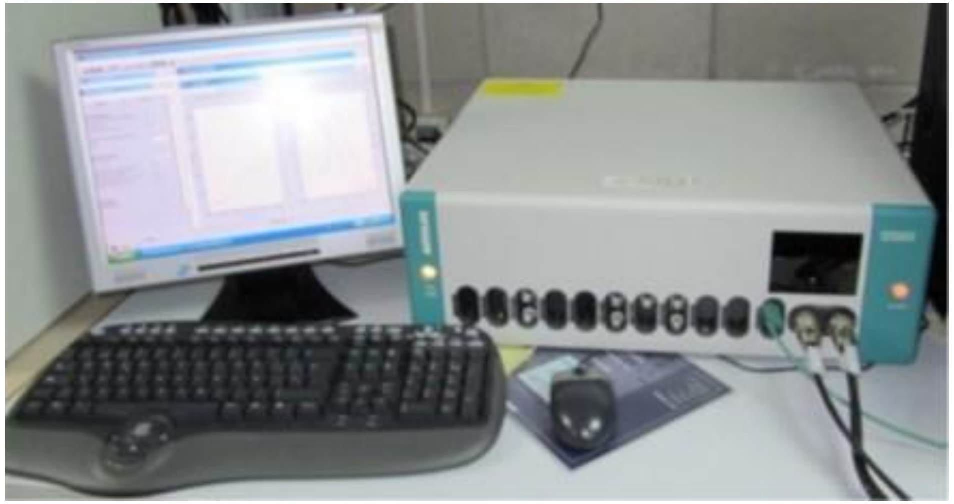
Coating D

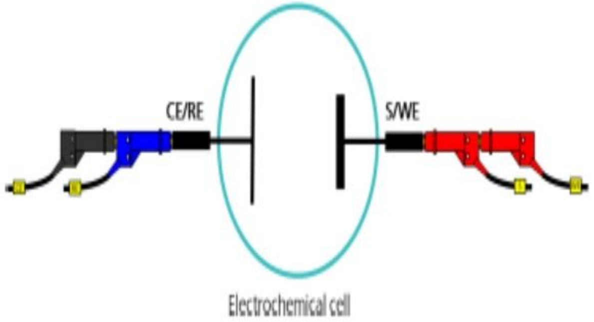

Coating	Adhesion rating	S.E mN/m	Blistering rating	Rusting rating	Comments
A	0	44	None	Ri 0	No visual signs of degradation
B	0	25	None	Ri 0	No visual signs of degradation.
C	0	44	None	Ri 0	No visual signs of degradation
D	0	<24	None	Ri 0	No visual signs of degradation

EIS Analysis

- PGSTAT20 AUTOLAB from Ecochemie®
- Vertical cell arrangement, synthetic brines (50 ml), r.t, open to air and continuous stirring
- Frequency range 100 kHz and 0.1 Hz (5 points per decade), AC potential perturbation of 200 mV (rms)
- Two-electrode configuration placed inside a Faraday cage.

The working electrode was the coated sample, and the exposed surface was 1 cm^2, a platinum mesh was the auxiliary (counter) electrode and the reference electrode was a platinum wire. The auxiliary electrode and the reference electrode were short-circuited to obtain more accurate measurements.





EIS Analysis

• The protective performance of the coatings is commonly assessed by estimating the polarization resistance (Rp). The Rp is the transition resistance between the electrodes and the electrolyte and can be used as a quantitative parameter to compare the corrosion resistance of different systems.

According to literature, the protective character of the coatings can be ranked as:

R_p $>10^8$ Ω·cm² excellent protection without noticeable penetration of electrolyte.

R_p 10^7-10^8 Ω·cm² good protection minimal electrolyte absorption.

R_p 10^6-10^7 Ω·cm² doubtful, the electrolyte creates a path the metal surface but there is not active corrosion yet

R_p $<10^6$ Ω·cm² poor, the coating is non protective,

The calculated R_p values have to be used with caution, and the analysis of the coating performance must be done attending all parameters extracted from the EIS plots, not by only one parameter.

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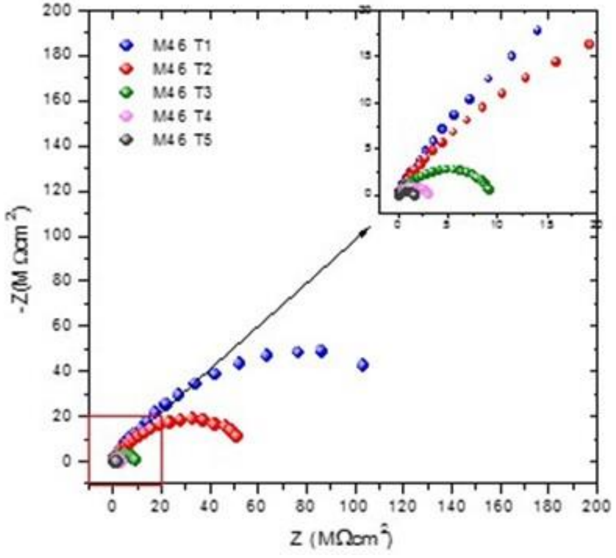
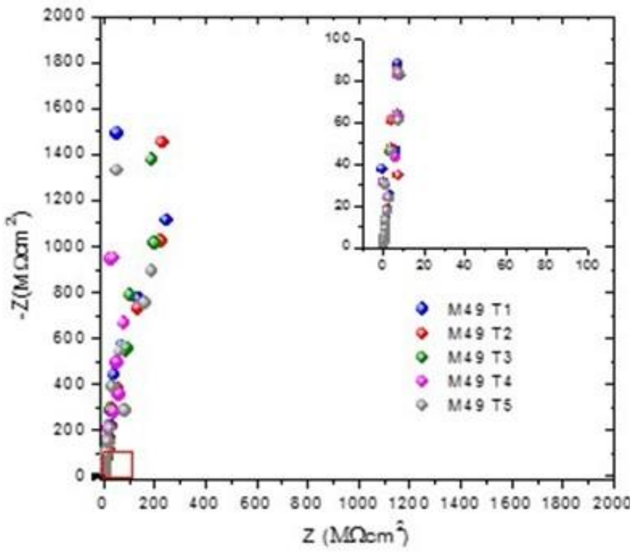
EIS Analysis

- The coatings were allowed to dry out at ambient temperature and pressure for 7 days prior to the EIS analysis.
- Upon subsequent re-immersion in the synthetic brines, the EIS measurements were carried at regular time intervals of 20 min. This was to analyse the electrolyte uptake into the coating layer. Coatings with significative deterioration show large permeability, while the opposite for resistant coatings.
- A period of 120 min was found as the time required to stabilize the impedance and reach steady state conditions. When the steady state conditions are reached, a detailed analysis of the barrier properties of the coating can be performed.

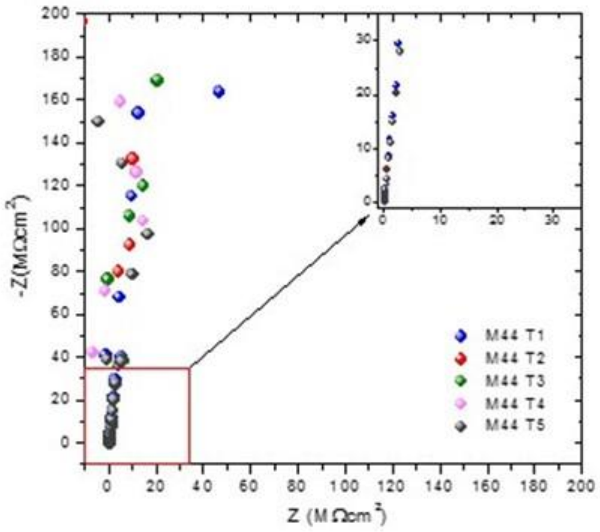
Coating A



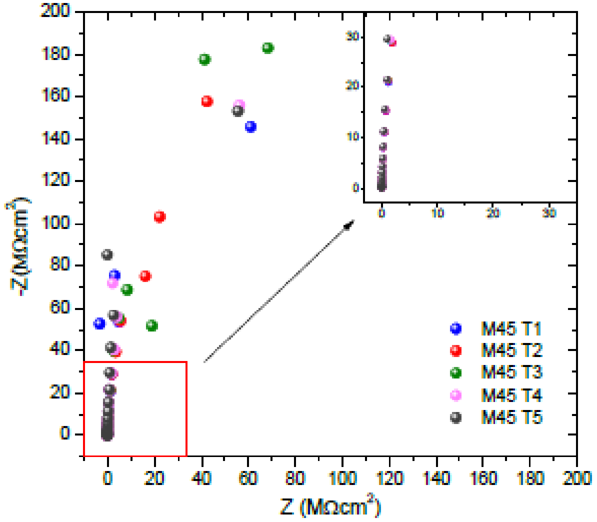
Coating B



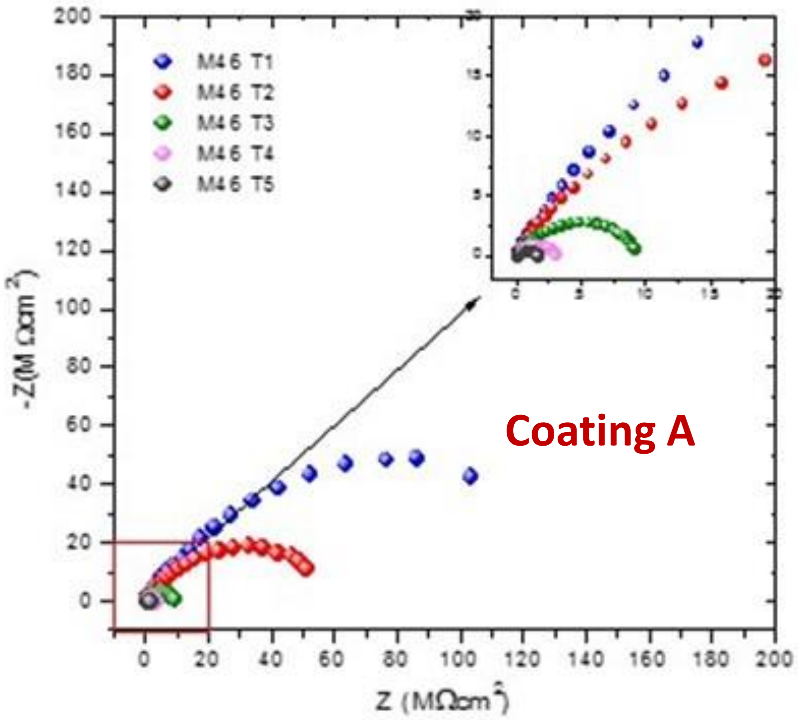
Coating C



Coating D

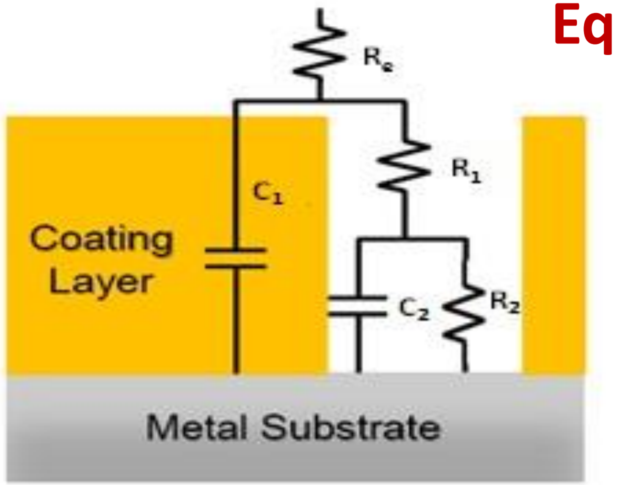


EIS Analysis



• The Nyquist plot changed gradually from a circular arc to a semicircle, whose radius decreased over time.

• The decrease of the impedance and the occurrence of a second time constant at low frequency reveals that, the electrolyte permeated into the coating/metal interface, causing electrochemical corrosion reaction of the metal substrate



Equivalent Electrical Circuit

R_s is the electrolyte resistance (brine resistance)
R_1C_1 is the time constant related to the barrier properties of the coating and R_2C_2 denotes the low frequency time constant accounting for the charge transfer resistance (R_2) and the double layer capacitance (C_2) corresponding to the corrosion process.
R_p is the sum of R_1 and R_2

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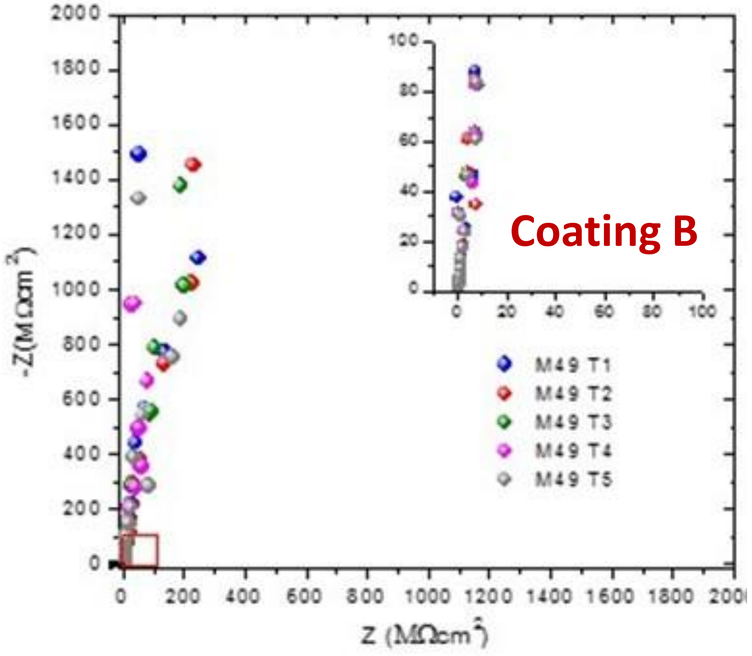
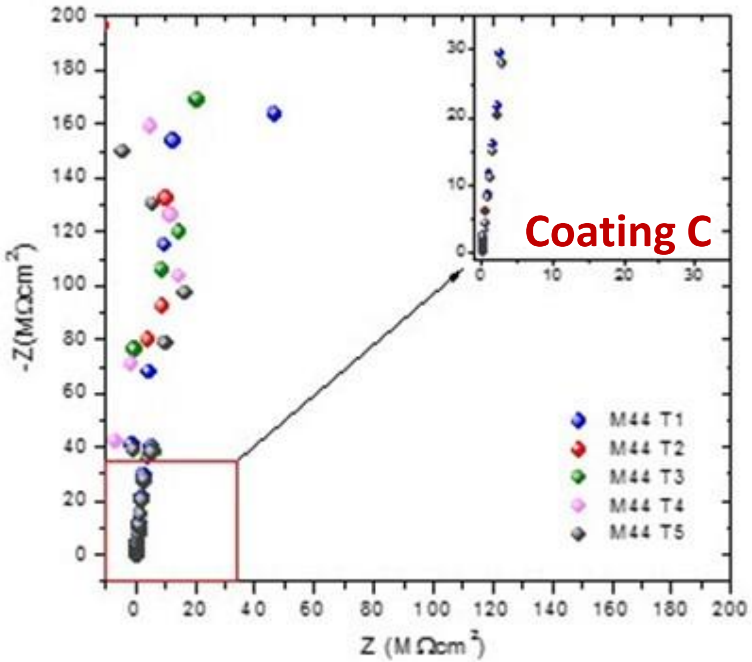
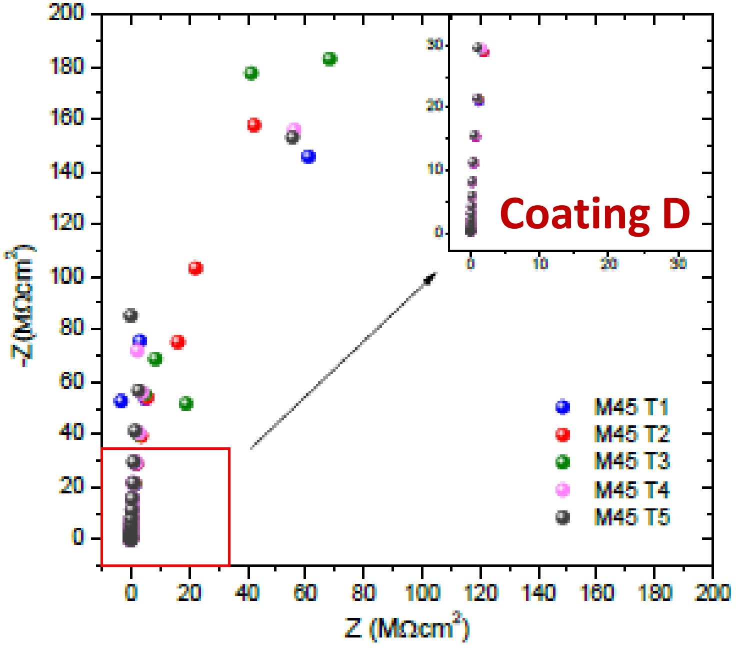
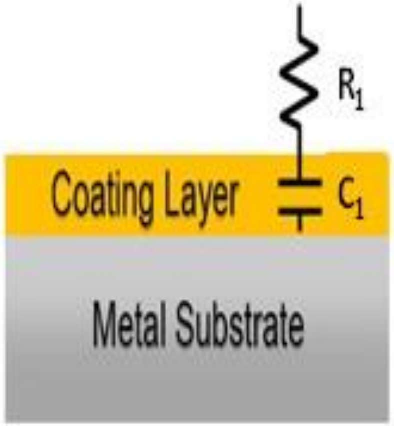
EIS Analysis







Equivalent Electrical Circuit



- The Nyquist plots of B, C, D showed an almost purely capacitive behaviour
- The high impedances and stability over time proved their excellent barrier properties

The coating adheres perfectly to the metal substrate, no surface imperfections. The EEC has only one time-constant which is associated to the coating

Rp is equivalent to R_1

EIS Analysis

T0	R_1 (MΩ·cm²)	C_1 (nF·cm⁻²)	R_2 (MΩ·cm²)	C_2 (nF·cm⁻²)	R_p (MΩ·cm²)
Coat A	5.45	0.47	1.57	3.37	1.62
Coat B	10×10^3	0.12	-	-	10×10^3
Coat C	98×10^3	0.08	-	-	98×10^3
Coat D	1×10^3	0.03	-	-	1×10^3

T5	R_1 (MΩ·cm²)	C_1 (nF·cm⁻²)	R_2 (MΩ·cm²)	C_2 (nF·cm⁻²)	R_p (MΩ·cm²)
Coat A	0.27	1.27	1.39	1.80	1.66
Coat B	7×10^3	0.13	-	-	7×10^3
Coat C	99×10^3	0.08	-	-	99×10^3
Coat D	2×10^3	0.04	-	-	2×10^3

- R_1 reflects the ability of the coating to resist electrolyte penetration. For B, C and D is in the order of GΩ·cm², and remained unchanged. B,C and D have excellent barrier properties. For A, R_1 is clearly lower and becomes even lower with time.

- R_2 is associated to the corrosion process, and its increment from T1 to T5 is due to the increase of the corroded area

Brasher-Kingsbury equation (volume fraction of water absorbed by the coating)

$\Phi = [(\log C1(t') / \log C1(t_1))] / \log(\varepsilon_w)$

ε_w is the dielectric constant of water ($\varepsilon_w \approx 80$)

Sample	C_{1t1} (nF·cm⁻²)	C_{1t5} (nF·cm⁻²)	Φ
Coat A	0.47	1.27	**23**
Coat B	0.12	0.13	**<0.05**
Coat C	0.08	0.08	**0**
Coat D	0.03	0.04	**<0.05**

- C_1 for B, C and D is very low and remain practically constant from T_1 to T_5, no geometric variation of the coating (no swelling), null or low brine absorption into the coating. Contrary, for A, the calculated brine uptake corresponds to a volume fraction of 23%

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Conclusions

• The autoclave-like tests are frequently used to qualify coatings for high P and T. **The incorporation of the EIS improves the reliability with which performance can be predicted, especially useful when not obvious coating degradation occurs.** **The sensitivity of EIS allows to detect the corrosion processes long before any visible damage occurs**

• Coatings A, B, C and D passed the initial screening and were analysed by EIS. Rp values for coatings B, C and D are very high, in the order of $G\Omega \cdot cm^2$ and the water uptake is below 0.1 their protection level is ranked as “excellent”. For coating A, the calculated R_p is in the range of $M\Omega \cdot cm^2$ and the water uptake is relatively high. The protection level is ranked as doubtful. At this stage, the electrolyte has reached the metal substrate but there are not visible evidences of corrosion yet.

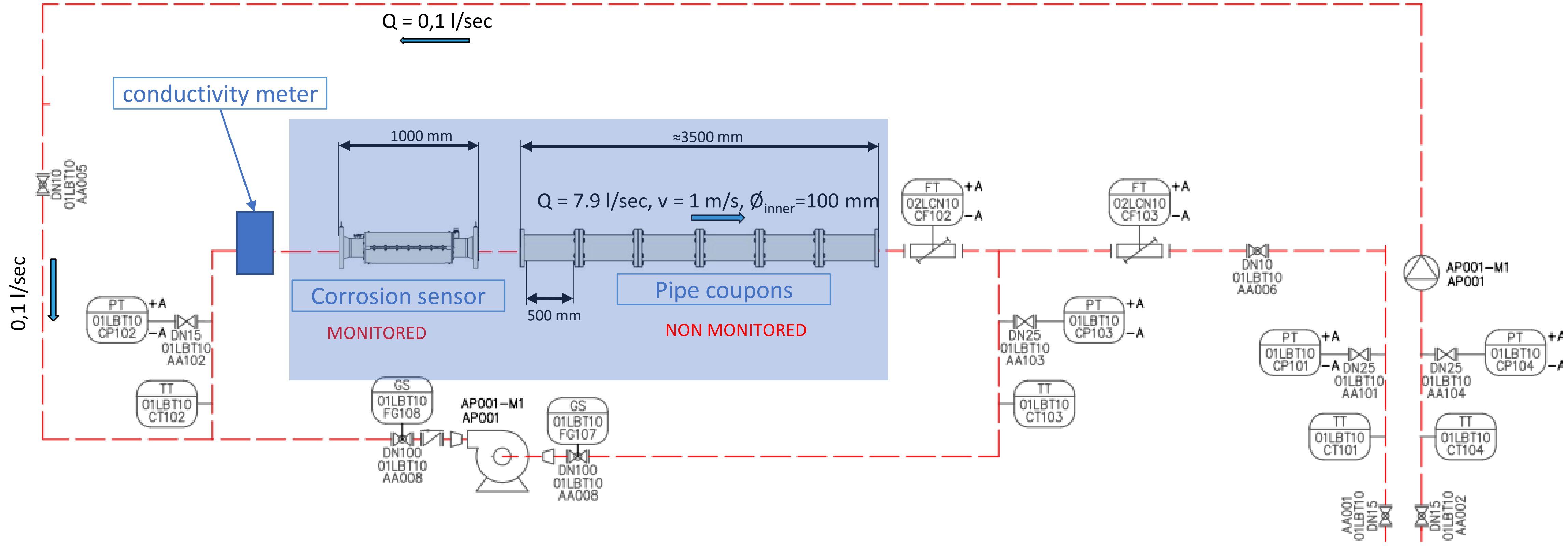
• **Coatings B, C and D are good candidates for internal pipe coating in geothermal installations.**

Laboratory testing cannot completely mimic all processes that occur in real operation, and the qualification of the coatings requires always a final validation under real operational circumstances

Demonstration

Demonstration and on site evaluation of the selected coatings

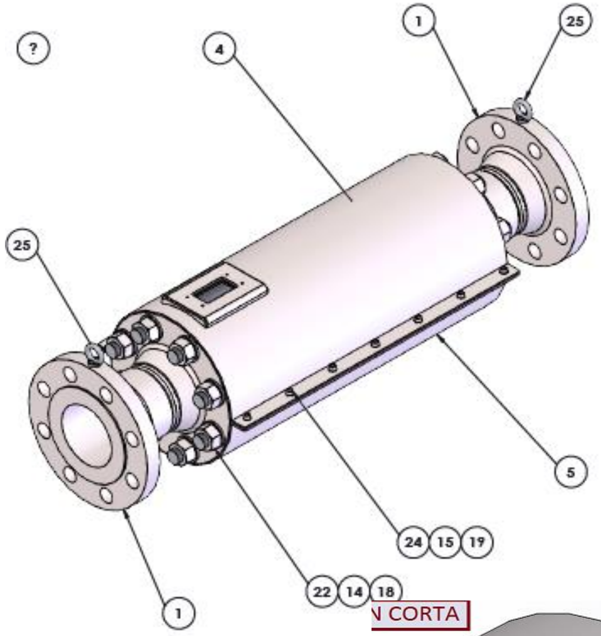
In total 6 coatings will be evaluated

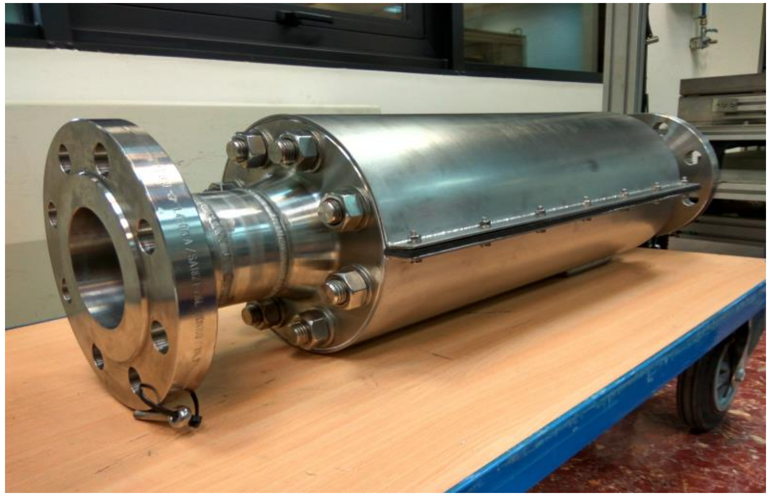


Demonstration

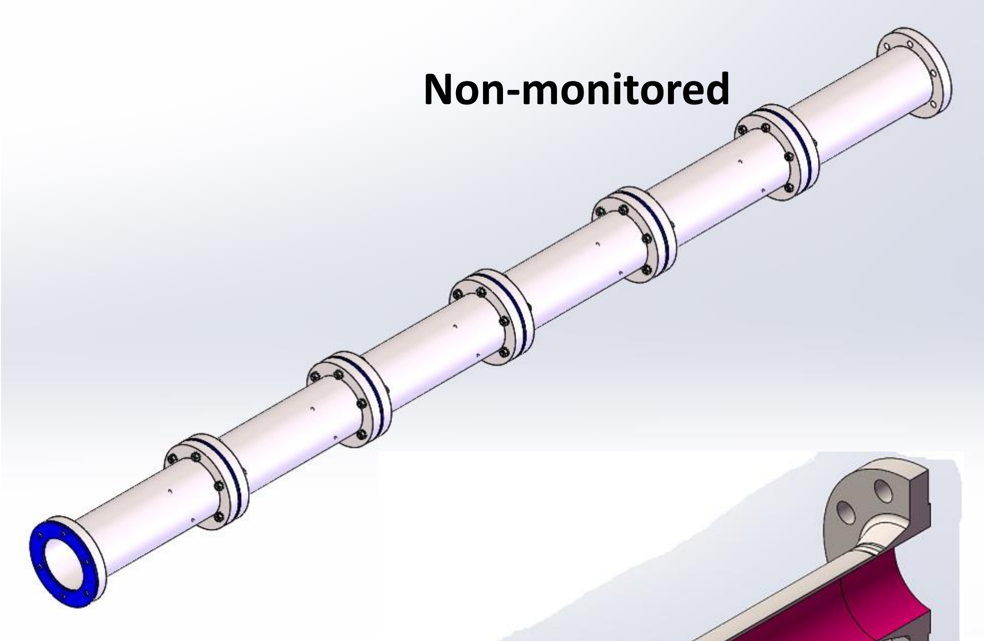
Demonstration

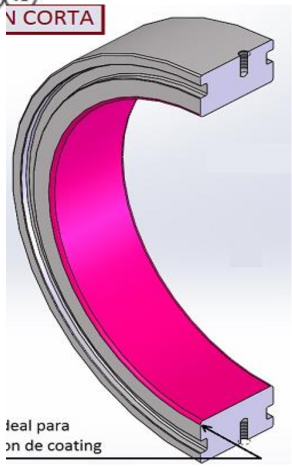
EIS monitored

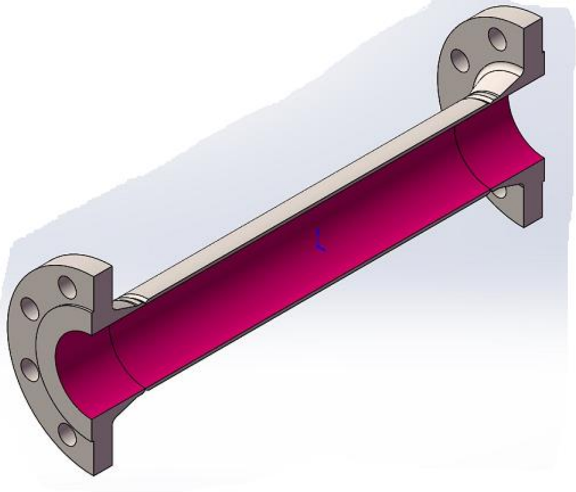




Non-monitored







Questions?

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