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Performance of novel Polymer Derived Ceramic (PDC) coatings developed for refinery piping systems and in-situ corrosion monitoring by EIS-based sensor

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| Background

Novel protective Polymer Derived Ceramic (PDC) coatings with improved corrosion resistance was developed in the context of the European project ACHIEF (*https://www.achief.eu/*). This project is aiming to introduce innovative materials to improve the energy performance of Energy Intensive Industries (EIIs) and reduce CO_2 emissions in the industrial processes.

A specific use case was identified in refinery pipes carrying corrosive fluids aiming for a reduction of the corrosion and/or erosion damage. Novel coatings with increased durability could increase service life of equipment and components, leading to a reduction of O&M operations and improving the overall performance and efficiency of the plant.

In this scenario, a novel PDC coating, containing polymer derived ceramic and ceramic charges, was developed to protect the inside of a stainless steel pipe (AISI 321) against corrosion in acidic environment. PDC are organic/inorganic materials formed by the pyrolysis of silicon containing polymer precursor (preceramic polymer precursor). Their properties (chemical composition, density) can be tailored at the molecular scale using suitable precursor and applying adequate thermal treatments. The processability techniques (spray, dip coating, brush, etc.) lead to a relatively low cost and easy approach to produce ceramic coatings, which provide excellent corrosion protection in high temperature and/or harsh environment.

In order to find the optimal composition for this particular case, analysis of the thermal conversion of suitable preceramic precursors and the addition of ceramic charges were assessed together with the integrity and morphology of coatings (by SEM) and the adhesion of the coating on substrates. Electrochemical Impedance Spectroscopy (EIS) was applied to select the best corrosion performance composition in the defined acidic conditions. Advances on upscaling the selected coating for pilot testing in industry will be showed.

Besides, a novel corrosion probe was also integrated in the refinery piping installation for in-situ and on-line monitoring using electrochemical techniques. The novel corrosion probe relies on the utilization of EIS method to determine the corrosion performance of the coated pipe. EIS is introduced as a useful tool not only at lab-scale but also for in-situ and real time estimation of the service life of components, corrosion resistance of novel coatings and prediction of failures in critical units, by correlating the process events to corrosion evolution.

The new EIS-based sensor system will facilitate the decision making and contribute to optimize the operation conditions, the coating/material selection and the maintenance costs of the plant.

| Methods I.

1. Materials under test

Different PDC coatings formulations were applied on flat samples of AISI321 stainless steel (1x1 cm^2) for the experimental study to optimize the coating for the final application. The electrochemical measurements were carried out in acidic solution, HCl 2M, at 60ºC. This solution was chosen because it approaches the conditions of the fluid found in the refinery piping system.

2. Electrochemical Techniques

Electrochemical experiments were performed in a conventional three-electrode cell arrangement with a thermostatic jacket. The counter-electrode was a Pt gauze of large surface area and a saturated calomel electrode (SCE) (E_0 = +0.24 V vs. SHE) as a reference. A Biologic VSP-300 Potentiostat was used to perform EIS tests. EIS spectra were recorded each 0,1, 2, 4, 8, 12, 16, 24, 36 and 48 h (from 10kHz up to 0,01 Hz and 50 mV r.m.s.) at 60°C.

Visual analysis at different magnifications, weight loss and Rp evolution, obtained by EIS fitting with R-RC circuit were used for the final evaluation of the coatings.

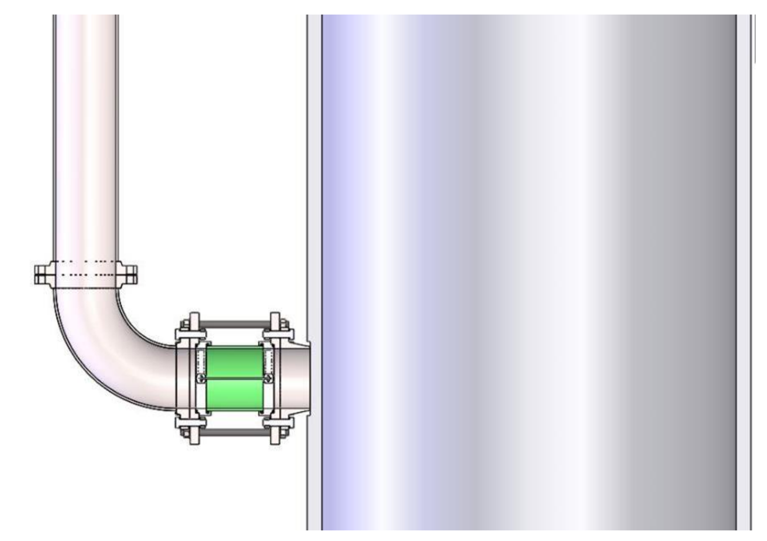
| Methods II.

Corrosion monitoring sensor design

The corrosion monitoring system to be integrated in the refinery pipe was designed by AIMEN based on the principles of a conventional 3-electrode-configuration cell for electrochemical measurements. For the design of the electrochemical probe, the following requirements should be accomplished:

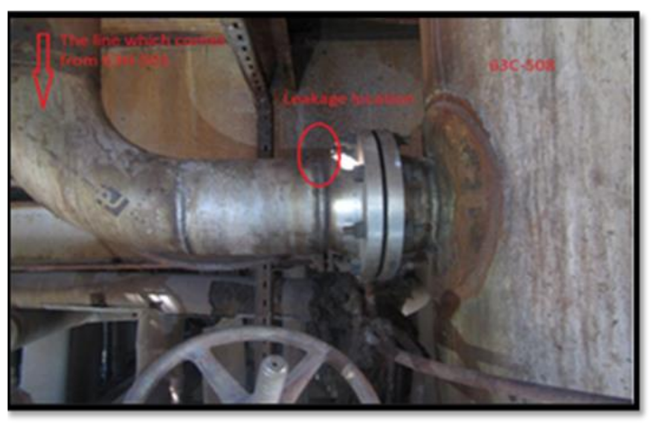
- Three electrodes configuration: the system requires three electrodes, a reference electrode (RE), a counter-electrode (CE) and a working electrode (WE). This configuration is selected as optimum to perform reliable EIS measurements.
- Dismountable: materials need to be easily dismantled once the testing campaign has been completed.
- Easy installation: the whole system (the probe and the data acquisition system) should be simple to install to avoid disruptions in the plant operation.
- Autonomous: Sensor operation should be unassisted since there are no personnel available at the plants to configure or collect data during its continuous operation. The measurements must be periodically scheduled and transmitted through wireless technology to an online server to be interpreted and analyzed by AIMEN.
- Resistant to operating conditions and adapted to the dimensions and geometry: the design and selected materials must withstand the harsh working conditions of the installation area and fluid chemistry.

Based on those specified requirements, a conceptual design of the complete system was created, including both the sensor geometry and the electrodes distribution. An outline of the described preliminary design of the probe manufactured is shown here

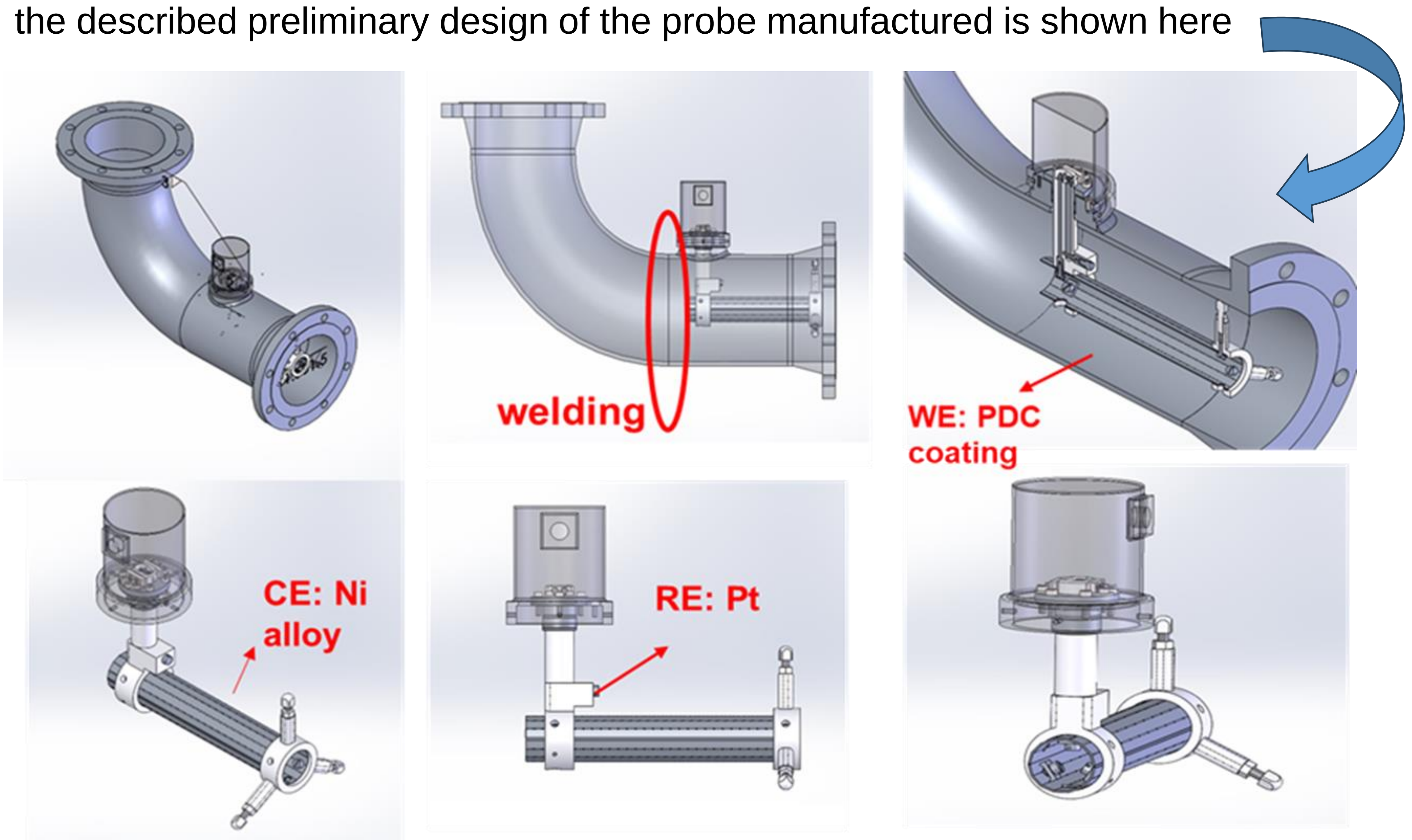


Detailed Drawing for Sensor Placement

MATERIAL LIST			
NO	QUAN.	PART NAME	MATERIAL
1	1	Long radius 90 Deg Elbow - 8"	ASTM A403 WP321
2	250 mm	Pipe 8" - Schedule 40	ASTM A 312 TP321
3	1	Pipe Flanges 8" - Flange Welding Neck - Class 150.	ASTM A182 F321



- Base metal **321 Stainless Steel**
- Outer diameter **8 inches**
- Thickness of the pipe **8.20 mm**



- The preliminary design allows to insert the sensor inside the welded pipe after the coating process.
- The probe is introduced in the coated section before the pipe installation and will be perfectly adjusted by telescopic pieces.
- It is needed to guarantee that the electrode will not move during the experiment and the contact points of the electrode will not damage the coating.

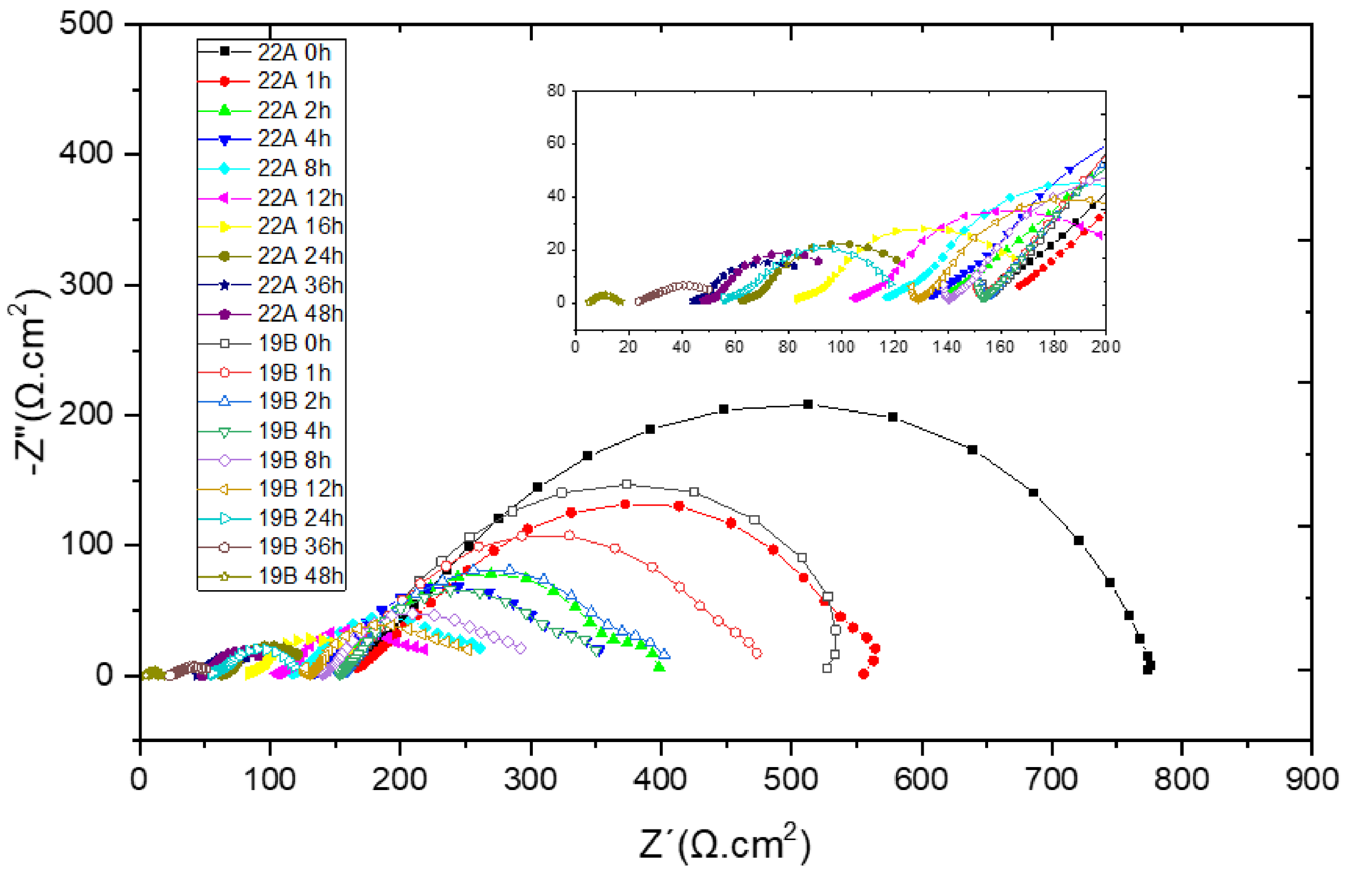
| Results I. PDC coating selection

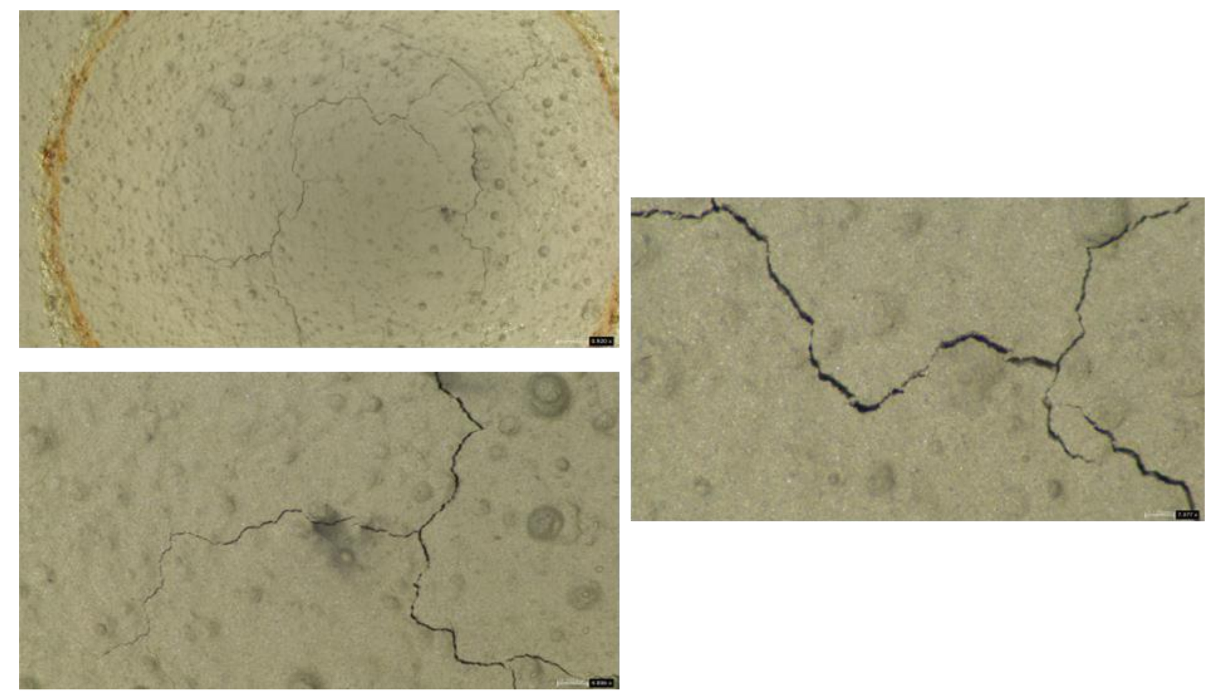
The PDC coatings were formulated by CEA in base of a Mixing of Silrès MK PDC (SiO_2) and SiC powder à Si, O, C.

The deposition process was spray coating with 360° spray gun. Fixed parameters for spray gun are: air flow = 300 L/min, nozzle opening: 1 lap and robot speed: 50 mm/s.

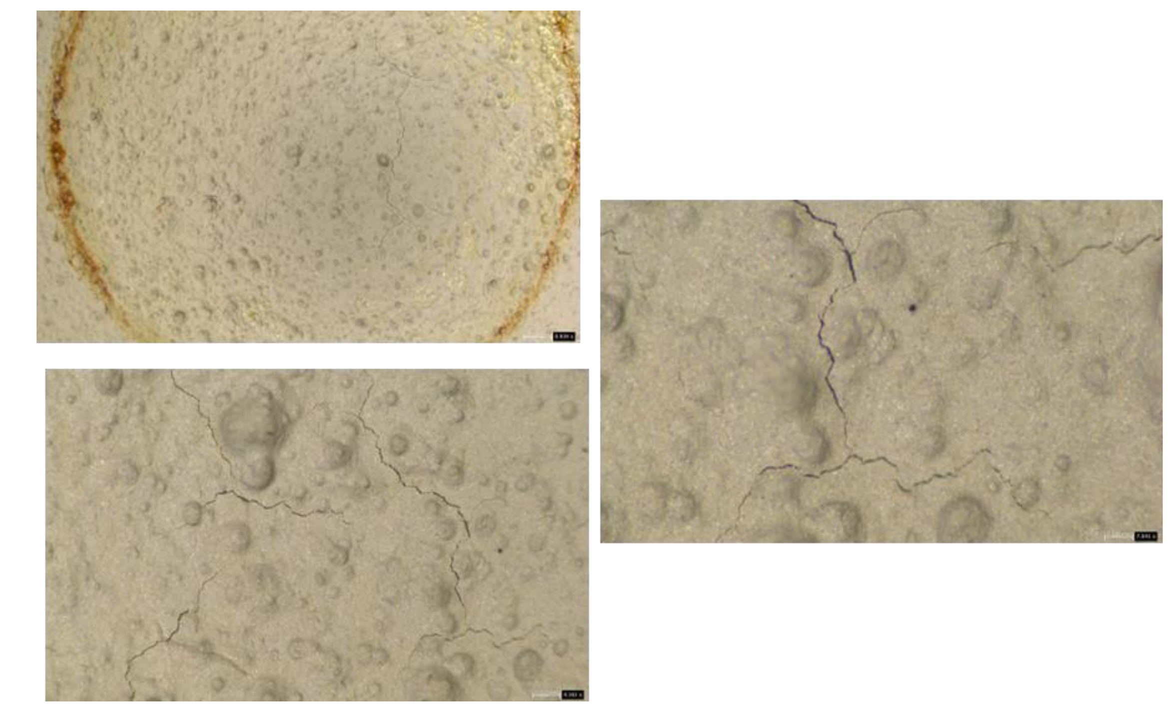
EIS measurements were recorded on 3 samples to obtain reproducibility. The average results are summarized in the following table.

Sample	Formulation	Formulation flow rate (cm^3/min)	Number layers	Rp 48h	Corrosion rate (mm/year)
REF	AISI 321	-	-		33,60
12	MK/SiC (50%)	200	1	10,55	3,47
13		200	2	30,09	2,23
14		100	2	11,95	2,06
15		100	4	14,60	4,25
16		100	6	24,94	5,40
18	MK/SiC (50%) + 16,6 wt.% solvent	200	1	9,98	3,72
19		200	2	25,05	1,92
20		100	2	5,48	3,62
21		100	4	20,23	3,78
22		100	6	55,16	1,53

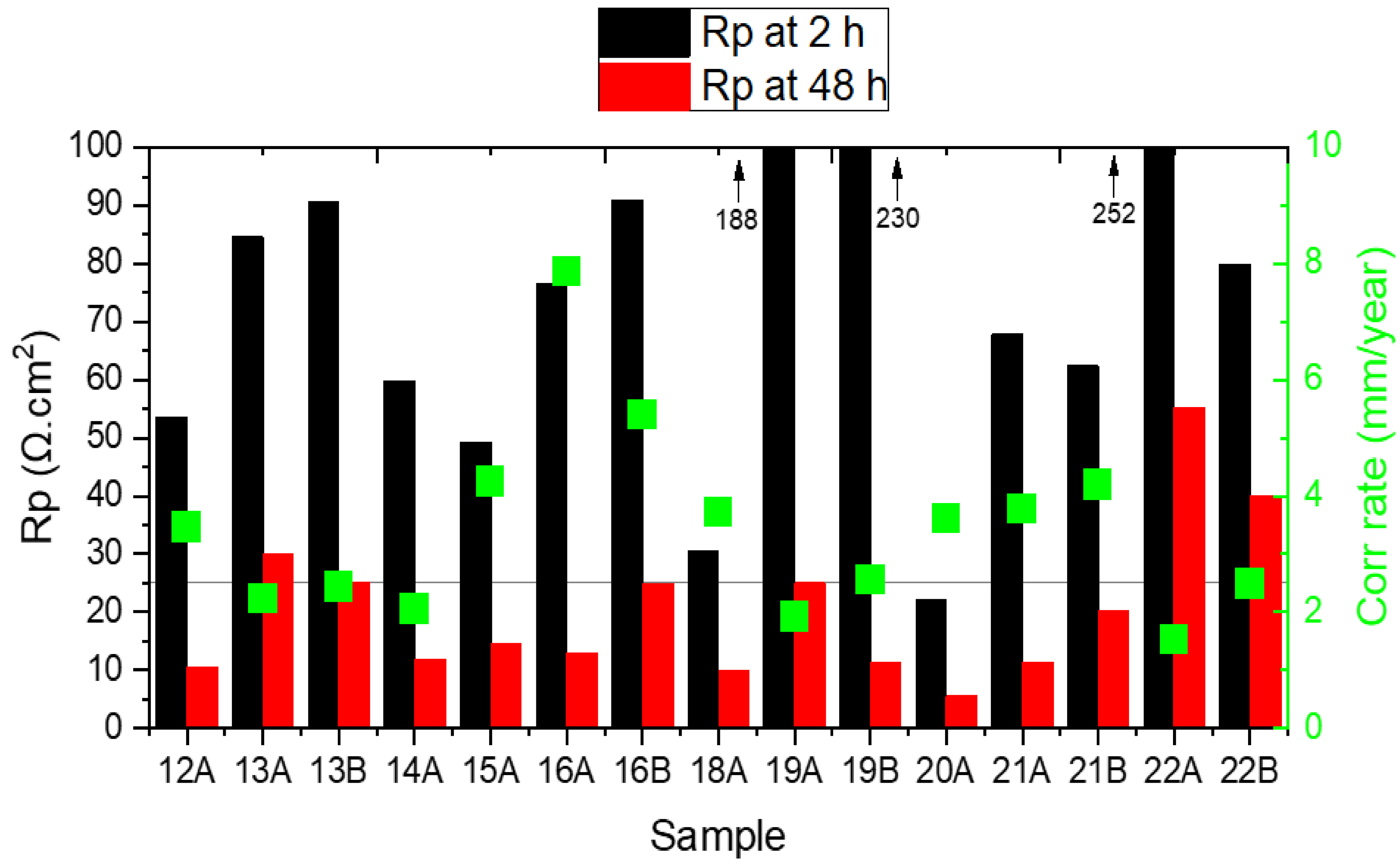




Sample 19: high cracks were detected on the coating after EIS tests



Sample 22: no cracks were detected on the coating after EIS tests



- Criteria to select best PDC formulations consist in finding the equilibrium between **corrosion rate** (lower than 3 mm/year) **and Rp at 48** h (higher tan 25 ohms at least).
- The results showed that higher number of deposited layers and higher thickness lead to higher Rp values after 48 h of testing and lower corrosion rates.
- **Best results are achieved for samples 22**

Results II. Corrosion monitoring sensor

The pipe will be coated with the previously selected PDC and the sensor will be integrated inside the pipe to monitor by EIS its corrosion resistance under real conditions. The complete system will be connected as show in the scheme below.

The new EIS-based sensor system will facilitate the decision making and contribute to optimize the operation conditions, the material selection and the maintenance costs of the plant.