

Expert report

Characterization of corrosion protection properties of NFRA product by impedance spectrometry

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Geographical location of the subject of the survey: MADIREL Laboratory, at the University of Aix-Marseille

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SUMMARY

I. Characterization

a. Preparation of samples;

b. Measurements

c. Test

1 - Coating

2 - Comparison

Characterization

a. Preparation of samples

In order to limit the influence of the material parameter all the samples will come from the same matrix and will all have the same assembly (see FIG. 1).

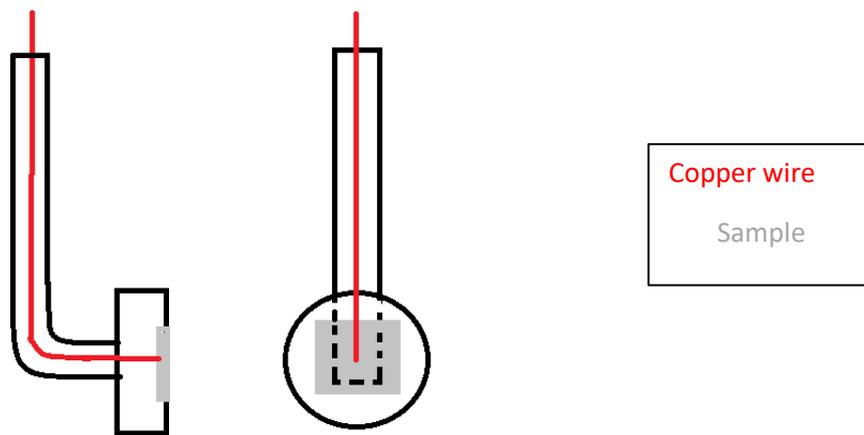


Figure 1, assembly diagram

The copper wire will be welded to the sample by arc welding in order to ensure a good electrical connection to the system; the whole will be covered with polyester resin in order to isolate the rest of the system in order to have just one surface of 1 cm^2 and to measure only the properties of the coating.

The samples which must undergo an oxidation in order to determine the influence of the protective power with respect to the degrees of oxidation of the product, will undergo electrochemical oxidation according to the following scheme:

- Low oxidation: $t = 20 \text{ s}$ and $V = 0.1 \text{ V}$
- Moderate oxidation: $t = 40 \text{ s}$ and $V = 0.1 \text{ V}$
- Strong oxidation: $t = 60 \text{ s}$ and $V = 0.1 \text{ V}$

The samples will be covered with a layer that will be about $30 \mu\text{m}$ thick and will be left for a minimum 48 hours to dry before the tests begin.

List of samples:

- Support Fe without oxidation (1)
- Support Fe Low oxidation (2)
- Support Fe Moderate oxidation (3)
- Support Fe Strong oxidation
- (4) Support Fe treated with Frameto (5)

b. Measurements

The measurement of impedance spectrometry will be carried out by the equipment of MADIREL laboratory.

List of equipment used:

- Zennium impedance spectrometer
- Platinum counter electrode
- Ag / AgCl reference electrode
- 0.05 M NaCl solution (sea water conditions)

A measurement with a Nyquist representation will be made for each sample. This representation will enable us to measure the impedance which will allow us to determine the fraction of water absorbed; When this fraction has reached 1 the coating will no longer be protective.

Working parameter:

- Voltage: - 0.05 to +0.05 V
- Frequency: 10⁻¹ to 10⁵ Hz 10⁻¹ à 10⁵ Hz

c. Test
i - Coating

After some measurement it has been observed that the system comprises like an RT circuit (see FIG. 2) and all the curves will be made.

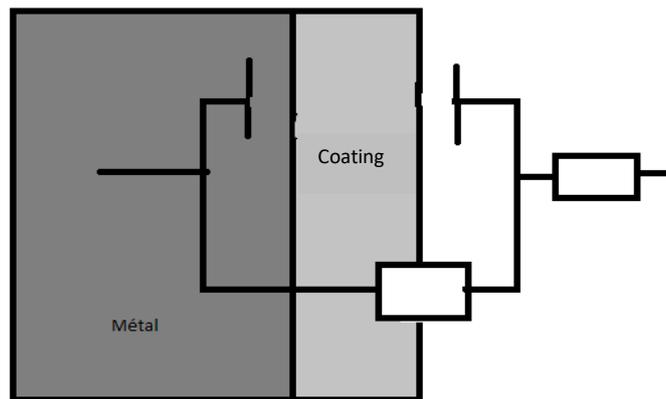


Figure 2, system diagram

In the following graph (see FIG. 3), the influence of the oxidation being minimal (see FIG. 4), the curves have been grouped together in order to facilitate reading.

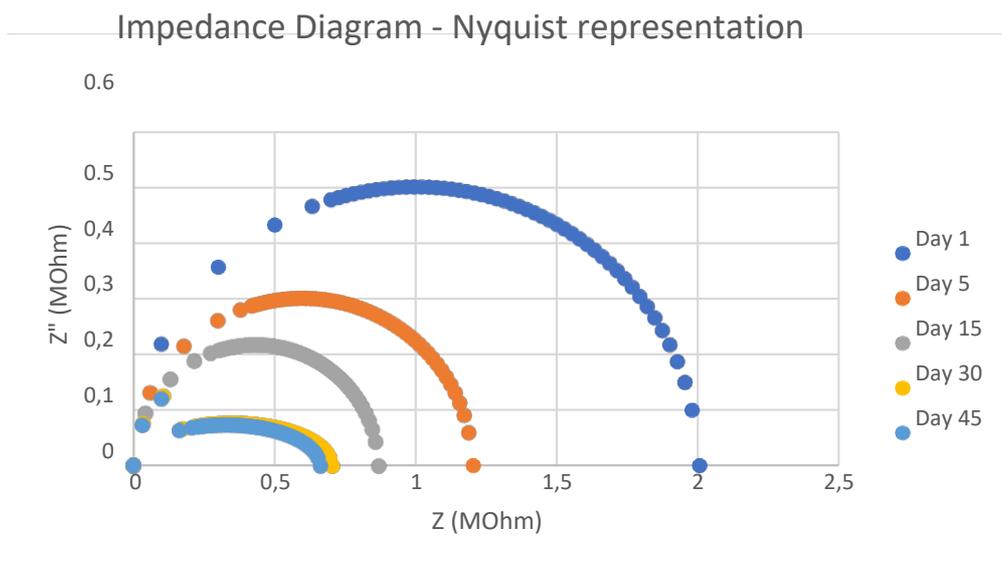


Figure 3, Coating result graph

As it is possible to observe, the impedance falls with time and begins to stabilize from about thirty days which will allow me to subsequently make a prediction about the lifetime of the coating.

From this graph it is possible to determine the value of the frequency (f_0) where the imaginary resistance (Z'') is the highest.

- (1) f_0 : 596 Hz
- (2) f_0 : 583 Hz
- (3) f_0 : 592 Hz
- (4) f_0 : 590 Hz

Thanks to this data, it is possible for me to determine the capacity (C) of the coating and to determine its evolution over time. In order to determine these values I will need the value of the transfer resistance (R_t).

| | Rt (MΩ) | | | |
|-----|---------|--------|--------|--------|
| Day | 1 | 2 | 3 | 4 |
| 1 | 2,0067 | 2,0102 | 2,0132 | 2,0072 |
| 5 | 1,2040 | 1,2104 | 1,2074 | 1,4134 |
| 15 | 0,8696 | 0,621 | 0.624 | 0.618 |
| 30 | 0.7023 | 0.7012 | 0.6982 | 0.6922 |
| 45 | 0.6672 | 0.6602 | 0.6572 | 0.6512 |

Figure 4, Table of different transfer resistance according to samples over time

| | C (C) | | | |
|-----|-------------|-------------|-------------|-------------|
| Day | 1 | 2 | 3 | 4 |
| 1 | 0.000133076 | 0.000135804 | 0.00013354 | 0.000134393 |
| 5 | 0.000221793 | 0.00022554 | 0.000222663 | 0.000190855 |
| 15 | 0.000307098 | 0.000439602 | 0.000430838 | 0.000436495 |
| 30 | 0.000380216 | 0.000389323 | 0.000385051 | 0.000389705 |
| 45 | 0.000400227 | 0.000413501 | 0.000409073 | 0.000414242 |

Figure 5, Table of different capacities according to samples over time

Not having the last points necessary to carry out the calculations for the prediction, you will find enclosed the incomplete graph.

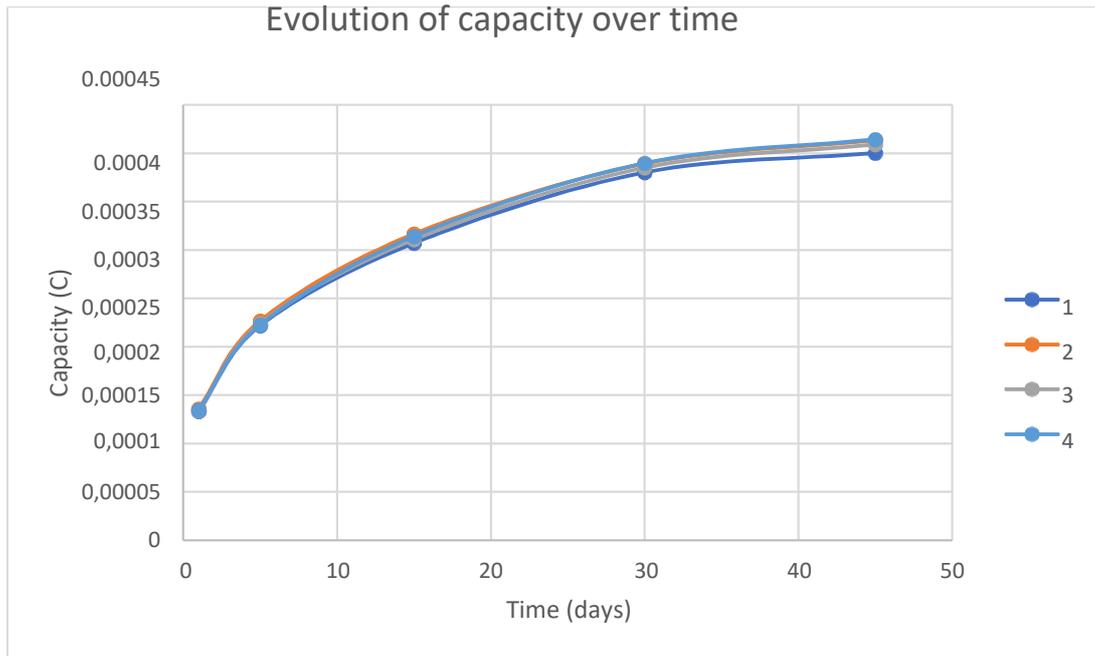


Figure 6, Coating result graph

The points that should follow should behave as an increasing linear function of the form $ax + b$.

According to the formula:

- At 45 days of experimentation the humidity level is 5% (0,05)

Thanks to these results I will be able to determine the moisture content of the coating and when this coating has reached a rate of 80%, CORRIZON will no longer be considered as protective (ref ISO 16773-2).

Intermediate note:

At this stage of the experiment, which has not yet been completed, it can already be seen that these intermediate and partial results make it possible, subject to confirmation at the end of all the measurements and their comparison with products already Tested with a similar objective, to consider that the **NFRA** product is positioned above the average, in the first tier, despite its remarkable very low application thickness (80µm for FRAMETO). Another particular element, visually the product **NFRA** seems to have a 'regenerative' power, the appearance of samples 2 (weakly oxidized) and 3 (moderately oxidized) exhibiting a significant improvement.

This particularity deserves a particular study, for which we do not have a standardized tool.