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**Monitoring of generalised corrosion: Ultrasonic Coda Wave Interferometry technique applied to Steel Corrosion in aqueous NaCl solutions.**

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### **Highlights**

Generalised steel corrosion in salted water monitored with Coda Wave Interferometry based technique.

## **Abstract**

This paper investigates a Non-Destructive Testing based on ultrasonic Coda Wave Interferometry technique to determine if it can be an efficient way to continuously and quantitatively measure the thickness loss due to corrosion on an S355 grade steel in 3 wt.% NaCl distilled water. To do so, several electrochemical experiments in open circuit potentials and imposed anodic dissolutions (from few to tens of micrometers) are performed at stable and varying temperatures (20-30°C) in aqueous NaCl. The thickness loss and corrosion rate are continuously measured with CWI thanks to a piezoelectric trasducer and verified post-experiment with an optical depth profile measurement.

## **Keywords**

Sensor

Generalised corrosion

Non-Destructive Testing

CWI

Electrochemical experiments

## **1. Introduction**

As corrosion of metallic structures can reduce their lifetime and lead to mechanical failure, it has to be considered in their design to prevent financial or safety issues [1-4]. Efficient measurement and corrosion detection are crucial to plan structural maintenance before it is too late. Despite the large number of existing corrosion sensors [5-8], Coda Wave Interferometry (CWI) technique [9] is an interesting choice that could be used to create new ones that will have the advantage of being a direct, non-destructive, continuous and very sensitive method to measure precisely the thickness loss of corroding metal.

This publication has been done in complement with the work done in collaboration with Farin et al. [9] to help develop a CWI-based sensor. This study has been carried out in the frame of the European Socorro II project, which aims to provide industries with computer tools to help them to take preventive actions on their corroding structures. To create this tool, a machine learning algorithm will be fed with corrosion data (direct and indirect techniques) from around the "Two-Seas" area to create a corrosion model. The more data are gathered and fed to the algorithm, the better it is expected to perform. The CWI technology is promising to provide a cheap, small-sized, continuous and direct technique to measure thickness loss on chosen steel grade that could be made into an autonomous system and easily installed in various locations around the North Sea area to gather corrosion data for this project.

The most straightforward and most broadly used technique to test and follow the corrosion evolution of a given material is to put coupons in natural or "accelerated" corrosion conditions and analyse it after a certain amount of time. Generally, the analysis consists of a thickness loss measurement [5]: corrosion products are removed from the surface and the coupons are weighted and compared to its initial weight to measure the mass loss induced by corrosion. Knowing the coupons size, an average thickness loss can then be calculated from the measured mass loss. The main issue with this technique is that coupons can only be used once per measurement and need to be handled each time manually, making this technique time and material-consuming. CWI technique is a Non-Destructive Testing that has been considered to automatically and continuously measure the thickness loss of a corroding metallic plate.

Coda Wave Interferometry (CWI), which has initially been developed for seismic wave analysis [10-11], has also been used to create Non-Destructive Testing (NDT) methods to follow biofilm growth on the metallic surface for agronomical applications [12-13]. This same technique has been recently adapted to corrosion monitoring [9]. CWI is an ultrasonic technique that relies on the same basic principle as the pulse echo technique. The idea is to generate an ultrasonic pulse within the material, then record and analyse the material response as the emitted ultrasonic waves are reflected at interfaces and defects. The main difference between CWI and pulse-echo is that instead of just

analysing the response time of the first wave packet arrivals to measure the thickness and detect a defect, the coda part (multiple echoes and reflections) is considered. Indeed, coda wave is theoretically more sensitive to any small perturbation occurring in the medium, such as temperature, velocity change, etc. To generate an ultrasonic impulse and record the response of the material, a piezoelectric transducer placed on the opposite side of the sample is a common choice, and it has the advantage of allowing post-experiment surface analysis if needed.

Nowadays, Electrical Resistance sensors (ER) and Linear Polarisation Probes (LPP) are the mainly used solutions to remotely follow corrosion evolution in natural exposition sites. ER sensors and LPP give quantitative corrosion rates but they only works with a specific material that must be designed and shaped to fit the sensors. ER is more robust and works in immersed and atmospheric conditions but the corrosion rates obtained by corrosion depth derivative, whereas LPP only works in immersed configuration and is less robust in the maritime environment when it tends to deteriorate quickly but gives instantaneous corrosion rates [[14].

In this work, which complements the previous technical developments [9], controlled electrochemical experiments are performed in parallel with ultrasonic sensor measurements to investigate the efficiency of ultrasonic CWI to monitor the corrosion of construction steels in aqueous 3 wt.% NaCl. The CWI technique used in this work is described in more detail in the previous publication [9]. In the present study, we will compare a CWI-based sensor to an existing solutions and focus on the precision of this technique, the conditions and the precautions required to obtain reliable and precise measurements of corrosion rates.

## **2. Material and experiments**

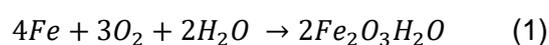
To evaluate the accuracy of the CWI technique for steel corrosion monitoring, a thermoregulated electrochemical cell has been coupled with a CWI measurement set-up. For this study, the S355 grade steel, provided by Thissenkrupp Steel Europe has been used. The chemical composition of this carbon steel is given in Table 1.

The corroding samples (Figure 1) are 5 by 5 cm, 3 mm thick square plates of S355 grade steel. Those plates were preliminarily polished with SiC grinding paper up to a 1200 grade and cleaned with ethanol to prevent premature corrosion. A piezoelectric transducer, both emitter and receiver (Figure 1.a) with a diameter of 2.6 cm, is glued with superglue on the face of the steel plate samples that will not be in contact with the electrolyte. Some samples were completely or partially varnished on the corroding side with a Flexible Silicon Coating (Electrolube). The varnishing details are given in the results section as they vary from one experiment to another.

The electrochemical cell (Figure 2) dimensions are 15-by-15-by-15 cm, and the volume of electrolyte put inside for all the experiments is 2.5 L. The Working Electrode (WE) is the steel sample, the Reference Electrode (RE) is a Saturated Calomel Electrode (SCE), and the Counter Electrode (CE) is a platinum plate electrode 8-by-8 mm. The CE and the RE are directly immersed from the top of the tank, whereas the steel sample (WE) is pressed with an adaptor against a hole on the side of the cell with an O-ring joint to maintain water-tightness. The adaptor was 3D printed so the sample could be pressed against the cell side without putting mechanical stress on the glued piezo-transducer and the welded wires on the samples back. The electrodes are connected to a potentiostat (model: Origaflex 500 mA by Origalys) in an inverted configuration so that the groundmass is connected to the sample to prevent “current leakage” during the imposed current phases of the electrochemical sequences.

Electrochemical sequences details are given alongside results as the sequence change depending on the experiment. Electrochemical cell temperature is controlled with a heat exchanger made of a glass tube that weaves in the cell. In this glass tube runs water whose temperature is regulated with a cryo-thermostat (model: Lauda RA8). The temperature in the electrochemical cell is continuously measured with a varnished thermocouple positioned as close as possible to the sample inside the cell.

Corrosion of S355 steel in water can be globally described as the reaction of iron, oxygen and water to form rust:



This will result in the consumption of the iron atoms at the surface of the steel surface and thus a reduction of the thickness of the plate. If the corrosion products are not adherent or not dense enough, this corrosion depth can be measured by ultrasonic techniques.

The CWI measurements setup (Figure 3) is composed of a function generator (Metrix GX 1050) connected to the emission part of the piezoelectric transducer and an acquisition board (14-bit, PicoScope 5444D, Pico Technology, 125MS/s) connected to the reception part of the piezoelectric transducer to record the sample response to the excitation with a 125 MHz sampling frequency.

The CWI technique is the same that the one used and detailed in the previous publication [9]. This technique consists of periodically sending the same ultrasonic excitation signal (a frequency-modulated chirp with frequencies varying from 5 MHz to 15 MHz) and measuring the sample response to this excitation. The sample response is then convolved with the time-reversed chirp function to obtain the impulse response of the sample. The coda part of this response, which is composed of the multiple reflections of the emitted waves off the sample opposite faces, is compared with a reference coda signal  $s_0$  measured at the beginning of the experiment (Figure 3). Since the multiple wave reflections are probing the sample many times, the coda is very sensitive to any change in the sample boundary conditions and material. To compare the measured coda signal  $s_x$  with its reference  $s_0$  in a defined time window  $[t_a; t_b]$  with  $t_a > t_b$  it is classical to use the decorrelation. The decorrelation (D) is very useful for investigating the global physical modification/evolution of a system. However, it cannot be used to obtain a quantitative corrosion depth value as it is influenced by all the physical modifications of the sample (like pressure-induced constraint, temperature etc ...).

Corrosion of S355 grade steel in NaCl 3wt.% distilled water can be assimilated to near homogeneous corrosion resulting in a thickness loss. This loss will result in a shorter travel time of the incident wave through the sample thickness. This time gain will accumulate as the ultrasonic wave goes back and forth multiple times in the sample (multiple reflections off the sample opposite faces), resulting in the fact that the later the time window is situated in the coda, the more this effect will be visible. This effect will make the reference coda signal look stretched compared with the coda signal measured for a smaller thickness. As shown in precedent work [9], this stretching of the response signal can be

computed. The coda stretching factor is mathematically determined by introducing an  $\alpha$  factor varying between -0.5% and 0.5% as follows in the reference response signal  $s_0$ :

$$s_0(t) \rightarrow s_0(t * (1 + \alpha)) \quad (2)$$

The coda stretching factor  $\alpha$  at a given time  $t_x$  is determined for the value of  $\alpha$ , which gives the best correlation  $D$  between the stretched reference coda signal  $s_0(t * (1 + \alpha))$  and the coda signal measured at this instant  $s_x(t)$ .

As temperature also modifies the ultrasonic wave propagation velocity in the material, it also influences the travel time and thus the coda stretching factor. As shown in [9], this temperature contribution can be corrected if a temperature measurement is close to the sample. Stretching from the temperature can be expressed like this:

$$s_0(t * (1 + \alpha_{raw})) = s_0(t * (1 + (\alpha_{corr} + \alpha_{temp}))) \quad (3)$$

Where  $\alpha_{corr}$  corresponds to corrosion coefficient, and  $\alpha_{temp}$  for temperature one.

So, the coda stretching factor from corrosion only can be obtained by removing the coda stretching factor of the temperature from the raw stretching factor.

If the temperature is stable or the temperature contribution to the coda stretching factor is mathematically compensated ( $\alpha_{corr} = \alpha_{raw} - \alpha_{temp}$ ) it is possible to convert a stretching factor to a corrosion depth using the following logic. If we consider that the stretching is only influenced by the corrosion thickness loss and if we only consider the time for an emitted ultrasonic wave to travel to the sample opposite face, be reflected and go back to the piezoelectric transducer, we obtain:

$$\text{For an uncorroded sample: } t_0 = \frac{2L}{c} \quad (4)$$

$$\text{For a corroded sample: } t_x = \frac{2(L-l_{corr})}{c} \quad (5)$$

With:

- $L$ : the initial thickness of the sample.
- $l_{corr}$ : the corrosion thickness loss.

- C: The longitudinal ultrasonic wave speed in the sample.

If the coda stretching factor is only due to thickness loss, in this condition, it will be calculated so that:

$$t_x = t_0(1 + \alpha) \quad (6)$$

$$(4), (5), (6) \rightarrow \frac{2(L - l_{corr})}{c} = \frac{2L}{c}(1 + \alpha) \rightarrow l_{corr} = -L\alpha \quad (7)$$

This equation is coherent with the result obtained for the coda stretching factor in the corrosion depth model developed in [9] in which for a 2 mm-thick plate, we obtained  $l_{corr}(\mu m) \approx -2004\alpha$ .

As said before, the stretching factor is also influenced by temperature. If we look at the same equation for a sonic wave going back and forth once (4) we can see that temperature will influence the flight distance due to material dilation and the ultrasonic wave speed  $C$ . [15]. An increase in temperature will result in an increase in the flight distance and a reduction in the speed of the ultrasonic wave, which will both contribute positively to the stretching factor  $\alpha$ .

If we consider only the dilatation of steel due to temperature variation using the dilatation coefficient ( $\gamma=11*10^{-6}$ ) and using the same logic as (7), but varying  $D$  with temperature instead of corrosion, we obtain :

$$\alpha = \sqrt[3]{1 + \gamma(T_x - T_0)} - 1 \quad (8)$$

(with  $T_0$  the temperature for the reference signal and  $T_x$  the temperature of the present measurement) and which corresponds to a modification of the coda stretching factor of 0.0004% per degree Celsius (dilatation coefficient is relatively stable for steel between 0-100°C). For a 2 mm thin plate, it corresponds to a shift of 0.006  $\mu m$  per degree on corrosion depth. If we now consider the modification of ultrasonic wave speed in the steel taking the data from the publication of [14] we can consider that in the 0-100°C domain, longitudinal ultrasonic wave speed can be defined as  $C (m.s^{-1}) =$

$6000 - b * T$  (with  $T$  the temperature in degrees Celsius and  $b$  a factor between 0.5 and 1. Using this equation combined with (4), varying  $C$  with temperature and keeping  $L$  constant, we obtain:

$$\alpha = \frac{b(T_x - T_0)}{6000 - bT_1} \quad (9)$$

Here, if we choose  $T_0 = 0$  °C and  $T_x = 1$  °C it corresponds to a shift of 0,008 % of stretching factor alpha for  $b = 0.5$  and 0.0167 % for  $b = 1$ , corresponding to a corrosion depth computation error between 0.16  $\mu\text{m}$  and 0.32  $\mu\text{m}$  per degree. Consequently, the influence of temperature on the ultrasonic wave speed in steel on the coda stretching factor  $\alpha$  is more critical than on the dilatation of the material. Those computations match the result obtained in [9] in which a change in temperature of 1 °C induced a stretching factor ( $\alpha$ ) shift of -0.0124 %.

Determining the influence of temperature on the coda stretching factor can be difficult because the dilatation coefficient and ultrasonic wave speed vary from material to material. The simplest way to obtain the influence of temperature on the stretching factor is to directly measure it by experimenting with a completely varnished sample which is protected from corrosion and only affected by temperature.

The influence of temperature and temperature correction will be investigated in this paper, but we will work at stable temperature for the first experiments. In order to check the accuracy of our corrosion depth measurement, surfaces were observed with an optical profilometer (Bruker Profilometer: Contour GT-K Automated) after each experiment. Several measurements were performed at the limit of the corroded area (after varnish removal with ethanol) to measure the corrosion depth (Figure 4) and compare it with the corrosion depth deduced from the CWI measurement.

### **3. Results**

#### **3.1 Corrosion detection with CWI**

In order to estimate the accuracy that can be expected on the corrosion depth from CWI, a first corrosion experiment has been conducted with an S355 steel 3 mm thick plate in NaCl 3 wt.% distilled

water. The electrochemical sequence was an open circuit potential for 5 days. The sample was partially varnished to prevent under-joint corrosion, the surface exposed to the electrolyte was a 3.8 cm<sup>2</sup> circle. As the coda signal is very sensitive to temperature, the temperature of the electrochemical cell is regulated at 29.5±0.5°C for this first experiment (Figure 5).

Polished S355 steel initial free potential in NaCl 3wt.% distilled water is around -0.4 V vs SCE evolving in a few hours to around -0.7 V vs SCE, which is coherent with the corrosion of S355 steel grade in NaCl 3 wt.% [8]. The coda stretching factor of the coda signal (Figure 6) increases steadily during the experiment. The coda stretching factor is then converted into a corrosion depth and gives a constant corrosion speed of around 1.0 μm.day<sup>-1</sup>.

After 5 days of immersion, the corrosion depth measured with the CWI technique was 5.1 μm (Figure 6). Corrosion products (mainly red rust) were cleaned from the surface with ethanol. Then, an optical profilometer was used to measure the corrosion depth and compare it with the CWI value. Over 5 measurements were performed along the edge of the corroded area and the corrosion depth on average was 4.5±0.5 μm.

The same experiment was performed with a completely varnished sample to investigate the possible contribution of the varnish and more largely the contribution of the experimental setup on the CWI signal stretching factor (Figure 7) and evaluate the baseline of the technique.

For the varnished sample, the coda stretching factor decreases rapidly on the first day of experiment and then more slowly over 5 days. Even if, in this case this stretching factor evolution does not correspond to a real corrosion depth (varnished sample) but rather to a drift of the corrosion depth measurement, it needs to be taken into account because it will influence the final result of the corrosion depth in the case of a non-varnished sample. This corrosion depth drift coming from the experimental set-up could explain the slight decrease observed at the beginning of the open circuit corrosion experiment (Figure 6). When real corrosion happens at the surface, this corrosion depth drift is rapidly small compared to the corrosion depth induced by corrosion, but it can shift it slightly.

### 3.2 Corrosion measurements with temperature correction

As explained in the experimental setup section, temperature variation will induce a stretching (dilatation/compression) on the coda part. In order to verify that the temperature influence on the coda stretching factor ( $\alpha$ ) can be corrected, the coda stretching factor in the experiment has been reproduced with the completely varnished sample but with temperature variation between 20 °C and 30 °C (Figure 8).

This experiment allows us to determine that the shift induced by a temperature increase of 1 Celsius degree on the coda stretching factor  $\alpha$  is -0.0123 %, which is close to the one from publication [9].

Thank to that we corrected the temperature contribution to the coda stretching factor by removing it from the raw stretching factor as follows:

$$\alpha_{corr} = \alpha_{raw} - \alpha_{temp} = \alpha_{raw} - (0.0123 * (T - T_o)) \quad (10)$$

With  $T$  the temperature at the time of the actual measurement and  $T_o$  the temperature at the reference measurement. The correction worked well, especially for slow temperature changes (e.g. from  $t = 25$  h to  $t = 85$  h and from  $t = 100$  h to  $120$  h) (Figure 8.b). The temperature influence is not completely compensated for quicker temperature changes (at  $t = 20$  h and  $t = 90$  h). However, such drastic temperature changes are rarely observed in natural environments. After 5 days, the corrosion depth is around  $-0.5 \mu\text{m}$  (Figure 8.c), coherent with the one obtained for the experiment with the varnished sample and fixed temperature.

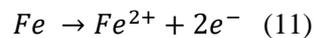
To complete those results, an experiment with an S355 grade steel sample with an unvarnished surface of  $3.8 \text{ cm}^2$  in NaCl 3 wt.% and controlled temperature variation between 20 and  $30^\circ\text{C}$  has been performed (Figure 9).

Again, temperature correction is better for slow than sudden temperature changes (Figure 9.a) (visible at  $t = 25$  h;  $t = 50$  h;  $t = 120$  h). The corrosion depth obtained for S355 grade steel reached  $4.5 \mu\text{m}$  after 5 days at open circuit potential, coherent with the  $5 \pm 1 \mu\text{m}$  corrosion depth measured with an optical profilometer and the corrosion depth obtained in the first experiment with stable temperature (Figure 6).

Those experiments demonstrate the efficiency of CWI in detecting corrosion and quantifying the rate of corrosion at the surface of a steel sample. In order to test the accuracy of this technique more quantitatively, more experiments with imposed electrochemical dissolution have been performed.

### 3.3 Quantitative continuous corrosion rate measurement with CWI.

To simplify the quantitative comparison with the final corrosion depth obtained from CWI, the one measured by optical profilometer and the ones extracted from literature, the imposed currents are converted in equivalent dissolution rate ( $\mu\text{m}\cdot\text{day}^{-1}$ ) with the hypothesis that all electrons contribute to the stoichiometric dissolution of iron following the reaction:



If we take the standard values for iron (close enough to steel) with a weight density of  $7.874 \text{ g}\cdot\text{cm}^{-3}$ , a molar mass of  $55.845 \text{ g}\cdot\text{mol}^{-1}$  and the Faraday constant, we obtain a dissolution rate of  $1 \mu\text{m}\cdot\text{day}^{-1}$  corresponding to a current of  $31,6 \mu\text{A}\cdot\text{cm}^{-2}$ . So, to give an example for our  $3.8 \text{ cm}^2$  sample, a dissolution current of  $1\mu\text{m}/\text{day}$  corresponds to an imposed current density of  $31.6 \mu\text{A}\cdot\text{cm}^{-2}$ , equivalent to an imposed current of  $120 \mu\text{A}$ .

A first experiment was performed on an S355 steel,  $3.8 \text{ cm}^2$  sample in NaCl 3 wt.%. An open circuit potential phase of a few hours was followed by an imposed current equivalent to a dissolution of  $5 \mu\text{m}\cdot\text{day}^{-1}$  ( $158 \mu\text{A}\cdot\text{cm}^{-2}$ ) (Figure 10). This experiment has been carried out with controlled temperature variations between 20 and 30 °C.

The corrosion rate calculated from the corrosion depth curves (Figure 10.c) gives a steady dissolution of  $4.5 \mu\text{m}\cdot\text{day}^{-1}$ . The corrosion depth expected from the current at the end of the experiment was  $30 \mu\text{m}$ , the corrosion depth deduced from the CWI technique is  $24 \mu\text{m}$  and the corrosion depth observed with the optical profilometer is  $35\pm 10 \mu\text{m}$ . The difference between the corrosion expected from the current and the CWI measurement (lower) came from the fact that not all the electrons sent in the system contribute to the  $\text{Fe} \rightarrow \text{Fe}^{2+}$  dissolution and are lost in other reactions/phenomena. The high

corrosion depth measured by the optical profilometer can be due to the fact that the corrosion is not perfectly homogeneous and we only measure the corrosion depth at the edge of the corroded surface.

To complete this study on the possibility of the CWI technique to get a continuous quantitative estimate of the corrosion depth, an experiment with different corrosion rates has been performed on S355 steel in NaCl 3wt % distilled water at a regulated temperature of  $29 \pm 0.5$  °C. The electrochemical sequence was composed of an open circuit potential (OCP) phase of 12 hours and imposed dissolution current phases of 1 hour each, respectively equivalent to the electrochemical dissolution of  $1 \mu\text{m}\cdot\text{day}^{-1}$  (IC1),  $5 \mu\text{m}\cdot\text{day}^{-1}$  (IC5),  $10 \mu\text{m}\cdot\text{day}^{-1}$  (IC10),  $20 \mu\text{m}\cdot\text{day}^{-1}$  (IC20) and  $40 \mu\text{m}\cdot\text{day}^{-1}$  (IC40). There are two free potential phases between the imposed current phases, one between IC10 and IC20 and one between IC20 and IC40. Those free potential phases are there to check if the imposed current is not disturbing the baseline of the experiment. This last experiment was conducted at a regulated  $29.5 \pm 0.5$  °C temperature (Figure 11).

During the imposed current phases, the potential rises from  $-0.73$  V (vs SCE) to  $-0.56$  V (vs SCE), which is close enough to the OCP to support the considered hypothesis that the electrons are mainly contributing to the dissolution of the steel. The final corrosion depth estimated with CWI after the experiment is  $4.2 \mu\text{m}$ , while the value obtained with the optical profilometer is  $4.5 \pm 0.5 \mu\text{m}$ , which is in very acceptable agreement. The corrosion rate measured with CWI is compared with the expected corrosion rate calculated from the imposed anodic current (Table 2). Except for the IC1 phase, the corrosion rates deduced from CWI are relatively close to the ones expected from the imposed current. The incoherence observed at IC1 may come from the imposed current being very close to the natural corrosion and thus difficult to differentiate, especially in just 1h.

#### **4. Discussion**

To test the performance of the CWI technique to measure corrosion depth, an electrochemical cell has been specially designed to make possible an ultrasonic measurement in parallel with an electrochemical corrosion experiment controlled with a potentiostat. CWI was able to monitor

corrosion depth over time in OCP and imposed dissolution with an accuracy of a scale of a few micrometres. The chosen parameters make measuring corrosion depth evolution over time possible during all the experiments. The corrosion of S355 steel in NaCl 3wt.% distilled water in our experimental conditions is a homogeneous generalised corrosion (verified with an optical profilometer). CWI depth loss measurement is very efficient for this kind of corrosion as the surface in front of the sensor is homogeneously affected by the corrosion and the corrosion depth model is making this assumption. If the corrosion is not homogeneous, the corrosion depth value is an average of the corrosion depth on the sample over the surface facing the sensor. As the system is designed now, it is impossible to differentiate homogeneous corrosion from localised corrosion by just looking at the coda stretching factor.

The corrosion depth model used to convert the coda stretching factor into thickness loss is accurate. For the experiments (Figure 6, 9 and 11), the values given by CWI method after 5 days is less than 0.5  $\mu\text{m}$  away from the measurement obtained with the optical profilometer, representing a 10% error. Our experimental setup and varnish baseline contribution to the corrosion depth calculated from the coda stretching factor is around 0.5  $\mu\text{m}$  over 5 days (Figure 7), but it is expected to be less and less important over time as this evolution is nonlinear. Considering that for this sample size, a classical mass loss measurement would be impossible without a precise weighting scale and the error would be more than 10%, the used technique could be an interesting alternative. Moreover, the corrosion rates computed with CWI in the last experiment (Figure 11) are less than 10% away from the rates expected with the imposed current. An interesting experiment could be to test dissolution rates of different electrodeposition electrodes or protective cathodes at different imposed currents.

The model tested to remove temperature contribution from the raw coda stretching factor is efficient but performs poorly for significant and quick temperature changes of about ten degrees in less than an hour (Figures 8, 9 and 10). However, this compensation is sufficient to obtain an accurate long-term measurement of the corrosion depth but needs to be considered carefully. As the thermocouple we used was located in the electrochemical cell, close to the sample but a few centimetres from it, this delay in temperature correction could be because the temperature measurement is not done directly on

the sample. That will be investigated and corrected in the future. Compared with ER sensors, CWI-based sensor precision is on the same order of magnitude ( $\sim 1\mu\text{m}$ ) and the corrosion rates is calculated the same way (thickness loss derivative). The CWI-based sensors drawback is that temperature needs to be measured in order to remove its contribution from the measurement but have the advantages that the corroding part of the sensor can be made with any metallic material as long as it's a plate whereas for ER the corrosion material has to be shaped and made specifically for the sensor. Also, in the case of CWI-based sensor, if the plate is not too corroded, it is possible to repolish and reuse the sensor.

The present work revealed that the CWI technique is accurate enough to compete with mass loss measurement due to homogeneous corrosion and Electrical Resistance sensors. As this technique is less time-consuming and gives a continuous depth measurement, it could be interesting to see if it performs well in other applications where mass loss and ER measurements usually are used. Salt spray tests and alternate immersion tests are planned in future work but the study of electrodeposition electrode degradation over time depending on the imposed current could also be investigated.

## **5. Conclusion**

A sensor based on Coda Wave Interferometry (CWI) was tested in a controlled electrochemical corrosion experiment to continuously measure corrosion depth on S355 grade steel in NaCl 3 wt.%. CWI technique applied to corrosion consists in periodically recording multiple echoes of an ultrasonic impulse emitted in the material thanks to a piezoelectric transducer, both emitter and receiver and following the evolution of those responses, looking at precise parameters influenced by corrosion. Corrosion of S355 grade steel in NaCl 3 wt.% corresponds to a homogeneous thickness reduction that mainly compresses the response signal. This compression can be considered as a stretching factor that can be extracted from the response signal to follow corrosion evolution. A model to convert this stretching factor into corrosion depth has been tested and verified experimentally by measuring the final corrosion depth with an optical profilometer. The value obtained this way was compared with the

one expected from the imposed electrochemical sequence and the one obtained with the CWI technique. Temperature variations also influence the coda stretching factor so temperature has to be maintained stable or the response signal has to be treated to remove the temperature contribution. A temperature contribution correction method was tested and validated. For this temperature correction to work, a temperature measurement as close to the sample as possible has to be performed. In addition, CWI is very sensitive to every physical change that modifies ultrasonic wave propagation in the material, so the experimental set-up and sensor have to be carefully designed, so their contribution to the response signal is stable and/or negligible during the measurement time. Due to this high sensitivity, CWI is potentially more sensitive than ultrasonic pitch catches sensors. That CWI technique can be used to obtain continuous quantitative measurements on small corroding samples without manipulating them and could give precious information on corrosion rates change as the corrosive environment evolves. Under specific conditions, those sensors could provide an excellent alternative to classical weight loss measurements that are time and material-consuming but also offer another way to remotely measure and follow corrosion evolution in various environments and can be used in parallel with others sensors.

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Table 1: Elemental composition of steel samples

Element	Fe	C	Si	Mn	P	S	Al	B	Cr	Cu	Mo	Nb	Ni	Ti	V
%	Bal.	0.177	0.016	1.5	0.015	0.01	0.04	0.0002	0.04	0.02	0.004	0.001	0.025	0.016	0.002

Table 2 : Imposed dissolution rates and dissolution rates measured with CWI sensor during the experiment corresponding to Figure 11.

	IC1	IC5	IC10	IC20	IC40
Imposed dissolution ( $\mu\text{m}\cdot\text{day}^{-1}$ )	1	5	10	20	40
Corrosion rate measured with ultrasonic CWI ( $\mu\text{m}\cdot\text{day}^{-1}$ )	0.69	4.99	10.10	23.28	47.01

Figure 1: (a) back side of S355 steel 5-by-5cm plate with piezo emitter/receiver glued and wired. (b) Partially varnished sample on a 3D printed support with the O-ring that will be used to maintain weathertightness with the electrochemical cell.

Figure 2 : Schematic and picture with corresponding elements of the experiment setup composed of an electrochemical cell coupled with a CWI emission/reception module

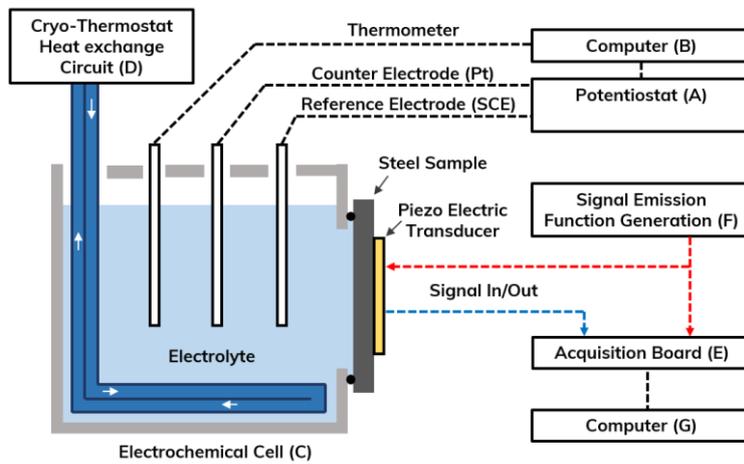
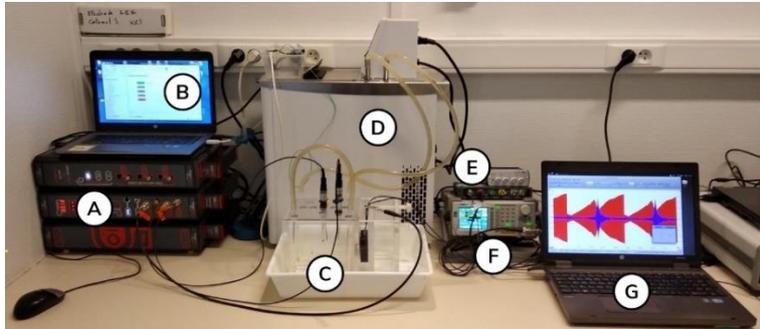


Figure 3: Schematic of the functioning principle of ultrasonic CWI technique applied to corrosion detection.

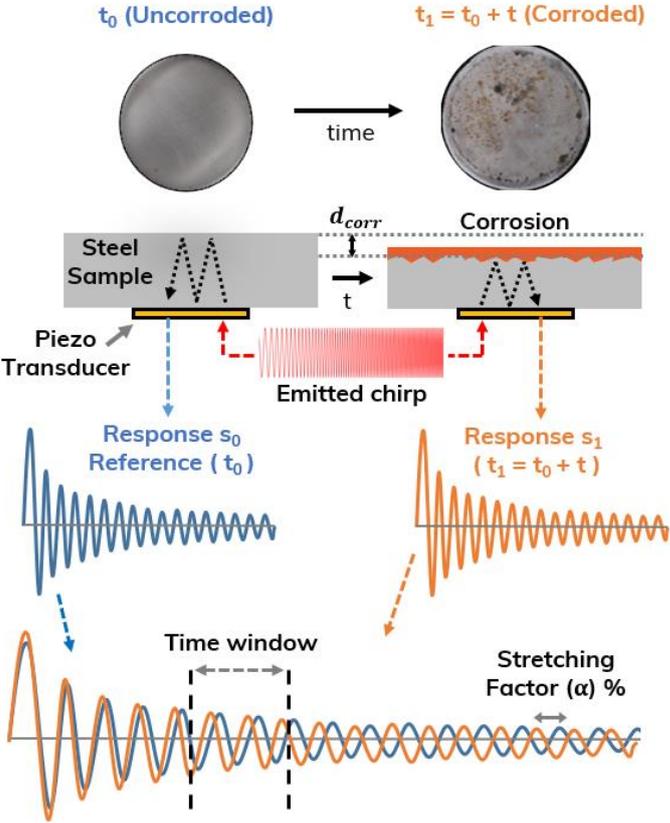


Figure 4: Topography (a) and corrosion depth profile (b) along orange dotted line measured with an optical profilometer at the edge of corroded area on S355 grade steel in NaCl 3 wt.% for 5 days at imposed dissolution rate of  $5\mu\text{m}\cdot\text{day}^{-1}$ .

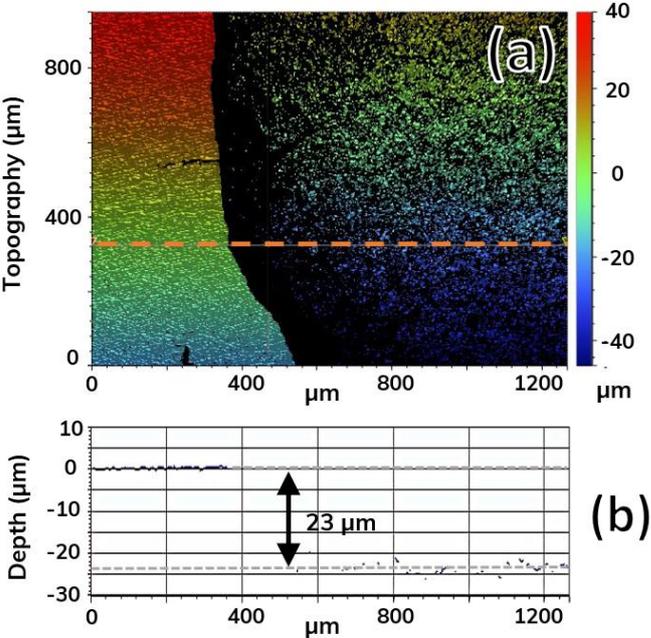


Figure 5 : (a) Open circuit potential, (b) temperature and (c) stretching factor of the coda signal) of S355 steel in NaCl 3 wt.% during 5 days with regulated temperature at  $29.5 \pm 0.5^\circ\text{C}$ .

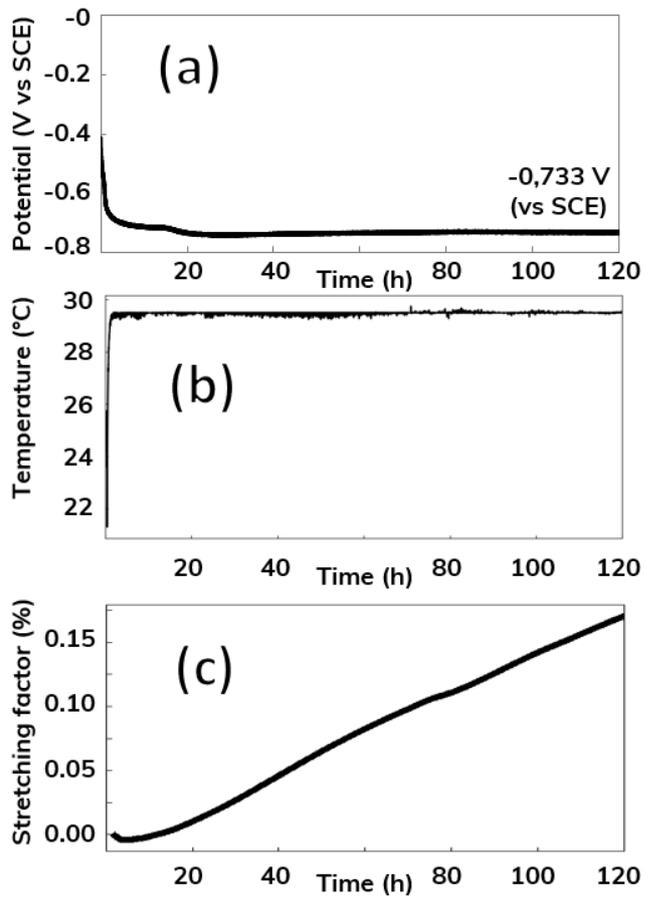


Figure 6 : Corrosion depth deviation measured by the sensor during 5 days on a completely varnished sample in NaCl 3 wt.% distilled water and regulated temperature at  $29.5 \pm 0.5^\circ\text{C}$ .

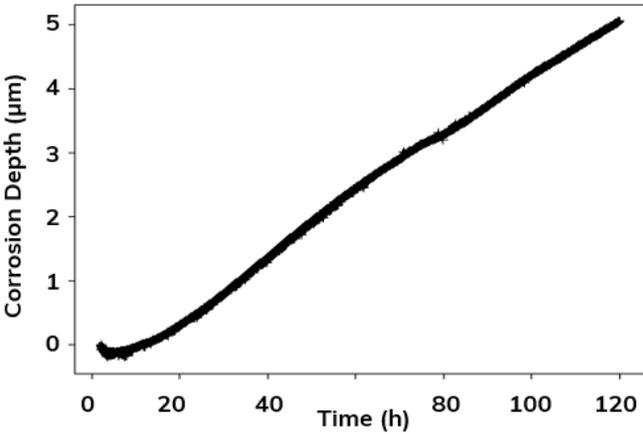


Figure 7 : Corrosion depth measurement “drift” measured with CWI during 5 days on a completely varnished sample immersed in NaCl 3 wt.% distilled water during five days at regulated temperature of  $29.5 \pm 0.5^\circ\text{C}$ .

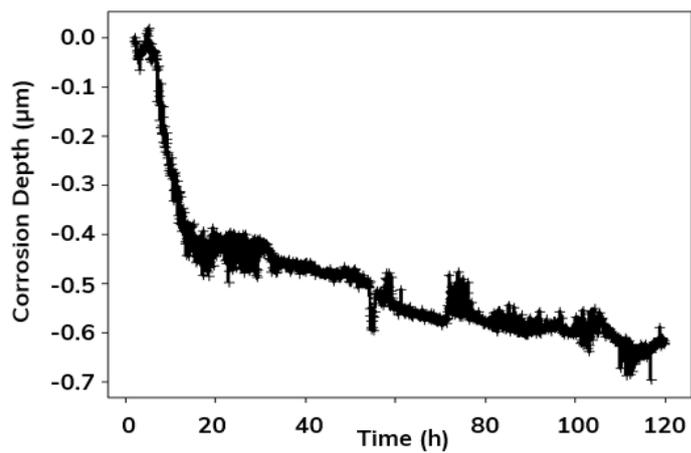


Figure 8 : “Virtual” corrosion depth deviation measured with the CWI technique during 5 days on a completely varnished sample in NaCl 3 wt.% distilled water and with controlled temperature variations between 20 and 30 °C).

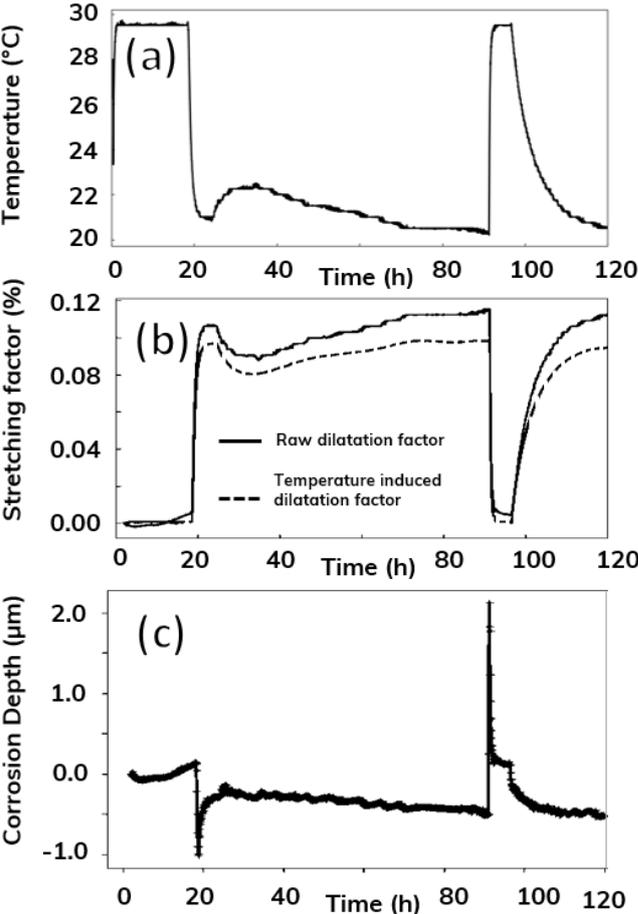


Figure 9 : Temperature, coda stretching factor and corrected corrosion depth measured with CWI during 5 days on a S355 steel sample in NaCl 3 wt.% distilled water and with controlled temperature variations at from 20 to 30°C).

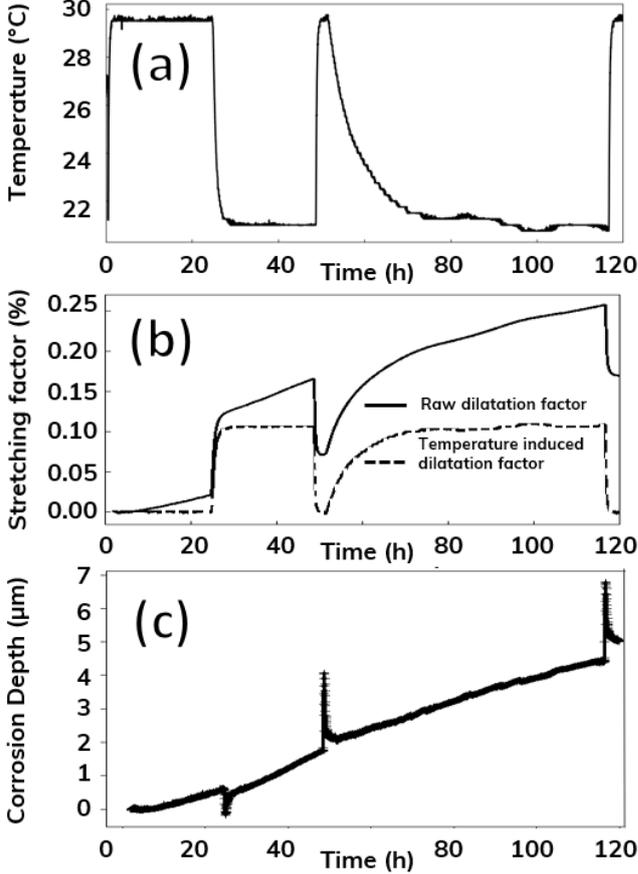


Figure 10 : Temperature, coda stretching factor and corrected corrosion depth measured with CWI during 5 days on a S355 steel sample in NaCl 3 wt.% distilled water at imposed dissolution current equivalent to  $5 \mu\text{m}\cdot\text{day}^{-1}$  and controlled temperature variations at (20-30°C).

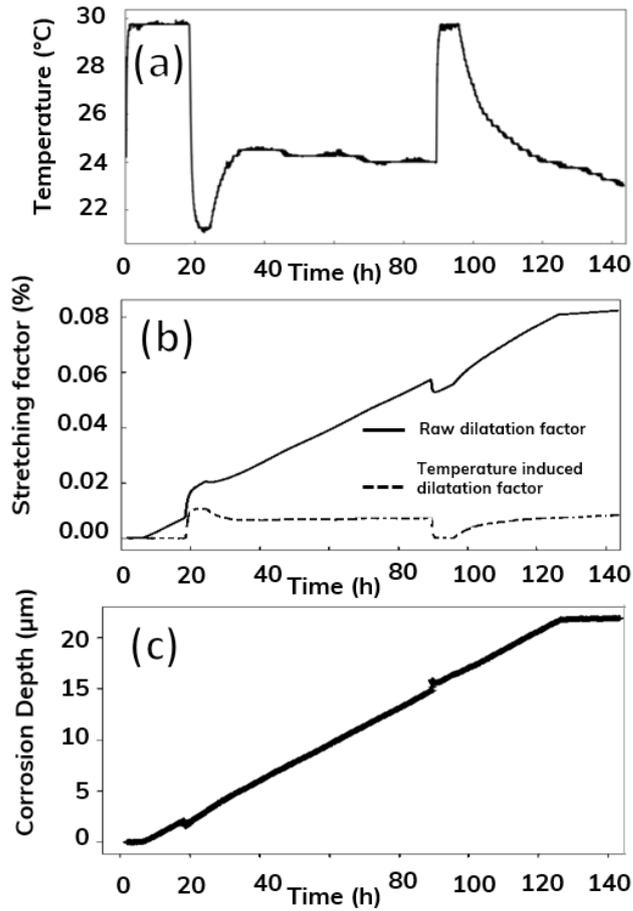


Figure 11 : Temperature (a.), potential(b.) and corrected corrosion depth (c.) (by CWI sensor) during an electrochemical sequence composed of OCP and imposed electrochemical dissolution phases at regulated temperature  $29.5 \pm 0.5^\circ\text{C}$ .

