DEMONSTRATION AT DEN HELDER

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Why this location

The impact of the North Sea on metal constructions at 3 different ports is selected in the SOCORRO project. The 3 measuring locations are spread out over the region, to be representative for any future measuring location at the North Sea: Shoreham (OP4), Den Helder (Endures, linked to PP13) and Oostende (linked to LP1).

The wide geographic spread of the demonstration sites enables to study and compare the corrosion behaviour in the Dutch, Belgian and English port areas. In the project description of SOCORRO, it is mentioned that corrosion is strongly depended on the environmental parameters, and therefore a comparison between ports with different conditions and geographical spread is necessary.

The port of Den Helder, located at the facilities of Endures in Bevesierweg 1 in 1781 AT Den Helder (NL), was selected as a demonstration site for the SOCORRO project as a port facility in direct contact with the North Sea. The Endures facilities are presented in Figure 1, a lab facility in the harbour of Den Helder and a raft exposure site in the harbour, close the North Sea. The exposure site in the port of Den Helder, the main naval base in the Netherlands, is representative for North Sea coastal water with high fouling pressure during a fouling season that runs from March to November. Seawater parameters such as temperature, pH, salinity and oxygen concentration are continuously monitored in the lab of Endures.

1. Endures Lab facility
2. Endures raft exposure facility in the harbour

Figure 1. Google maps image of the location of the testfacility in the harbour of Den Helder, The Netherlands.

Baseline/starting situation

Continuous monitoring of as well environmental parameters as the corrosion rate is performed by use of appropriate sensors. The sensors are connected by Wifi tot the internet, which enables to continuously follow up the measured parameters.

Both an environmental sensor (Scuba90) and a corrosion sensor (C-Cube) were installed. As on the raft infrastructure no electrical power was available, the probes are foreseen by electrical power by a battery pack or a solar panel.

Environmental sensor

A Scuba90 sensor, manufactured by Royal Eijkelkamp Soil & Water B.V. (Giesbeek, The Netherlands), was used to measure the environmental parameters. In the context of the SOCORRO project, only Scuba sensors were used, which measure specific environmental parameters that influence the corrosion rate. The measured physiochemical factors include temperature, pH, specific conductivity 25°C, salinity, dissolved oxygen, dry matter content, redox potential and chlorine content.

The Scuba90 sensor is 450mm in length and 90mm in diameter. The operating temperature varies within a range of -50°C to +50°C. The maximum operational depth of the sensor is 200 m, while the ion-selective electrode (ISE) can reach a maximum depth of 15 m. The sensor is supplied with a 12 V power supply and has a memory for 1,000,000 measurements (Royal Eijkelkamp, n.d.).

It is a multi-sensor probe equipped with several sensors capable of determining eight parameters (Royal Eijkelkamp, 2022): temperature, dissolved oxygen, specific conductivity of water, acidity (by a pH glass electrode), redox potential (ORP) and chloride concentration. The probe is presented in Figure 2.

The Scuba probe furthermore comes with two different attachments that serve to protect the sensors. These attachments can be securely attached to the sensors using threads. A sealed capsule is available to store the probe. Since the sensors must be stored in a humid environment, the sealed capsule is partially filled with water before being attached to the probe. The capsule is fitted with a copper mesh, which acts as a biofouling-resistant barrier. The copper mesh exhibits controlled solubility, slowly degrading and releasing copper ions. These copper ions cover the surfaces of the sensors and act effectively against the growth of biological organisms.

Scuba is connected to a 4G modem that uploads the data to the Telecontrolnet platform. Telecontrolnet is a platform where all data from the Scuba sensors come together. Here specific filters were applied to select only the sensors and parameters relevant for this project. Subsequently, a dataset was exported in the form of an Excel file. This Excel file was converted to a CSV file so that it was functional with the R program for the correlation analysis.

Corrosion sensor

For the SOCORRO project, a specific corrosion measurement system has been developed which measures corrosion of three different steel grades (S355, 316L and S235) and a micro-electrochemical cell that measures the rate of corrosion. These measurements are performed every 4 hours.

The working and reference electrodes are housed in a plastic housing filled with epoxy adhesive for protection against sea water. The LPR sensor from C-Cube (Delft, the Netherlands) has dimensions of 150 mm (length) x 60 mm (height) x 50 mm (width).

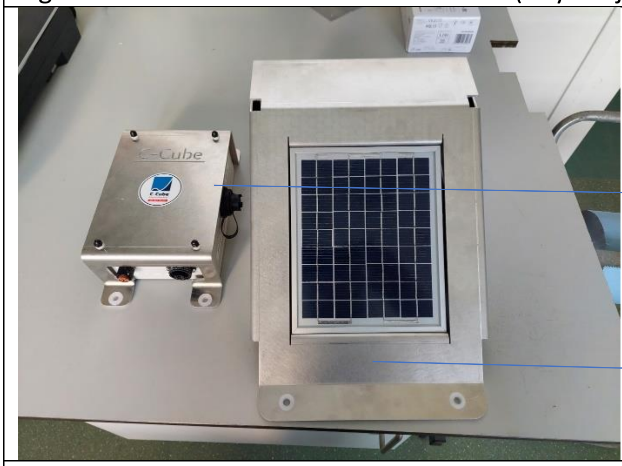
The sensor is connected to a separate C-Cube control box located in an easily accessible position. A potentiostat and a data logger are installed in the control cabinet. In addition, the control box contains a mobile antenna that transmits the measured data to the C-Cube network. The company collects all sensor data and sends it to an online database that is accessible to all researchers of the SOCORRO project.

Scuba90 Multi-sensor Probe with different sensors:
1: temperature sensor, 2: optical sensor (dissolved oxygen), 3: conductivity sensor, 4: pH glass, 5: ORP sensor, 6: fluorometer for chlorophyll determination; 7. reference electrode; 8. chloride sensor.

Protecting Cu mesh capsule

A 12 V power supply

Figure 2. Scuba90 environmental sensors (Royal Eijkelkamp)



Corrosion sensor box with 3 electrodes: Grade A (S325), S355 steel, stainless steel 316L.

Solar pannel

Figure 3. Corrosion sensor with solar pannel (C-cube).

Mass loss determination

For all corrosion tests, 3 samples were tested for weight loss for the 3 selected metals (Grade A, S355 and 316L). The samples were weighed before and once the rust layer was etched, to the nearest 0.1 g.

After testing for the designated exposure time, the samples were removed from the exposure site. The etching of the corrosion layer was done until the rust layer was completely removed. All samples were weighed immediately after.

The corrosion rate is expressed in µm/day and calculated from the specific weight loss Δm (in g/cm2) and the testing time test, as follows

$$\text{corrosion rate} = \Delta m / (\rho \cdot t_{test}) \qquad (1) \qquad \text{with } \rho = 7.86 \text{ g/cm3}.$$

The dimensions of each coupon were measured to the nearest 1 mm to ensure the correct calculation of weight loss with regard to the exposed area.

Construction

Installation

The raft exposure facility in the harbour of Den Helder is only reachable by boat. The raft is a floating metal platform, used for corrosion and anti-fouling testing, as presented in Figures 4 - 9.

For the installation of the environmental sensor, the sensors hardware (battery and Wifi module) were deployed with connections to the railing of the raft and the sensor itself was positioned ~ 1 meter under the water line, at the same depth of the samples to test. The installation is presented in Figures 10-13.

Also the corrosion sensor is mounted at het same depth under the water line and the solar panel and data loggers of the corrosion sensor were secured to the raft side railing. The installation is presented in Figure 14.

Figure 4. Location in the harbour of Den Helder.

Figure 5. Raft in harbour of Den Helder.

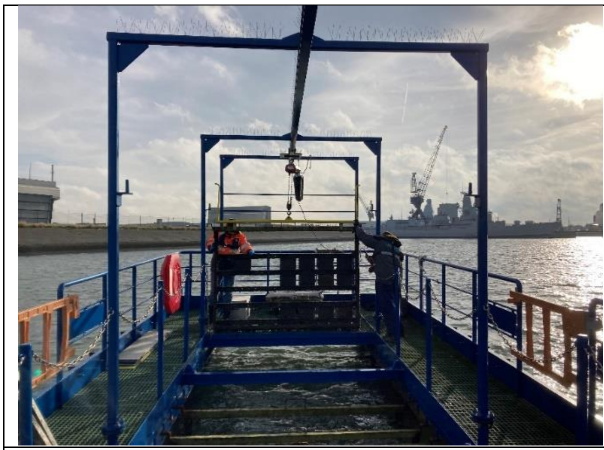


Figure 6. Metal framework on the raft to mount samples.

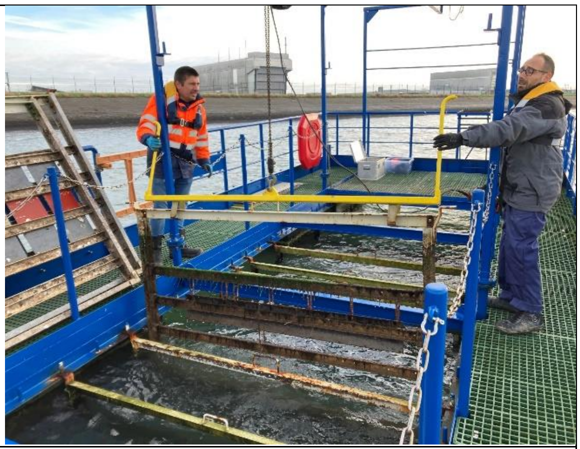


Figure 7. Positioning of rack to expose samples under the water level.

Figure 8 and 9. SOCORRO team (HZS, OCAS and Endures) to raft exposure site.

Figure 10 and 11. Positioning of the environmental sensor under the water line.

Figure 12-13. Mounting the battery pack and wifi module of the environmental sensor on the raft infrastructure.

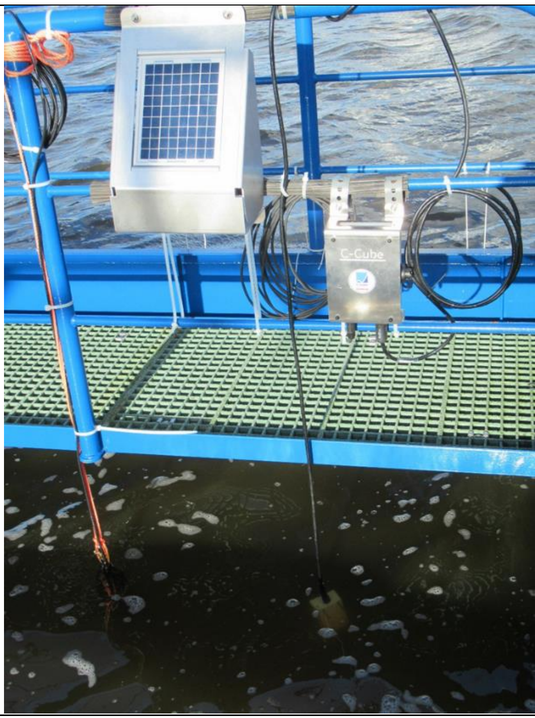


Figure 14. Installation of the corrosion sensor with solar pannel at the raft exposure site.

The final installation of the SOCORRO sensors and samples was completed and presented in Figures 15 and 16.

Figures 15 and 16. Final installation of the environmental and corrosion sensors together with the exposure samples (Grade A, S355 and 316L) on the SOCORRO demonstration site in the harbour of Den Helder.

Evaluation during exposure at the raft platform

Every month, the metal samples and sensors are evaluated. The metal samples are corroded and covered by biofouling organic matter, as seen in the figures 17-20, where the metals are presented after respectively 2 and 3 months of exposure 1 meter under the water line of the raft exposure site. The visual inspection and the corrosion data of the metal samples will be discussed in the next chapter Results.

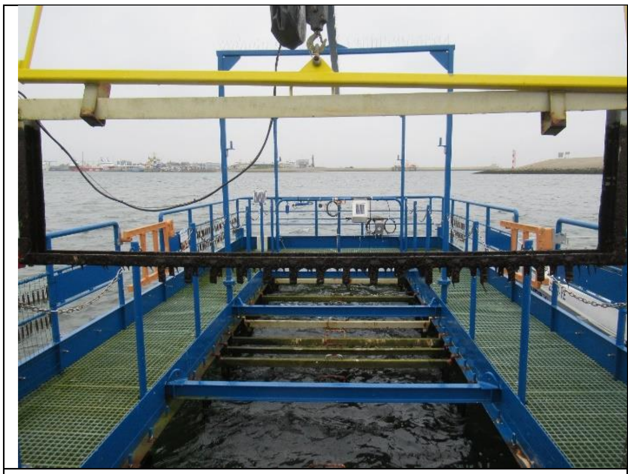


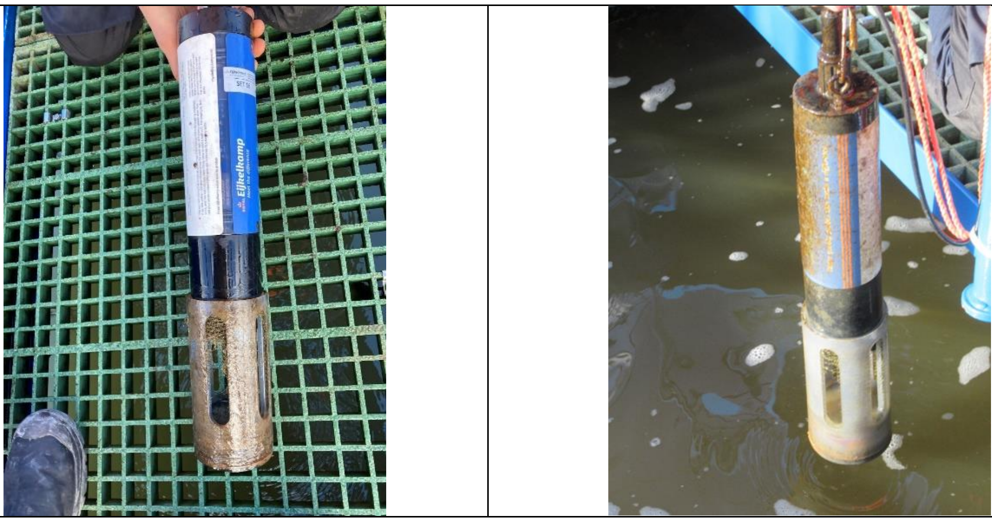
Figure 17. Rack mounted with metals after 2 months of immersion in the seawater at the raft.

Figure 18. Rack mounted with metals after 2 months of immersion in the seawater at the raft (detailed).

Figure 19. Rack mounted with metals after 3 months of immersion in the seawater at the raft

Figure 20. Rack mounted with metals after 3 months of immersion in the seawater at the raft (detailed).

Also a continuous evaluation of the sensors degradation is performed during the project. In figures 21 and 22 the status of the environmental sensor can be observed after 2 months of exposure. The protecting capsule with Cu mesh is working fine and protects the sensor to biofouling.



Figures 21 and 22. Environmental sensor after 2 months of exposure.

Results

The corrosion of the metal samples will be evaluated by the new corrosion sensor (ER-probe) and the mass loss determination of the metal coupons which were weighted before and after the exposure.

Corrosion rate by corrosion sensor C-cube

The corrosion monitoring sensor from C-cube is evaluated during the exposure at the raft in Den Helder. The sensor data read out provides on-line information of:

- The battery status in Volt
- Corrosion rate expressed in corrosion loss (mm) or corrosion rate (mm/year)
- Open circuit current in mA
- Potential (V) and Corrosion potential Ecorr (V)

The data output after 1 week and 4 months of exposure is presented in Figures 23-33. It can be seen that the battery status is full during the whole exposure of the sensor (Figure 23-24).

The corrosion loss (mm) is low the first week of exposure, as been be seen in Figure 25. During the first month of exposure, there is a steep increase in corrosion loss for S235 (Grade A) and S355 steel (Figure 26), where after 1 month of exposure the increase in corrosion loss is lower. After 3 months of exposure a stable corrosion rate is reached. Probably the corrosion loss will further increase in time. For 316L, the corrosion loss is nihil during the observed exposure time.

This behaviour is confirmed in the Figures 27 and 28, where the corrosion rate is shown. In the beginning of the exposure (Figure 27), the corrosion rate is high (0.175 mm/year) for steel, after 1 month of exposure the corrosion rate decreases, as seen in Figure 28. The corrosion rate reaches values below 0.05 mm/year. Also here the corrosion rate of 316L is almost nihil during the exposure time.

The corrosion potential (Ecorr) is a good indicator to evaluate the measurement performance of steel or stainless steel samples. As can be seen S235 and S355 show a Ecorr between -0.4 and -0.6V vs a reference electrode. 316L shows much more noble values of 0.1 to 0.4 vs a reference electrode.

1 week of exposure

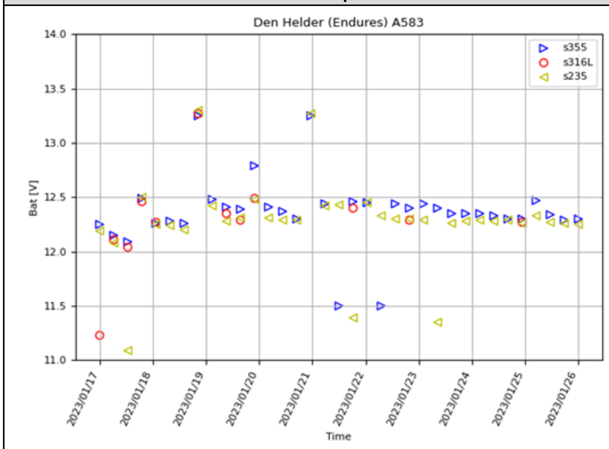


Figure 23. Battery status (V) after 1 week of exposure.

4 months of exposure

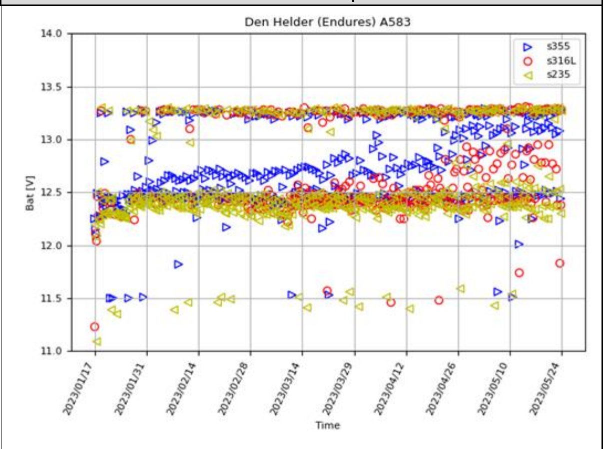


Figure 24. Battery status (V) after 4 months of exposure.

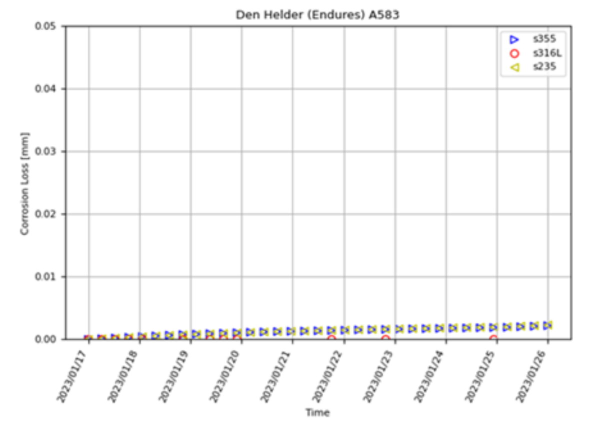


Figure 25. Corrosion Loss (mm) after 1 week of exposure.

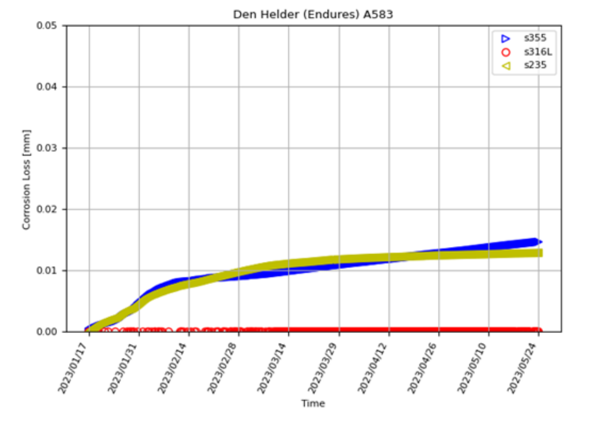


Figure 26. Corrosion Loss (mm) after 4 months of exposure.

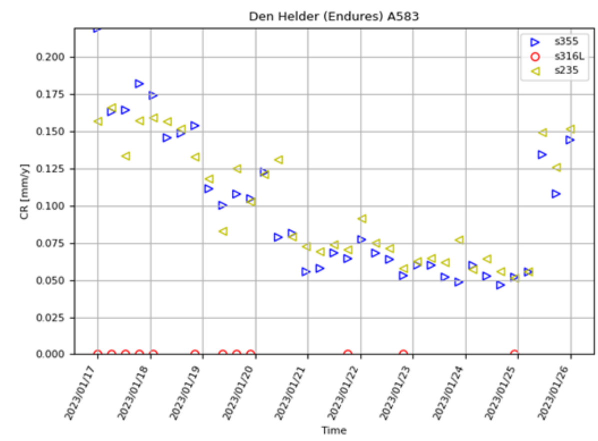


Figure 27. Corrosion rate CR (mm/year) after 1 week of exposure.

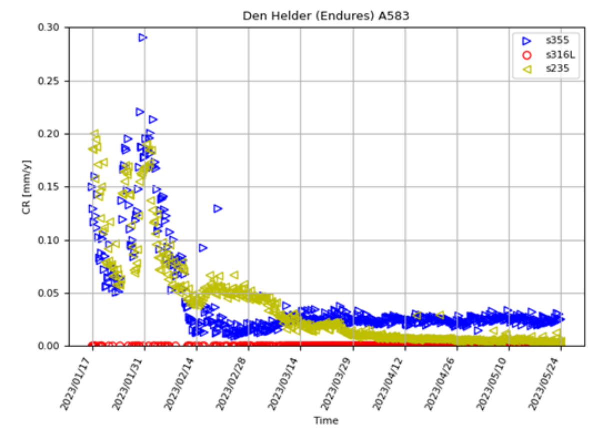


Figure 28. Corrosion rate CR (mm/year) after 4 months of exposure.

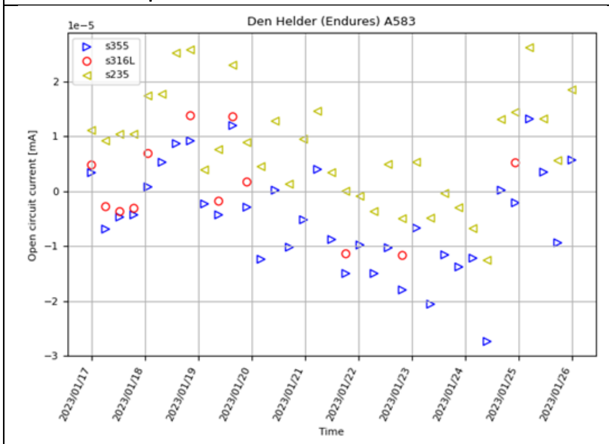


Figure 29. Open circuit current (mA) after 1 week of exposure.

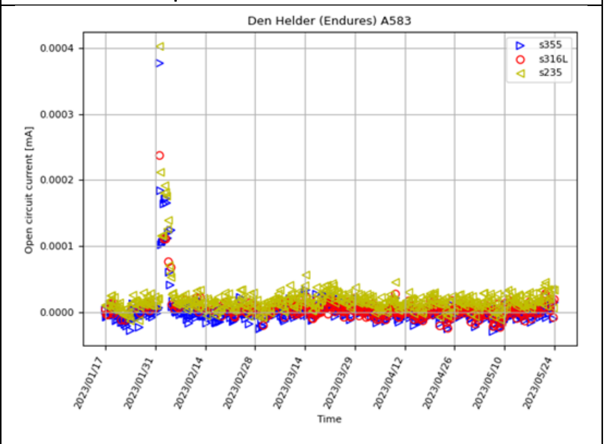


Figure 30. Open circuit current (mA) after 4 months of exposure.

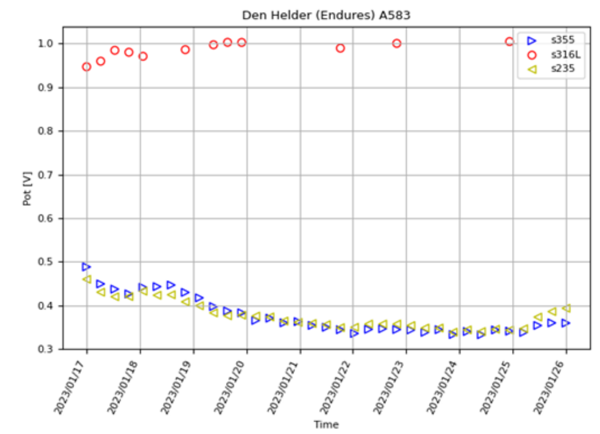


Figure 30. Potential (V) after 1 week of exposure.

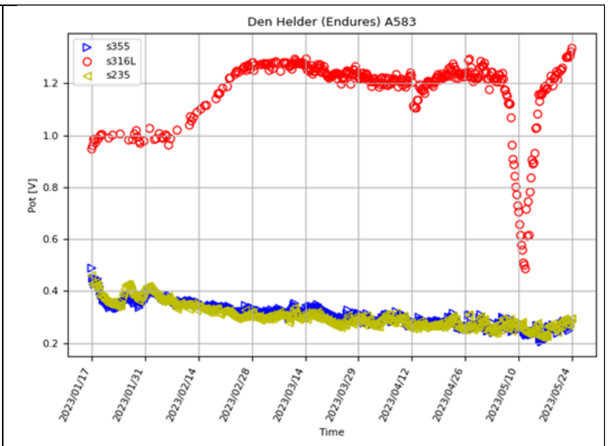


Figure 31. Potential (V) after 4 months of exposure.

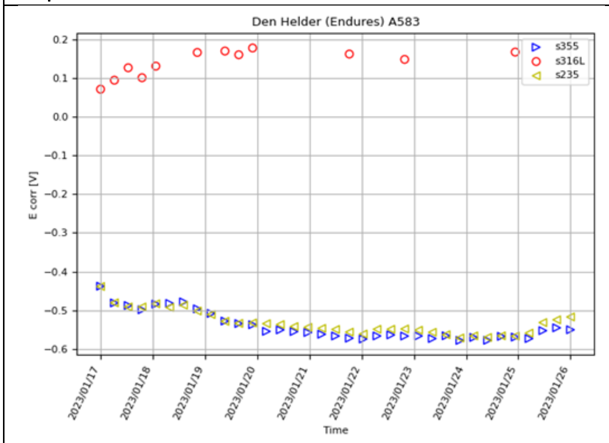


Figure 32. Ecorr (V) after 1 week of exposure.

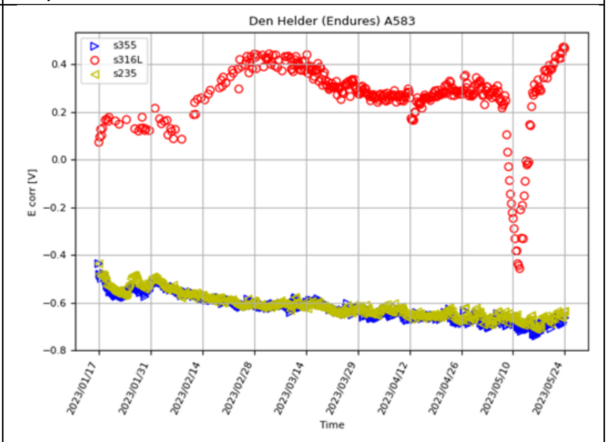


Figure 33. Ecorr (V) after 4 months of exposure.

The C-cube corrosion sensor is based on linear polarization (LP) to measure the corrosion rate of the metals. This is performed by applying a voltage of less than ±30 mV vs Ecorr to the metal. Within this voltage range, the resulting current response is linear if the anodic and cathodic regions are equal. This makes it possible to determine the polarization resistance (Rp), which is defined as the slope of the current-potential curve according to the Stern-Geary equation (Stern & Geary, 1957). The corrosion rate is the invers of the polarisation resistance. Important in this fitting procedure is the selection of the tangent of the anodic and cathodic polarisation curve. In the data output of the C-cube sensor the polarisation curves and automated fitting procedure can be observed, like presented in Figure 34 and 35. It is important to check the automated fitting procedures as a small change in tangent can cause huge errors in the determination of the final corrosion current.

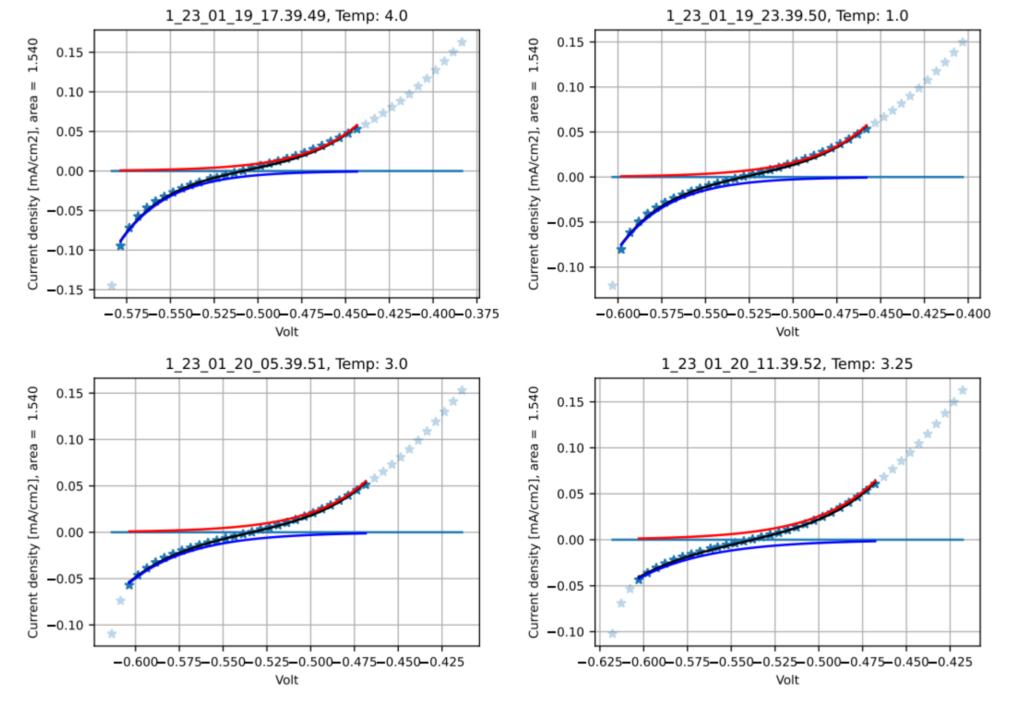


Figure 34. Current-potential plot to determine the corrosion current by a linear polarisation fitting procedure.

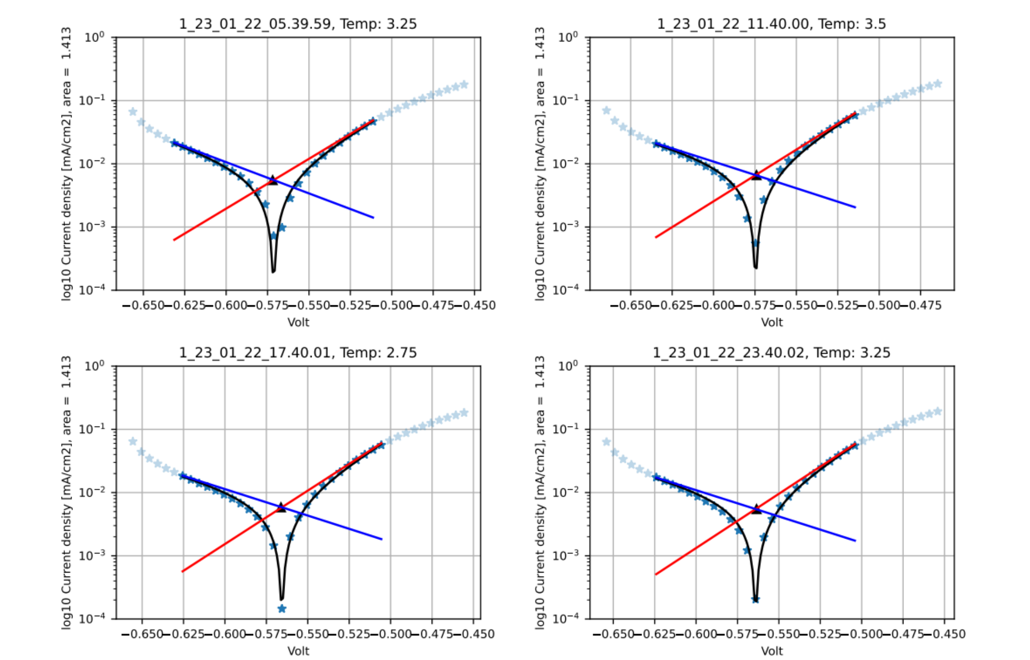


Figure 35. Log current-potential plot to determine the corrosion current by a linear polarisation fitting procedure.

The corrosion current is determined according to this procedure for the 3 metals and presented in Figure 36. The corrosion rate after 1 month is the highest and reach values of 90 and 100 µm/year for

S235 and S355 respectively. The corrosion rate for 316L is nihil. The corrosion rate decreases for month 2 and 3. The corrosion rate after 3 months is similar for S235 and S355 and reached 50 µm/year.

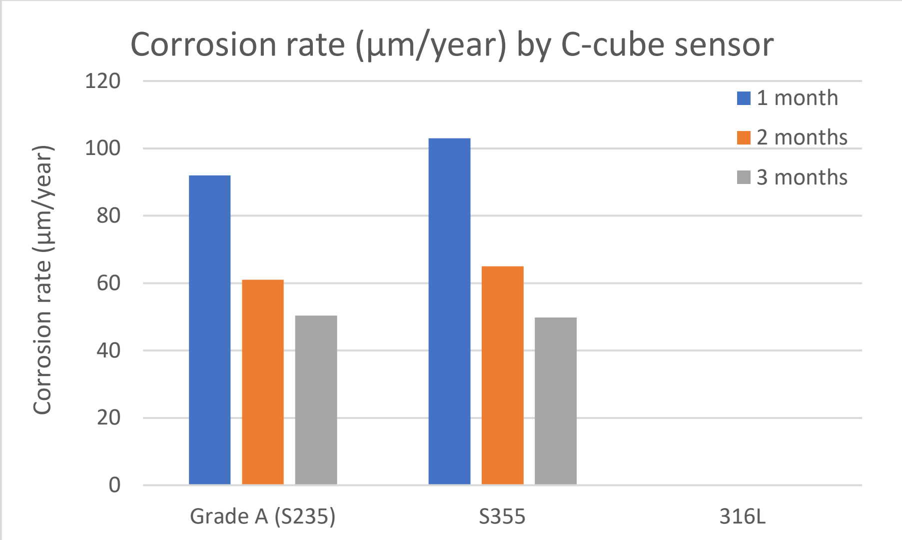
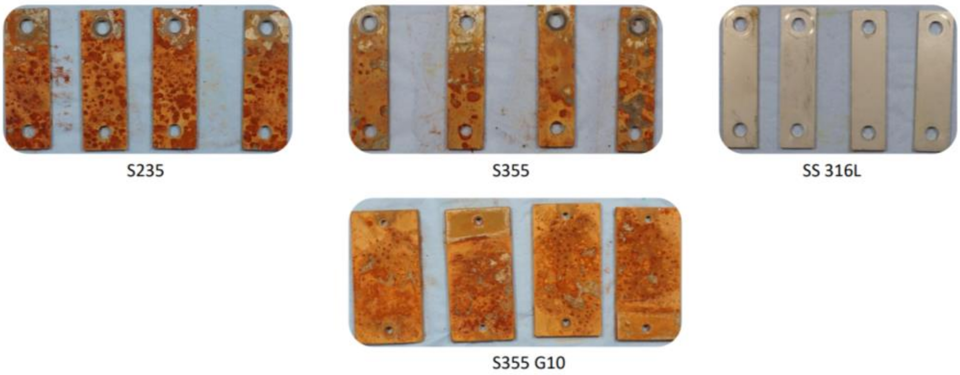


Figure 36. Corrosion rate (µm/year) for Grade A (S235), S355 and 316L by C-cube corrosion sensor during 3 months of exposure in the raft in the harbour of Den Helder.

Visual inspection and mass loss determination

At each evaluation time the metals are taken out of the exposure site, the fouling is removed and the samples are rinsed with water. The images are presented in Figure 37. A clear corrosion behaviour with orange coloured corrosion products are seen for S235 and S355 steel. For 316L no corrosion is seen.

After evaluation the corrosion products are etched in order to determine the mass loss after corrosion exposure. In order to have reproducible results, 3 samples per test condition are performed. In Figure 38 the samples are presented after etching.

<table>
<tr><th colspan="2">Metal samples after 1 month of immersion</th></tr>
<tr><td colspan="2">
</td></tr>
<tr><th colspan="2">Metal samples after 3 months of immersion</th></tr>
<tr><td></td><td></td></tr>
<tr><td>S235</td><td>S355</td></tr>
<tr><td></td><td></td></tr>
<tr><td>Ss316L</td><td>S355G10</td></tr>
<tr><td colspan="2">Figure 37. Visual inspection of the metal samples exposed to the demonstrator in Den Helder.</td></tr>
</table>

Metal samples after 1 month of immersion – after etching	
 S235  S355  SS 316L  S355 G10	
Metal samples after 2 months of immersion – after etching	
	
S235	S355
	
ss316L	S355G10
Metal samples after 2 months of immersion – after etching	
	
S235	S355

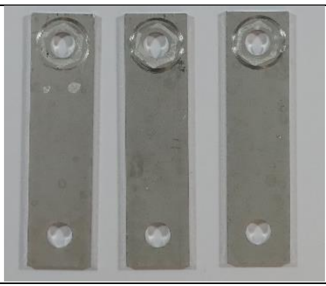
	
316L	S355G10

Figure 38. Metal samples exposed to the demonstrator in Den Helder – after etching of the corrosion products.

The mass of the metal coupons is determined before and after the exposure and the mass loss is calculated and expressed in µm per year, as presented in Figure 39. Also here it can be seen the general trend that the corrosion rate is the highest at the start of the exposure. A decrease in corrosion rate is seen in function of exposure time. The first month, the corrosion rate reached values of 300 and 270 µm/year for respectively S235 and S355. 316L shows hardly any sign of corrosion. After 3 months the corrosion rate decreased and the values for S235 and S355 are similar and reach ~200 µm/year.

As a reference material also S355G10, an offshore steel quality of S355 is exposed. Here the corrosion rate is lower than S355, which is expected as this steel grade is better resistant to corrosion in saline environment than S355.

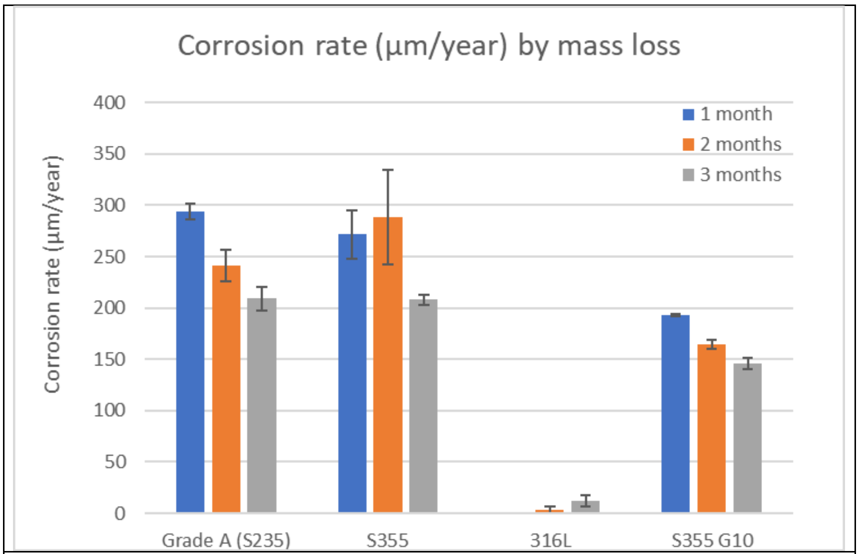


Figure 39. Corrosion rate (µm/year) for Grade A (S235), S355 and 316L by mass loss determination during 3 months of exposure in the raft in the harbour of Den Helder.

Comparison of the corrosion results

If the results of the mass loss determination and the corrosion sensor are compared, it can be seen that the general trends can be seen, as presented in Figures 40 and 41. For both methods the 2 steel grades S235 and S355 show clear corrosion during the exposure time, 316L showed hardly any sign of corrosion. For both methods, the highest corrosion rate is detected at the first month of exposure, the corrosion rate decreases in function of the exposure time. For both methods the corrosion rate after 3 months of exposure of S235 and S355 reached ~ the same value.

A big difference in the two methods is the absolute value of the corrosion rate. For the mass loss determination the corrosion rate is 3-4 times higher than he corrosion rate detected by the corrosion sensor C-Cube. This is a point of attention and needs to be followed up and checked in future exposure. A possible reason can be that the fitting procedure needs to be optimised.

Corrosion rate by mass loss

Material	Corrosion rate (mm/y) Average of 3 samples	Corrosion rate (µm/y) Average of 3 samples
S235	0,294	294
S355	0,272	272
SS 316 L	0,000	0

Figure 40. Corrosion rate (mm/year and µm/year) for S235, S355 and 316L by mass loss determination.

Corrosion rate by corrosion sensor C-Cube

Material (Sensor C-Cube)	Corrosion rate (mm/y)	Corrosion rate (µm/y)
S235	0,092	92
S355	0,103	103
SS 316 L	0,000	0

Figure 41. Corrosion rate (mm/year and µm/year) for S235, S355 and 316L by C-Cube corrosion sensor.

Plans for further use?

The demonstration site in Den Helder is evaluated now for 3 months. The evaluation will be maintained for the next 9 months. The adaptations that are made on the sensors (e.g. protecting Cu capsule) show that the sensors are able to function in the very severe conditions like the North Sea.

The corrosion prediction of the corrosion sensor shows a similar trend than the results obtained by mass loss determination, but the absolute values of the corrosion current show a factor of 3-4 difference. This needs to be further investigated in order to improve the corrosion prediction.

A correlated with the changed in environmental changes will be made with the long term corrosion data.