# Corrosion of steel and other wreckage in the Belgian North Sea

Kris De Baere<sup>1,\*</sup>, Sven Van Haelst<sup>2</sup>, Deirdre Luyckx<sup>1</sup>, Sven De Baere<sup>3</sup>, Nico Boon<sup>4</sup>, Sem van Halbeek<sup>1</sup>, Raf Meskens<sup>1</sup>, Remke Willemen<sup>1</sup>, Rob Melchers<sup>5</sup>

# <sup>1</sup> Antwerp Maritime Academy, Antwerp, Belgium <sup>2</sup> Flemish Maritime Institute, Ostend, Belgium <sup>3</sup> University of Ghent, Ghent, Belgium <sup>4</sup> Centre for Microbial Ecology and Technology, Ghent University, Ghent, Belgium <sup>5</sup> Centre for Infrastructure Performance and Reliability, University of Newcastle, Australia

# \*Corresponding author, kris.de.baere@hzs.be

# Keywords: Rate of corrosion, long term model, conservation of shipwrecks, MIC

SUMMARY: The near-coastal strip of the North Sea off Belgium has some three hundred shipwrecks mostly of steel construction, dating from both World Wars. Because many contain the remains of their crews and others, they are protected by Belgian law. Besides their cultural and historical value, these wrecks have a biological, environmental and economic importance. Preservation of the wrecks is an on-going issue. To-date, the rate of deterioration of the wrecks has been determined by comparing measured in-situ steel plate thickness with archived information about the ships' construction. The most applicable and general corrosion models are being used as a benchmark. The Melchers' corrosion model compared with the in-situ measurements showed a discrepancy that currently cannot be explained. This is important because the actual and likely future wreckage corrosion rate is required to refine our current view on the defining parameters for long term steel corrosion in stationary structures in the North Sea and also important for deciding how to preserve these wrecks for future generations. When validated against the in situ observed deterioration of the steel wrecks, it will be used in a project related to dumped chemical ammunition in the North Sea. At the end of World War I, Belgium was confronted with a huge amount of left-over chemical warfare, mainly of German origin. A cheap and fast solution was found in 1919 by dumping approximately 35,000 tons (most probably an underestimation) of gas shells, containing various toxic products such as yperite (mustard gas), as well as some conventional ammunition. on the Paardenmarkt, a silt bank east of the port of Zeebrugge, about 1000 meters from the shore. The material was forgotten until in 1971 when the harbour facilities of Zeebrugge were extended and several shells were brought to the surface. Their condition, after more than 100 years of immersion, is an important parameter for assessing the risks to the health and security of the local population. As direct observation is forbidden by the authorities, it was anticipated that the parametrized and tuned Melchers corrosion model would provide the best possible strategy to do so. The paper outlines the overall scope of both aspects of the project and describes the proposed approach for the corrosion studies.

#### **1** INTRODUCTION

Corrosion is a complicated process governed by many parameters such as temperature, water velocity, pH, dissolved oxygen, nitrate concentration, water depth, hydrostatic pressure, bacterial activity, pollutants, erosion and surface roughness. It is a major issue for infrastructures such as bridges, industrial facilities, coastal and harbour structures, ships, pipelines and other waterborne structures especially when positioned in or near the sea. A thorough understanding of the corrosion processes and rates allows for better estimates of the expected lifetime and reliability of different submerged structures, and for optimization of maintenance planning, construction design (corrosion-resistant materials, corrosion allowance, thickness and type of protective coating to be applied, quantity and position of sacrificial anodes, impressed current systems...), and the use of monitoring systems and tools.

Most corrosion studies focus on the initial corrosion processes, leading to assessments of corrosion rates that cannot be extrapolated to the longer time periods of 20-30 years, envisaged for the use of marine and maritime structures (port structures, drilling platforms, offshore energy platforms ...). However, are there any models available to describe corrosion on such a time scale? Initial modelling efforts were linear and not very consistent with reality. Several models were introduced in the 1930's - 40's. The most famous was the "Power Model" originally proposed and derived (approximately) by Tammann (1923) for relatively short-term atmospheric corrosion of copper. Later models (Paik et al., 1998; Qin et al., 2002; Guedes-Soares et al., 2005) used non-linear relations leading asymptotically to a zero-corrosion rate, as well as taking into account the retarding effect of a protective coating (as reviewed by Melchers, 2019).

This study applies the bi-modal model (Melchers, 2003), largely because it is based on physical and electrochemical principles. The model is robust and takes into account uniform as well as pitting corrosion in aerobic and anaerobic conditions, bacterial, environmental and manmade influences. In the model, five phases can be discerned (Figure 1). Phases 0, 1 and 2 are predominantly oxygen controlled while phases 3 and 4 are anaerobic. In the idealized case, the aerobic corrosion process starts with an initial instantaneous corrosion rate r0. Due to a progressive lack of oxygen, this rate diminishes and becomes nearly zero. At  $t_a$ , however, the corrosion rate picks up again under the influence of anaerobic and possibly bacterial corrosion processes with an initial corrosion rate of  $r_a$  to reach a constant rate  $r_s$  at time point B.

The Melcher's model is based on a large variety of field and relevant laboratory exposure tests, and it has been calibrated for a considerable number of environmental variables. As reviewed earlier (Melchers, 2018), it differs considerably from all other models proposed in the literature since these are all, essentially empirical based only on data for longer-term exposure of physical infrastructure, such as ships and offshore structures. However, this does not mean that these empirical models are necessarily more correct or more realistic. For example, the power-law has been applied to exposure periods much longer than for which it was originally developed. This ignored that the underlying corrosion processes change from initially being aerobic at the corrosion interface to being governed eventually by the hydrogen evolution cathodic reaction (Melchers, 2008). Additionally, this transition does not occur for the very special case of pure copper, for which the power law was developed, but it can be seen in a variety of other metals and alloys including steels, stainless steels, aluminium and copper alloys. Thus, simplistic curvilinear models are not appropriate, especially not when studying longer-term effects or complex materials.

In any case, it seems that the Melchers model is best suited for long-term corrosion modelling, particularly as it has been shown to be applicable to various steels and also to aluminium alloys, copper alloys (Melchers, 2018) and nickel alloys (unpublished). In addition, the model allows for longer-term exposure (well into phase 4), which is the time frame of interest here. In the present study, this model will therefore be used to analyse the long-term corrosion rates of structures in the North Sea, by parameterising the model with data obtained from shipwrecks. The longer-term outlook will then allow for further predictions on the condition and corrosion rates of other submerged structures and objects, such as windmills, historic artefacts and ammunition (combination of steel, copper, bronze, zamac) dumped after the World Wars.



Figure 1. Multi-phase model for long-term corrosion in marine environments showing the parameters defined in the text and in Table 1. The long-term corrosion rate becomes linear at t > B, due to a possibly increasing importance of microbiological influences over the involvement of oxygen. (based on Melchers, 2014).

#### 2 MATERIAL AND METHODS

#### 2.1 Parametrization of the Melchers model for the North Sea

For long-term corrosion (t >B) processes, the Melchers model described in the introduction can be simplified to become a linear curve with slope rs and intercept cs (Figure 1):

$$Corrosion loss = (c_s + [t - t_0] * r_s) * R_p$$
(1)

with cs being corrosion thickness at which the anaerobic activity becomes steady (in mm), t the total time of immersion (in years), t0 the time the original coating remains intact (in years) and rs the anaerobic

steady corrosion rate (in mm  $y^{-1}$ ). Rp is a factor that can be used to model the impact of micro-organisms (Melchers, 2014), as it is a function of the concentration of dissolved inorganic nitrogen (DIN) in the local environment, with:

$$R_{\rho} = \frac{\text{Corrosion loss with DIN}}{\text{Corrosion loss without DIN}}$$
(2)

To parameterize  $R_p$ , DIN as well as individual concentrations of ammonia, nitrates and nitrites in the neighborhood of the wreck sites were derived from data available at the Flemish Marine Institute (<u>http://www.vliz.be/en/request-data</u>). Moreover, to apply the Melchers model to the conditions in the North Sea, the parameters graphically presented in Figure 1, were calculated according to the equations in Table 1 (Melchers, 2008)). The temperature in the North Sea was set at an average of 12.5°C, again based on data provided by the Flemish Marine Institute.

Table 1. Model parameters for general corrosion and pitting under immersion conditions as function of the average seawater temperature T, as well as applied for the North Sea (T = 12.5°C). (Equations from Melchers, 2008).

Parameter	Unit	Equation	Value North Sea
<b>r</b> 0	mm y <sup>1</sup>	= 0.076 · exp(0.054 · T)	0.149
Ca	mm	=0.32·exp(-0.038·T)	0.20
ta	У	=6.61·exp(-0.088·T)	2.20
<b>r</b> a	mm y <sup>1</sup>	=0.066.exp(0.061.T)	0.141
Cs	mm	= 0.141 - 0.00133·T	0.12
r <sub>s</sub>	mm y <sup>1</sup>	=0.039·exp(0.0254·T)	0.053

#### 2.2 Corrosion measurements on shipwrecks

The Belgian part of the North Sea (BPNS, as defined, for example, by (Lescrauwaet, et al., 2013) contains numerous shipwrecks from a variety of sources and ages (see http://www.maritieme-archeologie.be/). Six of these wrecks (Table 2) were selected on the basis of a number of criteria such as water depth, under water visibility, general condition and position of the wreck on the sea bottom, distance from shore, surface traffic density, location in or outside protected or restricted area, availability of dive charters and, most importantly, the availability of reliable original construction data. The seventh wreck, the submarine UC-61, was found in very shallow coastal water near Wissant (France). Most of the time this wreck is immerged, but tidal effects and sand displacement may exceptionally allow the wreck to become visible and accessible at low tide. The wreck was visited on January 19, 2019. As the specific date at which each of the ships sank is known (Table 2), the duration of the immersion could be determined exactly.

The oldest wrecks in this study are three German submarines dating from the First World War. The U-11 is a German long-distance submarine (the only one of this type on the BCP) that sank on 12/12/1914 after collision with a mine. The wreck is considered to be a war grave. The UC-61 is a German minelaying submarine of the UC-II type. She was built in 1916 and beached on July 26, 1917 before surrendering to French authorities near Boulogne. The identity of the remains of the third German UB-III class submarine, situated on the Fairy Bank, is not completely clear. The wreck may be a submarine of the series UB-54 till UB-59 or UB-103 till UB-117. Most probably, the submarine sank after colliding with a mine in the Dover Mine Field in the first half of September 1918. The four others are shipwrecks dating between 1940 and 1972. The Torpilleur Bourrasque is one of a series of 12 French destroyers. She was built by Ateliers et Chantiers de France at Dunkirk; she collided with a mine and was lost off Nieuwpoort on 30 May 1940 during Operation Dynamo. The Birkenfels is a German merchant vessel built in 1951. On the 7th of April 1966, while on voyage from Bremen via Antwerp to the Persian Gulf with a cargo of 8.750 tons steel and general cargo, she came in collision with the German MV Marie Luise Bolton in dense fog, and sank, at about 1 mile south of Noordhinder Lightship. The Garden City was built as "Le Moyne d'Iberville" in France in 1949. She sank on 19 March 1969 after a collision with a Polish vessel MV Zaglebie Dabrowskie. Finally, the Sabrina II is a Belgian trawler built in 1963, which capsized on 12 May 1972 during fishing.

Diving excursions took place between February 2015 and April 2019 and were each time performed by recognized historic wreck divers led by Sven Van Haelst coauthor of this article. For the wrecks close to the shore a rigid inflatable craft (RIB) was used while for those further away the research vessels Simon Stevin of the VLIZ or the Belgica A962 of the BELSPO were engaged. *In situ* plate thickness measurements were performed with a Cygnus M2-Dive equipped with the S2C single ultrasonic Crystal Probe (Cygnus Instruments, USA), using multiple readings.

For each of the wrecks, an easily recognizable place was selected, of which the original plate thickness was known. Also, both sides of every measuring location were preferably exposed to open seawater (to allow the corrosion rate to be essentially similar on both sides). A few cm<sup>2</sup> of the fouling and the concretion were removed with a chipping hammer and scraper to allow the measurements to be taken. The next measurement was taken at a distance of about 20cm, resulting in N measurements per wreck (as specified in Table 2). Comparison with the original plate thickness allowed for a calculation of the corrosion rate at each individual spot.

NAME	VESSEL TYPE	DATE SINKING	DATE MEASURED	SOURCE CONSTRUCTION PLANS	POSITION	LEAST DEPTH (m)	N	Original plate thickness (mm)	Average current plate thickness (mm) ± SE	Average corrosion loss per side (mm)
U-11	U-boat WWI	12/12/1914	13/5/2015	Rössler, 2002	51°20,550'N 2°52,075'E	11	12	12	6.75 ± 0.106	2.63
UC-61	U-boat WWI	26/6/1917	19/1/2019	Ross, 2017	50°53,552'N 1°39,79'E	0	43	11.1	7.81 ± 0.093	1.64
UB-III Fairy Bank	U-boat WWI	First half September 1918	10/2/2015	Maritime Archeology Trust, 2008	51°26,795'N 2°19,992'E	16	1	12.5	8.85	1.83
Torpilleur Bourrasque	Torpedo boat	30/5/1940	16/4/2019	Construction Plans – Service historique de la défense, France	51°14,964'N 2°33,026'E	16	7	8	4.54 ± 0.033	1.73
Birkenfels	Cargo ship	7/4/1966	7/2018	Construction plans	51°38,99'N 2°32,268'E	20	15	7	4.60 ± 0.087	1.20
Birkenfels	Cargo ship	7/4/1966	12/05/2015	Construction plans	51°38,99'N 2°32,268'E	20	14	7	4.70 ± 0.016	1.15
Garden City	Cargo ship	19/3/1969	10/2/2015	Construction Plans – French Lines, Le Havre, France	51 <sup>°</sup> 29,141'N 2°18,321'E	15	2	8	4.93 ± 0.113	1.54
Sabrina II	Fishing vessel	13/5/1972	11/5/2015	Hoekman shipbuilding, pers. comm.	51°13,300'N 2°31,121'E	15	7	7	5.14 ± 0.131	0.93

Table 2. Overview of the shipwrecks used in this study. N = number of measurements taken on each ship; SE = standard error. The Birkenfels was visited twice.



Figure 2. Position of the wrecks used in this study, in the Belgian Part of the North Sea and the French coast

### 2.3 Determination of the impact of micro-organisms

DNA extraction was performed on metal collected from an anchor chain, recovered from the North Sea bottom during diving operations. The collected samples were mixed with lysis buffer, containing 100 mM Tris pH 8, 100 mM EDTA pH8, 100 mM NaCl, 1% polyvinylpyrrolidone (PVP40) and 2% sodium dodecyl sulphate. 200 mg of 0.1 mm glass beads was added to the samples after which they were disrupted in the PowerLyzer (Qiagen, Venlo, Netherlands) at 2000 rpm for 300 seconds. The samples were centrifuged at maximum speed for 5 minutes and the supernatant was added to a new tube containing 500  $\mu$ L of phenol:chloroform:isoamylic alcohol (25:24:1) at pH7. After mixing and subsequent centrifugation, the upper phase was added to a new tube containing 700  $\mu$ L of chloroform. After mixing and centrifugation, 450  $\mu$ L of the upper phase was added to a new tube containing 500  $\mu$ L of cold isopropanol and 45  $\mu$ L of 3M sodium acetate. The samples were mixed and stored at -20°C for one hour after which they were centrifuged at 4°C for 30 minutes. The supernatant was removed, and the DNA pellet dried prior to dissolving in 1X TE.

PCR was performed using a recombinant Taq DNA Polymerase kit, Fermentas (Thermo Fischer Scientific, Waltham, MA, USA), in 25  $\mu$ L reactions containing: 2.5  $\mu$ L 10x Taq buffer (+KCI – MgCl<sub>2</sub>), 0.5  $\mu$ L of 10 mM dNTP, 1.5  $\mu$ L of 25 mM MgCl<sub>2</sub>, 0.5  $\mu$ L of 10  $\mu$ M Primer 27f AGAGTTTGATCMTGGCTCAG, 0.5  $\mu$ L of 10 $\mu$ M Primer 1492r TACGGYTACCTTGTTACGACTT, 0.125  $\mu$ L of 5 U  $\mu$ L Taq polymerase, 0.065  $\mu$ L of 20 mg mL<sup>-1</sup> BSA (Roche Holding AG, Basel, Switzerland), 14.81  $\mu$ L PCR-water and 1  $\mu$ L undiluted sample. Amplification was run including initial denaturation for 7 min at 95°C, followed by 30 cycles of 1 min denaturation at 95°C, 1 min anneal at 55°C and 2 min extension at 72°C. A final elongation step was included at 72°C for 10 min. The product was run for 30 min at 100 V on a 2% agarose gel and was visualized using a UV transilluminator.

### 2.4 Determination of the composition of corrosion concretion

X-ray diffraction (XRD) was used to determine the composition of the concretion around the metal chain

shackle mentioned above using a D8 Discover XRD (Bruker), set-up for phase identification with a Co tube (K $\alpha$ 1 = 1.78897 Å) with a generator at 35 kV and 40 mA, a 1 mm slit behind the Polycap, long soller slits 0.35° in front of the detector, the lynx eye detector in 0 D mode with an opening of 13 mm, and a q/q configuration (continuous locked couple scan). The crystalline phases present in the analyzed sample could be identified by comparing the positions of diffraction peaks in the experimental pattern with those present in (experimental and simulated) patterns of known samples available in a database (Powder Diffraction File, International Centre for Diffraction Data, Swarthmore/USA).

## 2.5 Determination of calcium and magnesium

Seawater samples were taken at three depths at the location of the Torpilleur Bourrasque, with the deepest sample location set at 1 m above the wreckage. Calcium and magnesium ion concentrations were determined with an ionic chromatographer 883 Basic IC Plus, equipped with an Metrosep C6 column (Metrohm), using a mobile phase of 1.7 mM HNO<sub>3</sub> + 1.7 mM dipicolinic acid at a flow of 0.9 mL min<sup>-1</sup>, at a conductivity of ± 850-860 mS cm<sup>-1</sup>. All measurements were done in triplicate.

# 3 RESULTS AND DISCUSSION

# 3.1 Parametrization of the Melchers model for the North Sea

The Melchers model was parametrised for the North Sea, with parameter values as estimated and presented in Figure 1 based on the equations in Table 1. As most of the wrecks of interest have been immersed for a very long time (> 15 years), it is permitted to use the linear approximation of the Melchers model (Eq. 1).

The value for Rp in this equation can be determined with an empirical relation between Rp and the concentration of DIN for long term exposures (Melchers, 2014):

$$Rp = 1.375 \cdot DIN + 1$$
 (3)

with DIN expressed in mg N L<sup>-1</sup>. Values for DIN measured in the North Sea over considerable periods of time are known to vary between 0.3 mg N L<sup>-1</sup> (OSPAR, 2017) and 1.4 mg N L<sup>-1</sup> (Janssen, 1993), which are comparable with previously published average values of 0-30  $\mu$ M (0-0.4 mg N L<sup>-1</sup>) nitrate, 0-2  $\mu$ M (0.03 mg L<sup>-1</sup>) nitrite and 0-25  $\mu$ M (0-0.35 mg N L<sup>-1</sup>) ammonia for unpolluted coastal waters (Sharp, 1983). This suggests that there were perhaps only minor long-term changes over the period during which the shipwrecks were exposed.

Melchers (2014) considers a strong relationship between the availability of DIN for microbiological activity and the severity of the resulting corrosion. However, any assessment of DIN in the water surrounding the wrecks is only a proxy for the presence of anaerobic corrosion-enhancing micro- organisms. Sulfate reducing bacteria (SRB) are the most common corrosion-accelerating anaerobic bacteria, producing sulfide in their main energy metabolism, which can then be used as a marker for their presence, in the form of iron sulfides.



Figure 3. Chain used for DNA sampling and XRD analysis of the concrete layers. Corrosion & Prevention 2019 Paper 076 - Page 8





Figure 4. XRD analysis of (A) corrosion concrete depositions around a metal chain shackle retrieved from the bottom of the North Sea as well as (B) the surrounding sediments on the seabed. Red line represents raw data in figure 4A; blue line represents raw data in figure 4B. In both A and B, composition can be read as: Blue triangles: SiO<sub>2</sub>. Light green dots: CaCo<sub>3</sub>. Light blue triangles: K<sub>2</sub>CaMg(SO<sub>4</sub>)<sub>3</sub>. Red squares: Goethite (FeO(OH)). Dark red triangles: Lepidocrocite (FeO(OH)). Orange cross: K<sub>3</sub>FeO<sub>2</sub>. Dark green cross: Fe<sub>0.94</sub>O. Yellow: CaFeO<sub>3</sub>. Magenta triangle: Fe<sub>8</sub>O<sub>8</sub>(OH)<sub>8</sub>Cl

To obtain a clear view on the possible influence of MIC on the anaerobic corrosion rate at the bottom of the North Sea, it was attempted to determine the presence of bacterial cells or their metabolic end products. To this end, destructive sampling was needed. As it is morally and legally impossible to collect pieces of shipwrecks, samples were taken from a metal chain shown in Figure 3), not belonging to one of the shipwrecks, and salvaged in March 2018. Little is known about this piece of chain except that it has been on the bottom for a very long time, in any case more than 15 years.

To assess the presence of SRB, DNA sampling was attempted from the concrete layer around this iron chain shackle. The extraction yielded very low DNA concentrations and the subsequent PCR of 16S rRNA genes did not result any amplification of the genetic material (data not shown), probably due to very low amounts of bacteria and the presence of inhibitory compounds. Moreover, XRD analysis of a piece of an iron chain conserved under the same conditions as the shipwrecks in the rest of the study, however, indicates that the metal concretion (Figure 4A) probably contains SiO<sub>2</sub>, CaCO<sub>3</sub>, K<sub>2</sub>CaMg(SO<sub>4</sub>)<sub>3</sub>, FeO(OH), K<sub>3</sub>FeO<sub>2</sub>, Fe<sub>0.94</sub>O, CaFeO<sub>3</sub> and Fe<sub>8</sub>O<sub>8</sub>(OH)<sub>8</sub>Cl, whereas a seabed sample taken close by (Figure 4B) contained mostly CaCO<sub>3</sub> and K<sub>2</sub>CaMg(SO<sub>4</sub>)<sub>3</sub>. This analysis failed to demonstrate the presence of iron sulfides, which could function as a proxy for the historic presence and metabolic activity of SRB.

These results lead to the assumption that MIC is likely to be irrelevant for shipwreck corrosion in this part of the North Sea. Hence  $R_p$  can be taken as 1. Also, after a period of approximately 15 years on the sea bottom at 12.5°C the corrosion rate will then become ± 0.054 mm y<sup>-1</sup>.

#### 3.2 Shipwreck corrosion in the North Sea

Next, the results of the average measured corrosion losses on the studied shipwrecks were plotted against the time of immersion. Corrosion loss was compared with the multi-phase model of Melchers at 12.5°C in the absence of microbially induced corrosion (Melchers, 2008).

Under anaerobic conditions, the corrosion model (see Figure 1) involves a steep increase of corrosion loss starting from  $t_a$ , followed by a linear phase. The exact value of  $t_a$  may depend on environmental conditions and cannot be accurately estimated from the data at hand, as all considered shipwrecks have been immersed during many years; the minimum time of immersion being 43 years (Sabrina II). The first preliminary phase to be considered is a period preceding the actual multiphase model of Melchers, being the time frame during which the metal structure is still protected by a coating. The durability of coatings on shipwrecks has never been studied in detail. Even estimating the durability of modern coatings poses significant problems. A survey by Verstraelen et al. (2009) suggested that, on average, ballast tank coatings remain sufficiently intact for a period of 10.1 years. Calculations based on the equations given in Table 1 give a time interval between  $t_0$  and  $t_a$  of approximately 2.2 years, so that  $t_a$ . = 12.3 years (taking into account an intact period of 10.1 years) is considered a reasonable value for this research. The non-linear part was thus fitted to the data based on the theoretical value of  $t_a = 12.3$  years.

For the data at hand, even the power model shows that it provides close to a linear long-term trend for the corrosion losses:

Corrosion loss = 
$$\alpha$$
.  $(t - tb)\beta$  (4)

where  $t_b = 12$  years,  $\alpha = 0.16$  (95% confidence interval [0.032 ; 0.75]) and  $\beta = 0.57$  (95% confidence interval [0.18 ; 0.96]). This model is statistically significant (p = 0.012 < 0.05). For this model,  $t_a$  is reached at 12.3 years after sinking, when the tangent to the model has a slope of  $r_a = 0.141$ , based on the equations in Table 1.

The long-term linear part of the bi-modal model also was fitted to the data. Figure 5 shows that for the long-term evolution of average corrosion loss there is little difference between the linear and the non-linear model. A linear model could therefore be adopted to describe the long-term average corrosion loss

$$Corrosion \ loss = cs + t * rs$$
(5)

The linear North Sea model of Eq. 5 is essentially the same as Eq. 1, except that time t in Eq. 5 is the time after sinking (expressed in years). The long-term corrosion rate is estimated at  $r_s$ = 0.016 mm y<sup>1</sup> (95% confidence interval [0.0037; 0.028]), while the intercept is given by  $c_s$ = 0.46 (95% confidence interval [-0.46; 1.37]). This model is statistically significant (p=0.019 < 0.05).



Figure 5. Corrosion loss per side (mm) versus time in the water in years; the blue line corresponds with the linear North Sea model with a green 95% confidence and prediction band; the orange line corresponds with the Melchers model as parameterized for the North Sea; the red dotted line corresponds with the North Sea power model.

Comparison of the long-term linear model (displayed along with its 95% confidence and prediction bands in Figure 5) with the linear phase 4 of Melchers model (as defined in Figure 1) shows that the linear part of the latter hardly overlaps with the 95% prediction band of the measurements presented here. As such, the North Sea model is characterized by a long-term corrosion rate that is significantly lower than the long-term corrosion rate suggested by Melchers' multi-phase model. Once the corrosion becomes anaerobic and in the absence of active corrosion-accelerating bacteria, the corrosion rate in the North Sea, taken at 12.5°C, is estimated at  $r_s = 0.016$  mm y<sup>1</sup>. This is less than one third of the corrosion rate predicted by Melchers' multi-phase model, which is given by  $r_s = 0.054$  mm y<sup>1</sup> (Table 1).

#### 3.3 Corrosion of shipwrecks in the North Sea occurs at a very low rate

These findings, while preliminary, suggest that it might become necessary to refine our current view on the defining parameters for long-term steel corrosion of stationary structures in the North Sea.

Of course, this difference could be attributed to several parameters. Firstly, the structure and composition of the steel may cause some of the variation. The presence of sacrificial material or substances may promote the formation of a passivating layer. Older steel may on the one hand contain a number of impurities changing its sensitivity to corrosion; also, some of the ships used in this analysis (especially the ones dating from the First World War) are submarines, likely to have been built using different alloys, again complicating the corrosion rate.

One of the other options to provide an explanation for this discrepancy is the presence of higher amounts of calcium in the open sea than in the data used for the calibration of the original Melchers (2003) model. Present investigations for the likely mechanisms involved are focused on the effect of fresh, hard water entering the shallow coastal zone region through submarine groundwater discharges (UNESCO, 2004), noting that some of this has been considered previously for the effect of brackish water on corrosion (Melchers 2006). When biological influences on corrosion are a possibility (Little & Lee, 2007), attention must be given to whether critical nutrients for such corrosion are available in the local seawater (Melchers, 2014) and whether it is possible for such nutrients to reach the corrosion interface, presumably by diffusion through any rust and other layers. It is in this regard that the calcium carbonate layers that have been observed on the shipwrecks are likely to have played (and continue to play) a major role. Calcium carbonate deposits, particularly if aged, tend to be relatively impermeable (Green, 2016) and thus are likely to isolate the corrosion interface from nutrients and this may inhibit microbiological influenced corrosion.

Table 3. Calcium, magnesium and sulphate concentrations in different heights in the water column above the Torpilleur Bourrasque.

Location	Calcium (mg L <sup>-1</sup> )	Magnesium (mg L <sup>-1</sup> )	Sulphate (mg L <sup>-1</sup> )
Тор	460 ± 8	1225 ± 3	2813
Middle	451 ± 4	1233 ± 6	2776
Bottom	420 ± 7	1204 ± 7	2830

Indeed, most of the data sites on which the Melcher's model was based originally (Melchers, 2003) came from offshore sampling sites, or from locations where calcite deposition on steel had not been observed. For example, the effect of fresh water inflow, such as in estuaries and river mouths, conventionally associated with brackish waters, has its main effect on corrosion of steels as a result of the interplay between salinity and calcite deposition, with the latter well-known, from cathodic protection studies (Yang et al., 2015) to inhibit marine immersion corrosion (Melchers, 2006). It is likely that a parallel effect is at play in the lower levels of corrosion seen on the wrecks. This issue is under current investigation.

Calcium carbonate deposition as well as rust layers reduce the diffusion rate of  $O_2$  to the corroding surface (Elbeik et al., 1986). However, this does not mean that  $O_2$  ceases to play any important role in the corrosion process. On the inner part of the encrustation layer, its further build-up is essentially caused by the dissolution of water and the formation of Fe(OH)<sub>2</sub> which then converts to a magnetite layer. On the outside of that layer the magnetite continues to be oxidized by external  $O_2$ , which therefore remains the ultimate 'electron acceptor', except that the route is more tortuous (Evans and Taylor, 1972).

Several local conditions can be cited to support or enhance this mechanism. Firstly, in the case of the BPNS, hard and fresh ground water enters the coastal sea from the sandy sea bottom, as evidenced by the fact that Ca<sup>2+</sup> concentrations closer to the bottom were lower than upwards in the water column. By the time the fresh water reaches the top of the sand layers it would have deposited its calcite load, only then to be mixed with seawater and change from fresh to brackish and, finally, slightly diluted seawater. Moreover, as the shipwrecks are already rusting and the rust surfaces are slightly alkaline (pH around 10), they are the preferred surface for calcite deposition instead of the sediments at the bottom of the sea (Elbeik et al., 1986)

### 3.4 *Further applications of the corrosion model*

A lesser-known possible application of the model presented here is linked to the presence of historic ammunition dump sites in the North Sea. As mentioned in the introduction, the BPNS encompasses the dumping site of at least 35 000 tons of chemical warfare shells at the end of World War I on the Paardenmarkt, a sand bank situated 51°22'N & 3°15'E. The shells are currently covered with 2-6 m of sediment (Missiaen, 2013).

Of the shells found at the site, 65% consists of 77 mm grenades (Figure 6), 17 % of 105 mm grenades, 3.5% of 150 mm grenades and 14.5% is of unknown calibre (Stock & Lohs, 1997).



Figure 7. Structure of a German 77 mm gas shell. Original image in the public domain.

The shells contain between 2604 and 3991 tons of toxic substances (mustard gas, chloropicrin, phosgene, diphosgene and arsenic compounds), between 65 and 861 tons of trinitrotoluene and possibly between 924 and 14583 tons of other propelling explosive mixtures consisting mainly out of ammonium nitrate, carbon, nitrocellulose or nitroglycerine, and diethyldiphenylurea (calculations based on data obtained from various sources (Explosive Ordnance Disposal Belgian army, pers. comm.; General Staff - General Headquarters, 1918; Missiaen, et al., 2001).

What was an emergency solution at the time of dumping (1919-1920), is now turning into a major environmental and safety problem. The North Sea is increasingly being exploited intensively, for fishing activities, oil- and gas production, and recently energy generation by windmill farms. The danger of explosion or the release of toxic substances may pose serious consequences for safety and for the maritime environment. One of the major risk factors in the near future is the condition of the bomb casings. Due to current safety regulations, obtaining actual shell samples is not an option; hence, a combination of innovative modelling based on the results of the shipwreck analysis and short-term experiments (up to three years) to parameterize those models, offers the best strategy to determine the risk of fatal corrosion.

Five forms of corrosion may play a role. Firstly, each of the metal components of the shells (the cartridge, the shell and the fuze (Figure 7)), may be subjected to general, uniform corrosion. Additionally, galvanic corrosion may occur between the different metals, more specifically between the steel shell and the copper cartridge or the bronze fuze. For the shells the variability in the composition of the metals adds to the complexity of the problem. As the war progressed and raw materials grew scarce (Saul, 2012), any available material was used. German fuzes during World War I were made of brass, aluminium, steel or zinc (General Staff - General Headquarters, 1918). As the war progressed, less noble and more corrosive materials were used. If seawater can penetrate the shell, a reaction between water and the yperite (mustard gas) leads to the formation of aggressive hydrochloric acid, leading to an enhanced chemical corrosion from the inside out. Finally, erosion corrosion could have occurred before the ammunition was buried.

However, the corrosion conundrum becomes even more complicated, for several reasons. At a certain moment in time, at the latest at the time of the expansion of the port of Zeebrugge in the 1970s, the ammunition became covered by a sediment layer, likely rendering the corrosion anaerobic (Wang et al., 2005), affecting DIN concentration and raising the possibility again of the involvement of SRB at the site (Beech & Sunner, 2004). Also, the site is prone to freshwater upwelling (Vandenbohede & Lebbe, 2006) and release of natural methane, and has a shallow depth allowing UV penetration. Finally, just like the shipwrecks analysed, the shells were found to be covered with a layer of concretion, the importance of which is difficult to foresee at the present time. It is hoped that the present research project will contribute to a deeper understanding of the corrosion process, especially in seawater such as the North Sea, after decades of immersion.

### 4 CONCLUSION

The aim of the present research was to examine the long-term corrosion of steel in North Sea seawater by means of assessing the corrosion rate of steel ship and other wrecks. The empirical findings in this study provide a better understanding of the complex corrosion processes in a North Sea maritime environment. On the other hand, the generalizability of these results is subject to certain limitations typical for the North Sea environment, such as temperature, salinity, limited water depth and maybe UV light, hardness of the water. Regression analysis suggests that the corrosion rate of 0.012 mm y<sup>1</sup> in the North Sea seawater is lower than generally expected. To explain this discrepancy further research is needed, leading to a predictive model applicable to North Sea and similar environments. Application of such a model is likely to be helpful for the reduction of direct and indirect costs of steel constructions at sea and the development of an instrument where the potential environmental and safety impact of leaking World War I gas shell can be assessed. A better understanding of the mechanisms that underpin long term corrosion in seawaters such as the North Sea also is likely to lead to more effective protection methods and technologies.

#### 5 ACKNOWLEDGEMENTS

This project was partially funded by Internal Projects "Modellering van corrosie van de omhulsels van de giftige munitie op de Paardenmarkt" (Modelling the condition of the poisonous ammunition on the Paardenmarkt" and "Conservatie van historische Noordzeewrakken (Conservation of historical North Sea wrecks)" at the Antwerp Maritime Academy. The authors thank Yves Van Ingelghem (Free University of Brussels) and Geert Potters (Antwerp Maritime Academy) for his contributions to technical discussions. Raf Dewil and Sofie Houtmeyer (Catholic University of Leuven) provided the calcium and magnesium determinations. XRD analysis was done by Krista Van den Bergh at OCAS, Zwijnaarde, Belgium. Klaas Hoekman of Hoekman shipbuilding provided the construction details of the Sabrina II.

The main text of this contribution has been written by K. De Baere & R. Melchers. Statistical analysis of the data was done by D. Luyckx, DNA analyses was performed by N. Boon of CMET Ghent, The in situ plate thickness measurements were done by S. Van Haelst, S. De Baere did the corrosion analysis of the historical chain, S. van Halbeek, R. Willemen and R. Meskens contributed to the field- and data collection aspects of this work.

### 6 **REFERENCES**

- Beech, I. B., & Sunner, J. (2004). Biocorrosion: towards understanding interactions between biofilms and metals. *Current opinion in Biotechnology*, 15(3), 181-186.
- Elbeik, S., Tseung, A. C. C., & Mackay, A. L. (1986). The formation of calcareous deposits during the corrosion of mild steel in sea water. *Corrosion science*, *26(9)*, 669-680.

Evans, U. R., & Taylor, C. A. J. (1972). Mechanism of atmospheric rusting. *Corrosion Science*, 12(3),227-246.

General Staff - General Headquarters. (1918). Notes on German fuzes and typical French and Belgian fuzes. London: Harrison & Sons.

Green, G. (2016). Maritime Archeology, a technical handbook, 2nd edition. New York: Taylor & Francis.

- Soares, C. G., Garbatov, Y., Zayed, A., & Wang, G. (2005). Non-linear corrosion model for immersed steel plates accounting for environmental factors. *Transactions of the Society of Naval Architects and Marine Engineers*, 113, 306-322.
- Janssen, G. (1993). De eutrofiëring van de Noordzee en Waddenzee, een tussenbalans. Zien we al resultaten van het saneringsbeleid?. *H2O*, *26(4)*, 86-91.
- Lescrauwaet, A., Pirlet, H., Verleye, T., Mees, J., & Herman, R. (2013). Compendium Voor Kust En Zee: Een Geïntegreerd Kennisdocument Over De Socio-economische, Ecologische En Institutionele Aspecten Van De Kust En Zee In Vlaanderen En België. Oostende: VLIZ - Vlaams Instituut Voor De Zee.

Little, B. J., & Lee, J. S. (2007). Microbiologically influenced corrosion (Vol. 3). John Wiley & Sons.

Maritime Archeology Trust. (2008). *Forgotten wrecks of the first World War - SM U90.* Southampton: Maritiem Archeology trust.

- Melchers, R. (2003). Modeling of marine immersion corrosion for mild and low alloy steels—Part 1: phenomenological model. *Corrosion*, *59*(*4*), 319-334.
- Melchers, R. E. (2006). Modelling immersion corrosion of structural steels in natural fresh and brackish waters. *Corrosion Science*, 48(12), 4174-4201.
- Melchers, R. (2008a). Chapter 4, Corrosion wastage in aged structures. In R. Melchers, & J. Paik,

Condition assessment of aged structures (pp. 77–106). Cambridge: Woodhead Publishing.

- Melchers, R. E. (2008b). Development of new applied models for steel corrosion in marine applications including shipping. *Ships and Offshore Structures*, *3*(2), 135-144.
- Melchers, R. (2014). Long-term immersion corrosion of steels in seawaters with elevated nutrient concentration. *Corrosion Science*, *81*, 110-116.
- Melchers, R. (2018). A review of trends for corrosion loss and pit depth in longer-term exposures. *Corrosion and Materials Degradation*, 1(1), 42-58.
- Melchers, R. E. (2019). Predicting long-term corrosion of metal alloys in physical infrastructure. *npj Materials Degradation*, *3*(1), 4.
- Missiaen, T. (2013). Paardenmarkt Bank, a WWI ammunition dump site off the Belgian Coast. *De Grote Rede, 36,* 53-60.
- Missiaen, T., Henriet, J.-P., Van lancker, V., Charlet, F., Moerkerke, G., Lanckneus, J., & Halleux, L. (2001). *Paardenmarkt Site Evaluation*. Brussels: Office for Scientific, Technical and Cultural Affairs.
- OSPAR. (2017). Third OSPAR Integrated Report on the Eutrophication Status of the OSPAR Maritime Area, 2006-2014. OSPAR.
- Paik, J., Kim, S., Lee, S., & Park, Y. (1998). A probabilistic corrosion rate estimation model for longitudinal strength members of bulk carriers. *Journal* of *Ship* and *Ocean Technology*, *2*, 58-70.
- Qin, S., & Cui, W. (2002). Effect of corrosion models on the time-dependent reliability of steel plated elements. *Marine Structures*, *15*, 15-34.
- Ross, D. (2017). The World's Greatest Submarines. Florida: Amber.
- Rössler, E. (2002). The U-boat: The Evolution and Technical History of German Submarines. London: Cassell & Co.
- Saul, D. (2012). How Germany lost the WWI arms race. London: BBC.
- Sharp, J.H. (1983). The distribution of inorganic nitrogen and dissolved and particulate organic nitrogen in the sea. In E. J. Carpenter and D. G. Capone (ed.), *Nitrogen in the marine environment* (pp. 1-36). Academic Press, New York, N.Y.
- Stock, T., & Lohs, K. (1997). *The challenge of old chemical munitions and toxic armament wastes.* Oxford, Verenigd Koninkrijk: Oxford University Press.
- Tammann, G. (1923). Lehrbuch der metallographie: chemie und physik der metalle und ihrer legierungen. Leipzig: Voss.
- UNESCO. (Paris). Submarine groundwater discharge. 2004: UNESCO.
- Vandenbohede, A. & Lebbe, L. (2006). Occurrence of salt water above fresh water in dynamic equilibrium in a coastal groundwater flow system near De Panne, Belgium. *Hydrogeology Journal*, 14, 462–472
- Verstraelen, H., De Baere, K., Schillemans, W., Lemmens, L., Dewil, R., Lenaerts, S., & Potters, G. (2009). in situ study of ballast tank corrosion on ships (Part 2). *Materials Performance*, 48(11), 54-57.

Vlaamse hydrografie. (2019). Scheepswrakken op de bodem van de Noordzee. Retrieved 05 20, 2019,

- fromWrakkendatabank:https://www.afdelingkust.be/nl/wrakkendatabank.
- Wang, X., Duan, J., Li, Y., Zhang, J., Ma, S., & Hou, B. (2005). Corrosion of steel structures in sea-bed sediment. *Bulletin of Materials Science*, 28(2), 81-85.
- Yang, Y., Scantlebury, J., & Koroleva, E. (2015). A study of calcareous deposits on cathodically protected mild steel in artificial seawater. *Metals*, *5*(1), 439-456.

# 7 AUTHOR DETAILS

<b>Capt. Dr. Kris De Baere</b> (°1958) Obtained an academic master in Nautical Sciences in 1988 and his master mariners license f.g. in 1990. After 15 years at sea he returned to the AMA, as a lecturer, to pass on his love for the sea, mixed with a lot of knowledge and experience. In 2007 he started AMACORT, the corrosion research group and in 2011 his research work has been awarded with a PhD in Nautical Sciences.
Sven Van Haelst Maritime archaeologist Flanders Marine Institute Historic Wreck Diver
<b>Dr. Deirdre Luyckx (°1977)</b> obtained a PhD in Mathematics and a Master's degree in Statistical Data Analysis at Ghent University. She started working as a lecturer at Antwerp Maritime Academy in 2007, as such entering the fascinating maritime sector. Since then she is involved in strengthening the mathematical and statistical foundations of research and education at AMA. Her current interests include data analysis and visualization, with maritime applications, including the corrosion research of AMACORT
<b>S. De Baere (°1995)</b> Master in Archaeology

<b>Drs. Raf Meskens (°1968)</b> obtained the degree of Master in Nautical Sciences at the Antwerp Maritime Academy in 2008. He has a supplementary degree in Safety and Environmental Technology, obtained at Agoria, Sector Federation of the Technological Industry. After his maritime career he pursued a career on shore, first ten years as a P&I Surveyor and later on as head of the Logistics, Safety and Environmental Department at Antwerp Ship Repair. He joined the Antwerp Maritime Academy as a teacher in 2009
<b>Prof. dr. ir. Nico</b> is a Full Professor at the Center of Microbial Ecology and Technology (Ghent University) and leading the Microbial Community Engineering group. Since 1998 his research is focused on the applied microbial ecology of managed and engineered ecosystems. The areas of interests have been the development of (molecular) methods for the qualitative and quantitative description of microbial communities. During the last years, the research interests are focused on the development of new microbial ecological theories to link the microbial community structure to functionality.
S. van Halbeek Master Nautical Sciences
<b>Dra. ir. Remke Willemen (°1976)</b> Graduated in Nautical Sciences at the Maritime Academy in 1998. She continued her studies and obtained an engineering degree in Maritime Technology at the Technical University in Delft. Her professional career started as a surveyor and joined the AMA as a teacher in 2012. Shortly after, she completes the corrosion team of the AMA and since
<b>Robert E. Melchers,</b> Professor of Civil Engineering, The University of Newcastle, Australia, BE and MEngSc (Monash University), PhD (University of Cambridge, UK), Fellow, Australian Academy of Technology and Engineering, Honorary Fellow, The Institution of Engineers Australia. Awards include 2009 ACA Corrosion Medal, 2012 Jin S Chung Award (ISOPE), 2013 John Connell Gold Medal (The Institution of Engineers, Australia), 2014 Eminent Speaker, Structural College, The Institution of Engineers, Australia, 2006 and 2018 Guy Bengough Award (IOM3)