

INFLUENCE OF MARINE MICROORGANISMS ON CORROSION OF CHEMICAL MUNITION SHELL DUMPED IN THE BALTIC SEA

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Abstract

After World War II approximately 60 thousand tons of chemical munitions have been dumped in the Baltic Sea. Corrosion occurs due to chemical or electrochemical reactions between the environment and metal. Microbes change the electrochemical reaction at the biofilm/metal interface and either inhibit or accelerate the process of metal corrosion. Although the microbial inhibitory mechanism is environmentally friendly, the predictability of the results is not yet affirmed, as sometimes the same bacteria with an inhibitory property may also become aggressive. This review discusses mechanisms by which microbes may induce or inhibit corrosion in metals in specific condition of the Baltic Sea.

Key words: *marine microorganisms, corrosion, chemical munition, Baltic Sea*

1. INTRODUCTION

After World War II approximately 60 thousands ton of chemical munitions have been dumped in the Baltic Sea. It was mainly weapon of German origin, the action of dumping was conducted under the supervision of Allied and Soviet Armies. The toxic warfare, often dumped in relatively shallow waters and areas of active fishing, is a serious threat to the marine environment and also to the often densely populated European coasts. As many dumping operations were carried out stealthily, there is very little information about the place of its deposition and also it is not always clear who is responsible for the disposal. Some dump sites are located in the international water, beyond any particular nation's responsibility, although more of the dumping operations were carried out in the territorial waters near the borders of neighboring states (Missiaen & Henriet, 2002). The largest part of chemical warfare agents (CWA) which was stored in Wolfgast in Germany was dumped in the Baltic Sea and Skagerrak Strait (Beldowski, et al., 2014). Although there is no official record of the dumping sites, operations often took place in chaotic circumstances right after the war, there is also the lack of documentation and the loss of destruction of records (Tine, et al., 2010). As far as the Baltic Sea is concerned the most important dump sites are located in the Little Belt, close to Bornholm Island and in the Gotland Basin. Usually the British and American occupation forces sank approximately 41- 43 vessels in Skagerrak. They were containing approximately 150 000 t of chemical weapons and conventional ammunition. Other occupation forces nationalities like French also sank in Skagerrak two vessels containing 1500 t of chemical warfare agents. In addition substantial amounts of chemical weapons were dumped in the Baltic Sea (Table 1).

Table 1. Quantities of chemical munitions and warfare agents dumped in the Baltic Sea (Glasby, 1997)

Area	Quantities of munitions (t)	Estimated quantities of warfare agents (t)	Types of warfare agents
Bornholm Basin	35 300 (certain) to 43 300 (uncertain)	5300-6500	Mustard gas Viscous mustard gas Clark I Clark II Adamsite Chloroacetophenone Less certain Phosgene Nitrogen mustard Tabun
Area SW of Bornholm	Up to 15 000 (uncertain)	2250	Not known
Gotland Basin	2000	300	Not known
Little Belt	5000	750	Tabun Fosgene

Two vessels containing nerve agents (tabun) were sunk by Germans before the end of the war in the Little Belt near Denmark. Also Soviet Military Administration dumped approximately 32000 t of chemical munitions near Bornholm Island in the Bornholm Basins and 2000 t of chemical munitions in the Gotland Basin. The material that was sunk consisted of projectiles, aerial bombs, drums, mines and containers filled with CWA. The reason why those places were chosen for depositing of chemical munitions was hydrological conditions i.e. stable stratification with anoxic conditions developing below the halocline and very gentle bottom currents except for the period of seasonal flashing of the basins (Glasby, 1997).



Figure 1. Dumping of chemical munitions in the Baltic Sea (Bełdowski, et al., 2014)

There are also unofficial dump sites like Gdansk Deep and the Slupsk Furrow and probably transport routes from Wolgast Harbour to designated dumping sites (Bełdowski, et al., 2014). Objects that were thrown overboard were usually packed in wooden crates which within past years might have been washed ashore on the coast near the dumping sites.

2. CORROSION

Corrosion in marine industry has been known for almost 100 years. In the marine environment it used to refer to the refining industry, several and the harsh environments in which many platforms operate are also causing a considerable number of corrosion-related issues (Speight, 2015). The use of metals often impacts the environment during the life cycle of the material. Corrosion is typically identified by the appearance of rust on the steel surface of the offshore structure. The chemical reactions driving the corrosion process are caused by chloride attack — corrosion of steel occurs by an anodic reaction. The offshore structure is exposed to saline water throughout its whole lifetime. Sea water is the most corrosive natural environment that materials have to withstand but it is not as corrosive as many environments encounter in the refining industry, like mineral acids that are used in various processes.

Corrosion due to the presence of extreme corrosive element can be classified under several headings (Lewandowski & Beyenal, 2009, Maluckov, 2012, Speight, 2015, Coker, 2015).

- Uniform corrosion – which occurs as a decrease in metal thickness per unit of time or uniform deposit of corrosion products on the surface of the metal (it is also called general corrosion);
- Galvanic corrosion – which results from contacts between two different materials in a conducting, corrosive environment. It may result in a very rapid deterioration of the least resistant of the two materials leading to a fatal failure;
- Crevice corrosion – electromechanical oxidation reduction process. It occurs within localized volumes of stagnant trapped solution trapped in pockets, corners or beneath a shield of some description. The corrosive process is greatly accelerated if chlorine, sulfide, or bromide ions are present in the electrolyte solution. Crevice corrosion is considered far more dangerous than uniform corrosion as the rate at which it occurs can be up to 100 times higher;
- Pitting corrosion – this is characterized by deep, narrow holes that can penetrate inward extremely rapidly while the remainder of the surface stays intact. The perforation of a component can occur in a few days with no appreciable reduction in weight of the overall structure. Stainless steels are particularly sensitive to pitting corrosion in seawater environments.
- Intergranular corrosion – which progresses along the grain boundaries of an alloy and can result in the catastrophic failure of equipment, especially if tensile stress loads are present. A localized attack can occur while the rest of the material is completely unaffected. The presence of impurities in the boundaries or local enrichment or depletion of one or more alloying elements can be the catalyst for this type of corrosion.
- Stress corrosion cracking, which is a combination of tensile loading and a corrosive medium causing the initiation of cracks and then their growth. The time of the crash depends on specific application factors and can vary from just a few minutes to several years. Stress corrosion cracking is a very serious and permanent risk in many industrial applications where materials are often under mechanical loading for sustained periods or indeed permanently. In addition to selecting the correct materials, the risk of this type of corrosion can be avoided by stress relieving or annealing after fabrication of the assembly, avoiding surface machining stresses and controlling the corrosive environment.
- Microbiologically influenced corrosion (MIC) – this process is usually defined as a biocorrosion. The bacterial cells can colonize the metal surfaces causing damage. During the colonization of the solid surface the population of microorganism increase rapidly forming a kind of biofilm which covers the attacked surface.

There is also an increasing concern over the potential human health problems and ecological risk associated with the release of munitions chemical fills as the discarded military munitions have a continue to become older and corrode on the seafloor. Corrosion in the marine environment is dependent on the number of factors, including the time discarded chemical munitions is exposed to the marine environment, the type, quality and thickness of materials used in the construction, the availability of dissolved oxygen, seafloor current velocity, and the degree of burial within seafloor sediments. Additionally the presence, absence and conditions of protective coatings and microbiological processes can either accelerate or reduce the rate of corrosion. Given the large number of variables to be considered it would be difficult, if not impossible, to provide estimates of corrosion rates and time of corrosive penetration of these munitions based purely on the theoretical consideration of discarded military munitions (Silva & Chock, 2016).

2.1. Microbiologically influenced corrosion

No track of microbiologically corrosion can be found, that would distinguish this kind of corrosion from ordinary galvanic corrosion. Hence there are good reasons to believe that a universal mechanism of microbially stimulated corrosion does not exist (Lewandowski & Beyenal, 2009). MIC is caused by microbial communities attached to surface, known as biofilms, those microorganisms create prerequisites for MIC. A biofilm is composed of four compartments: the surface to which microorganisms are attached, the biofilm consisting of microorganism and a matrix, the solution of

nutrients and the gas phase. In each compartments there are several components and their number may vary (Lewandowski & Beyenal, 2009). Creating a biofilm depends on the surface characteristics of substrate such as: metal surface free energy, roughness, hydrophobicity and metallurgical feature. Hence the bicorrosion is the result of the synergetic interaction of the metal surface, abiotic corrosion products, bacterial cells and cells metabolites. Bacteria which affect metal surfaces the most exist in water and in land as sulfate-reducing bacteria, iron oxidizing/reducing bacteria, manganese-oxidizing bacteria and bacteria that secrete the mucus and organic acids (Maluckov, 2012). These organisms coexist in natural biofilms often forming communities able to affect electrochemical processes through co-operative metabolism which individual species have difficulties to initiate. Environment conditions also have influence on the rate of corrosion, parameters such as oxygen concentration, salts, pH value, redox potential and conductivity, which can be influenced by microorganisms growing at interfaces. Metabolic reaction in biofilm may be modified in many ways: biofilms create oxygen heterogenic near a metal surface, biofilm matrix increases mass transport resistance near a metal surface. Additionally metabolic reactions in biofilms generate corrosive substances, such as acids, and metabolic reactions in biofilms generate substances that serve as cathodic reactant (Lewandowski & Beyenal, 2009). Microorganisms implicated in MIC of metals such as iron, copper and aluminum and their alloys are physiologically diverse.

2.2. Bacteria influencing corrosion

Sulphate-Reducing Bacteria (SRB) are a group of ubiquitous, diverse anaerobes that reduce oxidized sulfur compounds, such as sulphate and tiosulphate, as well as sulphur to H_2S . Though SRB are strictly anaerobic (obligate anaerobes), some genera tolerate oxygen, and are even able to grow at low oxygen concentrations. Usually the activity of SRB is considered in terms of affecting by the sulphides generated by SRB, oil, gas and shipping industries. In terms of the Baltic Sea it can be considered as affecting the chemical munitions shells dumped in the sea, where exist the depletion of oxygen or even hypoxia. The effect of SRB on corrosion of various metals and their alloys in aquatic environments under anoxic as well as oxygenated conditions has been confirmed (Beech & Flemming, 2000). SRB gains energy for its growth from the reduction of sulfate to hydrogen sulfide with electrons usually derived from the degradation of organic matter or from molecular hydrogen, which is common fermentation product in sediment and in other anoxic settings. Iron sulfides (FeS) are the characteristic products of SRB-induced corrosion. They usually occur as a part of a mixture of mineral and organic deposits found on anaerobically corroded iron constructions. It was observed that serious corrosion damage of buried iron coupons in permanently anoxic marine sediment of the German North Sea was solely due to electrical microbially influenced corrosion (EMIC) in which SRB act as either direct or indirect catalyst (Enning & Garrelfs, 2014). *Bacillus* species is one of the SRB, usually found in the corrosive surfaces of metals in many environments, and some of them were identified as the dominant bacterial species. (Qu, et al., 2015). *B. subtilis* and *B. licheniformis* can inhibit the corrosion of cartridge brass, aluminum 2024 and carbon steel even in artificial seawater; microorganisms can colonize and form biofilm on metal surface in several days (Qu, et al., 2015). Other genera *Desulfovibrio spp.* strain can increase the rate of corrosion in comparison to abiotic conditions (AlAbbas, et al., 2013).

Metal-Reducing Bacteria (MRB) – these microorganisms are known to promote corrosion of iron and its alloys through reactions leading to the dissolution of corrosion-resistance oxide films on the metal surface. Numerous types of bacteria belong to MRB including those from genera of *Pseudomonas* and *Schewanella* (Beech & Flemming, 2000). *Pseudomonas sp.* was also observed by Machuca et al. (2013) on crevice corrosion of UNS S31803 and UNS N08825 in natural seawater. In the research were observed dominant populations of *Marinobacter Sp.*, *Thalassobius* and *Pseudoruegeria sp.* (Machuca, et al., 2013).

Metal-Depositing Bacteria (MDB) Many bacteria of different genera participate in the biotransformation of oxides of metals such as iron and manganese. Iron-depositing bacteria (e.g. *Gallionella* and *Leptothrix*) oxidize Fe^{2+} precipitated on the surface to Fe^{3+} . Bacteria from this genera are also capable of oxidizing manganous ions to manganic ions with concomitant deposition of manganese dioxide (Beech & Flemming, 2000).

Acid-Producing Bacteria (APB) and Fungi can produce capious quantities of either inorganic or organic acids as metabolic products. Microbially produced inorganic acids are nitric acid (HNO_3), sulphurous acid (H_2SO_3), sulphuric acid (H_2SO_4), nitrous acid (HNO_2) and carbonic acid (H_2CO_3) (Beech & Flemming, 2000).

Aerobic and anaerobic bacteria propagate within these biofilms by seeking out specific environmental niches within the structure of the biofilm and within layers of corrosion products formed on the metal surface. Biofilms, in and of themselves, contribute to general corrosion by restricting the diffusive flux of dissolved oxygen to portions of the metal surface onto which they have formed, creating localized differential aeration cells. Biofilm can also impede the outward diffusion of metabolites and corrosion products. It is the non-uniform colonization of marine microorganisms and biofilm distribution that often contribute to the patchy and unevenly swollen appearance of seawater submerged objects.

The low-oxygen environment within the deepest layers of the biofilm can support the propagation of anaerobic bacteria, including microaerophilic MDB (you may find also Iron Oxidizing Bacteria – IOB) and SRB. IOB derive energy from the oxidation of ferrous (Fe^{2+}) to ferric (Fe^{3+}) at near neutral pH and can generate significant dense deposits of iron oxide minerals, provided a sustained supply of Fe^{2+} . IOB accelerate corrosion by rapidly consuming Fe^{2+} , which can speed the oxidation of iron at anodic surface sites. SRB derive energy from the oxidation of organic compounds or molecular hydrogen while reducing sulfate (SO_4^{2-}) to sulfide (HS^-) to facilitate anaerobic respiration. HS^- then reacts with the dissolved Fe^{2+} to form iron (II) sulfide (FeS), a component of the black precipitate scale that is hallmark of SRB activity. SRB accelerates iron metal corrosion indirectly by the production of organic acids, hydrogen sulphide (H_2S) and hydrogen ion (H^+), with creating acidic microenvironments across the surface of the metal. However, it is also possible that SRB strains can also accelerate iron corrosion through the direct utilization of metallic iron (Fe^0) as the sole electron donor in sulfate respiration (Silva & Chock, 2016).

While IOB and SRB do contribute to accelerate corrosion, these specific bacteria do not act alone. Rather, and more typically, a diversified consortium of bacteria develops, including iron reducing bacteria, that as whole contributes to the corrosion of iron as a result of cooperative metabolism. Such microbial consortia accelerating the corrosion of steel shipwreck include the rapid deterioration of wrecks of the RMS Titanic and iron portions of the SS Central America (Silva & Chock, 2016).

3. HYDROLOGY OF DUMPSITES

The Baltic Sea is shallow semi-enclosed shelf sea characterize by high salinity gradients. It is connected to the Atlantic Ocean (The North Sea) through rather shallow basins of Danish Straits. Baltic is divided into six main regions: Gulf of Bothnia, Gulf of inland, Gulf of Riga, Baltic Proper (also known as Southern Baltic), Danish straits and Kattegat. The Proper Baltic can be additionally divided into four main smaller basins: the Arkona Basins at its western side, Bornholm Basins, the Bay of Gdansk and Gotland Basin situated at the eastern side (Bulczak, et al., 2016). The theoretical residence time of water in the Baltic is approximately 32 years. It is mainly physical processes which control water exchange in the Baltic Sea. In the southern part, such processes are directed mainly towards the east or north-east, with a counter current in the northern part of the Baltic. Correspondingly, less salty surface water is running-off along the northwest coast into the North Sea (Schiewer, 2008). In comparison to the oceans, salinity in the Baltic Sea, as a sea with limited contacts with the ocean, is different and more varied. The surface water is characterized by specific layout: with approximately 18 – 28 PSU in Kattegat, 10 – 20 PSU in Danish Strait, 6 – 10 PSU in the Baltic Proper and lower about 4 PSU in the eastern part of Gulf of Finland and Bothnian Bay. Salinity of the surface water is a consequence of the relation between components of water balance (positive climate balance and abundant inflow of fresh water into the sea). Characteristic for the Baltic Sea is the two-layer distribution of salinity in the vertical profile in which it is possible to distinguish the upper isohaline layer which is less salty and the more salty lower one. Those two layers are divided by halocline, within which there are significant changes of the salinity. Such arrangement is the same in the whole Baltic area, it is spatially varied. Halocline is observed at different depths in different basins. In mediocre situations on the longitudinal profile of the Baltic Sea -

from the Kattegat to the eastern end of the Gulf of Finland as well as from the Åland Sea to the northern coast of the Gulf of Bothnia - salinity is decreasing, and the isohalines gradually diminish. While diverging from the Danish Straits, densification of isohaline is decreasing, indicating the progressive reduction in the vertical distinction of salinity caused by a small inflow of more salty waters. In the deeper layer salinity is 30-100% larger than on the surface. There are characteristic clusters of more saline water in the bottom densities. The more salt water in them, the higher the density, isolating the dents (hollows) from the environment, makes circulation more difficult, and affect the environment conditions (Cyberski, 2011).

The salinity influences oxygenation of the bottom sediments and deeper water layers. The Baltic Sea is naturally prone to hypoxia due to a restricted water exchange with the ocean and a long residence time above 30 years. The dense saltwater inflows brings new supplies of oxygen to bottom waters, but at the same time enhances stratification, creating larger bottom areas that experience hypoxia. (Carstensen, et al., 2014). According to the report given by Swedish Meteorological and Hydrobiological Institute (Hansson & Andersson, 2013) there occurs hypoxia in the Baltic Proper, anoxic conditions affected approximately 15% of the bottom areas in the Baltic Proper, including Gulf of Finland and the Gulf of Riga. Better oxygen situation is in Bornholm Basins, Arkona and southern Eastern Gotland Basins, where due to small inflows from the North Sea the oxygen conditions may temporarily improve (Figure 2). The inflow of oxygen seems to be important for the apparent oxygen removal. The inflow gives sufficient supply of oxygen to balance the oxygen removal. The oxygen budget suggests the deepwater inflow to be the main supply of oxygen except for periods with stagnant conditions in which case the diffusive supply from surface waters is dominant (Pers & Rahm, 2000).

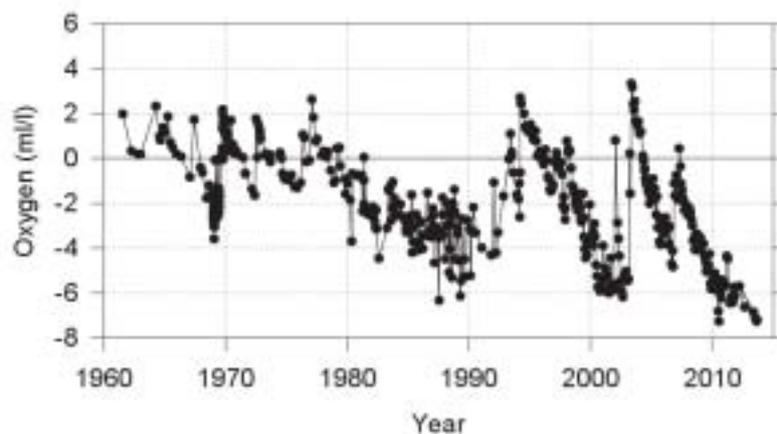


Figure 2. Oxygen at Eastern Gotland Basin, 1960 – 2013 (Hansson & Andersson, 2013)

Not only halocline has influence on oxygen concentration in the sea water, also nutrient concentration such as nitrogen and phosphorus may change decline the amount of oxygen in the bottom waters. Falkowska (Falkowska, et al., 1998) during research led in the Gdansk Deep, observed that during increase of phosphorous and nitrogen compounds under the halocline there was significant fall in oxygen content. They observed negative correlation between those compounds, what was also confirmed by Gustafsson (Gustafsson, 2001). There is one more factor on which oxygen level depends – temperature. The increasing bottom water temperature may result in more frequent occurrence of oxygen depletion even if other forcing variables such as water exchange or nutrient supply, remain constant.

During cruise on assessment of corrosion of chemical munitions dumped in the Baltic Sea on research stations, several parameters were measured: dissolved oxygen concentration, salinity and temperature. In the area of Little Belt oxygen concentration in the bottom layer was about 3,22 ml/l, which indicates the depletion of oxygen in the bottom layers. There were also termocline observed on the depths of 12 – 24 m, and halocline (Figure 3). Previously depletion of oxygen also was noted by (Ærtebjerg, et al., 2003), who stated that it was dependent on temperature and supply of organic matter from phytoplankton

primary production. An inflow of oxygen was supplied to the bottom water during inflow from Skagerrak and vertical mixing of water column (Pers & Rahm, 2000, Ærtebjerg, et al., 2003).

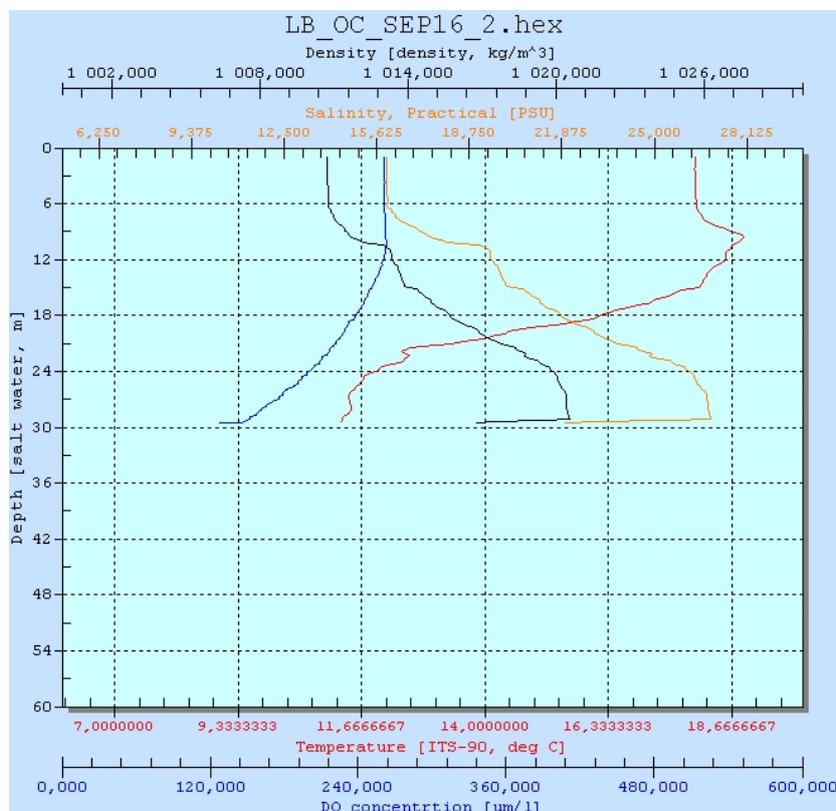


Figure 3. Dissolved oxygen, salinity and temperature in Little Belt.

Small amount of oxygen may induce grow of microorganism (bacteria, archaea and fungi) that mineralized organic material which accumulates in marine sediments. This is due to the fact that depending on oxygen conditions the organic matter degradation can occur via various pathways and with different intensity. The oxic zone is, however, only mm-to cm thick and much of the organic matter mineralization takes place within the anoxic sediment. When oxygen has been depleted or entirely consumed other oxidants are used in the deeper sediment layers, i.e. Mn (IV) oxide, nitrate, Fe (III) (hydr)oxides, sulfate and carbon dioxide. In the areas where the dissolved oxygen concentration in near-bottom water drops below $2\text{ml}\cdot\text{l}^{-1}$, sulfate reduction becomes the dominant pathway for mineralization of organic matter reaching the seafloor. Hydrogen sulfide, which forms in this process, may diffuse to near-bottom water where it is re-oxidized. It can also react with iron (II) resulting in the formation of amorphous iron monosulfides and subsequently, thermodynamically more stable, pyrite. Hypoxia also stimulates nitrogen accumulation in the ecosystem, which is connected to the inhibition of denitrification and anaerobic ammonium oxidation (anammox). This is due to the fact that nitrate produced during nitrification is a substrate in both aforementioned processes, and that nitrification can only occur under oxic conditions. Moreover sulfate reducing bacteria (SRB), ubiquitous in marine sediments, have the genetic potential to fix molecular N (Pers & Rahm, 2000, Lukawska-Matuszewska & Kielczewska, 2016).

Organic matter mineralization using a variety of oxidants is influencing the evolution of pH in marine environment. According to Ulfso et al. (2011) effects from biogeochemical processes on the evolution of pH are therefore predicted to be most pronounced along the redox gradient following the transition between oxic and anoxic conditions in low-salinity environments where there is a wide range of reactants and limited buffer capacity (Ulfso, et al., 2011). Research led in the Gotland Deep showed

that concentration of oxygen, pH reflects the combine effect from physical process and biogeochemical activity (Ulfsbo, et al., 2011). In the Baltic Sea pH of water varies between 7,247 below halocline to 8,5 on the surface. This may indicate limited microbial activity and organic matter mineralization. Also pH of the samples taken during the cruise varies from 8,26 – 6,72 (Table 2). In the little Belt (station LBOCSEPT16-1) change in the pH coincided with the gradient in oxygen concentration. In the bottom water with low oxygen or anoxic conditions, pH was low (~ 6,72).

Table 2. pH measurement in the Baltic Sea (September 2016)

Station	Water	Deeper sediment layer	Surface sediment layer
KHOCSEP16-5	8,18	7,32	7,26
PBOCSEP16-1	8,58	-	-
KHOCSEP16-1	8,26	-	7,01
RSOCSEP16-1	8,07	8,22	7,95
LBOCSEP16-2	7,66	6,84	6,72
PBOCSEPT16-1	-	7,65	7,95

4. CHEMICAL WARFARE AGENT SHELL COMPOSITION AND CONDITION

Place of deposition of chemical munitions in Baltic Sea are characteristic of low oxygen concentration. Depending on the area in which chemical munitions were sunk, they may be covered by mud or entirely exposed. In literature there is a lack of information on the composition of the casing of munitions. In research carried out in Hawaii concerning the retrieval and corrosion analysis of discarded military munitions in ocean water were the projectiles were retrieved using a Remotely Operated Underwater Munitions Recovery System from the shallow waters of the Waianae Coast. Using Optical Emission Spectroscopy (OES) the elemental composition of the steel and copper samples that were cut from the steel projectile casing and copper driving band were determinate (Table 3).

Table 3. Elemental compositions (wt.%) of the steel and copper samples from the projectile (Li, et al., 2016)

Elements	C	Mn	P	S	Cr	Si	Ni	Mo	Cu	Al	Fe
Projectile steel	0.7	0.55	0.02	0.013	0.03	0.1	0.08	<0.01	0.1	0.01	Balance
UNS G 10690	0.65–0.75	0.40–0.70	0.040 max	0.050 max	0	0	0	0	0	0	Balance
Elements	P	Pb	Fe	Sn	Zn	Ni	Mn	Cu			
Projectile copper	0.0163	0.01	<0.01	<0.01	<0.01	<0.01	<0.01	99.97			
UNS C12210	0.015–0.025	0	0	0	0	0	0	99.90 min			

After the immersion in seawater, the projectile will begin to corrode and form a rust layer. Benthic organism may attach and form colonies on the rust layer, usually with the protective calcium carbonate exoskeleton. During the corrosion process, Fe^{2+} generated at anodic regions on the steel/rust interface increases the excess positive charge and also the acidity by Fe^{2+} hydrolysis. The excess positive charge at the steel/rust interface attracts Cl^- ions from seawater, rendering higher Cl^- concentration in the inner rust layers (Li, et al., 2016). Silva and Chock (2016) stated that the integrity of the munitions dumped in the Hawaii ranged from intact and nearly pristine to highly deteriorated. That state of observed corrosion varied within similar typed of munitions located in the same general area, as well as between different types of munitions distributed over a wider region. The observations were similar to those provided from the corrosion of chemical munitions in the Baltic Sea (Silva & Chock, 2016).

4.1. Possible microbial community contribution to corrosion.

As was stated in the Hawaii research, although microbial-induced corrosion and mineralization processes cannot be confirmed from a purely visual evaluation of these munitions, microbial corrosion processes appear to have occurred, as evidenced by tubercle-like growths and the presence of laminated corrosion deposits, observed on many of the dumped military munitions encountered that can cause anaerobic metal-corroding bacteria, including SRB species (Silva & Chock, 2016). The tubular corrosion features observed were compared to the tubicle or ‘rusticle’ features observed on the wreck of the RMS Titanic (Cullimore, et al., 2002). Similar corrosion structures have additionally been observed on offshore oil production infrastructure water conveyance pipes, and within groundwater wells (Silva & Chock, 2016). That kind of corrosion is reported to be of microbial origin. Additionally in the HUMMA study area there were observed formations skirt-like and pedestal features, which may be microbially-mediated (Figure 4). According to the authors, that type of sediment cementation generally results from bacterial mineralization of organic matter (or other potential electron donor source), the reduction of various available electron acceptors (e.g. nitrate, Mn (IV), Fe (III), sulfate), and the formation of carbonate minerals within sub-oxic or anoxic aquatic sediment environments.



Figure 4. Examples of corrosion skirt features observed: (a) bomb casing, (b) ammunition box, (c) aerial depth bomb, (d) discarded depth charge (Silva & Chock, 2016).

By this mechanism, sediments at the sediment–water interface would have limited cementation potential given the abundance of dissolved oxygen within these surficial sediments. However, dissolved oxygen can decline considerably within the first few centimeters of the surface and could support anaerobic bacteria capable of facilitating sediment cementation. If microbially-induced processes are in fact responsible for the formation of these corrosion skirt and pedestal features, it appears that this activity is restricted to the immediate vicinity of and/or beneath the observed dumped military munitions, as evidenced by the lack of cementation of the surrounding seafloor sediments within the study area. It is possible that the very presence of these munitions, and non-munitions objects, on the sea bottom sets a favorable environmental niche directly beneath these objects that supports anaerobic processes, including microbially-induced accelerated corrosion at the base of these objects and biogeochemical cementation of seafloor sediments beneath these objects. Some of the objects studied during HUMMA project were significantly damaged by the corrosion. However, so far it is difficult to study the corrosion underside the objects because of potential leakage, and thus it cannot be confirmed, but the diffusive release of chemicals to an anaerobic sediment environment beneath the munitions could provide a steady source of carbon and/or nitrogen to support microbial mechanism (Silva & Chock, 2016).

4.2. Possible microbial community contribution to corrosion.in the Baltic Sea

The study on biofilm development on stainless steel in the Baltic Sea water observed “mushroom” like structures of $>10\ \mu\text{m}$ in diameter, more than 100 per mm^2 . It was observed to have grown in size of the structures with increasing open circuit potential. Mushroom like structures in observed research were very often asymmetrical in shape, and sometimes had other organism attached such as diatoms and non-biological material. After 56 days biofilm structures achieved size up to 100 μm from the steel surface into the seawater. On the stainless steel different biofilm was observed – highly permeable in structure forming uniform mats not individual mushrooms. Marine oxidizing organic matter bacteria can contribute to cathodic reaction of the steel and consumption of the oxidized passive layer of the stainless steel (Mattila, et al., 1997).

Also in the Baltic Sea sulfate-reducing bacteria were observed. Despite the fact, that they are present mainly in the anoxic sediments, Bussmann and Reichardt (1991) were epizootic SRB on clam *Arctica islandica*, which can survive temporarily anoxia. As dominating bacteria strain form genera *Desulfovibrio spp* were observed (Bussmann & Reichardt, 1991). Their presence was noted also by Mudryk (2000) in the Gulf of Gdansk (Mudryk, et al., 2000). At the dumping sites there were also single macrozoobentos organism found mainly from bivalvia, priapulida, crustacean and polychaets worms. The most abundant were meifaunal organisms such as nematoda, harpacticoida, kinoryncha, ostracoda, acarina, turbellaria, polychaeta (Kotwicki, et al., 2016). There is a possibility that they also may be colonized by epizootic SRB. Bacteria from *Desulfovibrio spp.* strain as a SRB can increase the rate of corrosion in comparison to abiotic conditions (AlAbbas, et al., 2013). In the dumpsite microbiota of the near-bottom water are also represented by microorganisms mainly by genera *Pseudomonas*, *Bacillus*, *Arthrobacter*, *Achromobacter* from which *Pseudomonas* and *Bacillus*, genera were dominating (Medvedeva, et al., 2009). Those species are also involved in MIC. Thus its presence may also contribute to the rate of corrosion, especially in anoxia condition, which are observed in the dump sites.

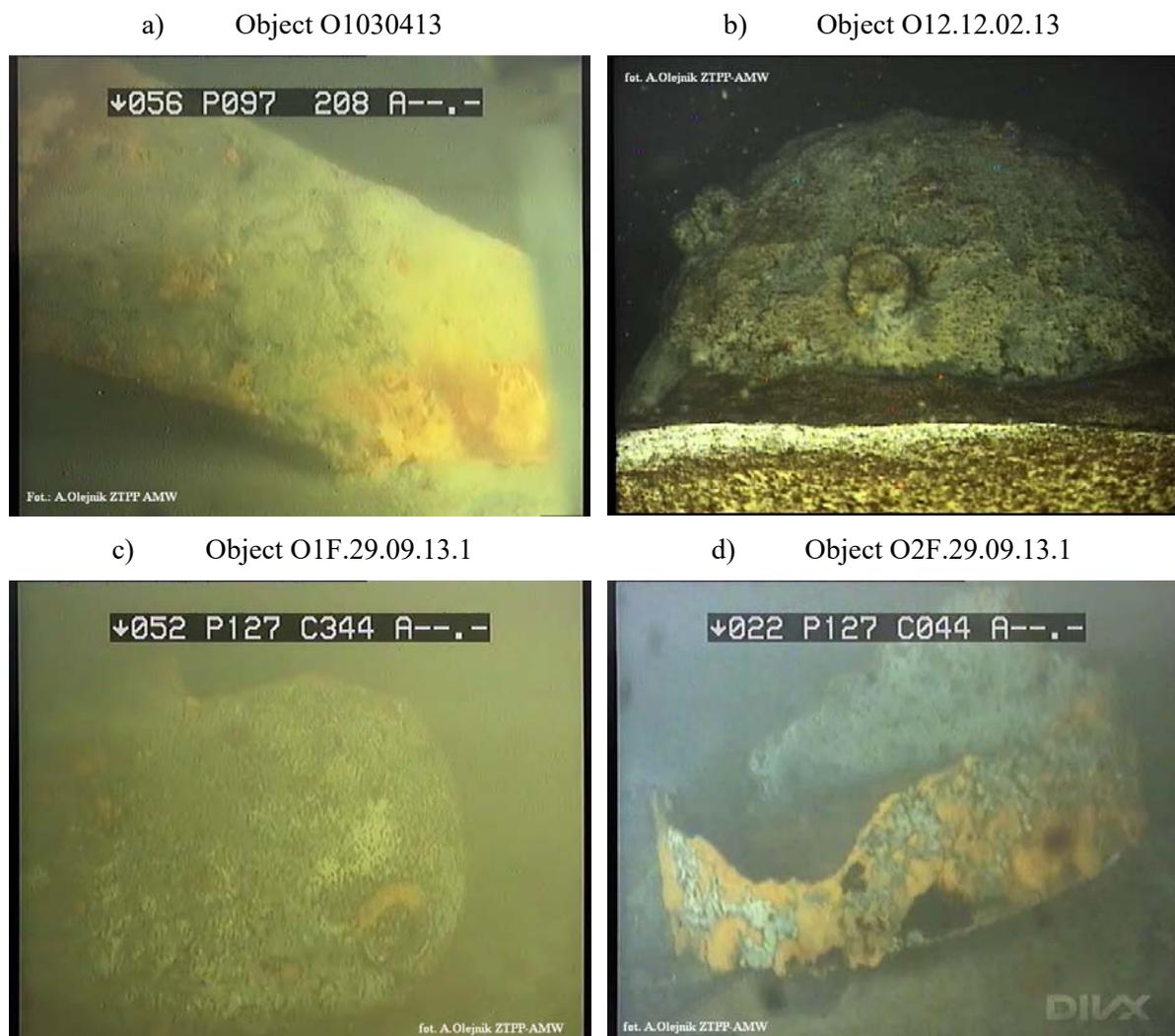


Figure 5. Examples of corrosion of post war munitions found in the Baltic Sea a: (Olejnik & Stoltman, 2013b) b: (Olejnik & Stoltman, 2013a) c, d: (Olejnik & Stotman, 2013c)

During CHEMSEA research led in years 2013-2014 several objects were found on the bottom of the Baltic Sea. Some of them were completely covered with mud and buried in the sediments, thus during operating with the ROV it was difficult to recognize the objects and also check its state of corrosion. However, there were also objects laying on the seafloor with visible sign of corrosion (Figure 5). There can be observed structures similar to “mushroom”, which can indicate the role of bacteria in the corrosion. Thus the analysis of the sediments and munitions shells for the presence of microorganisms needs to be performed in order to confirm the occurrence of the bacteria causing MIC. Unfortunately, because of the sediments and the full coverage of dumped munitions it was also difficult to see the skirt-like structures close to those observed in Hawaii, however they cannot be excluded.

5. CONCLUSIONS

It is well known that the formation of biofilms is the result of a complex series of actions, involving interactions between physical, chemical and biological processes and that different biofilm microbes respond to changes in their environment with dissimilar growth patterns. It can be expected that microbial attachment may be influenced by the nature of the passivating film formed on the alloy surfaces and by the microstructure of the alloys. Chemical composition and microstructure may have a strong influence on the composition and thickness of oxide films. However, the structure of passivating films is continuously altered with exposure time by the chemical and biological species in the environment and microbial-surface thus interactions become a more complicated process. The biofilm community structure developed on stainless steel can change with time exposure. According to research microbial diversity may be higher in biofilms developed under aerobic conditions than anaerobic conditions, however the corrosion in aerobic conditions is more severe. It is well known that microorganisms vary in their need for, or tolerance of, oxygen. Aerobes are species able to grow at full oxygen tensions and utilize oxygen in their metabolism while strict anaerobes may be inhibited or even killed by oxygen. But there is also a wide variety of microorganisms that can live between those two extreme under both oxic and anoxic conditions (Machuca, et al., 2013). The phenomena of microbial adhesion and biofilm formation on corroding surfaces are far from being simple and uniform. This is a very complicated system affected by many factors and the evaluation of the relative contributions of these factors is extremely difficult (Machuca, et al., 2013). Microbial diversity is higher in biofilms developed under aerobic conditions than under anaerobic conditions.

Hydrological conditions in the Baltic Sea are favorable to development of MIC. Parameters such pH, small amount of oxygen may provoke grow of a microorganism (bacteria, archea and fungi). This is due to the fact that depending on oxygen conditions the organic matter degradation can occur via various pathways and with different intensity. Although there is lack of information on microbiological influenced corrosion, and this area is not yet fully developed. Currently research on the rate of corrosion is being conducted within DAIMON project, however microbiological corrosion is not included. Taking into account the threat posed by chemical munitions buried at the bottom of the Baltic Sea, attention to the problem of microbial corrosion will allow you to assess the rate of corrosion more accurately and predict the future effects and time of CWA spreading the marine environment.

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