

DETERMINATION OF THE CHEMICAL COMPOSITION OF SHELLS OF CHEMICAL MUNITIONS IN THE ESTIMATION OF THE RATE OF CORROSION OF CHEMICAL WEAPONS DUMPED IN THE BALTIC SEA

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Abstract

About 15 000 t of chemical warfare agents placed in about 600 thousand pieces of ammunition and containers, were sunk in the Baltic Sea. The ammunition – mostly artillery shells and aerial bombs and containers – mainly barrels. Ammunition and containers undergo slow corrosion, which leads to releasing toxins into the environment. The corrosion rate depends on numerous environmental factors as well as on the type of ammunition bodies, material and container walls. This article presents the results of previous studies – determination of the chemical composition of munitions bodies and containers.

Key words: *chemical munitions, chemical warfare agents, corrosion, Baltic Sea*

1. INTRODUCTION

Chemical ammunitions were first used on the mass scale during World War I. Since then, countries engaged in military conflicts have extremely often used this type of new and very effective weapon. The greatest amount of it was produced before the beginning of and during World War II. Despite preparations made for a chemical war, during World War II none of the belligerents used chemical weapons in combat actions. For this reason huge quantities of them remained in many countries' warehouses. It is estimated that, after the war, chemical weapons were owned by about 60 countries (Konopski, 2009) and the world wide reserves of warfare chemical agents (CWA) were evaluated as minimum 500 thousand tons (Robinson & Leitenberg, 1971). In Germany there remained about 100 thousand tons (Makles & Śliwakowski, 1997), in USA about 146 thousand tons of CWA, in Great Britain about 55 thousand tons, and the reserves of the Soviet Union were evaluated as minimum tens of thousands tons of CWA (Konopski, 2009). Significant amounts of CWA were also in the possession of Japan, Italy and France. The owner countries kept considerable amounts of the already produced CWA in their military arsenals. This was not the case of Germany. Under the Potsdam Agreement, the arsenal of chemical weapons of the Third Reich was seized by the allied troops with the recommendation of destruction. Dumping was the easiest and cheapest way of getting rid of toxins. Most of the German chemical weapons were dumped in the Northern and the Baltic Sea. Along with the process of destructing the German chemical weapons, the allies also got rid of their old or decomposed ones.

As it turned out over time, munition dumping did not solve the problem. The ammunition lying on the bottom has become a problem for contemporary marine economy and tourism. The exploitation of the sea bottom (marine industry, construction of wind farms, dredging works, construction of underwater gas pipelines, lying power cables) in the vicinity of dumping areas connects with the risk of displacing the ammunition and releasing warfare agents to the environment and its contamination. Bottom fishing causes risk of ammunition sweeping, exposing of the fishermen's health or displacing it in other regions, and in the effect enlargement of the area of dumped chemical munition. These and many other factors force countries, in whose waters the dumping was carried out, to counteract those threats. One of the methods is the extraction of outdated chemical ammunition and containers filled with CWA, and destruction on land or sea. Specially prepared devices are used for this purpose. Many countries have practiced such activities for several years. They are, for example, Japan, Belgium, Italy or USA. However, it should be noted here that the condition for clearing the sea bottom of the chemical munitions is good technical condition of chemical ammunition or containers filled with CWA.

In order to evaluate the technical condition of chemical ammunition dumped in the Baltic Sea, one has to evaluate its corrosion degree. Except for the environmental factors (oxidation of the bottom waters,

water solution pH, water temperature and salinity, pressure and dynamics of bottom waters), time, which the ammunition spends in water and type of the ammunition, have the influence on degree of corrosion. The German chemical ammunition was dumped in 1946 – 1947, that is about 70 years ago. Chemical munitions were contained in various means of transport: bombs, missiles, grenades, mines, etc. Although, not all stockpiles of CWA were placed in ammunition. Especially at the end of the war significant part of CWA was also kept in barrels.

There is no information in available literature about the chemical composition of material, of which bodies of the chemical ammunition or barrels, in which CWA were kept, were made. Material is mostly described as a steel. Taking into account the fact of various steel corrosion resistance depending on the chemical composition, evaluation of technical condition without the knowledge of the steel type is loaded with a big mistake. The primary goal of the article is to determine chemical composition of steel bodies of chemical ammunition and barrels, also determining the technology of its performance. The information will enable, in the future, conducting corrosion researches on the materials with features and composition similar to those, from which chemical ammunition was made, and in the result proper estimation of technical condition of chemical weapon dumped in the Baltic Sea.

2. DUMP SITES

Dumping as a method of destruction of chemical ammunitions, was used until the beginning of the 1970's. Chemical weapons were dumped by, among others,: USA, Great Britain, France, Japan and Russia, by placing them in the nearby seas and oceans (Fabisiak, et al., 2012), sometimes also inside the country: in lakes and rivers (Long, 2009). It is estimated that, this way of destruction was performed by 40 countries – owners of chemical weapon (Carton & Jagusiewicz, 2009). It is evaluated that, in the seas and oceans one dumped over 1 million tons of chemical ammunition, and only USA, from 1918 to 1970, dumped about 350 000 tons (Smart, 1997).

2.1. Chemical ammunition dump sites in the world

Currently, the dumped chemical weapons can be found in various amounts in oceans, seas, lakes and even rivers. It was very often dumped mixed with conventional weapon, making these areas more dangerous. Chemical weapons were often dumped near the places, in which they were gathered, so that these operations could be as cheap as possible. They were dumped in Atlantic, Pacific and Indian Ocean, at the coasts of north and east Canada and United States, in Gulf of Mexico, the coast of Australia, New Zealand, India, Philippines, Japan, Great Britain and Iceland, at the Caribbean, Black, Red, Mediterranean, North and Baltic sea. Currently there are 127 areas of chemical ammunition documented in detail, in which USA only performed 74 droppings (Ong, et al., 2013). The list is still open. It is assumed that, there are over 300 chemical ammunition dumping sites. Areas of chemical munitions dump sites are presented in the Figure 1.

Dumping the chemical ammunition was not a safe method of its reprocessing. The intense use of the seas, exploitation of their bottoms have led to more and more frequent encounters with ammunition filled with deadly poisons. The dumped weapons again became a problem. There were more and more situations when chemical ammunition or released toxins were fished up with catch. More and more people connected with the sea were registered with burns or poisoning by those agents. Ammunition is increasingly being thrown into the beaches, causing them to be contaminated, thereby endangering tourists and coastal residents. The problem of the dumped ammunition came back not only to the countries which were destroying it, but also touched other coastal countries, on which waters the ammunition was dumped.



Figure 1. Selected areas of chemical munition dump sites (Andrulewicz, 2011).

Nowadays the problem of the chemical weapons lying on the bottom of seas and oceans has to be solved by, among others, Americans and Canadians as off their coasts were dumped over 27 000 tons of CWA and over 400 000 bombs and rockets filled with poisonous gas. Especially dangerous are 8 000 tons of poison dumped in the area of Hawaii (Carton & Jagusiewicz, 2009). Australia also copes with the problem of dumped chemical ammunition, as they had dumped off the eastern part of its shores over 21 000 tons of CWA. Japan has the same problem, between 1945 and 1948 they dumped over 6 600 tons of CWA near the mainland. So far, Japanese research has verified 44 locations of chemical weapons dumping on its coast, but it is estimated that there are still about 140, many of which can be found in inland waters: lakes and rivers (Walker, 2012).

Sea areas of Europe were also influenced by contamination with chemical ammunition. On the shallow coastal waters of Belgium, at the sandbank “Paardenmarkt” 35 000 tons of ammunition were dumped, of which 1/3 was ammunition filled with CWA (about 500 tons of CWA). One of the dump sites is located almost 1,5 km from famous Belgian health resort Knokke-Heist (Francken & Hafez, 2009). About 1 million tons of ammunition was dumped in the Beaufort’s Dyke trench at the depth from 200 to 300 meters and maximum width of 3,5 km, at the part of 50 km between Scotland and North Ireland, including also large amount of chemical ammunition. The place was considered the largest underwater dumping site of ammunition near the Great Britain (Carton & Jagusiewicz, 2009).

2.2. Chemical ammunition dump sites in the Baltic Sea

About 300 000 tons of chemical ammunition was found after II World War in the area of Germany. It was assembled in the port of Wolgast, and from there a special transport was planned to transport it and dump in one of the oceans at a depth of at least 4 km. For this purpose one set the area of Faroe Islands at the Atlantic Ocean. Although, the operation was not successful, mainly because lack of proper vessels for the transport of dangerous substances and high costs. Finally, a decision was made to dump the poisonous substances in the Baltic Sea. Various dumping techniques were used: dumping small amounts from individual ammunition, barrels, canisters, to huge bombs, rockets, and often even entire ships loaded with chemical ammunition and CWA. The operation of dumping post-war chemical ammunition in Baltic Sea was conducted until 1947 (Fabisiak, et al., 2012). Eventually almost all German weapon seized by allies was dumped in the Baltic Sea. It is evaluated that, in Baltic one dumped, in total, from 360 000 to 385 000 tons of ammunition, from which over 40 000 tons was chemical ammunition including about 13 000 tons of CWA (Carton & Jagusiewicz, 2009). The weapons were dumped in the southern-east part of Gotland Depth (about 2 000 tons), in eastern part of Bornholm Depth (about 32 000 tons), in Mały Belt strait (about 5 000 tons), and in Mäleskär area, east of Sweden (about 20 000 tons)

(HELCOM, 1994). Moreover, it was confirmed that, chemical munition was also dumped in the areas on the east (about 8 000 tons) and southern-west (about 15 000 tons) from Bornholm. Until this day neither the amount, nor the type of dumped chemical ammunition and CWA, has been verified (Kasperek, 1999).

Chemical munition was dumped in Baltic Sea long after 1947, by the armies of former East Germany and Soviet Union. Unless in the case of USSR these activities were not documented, and the amount and type of CWA verified (Kasperek, 1999), in the case of East Germany declassified documents show that from 1959 to 1965 about 60 tons were dumped in the east area, and 120 tons in the southern west area from the island of Bornholm, mainly bombs, missiles and barrels containing sulfur mustard, phosgene, adamsite and CLARK I and II (Knobloch, et al., 2013).

The collected documentation and statements of witnesses indicate that, the amount of dumped agents can be greater, and droppings were performed also in the other regions of Baltic Sea. It is assumed that, the ammunition was dropped already during the transport to the designated dumping sites. Research conducted since 2011 within the framework of project CHEMSEA presented that, CWA is located also in the Gdańsk Depth, which was, until recently, assumed to be the area of dumping only conventional ammunition. Official and unofficial areas of chemical ammunition dump sites are shown in the Figure 2.



Figure 2. Areas of chemical ammunition dump sites in the Baltic Sea (Bełdowski, et al., 2014).

3. ESTIMATED TECHNICAL CONDITION OF DUMPED CHEMICAL AMMUNITION

It is evaluated that, CWA were located in about 600 000 pieces of ammunition and containers (barrels, canister). Chemical ammunition mainly consists of artillery missiles, aerial bombs (50, 250 and 500 kg), mines, makeshift mines, candles and smoke grenades. Containers are mostly barrels and canisters. The amount and type of dumped, in Bornholm Deep, chemical ammunition and containers filled with CWA, is shown in the table 1. Theoretically evaluated speed of overall corrosion of metal bodies of ammunition and containers is 0.05 – 0.1 mm in a year (Witkiewicz, 1997). Local and contact corrosion can be much faster. Taking the above into account, we can evaluate that, the thickness of ammunition bodies and walls of containers decreased by 3.5 – 7 mm in relation to the original thickness.

The speed of corrosion is conditioned by the environment in which the ammunition is located, and also the type of material, of which the ammunition and containers were made. On the basis of theoretical considerations, taking into account thickness of the ammunition and containers walls, time after which the toxic agents can penetrate into environment was evaluated from 8 to 390 years (Witkiewicz, 1997). It appears that, the process of penetrating of toxic agents into the sea water last for a while and it will

still take a very long time. The course of this process depends, mainly, of the type of the ammunition or containers, in which the toxic agents were located. For instance, time in which the toxic agents can extract from the thin-walled contained was evaluated from 8 to 30 years, and from thick-walled artillery missiles – 150 mm from 100 to 390 years (Witkiewicz, 1997).

Table 1. Number and type of objects in Bornholm Basin in 1947 (Missiaen, et al., 2010)

| Type of CW | S-mustard | Other As-cont | Adamsite | CN | Others | Total |
|----------------------|-----------|---------------|----------|--------|--------|---------|
| Aircraft bombs | 65 779 | 8 338 | 7 388 | 4 785 | - | 86 290 |
| Artillery shells | 302 926 | - | 29 639 | 49 702 | - | 382 267 |
| High-explosive bombs | 31 442 | - | - | - | - | 31 442 |
| Mines | 9 590 | - | - | - | - | 9 590 |
| Encasements | 487 | 1 434 | 693 | - | 55 | 3 166 |
| Smoke grenade | - | - | 32 250 | - | - | 32 250 |
| Cans | - | - | - | - | 7 234 | 7 234 |
| Containers | - | 924 | - | - | - | 924 |
| Drums | - | - | 6 927 | - | - | 6 927 |
| Total | 410 224 | 10 696 | 76 897 | 54 487 | 7 786 | 560 090 |

4. HYDROLOGICAL CHARACTERISTICS OF DUMP SITES OF CHEMICAL WEAPONS IN THE BALTIC SEA

Current research shows, that the chemical ammunition was dumped not only in deep-water zones of Baltic, but also at the shallower waters. Therefore, when evaluating the speed of corrosion we should take into consideration various environmental conditions that can influence corrosion processes. For analysis of this problem, depending on the hydrological conditions associated with the influence of the rippling of sea currents, Baltic bottom was divided into three zones: deep-water zone (below 60 m), middle zone (10 – 60 m), which extends between depths and coastal zone, and surf zone (strip of coastal zone from the beach to the depth of 10 m) (Andrulewicz & Wielgat, 1997).

4.1. Deep-water zone

Currents capable of moving large surface sediments at considerable distances can occur in Bornholm and Gotland Deep (ICES/HELCOM, 1997). Sedimentation tempo is, in this area, on the average about 1mm/year. Although, sedimentation can be periodically disturbed by stronger currents, but not stronger than 20 cm/s (Andrulewicz & Wielgat, 1997). It means that, dump sites of chemical ammunition can be both covered with the layer of sediments and entirely exposed.

The center of the dump area in Bornholm Basin is at about 20 Mm east from the Bornholm Island, and its surface is evaluated on about 256 square miles. The depth of the water region in this region vary from 70 to 105 m, and most of the bottom is covered with mud of thickness of 5 – 6 m. Waters at the water region are stratified: upper layer of thickness of 50 m, is brackish water with salinity of 7 PSU, and bottom layer is water with salinity of about 16 PSU, originating from inlets of North Sea. The stratification effectively inhibits the vertical exchange of water. Vertical exchange of bottom layer waters is also slight, because bottom waters at the Bornholm Basin are mostly weak. Temperature of bottom waters during the year varies from 5 to 6°C, and its oxidation is poor, even hydrogen sulfide is present occasionally. Therefore, it can be assumed that reduction conditions occur in bottom sediments, what reduces tempo of corrosion of metal containers and is conducive to long-lasting preservation of

ammunition in unchanged condition. Physicochemical parameters in area of Bornholm Deep is presented in the Figure 3a.

In the dump area in Gotland Basin the depth of the sea is between 70 and 120 m. Hydrographic conditions there are similar to the conditions observed in Bornholm Basin, with slightly lower values of bottom water salinity – to 12 PSU. Stratification of water masses is very stable. Mostly weak bottom current occur here, although, similarly to Bornholm Basin, periodically strong currents occur – over 20 cm/s, what cause, that chemical ammunition and CWA containers can be in some periods covered with thin layer of mud, in other – entirely exposed. Physicochemical parameters in area of Gotland Deep is presented in the Figure 3b.

Taking above into account, chemical ammunition located in deep-water zone, can still lay there untouched. It is probably immersed in mud or covered with a thin layer of it, we also cannot exclude that it can be exposed.

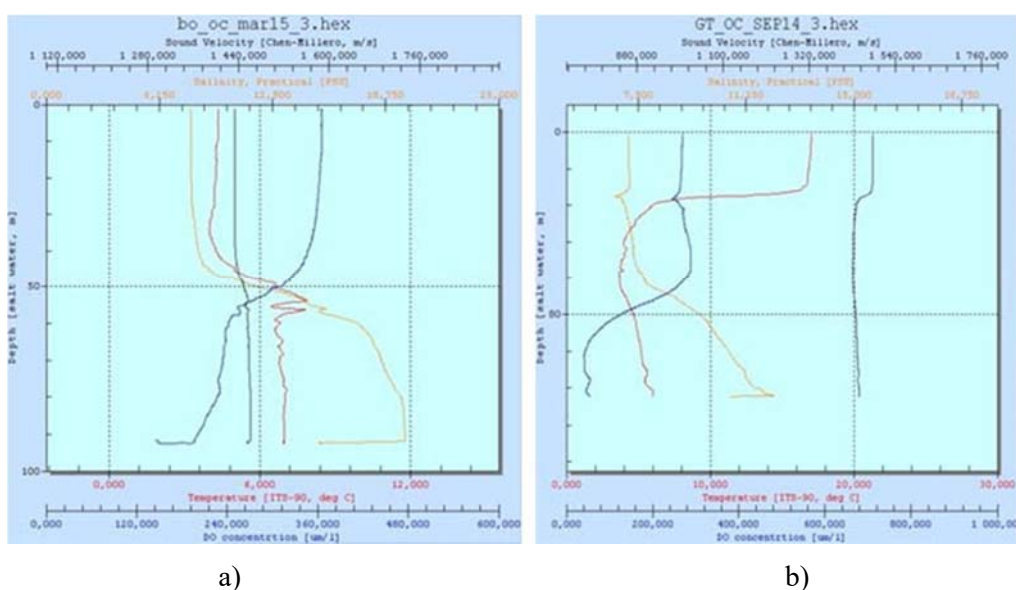


Figure 3. Physicochemical parameters in area of a) Bornholm Deep, b) Gotland Deep.

4.2. Middle zone

The chemical ammunition located in this area originates from dropping, which took place during the ammunition transport to target dump sites in Bornholm and Gotland Deeps. Probably, there is also part of ammunition dumped in wooden chests which drifted into shallower sea areas. It is not excluded that there is also ammunition loaded with deep-sea fishing nets or fishermen caught while fishing in munitions areas (areas where fishing in the bottom zone is prohibited) and then discarded in other areas. Due to meaningful dynamics of middle zone waters the permanent sedimentation does not take place here, therefore, ammunition is not covered in mud. Wave impact can reach up to a depth of 40 m. Also strong currents, over 40 cm/s take place here, although, their impact is too poor to cause horizontal movement of heavy objects. Because of the movement of water masses above the bottom, the phenomenon of unconditioned immersion of heavy objects in sand at the bottom occur. The zone is also intensively swept, therefore, war originated objects can easily get into fisherman's nets. Due to the fact that, layers of water of this zone are located over thermocline, oxidative conditions occur, what favors the corrosion of metal containers (Andrulewicz & Wielgat, 1997). Physicochemical parameters of the area of Słupsk Furrow are shown in Figure 4.

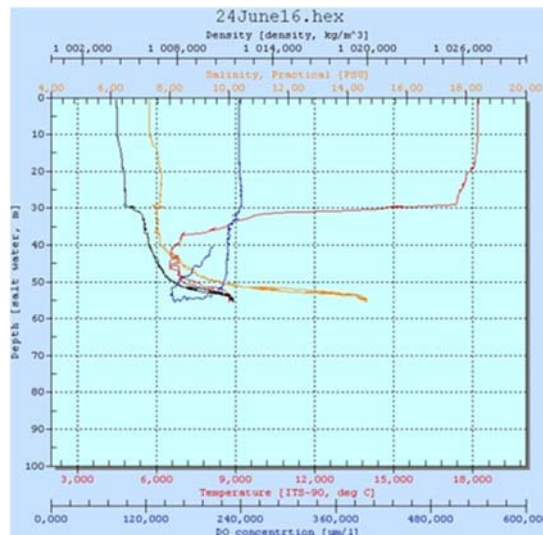


Figure 4. Physicochemical parameters of Słupsk Furrow area.

Southern regions, and also southern east of Bornholm, are relatively shallow parts of the sea (depth of 30 – 40 m). The waters are of salinity about 7,5 PSU and temperature of water conforms with seasonal changes of air temperature. They are mostly well mixed in the whole capacity.

To sum up, chemical ammunition in this zone can be covered in sand just below the sediments layer. Missiles, that immersed earlier and deeper, probably have deep corrosion pitting, and those which immersed later and shallower probably corroded entirely. Hardened blocks of mustard gas of specific light weight probably do not immerse in bottom sediments and can get into fisherman's nets during sweeping.

4.3. The Little Belt

In straits, gulfs and reservoirs of the Baltic Sea are other conditions than in the open sea. Sea depth in area of the Little Belt is about 30 m. The bottom is covered in mud of thickness to 8 m. Bottom sediments accumulate in this region in tempo of 1 – 2 mm per year. Thus, after 70 years, the thickness of the sediment layer can reach 14 cm. Surface current flows in north-east and south-east directions with velocity from 0,5 to 1,0 knot (Andrulewicz & Wielgat, 1997). Physicochemical parameters in region of Mały Belt at the area of dump sites of conventional and chemical ammunition is shown in the Figure 5. Most of the chemical ammunition from the Little Belt strait was extracted and destroyed. Possible remains sank into bottom sediments.

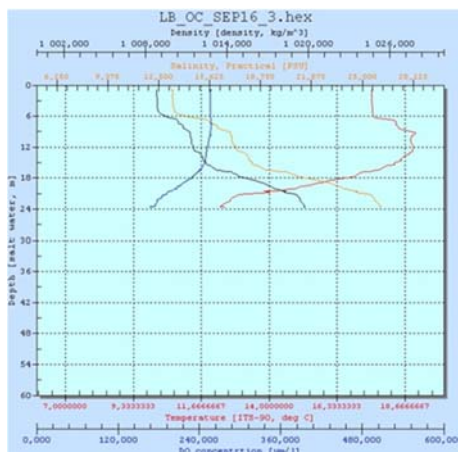


Figure 5. Physicochemical parameters in region of Mały Belt at the area of dump sites of conventional and chemical ammunition

4.4. Surf zone

Stretching along the shore and reaching the 10 m isobath surf zone has mostly sandy, partially rocky-sandy bottom. The zone is under a strong influence of waves and currents. Especially endangered on dynamic sea actions are vast parts of open shores. In the surf zone, in the time of strong storms, sea bottom continuously changes its configuration. Heavy metal objects at the bottom of this zone can be alternately covered with sand (even several meters deep) or periodically uncovered, and even ejected to the shore by storm waves and currents (Andrulewicz & Wielgat, 1997).

Missiles and other types of ammunition that were found in this zone were most likely dragged there. They could have also remained there since the time when it drifted after being dropped to the sea in wooden chests, and sank near the shore.

5. RESEARCH

Knowledge of environmental conditions in the area of dumping and type of ammunition dumped in Baltic, allow only to evaluate, often incorrectly, the course of processes of corrosion reprocessing of metal bodies of chemical ammunition or containers. Information about the forecasted time of unsealing of chemical munitions appears on the basis of such estimates available in the literature (Witkiewicz, 1997), (Granbom, 1996), (Surikov, 1996). According to the data, time, after which toxic agents will get out of the thin-walled containers (barrels), was estimated on 8 -30 years, and from artillery missiles of thicker-walls – from 100 to 390 years.

In order to precisely evaluate the processes of corrosion reprocessing, and in the same time evaluate current technical condition of dumped munition or containers filled with CWA, it is crucial to make tests in-situ in dump sites or (and) ex-situ in laboratory. Coupon corrosion measurement is thought to be the best method for those tests (Jurczak & Fabisiak, 2017). Knowledge of the chemical composition of chemical ammunition bodies (containers) will allow making samples (coupons) from steel of proper chemical composition, according to currently used materials (steel). The coupons can then be taken under corrosion testing.

There is a lack of information in the available literature concerned with the chemical composition of steel, of which bodies of chemical weapon were made. Therefore, it was decided to find out the chemical composition and production technology of ammunition from before 1946, by testing original ammunition bodies, which were used as chemical weapons. Special attention was paid to the artillery shells and chemical aerial bombs, because most of this type of ammunition was dumped in Baltic Sea. Material for testing was acquired from museums in Pomeranian voivodship: Museum of Kaszuby and

Military Devices in Goręczyno and Engineer Museum EXPLOSIVE in Dąbrówka, also Military Institute of Armament Technology in Zielonka, near Warszawa.

Tested objects: two German artillery shells Jgr. 18 A.B, 75 mm (il. 6) and 105 mm (il. 7), Russian artillery shell YKh 354, 76,2 mm (il. 8), and two KC-205 bombs (il. 9.). A Russian artillery shell was used in testing, because while dumping the German chemical weapon, Russians also got rid of their obsolete ones.

Artillery shells in the future will be used in corrosion tests – shells will be used for making coupons. KC-250 bombs were used only in non-destroying tests in order to evaluate the chemical composition of the bomb.

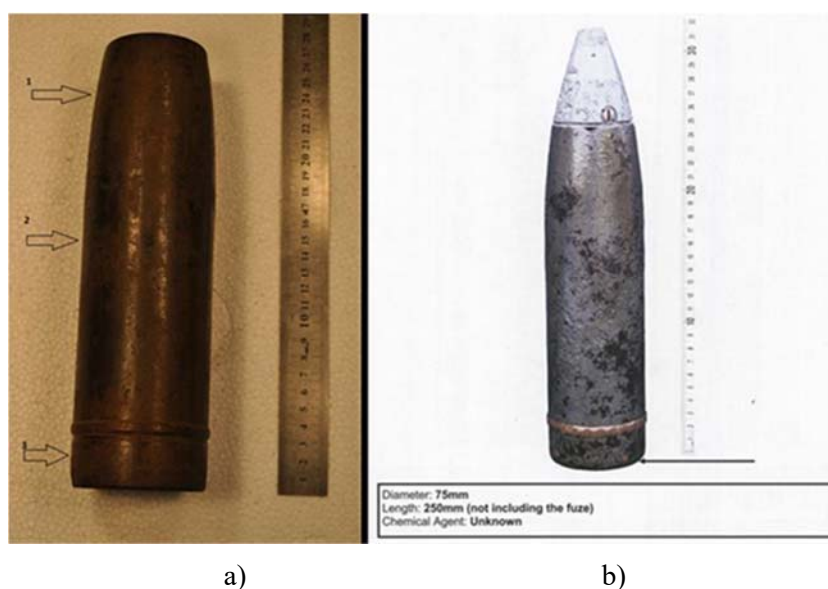


Figure 6. Artillery shell Jgr. 18 A.B, 75 mm, a) (Baranowski, 2016a), b) (Osborn & White, 2011)

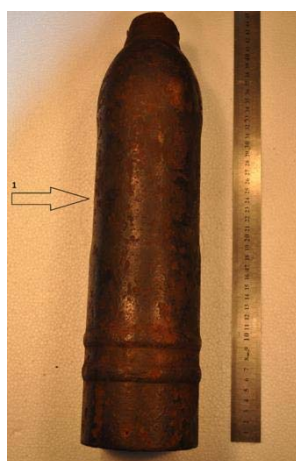


Figure 7. Artillery shell 105 mm (Baranowski, 2016b)



Figure 8. Artillery shell Jgr. 18 A.b, 75 mm, a) (Baranowski, 2016c), b) (Osborn & White, 2011)



Figure 9. KC-250 bomb (Osborn & White, 2011)

The chemical composition of steel used to make the ammunition bodies was specified with X-ray Energy Dispersive Spectroscopy (XEDS) method. The study was conducted using a scanning electron microscope system Quanta 3D FEG of FEI in Military University of Technology. Quanta 3D FEG is a scanning electron microscope, equipped additionally with an ionic column (FIB) and X-ray spectrometer EDS and WDS. EDS spectrometer is used for detection of all elements including beryllium. Its resolution is about 130 eV. Samples for chemical composition study in form of steel chips were acquainted by drilling the shell in three places: bottom, middle and top (il. 6, 7,8).

Steel type was defined by observation of the ammunition samples with XEDS method. Test results are shown in table 2. Literature data on the chemical composition of steel used to make the German conventional ammunition, are shown in Table 3. An example of the structure of artillery shell body Jgr. 18 AB, 75 mm, is shown on Figure 10.

Table 2. Chemical composition of artillery shells and aircraft bomb.

| Type of munition | Element [wt %] | | | | | | | | |
|---|----------------|------|------|------|------|------|------|------|------|
| | Fe | C | Si | Mn | S | Cu | Cr | Ni | Al |
| German artillery shell 75mm Jgr. 18 AB | 98.20 | 0.29 | 0.39 | 1.16 | 0.14 | - | - | - | - |
| Russian artillery shell 76,2mm YKh 354 | 97.27 | 0.40 | 0.35 | 1.79 | 0.20 | - | - | - | - |
| German artillery shell 105 mm | 97.71 | 0.31 | 0.30 | 1.09 | 0.22 | - | - | - | 0.37 |
| Aircraft bomb KC-250 | 98.96 | b.d* | - | 0.73 | - | 0.11 | 0.05 | 0.05 | - |
| Aircraft bomb KC-250 | 98.83 | b.d* | - | 0.74 | - | 0.25 | - | 0.07 | - |

*the collected data shows that, carbon content in aerial bombs KC-250 was lower than 1,5% (Koehler, 2017)

Table 3. Chemical composition of steel St37 (Koehler, 2017)

| Type of material | Element [wt %] | | | | | |
|------------------|----------------|-----------|-----------|-----------|-----------|-----------|
| | C | Si | Mn | S | P | N |
| Steel ST37 | max. 0.17 | max. 0.30 | max. 1.40 | max. 0.05 | max. 0.05 | Max. 0.01 |

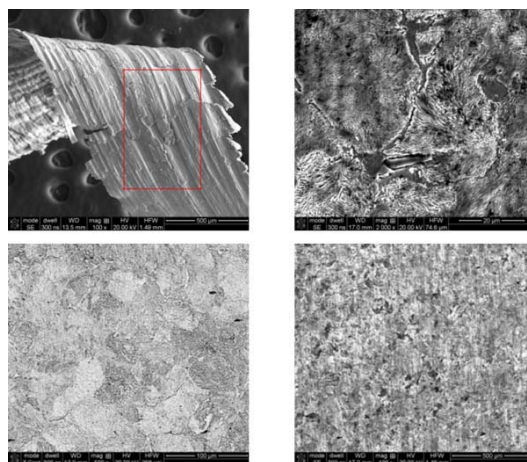


Figure 10. Steel microstructure of artillery shell body construction Jgr. 18 AB, 75 mm, with varying magnification

6. RESEARCH RESULTS

The chemical analysis of steel composition (Tab. 2) shows that, artillery shells were produced of carbon steel with carbon content of 0,3% in case of German shells, and 0,4% - Russian. The amount of carbon is characteristic of hypoeutectoid steel (carbon content below 0,8%). The structure of this type of steel consists of two components: ferrite and perlite, as the content of carbon in the steel increases, the perlite content in the structure increases. Microscopic analysis of bodies structure (XEDS) also confirmed it, it

showed that it is a steel of ferrite-perlite structure, of content $C=0.3\div0.4\%$. This type of steel is a mixture of ferrite and cementite Fe_3C of a band structure. In greater magnification bands form alternating ferrite and cementite tiles, which distance varies with the increase in cooling rate. Exemplary picture of artillery shell 75 mm Jgr. 18 AB body structure is shown on the Figure 10. It shows typical structure of carbon steel.

Structural research and hardness measurements show that the missiles were made of hypereutectoid carbon steel of carbon content 0,8%. The structural research shows typical perlite structure with visible elements of second order cementite grid after grain boundaries (il. 10). Perlite grains are dark areas of tile structure, showed on the Figure 9. Determined, average hardness value in three areas of the shell (upper part, middle and bottom – il. 5) is HV 295 (HB 279), and actual thickness of the body, determined by ultrasonic method, is 10 mm. The tensile strength limit for the body material at the determined hardness is estimated at approximately $R_m=600\div800$ MPa (Jurczak & Fabisiak, 2017). Content of silicon and manganese in steel, to upper limit value, proves that to perform artillery shells one used steel of higher quality, which is equivalent to a higher corrosion resistance of the bodies.

KC-250 aerial bombs are also made of carbon steel, but without the silicon admixture and nearly half the manganese content compared to the artillery shells. This proves that, aerial bombs were produced from the lower quality of steel, in comparison to artillery shells. It should be expected that, in this case, corrosion will proceed slightly faster. Slight amount of Cu, Cr and Ni are acceptable random admixtures e.g.: scrap metal, and do not have much influence on steel quality and its corrosion processes. Analyzed artillery shells and KC-250 bombs were general means of carrying conventional ammunition. Thickness of bodies of conventional artillery shells and aerial bombs was about 10 mm (Koehler, 2017). The same type of steel was used in performing chemical ammunition, however thickness of body walls of chemical shells and aerial bombs was significantly smaller than of conventional ammunition. Available data inform, that bodies of chemical ammunition are of thickness from 2 to 2,5 mm (Koehler, 2017). Construction of chemical ammunition was identical to conventional ammunition, differences were visible only in location of fuze and reduced amount of explosives. All other elements of construction were the same (Koehler, 2017).

Collected, but not yet published, information (Koehler, 2017) indicates that, ST37 steel was used as the main material for production of the German ammunition. It was produced by Sthalguss (cast steel), and Grauguss (grey cast iron) facilities. The chemical composition of this steel (Table 3) is very close to the chemical composition of the steel used to make the artillery shells which were tested (Table 2).

Significant elements influencing the rate and type of corrosion, are additional details of missile construction, as, for example: leading rings of missiles (il. 11). Analysis showed that, the leading ring is structurally clean copper, pressed with ferritic steel mounted directly on the body (il. 12). This material combination cause, that in sea water, beside the general corrosion, the process of galvanic corrosion will also take place in the area of the leading ring mounting.



Figure 11. Leading ring of the shell 75 mm I GR. 18 AB

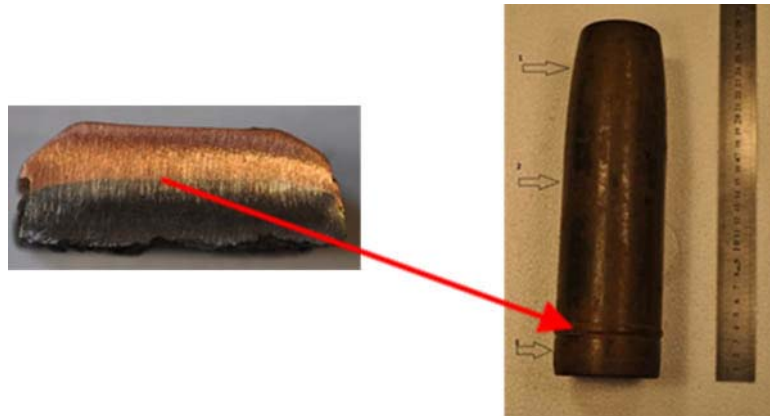


Figure 12. picture of leading ring of shell 75 mm I GR. 18 AB

However, not only the chemical composition of constructional material of ammunition body, but also the technology of its production will decide about corrosion susceptibility of ammunition. Anticorrosive protection of munition has also to be taken into account. The ammunition, including chemical, made before the war, especially that produced during it, was meant to be used as soon as it was possible after the production. That is why, it was not secured with anticorrosion agents, even for economic reasons. Yet the aspect should be taken into consideration in evaluation of corrosion reprocessing of ammunition performed after the war.

A significant fact, which has to be taken into account when evaluating the technical state of the dumped chemical ammunition, is that at the end of the war, because of the rush and savings, the steel used to make the ammunition, could be of much worse quality, and the corrosion processes can take place faster.

While selecting the steel to corrosion testing lexicon of materials science (LM) is used most often. The obtained research results showed 100% match for several dozen items of currently produced materials. Yet, most similar, in terms of chemistry, type of steel, which can be used for corrosion testing, is C 80 steel.

7. SUMMARY

Evaluation of the external and internal factors is necessary to determine the corrosion rate of construction reprocessing of ammunition dumped in the Baltic Sea. External factors are physicochemical features of sea environment, internal factors are features of constructional material, especially chemical composition and technology of its production.

Ammunition dumped in the sea can be located in three corrosion centers: water, surface layer and deeper layer, in which corrosion rate varies. Physicochemical parameters of Baltic Sea waters are determined by seasonality, but the most essential parameter determining the corrosion process is the environment oxygenation. Lack of oxygen, especially in deep water regions, in places where the ammunition is covered by mud, strongly prevents the process of corrosion.

Ammunition lying on the bottom is subjected to pressure (stress) whose magnitude is dependent on the depth. It has to be taken into consideration that hydrostatic pressure that act upon the ammunition intensifies the corrosion process (stress-corrosion).

Slight differences in pH values in chemical ammunition dump sites show that corrosion processes of carbon steel will progress at about the same rate.

Literature data shows, that St37 steel, shaped by cold extrusion, represents the bulk of the German chemical weapons.

In some cases materials used to make the component parts of ammunition bodies were not the same as the ones used to make the bodies themselves, e.g. copper was used to make leading rings. Therefore, the rate of corrosion at the point of contact of these extremely potential, in the presence of sea water, materials becomes more intense.

At the same time to perform micro-analysis and structural research from one micro area and to realistically and actually assess the chemical composition of the material within the structure mentioned above, all ammunition bodies should be tested. In this way, discrepancies in the chemical composition assessment are eliminated resulting from, for example, the retrieval of test material from different places of the ammunition body or sheet metal. Additional questions, such as micro- or hardness, are the decisive factor in questioning chemical composition.

Those tests were made in evaluating artillery shell Jgr. 18 A.B., 75 mm, where hardness at the level 279HB indicates carbon steel (hypereutectoid steel) of carbon content about 0,8%. Minimum thickness of the ammunition body of this ammunition is 10 mm and with standard rate of corrosion reprocessing in Baltic Sea waters, which is 0,05 mm/year, we should evaluate the period of tightness of this construction on about 200 years.

Samples for the corrosion tests – coupons – should also be made of original material. In selecting counterparts of the currently produced steel used in corrosion tests, one should buy steel with metallurgical certificate confirming its chemical composition and features. A lack of these documents creates further doubts.

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