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Assessment of corrosion of mercury canisters in the keel of U864

Marstrand AS

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Objective:

The objective is to evaluate the current condition of the mercury cannisters and compare with the conclusions made in 2008 made by DNV (Section 6.1 - in DNV report No. 23916-1)

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1 EXECUTIVE SUMMARY

DNV has been requested to assess corrosion scenarios relevant to mercury canisters located inside the keel of the U-864 submarine and compare with the conclusions from the previous report issued in 2008 *"Salvage of U864 – Supplementary Studies – Study No. 1: Corrosion" report no. 23916-1, revision no. 01*. The assessment considers long-term exposure conditions and potential influencing factors on corrosion of carbon steel.

The possible influence of mercury on corrosion of carbon steel has also been evaluated. Mercury is considered a poor cathode due to its strong polarizing behaviour, resulting in inefficient galvanic coupling with carbon steel. While certain mercury compounds can form in seawater conditions, there is limited supporting evidence in the literature to quantify such effects towards corrosion of carbon steel. Consequently, no additional corrosion rate has been attributed to mercury exposure.

Two main exposure scenarios have been identified as relevant: (i) canisters located inside the keel boxes containing stagnant seawater and/or sediments and (ii) canisters buried in seabed sediments outside the keel boxes. Except for canisters located close to the sea floor, the seawater/sediments in contact with canisters are predominantly oxygen-free (anoxic).

The following conclusions were drawn:

- For the canisters inside the keel boxes containing trapped seawater, the maximum long term corrosion rate for canisters located near open seawater is expected to be in the order of 0.01-0.03 mm/year. For canisters located in oxygen-free conditions further away from the interface (typically after approximately 1 keel box), the general corrosion rate will likely be 0.001-0.005 mm/year
- For canisters buried in the upper sediments, either inside or outside the keel boxes, the formation of corrosion product layers on the surface of the canisters will result in maximum expected long term general corrosion rates in the order of 0.04-0.05 mm/year. The upper sediments may support bacteria that can cause microbiological induced corrosion (MIC). MIC will typically cause localized corrosion with corrosion rates up to 0.1 mm/year. Canisters exposed to oxygen-free conditions (buried deep (> 1m) in the stiff clay sediments) with low MIC activity will likely experience corrosion rates of 0.001-0.005 mm/yr
- For canisters freely exposed to seawater on the seabed, the conclusions from the assessment done in 2008 is still applicable

Overall, the uniform corrosion rate of carbon steel canisters located in the buried keel boxes is expected to be relatively low, with rates governed primarily by environmental conditions rather than mercury-related effects. Most of the canisters are probably located relatively deep in the sediments where the environment is oxygen-free with limited microbial activity. Expected corrosion rates under these conditions are 0.001 to 0.005 mm/year. It is therefore unlikely that there will be any leakage of mercury from these canisters in the next 15 years. However, for the canisters exposed close to the interface of the sediments and the seabed, higher corrosion rates are expected, resulting in wall perforation.

These conclusions are well aligned with the DNV report 23916-1 issued in 2008.

2 INTRODUCTION

The German submarine U-864 was sunk on February 9, 1945, after being struck by a torpedo fired by the British submarine Venturer. The incident occurred about two nautical miles west of the island of Fedje in Hordaland. At the time, U-864 was traveling from Germany, passing through Norway, in route to Japan. On board was a shipment of wartime supplies, including roughly 67 tons of liquid metallic mercury (Hg) stored in carbon steel containers within the keel, according to historical records. The torpedo impact caused the vessel to break into two sections. These wreckage fragments were later located by the Royal Norwegian Navy at depths ranging from approximately 150 to 175 meters.

Several excursions were done over the years to assess the conditions of the wreck and also estimate the hazards posed by the large mercury content, that is known to have already contaminated the seabed around the torpedoed submarine. Focus has been put to identify the actual conditions of the remainder of the canisters in terms of corrosion degree, given that these are exposed to subsea conditions for more than 80 years.

DNV have been commissioned by Marstrand AS to perform a corrosion evaluation of the canisters containing mercury that are still inside the U-864 wreck. This is to assess whether these canisters will start leaking mercury as result of corrosion in the next years.

2.1 Scope of work

The scope of work is to:

- Familiarize with the DNV report No. 23916-1 and failure investigation report made by AGR Emi Team AS
- Understand the layout of the submarine and different exposure scenarios for the mercury cannisters
- Kick-off meeting to clarify objectives and scope of work, identify lacking information, facts and assumptions
- Evaluate the condition of the mercury cannisters based on current available information such as inspection data and laboratory investigation reports
- Literature review on the effect of mercury on the corrosion of carbon steel in seawater
- Identify different exposure scenarios that can affect the corrosivity of mercury steel cannisters
- Compare the current assessment with Sec. 6.1 in DNV report No. 23916-1 /1/

3 SCENARIO DESCRIPTION

After being torpedoed, the submarine was split into two parts, referred in previous documents as bow and stern parts. Some of the mercury canisters exploded together with the submarine, while others were scattered on the seabed. Some of the latter have been retrieved on previous excursions. The remainder of the mercury canisters from the U-864 are still expected to be located in the keel (Figure 1). Previous analysis stated that there were at least 2 types of canisters, but all of them were assumed to have had originally 5 mm of wall thickness /1/.

An excursion in 2014 excavated the seabed sediments to access two compartments of the keel where the canisters were expected to be /4/. However, the chambers were empty, and the only canisters found were the ones buried in the sediments that were unearthed during the excavation. In 2025 another excursion tried to map the location of the canisters by using electromagnetic data from the wreck but failed to precisely determine their location.

Previous excursions to the wreck indicated that the rest of the canisters are most likely in the bow part of the keel, as shown in Figure 2 /2/. The biggest challenge faced in this investigation is to properly determine the condition of the buried keel and the canisters, and the exact environment where they are exposed i.e., seawater, buried in sediments, etc.

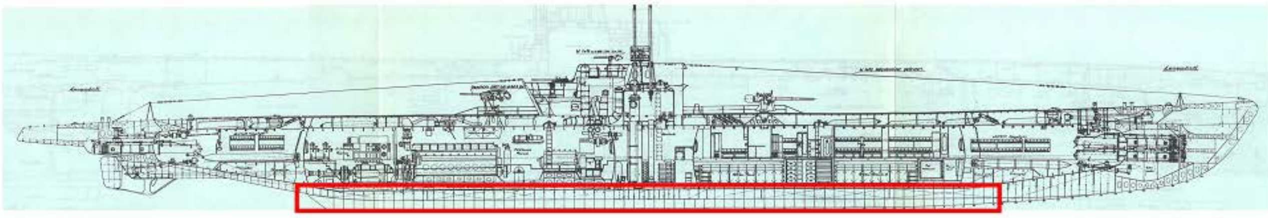

Figure 1. IX D2 submarine type. The area marked in red shows the keel, where the mercury canisters were stored /3/.

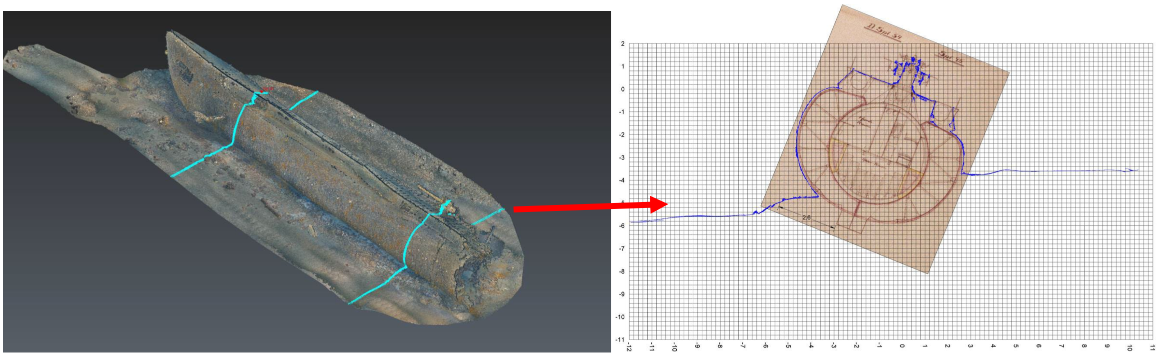

Figure 2. Cross profile of the bow part, estimating location of the buried keel /2/.

Previous reports stated that the keel is most likely completely intact, which suggests that the canisters are expected to be in the same position inside the keel chambers. A report from 2014 compared the U-864 with the structure of another torpedoed German submarine, U-534, that was salvaged in the 90's, in order to draw observation about the keel characteristics, shown in Figure 3 /3/. These are comparable since both submarines have the same type (IX D2) and both were cargo loaded in the same port in Germany (Kiel), sharing several similarities.

Figure 3. Pictures from the keel of the submarine U-534.

From the pictures it is clear that the keel had openings that allowed seawater to flood the chambers to avoid trapped air and enable pressure equalization, meaning that the canisters had been exposed to seawater at all times before being buried. Besides the assumption that the keel is most likely intact, upon burial of the structure, it is also expected that some of the sediment got in the chambers.

Thus, the most likely exposure scenarios for the mercury canisters inside the keel are:

1. Inside the intact keel - seawater from the originally flooded chamber.
2. Buried in sediments – either inside the wreck or loose outside the keel (assuming keel is not intact or sediments have been able to fill the keel).

4 ASSESSMENT

This assessment concerns only the non-torpedoed canisters that should be intact from the explosion/hit and having corrosion degradation as the only mechanism for failure. For canisters freely exposed to seawater on the seabed, the conclusions from the assessment done in 2008 is still applicable /1/.

4.1 Expected corrosion conditions for each exposure scenario

4.1.1 Inside the intact keel boxes containing seawater from the originally flooding

The canisters have been exposed to seawater before the submarine was sunk due to the holes on the keel box walls, as shown in Figure 3. The exposure time before the sinking has been short (weeks), and not enough to promote any significant corrosion damage during the transport. When the submarine was sunk, it is assumed that the seawater inside the keel boxes was trapped upon burial in the sediments, meaning that the keel boxes were sealed off from any convective supply of oxygen and organic materials. In these conditions, oxygen was rapidly consumed by microbial respiration and oxidation of reduced species. Experimental and field studies show that oxygen depletion in marine systems can occur over short time scales (hours to days), with anoxic conditions developing quickly in environments with limited mixing or diffusion /5/.

Consequently, seawater trapped within buried or sealed keel boxes of U-864 would be expected to become oxygen-depleted relatively quickly after burial, resulting in a low-oxygen or anoxic environment and correspondingly reduced corrosion rates compared to freely exposed seawater.

Anaerobic activity that would lead to microbiologically induced corrosion (MIC) is not expected to be high in this case, since the bacteria need constant supply of nutrients, and considering the sealed-off conditions it is not expected any MIC contribution to the corrosion of the canisters. There is a possibility that some keel chambers are close to the top part of the sediments, which would provide a scenario where some replenishment of seawater inside is possible. Nevertheless, in the worst case these are treated as freely exposed to seawater, and that is already covered by the report from 2008 /1/.

Since no canister has been retrieved from inside the keel up to this day, it is not possible to determine the exact general corrosion rate, but the maximum values are expected to be in the range of 0.01 to 0.03 mm/year. These rates are conservative and agree with previous report from 2008 /1/. For canisters located in oxygen-free conditions further away from the interface (typically after approximately 1 keel box), the general corrosion rate will likely be 0.001-0.005 mm/year

4.1.2 Buried in sediments

For canisters buried in sediments, these can be either loose after the impact, or still inside the keel but in contact with sediments that could have gotten in through the openings. Corrosion-wise, these 2 conditions are very similar, and will be treated as the same.

For buried structures, studies have shown that corrosion evolve over time following 2 modes; transitioning from an initial oxygen-controlled mode towards a diffusion-limited and anaerobic mode, in which nutrient transport to the steel surface is corrosion rate-controlling /6/. Figure 4 shows a typical representation of the corrosion evolution over exposure period for buried steel. Considering the information given that the canisters are located 2-4 m deep, it is assumed that no oxygen is available.

Here, MIC is more likely than the scenario discussed in Section 4.1.1 and will be dependent on the burial depth and the corrosion products coverage on the canisters. The general understanding in the literature is that MIC activity is reduced with depth, but that is highly dependent on availability of nitrogen and organic matter, which is dependent on the characteristics of the seabed soil /7/. A report from 2005 indicated that the soil around the U-864 is low in total organic carbon (TOC), which is essential for microbial activities (MIC) /8/. Also, the report supports the assumption that the canisters are likely buried in a stiff clay layer, that provides low permeability, low organic content and poor nutrient flux.

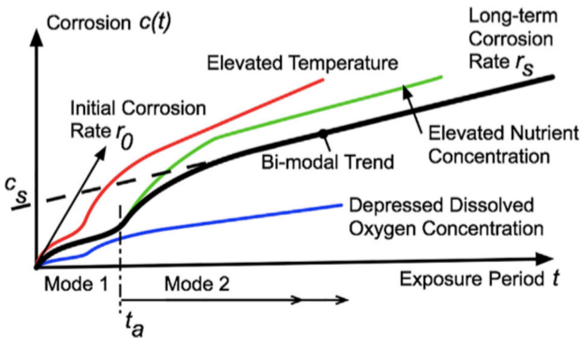

Figure 4. Schematic bimodal representation of the development of corrosion loss c(t) as a function of increased period of exposure (t) /6/.

On top of that, it can be considered that the canisters have developed a corrosion product layer over the years, that creates another diffusion barrier for organic matter supply to feed any bacteria that could promote MIC. Combining that, with the cold conditions on the seabed outside Fedje, the maximum general corrosion rates are expected to be in the range of 0.04-0.05 mm/year for buried canisters. It is likely that the corrosion rate for steel buried in stiff clay is significantly lower, e.g., 0.001-0.005 mm/year.

It should be notes that if the upper sediments may support bacteria that can cause microbiological induced corrosion (MIC). MIC will typically cause localized corrosion with typical corrosion rates up to 0.1 mm/year.

4.2 Effect of mercury on the corrosion of carbon steel in seawater

4.2.1 Galvanic coupling

Mercury (Hg) is known for its amalgamation behaviour when in contact with metals such as oxide-free aluminium, silver and gold. Its liquid state allows high atomic mobility allowing rapid diffusion of Hg into the grain boundaries of such metals. On the other hand, its effect towards carbon steels (iron) is very limited due to the strong metallic bonds found in these materials, which leads to poor solubility in Hg.

However, special attention has been raised on the possible contribution of the mercury present on the seabed acting as an accelerator of the corrosion processes on the carbon steel due to galvanic coupling. In a galvanic cell, in order to have a sustained galvanic current flowing, one metal will act as the anode, losing electrons, and the other metal as the cathode, gaining electrons. The tendency for losing and gaining electrons is highly dependent on the electron energy levels in the atoms that forms the metal. These electron energy levels are called electron shells. Each electron shell (s, p, d and f) has a maximum number of electrons that they can hold, and the more each shell is filled, the more stable and reluctant for electron transport the atom is, resulting in poorer abilities for sustaining a galvanic current.

Mercury's electronic configuration displays an electronic d-shell full of electrons, making Hg chemically stable. Due to its high atomic mass, the 6s electrons are relatively contracted and weakly shared, creating strong polarizing abilities for Hg. Therefore, although being electrochemically nobler than iron, its strong polarizing behaviour leads to large variations in potential with small galvanic currents, which would suppress any galvanic coupling, making Hg a poor electrode for the development of cathodic reactions /9/. Thus, the effect of galvanic corrosion between mercury and the steel canisters is insignificant.

4.2.2 Formation of mercury chloride

The reviewed literature indicates that oxidation of Hg in seawater/sediments is possible under bio-catalytic activity (MIC). In marine sediments, the prevailing geochemistry (particularly sulphide availability) may favour the formation of HgS rather than chloride complexes. However, there is no supported evidence in the literature that these compounds will directly affect corrosion of carbon steel.

5 CONCLUSIONS

DNV have assessed the corrosion scenarios that the mercury canisters inside the keel of the U-864 might be exposed to. Two most likely conditions are discussed: exposed to oxygen-free seawater inside the intact keel boxes or buried in sediments inside or outside the keel boxes. The following conclusions were drawn:

- For the cannisters inside the keel chamber containing trapped seawater, the oxygen-depleted environment will result in maximum corrosion rates in the order of 0.01-0.03 mm/year.
- For structures buried in the upper sediments, either inside or outside the keel, the low diffusion of nutrient supply to MIC, combined with the corrosion product layer formed on the surface of the canisters, will result in maximum general corrosion rates in the order of 0.04-0.05 mm/year
- The upper sediments may support bacteria that can cause microbiological induced corrosion (MIC). MIC will typically cause localized corrosion with typical corrosion rates up to 0.1 mm/year.

The maximum corrosion rates in both cases are expected for the canisters located near the interface of the sediment/seawater, while canisters in oxygen-free conditions (buried deep in the sediments) will likely experience corrosion rates of 0.001-0.005 mm/year.

The canisters freely exposed to seawater on the seabed are still treated as per the assessment done in 2008 /1/

The potential galvanic effect of mercury and mercury compounds to corrosion on carbon steel were also investigated. The main conclusions are:

- Mercury is a poor cathode due to its strong polarizing character, resulting in an inefficient galvanic coupling with carbon steel.

Considering the data available in the literature it is not believe that mercury speciation is a concern for the scenario assessed in this report. The current assessment agrees with the previous analysis conducted in 2008 by DNV /1/.

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