Microbiologically Influenced Corrosion (MIC)

from a Surveyor's Point of View

Discussion Paper

1. Introduction

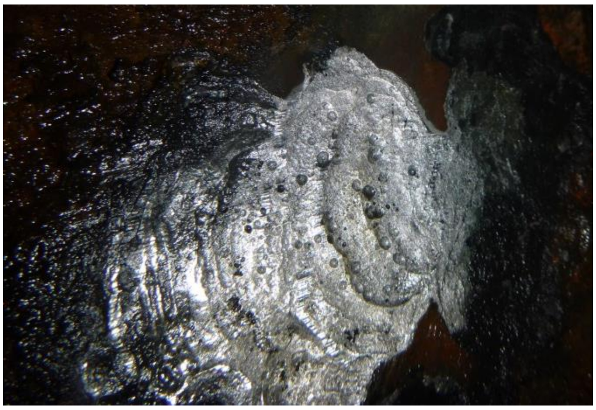
As marine surveyor, with a significant part of my work being on steel hulls and inland waterways, I often come across a specific corrosion, which has never been studied carefully in this environment and has a variety of explanations from various surveyors. This discussion paper aims to narrow down the possible causes by eliminating non-viable options and to suggest a credible alternative explanation, but most importantly, it is meant to raise awareness amongst surveyors of the symptoms of this corrosion and it's very serious effect on the structural integrity of the vessels.

2. Presentation

This corrosion is characterised by pits with a shiny metallic appearance, often surrounded by brown deposits and is found below or at the waterline.

But this becomes visible only after the hull is washed, while before the wash, the appearance is very different and does not suggest the existence of corrosion damage under the layers of biological fouling and corrosion products buildup, as shown on the picture below.

Here is a link to a video I have taken on how the corrosion damage is revealed after scraping and water wash - https://youtu.be/PpyCgR5yaYM ………and a close-up picture of the pit which was hidden under the deposits.



Very often, after the hull is washed, this pitting is found to be relatively shallow (about 1mm depth), but very large diameter individual pits, often merging into large pools.

From the surveyor's point of view, it is important that sometimes the pits are extremely deep and even have gone through the plate. I will come back to this finding later, but the pictures below illustrate a boat which was due blacking and the boatyard stopped washing it, as holes in the hull were being discovered. This boat is a very good example, on the first picture - a washed section of the hull is shown, while on the second picture, an adjacent (not washed) section is shown with plate thickness and pit depth marked in red. It is easy to see how a surveyor could miss (and in this case has actually missed) severe pitting and holing of a hull which is giving normal ultrasound thickness measurements.

This corrosion is also often found to affect the welds and creep under as demonstrated on the pictures below. In some cases, when the fillet weld between the base and side plates was ground, it was found that the corrosion has gone completely through the weld face and only the internal fillet weld was ensuring watertightness.


3. Myths

The UK surveyors community has been divided into two groups when it comes to the existence and the effect of Microbiologically Influenced Corrosion (MIC) on steel vessels; one group is sceptical about the existence of MIC in general, or is of the opinion that it occurs, but not on steel hulls in normal use, basing their views on the idea that bacteria can live only in stagnant waters. This group has alternative explanation to the symptoms and I will talk about this below. The second group is of the opinion that MIC can be found on steel hulls and although it uses scientific language in their publications, does not offer practical advice and does not analyse the problem from the surveyor's point of view. It also offers bleaching of the hull as a cure without addressing the practicalities of such treatment or the extent of its effect on the hull and on the environment.

3.1. Myth No:1 "The shiny pits are actually the bare metal surface of the hull plating caused by electrolytic corrosion or electrolysis…."

Similar symptoms have been observed by the Health and Safety Executive sponsored study on mooring systems in Scotland and the picture below is from a chain link which has no electrical contact with dissimilar metals and no external power sources had been applied there.

I have also observed the same symptoms on piling which is not electrically connected to other metals and also on a boat which had been with no batteries on board, no electric systems or power at all and not galvanically connected to any other structure for more than 2 years. The silvery deposits appeared after the wash (pictures 1 and 2 below). The fact that the silvery surface is discovered under a film/crust is also evidence that there was no currently active galvanic corrosion or corrosion caused by external source, as if that was the case, the corroding metal would have been exposed.

This silvery material is sometimes found suspended in the thick layer of corrosion products and not attached to the hull, as shown on the picture below and in this video - https://youtu.be/ebxXemW6yrQ. It comes to show that this is not the hull metal, but rather a product of a corrosion process (such as Mackinawite, Pyrite or other FeS crystalline structure associated with Sulphate Reducing Bacteria (SRB) activity.) I have also tried to polish mild steel and the surface can never be as bright as this silvery substance.

3.2. Myth No:2 “The silvery metal is the anode material (Zn or Mg) deposited on the pit surface”

First of all the cathodic protection does not work by depositing the anode material on the cathode. Rather, in a simplified explanation, the cathode is flooded with electrons released from the anode, thus not allowing oxidation of the protected metal (the cathode). It is also impossible to have these two processes going simultaneously; one corroding the plate and creating pits, while the other is depositing anode material in this very same pit at the same time! In addition, I have a real live example of a hire boat which has never had hull anodes or shore power and was displaying the same symtoms.

3.3. Live examples

I find that “electrolysis” is often used as a blanket term when some sort of corrosion is discovered, while it relates to a method or technique rather than a condition. It is often forgotten that the corrosion, in general, is always an electro-chemical process and to explain it, one has to identify the presence of the four elements: anode (where the oxidation happens and metal is lost), cathode (where the reduction happens), conductor to connect the cathode with the anode and electrolyte to close the circle. Often it is hypothesised that electricity flow within a galvanic couple or from external power source causes the symptoms described above, but here is one of the real live examples I have come across, which disproves this hypothesis; A narrow boat was taken out of the water for blacking, it came under its own power and the owner did not report any leaks. When the boat was pressure washed, numerous holes in the bottom of the silvery pits were discovered – examples on pictures 1 and 2 below. Some of them were rather large and definitely capable of sinking a boat which did not even had a bilge pump. Apparently these pits (and holes!) were there already and not a result of an active electric current flow. What was keeping this boat still afloat was the biofilm and corrosion product buildup which was blocking the holes! If the pits were caused by an electricity flow between a galvanic couple or an external power source, the pits would have displayed bare metal surface as they were the anode side and were losing metal. We all know how the hull anodes look when they are working normally – bare metal with pitted surface……In this case however, everything has been happening in the isolated site under the crust/film, typical for microbiologically influenced corrosion as discussed and illustrated in section 4 below.

4. Does MIC exist at all?

There is a belief in the yacht and small craft boat industry that MIC simply does not exists. This is mostly due to the perception that bacteria lives only in a stagnant environment and causes some sort of a decay, which is certainly not the case here. MIC is a complex process and very often a combination of different processes. The sulphate reducing bacteria (SRB), which are one of the main causes of MIC, are wide spread and can live in almost any water condition; high or low temperature, salinity, PH, pressure…….and even though SRB has anaerobic digestion, it can survive in a “resting stage” in oxygen rich waters and then become active under a biofilm formation such as on a neglected steel hull.

There are many scientific papers dealing with the microbiologically induced corrosion and it has been around for a long time. MIC is very often a combination of many processes happening in parallel and influencing each other. Below is an illustration of different types of MIC, which could be taking place on the metal hull in the presence of SRB, as discussed in a paper by Dennis Enning and Julia Garrelfs of Max Planck Institute for Marine Microbiology, Bremen, Germany.

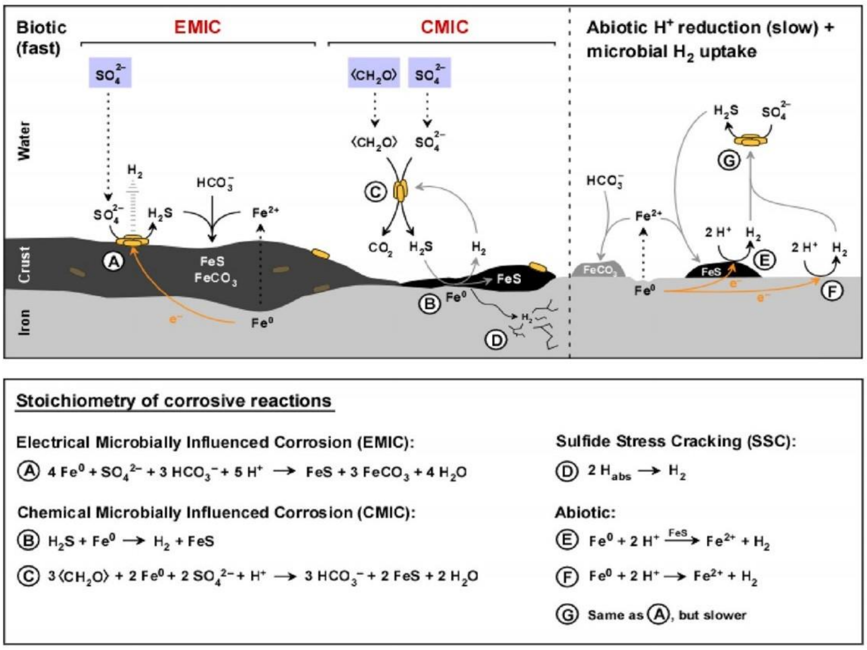


FIG 4 Schematic illustration of different types of iron corrosion by sulfate-reducing bacteria (SRB) at circumneutral pH. Biotic and abiotic reactions are shown. Depicted biotic reactions tend to be much faster than abiotic corrosion reactions. SRB attack iron via electrical microbially influenced corrosion (EMIC) or chemical microbially influenced corrosion (CMIC). Stoichiometry of the illustrated reactions is given in the lower panel of this figure. Please note that all depicted processes may occur simultaneously on corroding metal surfaces but differ in rates and relative contributions to corrosion. (A) Specially adapted lithotrophic SRB withdraw electrons from iron via electroconductive iron sulfides (EMIC). Excess of accepted electrons may be released as H_2 (via hydrogenase enzyme). Participation of possibly buried (encrusted) SRB in sulfate reduction and hydrogen release is currently unknown. (B) Biogenic, dissolved hydrogen sulfide reacts with metallic iron. (C) Overall representation of CMIC. Organotrophic SRB produce hydrogen sulfide which reacts with metallic iron. (D) Sulfide stress cracking (SSC) of iron due to biogenic hydrogen sulfide. (E) Catalytic iron sulfides may accelerate reduction of H^+ ions to H_2. (F) Slow, kinetically impeded reduction of H^+ ions to H_2 at iron surfaces. (G) Consumption of H_2 from reaction E or F by SRB does not accelerate the rate of H_2 formation (no "cathodic depolarization"; see the text). Note that CMIC quantitatively depends on the availability of biodegradable organic matter (here schematically shown as carbon with the oxidation state of zero, CH_2O).

5. How can we prove that these symptoms are a result of MIC and not something else

Scientists and consultants who have been involved in the research of MIC and also have worked for world-leading oil and gas companies' in-house or independent laboratories such as DNV (https://www.dnv.com/services/microbiologically-influenced-corrosion-threat-assessment-208330#dropdown-sector-Maritime) , advise that to prove that certain corrosion is influenced by a microbiological process, multiple lines of investigation should be pursued.

6. My research

Following the advice from the experts, my research followed these steps:

6.1. Identify cases of corrosion with similar symptoms as discussed above.
I have examined over 30 steel hull boats in various parts of the inland waterways, including the Grand Union Canal, Oxford Canal, Kennet and Avon Canal, Shropshire Canal….. River Thames, Severn, Wey….steel piling in and out of marinas.

6.2. Eliminate other, abiotic possible causes for the corrosion.
I have eliminated other possible causes as discussed above, but most importantly, all the boats which I examined, had a film of biological fouling and corrosion product buildup over the silvery pits, which is a certain indicator that no external electrical current or galvanic action between dissimilar metals was causing the corrosion and that the silvery spots/pits

were not bare steel. I have also polished steel and magnesium with jewellery tools and they were nowhere near as bright as the silvery appearance of these pits.

6.3. Examine the corrosion products for presence of Iron Sulphides (FeS)
Iron Sulphides are products of SRB influenced corrosion. They are normally not a product of abiotic corrosion, hence their presence in the corrosion products buildup is a very strong indicator of MIC. A simple field test to discover iron sulphides is to treat them with hydrochloric acid and check if hydrogen sulphide gas (H_2S) is released (rotten eggs smell or positive test with lead acetate paper). This test was also used in the Health and Safety Executive sponsored study on mooring systems in Scotland.

I have treated corrosion products taken from the silvery pits with hydrochloric acid and compared it with corrosion products taken from above the waterline. The following video shows bubbles (which smelled like rotten eggs) being released from corrosion products from the base plate of a narrow boat on the Grand Union Canal – https://youtu.be/y4xvlAuO47I. The pit, after it was cleaned, is shown on the picture below.

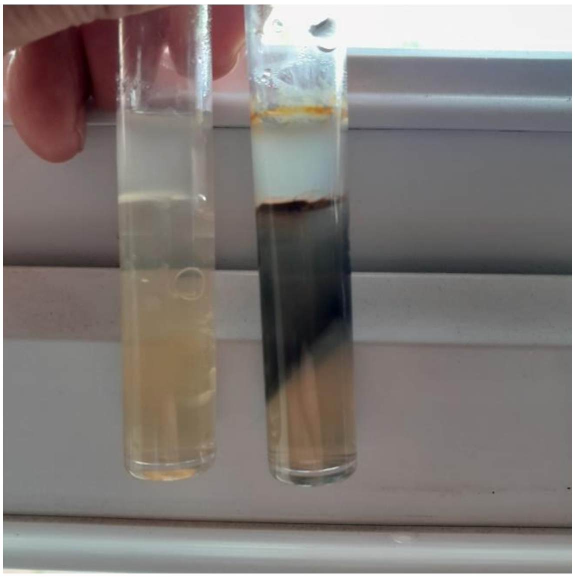
I have also compared the corrosion products from a silvery pit on the bottom of a barge on the Thames and corrosion products around its hatch coamings by adding hydrochloric acid and inserting lead acetate paper to test for hydrogen sulphide. The dark paper indicates presence of hydrogen sulphide – the right test tube on the picture below is with the corrosion product found in the bottom pit, the left is the corrosion product found around the hatch on deck.

I have conducted at least 20 such experiments and every time, the corrosion products from the silvery pits released hydrogen sulphide.

6.4. Confirm presence of Sulphate Reducing Bacteria (SRB) in the water and more specifically in the film covering the corroding steel.

I have discussed a test method for detecting SRB with Dr Robert Edyvean (University of Sheffield) and Dr Tony Rizk (University of Manchester) and implemented it on at least 4 boats at different locations. They all came back positive on the presence of SRB, mostly "moderate" according to the reference scale. The control samples (water taken from the site), have also been mostly positive, i.e. they also showed presence of SRB.

The most convincing test however, was the one where instead of using water from the canal or river (which usually also contains SRB) as a control sample, I used bottled mineral water which contains Sulphates, but no SRB. I took corrosion products from the boat's hull when it had been out of the water for a couple of hours and put them in a test bottle filled with mineral water. Then I let it stay for a couple of hours. After that, I filled one test tube with clean mineral water from the same bottle (control sample) and the other from the test bottle with the corrosion products (test sample), then incubated the two samples together. I was able to see some SRB growth (the test gel turning black) in the test sample on the first day and on the second, the growth had turned black already, while the control sample remained unchanged (indicating no SRB present). Below are pictures taken in sequence on day zero (in the incubator), day one, day two and day three. The control sample is on the left, the test sample is on the right. This experiment shows that SRB were present in the silvery pits and in the film which develops over them. It has also eliminated the chance of false positive results which can be caused by the use of canal or river water for the samples. Where I have scraped the corrosion products/film from the pits, the plate had the typical silvery deposits and other undisturbed corrosion formations can be seen in the vicinity – picture 5 below. Note that the boat had been out of the water for a couple of hours already, hence the bacteria will stay alive even in damp and oxygen-rich conditions.



With these multiple lines of investigation, I have shown that the most likely cause for the corrosion with the specific symptoms discussed above and which is very wide spread on inland waterways, is indeed SRB Microbiologically Influenced Corrosion.

7. What is the value of this research from the surveyor's point of view.

The current controversy surrounding the MIC is not good for the industry and I felt that a structured research would be of benefit and could raise the awareness. Personally, I have drawn conclusions and adopted strategies, which might be beneficial from the surveyor's point of view:

7.1. With MIC present on the hull, visual observation and hammer sounding opportunities and reliability is greatly reduced. A relevant example is given in point 2 above, where the surveyor was misled by the relatively good thickness measurements and did not have a good opportunity to visually examine the unwashed hull. Hammer sounding a base plate with a 10mm thick layer of marine growth and corrosion products from MIC is not very reliable.

7.2. Boats with MIC take a lot longer to prepare sample patches and it is extremely important to clean the corrosion products from as many pits as possible to assess depth. I use 3-pack Tercoo disks on a battery drill. These clean the pits from the corrosion without grinding sound metal. I also look for corrosion product formations which have brown-coloured tips or have opened in the centre as a volcano crater, as this is where the deepest pits are expected. Other areas which I am particularly careful about are near sharp edges (chines, sternpost….)as the MIC is accelerated if the biofilm/corrosion product buildup is periodically disturbed/broken off, which gives the opportunity for the bacteria to reach new fresh metal. This also happens a lot around the bow thruster propellers and where the rudder is striking the counter. The filet welds are also a prime suspect, as MIC will be accelerated in crevices with access to fresh metal and anaerobic conditions.

7.3. If the findings from the sample patches are of concern, i.e. deep silvery pits (but remember it will not be silvery until you wash it), crevices in weld seams, tapered/corroded sacrificial edge………then I would like to see the boat pressure washed or my report will be full of disclaimers.

7.4. Because of the current controversy, I prefer not report my findings as MIC. However, I also do not offer untenable opinions on the cause of the pitting or recommend bleaching as it has only a very short-lived effect on a boat hull (SRB will start to regrow in the first hours after launch in a SRB rich canal or river waters) and can be harmful to the environment and to the metal as well…… MIC is like Voldemort from Harry Potter - "The one whose name should not be spoken" and that is why I usually describe the pitting in terms of its density, area and depth and recommend the usual and regular hull treatment and inspection. After all, there is not much more one can do about the corrosion prevention or the treatment of the hull anyway ……and it is sufficient if inspection and maintenance is carried out regularly, but often it is not.

7.5. I still carry HCL (hydrochloric acid) and lead acetate paper in my toolbox to test the corrosion products for the presence of FeS, although I can now reliably predict the outcome by visually examining the corrosion.

8. Credits

In my research I have consulted papers from the following sources and have had meetings in person or on Zoom with the lead scientists:

8.1. Trevor Osborne – Deepwater Corrosion Services UK, past President and Fellow of the Institute of corrosion
8.2. Inspections for Accelerated Corrosion on Marine Steel Piles by JB Christie of Aberdeen Harbour Board
8.3. Dennis Enning - Professor of Industrial Microbiology and Julia Garrelfs of Max Plank Institute for Marine Microbiology, Germany
8.4. Karsten Pedersen – Senior Principal Scientist (CEO, Docent), Microbial Analytics Sweden AB
8.5. Microbiologically Influenced Corrosion of mooring systems for floating offshore installations – Joint industry project sponsored by the Health and Safety Executive Scotland
8.6. Susmitha Purmina Kotu Ph.D. Corrosion management at DNV GL USA, who also have some wonderful webinars on the subject – available on their website.
8.7. Dr Tony Rizk - University of Manchester and CEO Halo Sealing Systems Ltd.
8.8. Dr Robert Edyvean –Department of Chemical and Biological Engineering ,The University of Sheffield, past President and Fellow of the Institute of Corrosion
8.9. All boatyards where I have inspected boats ….P&S Marine, 4AllMArine, Highline Yachting, Uxbridge, Pyrford, Stanstead, Better Boating, Oxford Cruisers, Overwater, North Kilworth, Norton Canes, Upton, Cropredy, Tewkesbury, Aston, Devizes, Thames and Kennet, Salters Steamers…….and many more.

I am happy to discuss this subject with people who have interest in it or ideas for development.

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