

REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to the Department of Defense, Executive Services and Communications Directorate (0704-0188). Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ORGANIZATION.					
1. REPORT DATE (DD-MM-YYYY) 04-03-2014		2. REPORT TYPE Journal Article		3. DATES COVERED (From - To)	
4. TITLE AND SUBTITLE Microbiologically Influences Corrosion of Pilings				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER 0601153N	
				5d. PROJECT NUMBER	
6. AUTHOR(S) Brenda J. Little and Richard I. Ray				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER 73-4635-03-5	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Naval Research Laboratory Oceanography Division Stennis Space Center, MS 39529-5004				8. PERFORMING ORGANIZATION REPORT NUMBER NRL/JA/7330--13-1810	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research One Liberty Center 875 North Randolph Street, Suite 1425 Arlington, VA 22203-1995				10. SPONSOR/MONITOR'S ACRONYM(S) ONR	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release, distribution is unlimited.					
13. SUPPLEMENTARY NOTES					
20151013128					
14. ABSTRACT Sheet piles, used as retaining walls, wharfs, and piers, are typically made of unprotected carbon steel (CS). This type is affordable and the general corrosion rate (wastage) is predictable. Despite the long and successful use of CS sheet pilings, there are reports of localised corrosion of CS pilings that have been identified as microbiologically influenced corrosion (MIC) ie, corrosion that is a result of the presence and activities of microorganisms. Microorganisms can produce localised attack including pitting, enhanced erosion corrosion, enhanced galvanic corrosion, stress corrosion cracking, and hydrogen embrittlement of CS. Microorganisms do not produce a unique corrosion morphology in CS that could not be produced abiotically.					
15. SUBJECT TERMS microbiologically influenced corrosion, carbon steel pilings, iron-oxidising bacteria					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	18. NUMBER OF PAGES 3	19a. NAME OF RESPONSIBLE PERSON Brenda Little
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NUMBER (Include area code) (228) 688-5494

Microbiologically influenced corrosion of pilings

Brenda J. Little, *senior scientist for marine molecular processes,*
Richard I. Ray, *physical scientist and* Jason S. Lee, *materials engineer,*
Naval Research Laboratory, Mississippi, United States

Sheet piles, used as retaining walls, wharfs, and piers, are typically made of unprotected carbon steel (CS). This type is affordable and the general corrosion rate (wastage) is predictable. Despite the long and successful use of CS sheet pilings, there are reports of localised corrosion of CS pilings that have been identified as microbiologically influenced corrosion (MIC) i.e. corrosion that is a result of the presence and activities of microorganisms. Microorganisms can produce localised attack including pitting, enhanced erosion corrosion, enhanced galvanic corrosion, stress corrosion cracking, and hydrogen embrittlement of CS. Microorganisms do not produce a unique corrosion morphology in CS that could not be produced abiotically.¹

Corrosion of pilings in marine and estuarine environments

Accelerated low water corrosion (ALWC) is a particularly aggressive form of localised corrosion that has become a high profile problem, associated with unusually high corrosion rates of unprotected or inadequately protected CS pilings in marine and estuarine waters. The UK Institution of Civil Engineers described ALWC as "a matter of national importance".²

ALWC is a global phenomenon having been reported in all climatic conditions on unprotected steel pilings in contact with saline water (i.e. seawater and brackish water) that is subject to tidal influences.^{3,4} A survey of port and harbour authorities in five Western European countries concluded that at least 13 percent of the ports were affected by ALWC.⁵

The term ALWC does not define a corrosion mechanism. Instead the term denotes the precise location of the corrosion on the exposed pilings (see

Figure 1). Average corrosion rates in the range of 0.3 to 1.2 millimetres per side per year have been reported. ALWC has a distinct appearance, patches of lightly adherent, bright orange and black (iron sulphide rich) deposits over a clean, shiny and pitted steel surface.⁶

As pits deepen and become more numerous, they overlap, producing terraced holes. Corrosion products contain magnetite, iron sulphides, and green rust (an unstable iron oxy-hydroxide sulphate complex).

Mechanisms and mitigation

A report by Gehrke and Sand concluded that ALWC was due to the combination of sulphate-reducing bacteria (SRB) and sulphur oxidising bacteria (SOB) in the fouling layers on the pilings.⁶ The organisms co-populate the same spatial regions on the pilings. At low tide the biofouling layer is oxygenated whereas at high tide anaerobic areas develop. Sulphides produced by SRB are converted to sulfuric acid by SOB, creating an extremely corrosive environment. (see Figure 2a).

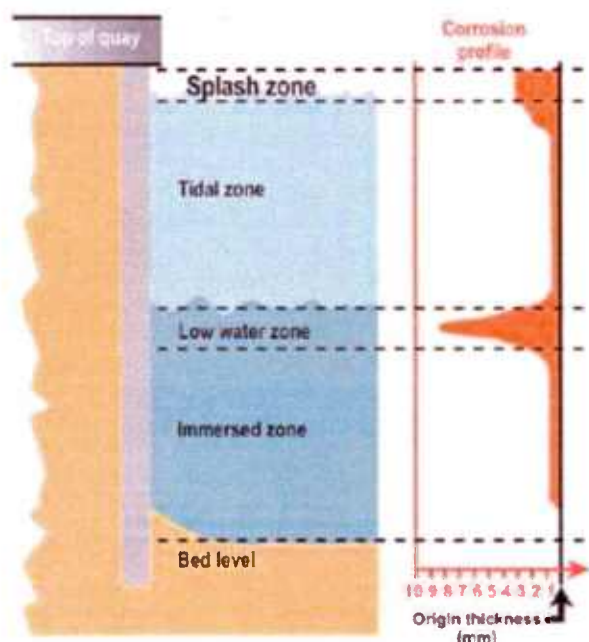


Figure 1: Schematic of ALWC illustrating relationship of water level and degree of corrosion. Taken from Koczyński (PII 2919).

Meleher and Jeffrey found: "The increased occurrence of ALWC reported in recent years is most likely the result of elevated levels of water pollution in the waters to which the steel piling has been exposed over its lifetime, irrespective of whether water pollution is currently decreasing."ⁱⁱⁱ

A later review of data from a 27-year period related to ALWC concluded that the severity of ALWC correlated with the concentration of dissolved inorganic nitrogen (DIN), "a critical nutrient for microbiological (bacterial) activity in seawater." It is suggested that this observation could be used to predict the long-term risk of ALWC.ⁱⁱⁱ It has also been reported that protective coatings, sacrificial anodes or impressed current cathodic protection were effective in mitigating ALWC.^{iv}

Corrosion of pilings in freshwater environments

Accelerated corrosion has been reported for CS pilings in the Duluth-Superior Harbour (DSH), Minnesota, a fresh water estuary.⁵ DSH pilings that are over 30 years old are either completely or partially perforated by localised corrosion (see Figure 2b). The corrosion extends from the air/water interface to a depth of about 3 metres, but with decreased attack from 1.2 to 3 metres. The position of the air/water interface is not significantly influenced by tides. Below 3 metres where zebra mussel attachment begins there is little corrosion. Corroded DSH pilings have an orange rusty appearance characterised by tubercles, dense mounds of corrosion products (see Figure 3). The average pit depth, a measure of localised corrosion, in a three-year study ranged between 670 micrometres to 788 micrometres, 7-8 percent of the total thickness of the coupons. Pit depth varied with location and increase in pit depth was not linear over the three-year exposure.

Mechanisms and mitigation

A 2009 study has demonstrated that corrosion of carbon steel pilings in DSH was due to deposition of copper under tubercles of iron-oxidising bacteria (IOB). IOB oxidise iron and produce dense deposits of intact and/or partly degraded remains of bacterial cells mixed with amorphous hydrous ferric oxides. A galvanic couple was established between the copper layer and the iron substratum. In laboratory experiments, the galvanic current depended on the concentration of dissolved copper in the lake water.^{vi} A recent study used genetic techniques to quantify the abundance of IOB at multiple sites in the DSH over multiple



Figure 2a: (Left) Piling deterioration due to ALWC. Figure 2b: (Right) Corrosion of piling in Duluth Superior Harbour.

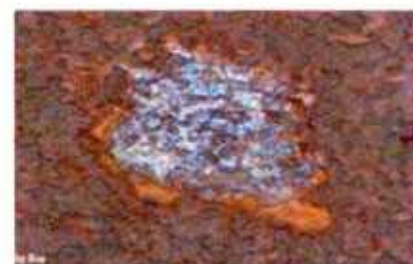
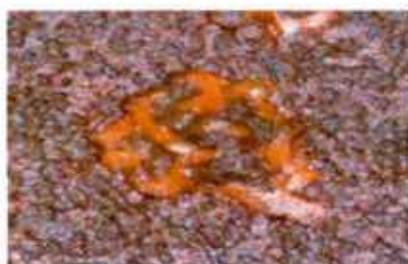


Figure 3: Tubercle on carbon steel exposed in Duluth Superior Harbour before (left) and after (right) removal of tubercle.

years. They demonstrated that tubercles in the DSH were enriched with IOB compared to the biofilm on adjacent surfaces. However, long-term corrosion was not related to IOB abundance or dissolved copper concentration.^{vii} Both studies concluded that a combination

of microbiological and chemical factors influenced the rate of corrosion. An additional report evaluated coatings for DSH pilings over a four-year period. Some of the coatings provided an effective barrier that prevented tubercle formation and MIC.

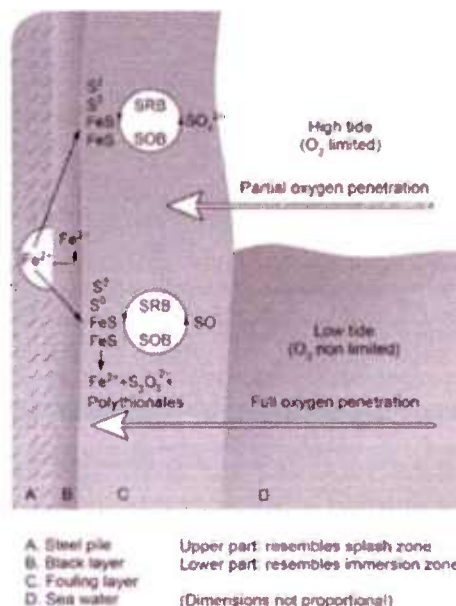


Figure 4: Schematic representation of the chemistry and reactions associated with ALWC. Reproduced with permission from NACE International, Houston TX. All rights reserved. Copyright NACE International 2003.

Diagnosing MIC in harbours

The involvement of microorganisms in the corrosion of CS pilings cannot be surmised by evaluating the morphology of the localised corrosion. Furthermore quantification of bacterial types does not provide a predictive capability. The following are required for an accurate diagnosis of MIC: a sample of the corrosion product or affected surface that has not been altered by collection or storage, identification of a corrosion mechanism, identification of microorganisms capable of growth and maintenance of the corrosion mechanism in the particular environment, and demonstration of an association of the microorganisms with the observed corrosion.

In summary

Corrosion rates for ALWC and corrosion in DSH are similar i.e. 0.3 millimetres

per-year and higher. However, there are obvious differences in the observations in DSH and reports of ALWC (see Figure 4). ALWC is in the low water zone, just below the tidal zone, in saline waters containing gram per litre quantities of sulphate. DSH is a fresh water harbour with milligram per litre concentrations of sulphate. Corrosion in DSH is localised to the top 3 metres below the surface of the water and water depth is not significantly influenced by tides. Despite these differences both ALWC corrosion and corrosion in DSH have been attributed to MIC. In both cases, a combination of biological, chemical and physical events contribute to the corrosion. The specificity of metal/microbe/electrolyte interactions makes it difficult to predict the likelihood and rate of MIC in harbours. MIC on CS pilings can be prevented.

References

- ¹Little BJ, Lee JS. 2007. Microbiologically Influenced Corrosion. Hoboken, New Jersey: John Wiley and Sons, Inc.
- ²Breakell JE, Foster K, Siegwart M. 2005. Management of Accelerated Low Water Corrosion in Steel Maritime Structures. C634. London: Construction Industry Research & Information Association (CIRIA)
- ³Johnson D, Moulton JM, Karins R, Resnick B, Confete M, Chao WT. 1994. Low water corrosion on steel piles in marine waters. EUR 17868
- ⁴Kopczynski B. 2010. Accelerated low-water corrosion in harbours. Port Technology International 46:116-118
- ⁵Chenng CWS, Walsh FC, Campbell SA, Chao WT, Beech IB. 1994. Microbial Contributions to the Marine Corrosion of Steel Piling. Int Biodeter Biodegr. 34(3-4):259-274
- ⁶Gehrke T, Sand W. 2003. Interactions between microorganisms and physicochemical factors cause MIC of steel pilings in harbours (ALWC). Paper presented at: CORROSION

/ 2003, San Diego, CA.

⁷Melchers RE, Jeffrey R. 2010. Corrosion of vertical steel strips exposed in the marine tidal zone and implications for ALWC. Paper presented at: CORROSION / 2010, San Antonio, TX.

⁸Melchers RE. 2013. Influence of Dissolved Inorganic Nitrogen on Accelerated Low Water Corrosion of Marine Steel Piling. Corrosion. 69(1)

⁹Kumar A, Stephenson LD. 2005. Accelerated Low Water Corrosion of Steel Pilings in Seawater. Paper presented at: CORROSION / 2005, Houston, TX.

¹⁰Marsh CP, Beitelman AD, Buchheit RG, Little BJ. 2005. Freshwater Corrosion in the Duluth-Superior Harbour, Summary of Initial Workshop Findings. ERDC/CERL SR-05-03.

¹¹Ray RL, Lee JS, Little BJ. 2009. Factors contributing to corrosion of steel pilings in Duluth-Superior Harbour. Corrosion. 65(11):707-717.

¹²Hicks RE, Oster RJ. 2012. Developing a Risk Assessment Tool to Predict the Risk of Accelerated Corrosion to Port Infrastructure, Final Report. Great Lakes Maritime Research Institute.

About the author



Brenda J. Little is senior scientist for marine molecular processes at the Naval Research Laboratory. Dr Little has worked in the field of microbiologically influenced corrosion for 30 years. She serves on the editorial board for Biofouling and is a NACE International Fellow.



Richard I. Ray is a physical scientist at the Naval Research Laboratory. Mr Ray has worked in the field of microscopy for 20 years and has developed protocols for imaging biofilms and biological materials.



Jason S. Lee is a materials engineer at the Naval Research Laboratory. Dr Lee has worked in the field of corrosion for 14 years.

About the organisation

Naval Research Laboratory (NRL) is the corporate research laboratory for the US Navy and Marine Corps and conducts a broad program of scientific research, technology and advanced development. NRL has served the navy and the nation for over 85 years and continues to meet the complex technological challenges of today's world. NRL publication NRL/JA/7303 -13-1810. Funding provided by ONR (Dr L. Chriscy).

Enquiries

Brenda J. Little
Naval Research Laboratory
Code 7303, Stennis Space Centre
MS 39529, US
Tel: +1 (228) 688 4494
Email: brenda.little@nrlssc.navy.mil