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Freshwater Corrosion in the Duluth – Superior Harbor

Summary of Initial Workshop Findings, 9 September 2004

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Final Report

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ABSTRACT: This report reviews the potential causes of accelerated corrosion of sheet pile and other steel structures in the Duluth-Superior Harbor and makes recommendations for addressing the problem. The authors met in Duluth (September 2004) to examine harbor corrosion and consult with interested parties. The corrosion appears as pock marks primarily in the 4 feet just below the water surface. The corrosion extends down to about 10 feet, but decreases from 4 feet below the surface to 10 feet. The corroding pock marks are covered by an orangish coating that tends to cover the corroded pit. Water chemistry, dissolved oxygen content, and dissolved chlorides from de-icing salts seem to be the most likely agents of accelerated corrosion of 12 causes discussed. A lack of data made it unclear whether microbiological factors or functional harbor changes are unduly influencing corrosion in the harbor. The authors recommend immediately quantifying the corrosion rate, conducting a water chemistry analysis, checking for microbiologically influenced corrosion, testing for stray DC currents, and assessing the condition of critical steel structures. They encourage long-term monitoring of corrosion in the Duluth-Superior Harbor and other Great Lakes ports, as well as developing a condition-based strategy for steel replacement and repair.



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Preface

This special report was prepared for Headquarters, U.S. Army Corps of Engineers, as part of Proponent-Sponsored Engineer Corps Training project 009, “Corrosion Control,” in cooperation with the National Sea Grant College Program, National Oceanic and Atmospheric Administration, U.S. Department of Commerce. The Sea Grant Technical Monitor was Jeffrey L. Gunderson.

The work was coordinated through the Materials and Structures Branch (CF-M) of the Facilities Division (CF), Construction Engineering Research Laboratory (CERL). The CERL research project manager was Dr. Charles P. Marsh. The technical editor was Gordon L. Cohen, Information Technology Laboratory – Champaign. Martin J. Savoie is Chief, CEERD-CF-M, and L. Michael Golish is Chief, CEERD-CF. The Technical Director of the Facilities Acquisition and Revitalization business area is Dr. Paul A. Howdyshell, CEERD-CV-ZT. The Director of CERL is Dr. Alan W. Moore.

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1 Introduction

Background

Duluth – Superior Harbor is formed by the St. Louis River estuary and is protected from Lake Superior by a long sand spit. There are two openings that allow water exchange with Lake Superior and provide navigational entries. The St. Louis River is a dark-water river that drains a large portion of northeastern Minnesota. Water quality information is available from the Minnesota Pollution Control Agency (<http://www.pca.state.mn.us/data/eda/index.cfm>).

Steel sheet piling in the Duluth – Superior Harbor (DSH) is reported to be corroding at an accelerating rate. Based on observations of both older and newer sheet pile installations, the increased rate of corrosion appears to have begun in the late 1970s. Owners and managers of sheet pile structures in DSH are facing an expensive problem. About 13 miles* of steel sheet piling and numerous wooden docks held together with steel fasteners are located around the harbor. Steel columns supporting highway bridges and the giant steel ore docks through which millions of tons† of taconite are shipped each year are also corroding. The main concern is that the strength and structural integrity of the docks will decrease to dangerous levels much sooner than expected. The installed cost of replacement steel sheet piling is \$1,500 or more per lineal foot, and that figure implies a problem that may cost more than \$100 million to correct. It is not known with certainty why corrosion rates may have accelerated in the late 1970s, but a number of changes that occurred within that timeframe may have contributed to the problem.

The Western Lake Superior Sanitary District (WLSSD) went online in 1978 and consolidated Minnesota industrial and municipal discharges into a single waste treatment plant, which had a significant positive impact on river water quality (St. Louis River Remedial Action Plan 1993). Possible impacts of the WLSSD on

* 1 mile = 1.6 km.

† 1 ton = 907.1 kg.

harbor corrosion include (1) an increase in dissolved oxygen levels, (2) concentrated chemicals from industrial sources that had previously been distributed throughout the river, and (3) the addition of sulfate compounds used to dechlorinate effluent. The WLSSD plant is located the lower St. Louis River, the area where the highest corrosion rates have been observed. Water quality information has been collected in the river and harbor since 1973. WLSSD no longer chlorinates or dechlorinates its discharge.

Another possible influence on corrosion rates is a high-voltage direct current (DC) power line constructed in the 1970s, which runs from North Dakota to Duluth. Minnesota Power has stated that the 250 kV DC line returns current via conductors, but occasionally operates with a ground return. The company has indicated that if it operates under ground return, it must operate in a reduced mode. Minnesota Power indicated that the ground return is oriented northwest from the site and away from the DSH. DC power lines have been associated with accelerated corrosion of a variety of steel structures, and concern has been expressed that this power line may be related to the reported changes in corrosion rate.

A third change occurred in the 1970s when the Duluth water treatment facility began filtering water to remove asbestos fibers. As part of this process alum (aluminum sulfate) was added to the water. Along with chlorine and fluoride additions, this treatment tended to decrease pH from about pH 8 to pH 7, which caused corrosion problems in Duluth water lines. Plant operators added zinc orthophosphate and tripolyphosphate to try to coat the pipes and prevent the corrosion. Then, around 1986, they abandoned that effort and began trying to raise the pH to 9 by adding sodium hydroxide. That treatment mode continues today. Meanwhile, it has been speculated that whatever caused corrosion of the city water lines may have been transferred to the harbor through WLSSD. However, it also was discovered that some Duluth steel water mains corrode due to electrolysis.

In addition to the three major changes discussed above, other possible influences on accelerated corrosion in DSH include an increased use of road de-icing salts, ionization of water by underwater power lines, tannic acids from waterways that drain into the harbor, stray electric voltage from various sources, a proliferation of corrosion-influencing microorganisms, goose droppings, etc.

The characteristics of the subject corrosion have been described by a diver and structural engineer working for a Duluth engineering firm. The diver has described the corrosion as pock marks primarily in the 4 feet just below the water

surface. The corrosion extends down to about 10 feet, but decreases from 4 feet below the surface to 10 feet. Below 10 feet there is very little corrosion. Zebra mussel attachment begins at 10 feet below the surface and extends to the bottom of the sheet pile. The corroding pock marks are covered by an orangish coating that tends to cover the corroded pit. Another aspect of the corrosion is that it also appears upstream from the harbor, albeit to a lesser extent. A seiche could be one possible factor in the upstream distribution of accelerated corrosion through a brief reversal of river flows, moving some Lake Superior water and corrosion-related contaminants from the lower harbor up-river.

To determine the cause of the accelerated corrosion reported at DSH, the Duluth Seaway Port Authority has sought external assistance from experts working within both the public and private sectors. In order to provide a forum for discussion and technical information exchange, the port authority organized a workshop featuring scientists and engineers with expertise in corrosion processes, materials, and corrosion protection technologies.

Objective and Scope

This report documents and summarizes the initial findings of a workshop and panel discussion held 8 – 9 September 2004. All discussion and preliminary recommendations are based on limited available data, including information gathered by the Minnesota Sea Grant program, qualitative observations by members of the expert panel, and anecdotal reports from the field. Definitive conclusions about the causes and appropriate mitigation of DSH corrosion will require data gathered through formal measurement, testing, and engineering analysis.

Approach

To help provide focus for possible research and mitigation projects, a partnership was formed to examine the problem of accelerated DSH corrosion. The partnership was composed of the Minnesota and Wisconsin Sea Grant programs, the Duluth Seaway Port Authority, the Natural Resources Research Institute, the U.S. Army Corps of Engineers (USACE), and Krech Ojard & Associates, Duluth, MN. The partnership served as a steering committee that determined the expertise required, selected an expert panel, and planned and facilitated the expert panel meeting. The steering committee included the following members:

Dave Bowman, USACE
Gene Clark, Wisconsin Sea Grant
Don Fosnacht, Natural Resources Research Institute
Jeff Gunderson, Minnesota Sea Grant
Al Klein, USACE
Al Mozol, USACE
Carl Richards, Minnesota Sea Grant
Chad Scott, Krech Ojard & Assoc.
Jim Sharrow, Duluth Seaway Port Authority
Ray Skelton, Duluth Seaway Port Authority

The steering committee also developed the following list of fundamental questions for the expert panel to address:

1. Is there accelerated corrosion and is it different than seen in other freshwater ports?
2. What is the spatial extent of corrosion?
3. What are likely causes of the corrosion?
4. What research/monitoring is needed?
5. How should the research/monitoring needs be prioritized?
6. What can be done to mitigate the problem?

The names, affiliations, and areas of expertise of individuals selected for the expert panel are presented in Appendix A.

The expert panel met on 8 and 9 September 2004 in Duluth. The agenda is presented in Appendix B. Stakeholders, university researchers, agency personnel, and other interested parties were invited (Appendix C). The workshop included a facilitated discussion to allow participants to ask questions and provide additional information to the panel about DSH corrosion issues. The workshop ended with a media briefing for local journalists.

2 Summary of Expert Panel Discussions

Evidence for Accelerated Corrosion

Based on multiple sources of information and observation, corrosion of steel structures appears to be worse in the Duluth-Superior Harbor (DSH) than in other freshwater environments. Anecdotal reports, direct visual observations by the panel of experts, pit depth data (Krech Ojard & Associates), and dissolved oxygen data support inferences of an abnormally high corrosion rate. Appendix D provides an analysis of limited pit depth data taken from multiple locations within DSH with respect to duration of exposure for various time periods. These findings are compared with published pit depth corrosion data for comparable materials as exposed in three freshwater rivers. Some assumptions and extrapolation were necessary given the limitations of the available data, but the findings are based on the only known available direct quantitative measurement of corrosion at sites within DSH. Appendix D also includes an analysis of inferred corrosion rates based on historic dissolved oxygen (DO) data. These corrosion rate estimates, made from dissolved oxygen measurements near the Burlington Northern Bridge, suggest an increase in corrosion rates from about 12 mils* per year (mpy) during the 1970s to 22 mpy during the 1980s. In addition, total thickness losses estimated from this analysis at least appear to generally coincide with actual observations of corrosion thickness losses of sheet pile across the harbor. Reports suggest that corrosion outside the harbor in Lake Superior is not as severe.

Taken together, it appears that there is cause for concern and a need for formal scientific investigation. Such investigation should first substantiate and quantify the effect, determine its cause or causes, and then provide informed recommendations for proactive mitigation and cost-effective management. One question of wider and potentially even greater impact is whether the situation in DSH is an isolated case, or typical of other ports within the Great Lakes. That question is beyond the scope of this effort, but it is noted that, at this time, there

* 1 mil = 1 milli-inch, or 0.0254 mm.

is no systematic coordinated monitoring and reporting of corrosion rates or projected condition of sheet pile for any ports in the Great Lakes waterway system.

Possible Causes

Typical sheet pile corrosion is most severe in the splash zone and just below the mud line. Without direct quantitative measurements of corrosion from the site of the problem it is not possible to definitively state a cause. However, based on their collective experience, the expert panel compiled an inclusive list of possible causes. Each cause was discussed in terms of its likelihood of contributing to the corrosion problems in the DHS. Each potential cause is listed in Table 1 and discussed below. Some potential causes of accelerated corrosion are closely interrelated, as noted in the discussions.

Table 1. Estimated importance of possible causes of harbor corrosion.

Possible Causes of DHS Corrosion	Assessment of Significance
Water chemistry	Significant
Temperature	Not significant
Dissolved oxygen content	Significant
Dissolved chlorides from de-icing salts	Significant
Microbiologically influenced corrosion	Not clear (further analysis)
Stray current corrosion	Not significant (but check)
Storm water runoff / sewage discharge (related to water chemistry)	Not significant (of itself)
Ballast discharge	Not significant
Zebra mussels	Not significant
Metallurgy of steel	Not significant
Water electrolysis from power distribution	Not significant
Functional changes within the harbor	Not clear (bear in mind)

Water Chemistry

Because corrosion is an electrochemical process, water chemistry matters a great deal. At a fundamental level, total ion concentration in the electrolyte determines the relative resistance to electric currents and therefore it affects the rate of corrosion. Some preliminary measurements of total dissolved solids (TDS) were taken and then translated into terms of water resistivity, which is a standard corrosion engineering parameter. Three measurements in different locations consistently returned values of about 4,500 – 4,700 ohm-cm, which falls within a typical range for fresh waters. For comparison, some similar measurements from the Cuyahoga River at Cleveland, OH, returned values of about

1,250 ohm-cm, and seawater values are generally measured to be on the order of 23 ohm-cm.

Another aspect of water chemistry is pH. In different regimes of pH — admittedly some rather extreme in the context of a freshwater environment — the predominant mechanism of corrosive degradation may differ. The possible presence of dissolved tannins related to biological decomposition in connected rivers is also a factor that could affect pH, dissolved oxygen content, microbiology, and other aspects of water chemistry. Furthermore, water chemistry also can serve to preferentially favor certain flora and fauna (both native and non-native species) that can influence corrosion. Given the multiple and potentially widespread effects that are possible from either global or localized changes in water chemistry, this factor is significant and requires quantitative testing for purposes of definitive characterization.

Temperature

Corrosion involves a complex of related chemical reactions, all of which occur at a rate affected by ambient temperature. The so-called *rate limiting step* is dependent on the slowest of these interrelated reactions. Given the Arrhenius dependence of chemical reactions,* the presence of a significantly elevated temperature could have a significant effect on corrosion rate. However, there is no evidence of currently elevated temperatures or recent changes toward elevated temperatures, on average. If anything, the generally cold climate argues against that. Temperature does, however, have other effects. As temperature rises the limiting solubility of dissolved gases, such as oxygen, decreases. Also, with other factors being equal, an increase in temperature promotes the occurrence of bio-fouling which, with some exceptions, tends to effectively act as a low-grade protective coating. Subject to future findings to the contrary, temperature is not thought to be a significant factory in DSH accelerated corrosion.

Dissolved Oxygen Content

Dissolved oxygen is critical in the cathodic electrochemical action responsible for producing the negatively charged hydroxyl ions that serve to complete an electrochemical corrosion circuit or *cell*. When a positively charged metal ion leaves the steel to complete this circuit, it is incorporated into a corrosion product either as a deposit on the steel or into solution. Countless corrosion cells can form and

* Arrhenius dependence: a strong exponential dependence ($e \cong 2.1828$) of chemical reaction rate on temperature.

discharge continuously over time, and dissolved oxygen content is a primary variable affecting the reaction. Appendix D presents more technical detail related to this oxidation process.

Dissolved Chlorides From Roadway De-Icing Salts

The pH regime of the DSH (somewhere near neutral, or slightly alkaline) makes another cathodic reaction worth mentioning. Given the local topology and land use contributing runoff into the DSH, roadway de-icing salts could be a significant chloride source giving rise to chloride ions. Similar to hydroxyl ions as noted above, chloride ions serve to complete the circuit in electrochemical corrosion cells. Owing to their strong electro-negativity, chlorides are also locally depolarizing (another detrimental effect). A passivating film normally forms over a corroding surface, significantly decreasing the rate of degradation. Chloride ions continuously disrupt the formation of this passivating film, which leads to higher corrosion and pitting rates. Although an aspect of water chemistry, dissolved chlorides are sufficiently important to consider separately.

Microbiologically Influenced Corrosion

Microbiologically influenced corrosion (MIC) is a general term for corrosion resulting from the presence and activities of microorganisms. One example of MIC now being studied is called accelerated low water corrosion (ALWC), which is reported to be a growing problem affecting European ports. Microbiologically mediated reactions can alter both rates and types of electrochemical reactions, but they do not result in a unique manifestation of corrosion. Microorganisms can cause pitting, crevice corrosion, differential aeration cells, metal concentration cells, selective de-alloying, increased erosion, and increased galvanic corrosion. It is not clear if this factor is significant; further analysis is advised.

Stray Current Corrosion

The corrosive loss of metal from a submerged surface can be thought of as a current of positive ions leaving the structure. The natural electromotive potentials driving this action are typically small — on the order of 1.5 volts of direct current (VDC) or less, depending on the materials and electrolyte. However, additional DC flows can be introduced into the local environment of a submerged metal structure, either intentionally or not. Some typical sources of such stray DC flows are cathodic protection (CP) systems from impressed current type systems, electric rail transit systems, welding operations, and underground DC power lines. Another source of stray current occasionally observed on long pipelines,

although not usually considered significant, is *Telluric current*. These currents occur below the Earth's surface as a result of charge flows or rearrangements in the upper atmosphere. Alternating current (AC) is often incorrectly cited as the source of stray current corrosion, but AC does not contribute to corrosion of buried or submerged steel structures.

When present, stray DC will follow the path of least resistance such as a nearby buried pipeline. When stray DC flows through a submerged metallic structure, significant localized corrosion can occur rapidly where the current leaves the structure.

Although a high-voltage DC power line terminates in the region of some DSH corrosion sites, observations do not suggest that it has had a significant effect on harbor corrosion. However, given the potential severity of even intermittent DC flows, this possibility needs to be conclusively tested. Although testing is highly recommended, stray currents are considered insignificant agents of harbor corrosion based on what is known at this time.

Storm Water Runoff and Sewage Discharge

This source of inputs to DSH affects water chemistry and dissolved oxygen. A concern related to sewage discharge is the addition of sulfates to the harbor. Also, any unintended release of waste material during a prolonged or inundating rain, for example, could promote the preferential growth of certain types of bacteria (e.g., coliform family) and thereby modify the harbor ecosystem. Chlorides from de-icing salts, previously discussed, are delivered to the harbor through runoff. Finally, adverse chemistry from rain water (e.g., acid rain) could also be concentrated in the harbor although that is not suspected to be the case here. Water chemistry and de-icing salts are being considered separately by the expert panel, and no observations suggested that runoff or sewage discharge in and of themselves constitute a corrosion problem for DSH. Therefore, subject to later findings to the contrary, this factor is thought to be insignificant.

Ship Ballast Discharge

Visiting ships may discharge chemical or biological matter that could contribute to harbor corrosion from ballast tanks or ship operations. Any chemical discharge is unlikely to make a significant difference after the effects of dilution and natural breakdown are accounted for; the dual requirement of environmental persistence and corrosiveness make such a possibility unlikely. However, it is possible that non-native species may be introduced through ballast

discharge. Such a release would have to coincide with a favorable environment in which a non-native species could flourish. Observations to date do not suggest that anything like this has occurred. As noted above in the discussion of MIC, potential biological agents of corrosion should be formally investigated. However, the panel agreed that ballast discharges probably are not significant sources of harbor corrosion.

Zebra Mussels

Zebra mussels continue to spread within the Great Lakes. In 1999 two members of the panel conducted a study to assess sheet pile condition in Cleveland, OH, along the Cuyahoga River. At that time, Lake Erie was infested with zebra mussels and the mussels were making their way up river in increasing concentrations. Corrosion rate measurements suggested the covering by zebra mussels served to partially protect the underlying sheet pile from corrosion; measured rates of corrosion were somewhat lower compared with non-infested regions. In DSH, zebra mussels are abundant on the sheet pile at a depth of about 10 feet and below. This distribution is thought to be a result of the cold winters or ice scour. On sheet pile steel directly covered with zebra mussels, there is not likely to be significant corrosion. A related situation worth considering is an 'area effect' whereby a large cathodic area concentrates and aggravates corrosion from a small anodic area of steel not covered by zebra mussels. One conjecture is that a widespread corrosion current, if present, could be concentrated by the electrically insulating presence of the zebra mussels to preferentially affect the upper, uninfested portion of the sheet pile.

Other dissimilar electrolyte effects to consider are anodic regions of lower pH or higher chlorides, which give rise to a potential difference as characterized by the Nernst equation.* Also, the possible effects of zebra mussel infestation on the corrosion of noninfested areas of sheet pile are worthy of scrutiny. However, this factor is not now considered to be highly significant because large colonies of zebra mussels were only detected after 1998 while the subject corrosion appears to have started accelerating in the late 1970s.

* Nernst equation: an equation expressing the relation between the potential or energy level of a metal to the ion concentration in an electrolyte surrounding that metal.

Metallurgy of Steel

In most sheet pile, localized variations in alloy content, retained stress, and other similar factors give rise to small, usually shifting region of anodic and cathodic areas. In the case of pitting corrosion, less shifting occurs and the corrosion becomes more localized. Typically, cost determines the choice of common steel alloys, and this is the general case with DSH sheet pile, with ASTM A328 steel being the most common. The metallurgical effects are minor for these steels. More expensive materials, such as high-tensile strength steel, typically have poorer corrosion performance, but those materials are not in widespread use within DSH. Subject to future findings to the contrary, this factor is thought to not be significant in DSH accelerated corrosion.

Water Electrolysis from Power Distribution

Among many public comments, one request was to consider the corrosive effects of the possible byproducts of water electrolysis. That suggestion presumes that electrolysis is taking place, but this condition has not been established. At standard temperatures and pressures, the splitting of water requires a minimum of 1.2 VDC. This degree of potential gradient within a small space is unlikely to be present, and electrolysis was not observed at any of the locations visited. The electrolysis of water results in hydrogen and oxygen gas; the former can impact pH and the later can alter the dissolved oxygen concentration (see above). Comparatively, stray current corrosion would be a more likely mechanism should the power distribution system turn out to be involved. Subject to future findings, this factor is thought to not be significant.

Functional Changes Within the Harbor

Over the 35 years under consideration, it is difficult to know which changes in harbor use may have affected corrosion of sheet piles and support H-piles. Some of the changes that have occurred would include types of cargo ships using the harbor, changes in cargo and associated loading/unloading facilities, the rate of ship traffic, harbor modifications, and policy changes pertaining to ship discharge. Lacking a formal study it is unclear whether functional changes have significantly affected corrosion rates. Therefore, the panel believes changes in harbor use should be investigated as a possible cause of accelerated corrosion.

Potential Solutions

The risk in presenting potential solutions to a problem before definitively defining its causes is that the analytical process may be unduly influenced. However, it is useful to categorize the range of possible options that are available when addressing corrosion problems. General categories of solutions, as presented by the expert panel, are discussed below.

Cathodic Protection (CP)

There are two basic types of CP system: impressed current and sacrificial (also called galvanic). An *impressed current* CP system uses an electric power source to introduce an engineered DC flow between a submerged or buried steel structure and an installed anodic electrode. A *sacrificial anode* CP system operates off the native (i.e., natural) difference in electric potential between a steel submerged or buried steel structure and a mass of metallic material (usually a zinc or aluminum alloy) that is anodic compared with the structure. A sacrificial system requires no external source of electric power, and it consumes the anodic material as part of the corrosion protection process.

Impressed Current System. Although an impressed current CP system could be applied to affected structures located in MSH, the electric current demand would be very high. Even before accounting for resistance associated with delivering the protective current, the requirement for a representative structure would amount to thousands of amperes. Delivering that amount of current would require a significant initial capital cost to provide multiple anode beds and banks of rectifiers. Furthermore, the resulting power bills would be prohibitively high, especially considering that the local water resistivity is about 4,500 ohm-cm. Therefore, impressed current CP would not be a viable overall solution for accelerated corrosion throughout the greater DSH. However, for smaller critical portions of the sheet pile or H-piles where dielectric isolation can be achieved, impressed current CP could be selectively applied.

Sacrificial Anode System. This type of system has the advantage of being simpler in design than an impressed current system, and it requires less maintenance. However, the overall current output and protective current distribution is limited in comparison with impressed current CP. In DSH applications, the tons of galvanic anodes required to implement and maintain a sacrificial system would be even more expensive than the cost of impressed current CP. There would also be design problems associated with effective permanent placement of galvanic anodes given the winter icing and scour conditions. The relatively high

water resistivity also would be problematic, as it would be for impressed current CP. Consequently, galvanic anodes could only be considered for limited and highly localized applications, and even in such cases they would probably be cost-prohibitive.

Corrosion-Resistant Alloys

Some structural alloys resist corrosion in immersed environments more ably than conventional materials, but they tend to be expensive. If other alloys were used in harbor structures they must not be connected with existing sheet pile, otherwise destructive galvanic effects would occur. The same also would be true of in-kind replacement because new steel, when connected to old steel, will quickly corrode in order to achieve a comparable native potential. Barring the availability of cost-competitive production or a source of more corrosion-resistant metal alloy sheet piles, this does not appear to be a promising solution. Nevertheless, it may be prudent to investigate costs for stainless steel, copper steel, high-strength low-alloy (HSLA) steels, and other corrosion-resistant materials before completely ruling out this approach.

Non-Metallic Advanced Materials

Sheet pile fabricated of non-metallic materials such as fiber-reinforced polymers are available, but they are unproven in this type of service and in harsh environments. In general, polymer materials have a *glass transition temperature* below which they become brittle and prone to fracture. There are also other performance issues related to their ductility, tensile strength, and ultraviolet degradation. Advanced non-metallic materials do not ‘rust,’ but they do degrade in other ways. In the future, cost-effective and viable sheet pile may be made of non-metallic or other advanced materials (e.g., glassy steel or fullerene carbon reinforcement) may be available, but at this time there are no affordable, performance-tested alternatives of this nature on the market.

Protective Coating Systems

Protective coatings are appropriate both for existing and new structures. A coating system was observed on one structure in the harbor. Even though the coating film thickness was minimal it did appear to provide some corrosion protection. The coating had sustained damage due to impacts from floating ice or debris, but revealed no notable deterioration due to outside electrical or chemical factors. The Corps of Engineers publishes standard coating specifications for sheet pile and other freshwater structures, and many of these systems have suc-

cessful performance histories that span decades. The problem is that coating sheet pile in place is difficult and relatively expensive. Coating systems that are suitable for underwater application are very costly and typically inferior to coatings applied to dry substrates. Devices called coffer dams can be used to provide a dry setting under water to coat sheet pile in place, but water from the land side of the pile typically seeps through joints and perforations before the coating fully cures, and this results in numerous early failures. A cost/benefit evaluation of coating existing piles in place may be considered, but conducting a formal study could require years of observation after which time the exact same formulation of the commercial products tested may no longer be available. The most dependable approach is to coat all new piles before installation with a performance-tested coating system that has a proven service record.

Condition Based Maintenance and Management

For a problem of the magnitude that is suspected, a phased solution ultimately will be needed. For virtually any structure or mechanical system, repair is cost-effective if degradation is identified soon enough. After some point, however, replacement is a more cost-effective option than a massive repair program. The challenge is to reliably assess the condition of each sheet pile section in order to (1) determine whether maintenance or replacement is the better option, (2) prioritize among multiple efforts within budget limits, and (3) project future work and overall infrastructure condition using alternative funding scenarios. This approach is the essence of condition-based maintenance and management. Tools and engineering guidance are available and, if applied consistently, condition-based maintenance and management provide superior mitigation of problems more affordably than any ad hoc approach. In addition to avoiding catastrophic failures, this approach provides better opportunities to organize and plan for the inevitable replacement of steel in the harbor.

3 Recommendations

The following recommendations are preliminary and subject to revision based on future findings. The short-term recommendations are considered to be urgent and should be considered for immediate implementation. The long-term recommendations are less immediately urgent but are nevertheless considered by the expert panel to be necessary for ongoing effective management of DHS accelerated corrosion.

Short-Term

1. Corrosion Rate Monitoring

In order to establish and quantify the problem, the rate of corrosion should be immediately measured at a number of sites. All measurements should be made according to existing industry standards by corrosion engineer certified by the National Association of Corrosion Engineers (NACE). These measurements will also help to establish a baseline for future reference. Initially, locally induced polarization testing methods should be used. Thereafter, either polarization or coupon weight loss methods should be employed to capture ongoing or seasonal changes. Longer-term, less-frequent corrosion rate measurements should be made at a small number of select monitoring sites.

2. Water Chemistry Analysis

Water chemistry analyses focused on corrosion-related parameters should be made at a number of representative sites and depths. Given the probability of seasonal variations, these analyses should be performed for at least 2 years. Data should at minimum include measurements of pH, total dissolved solids, dissolved oxygen content (at the time of sampling), various metals and compounds concentrations (e.g., sodium, calcium, magnesium, sulfate, chloride, iron, copper, zinc, silica, orthophosphate, ammonia, tannins, etc.), conductivity, Ryznar index, Langelier index, and Larson index. Longer-term, less-frequent sampling at a few sites should be continued for monitoring. All testing should be performed by a certified laboratory.

3. Corrosion Product and MIC Analysis

Corrosion product should be characterized and the presence of MIC activity should be investigated. Such investigation may confirm one or more specific corrosion mechanisms, and should at least eliminate various other mechanisms from consideration. Measurements should be made according to all applicable industry standards as performed by qualified personnel.

4. Stray Current Testing

Of the various possible sources of stray DC flow, two are relevant to any formal investigation of DSH accelerated corrosion:

- DC loading equipment such as ore conveyor systems reported to operate in the vicinity of the sheet pile DSH sheet pile
- high-voltage DC (HVDC) electric transmission systems.

Because both potential sources of stray current vary dynamically during operation, testing to determine if these are impacting the sheet pile would be relatively simple. The corrosion potential of the steel may be measured as a function of time (generally over a 24- or 48-hour period) using synchronized digital recording volt meters. Measured changes in corrosion potential can be compared with the operations of the HVDC and the DC loading equipment to assign any detected source of the influence. If no such time correlations are observed, then stray current can be ruled out as a factor in DSH accelerated corrosion.

Tests capable of determining the presence and source of any stray current corrosion should be performed by a NACE-certified corrosion engineer in accordance with all applicable industry standards.

5. Critically Needed Condition Assessment and Structural Characterization

Where life-safety issues or economic losses are of high potential concern, focused condition assessment and structural characterization activities are advisable. The most appropriate method of characterization will differ according to the specific situation, but nondestructive ultrasonic thickness measurement techniques in conjunction with an appropriate number of confirmatory through-hole micrometer measurements should be considered.

Long-Term

1. Condition-Based Inspection Strategy for Repair/Replace Management

Given the wide extent and age of installed metallic structures in DSH, the cost-effective management of this infrastructure will become increasingly problematic without a coordinated maintenance management strategy. Deferred projects, emergency repairs, and inaccurate budget projections will increasingly become the norm without a systematic, proactive means of tracking current and projected condition. It is recommended that an existing management tool be adopted or adapted to meet the needs of DSH and consistently applied. One category of tools developed for such purposes is the Engineered Management System (EMS). EMSs are available for sheet pile structures as well as other infrastructure systems such as pavements, roofs, and vertical structures. An EMS encompasses a methodology of objective, repeatable visual inspection and assessment used in conjunction with an engineer-developed condition index. The inspection and assessment produces a condition 'score' that is tracked over time at a specific site, sometimes in conjunction with predictive degradation models that help infrastructure managers project future condition. By maintaining this capability, various maintenance management scenarios can be quickly developed and examined in order to make optimal use of limited resources. A major benefit of this approach is the avoidance of catastrophic structural failures or unacceptable economic losses.

2. Ongoing Monitoring

An ongoing monitoring program is recommended for both water chemistry and corrosion rate measurements. The frequency and number of sites will be reduced compared to the initial efforts. The specifics of the program should be determined after assessing the variability obtained from initial characterizations.

3. Develop a Standard Replacement Design Using Both Coatings and CP

Probably the most cost-effective solution to accelerated corrosion affecting steel sheet piles in DSH would be to install a new pile structure in front of and parallel to existing deteriorated sections. This approach is typically executed by driving new pile where needed and attaching it to existing dead-man anchorages. The technique provides lateral support to the new pile but, as noted previously, creates a galvanic corrosion problem as the new pile corrodes at a substantially faster rate than even the existing pile as the native potentials of the two structures equalize. To avoid this phenomenon it is essential to anchor new

sheet pile to the old pile using electrically insulating materials that prevent current from flowing directly between the two piles.

Even if the new sheet pile is electrically isolated from the old in terms of mechanical connections, excessive corrosion will nevertheless occur if the steel is installed without a protective coating. The corrosion rate for the new bare steel pile would reflect the accelerated rates of the past 25 years. However, because all coatings will have a number of small flaws (called *holidays*), new coated piles will still have small, electrically conducting sites where pitting corrosion will occur. The rate of pitting attacks at holidays can be as much as five times greater than the general corrosion experienced uniformly across bare metal. A common solution to this vulnerability is to design sacrificial CP specifically to prevent pitting at the coating holidays. The cost of galvanic anodes for this purpose typically is less than 10% of the coating cost and about 1 – 2% of the overall repair cost.

The expert panel recommended developing a standard design specification for a replacement steel sheet pile section, both coated cathodically protected, to use adjacent to deteriorated sheet pile. It is recommended that such a design be incorporated into applicable regulations. The replacement section design should include all engineering drawings, calculations, coating and material specifications, and details needed to ensure acceptable long-term performance.

4. Initiate a Corrosion Characterization Survey of Other Great Lakes Port Facilities

While not explicitly within the scope of this effort, corrosion characterization surveys of other Great Lakes port facilities are recommended to determine the extent of accelerated corrosion in the Great Lakes. Formal coordination of research and technical information exchange could help to avoid redundant efforts, save time, and avert significant hazards or economic losses.

Appendix A: Expert Panel Members

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Appendix B: Workshop Agenda



Duluth – Superior Harbor Accelerated Corrosion Expert Panel Meeting September 9, 2004



The expert panel will address the following questions.

1. *Is there accelerated corrosion and is it different than seen in other freshwater ports?*
2. *What is the spatial extent of corrosion?*
3. *What are likely causes of this corrosion?*
4. *What research/monitoring is needed?*
5. *How would you prioritize the research/monitoring needed?*
6. *What can be done to mitigate the problem?*

THE AGENDA

8:30	Introductions and description of the agenda
8:45	Overview of problem
9:15	Overview of information collection
9:35	Overview of Expert Panel process (charge to the panel)
9:45	Facilitated meeting – Panel discusses the list of questions. Facilitator allows audience participation as appropriate
10:30	Break
10:45	Continue facilitated panel meeting
12:00	Lunch (on your own)
1:15	Continue facilitated panel meeting
3:00	Summarize outcomes of the day
3:30	Adjourn

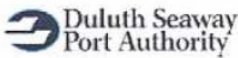
THE PANEL

<u>Expert</u>	<u>Expertise</u>	<u>Affiliation</u>
Charles Marsh	Great Lakes corrosion	US Army Corps of Engineers
Alfred Beitelman	Protective coatings	US Army Corps of Engineers
James Bushman	Electrical induced corrosion	Bushman and Associates
Brenda Little	Microbial induced corrosion	Naval Research Laboratory
Rudy Buchheit	Metallurgy and corrosion	Ohio State University

SPONSORS








THE LOCATION

Minnesota Pollution Control Agency
Fourth Floor Conference Room
525 South Lake Avenue
Palucci Building, Canal Park
Duluth, MN

THE STEERING COMMITTEE:

Dave Bowman, US Army Corps of Engineers
Gene Clark, WI Sea Grant
Don Fosnacht, Natural Resources Research Institute
Jeff Gunderson, MN Sea Grant
Al Klein, US Army Corps of Engineers
Al Mozol, US Army Corps of Engineers
Carl Richards, MN Sea Grant
Chad Scott, Kreech, Ojard and Assoc.
Jim Sharrow, Duluth Seaway Port Authority
Ray Skelton, Duluth Seaway Port Authority

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Contact:

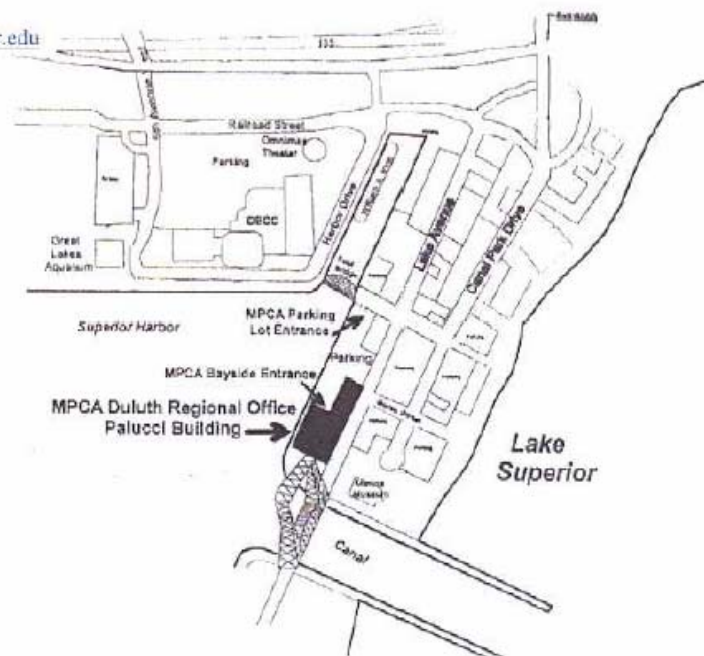
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Appendix C: Invitation List for Corrosion Workshop

Azcon Corp.	AGP Grain Limited
Rodd Secrist, General Manager	Tom Miller, Superintendent
Burlington Northern Santa Fe No. 5 Taconite Facility	Cargill Inc.
Mike Weston, Terminal Manager	Roger Juhl, Elevator Superintendent
C. Reiss Terminal	Cenex Harvest States
Michelle Joki, Office Manager	Lance Helgeson, Superintendent
Cutler-Magner Company	General Mills Elevator
Clarence LaLiberte, President	A. Douglas Christiansen, General Manager
Cutler-Magner Company, Superior	Peavey Company - Connor's Point Elevator
CLM Corp., Lime Plant	Mick Sertich, Superintendent
Duluth Missabe & Iron Range Railway Company General Offices	Superior Harbor Commission
Duluth Missabe & Iron Range Railway Company	Jason Serck, AICP, City Planner
David Torgersen, Manager, Dock Operations	U.S. Coast Guard
	Cdr Hung M. Nguyen, Captain of the Port & Marine Inspection
	Lcdr Mark Ledbetter
Hallett Dock Company	Fraser Shipyards Inc.
Jeremy Fryberger, President	Trevor White, Vice President & General Manager
William McGiffert, Vice President Operations	
Michael McCoshen, General Manager	
Lafarge North America	Mark McShane, Director
Carl Hanson, Manager	Property Management Division
Lafarge North America	Tim Beber
Barry Pigeon, Manager	
Lake States Lumber Inc./Innovative Pine Technologies	MPCA
John Stauber, Manager	Pat Carey
Lake Superior Warehousing Company, Inc.	Duluth Port Authority
Gary Nicholson, President	Adolf Ojard
Denise McDougall, Warehouse Coordinator	
Midwest Energy Resources Company	Duluth Port Authority
Fred Shusterich, President	Jim Sharrow
Marshall Elder, Manager, Terminal Operations	
Northland Bituminous (at Northland Pier)	Duluth Port Authority
c/o Northland Constructors Inc.	Ray Skelton
Jim Holmgren, President	
St. Lawrence Cement Inc.	UMD
David Sobczak, Terminal Manager	Carl Richards
UMD, Sea Grant	UMD
Jeff Gunderson	Emmanuel Ugo Enemuoh

UW, Sea Grant	UM-Twin Cities
Gene Clark	Watertalk
UW, Sea Grant	US Army Corps of Engineers
Jim Hurley	Al Klein
UMD, Sea Grant	US Army Corps of Engineers
Marie Zhuikov	Al Mozol
UMD, Sea Grant	Minnesota Power
Cindy Hagley	Lynn Crane
UMD, NRRI	WLSSD
Don Fosnacht	Kurt Soderberg
UMD, NRRI	WLSSD
Joseph M. Mayasich	Joe Stepun
UMD, NRRI	Rep. James Oberstar
Jerry Niemi	U.S. House of Representatives
UMD, NRRI	Bill Richard
Rich Axler	Oberstar office
UMD, NRRI	Jackie Morris
Mike Lalitch	Oberstar office
UMD	Sen. Mark Dayton
James P Riehl	U.S. Senate
UMD	Tom Huntley
Randy Hicks	MN Representative
UMD	Herb Bergson
Bilin Tsai	Duluth Mayor
UMD	
Bob Carlson	
UMD	
Tim Holst	
UMD	
Eric Brown	
UMD	
Steve Coleman	
UMD	
A. Rashid Hasan	
UMD	
Stanely Burns	
UMD	
Dave Wyrick	
UMD	
John Hiller	
UMD	
Vince Magnuson	
UMD	
Kathryn Martin	

Appendix D: Preliminary Evidence of Accelerated Corrosion

Pit Depth Analysis

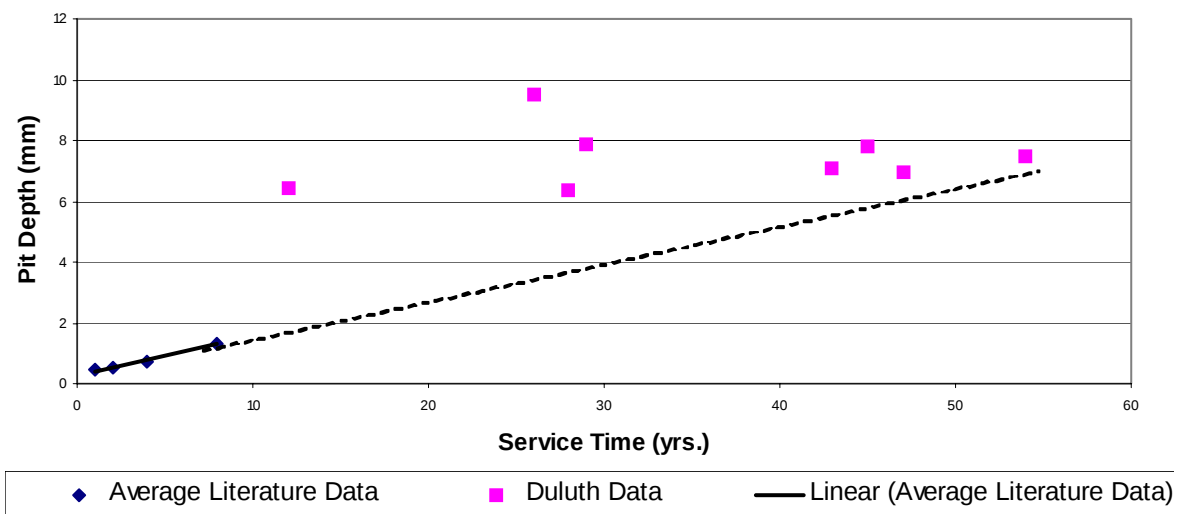
In the graph below the maximum pit data gathered from multiple sites by Krech Ojard & Associates is analyzed with respect to literature data published* for three freshwater rivers (Monongahela River – Charleroi, PA; Allegheny River – Kittanning, PA; Mississippi River – Winfield, MO). The comparison is for the plain carbon steel results only. For each period (1, 2, 4, and 8 years) the data from all three rivers were averaged together. One of the main concerns is that corrosion rate data is typically used for comparing the corrosive effects of differing environments. The pitting process is not well understood (e.g., determination of initiation time, the role of passivity and passive film breakdown with respect to local environmental conditions, etc.) and is not necessarily representative of the relative corrosiveness between two environments. However, given that this was the only direct quantitative data available and that there was applicable published data to compare it to, this somewhat flawed analysis was undertaken. Another caveat to point out is that each DSH data point is a single measurement. Therefore, statistical analysis as to mean, variance, error, etc. is not possible. Further, maximum pit depth may not have been measured according to generally accepted practices, such as with a lever type pipeline pit gage, or a L.S. Starrett Co. type device.

With that said, the following interpretation is of interest. The conjecture is that approximately 30 years ago the ongoing rate of corrosive degradation in DSH underwent a significant and, thereafter, persistent increase. As shown on the following graph, the four data points for 30 years or less exposure show a significant increase in maximum pit depth compared to the linear projection from the collective freshwater data. This is in marked contrast to the four data points for exposure times exceeding 40 years. One interpretation of this is that longer ex-

* *Metals Handbook*, 9th ed., Vol. 1, Properties and Selection: Irons and Steels, American Society for Metals, Metals Park, OH, 1978, p.737.

posures include an increasingly longer proportion of service life in the “low corrosion” regime where the time-averaged rate of maximum pit growth would be less. The net effect for these older samples is a shallower maximum pit depth than would be expected under a more constant corrosion rate.

Comparison of Pit Depth Thickness Measurements at Various Locations on Duluth Harbor Sheet Pile Compared with Averaged Published Pit Depth Measurements for Comparable Materials in Fresh Water



Estimated Steel Thickness Loss Based on Dissolved Oxygen Data

Estimates of thickness losses of steel sheet pile were made from dissolved oxygen (DO) measurements from April 1974 to October 1987 from DO data collected in the Duluth-Superior Harbor at the Burlington Northern Bridge water chemistry monitoring site. The analysis suggests a nominal corrosion rate of about 12 mils per year from 1974 to 1979, followed by an increased corrosion rate of about 22 mils per year from 1979 to 1987. A total thickness loss of about 250 mils is estimated, which is consistent with observations of thickness losses due to sheet pile corrosion. This apparent increase in corrosion rate through the 1980s suggests that a change in the DO content in the harbor may be a contributing, or perhaps a dominant factor in accelerated sheet pile corrosion. The analysis and assumptions underlying these estimates are as follows:

Corrosion mechanism assumed. A primary environmental variable affecting the corrosion rate of steel in natural fresh waters is the DO content. In this analysis, the corrosion cell reaction for steel is treated as the oxidation of iron coupled to the reduction of oxygen dissolved in water:



The reactions are coupled by the fact that electrons produced by oxidation of iron are consumed by reduction of DO. $\text{Fe}(\text{OH})_2$ can react further with DO to form $\text{Fe}(\text{OH})_3$, Fe_3O_4 and Fe_2O_3 . None of these subsequent reactions result in further metal wastage directly and were not considered in this analysis.

Because all of the electrons produced by the oxidation of iron are consumed by the reduction of DO, the current associated with the reduction of oxygen must equal the current associated with oxidation of iron. In natural waters, the reduction of oxygen on metal surfaces is typically mass transport limited, and *mass transport limited oxygen reduction was assumed in this analysis*. For a planar surface, the current density characterizing the rate of oxygen reduction is given by:

$$i_{\text{lim}} = \frac{nFDC_B}{\delta} \quad (\text{eq. D.3})$$

where i_{lim} is the limiting reaction rate current density (A/cm^2), n is the number of equivalents of electrons reacted per mole of oxygen reduced (4 eq/mol per eq. D.2), F is Faraday's constant (96,500 C/eq), D is the diffusivity of DO in water ($8 \times 10^{-6} \text{ cm}^2/\text{s}$) and δ is the diffusion layer thickness ($2 \times 10^{-2} \text{ cm}$). The values for D and δ are approximate but believed to be appropriate for this analysis. C_b is the DO concentration (moles O_2 per cm^3 water). DO measurements were reported in part per million by weight (ppmw). One ppmw O_2 was taken to be 3.13×10^{-10} moles O_2 per cm^3 water. In this analysis, F is a constant by definition, and the terms n , D and δ were treated as constants throughout the analysis.

Corrosion rate calculation. The rate of oxygen reduction and iron oxidation in eq. D.1 and D.2 are precisely coupled because all electrons produced by oxidation of iron are consumed by reduction of oxygen. *Assuming that the oxidation and reduction reactions occur uniformly across the sheet pile surface (a fair assumption in the case of uniform corrosion), the current densities for each partial reaction are exactly equal:*

$$i_{\text{oxidation}} = i_{\text{lim}} \quad (\text{eq. D.4})$$

In eq. D.4, $i_{\text{oxidation}}$ is the corrosion current density of the steel sheet pile and i_{lim} is the current density for the oxygen reduction reaction. A modified form of Fara-

day's law was used to compute the rate of thickness loss of the steel sheet pile from $i_{\text{oxidation}}$:

$$r = 0.129 \frac{A i_{\text{oxidation}}}{nD} \quad (\text{eq. D.5})$$

where r is the corrosion rate (mpy), A is the atomic weight of iron (55.8 g/mole), $i_{\text{oxidation}}$ is taken from eq. A.4, n is the number of electrons reacted per mole of iron oxidized (2 eq/mol), and D is the density of steel (taken as the density of iron in this calculation, 7.7 g/cm³).

To estimate corrosion rate, the DO concentration data was used to compute the limiting current density for oxygen reduction according to eq. A.3, and the corresponding rate of sheet pile corrosion rate was calculated from eqs. D.4 and D.5.

Thickness loss calculation. The DO measurement data set consisted of the numerical values of the DO content and the dates on which the readings were made. From year to year, the number and frequency of measurements varied resulting in intervals of varying time between measurements. To estimate thickness losses, a corrosion rate was computed from a DO measurement, and that rate was multiplied by the time elapsed until the next DO measurement:

$$\Delta T_i = r_i \cdot t_i \quad (\text{eq. D.6})$$

In this expression ΔT_i is the thickness loss due to corrosion during the interval (mils), r_i is the corrosion rate for the interval (mpy), and t_i is the length of the time interval (years). Cumulative thickness loss at any time, $T(t)$, is then given by the sum of the thickness loss increments:

$$T(t) = \sum_{i=0}^i \Delta T_i \quad (\text{eq. D.7})$$

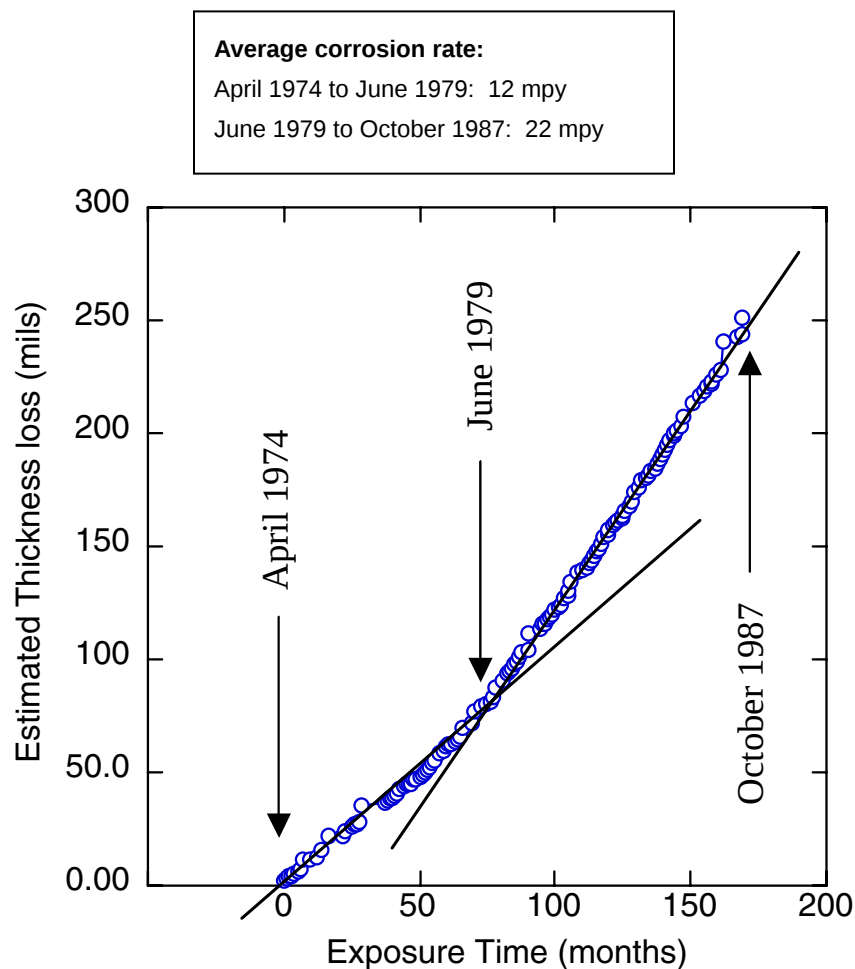
Eq. D.7 was used to construct the plot of total thickness loss versus time.

Assumptions. There are several implicit assumptions in this analysis not noted above.

- 1) The effect of temperatures is not accounted for. Temperature ranges from about 32 – 70 °F across the harbor during an annual cycle. This will affect the

value of the diffusivity for DO used in eq. A.3. Overall, this effect is thought to be minor.

- 2) This analysis does not account for effects on corrosion rate by corrosion product films, biofilms, or deposits of any type on the sheet pile surface. These layers can have either inhibiting or accelerating effects, which cannot be judged without additional information.
- 3) This analysis applies to a uniform corrosion mode. Corrosion of sheet pile is somewhat localized.
- 4) This analysis assumes that the area suffering corrosion and the area supporting reduction of DO are nominally equal.



Estimated thickness loss as a function of time from April 1974 to October 1987 derived from dissolved oxygen measurements made near the Burlington Northern Bridge in Duluth-Superior Harbor.

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ABSTRACT This report reviews the potential causes of accelerated corrosion of sheet pile and other steel structures in the Duluth-Superior Harbor and makes recommendations for addressing the problem. The authors met in Duluth (September 2004) to examine harbor corrosion and consult with interested parties. The corrosion appears as pock marks primarily in the 4 feet just below the water surface. The corrosion extends down to about 10 feet, but decreases from 4 feet below the surface to 10 feet. The corroding pock marks are covered by an orangish coating that tends to cover the corroded pit. Water chemistry, dissolved oxygen content, and dissolved chlorides from de-icing salts seem to be the most likely agents of accelerated corrosion of 12 causes discussed. A lack of data made it unclear whether microbiological factors or functional harbor changes are unduly influencing corrosion in the harbor. The authors recommend immediately quantifying the corrosion rate, conducting a water chemistry analysis, checking for microbiologically influenced corrosion, testing for stray DC currents, and assessing the condition of critical steel structures. They encourage long-term monitoring of corrosion in the Duluth-Superior Harbor and other Great Lakes ports, as well as developing a condition-based strategy for steel replacement and repair.					
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