



Miles of steel sheet piling and structures are corroding at an unusually accelerated pace in Duluth-Superior Harbor. The cause is still under investigation. All photos courtesy of Gene Clark, Wisconsin Sea Grant Institute.

# Mystery in Minnesota

*Duluth harbors unusual corrosion.*

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**S**ilently, insidiously, corrosion has raised the ante in Duluth-Superior Harbor (Duluth, Minnesota), where steel sheet pilings are rusting away at an unusually accelerated rate: The thick plates, generally expected to last 50 years in this type of service, are exhibiting perforations after less than 10 years. This rate of corrosion is not common in freshwater harbors, and it promises expensive repairs if the cause is not identified and mitigated.

Thirteen miles (20.8 km) of steel sheet piling and structures are corroding around the harbor, menacing the structural integrity of docks and loading facilities. Replacing the failing steel will run \$1,500 or more per linear foot: The Duluth Seaway Port Authority estimates up to \$100 million in repairs may be required for steel that is weakened by corrosion.

Comparisons of sheet piles of different ages within the harbor indicate that the increased rate of corrosion began in the late 1970s. Underwater inspections reveal that the corrosion is widespread, affecting all types of steel piling buttressing the docks. Most of the steel is riddled with small pits in diameters of 0.25 to 1 in. (6 to 25 mm), primarily in the first 4 to 6 ft (1.2 to 1.8 m) below the waterline, and tapering off around 10 ft (3 m). (Below 10 ft, there is very little corrosion, despite the colonies of zebra mussels that begin at that depth and range to the bottoms of the steel plates.) Some of the steel beams supporting the dock structures have holes the size of footballs (these are being repaired). The pits of corrosion are described as having an orange coating that generally covers the pits.

Similar corrosion, to a lesser extent, also appears upstream from the harbor; however, reports suggest that in general, corrosion outside the harbor is not as severe. Investigators posit that the limited amount of accelerated corrosion upstream may be due to a seiche (an oscillating wave resulting from seismic or atmospheric disturbance), which could briefly reverse water flow and move some of the harbor water, with its corrosion-causing contaminants, up river.

To look into the problem, a steering committee was formed by the Wisconsin Sea Grant Institute (Madison, Wisconsin), Minnesota Sea Grant College

Program (Duluth, Minnesota), the Duluth Seaway Port Authority, the U.S. Army Corps of Engineers (Washington, D.C.), Krech Ojard & Associates (Duluth, Minnesota), and the University of Minnesota-Duluth and its Natural Resources Research Institute. The committee recommended that the corrosion problem be reviewed by an independent group of experts. Subsequently, a panel of five experts in corrosion, microbiology, and chemistry was assembled, including Charles Marsh and Alfred Beitelman, materials research engineers with the Army Corps of Engineers; Rudolph Buchheit, a professor of materials science and engineering at Ohio State University (Columbus, Ohio); James Bushman, a NACE-certified independent corrosion engineer; and Brenda Little from the Ocean Sciences branch of the Naval Research Laboratory (Diamondhead, Mississippi).

The panel visited areas of the port where accelerated corrosion was particularly apparent, then met to discuss their observations and review the information gathered by the steering committee. A number of



Most of the corroding steel sheet pilings and beams—which may require up to \$100 million to repair—are riddled with pits.



Researchers examined 12 possible causes of the accelerated corrosion; the exact cause still remains a mystery.

stakeholders, researchers, and other interested parties also participated in the meeting.

## Possible Causes

Twelve possible causes of the accelerated corrosion were examined: water chemistry, temperature, dissolved oxygen (DO) content, de-icing salts, microbiological activity, stray current, storm water runoff/sewage, ship's ballast discharge, zebra mussels, metallurgy of steel, water electrolysis, and functional changes within the harbor.<sup>1</sup> Of those, the panel found water chemistry, DO, and de-icing salts to be significant potential causes that should be investigated first. They also cited microbiological activity and functional changes as meriting further consideration.

## Water Chemistry

As total ion concentration in the electrolyte determines resistance to electric currents (and thus the rate of corrosion), preliminary measurements of total dissolved solids were taken at different locations in the harbor. The measurements consistently showed values of 4,500 to 4,700  $\Omega$ -cm—within the typical range for fresh waters. The panel's report noted that pH and dissolved tannins could also be significant factors, and that additional testing should be performed to quantify these characteristics of the harbor water.

## Dissolved Oxygen

An analysis of DO measurements collected in the harbor from April 1974 through October 1987 showed a corrosion rate of 12 mpy (305  $\mu\text{m}/\text{y}$ ) from 1974 to 1979. The rate increased to 22 mpy (559  $\mu\text{m}/\text{y}$ ) from 1979 to 1987. This increase suggests that a change in DO in the harbor may be contributing to

the accelerated corrosion. The effect of temperature on DO content was not considered, as it was thought to have little effect in this instance.

## De-icing Salts

Roadway de-icing salts may be a significant source of chloride in the harbor waters, as local topology and land use feed significant runoff into the harbor. Chloride ions, which disrupt passivating films, can contribute significantly to corrosion.

## Other Possibilities

Results of the initial investigation do not make clear whether microbiologically influenced corrosion (MIC) is a significant factor in this instance; therefore, the panel feels the possibility of MIC should be explored in greater detail. (One type of MIC, accelerated low water corrosion [ALWC], is reported to be a growing problem in European ports.)

"The similarities and differences between the corrosion of sheet piling occurring in Duluth freshwater harbors and ALWC in saline waters are striking," says Little. "ALWC is a global phenomenon, having been reported around the world 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.

"The detailed mechanism of ALWC in marine/estuarine environments continues to be a matter of some debate," she continues, "but several research groups have concluded that it is a form of MIC due to combination of sulfate-reducing bacteria (SRB) and thiobacilli in the fouling layers on the pilings. The organisms occur together, separated by the oxygen gradient in the biofilm. At low tide, the biofouling layer is oxygenated, whereas at high tide, anaerobic areas develop. The sulfides produced by the SRB in the anaerobic regions and sulfuric acid ( $\text{H}_2\text{SO}_4$ ) resulting from the thiobacilli in the aerobic regions combine to produce an extremely corrosive environment." However, Little adds, there are no data at this time to indicate that this type of mechanism is at work in the Duluth-Superior Harbor.

Three significant functional changes in the harbor were noted by the panel as possible contributing factors that should be investigated. One change occurred in 1978, when industrial and municipal sanitary discharges were consolidated into a single waste treatment plant, located in the area where the highest corrosion rates have been observed. This improved water quality significantly; however, it may also have increased DO levels, concentrated chemicals from industrial sources that were previously distributed along the river, or raised the level of sulfate compounds (used to dechlorinate effluent) in the harbor. The treatment plant no longer chlorinates or dechlorinates its discharge.

Another change was effected with the installation of

a high-voltage direct current (DC) power line, which runs from North Dakota to Duluth, in the 1970s. The 250-kV line returns current through conductors, but occasionally operates under a ground return, oriented northwest of and away from the harbor.

The third change also occurred in the 1970s, when a local water treatment facility began filtering for asbestos fibers. Aluminum sulfate is added to the water as part of this process. Combined with chlorine and fluoride additions, this treatment decreased pH from 8 to 7, causing corrosion problems in Duluth water lines. Plant operators initially added zinc orthophosphate and tripolyphosphate in an attempt to coat the pipes. In the mid-1980s, they switched tactics and tried to raise the pH to 9 by adding sodium hydroxide (NaOH). This treatment continues today. The panel speculates that whatever caused corrosion of the city water lines may have been transmitted to the harbor through the waste treatment facility.

## Finding a Solution

The panel's initial activities served to identify primary cause candidates for further investigation. A substantial amount of data gathering and analysis remains to be done before the cause of the accelerated corrosion can be positively identified and a solution put in place.

Upon completion of its initial review of the condition of the steel plates and other available data, the panel drew up a list of short-term and long-term recommendations.

## In the Short Term

Among its proposals for the near future, the panel suggested tracking the rate of corrosion at a number of sites in the harbor to establish a baseline and to capture seasonal or other changes. Detailed water chemistry analysis should be performed for at least two years, the panel specified, and corrosion product collected from the steel piling should be characterized, as well as tested for microbiological activity.

To determine whether stray current contributes to the accelerated corrosion, the panel proposed examining DC loading equipment (such as ore conveyor systems) that is used at the harbor, as well as high-voltage electric systems in the area.

Finally, the panel emphasized the need for immediate, detailed assessment of the condition and structural integrity of the pilings, so as to identify any risks to persons or property.

## Looking Ahead

For the long term, the panel advocated a condition-based inspection regime to manage repair and replacement, aimed at avoiding a spiraling cycle of emergency repairs and unanticipated expenses. Monitoring of water chemistry and corrosion rates should be ongoing, the panel counseled, and other port facilities in the Great Lakes should be surveyed to determine whether acceler-

ated corrosion is occurring in other areas.

Finally, the panel proposed installing a new pile structure, in front of but electrically insulated from the existing pilings. The new structure, they specified, should be protected with an appropriate coating and cathodic protection.

## Acknowledgment

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## Reference

1. C.P. Marsh, J. Bushman, A.D. Beitleman, R.G. Buchheit, B.J. Little, "Freshwater Corrosion in the Duluth-Superior Harbor," U.S. Army Corps of Engineers, ERDC/CERL SR-05-3, March 2005. **MP**

## Duluth-Superior Harbor Corrosion Study Update

- **Funding:** The steering committee continues to pursue multiple sources of study funding. To date, the State of Minnesota has appropriated \$100,000 and the U.S. Army Corps of Engineers was approved \$300,000 (FY 06 budget) for the initiation of studies to determine the causes of the corrosion. The steering committee is seeking similar levels of federal funding for FY 07, approaching the State of Wisconsin for a grant similar to the Minnesota appropriation, and soliciting financial support from owners of dock facilities throughout the harbor.
- **Short-term studies:** A coating test is underway, and a limited-scope MIC test has been initiated with sample coupons from several locations around the harbor.
- **Water quality database:** Existing water quality data is being collected and cataloged in a database. Specific water quality parameters pertinent to the study will be included and the database will be updated as additional information is collected.
- **Existing structure evaluations:** Existing harbor structures will be catalogued. Divers will inspect each facility in the harbor. Additional parameters will be measured, such as thickness loss due to corrosion, analysis of water samples and light intensity near the structures, and water clarity.
- **New developments:** Updates on the mystery will be posted as they become available at [www.seagrant.wisc.edu/coastalhazards](http://www.seagrant.wisc.edu/coastalhazards), or you can contact Gene Clark with the Wisconsin Sea Grant Institute at [grclark@aqua.wisc.edu](mailto:grclark@aqua.wisc.edu).