NATIONAL MARINE SANCTUARIES LESSON PLAN

The Iron Cheesebox

Theme
National Marine Sanctuaries (U.S.S. *Monitor*)

Links to Overview Essays and Resources Needed for Student Research
http://monitor.nos.noaa.gov/

Subject Area
Chemistry

Grade Level
9-12

Focus Question
How can cultural resources be protected from natural processes that tend to destroy historically important artifacts?

Learning Objectives
- Students will be able to describe at least three oxidation/reduction reactions involved in the corrosion of iron in sea-water.

- Students will be able to define and discuss the major steps in conserving marine archeological artifacts.

- Students will be able to discuss at least three options that were considered for preserving the wreck of the U.S.S. *Monitor.*

Materials Needed
- (optional) Computers with internet access; if students do not have access to the internet, download copies of materials cited under "Learning Procedure" and provide copies of these materials to each student or student group
- (optional) Materials for demonstrating cathodic protection (see "Learning Procedure," step 3)

Audio/Visual Materials Needed

None

Teaching Time

One or two 45-minute class periods, plus time for student research

Seating Arrangement

Classroom style or groups of 3-4 students

Maximum Number of Students

30

Key Words

U.S.S. *Monitor*
Archeology
Artifact
Corrosion
Oxidation
Reduction
Archeological conservation
Cathodic protection

Background Information

In January, 1862, Continental Iron Works launched one of the world's strangest ships. To some it resembled a tin can floating on a shingle. Others simply called it "a cheesebox on a raft." But the 172 ft U.S.S. *Monitor* was a highly innovative vessel that included a rotating gun turret, a sheet iron hull capped with an armored belt designed to resist the largest cannon shot, a forced-air ventilation system, and below-waterline flush toilets. Two months later, the *Monitor* proved itself in a four-hour battle with the Confederate ironclad ship CSS *Virginia* (ex-USS *Merrimack*). Though neither ship yielded to the other, the *Virginia* was prevented from breaking the Union blockade of the James River, and resulted in instant hero status for the *Monitor* and its crew. But less than a year after her launch, the *Monitor* lay broken and upside down under 240 feet of water on the bottom of the Atlantic Ocean, a victim of the wicked winter storms common to the North Carolina coast off Cape Hatteras. After more than a century, the wreck of *Monitor* was discovered in 1973.

Two years later the wreck site became the United States' first National Marine Sanctuary, with a 1-nautical mile diameter protected area around the remains of the *Monitor*. Since then, the *Monitor* has been the subject of numerous expeditions to study and preserve this significant piece of our maritime heritage. Many organizations participated in the effort using sophisticated equipment for deep-diving, mapping, photography, and underwater salvage, and recovered more than 1,100 artifacts. But these expeditions also revealed that the Monitor's hull was deteriorating at an alarming rate.

As the *Monitor* sank, the hull began to roll in the water column. The ship impacted the bottom stern-first, gun turret broke free and landed upside down on the sea bed, and the inverted hull landed partially on top of the turret. This left an area of the ship's deck resting on the gun turret, only partially supported above the bottom. Now 130 years later, tons of iron armor on the hull threatened to snap the deck in half. As the wood and metal of the deck deteriorated, there was increasing danger that the hull would collapse and bury the rest of the ship beneath tons of debris.

In 1996, the U.S. Congress directed the Secretary of Commerce to produce " a long-range, comprehensive plan for the management, stabilization, preservation, and recovery of artifacts and materials of the U.S.S. *Monitor*." A year later, the National Ocean and Atmospheric Administration's (NOAA) National Marine Sanctuary Program released a plan that identified eight options:

1. Non-Intervention—no preservation action is undertaken and nature is allowed to take its course;
2. In Situ Preservation by Encapsulation—the *Monitor* is buried to significantly reduce deterioration;
3. In Situ Preservation by Shoring—structural support is provided to sections of the hull that are in greatest danger of imminent collapse;
4. In Situ Preservation by Cathodic Protection—modern technology for protecting vessels against corrosion is used to slow deterioration of metal components of the *Monitor*;
5. Selective Recovery of Artifacts and Hull Components—significant artifacts and major hull components that can be recovered with reasonable efforts are recovered;

6. Selective Recovery Followed by Encapsulation—a combination of above options;
7. Selective Recovery Combined With Shoring—another combination of above options;
8. Full Recovery—the entire wreck of the *Monitor* is raised from the bottom and preserved.

While the last option might seem to offer the best protection, this would be an extremely expensive solution and it might be impossible to keep the vessel from falling apart during salvage. In addition, the notoriously bad weather off Cape Hatteras that sank the *Monitor* in the first place continued to cause delays in efforts to study the wreck. Meanwhile, the wreck continued to deteriorate, threatening a catastrophic collapse that would make recovery even more difficult. In the end, managers chose "Selective Recovery and Stabilization (shoring)" as the most practical option. The effort culminated in August 2002 with the recovery of *Monitor's* gun turret. Many other artifacts were recovered during previous expeditions, including the ship's anchor and propeller, its steam engine, hydrometers and thermometers (some still working!), dinnerware, a brass signal lantern, and a jar of pickle relish. The relish looked and smelled quite good, but was found to have a high lead content, probably from curing in a lead-glazed crock before being transferred to the jar. The signal lantern had a red lens, and may have been the last thing seen by the Monitor's crew before the ship sank.

See the Ocean Explorer websites *http://oceanexplorer.noaa.gov/explorations/monitor01/monitor01.html* and *http://oceanexplorer.noaa.gov/explorations/monitor02/monitor.html* for details of *Monitor* expeditions, and *http://www.magazine.noaa.gov/stories/mag55.htm* for an online magazine article about the gun turret recovery.

In this lesson, students will investigate some of the processes that contribute to deterioration of underwater artifacts and options that resource managers may use to overcome these processes.

Learning Procedure

1.

If you want to introduce your students to marine protected areas, have them complete the "Water Parks" lesson, or direct them to "MPA Education Poster Site Descriptions" and "MPA Poster Activity Sheet " at *http://mpa.gov/information_tools/education/pdfs/Poster04companion.pdf* and *http://mpa.gov/information_tools/education/pdfs/mpaposter_activity.pdf*. Have each student complete one version of the MPA Subject Review, then lead a discussion to review the answers.

2.

Briefly review the chemistry involved in typical processes of iron corrosion. Students should understand that most corrosion processes are electrochemical; that is, they involve the flow of electrons from one substance to another. If you want to have students do a hands-on activity related to corrosion, see the Ocean Explorer "Galvanic vs. Titanic" lesson at *http://oceanexplorer.noaa.gov/explorations/04titanic/edu/media/Titanic04.Galvanic.pdf*.

In the case of iron corrosion, metallic iron (Fe_s) in contact with water loses electrons (is oxidized) to form ferrous (Fe^{2+}) ions and a small hole or pit is produced on the metal surface where the oxidation has occurred.

In acid solutions, the electrons produced by the corrosion reaction react with hydrogen ions (H^+) to form atomic hydrogen:
$2H^+ + 2e^- \text{-->} H_2$
As hydrogen ions are consumed, hydroxide (OH^-) ions appear.

When oxygen is present, an alternative reaction is
$O_2 + 4e^- + 2H_20 \text{-->} 4OH^-$.

Hydroxide (OH^-) ions react with ferrous (Fe^{2+}) ions to produce insoluble ferrous hydroxides or green rust:
$Fe^{2+} + 2OH^- \text{-->} Fe(OH)_2$

In seawater, ferrous (Fe^{2+}) ions can also react with chloride (Cl^-) ions to form ferrous chloride ($FeCl_2$).

The ferrous (Fe^{2+}) ions also react with hydrogen ions and oxygen to produce ferric (Fe^{3+}) ions:
$4Fe^{2+} + 4H^+ + O_2 \text{-->} 4Fe^{3+} + 2H_2O$

The ferric (Fe^{3+}) ions react with hydroxide ions to produce hydrated ferric oxides (also known as ferric hydroxides):
$Fe^{3+} + 3OH^{-} \rightarrow Fe(OH)_3$

$Fe(OH)_3$ is loose porous rust, which can form a crystal containing water ($Fe_2O_3.H_2O$) which is the familiar red-brown rust.

Remind students that most metals tend to become oxidized (that is they tend to lose electrons) and that metals can be arranged in an "Electromotive Series" according to the strength with which they "hold on" to their electrons. Metals lower in the Series tend to give up their electrons more readily than metals that are higher in the Series. When two metals with different electromotive strengths are electrically connected and submerged in an electrolyte (such as seawater), electrons will flow from the metal lower in the electromotive series, causing this metal to form oxides or other compounds and resulting in corrosion (this is also the process through which batteries produce an electric current).

In the absence of oxygen, corrosion can still take place if sulfate-reducing bacteria are present. These bacteria reduce sulfates (SO_4^{2-}) to sulfides (S^{2-}), and the sulfides can react with ferrous (Fe^{2+}) ions to produce ferrous sulfide (FeS). This process is a major cause of deterioration on another famous shipwreck, the R.M.S. *Titanic*. Complex communities of bacteria and fungi have produced structures called "rusticles" that superficially resemble icicles or stalactites. Rusticles are built up in ring structures and are highly porous, with channels and reservoirs that allow water to flow through. Up to 35% of rusticles' mass consists of iron compounds (iron oxides, iron carbonates, and iron hydroxides).

3.
Have students or student groups complete the "*Monitor* Subject Review Worksheet." You may want to direct students to the websites listed under "Resources," or allow them to discover the necessary information on their own.

Lead a discussion of students' answers (refer to "Background Information" for answers to the first five questions). Students should realize that almost all material objects have a finite existence and are subject to a variety of processes that cause their deterioration. Overall, this is a very good thing, since these are essentially processes of recycling that keep us from drowning in garbage. But when objects have cultural or historical value, we may think it is important to keep them intact for future generations. Students should understand that the process of preserving artifacts from archeological sites is known as "conservation," and in the case of marine sites can be quite involved. You may want to tell students that the major steps in a typical conservation process are:

1. Initial documentation (detailed descriptions, photographs, x-rays, detailed notes on location and conservation procedures)
2. Storage prior to treatment
3. Mechanical cleaning
4. Preliminary evaluation (since marine artifacts are often heavily encrusted, it is frequently impossible to decide on appropriate cleaning and preservation techniques until after mechanical cleaning is completed)
5. Treatment (often chemical or electrochemical cleaning)
6. Rinse
7. Drying
8. Sealing
9. Storage
10. Periodic inspection

In the case of the *Monitor* (and many other archeological sites), deterioration of iron was particularly significant and problematic.

Strong currents, high temperatures, and a saline environment all contribute to corrosion of the ship's iron-containing components. While the encapsulation (burial) option would provide additional support to the hull of the ship as well as reduce exposure to dissolved oxygen and ocean currents that accelerate corrosion rates, this option would also make the ship inaccessible.

The tendency of metals to become oxidized is the basis for the cathodic protection strategy: If a metal such as zinc were attached to *Monitor's* hull, the zinc would suppress corrosion of the hull because zinc is lower in the electromotive series than iron. Unfortunately, this would not reverse the extensive deterioration that has already occurred and would not affect deterioration of other components of the ship such as parts made of wood.

Cathodic protection can be easily demonstrated by attaching a small piece of zinc (available at boating supply stores) to a steel washer, and placing the assembly in a glass jar filled with household bleach. A second washer should be placed in another jar filled with bleach. Observe the jars over several days to see how the zinc affects corrosion of the washer.

When iron artifacts from marine sites are taken out of seawater, corrosion processes can accelerate because air contains much more oxygen than water. The greatest damage is caused by iron chlorides that form ferric oxide or ferric hydroxide and hydrochloric acid. The acid speeds up the oxidation of non-corroded metal to ferrous chloride and hydrogen or ferric chloride and water. In addition, iron in ferrous (Fe^{2+}) compounds may be oxidized to the ferric (Fe^{3+}) state, which will crumble off the surface of an artifact. For this reason, it is critical that iron artifacts are stored in a solution that will inhibit further corrosion. This usually means an alkaline solution with a pH between 10 and 13. For similar reasons, encrustations covering or containing iron artifacts should be left intact during storage since they provide a protective coating that retards corrosion. Before conservation can proceed, however, artifacts must be separated from encrusting materials. Separation usually involves careful work with pneumatic chisels, picks, etc.

Ironically, the same chemical processes that cause corrosion can also be used to clean artifacts. "Galvanic cleaning" involves covering the artifact with aluminum foil or zinc granules in a container of 10 to 20 percent sodium hydroxide. The aluminum or zinc oxidizes, while the iron is reduced. This is one of the oldest and simplest cleaning techniques, but does not work well for large objects.

Electrolytic reduction is a related, but better, technique that involves connecting the artifact to an electric circuit in a container of an electrolyte (a solution that conducts electricity). The artifact is connected to the negative terminal (cathode) of a source of direct current. A steel mesh is wrapped around the artifact and connected to the positive terminal (anode) of the power supply. When current is passed through the circuit, the artifact receives electrons and some of the positively charged metal ions in corrosion compounds on the surface of the artifact are reduced to a metallic state. At the same time, chlorides and other negatively charged ions from the corrosion compounds are drawn away from the artifact to the positively charged anode.

Once an artifact is cleaned, it must be rinsed in multiple changes of water to remove the last traces of chlorides, then dried to remove the last traces of water (usually by soaking in alcohol), and finally sealed to prevent future exposure to water (usually with special waxes). Cleaning, rinsing, drying, and sealing take time. One cannon, for example, required 20 days for mechanical removal of encrustations, 251 days of electrolytic cleaning, seven days of rinsing, 15 days of dehydration in alcohol, and two days soaking in microcrystalline wax. Conservation of the *Monitor's* anchor required almost three years to complete; the cast iron propeller took almost seven years.

The Bridge Connection

http://www.vims.edu/bridge/ – In the navigation menu on the left side of the page, click on "Ocean Science Topics," then "Human Activities," then "Heritage," then "Archeology."

The Me Connection

Have students write a brief essay from the standpoint of a National Marine Sanctuary manager, describing the pros and cons of spending large sums of money to study and/or salvage shipwrecks like the *Monitor*. You may want to remind students that National Marine Sanctuaries are responsible for managing living resources as well as cultural resources, and that (like all government agencies) budgets are limited.

Extensions

Visit *http://www.monitorcenter.org/index.html* for more information about the *Monitor*, her crew, and archeological investigations of the wreck site.

Resources

http://monitor.nos.noaa.gov/ – Web site for the *Monitor* National Marine Sanctuary *http://www.monitorcenter.org/index.html* – U.S.S. *Monitor* web site presented by the Mariners' Museum

http://www.mariner.org/monitor/ – Monitor Web site presented by the Mariners' Museum

http://www.magazine.noaa.gov/stories/mag55.htm – NOAA online magazine article about the recovery of *Monitor's* gun turret

http://news.nationalgeographic.com/news/2003/12/1204_031205_monitor.html – National Geographic online article about the *Monitor*

http://nautarch.tamu.edu/class/anth605/File9.htm
http://nautarch.tamu.edu/class/anth605/File10a.htm
http://nautarch.tamu.edu/class/anth605/File10b.htm – Portions of the Conservation Manual for a course in Conservation of Archaeological Resources at Texas A & M University

National Science Education Standards

Content Standard A: Science as Inquiry
- Abilities necessary to do scientific inquiry
- Understandings about scientific inquiry

Content Standard B: Physical Science
- Structure of atoms
- Structure and properties of matter
- Chemical reactions

Content Standard E: Science and Technology
- Abilities of technological design
- Understandings about science and technology

Content Standard F: Science in Personal and Social Perspectives
- Natural and human-induced hazards

Content Standard G: History and Nature of Science
- Historical perspectives

Links to AAAS "Oceans Map" (aka benchmarks)

5D/H3 – Human beings are part of the earth's ecosystems. Human activities can, deliberately or inadvertently, alter the equilibrium in ecosystems.

NATIONAL MARINE SANCTUARIES WORKSHEET

The Monitor Subject Review

1. What was the length of the U.S.S. *Monitor*?

2. What caused the *Monitor* to sink?

3. How long was it from the time the *Monitor* sank to the time its wreck was discovered?

4. How large is the protected area in the *Monitor* National Marine Sanctuary?

5. List five options that were identified for preserving the *Monitor*.

6. What oceanographic factors at the *Monitor* wreck site contribute to corrosion of the ship?

7. How would encapsulation help preserve the *Monitor*?

8. What is cathodic protection, and why does it work?

9. What is "archeological conservation"?

10. Why is it important that iron artifacts from marine archeological sites are not allowed to dry out?

11. What is "galvanic cleaning?"

12. What is "electrolytic reduction?"

13. Once an artifact is cleaned, what further steps are needed to complete the conservation process?

14. How much time was required for conservation of the *Monitor's* anchor and brass signal lantern?