Corrosion of Iron

Demonstration and Inquiry

Introduction

Rust is expensive! The cost of iron corrosion—for equipment maintenance, repair, and replacement—exceeds $300 billion per year in the United States alone. What kinds of chemical treatments, surface coatings, or combinations of metals will prevent the corrosion of iron?

Concepts

- Corrosion
- Half-reactions
- Oxidation–reduction
- Activity of metals

Background

When iron metal is exposed to oxygen and water, a familiar result is observed—rust. The rusting process consists of several steps. In the first step, iron is oxidized to iron(II) ions, Fe^{2+}, and oxygen from the air is reduced to hydroxide ions, OH^-. This oxidation–reduction reaction takes place via two separate half-reactions (Equations 1 and 2).

Oxidation half-reaction: $$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^- \qquad \textit{Equation 1}$$

Reduction half-reaction: $$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq) \qquad \textit{Equation 2}$$

Combining the oxidation and reduction half-reactions so the electrons "cancel out" gives the balanced chemical equation for the overall reaction of iron, oxygen, and water (Equation 3). Notice that two iron atoms are oxidized for every oxygen molecule that is reduced—the number of electrons gained by one oxygen molecule is equal to the number of electrons given up by two iron atoms.

$$2Fe(s) + O_2(g) + 2H_2O(l) \rightarrow 2Fe^{2+}(aq) + 4OH^-(aq) \qquad \textit{Equation 3}$$

Fe^{2+} and OH^- ions may combine to form solid iron(II) hydroxide, $Fe(OH)_2$ (Equation 4), which reacts further with oxygen and water to form hydrated iron(III) oxide, $Fe_2O_3 \cdot nH_2O$ (Equation 5). The latter is the reddish-brown solid commonly known as rust.

$$Fe^{2+}(aq) + 2OH^-(aq) \rightarrow Fe(OH)_2(s) \qquad \textit{Equation 4}$$

$$4Fe(OH)_2(s) + O_2(g) + xH_2O(l) \rightarrow \underset{\textit{Rust}}{2Fe_2O_3 \cdot (x+4)H_2O(s)} \qquad \textit{Equation 5}$$

Inquiry Approach

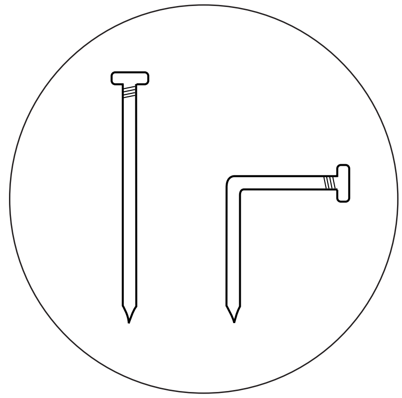
The purpose of this guided-inquiry activity is to observe a "standard test" for iron corrosion, interpret the results in terms of the chemical model for corrosion, and investigate materials that will reduce or prevent corrosion.

Demonstration Questions

The demonstration illustrates the standard test method and provides evidence for the electrochemical nature of corrosion. Two iron nails were cleaned and sanded, and one of the nails was bent to a 90° angle. The nails were placed in a Petri dish and covered with warm agar containing two indicators. Upon cooling, the agar formed a stable, semi-solid gel. Phenolphthalein, an acid–base indicator, was added to detect the formation or presence of hydroxide ions. Phenolphthalein is colorless in acidic or neutral solutions but turns bright pink in basic solutions (pH > 8–10) due to reaction with OH^- ions. Potassium ferricyanide, $K_3Fe(CN)_6$, was added to detect the formation or presence of iron(II) ions. Ferricyanide ions react with Fe^{2+} ions to form a dark blue mixed iron(II)/iron(III) compound, $Fe_3[Fe(CN)_6]_2$, commonly known as Prussian blue (Equation 6).

$$3Fe^{2+}(aq) + \underset{\textit{Yellow}}{2Fe(CN)_6^{3-}(aq)} \rightarrow \underset{\textit{Prussian blue}}{Fe_3[Fe(CN)_6]_2(s)} \qquad \textit{Equation 6}$$

1. Observe the nails and the indicator colors in the standard corrosion test. Record observations in the diagram below.



2. Which parts of the straight nail (the control) oxidized most readily? What evidence supports this? Suggest a possible reason for the observation.
3. Compare the results obtained for the bent nail versus the control. Did bending the nail change where oxidation of the metal was most likely to start or the amount of rust that was observed? Explain.
4. According to the electrochemical model for iron corrosion, the corrosion process takes place via two separate half-reactions. Electrons flow through the metal, like electricity through a wire, from the site where iron is oxidized to the site where oxygen is reduced. Do the indicator color changes support this model for iron corrosion? Explain.

Inquiry Design and Procedure

1. Study the mechanism of the corrosion process (see the *Background* section) and the evidence for this mechanism (see the *Demonstration Questions*).
2. Form a working group with two other students and brainstorm the following questions.
   - What chemical additives might reduce or prevent the corrosion of iron?
   - What type of surface coatings might inhibit the corrosion of iron?
   - What combinations of metals might prevent the corrosion of iron?
   - What other types of metal treatment might reduce the corrosion of iron?
3. Choose one *general* type of metal treatment and develop an "if/then" hypothesis to describe its effect: If a nail is combined or treated with ________________ , then the amount of corrosion should ________________, because __________________________.
4. Read the list of *Materials* that may be provided along with the *Safety Precautions* for their use. Design a "fair test" experiment to test the group hypothesis using these materials. Choose at least 3–4 *specific* examples of metal treatment that may provide evidence both *for and against* your hypothesis.
5. What other variables might affect the test? How can these variables be controlled?
6. Write a detailed, step-by-step procedure for your experiment and verify the procedure and the required safety precautions with your instructor. Design a data table or worksheet to record observations and results.
7. Carry out the experiment and record observations results.

Materials (*for each group of students)*

Agar, 1.5 g*

Labels and/or marker pen

Distilled or deionized water, 150 mL*

Iron nails, 4

Phenolphthalein indicator solution, 1% in alcohol, 1 mL

Potassium ferricyanide solution $K_3Fe(CN)_6$, 0.1 M, 1 mL

Beaker, 400-mL

Hot plate or Bunsen burner

Chemical additives or test solutions†
(NH$_4$Cl, HCl, NaHCO$_3$, NaCl, Na$_2$(C$_2$O$_4$)

Metal wires, strips or ribbons†
(Al, Cu, Pb, Mg, Sn, Zn)

Petri dishes with covers, disposable plastic, 2

Pliers

Sandpaper or steel wool

Spatula

Stirring rod

Surface coating materials†
(Glue, paint, lotion, wax, nail polish, markers, petroleum gelly, grease, tape, etc.)

Weighing dish

**Prepare a 1% suspension of agar in boiling water. Dissolve 1.5 g of agar along with 1 mL each of the two indicators in 150 mL of boiling water to give enough agar for two corrosion tests (Petri dishes).*

†Extra materials needed to test each working hypothesis. Consult with your teacher.

Safety Precautions

Potassium ferricyanide solution is a skin and eye irritant. Contact with concentrated acids may generate a toxic gas; avoid contact with strong acids. Phenolphthalein is an alcohol-based solution—it is a flammable liquid and moderately toxic by ingestion. Keep away from flames and other sources of ignition. Avoid contact of all chemicals with eyes and skin. Wear chemical splash goggles, chemical-resistant gloves, and a chemical-resistant apron. Wash hands thoroughly with soap and water before leaving the lab. Please review current Material Safety Data Sheets for additional safety, handling, and disposal information.

Post-Lab Questions

1. Do the observations and results support the hypothesis? Describe the evidence both for and against the hypothesis.
2. Suggest a possible explanation, *based on the evidence*, for the results of the experiment. Do the results raise any additional questions about how corrosion occurs or how it may be prevented?
3. Prepare a poster or computer presentation summarizing the design of the experiment and the results. Discuss the findings with the class.
4. Based on class results, compare the effectiveness of different metal treatments in reducing or preventing corrosion. Write a summary citing the effectiveness, advantages, and disadvantages of various methods of corrosion prevention. Research and include in the summary at least one “real-world” example of corrosion protection.

Teacher's Notes for Guided Inquiry

Corrosion of Iron

Demonstration Procedure

1. Clean two iron nails with sandpaper or steel wool. Bend one of the nails at a 90° angle using two pairs of pliers. Use "bright common" (all-purpose) nails for this experiment. Do not use galvanized nails!
2. Obtain 75 mL of distilled or deionized water in a 250-mL beaker and heat the water to boiling on a hot plate.
3. Add 0.75 g of powdered agar to the boiling water. Stir continuously until the agar forms a uniform suspension. Be careful not to burn the agar.
4. Carefully remove the beaker from the hot plate and add 5 drops of 1% phenolphthalein solution and 10 drops of 0.1 M potassium ferricyanide solution. Stir to mix. (The suspension will be yellow in color.)
5. Allow the agar to cool but not harden.
6. Place the two cleaned nails (step 1) in the bottom of a disposable plastic Petri dish. Make sure the nails are not touching.
7. Pour the agar suspension into the Petri dish so that the nails are completely submerged and covered with agar.
8. Cover the Petri dish and set it aside for later viewing—24 hours is optimum, although indicator color changes may be apparent after about 30 minutes.

Disposal

Consult your current *Flinn Scientific Catalog/Reference Manual* for general guidelines and specific procedures governing the disposal of laboratory waste. The Petri dishes and their contents may be discarded in the trash (solid waste) according to Flinn Suggested Disposal Method #26a.

Connecting to the National Standards

This laboratory activity relates to the following National Science Education Standards (1996):

Unifying Concepts and Processes: Grades K–12
Evidence, models, and explanation
Constancy, change, and measurement

Content Standards: Grades 9–12
Content Standard A: Science as Inquiry
Content Standard B: Physical Science, structure and properties of matter, chemical reactions
Content Standard E: Science and Technology

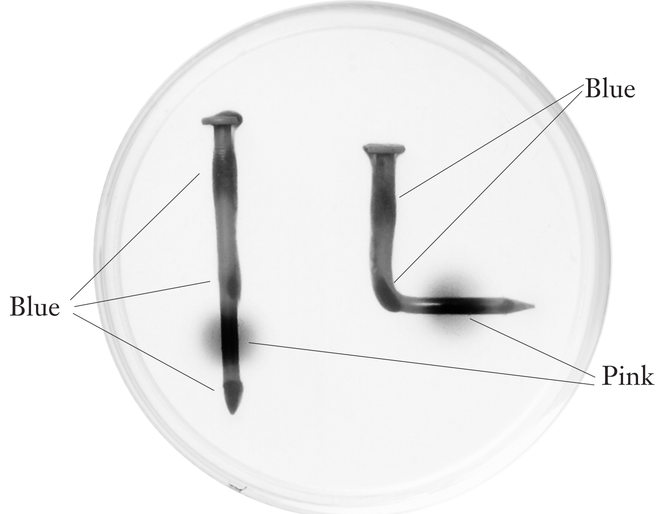
Teaching Tips

- For best results, schedule at least two 50-minute periods for completion of this activity. Students will need one day to observe the standard test method demonstration (see the *Pre-Lab Activity*) and plan their investigation (see the *Procedure*), and a second day to prepare the nails and gels for the corrosion test.
- Student preparation is an essential element for success in a student-directed inquiry activity. To ensure a safe lab environment, the teacher should review each group's procedure, including any necessary safety precautions, before allowing students to work in the lab.
- Agar gels may be prepared using dilute solutions of acids, bases, salts, oxidizing agents, reducing agents, etc., rather than water (see the *Demonstration Procedure*). Some test solutions will interfere with the use of the indicators. Any basic solution will give a pink gel with phenolphthalein, but potassium ferricyanide can still be used to detect the formation of Fe^{2+} ions. If an acidic solution is used, any hydroxide ions generated during the reaction will neutralize the acid and likely will not cause color change with phenolphthalein. "Rainbow acid universal indicator" available from Flinn Scientific (Catalog No. U0012) may give detectable color changes in an acidic gel.
- The concept of a "fair test" is used to get students to think about the design of their experiment. Students may predict, for example, that a water-resistant (impermeable) coating will prevent corrosion. Is it fair to test only water-resistant coatings? Students must identify the condition they wish to manipulate (the independent variable) and the response they wish to observe or measure (the dependent variable). A "fair test" experiment is one in which all other experimental

conditions are kept the same (the controlled variables).

Answers to Demonstration Questions *(Student answers will vary.)*

1. Observe the nails and the indicator colors in the standard corrosion test. Record all observations in the diagram below.



2. Which parts of the straight nail (the control) oxidized most readily? What evidence supports this? Suggest a possible reason for the observation.

   Oxidation of iron appeared to originate at two sites—the head and the tip of the nail. The evidence for this is the location of blue areas in the gel where Fe^{2+} ions were produced. Oxidation originates at points on the nail that have been "stressed" in the manufacturing process. ***Note to teachers****: Metalworking causes dislocation of iron atoms and creates defects in the crystal structure.*

3. Compare the results obtained for the bent nail versus the control. Did bending the nail change where oxidation of the metal was most likely to start or the amount of rust that was observed? Explain.

   Bending the nail changed the location at which oxidation originated. The blue color due to reaction of Fe^{2+} ions with ferricyanide indicator began at the 90° bend in the nail and proceeded in either direction away from the bend. The head and the tip of the nail were surrounded by pink areas in the gel, indicating the presence of OH^- ions. Both nails were covered with rust after 24 hours.

4. According to the electrochemical model for iron corrosion, the corrosion process takes place via two separate half-reactions. Electrons flow through the metal, like electricity through a wire, from the site where iron is oxidized to the site where oxygen is reduced. Do the indicator color changes support this model for iron corrosion?

   The indicator color changes suggest that oxidation and reduction occur at different sites on the nail—there are distinct and separate blue and pink regions in the gel. The blue areas indicate the presence of Fe^{2+} ions due to oxidation of iron atoms. The pink regions indicate the presence of OH^- ions due to reduction of oxygen in the presence of water.

   Note to teachers**:** *Evidence from other experiments also supports the electrochemical model of corrosion. First of all, the reaction requires water (about 40% relative humidity is required). Water is required for migration of ions and to neutralize charge buildup in an electrochemical reaction. Secondly, two distinct types of corrosion damage are generally observed—pitting or cracking in the metal structure where iron atoms have been lost, and the buildup of rust deposits. The two types of corrosion damage occur at different locations on the metal surface. This suggests a two-fold process. Oxidation results in the release of electrons and gives rise to pits and cracks in the iron surface where the iron has dissolved. The electrons flow through the metal, as they might through a wire that conducts electricity, until they react with oxygen and water to produce hydroxide ions. In the presence of water or moisture on the metal surface, the Fe^{2+} ions migrate until they reach the region where OH^- ions have been produced. There they combine with OH^- ions or react further with oxygen to form rust. The formation of rust at sites far removed from where the iron has dissolved is compelling evidence for the electrochemical nature of the rusting process.*

Sample Results and Conclusions

Chemical Additives

A neutral salt (NaCl) environment accelerates the corrosion of iron. A basic salt ($NaHCO_3$) or a reducing salt ($Na_2C_2O_4$) environment prevent the corrosion of iron.

Possible Explanations: Electrolytes increase the rate of an electrochemical reaction. High concentrations of OH^- ions—a product of corrosion—shift the position of equilibrium for reduction of oxygen to hydroxide ions. A reducing agent provides an alternative source of electrons for the reduction of oxygen. (The reducing agent competes with iron as the site of oxidation.)

Surface Coatings

Water-resistant coatings (wax, grease, nail polish) inhibit the corrosion process—neither oxidation nor reduction products are observed in the gel. The nail must be *completely covered* for corrosion protection to be effective. Any breaks, no matter how small, in the coating act as sites for iron oxidation. Water-resistant coatings that adhere to the metal surface (transparent tape, wax, and nail polish) appear to be most effective. Petroleum jelly inhibits the corrosion process for a short time (1–2 hours), but does not provide long-term corrosion protection.

Painting a nail with water-permeable latex paint also protects the nail against corrosion. Again, however, any break in the coating where the nail is not covered provides a site where the redox reaction is initiated. Latex paint, even when dry, is water-permeable. This suggests that the ability of the coating to adhere to the nail may be a crucial variable. Elmer's® glue, a water-based coating that adheres to the metal, increases the amount of corrosion that is observed. This is probably not a good "fair test" subject, however, because glue contains many chemical additives.

Possible Explanations: Water is necessary for corrosion to occur. Simple hydrocarbon-based, water-resistant coatings, such as wax or silicone grease, provide effective, long-term corrosion protection by preventing contact of the nail with water. The rigidity of the coating is a co-variable but is not a necessary condition. The ability of the coating to adhere to the metal is another co-variable. For water-permeable coatings, it is difficult to isolate the critical variable—is it the rigidity of the coating, its ability to adhere to the metal, or its chemical composition?

Combinations of Metals and Metal Activity

Combining a nail with a metal that is more active than iron (magnesium, aluminum, and zinc) protects iron against corrosion—no rust is observed and there are few or no blue regions in the gel. Pink sites in the gel verify that reduction of oxygen is still taking place when these more active metals are present. Zinc is the most effective "second metal" in reducing the corrosion of iron. Magnesium gives unreliable results—sometimes it prevents corrosion entirely (as it should), while other times it prevents corrosion only where it is attached to the nail. Metals that are less active than iron (copper, lead, and tin) do not protect iron against corrosion.

The more active metal does not have to be wrapped around the nail to offer corrosion protection—it only needs to make "electrical contact" with the iron in one location. More active metals protect iron against corrosion even if the less active metal is not sanded or polished before use.

Possible explanations: The activity series of the metals lists the metals in order of reactivity. Reactivity can be defined as the ease of oxidation. Metals at the top of the activity series are said to be more active—they are more reactive and more easily oxidized. When two metals are present together and both are exposed to oxygen and water, competition between the two results in the more reactive (more easily oxidized) metal reacting preferentially with oxygen. The more reactive metal protects the less reactive metal from the oxidizing effects of oxygen. The activity series for metals is: Mg > Al > Mn > Zn > Cr > Fe > Co > Ni > Sn > Pb > Cu > Ag > Au

Reference

This experiment has been adapted from *Flinn ChemTopic™ Labs*, Volume 16, *Oxidation and Reduction;* Cesa, I., Ed., Flinn Scientific: Batavia, IL, 2004.

Iron Corrosion—Guided Inquiry Activity is available as a Student Laboratory Kit from Flinn Scientific, Inc.

Catalog No.	Description
AP7186	Iron Corrosion—Guided Inquiry Activity

Consult your *Flinn Scientific Catalog/Reference Manual* for current prices.