



Should we do more to save Cultural Monuments from Corrosion ?

Teacher Notes

Student worksheet 1 Reacting copper and iron (and zinc)

Procedure:

1. Prepare 200 ml of agar-agar solution. Measure out a mass of 2.0 grams of powdered agar-agar. Heat 200 ml of water to boiling. Remove the water from the heat and add the agar-agar powder slowly while constantly stirring. Once the agar has dissolved, add 5 drops of phenolphthalein solution or 5 drops of bromothymol blue.
2. Take two nails (or strips of pure iron) and wrap them in the strips of metal. One nail should be wrapped with zinc metal and the other nail wrapped with copper metal. Place these two wrapped nails into a petri dish. Be sure the nails do not touch. (The zinc and copper metals should be rubbed down and cleaned with sandpaper before they are wrapped around the nails). Make sure the nails are not galvanized or have some other type of coating. The idea is to use **iron**.
3. Slowly pour the agar-agar solution into the petri dishes to a depth of about 0.5 cm above the nails and metals.
4. Allow the petri dishes to remain untouched for a day or two. From time to time make observations. At the end of the next day and then at the end of the second day make and record observations.

Questions:

1. What changes did you observe in the petri dish? Why did the color changes occur where they did?
2. In which nail did the iron of the nail corrode?
3. Why did the iron nail corrode in the one situation and not in the other?
4. Explain "corrosion" or "rust" in an electrochemical point of view.
5. What does the "pink" color (if phenolphthalein was used) indicate?
6. What is a cathode and what is an anode?
7. What is oxidation?

Teacher notes

Materials: -

- Iron nails
- Petri dishes
- Agar-Agar solution
- Phenolphthalein solution
- Strips of zinc and copper metal
- Sandpaper

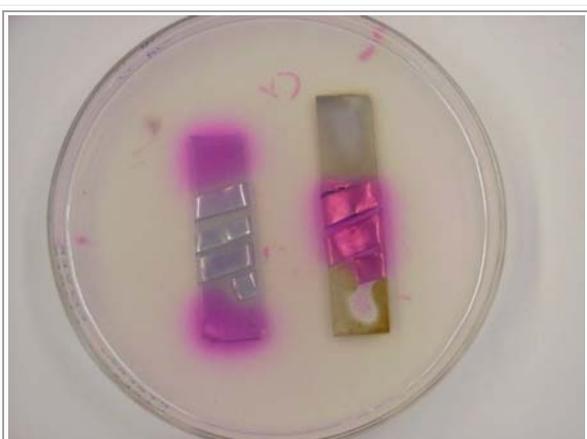
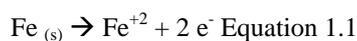


Figure 1. Using Phenolphthalein as indicator.

Iron wrapped in zinc is on the left and iron wrapped in copper is on the right.

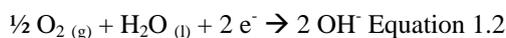
Explanations:

1. As can be seen in Figure 1, the iron strip which is wrapped in copper corroded. Pink color is found around the copper strip and the iron can be seen to be turning orange-yellow. This is only after 5 hours. More corrosion would be visible days later. The second strip of iron is not corroded. Pink is found on the iron and nothing by the zinc strip. The color changes occurred where they did as a result of the corrosion.
2. In the strip of iron wrapped with copper the iron corroded. Iron metal oxidizes faster or more easily than does the copper. It is said that the iron is oxidized and the copper is reduced. What is happening is that the iron is losing electrons and the copper is gaining electrons. The copper is considered the cathode in this case and the iron is considered to be the anode. The iron metal loses electrons and turns into an iron ion according to this equation:



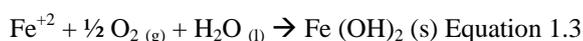


These two electrons travel through the iron metal to the copper. At the copper there is water and oxygen which take the two electrons and use them to form hydroxide ions as in Equation 1.2:



This excess of OH^- produced causes the solution next to the copper to be pink. Hydroxide ions (OH^-) make a solution to be basic which turns pink in the presence of phenolphthalein.

What ultimately happens in the case of the iron metal wrapped with copper is that the iron metal loses two electrons which are used by water and oxygen to make hydroxide ions. It is evident that the hydroxide ions are formed at the copper surface because of the pink that exists around the copper. The iron ions that are formed react with oxygen and water to form "rust" as is seen in Equation 1.3:



This $\text{Fe} (\text{OH})_2 (\text{s})$ combines with a second molecule of $\text{Fe} (\text{OH})_2 (\text{s})$ in the presence of oxygen to form iron(III)oxide (the more common form of rust) and water.



Thus iron "rusts" and the copper does not react with anything.

In the other situation in which iron is wrapped with zinc the opposite occurs. In this case zinc is oxidized faster or more easily than the iron and therefore it undergoes a very similar reaction as did the iron in the last example. Here zinc loses two electrons and forms a Zn^{+2} ion. On the surface of the iron the same reaction occurs as did on the copper. Water and oxygen combine with the two electrons to make hydroxide ions, which turn the solution next to the iron surface pink. In this case the zinc is considered to be the anode and the iron is considered to be the cathode.

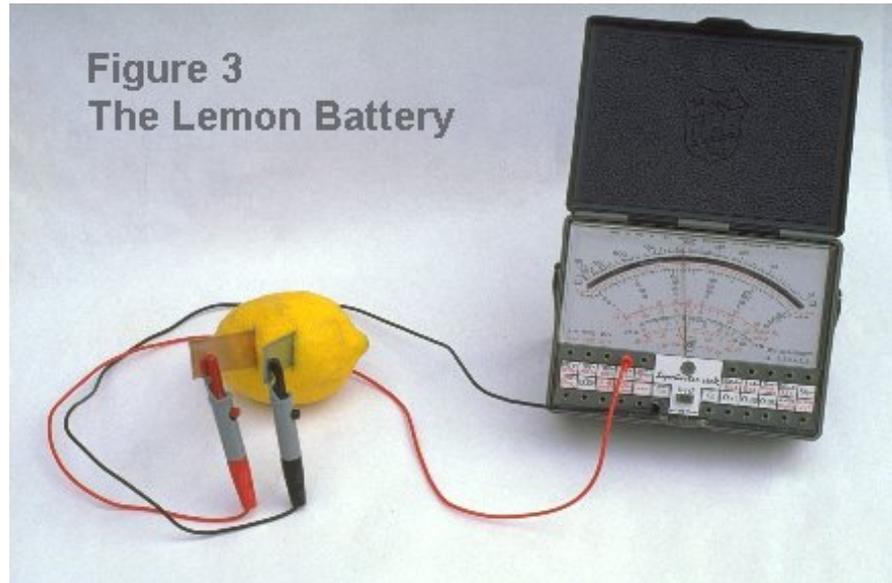
3. The iron of the nail which is covered with copper corroded.
4. See number 1.
5. See number 1.
6. The pink color indicates that hydroxide ions are produced. This indicates a chemical reaction has occurred. The location of the pink indicates that the metal nearest to it was producing the hydroxide ions, and therefore, was the metal "gaining" electrons. This metal which "gained" electrons is said to have been "reduced" while the metal which "lost" the electrons is said to have been "oxidized" or "rusted" or "corroded".
7. The cathode is the place in an electrochemical cell **to where** the electrons travel.
8. The anode is the place in an electrochemical cell **from where** the electrons came.

9. Oxidation is the "loss of electrons". It is usually comparable to "rusting" or "corroding" because the metal loses electrons, turns into an ion, and therefore, there are less "metal" atoms around. Thus the metal is said to have corroded.

Reacting Copper and Zinc – the Lemon Battery △

Materials:

- a lemon
- a strip of copper
- a strip of zinc
- a voltmeter
- two cables with alligator clips
- a thermometer or clock with an LCD display



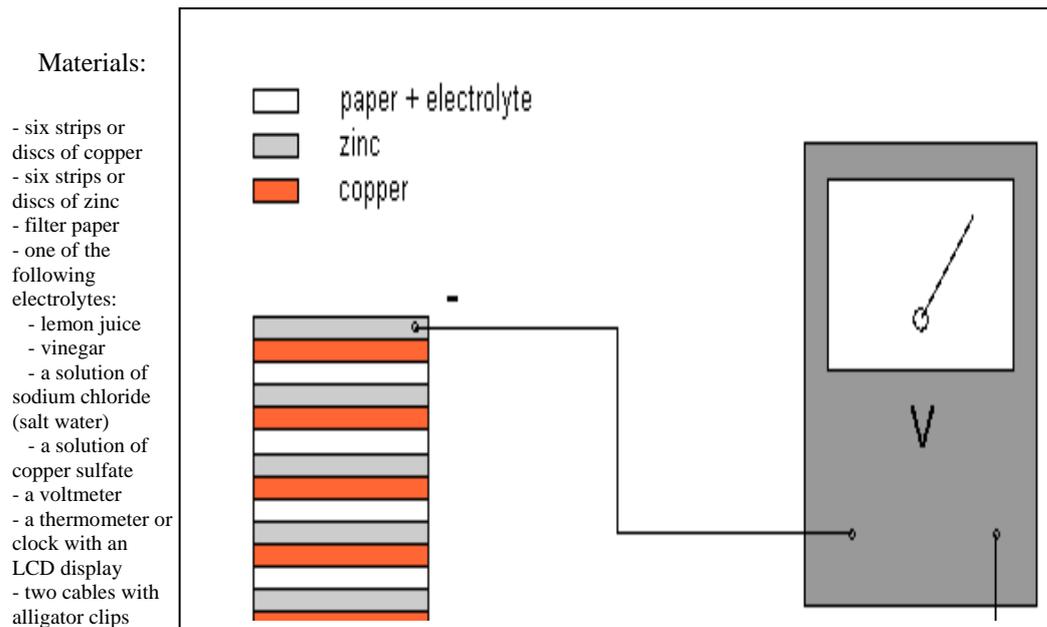
1. Roll the lemon firmly with the palm of your hand on a tabletop or other hard surface in order to break up some of the small sacks of juice within the lemon.
2. Insert the two metal strips deeply into the lemon, being careful that the strips not touch each other.
3. Using the voltmeter, measure the voltage produced between the two strips (figure 3). It should show to be about one volt.

It is possible to use other electrolytes, whether it be an acid, base or salt solution. The lemon battery works well because the lemon juice is acidic. Try the same setup with other types of solutions. As you may know, other fruits and vegetables also contain juices rich in ions and are therefore good electrical conductors. You are not then, limited to using lemons in this type of battery, but can make batteries out of every type of fruit or vegetable that you wish.

Like any battery, this type of battery has a limited life. The electrodes undergo chemical reactions that block the flow of electricity. The electromotive force diminishes and the battery stops working. Usually, what happens is the production of hydrogen at the copper electrode and the zinc

electrode acquires deposits of oxides that act as a barrier between the metal and the electrolyte. This is referred to as the electrodes being polarized. To achieve a longer life and higher voltages and current flows, it is necessary to use electrolytes better suited for the purpose. Commercial batteries, apart from their normal electrolyte, contain chemicals with an affinity for hydrogen which combine with the hydrogen before it can polarize the electrodes.

Volta's Pile

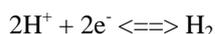


Place each zinc disc on a copper disc. You should have six sets of Cu-Zn disc pairs. As shown in fig. 11, build a stack or "pile" of these pairs of discs, with a disc of electrolyte soaked filter paper separating each pair from its neighbors. Be careful that the solution does not dribble down the side of the stack as this can cause a short circuit between the elements of the pile. Note that the sequence of the elements is as follows: Cu, Zn, electrolyte, Cu, Zn, electrolyte, etc. When the device is all arranged as specified, measure the voltage between the the bottom element of Cu and the top element of Zn. You should see 6.6 volts or 1.1 volt per pair of elements. The voltage generated is also dependent upon the electrolyte used and it's concentration. As you may have done with the lemon battery, try to power a small LCD electronic device such as a clock, thermometer or even a calculator.



Measuring potentials of reduction

Another method of explaining the function of a battery lies in the oxidation reduction reactions at the electrodes. Oxidation reduction reactions involve the transfer of electrons from one chemical element to another. The tendency of an element to acquire or give up electrons is measured as electrical potential compared to that of a special hydrogen electrode, which is considered by convention to have zero electrical potential at 25°C. At this electrode, the following reaction occurs:



To make these measurements, use is made of a cell with one electrode of hydrogen and the other of the material to be measured. The voltage produced indicates the potential of reduction of the new material in terms of positive or negative volts in respect to the hydrogen electrode. Chemical elements that have a positive potential of reduction tend to be reduced, that is to acquire electrons, while elements that have a negative potential tend to oxidize, that is to give up electrons.

At this point, the voltage produced by a battery can be calculated by finding the difference between the potentials of reduction of the two half cells: $E = E_1 - E_2$ as shown below.

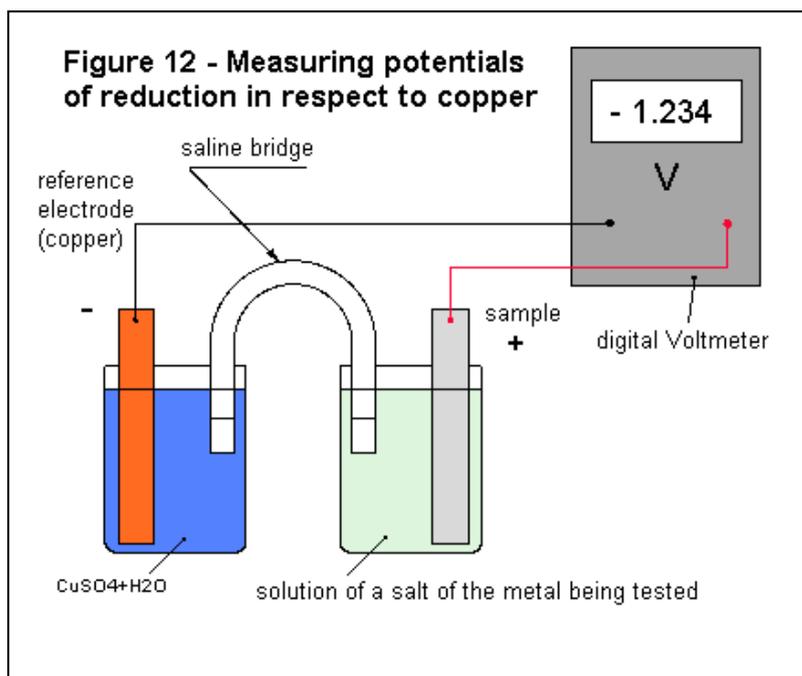
	reaction	potential of reduction (V)
E_1	$\text{Cu}^{++} + 2\text{e}^- = \text{Cu}$	+ 0.342
E_2	$\text{Zn}^{++} + 2\text{e}^- = \text{Zn}$	- 0.762

In this case, the voltage generated would be:

$$E = +0,342 - (-0.762)$$

$$E = +1.104 \text{ V.}$$





Materials:

- a strip of copper
- various materials to try as electrodes
- two beakers or appropriate containers
- plastic tubing
- cotton
- 50 g. of copper sulfate (CuSO_4)
- 50 g. of a sulfate of the same element as the electrode you want to try
- 5 g. potassium nitrate (KNO_3)
- 5g. sodium chloride (NaCl) as an alternative to the potassium nitrate
- 1/2 liter of distilled water
- a voltmeter (it is best to use a digital model because the high input impedance will not affect the voltage as much as a low impedance analog model)
- a cable with alligator clips
- sandpaper

Fill the container having the copper conductor with copper sulfate solution in the concentration of 1M. Fill the other container with the appropriate solution also in the concentration of 1M. Connect the negative side of the voltmeter to the copper electrode and the positive side to the electrode of test material and measure the voltage.

In order to get valid test measurements, it is necessary to have clean electrodes. Use the sandpaper to clean off any oxides or any other coatings or contamination so that the surfaces of the electrodes are clean and bright. Some metals oxidize very easily, such as aluminum, titanium, and magnesium. In the case that you are using a metal that oxidizes quickly, clean the electrode with sandpaper just before placing it in the electrolyte and then, during the experiment, wait a few moments for the chemical reaction to remove the slight amount of oxide that formed while you were cleaning it. You will see the voltage slowly rise to a maximum value. Note this reading as it represents the potential of reduction of the material under test with respect to copper. If the voltage starts immediately to drop, use the highest observed reading as the maximum value.

The voltages that you record are relative to copper. In order to obtain the value relative to hydrogen, that is the standard value, you would factor out the standard value of copper (Cu/Cu^{++}). For example, if you measure the voltage between zinc and copper with this setup, you should see -1.1 volts output. By



adding -1.1 and $+0.34$ (the standard value for copper) you get -0.76 volts which is exactly the potential of reduction for zinc (Zn/Zn^{++}) relative to hydrogen.

Questions on bronze monuments the teacher may wish to ask

1. The statue of Marcus Aurelius had been on the top of Capital Hill in Rome for 2000 years. This is the only one of numerous riding cavalier statues which exists today. Others were destroyed by early Christians. At the end of the seventies it was moved to the laboratory. Much of the monument's detail in bronze had been destroyed and looked like a sieve with many holes. The ancient gold cover existed only in the form of small islands.
What do you think, besides time, caused the bronze destruction?
2. Why is modern bronze, containing Zn, less stable than ancient bronze containing Sn? Why is the surface of statues made from bronze containing very little amount of Sn covered with white dots?
3. What do you think was the reason for the Callos of Rhodes destruction, taking into consideration that this statue was made of bronze sheets, which were clamped on an iron bearing construction?
4. Sometimes to protect bronze sculptures they are covered by special films, consists of oxides and hydrosalts of copper. Why is sulphate and nitrate but not hydrocarbonate of copper(I) and (II) formed in cities with highly developed industry for producing protection films?

Patinas

The surface of every monument made of metal has a natural or protective-decoration cover which prevents the metal from further oxidation. These are called patinas. Patina is a more or less stable coloured film, formed as a result of complicated and multistage interactions of the upper layer of the sculpture material with acids, salts and gases in the atmosphere.

Non-natural cover are usually combinations of non-natural patinas and organic compounds, such as compositions from natural and synthetic wax, natural and synthetic drying oil, polybutylmethacril varnish and others. It is known that some monuments were painted with drying oils and covered with a black pigment. Of course in these cases the surface of the monument loses its characteristic glitter of bronze and gains a varnish-like structure.

Some types of patinas are used in the restoration of monuments around the world are made from the following chemical composition- (a) basic copper oxides (I) and (II) and (b) basic copper sulphates (I) and (II), Sb(II), Bi(III) (c) basic salts of copper (carbonates, sulphates, nitrates, chlorides)



Oxide films on the surface of small bronze objects are obtained by heating in a flame, leading to the formation of black copper oxide by oxidation by the atmosphere. Larger objects are heated in special furnaces. Making patinas is an usual operation which is made after sculptures have been cast. Sulphate films are stable only in conditions of low atmospheric humidity. Non natural patinas made on the basis of basic salts are very similar to natural patinas but they are less mechanically stable. However the quality of films influence by atmospheric conditions gets better with time, if the patina composition and way of making have been chosen correctly. It is not recommended to use non-natural patinas, containing carbonate ions in towns which are situated on the sea coast and industrial centres, because carbonate ions can be easily replaced with sulphate ions (contained in the air). In these cases, it would be better to use films, containing basic copper sulphate or nitrate (strong acid salts).

To protect monuments in coastal areas chloride ions are introduced into the composition of the patinas. Because chloride ions could be corroding agents, In the presence of a water film (on the bronze surface) copper, in the presence of chloride ions, oxidises in the air to form a thin and considerably stable light green film which protects the inner bronze layers from further oxidation. This film ($\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$) is called atakamit.

Carbon dioxide gas causes a transformation of atakamit to the green coloured malachite $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$. Green patina tends to show old age of the monument. If in the air there is a lot of sulphur compounds, this could lead to the formation of the green coloured film containing $\text{Cu}(\text{OH})_2 \cdot \text{CuSO}_4$. Climate conditions greatly influence the physical-chemical processes occurring on the surface of the sculptures. The most important factors are compounds polluting the atmosphere and the humidity.

Possible additional tasks

1. Bronze sculptures were created in very ancient times. In the 19th century cast iron was introduced into the practice of making sculptures. In the 20th century sculptures began to use steel and titanium. What metal is least likely to corrode ?
2. The famous monument of the bronze cavalier in St. Petersburg is constructed on an iron arc like a horseshoe, which is connected to the bronze sculpture with the help of bronze braces. During restoration in 1978, a steel framework was not only very carefully cleaned from dirt and rust, but was painted with red lead. It was very difficult to work inside the sculpture. Infrared lamps were used to make the drying process of the paint faster. However, restorers painted the inside of the sculpture several times.

Why was this done ?

Answer: it is necessary to isolate the iron framework from the bronze sculpture material



3. Usually bronze sculptures have thin walls (1.5 mm up to several millimetres in thickness). They are usually fixed on the pedestal of the monument with the help of a special iron or steel framework. Unfortunately, due to the influence of accumulating water surrounding the sculpture, the bronze is being destroyed. How can you explain that in the horse sculpture, the most noticeable destruction (even holes) is on the lower part of the legs?

Answer: The iron framework is rusting. This is more rapid where it is in contact with the bronze. The oxidation product (rust) has a largely volume than the iron and cracks appear in the very narrow places (for example the lower parts of the legs)

4. Cracks in bronze sculptures are often sealed with an alloy of lead and tin. What properties of these materials make them suitable for this process ? Why is their usage not the most convenient way to restore bronze sculptures?

Answer: Lead and its alloys are fusible materials and it is thus easy to use them to restore cracks in the bronze sculptures. However, in using them we break the principle of not using different metals in contact and this leads to electrochemical corrosion.

Statue of Marcus Aurelius

Over time little cracks appeared in the gilt. Water accumulated in the cracks. This water, together with substances in the air, formed a conducting medium and allowed an electrochemical process to occur between the gold and the bronze. As a consequence the statue became an enormous battery. The metal corroded and little holes appeared in the statue.

What is bronze ?

Bronze is made from mixing copper and tin (or copper and zinc as is preferred today) in a furnace, melting the metals and, on cooling, forming sheets of a fairly soft metal that can be hammered into shapes or carved with a sharp instrument. It is a dark brown/black colour on the surface, but on scratching reveals a bright orange/brown colour similar to copper. Bronze is typically 80% copper.

The reactivity of metals can be expressed in a table, the most reactive metals given first. Such a table is given below:

Ca Mg Al Zn Fe Sn Pb H Cu Ag Au (K and N have been omitted as their reactivity is too great to be considered for sculptures)

Although not a metal, hydrogen is included as a reference. With this, the same table can be used as an electrochemical series; metals above H establishing a negative potential compared to hydrogen and those below H, a positive potential.