UNIT 11: OXIDATION-REDUCTION

LAB	ARTICLE
#29: SILVER NEEDLES	FLAKING AWAY
#30: PERCENT COMPOSITION OF A PENNY	ARTISTIC CHEMISTRY: A BEAUTIFUL COLLABORATION

From Ferraris to Ford Pintos, almost every car is fighting a losing battle to rust.

By Christen Brownlee

The old-style Volkswagen Beetle: Is it a classic car, or an endangered species? The answer depends on where you live. Although there are few classic cars hanging around the northern states or on the coastlines, plenty of vintage automobiles still exist in the mild southern climates and in America's interior states.

The reason that Volkswagen Bugs and other older cars are dropping like flies isn't the typical habitat loss or human encroachment that's plaguing other endangered species. Classic car fleets are constantly shrinking due to a chemical reaction that you're no doubt already familiar with: rusting.

But why does rust unequally strike cars in the snowy states and coastal towns but leave vehicles elsewhere virtually untouched? And more importantly, how can you keep your beloved grocery-getter safe, no matter what parking place you call home? Read on to get the lowdown on how rust works and what measures you can take to stop corrosion in its tracks.

Electron swap meet

Like all types of corrosion, rust is actually a chemical bargain, with two reactions in one: reduction, in which some atoms gain electrons, and oxidation, in which other atoms lose electrons. With all those electrons flowing from one place to another, rust-making is also considered an electrochemical reaction. According to John Scully, a corrosion expert at the University of Virginia in Charlottesville, the redox reaction that forms rust needs just three ingredients to take place: an anode, or metal that readily gives up electrons; a cathode, or substance (in this case, oxygen) that easily accepts electrons; and an electrolyte solution, which shuttles ions between cathode and anode.

Most cars are made mostly of steel, a tough mixture of iron, carbon, and small amounts of other ingredients like manganese, silicon, phosphorus, and sulfur. It's the iron part of steel that corrodes to make rust.

Iron doesn't hold onto its electrons very tightly, says Scully, making it the perfect anode for an electrochemical reaction to take place. Other metal atoms in the steel mixture, or even another point on the piece of iron, make excellent cathodes. Steel has a nonuniform surface because the chemical composition is not completely homogeneous. Also, physical strains leave stress points in the metal. These defects create anodic regions where the iron is more easily oxidized than it is at others (cathodic regions). However, without a bridge to connect potential anodes and cathodes, rusting would be such a time-consuming process that cars would virtually last forever.

The water on the steel surface is a solvent for ions produced when the iron metal at the anodic region loses electrons (is oxidized to form ferrous ions) and the electrons are conducted through the metal to the cathodic region where they react with water and oxygen from the air to form hydroxide ions, as shown in these equations:

$$2Fe \rightarrow 2Fe^{2+} + 4e^- \text{ (oxidation at anodic sites)}$$

$$4e^- + O_2 + 2H_2O \rightarrow 4OH^-$$
(reduction at cathodic sites)

The ions in this electrolyte solution can migrate together and react to form ferrous hydroxide, which reacts further with oxygen from the air to oxidize the ferrous ion and form insoluble ferric oxide, the chemical name for rust, as shown in these equations:

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$$
(formation of ferrous hydroxide)

$$4Fe(OH)_2 + O_2 \rightarrow 2Fe_2O_3 + 4H_2O$$
(oxidation to ferric oxide or red 'rust')

The movement of ions through the electrolyte solution completes the electric circuit that allows the electrons from iron to move from the anode to the cathode.


MIKE CIESIELSKI

A redox reaction on wheels. The bumper of this vehicle wears the product of the reaction between iron and oxygen—rust!

But all this still doesn't explain why colder climates and coastal areas get an unfair share of rust. The magic ingredient that both areas share—which is missing in the basic recipe for rust—is a high abundance of salt. Coastal areas have plenty of salt sailing through the air from ocean spray, and with each cold, snowy winter, northern states smear tons of rock salt on roads to lower the freezing point of water and help keep roads free or ice and snow. [See "Salting Roads: The Solution for Winter Driving" in this issue]

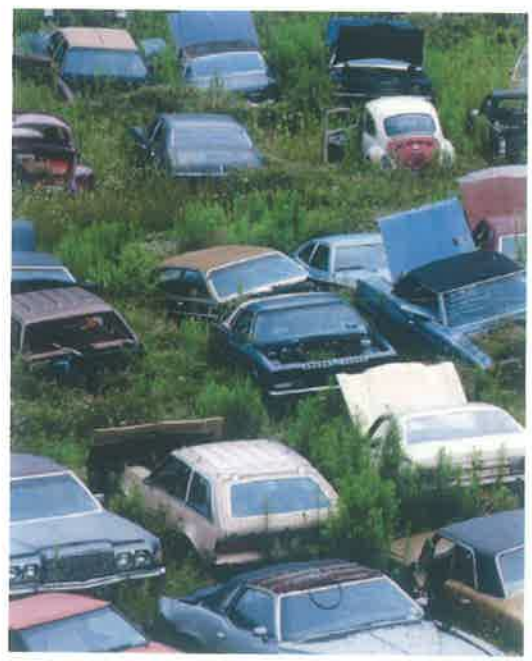
Salt speeds rust's redox reaction along by making water a better conductor. "Salt allows the anode and cathode to be in touch even better," says Scully, making corrosion happen even quicker. Also, chloride ions form very stable complex ions with Fe^{3+}, which helps dissolve iron and accelerate corrosion.

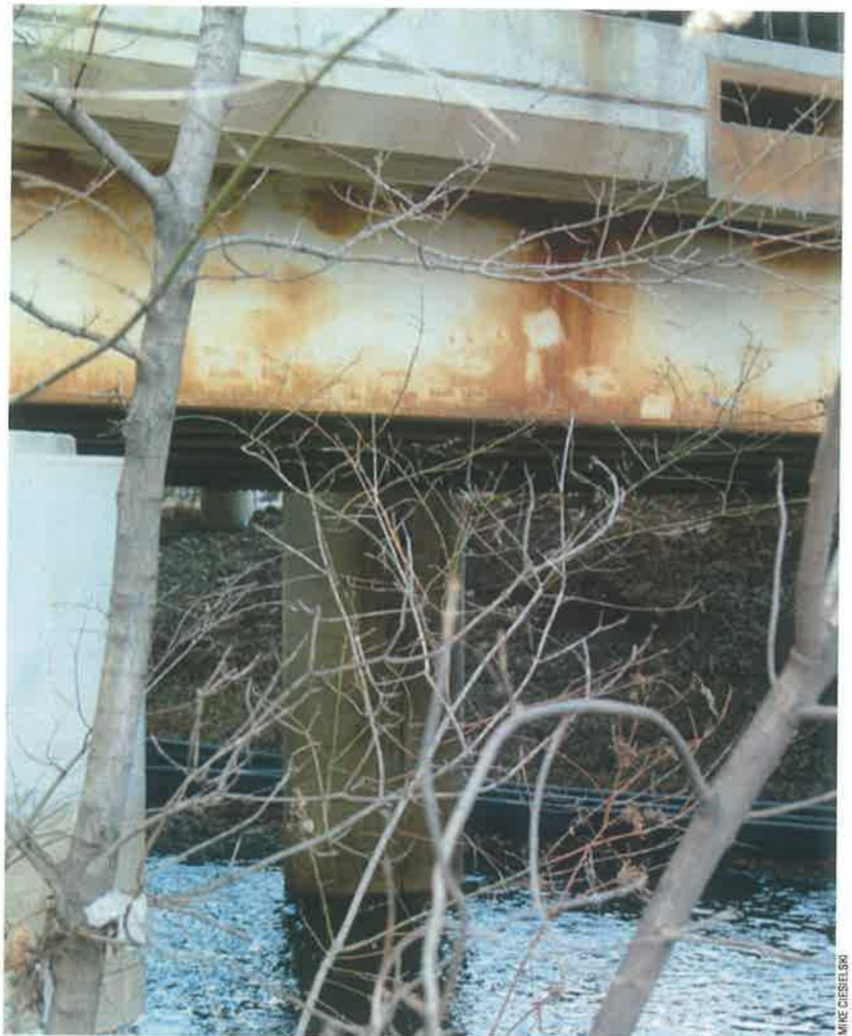
Costly corrosion

Scully points out that iron can't help rusting—existing as an oxide in its thermodynamically favored state. In fact, the metal rarely exists in a pure state in nature. Before it becomes a side panel in your car, engineers must convert rusty iron ore into a pure metal.

With rust being iron's favored state, it is of little use trying to fix rust after it has already happened. By putting energy into rust, it's possible to plate metal back onto a car, says Scully. However, it's also incredibly costly and impractical. Plus, by the time most car owners notice a rust spot, a significant amount of iron has already sloughed off of the car, lost to wind and rain.

One solution to stopping iron's thermodynamic conversion, says Scully, would be to make cars out of a metal that doesn't corrode, such as gold or silver. "Converting to an oxide isn't thermodynamically favorable



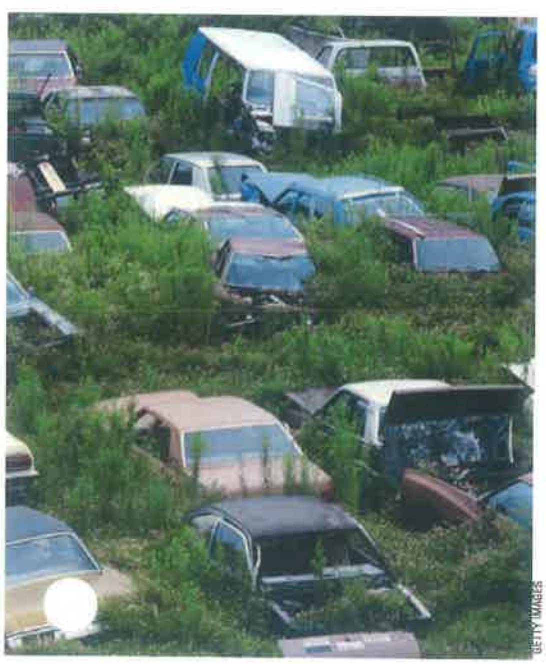


MIKE CIESIELSKI

It's not only cars that are rusting away. Corrosion costs the United States a whopping $276 billion per year!

MIKE CIESIELSKI

This student investigates the role of salt on the rate of rusting by putting nails in various salt water solutions.



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reaction for these metals, so they won't corrode spontaneously," he says. "Archaeologists can dig up gold coins that have survived through the ages without corroding."

But while driving a gold car might make you feel like a million bucks, making such a vehicle would cost substantially more. Not to mention the fact that these soft metals would be unable to support the car's weight and would squash like putty in a collision!

Even using noncorroding metals that are cheaper than gold or silver, such as stainless steel that Deloreans are made of, is still more expensive than using the plain steel that most cars are made of today.

The best way to prevent corrosion is still the cheapest. A good coating of paint removes the connection between anode and cathode by preventing water from making contact with steel. Without water, rusting slows down to a snail's pace.

Today's high tech paints have evolved far from being just a simple barrier, says Scully. Researchers are currently working on paints that release rust inhibitors on demand when paint's seal on steel is breached, for example, when the paint on a car is scraped or scratched. Other "smart paints" that ooze together to close gaps whenever a car's panels get scratched are also in the works.

Although rust is a big deal for car owners, it's an even bigger deal for industries that rely on machines with metal parts, ranging from farm tools to factory equipment to fighter jets. According to Scully, corrosion costs the United States a whopping annual toll of about $276 billion in lost goods and services. With the exorbitant cost of new military equipment, the Department of Defense (DOD) is one of the largest investors in antirust research, says Scully. Scientists at the DOD hope they can keep the aging Blackhawk helicopters and B52 bombers that are currently in use running smoothly for decades to come—a cost savings of millions of dollars per machine.

But one military asset sometimes harmed by corrosion is extremely difficult to put a price on, says Scully. "If a soldier goes to war and the rifle he's using to protect himself doesn't fire when he needs it to, how do you estimate the cost of corrosion then?"

Christen Brownlee is a contributing editor to *ChemMatters*. Her article "Super Fibers" also appears in this issue.

ARTISTIC CHEMISTRY

A Beautiful Collaboration

MARK SCHWENK, WWW.FROGVALLEY.COM

By Helen Herlocker

In Frog Valley, W.Va., Mark Schwenk, a metal artist and photographer, has been building and operating a pottery kiln for the past 3 years. Visitors enjoy going to his studio because they are in for a show! Schwenk opens the kiln, grabs a red-glowing pot with metal tongs, and plunges it into a metal trash can stuffed with shredded paper. Flames shoot skyward! Then, Schwenk slams the lid down, and the flames are replaced by a small emission of black smoke. After a few minutes, Schwenk removes the pot, still very hot, and dips it in a tub of water, where the billowing steam captures the attention of a crowd of visitors. When the pottery piece is cleaned, it has a beautiful shiny and colorful glaze.

Schwenk makes Raku pottery, an increasingly popular art form that is also a fun way to fire pottery. He is one of seven artisans working together as part of an artist collective called Frog Valley Studios. The other artisans create craft from metal, ceramics, and glass, which attract many visitors throughout the year.

I work at Frog Valley Studios as a volunteer apprentice. I help Schwenk and a stained-glass artist named Veronica Wilson with pottery and stained glass. I find Raku pottery and stained glass fascinating. Let me show you around!

Red-hot pottery

It's hard to imagine a craft as basic as pottery, which consists of making pots out of clay—a naturally occurring material composed mainly of fine-grained minerals. Essentially, pottery consists of sculpting pots by hand, decorating them with a glaze, and heating them to high temperatures in a kiln so they can harden before letting them cool down outside.

But unlike traditional pottery, Raku pottery is more exciting. Sculpting a Raku pottery piece and glazing it is similar to traditional pottery, but unlike the gradual heating and gradual cooling of the everyday pottery kiln—a process that takes at least 8 hours—a Raku kiln is best described as "fast and furious." The pots sit in a chamber, exposed to a fuel-rich flame that rapidly heats them to 1,800 °F.

What Schwenk shows his visitors a few times per year is the most spectacular part of the process, but also—according to many—the most fun and enjoyable. This unusual form dates back to the mid-16th century when Sen no Rikyu, a Japanese tea master and former Zen monk started firing pieces in such a way that each bowl presented its own unique shape, texture, and surface features. Today, Raku potters produce pieces which, like those of Rikyu, have singular forms and features. In short, every piece is a surprise!

MARK SCHWENK, WWW.FROGVALLEY.COM

A finished piece from a Raku firing: metallic features provide color and sheen.

What happens in the trash can is an example of oxidation-reduction, or redox, reactions—among the most common and most important chemical reactions in everyday life. A redox reaction involves both oxidation (loss of electrons) and reduction (gain of electrons). In this case, the elements are the

PHOTOS: MARK SCHWENK, WWW.FROGVALLEY.COM

A lid is placed on a trash can containing hot pots.

Above: Glazes rich in metallic oxides and carbonates are applied to a pot before it is fired in a kiln.

Left: A pot, hot from the first Raku firing, is plunged into a container filled with paper and straw, which burn. The red-hot interior of the pot is visible in the photo.

metals in the glaze, which either lose or gain electrons. The elements that lose electrons are "oxidized" and those that gain electrons are "reduced."

The glazes contain metals of either the oxide ion (O^{2-})—such as copper(I) oxide (Cu_2O) and silver oxide (Ag_2O)—or the carbonate ion (CO_3^{2-}), such as cobalt(II) carbonate ($CoCO_3$) and copper(II) carbonate ($CuCO_3$).

The burning in the trash can occurs because of the presence of three elements: heat, fuel, and oxygen. With the lid cutting off a supply of atmospheric oxygen, the nearest available source of oxygen is the glaze compounds, which all contain oxygen.

The metals in the glaze components are reduced, while the carbon or carbon monoxide coming from the combustion is oxidized. For example, in the case of copper oxide (Cu_2O), which is actually a crystal composed of the ions Cu^+ and O^{2-}, the following redox reactions occur in the can:

Reduction: The copper ions are reduced into elemental copper:

$$Cu^+ + e^- \rightarrow Cu$$

Oxidation: The carbon is oxidized into carbon dioxide in the presence of carbon or carbon monoxide:

$$CO + O^{2-} \rightarrow CO_2 + 2\,e^-$$

or

$$C + 2\,O^{2-} \rightarrow CO_2 + 4\,e^-$$

The combination of both reduction and oxidation reactions leads to either of the following reactions:

$$2\,Cu_2O + C \rightarrow 4\,Cu + CO_2$$

or

$$Cu_2O + CO \rightarrow 2\,Cu + CO_2$$

The end result is a shiny copper coating on the surface of the pot that replaces the copper oxide that was present in the glaze before the combustion occurred.

What makes Raku pots unique is the presence of different metallic streaks that would not form if the pots were left outside to cool down after being taken out of the kiln.

Art on glass

Another art form that is gaining popularity is stained glass. To picture what stained glass looks like, imagine a beautiful painting that you like. Now imagine the painting with sunlight streaming through. That's essentially what a stained-glass window looks like. It consists of small pieces of glass that are carefully shaped and assembled to form a design or a picture. Stained glass is also used to make lamps, boxes, and decorations, and anyone can learn this craft.

At Frog Valley, stained-glass artist Veronica Wilson created a stained-glass window featuring Appalachian wildlife—frogs, birds, luna moths, turtles, and a brightly coiled snake. In the sunlight, the stained-glass window looks like a brilliant array of colored glass pieces—some smaller than your little finger nail—held in place by a metallic support network.

Wilson explains that her work, with its small scale and tiny mosaic pieces, is actually a scaled-down version of the stained-glass windows that grace cathedrals and churches. To create such windows, artists connected large window pieces with a reinforcing material called a lead came (Fig. 1), which was soldered at the junctions between the window pieces.

ANTHONY FERNANDEZ

Figure 1. A stained-glass window commonly seen in churches consists of many small pieces of glass that are all soldered to each other with supporting channels called lead cames. Shown here are two pieces of glass (labeled "3") that are soldered with two U-shaped cames (labeled "1") and one H-shaped came (labeled "2").

Wilson uses bits of colored glass to form small flower petals, insect wings, stems, and leaves. But instead of using lead cames, she fastens them in place with a different technique. First, she draws the shapes on paper, glues them lightly on a piece of colored glass, and then cuts around them (Fig. 2).

Using a glass-cutting tool, which she holds like a vertical pencil, she scores the surface around each shape. Then, she lightly taps on the underside of the glass to weaken the scored line and applies a downward pressure with glass pliers on each side of the scored line to make the break. When the small pieces are assembled together, the work looks like a colorful jigsaw puzzle.

Figure 2. The artist first draws patterns on paper and then reproduces them on the glass before cutting the pieces of glass.

PHOTOS: MARK SCHWENK, WWW.FROGVALLEY.COM

Figure 3. Each piece of glass is wrapped with copper foil because solder adheres to metal but not to glass.

To put the small pieces together, Wilson uses copper foil, a spool of lead-tin solder, and a cleaning agent. First, Wilson edge-wraps each piece of glass with a narrow strip of copper foil—today's foil is available in spools with a backing of adhesive—which she attaches to the glass (Fig. 3).

Then, she applies the cleaning agent to the copper. The cleaning agent is hydrochloric acid (HCl), which is formed by exposing zinc chloride ($ZnCl_2$) to moisture and heat, which leads to hydrous zinc chloride ($ZnCl_2{\cdot}2H_2O$). At high temperatures, hydrous chloride decomposes to hydrochloric acid and zinc oxychloride [$ZnCl(OH)$], giving off water vapor (H_2O) in the process:

$$ZnCl_2{\cdot}2H_2O \rightarrow ZnCl(OH) + HCl + H_2O$$

Hydrochloric acid removes any oxides that are present on the surface of the copper foil, so that only copper is exposed to the solder:

$$CuO + 2\,HCl \rightarrow CuCl_2 + H_2O$$

The product, copper(II) chloride ($CuCl_2$), is soluble in water and easily washes away. What is left is a surface of pure copper, to which the tin-lead solder can bind.

The solder is a mixture of metals with low melting points. Wilson uses a tin-lead 50:50 mixture. She heats the copper base and moves the hot iron to melt a bead of solder into place (Fig. 4). When the tin-lead metal cools down, it adheres to the copper and holds the glass in place.

Figure 4. Molten solder flows onto the seams and creates a "came."

Wilson then applies a thin shiny coating called a liquid patina to give the desired color to the solder line and to protect the cooled solder from further oxidation. Days, sometimes weeks, in the making, the piece is finally ready to be metal-framed and mounted in a sunny window where it blooms to life!

Want to give it a try?

After seeing the art pieces at Frog Valley Studios, I wanted to become familiar with how stained glass and Raku pottery are created. So, I simply showed up and volunteered to help the artists with the many steps involved in the production. Hours of free help is hard to turn down! And they became valuable and fun lessons.

You may want to try Raku pottery or stained glass. Classes are offered throughout the United States, and chances are, classes are available near you. While you learn about the properties of the materials and how they interact with each other, you will discover that it really is all about chemistry! ***CM***

Check out the video podcast on artistic chemistry at: www.acs.org/chemmatters

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