Dissolving Limestone the Natural Way
(or how sinkholes and caves are formed)

By Tracy D. Branam

Materials needed:

- Red cabbage pH indicator solution (see supplement)
- Plastic elbow straws or ¼-inch tubing
- Several clear plastic cups, small jars, or 250-ml beakers, with covers if possible
- Plastic spoons or glass rods for stirring
- Baking soda
- Vinegar
- Clean, 20-oz plastic soda bottle or equivalent-size plastic or glass container with narrow mouth
- Plastic funnel that fits opening of soda bottle
- Eye dropper
- Cork stopper to fit soda bottle
- Cork borer or drill to create ¼-inch hole in cork
- Tape
- Several small pieces of limestone (no dolomite!) with fresh surfaces

Optional:

- A 1:10 dilution of hydrochloric (muriatic) acid (HANDLE WITH CAUTION, CAN CAUSE SEVERE BURNS!)
- Safety goggles and gloves for handling concentrated hydrochloric acid
- Balance for weighing limestone pieces
- Short candle
- Wide-mouth jar taller than candle

Procedure:

Step1: Preparing the distillation apparatus

Bore a hole in the cork just large enough for a straw to go through. Insert the short end of the elbow straw through the top of the cork until at least ½ inch of straw sticks out the bottom of the cork. Attach the short end of another elbow straw to the long end of the one sticking out of the cork. You may have to crimp it to get the second straw to fit into the first. Carefully cover the straw junction with tape to seal the connection.

Step 2: Setup, generation, and explanation of carbonic acid formation

Fill one glass for each acid being used plus one for the gas distillation with about 100 ml (about ½ cup) of water and 20 ml (about 1 tablespoon) of red cabbage pH indicator. Note the color and corresponding approximate pH value using the table (next page). To one glass add diluted hydrochloric acid (prepared by adding 1 part concentrated acid to 9 parts distilled water) one drop at a time, stirring with a plastic spoon between drops, until indicator color is red (use of hydrochloric acid is optional). Note the number of drops it takes to turn the indicator red.

Repeat process with a second glass, using vinegar. Place the funnel over the opening of the soda bottle and put in 2 to 3 tablespoons of baking soda, add about 100 ml of vinegar, remove funnel, and quickly place the cork in the opening. Place the other end of the tubing near the bottom in a glass of indicator solution and allow the setup to sit until bubbles stop coming out of the straw. Carefully grasp the soda bottle, hold the straw in the indicator solution, and swirl the mixture to generate more gas bubbles. Note the color change to the indicator solution. It should change from blue or violet to a pinkish-purple instead of a red color. This is because the gas that is produced, carbon dioxide (CO_2), combines with water to produce a weak acid called carbonic acid (H_2CO_3); hydrochloric acid (HCl) is a strong mineral acid and vinegar (acetic acid, H_3CCOOH) is an organic acid somewhat weaker than hydrochloric acid but stronger than carbonic acid.

Carbonic acid is the natural acid that forms in the soil when microbes break down organic material, releasing carbon dioxide, which combines with pore water in the soil. The acid will either be transported (flushed by rainwater) down through the soil until it contacts bedrock, or it will migrate to an outwash location such as a stream or seep. If the bedrock that the carbonic acid encounters is limestone, then a slow dissolution reaction occurs. If there is a fracture in the bedrock that channels the carbonic acid-rich water through it, then dissolution will be concentrated along the fracture, causing it to enlarge, leading to the formation of sinkholes and caves that slowly form over thousands of years.

pH	2	4	6	8	10	12
Color	Red	Purple	Violet	Blue	Blue-green	Greenish yellow

Step 3: Comparison of acid neutralization (or limestone dissolution) rates

The neutralization of carbonic acid by limestone occurs at a very slow rate; therefore, this demonstration works best as a full-day demonstration where the results are not fully realized until afternoon, if the experiment is started in the morning.

Place similar-sized pieces of limestone in each of three glasses filled with 100 ml of water and 20 ml of red cabbage indicator solution. [NOTE: Use glasses with lids if possible.] Limestone pieces should be small enough to be completely submerged in the liquid. Let sit overnight; when ready to start the demonstration the next day, note the color of the solution (it should be blue). Carefully (while wearing safety glasses and gloves) add enough hydrochloric acid with an eyedropper to one glass to change the pH indicator color to red, remembering to count the number of drops added and stirring or swirling the liquid as drops are added. Cover the glass and set aside.

Repeat the process on a second glass, only this time use the same number of drops of vinegar as was used with hydrochloric acid. Notice that the color does not turn quite as red, since vinegar is a weaker acid.

Now set up the distillation apparatus by placing 2 to 3 tablespoons of baking soda through the funnel into the bottle and adding 100 ml or ½ cup of vinegar, quickly capping with the cork/tubing, and inserting the open tube end deep into the 3rd cup containing indicator solution and limestone, swirling the soda-vinegar mix occasionally to keep the effervescence going. Add more vinegar to the bottle and swirl again to release additional CO_2. The indicator color changes much less for the carbonic acid formation than the other two acids. Cover the glass and set next to the other jars. Record the indicator colors for each glass.

If the reactions are performed early in the day, one or more of the solutions should have changed color again back to violet or blue by the end of the day, depending on how much limestone is in the glasses and the size of the limestone pieces. For faster reactions, place several small limestone pieces in each glass instead of one large one. Be sure to label each glass with the name of the acid that was added to it and note which one turns blue first.

Explanation:

In nature, carbonic acid, which is very weak, is the most common acid formed. As this experiment demonstrates, it does not create as strong an acidic environment as the mineral acid HCl or the organic acid H_3CCOOH. This weak acid is more quickly neutralized by the presence of limestone than the other two acids, which means it is dissolving less limestone than the other two acids. Because of its weak acid properties, carbonic acid reacts slowly with limestone, requiring large quantities to dissolve even an small amount of limestone. This demonstrates how long it takes for karst features such as large sinkholes and caves to form given that the dissolution rate is so slow.

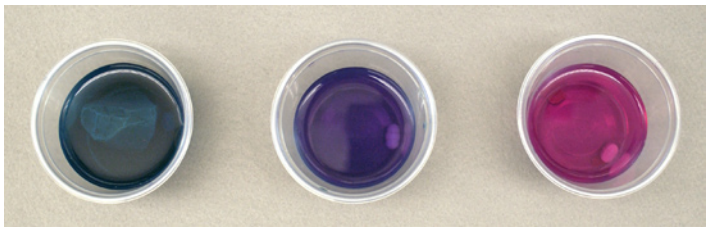
Optional:

Properties of carbon dioxide gas

To demonstrate that the gas being generated is not just breathable air, place a candle in a glass jar and light it. Start the CO_2-generating process by adding the baking soda and vinegar. After capping, point the open end of the tube into the jar containing the candle. Note what happens. Without oxygen, the candle dims; if enough CO_2 is introduced, the flame goes out.

Measuring limestone dissolution amounts

To gauge how much limestone is dissolved by acids of different strengths, weigh each piece on a balance prior to placing the limestone pieces in the indicator solutions. Place weighed pieces of limestone in each of three glasses and repeat Step 3 above, being sure to cover the containers between additions. Repeat this process for at least 5 days. After the experiment, allow each piece to dry a few days, re-weigh, and compare the amount dissolved by each acid. This will provide a more empirical way of appreciating just how slow the dissolution of limestone by carbonic acid can be.



Supplement: Red Cabbage pH Indicator Solution

(From the Web page: http://chemistry.about.com/library/weekly/aa012803a.htm)

Materials needed:

Red cabbage
Knife for cutting cabbage or food processor
Boiling water
Filter (coffee filters work well)
Large jar or beaker for holding filtered cabbage water

Procedure:

Cut cabbage into pieces and place in jar or beaker and pour boiling water over cabbage. Allow at least 10 minutes for the color to leach out of the cabbage. Decant the liquid through the filter (make sure the filter is supported by a funnel or strainer) into a beaker or jar. You now have a pH indicator. To test the color range place 50 ml (about 1/4 cup) cabbage indicator in enough small clear cups or small jars to test as many of the following materials as you can: muriatic acid, vinegar, lemon juice, baking soda, antacids, seltzer water, household ammonia, washing soda, cream of tartar, and lye.