acid-etching crystals

by Ryan Coppage, PhD

Crystalline pottery follows a history of experimentation with glaze chemistry and firing techniques. Curiously, instead of adding colorants, acid-etching the colorants from surface crystals creates striking silver effects.

Defining the Terms

Carcinogen: A material that is known and reported to be cancer-causing in relatively high prevalence for humanity.

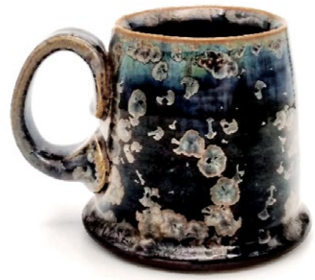
Crystalline Pottery: Fired ceramics characterized by the presence of visible zinc-silicate crystals in a ceramic glaze. The crystals are grown to various sizes and number of rings during specific firing ramps.

Doping: The absorption of color centers (pigment atoms) as a zinc-silicate crystal grows, in which the absorbed pigments then color the entire crystal.

Leaching: The process of heavy metals being pulled from the surface of a glaze over time, or being preferentially pulled out of a glaze for a color change.

Crystalline Surfaces

Crystalline pottery is surprisingly old. There were zinc-silicate crystals on pots in the Art Nouveau era of France—over 100 years ago. With that said, in their freshly-fired states, most crystals are low-contrast compared to their backgrounds: rutile makes gold crystals on a white background, copper carbonate or oxide makes green on green, cobalt makes blue on blue, and so forth. Most silver crystals, however, are actually made from acid-etching the colorants out of the crystals that grow on the surface.



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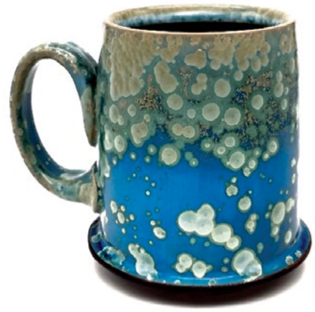

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1 A crystalline mug acid-etched, neutralized, and then boiled in water to remove any excess salts left behind from the processes. **2** A crystalline mug in which cobalt was removed from the crystals through acid etching, base neutralization, and boiling in water to remove any unwanted salts.

Ceramic crystals are the result of a solid-state chemical reaction that takes place at a very high temperature. Most of the time, a crystalline glaze is 25% silica and 25% zinc oxide—in nearly 1:1 ratios of one another. This allows for the formation of zinc-silicate crystals, which grow between about 2000–1400°F (1093 and 760°C). In doing so, they pick up whatever pigment metal atoms happen to be around the glaze. This process is called color doping. Cobalt atoms make crystals blue, copper atoms make them green, rutile crystals (as this is a titania crystal, not an atom) make them gold, etc. The pigments sit in the zinc-silicate crystalline structure, which would otherwise just appear silver.

Crystals also break up the surface of the glaze, making them porous and good candidates for leaching. The release of heavy metals can be hazardous. For example, a glaze with an orange background with blue crystals is likely to contain nickel, which is a carcinogen. The glaze will contain open spots on the crystals, where nickel could leach out of the surface, such that this type of glaze should not be used on a surface that comes into contact with food. However, on the other side of that coin is the opportunity to force leaching as much as possible to either change the crystal color or remove hazardous materials that could possibly be leached out later (1). Since crystalline glaze surfaces are a prime candidate for leaching, they can also easily be taken advantage of for changing crystal color—by removing the dopants picked up during firing. That means that the low contrast of blue background and blue crystals for cobalt can become blue background and silver crystals (2), for example.

Materials Needed

For this process with a crystalline-glazed pot, I recommend extreme care, gloves, eye protection, a respirator, three 5-gallon buckets with lids, and access to a dishwasher or at least a large pot for boiling water.

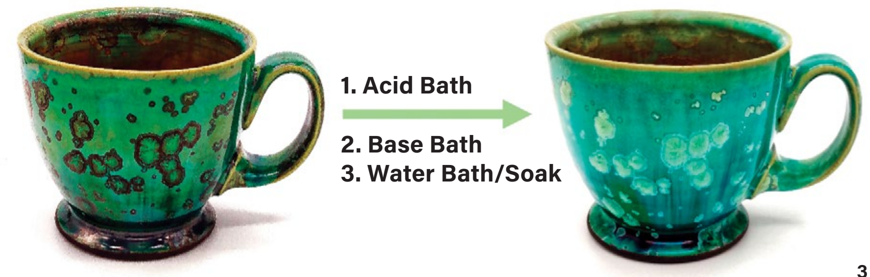
Muriatic acid (HCl) is a common concrete etchant that can be found at most home improvement stores for around $12 per gallon. I do not buy the low-vapor kind, as that's also incredibly diluted. HCl is a gas dissolved in water, so if you're buying low vapor, you're really just paying for less HCl to start with.

This can be mixed in a ratio of 1 part muriatic acid to 4 parts water in a 5-gallon bucket, to only about 3 gallons of total volume. This will do all of your etching leg-work, while the rest of the process is just cleaning the HCl out of the crystals after they have been etched.

Next, put 3–4 gallons of water in a second bucket, and add in 5 pounds of baking soda. This will be your neutralization bath. The reaction below shows how it works:

$$HCl + NaHCO_3 \rightarrow NaCl + H_2O + CO_2$$

Finally, set up your third bucket with 4 gallons of water. This bath will pull the initial extra NaCl (salt) out of the crystalline pockets after neutralization. **Note:** These three buckets must be set up outside (especially the first!), as HCl is a vapor and will escape from the first bucket every time it is opened.



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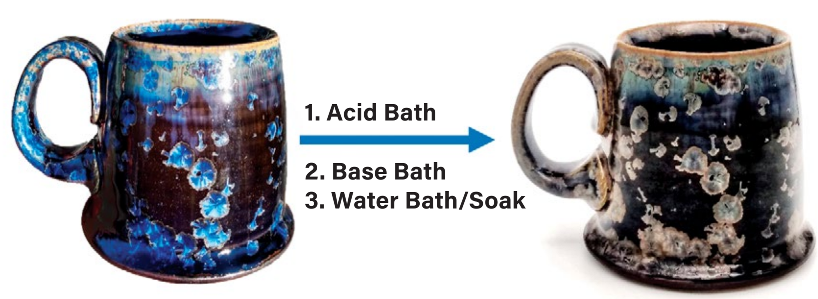

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3 Acid-etching of a copper-oxide crystalline surface through the process described below, in which copper is pulled out of the crystals seen at left to make the lighter colored ones seen at right. **4** A crystalline glaze with 7.5% manganese oxide and 2% cobalt oxide, in which the cobalt is preferentially leached out of the crystals (left)—to make silver crystals with gold rings over a black background (right).

Acid-Etching Process

While wearing long sleeves, gloves, a respirator, and eye protection, grasp the crystalline-glazed pot with tongs and carefully lower it into the acid bath. Lower it slowly to prevent any splashing, then seal the lid back on the bucket. (As HCl is a gas, leaving the lid off lets HCl escape and the concentration of your muriatic acid decreases over time. So, while letting it soak, seal the lid.) The acid solution will seep into the glaze crystals, which are actually open on the surface, and dissolve the cobalt or copper atoms, leaving the zinc-silicate crystal in place.

The desired color change in the crystals determines the amount of time that it is left in the acid bath. For full silver, I leave a pot in overnight. For less, aim for 1–2 hours. The color change isn't visible when wet—only when the surface has dried.

When it is time to take the vessel out, put your gloves, glasses, long sleeves, and respirator back on and pull the piece out of the acid bath with tongs, pouring any extra liquid out of it back into the bucket (closer to the surface than farther away, slowly and carefully—no splashing!). Transfer it to your base/neutralization bucket (I have the three buckets set up in a row on my driveway: acid, then base/neutralization, then water). As the vessel enters the base/neutralization bath, it will fizzle and bubble; that is CO_2 forming from the equation above. Let the piece sit in the bath for 3–4 hours, take it out, and let it soak in the water bath overnight to pull any residual salt out of the crystals.

Depending on the length of the soak, there may be extra salts left on the surface. For this, I boil the vessel in water on my stovetop or run it through the dishwasher on a hot cycle a few times. If left in the base neutralization bath too long, you will see salt crystals growing out of the glaze crazing and crystals. These can be wiped off with a non-metal scouring pad and then the piece can be washed in a dishwasher/boiled on the stovetop to remove any excess salt, until you have something akin to figure 4.

In my experience, the acid-etching process works best with cobalt carbonate/oxide and copper carbonate/oxide, but does not work with rutile, neodymium, or when cobalt is used in combination with neodymium. It will pull most of the copper out of crystals, but they do retain greenish tints (3); however, it seems as though almost all cobalt colorant can be removed from crystals, making them turn bright silver (2, 4). **Note:** To dispose of the muriatic-acid bucket, purchase 5-pound boxes of baking soda. Slowly pour the baking soda into the acid bucket, until it no longer fizzes, effectively making a giant bucket of salt water. Leave the lid off and let the water content evaporate off over a couple weeks. The remaining salt/bicarbonate can be thrown away in the trash. There will be trace amounts of copper, etc., but in solid waste, this is less severe than throwing away electrical wiring/old electronics.

It should be noted that I would not consider any of these cobalt-containing mugs safe to drink out of prior to the acid-etching process, but after going through an acid bath of this strength (way more stringent than any tea or coffee you could ever put into it), they are no longer susceptible to heavy-metal leaching—as Andy Boswell has also argued for his crystalline works.

The absence of leaching has been lab tested via a standard leach test consisting of a 72-hour soak in vinegar followed by looking for discoloration of the vinegar or discoloration of the glaze. For those who try this process, it is important to test your own pieces for leaching. No observable color change was detected after aggressive soaks in muriatic acid (as per the acid strength of HCl vs acetic acid). I also use a tenmoku liner glaze in all crystalline pots to reduce surface pocketing/leaching/porous nature for retention of beverages.

What It All Means

While some crystals are actually poisonous/carcinogenic and possessing of low-contrast color combinations, this process allows to both increase the contrast between the ceramic crystal and background color and, after leach testing, make them safe for use—at least for the case of cobalt.

the author *Ryan Coppage is currently chemistry faculty at the University of Richmond. He fiddles with various glaze projects and makes a reasonable number of pots. To see more, visit www.ryancoppage.com.*