An Oxidized Bisque Firing

by Steve Davis

Appears in the Jul/Aug 2018 issue of Pottery Making Illustrated.

Many clay and glaze faults in ceramic wares are caused by incomplete burnout (oxidation) of carbon and sulfur during the bisque firing. These faults are observed after a glaze firing, but the problems arise during the bisque firing. These initial problems can be attributed to a kiln operator's lack of understanding about the chemistry that occurs during this first, critical firing.

Carbon

Many materials used in ceramics contain carbonaceous matter, including organic carbon and inorganic carbon from clays, whiting, dolomite, and talc. This carbon must be burned out (oxidized) during the bisque firing to ensure the best results possible in glaze firings. Bloating, black coring, pinholing, blistering, and poor color development are all the result of incomplete carbon burnout. To achieve the complete burnout of carbon, you need the following components: oxygen, time, and temperature.

Oxygen

Oxygen is the most critical component. Without sufficient oxygen in the kiln chamber, carbon in the clay will have difficulty forming carbon monoxide and dioxide gases that allow carbon to vacate the clay. If oxygen is in short supply, carbon will take oxygen from sources including red iron oxide (Fe_2O_3) that comes from ball clays, kaolins, fireclays, and particularly red clays. When carbon atoms strip oxygen atoms from red iron oxide (Fe_2O_3), the red iron oxide is converted into black iron oxide (FeO), which is a more powerful flux than the feldspars we add to clay bodies. The chemical equation representing the transformation from one form of iron to the other is: $Fe_2O_3 + C \gamma 4FeO + CO_2 \eta$. Starting at 1650°F (899°C), the walls of the wares become progressively sealed by the fluxing action of the black iron oxide. When this same clay is then fired for a second time in a glaze firing to maturation, the clay wall will be over-vitrified and soft from the fluxing action of the black iron oxide. Gases from carbon and sulfur that are trapped in the soft, sealed clay wall will expand to form pockets (bloating). In iron-bearing and black clay bodies, the bloats will be small to large pockets where gases have gathered together. In porcelain bodies, islands of trace iron exist that can form pimple-sized bumps in the clay wall.

In low-fire ceramics, temperatures are not high enough for bloating or melting to occur, but the carbon can cause faults such as black coring, pinholes, blisters, and poor color development in glazes and underglazes.

Time

Proper carbon burnout requires time for the oxygen to penetrate the ware and form carbon monoxide and dioxide gas. Much thicker pieces, dense loads, and high-iron clays require substantially more firing time for proper oxidation of the carbon. Sometimes the carbon content of the ware can be much higher than normal due to changes in raw materials.

Increased carbon content can cause problems that would not normally occur with established firing procedures that have been used for years, but now have to be planned for.

Temperature

Organic carbon burns out (oxidizes) from 300–600°F (149–316°C). Inorganic carbon from clays and ceramic materials burns out (oxidizes) from 1292–1652°F (700–900°C). Sulfur in various forms will oxidize from 1292–2102°F (700–1150°C).

Kilns must be well vented throughout these temperature ranges, especially from 1292–1652°F (700–900°C), and the firing should proceed slowly through this temperature range to allow oxygen time to oxidize all of the inorganic carbon and sulfur in the clay.



Proper placement of the ceramic fiber blanket lid prop on an electric kiln shields the control box from excessive heat while venting combustion gases.

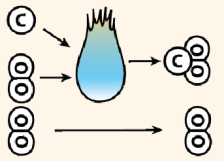
Venting Electric Kilns

Just because a kiln is powered by electric elements, doesn't mean that it's oxidizing your wares during firing. There are too many carbon sources coming from clays and glazes. Oxygen must be supplied to the kiln through venting by one of two methods. One method is to install a kiln vent, which is the most effective way to introduce oxygen. The other method is to prop the lid open to ¾ inch and remove all of the spy hole plugs. Venting should be done from the start of the firing and continue until the inside of the kiln chamber has achieved 1700°F (927°C). A good prop for the lid is a 2½-inch deep × 12-inch wide × 1-inch thick piece of ceramic fiber blanket. It will compress to ¾ inch. If placed on the rim of the kiln wall next to the control box, it will shield the control box from excessive heat. Be sure to not place the lid prop over the air gap between the kiln wall and the control box. This needs to be clear so cool air can flow upward (convection) between the kiln wall and controller. When 1700°F (927°C) is achieved, use a pair of leather gloves to carefully remove the lid prop and place it in a location where it will cause no bodily harm or become a fire hazard while it cools. Keep the lid closed for the remainder of the firing. The spy holes should remain open.

Loading Electric Kilns

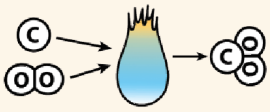
It's your job to make it easy for this process to work. You should load the kiln in a manner that allows for enough space between the wares for the exchange of gases throughout the clay wall. Another consideration is the space between the kiln shelves. There needs to be enough shelf height above the wares to allow the elements to emit radiation (electromagnetic wavelength of light) onto the wares. Having an element visible below the shelf so that the radiation can emanate down on the pieces is ideal. Due to the static movement of air throughout electric kilns, heat has a tendency to rise to the top of the kiln via convection, resulting in wares at the top of the kiln being fired to a higher temperature than wares in the bottom of the kiln. It's best to load tall and loose at the bottom of the kiln, and short and dense from the middle to top of the kiln so as to balance out the heat throughout the kiln.

Firing Atmospheres—by Hal Frenzel



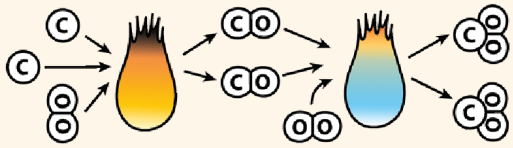
$C + 2O_2 \rightarrow CO_2 + O_2 + heat$

Oxidation: When excess oxygen is present in the kiln; it plays no part in combustion. However, it does absorb heat energy that would otherwise help fire your ware. In this way, it does contribute to fuel consumption.



$C + O_2 \rightarrow CO_2 + heat$

Neutral: When exactly two oxygen atoms are present for each carbon atom; neutral combustion occurs, creating carbon dioxide and heat. This assumes complete turbulence and circulation in the kiln so that every atom finds a partner. This is difficult, even in efficient kilns, so some excess oxygen is needed to avoid reduction.



$2C + O_2 \rightarrow 2CO + heat$, and later, $2CO + O_2 \rightarrow 2CO_2 + heat$

Reduction: When an excess of carbon (fuel) or a shortage of oxygen (air) is introduced, incomplete combustion takes place. Carbon monoxide (as opposed to carbon dioxide) is produced along with heat, though not as much as would be produced during complete combustion. The carbon monoxide then looks for more oxygen, which it takes from oxides in the clay and glaze in the kiln. This is also the reason yellow flames shoot out through spy holes when a kiln is in reduction—the carbon-rich fuel is following the oxygen supply.

Time	Temp	Gas	Damper/Air	Comments

Gas Kiln Bisque Firing Chart

Bisque Firing with a Gas Kiln

In a gas kiln, oxygen supply is a little trickier. Gas-fired kilns are basically a box where air and fuel are mixed and ignited. The air:fuel ratio is the focus. In natural-draft kilns, fuel comes through the body of the natural-draft burner under pressure. This flow of gas entrains around 50% of the air requirement (primary air) through the burner. Air and fuel are mixed in the burner and the kiln chamber. The other 50% of the required air comes through the burner ports (secondary air). The damper on both updraft and downdraft kilns controls this secondary air and the atmosphere of the kiln.

To achieve a reliable, oxidized bisque firing with a gas kiln, a kiln chart (see below) that lists the gas pressure and corresponding damper settings must be employed. As the kiln temperature increases, combustion gases will expand throughout the kiln chamber. The air:fuel ratio will change toward a reduced atmosphere (reduction of oxygen), due to the greater pressure of the fuel verses the pressure of the air. Complete combustion—total conversion of carbon to CO2—is what we are seeking in oxidized bisque firings.

Creating the Firing Chart

In order to guarantee that there is always ample oxygen supplied to the wares, a firing chart should be established at a temperature equal to, or above the bisque temperature. It's critical to use repeatable methods of measuring the gas pressure and damper settings.

Clean out the kiln, burner ports, and burners. Check the orifices for spider nests, and inspect the flue area for obstructions. Debris in the burner port can cause an area of local reduction within the kiln that may not be noticed during a firing.

If the kiln doesn't have one already, install a gas gauge between the burners and the gas control valve.

Mark the damper indicating the location of the damper openings of inch or half-inch increments.

Fire the kiln empty up to cone 04 and make notations on a kiln chart that include time, temperature, gas pressure, damper setting, and comments.

Create a chart that shows the ideal damper setting and gas pressure for different stages of the firing using the following steps.

At cone 04, note the maximum amount of gas pressure used. Push the damper in until a flame is visible in the damper area. If the damper area is not visible, observe the flame coming out of the spy hole.

Now, incrementally back out the damper until the flame disappears. It may take a minute for the kiln atmosphere to adjust.

Once the kiln is in an oxidizing mode (lack of flame), make a note of the damper setting that corresponds with the gas pressure reading. This combination of damper setting and gas pressure should be used in the latter stage of the firing to reach cone 04.

From here, the ideal settings to produce an oxidizing atmosphere at lower temperatures can also be determined.

Lower the gas pressure by ½ inch, and repeat the same damper adjustments as listed above. This allows you to establish the corresponding damper settings to achieve an oxidizing atmosphere for lower gas pressure readings.

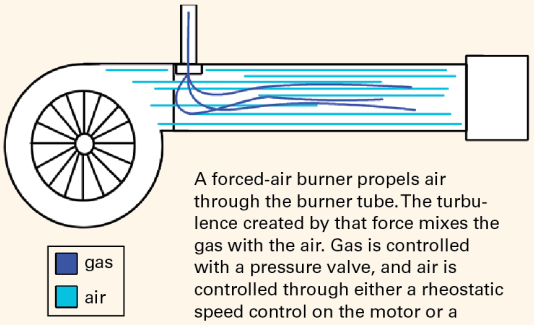
Continue this process until you're down to 1 inch of gas pressure.

This chart is created at a temperature (cone 04) that guarantees your kiln atmosphere will be oxidizing at lower temperatures. Tip: It's best to make the kiln chart at night when the flame is more visible.

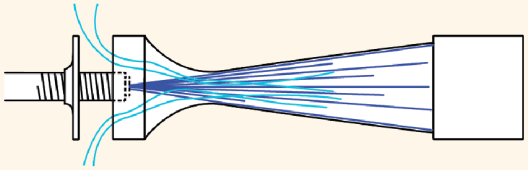
Once this chart is established, it should be easy to achieve a well oxidized bisque.

Remember that oxygen, time, and temperature must be taken into account when bisque firing.

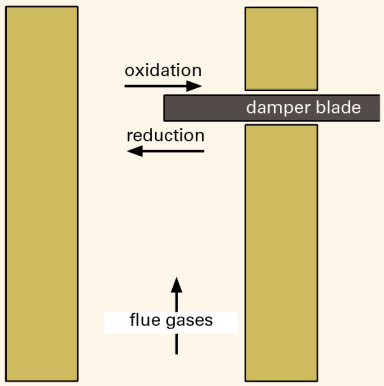
Firing Controls—by Hal Frenzel



A forced-air burner propels air through the burner tube. The turbulence created by that force mixes the gas with the air. Gas is controlled with a pressure valve, and air is controlled through either a rheostatic speed control on the motor or a manual inlet cover flap that blocks the air from entering the blower.



An atmospheric burner operates according to the force of gas through a narrow throat in the burner body. This creates low pressure behind the opening and draws air into the burner with the gas. As the gas is increased, more air is drawn into the burner, and the appropriate ratio of gas and air for combustion is maintained. Gas is controlled with a pressure gauge, and air is controlled by a plate at the back of the burner.



A damper is usually a piece of refractory material, often a kiln shelf, that is placed in the path of the flue gases as they travel up through the chimney stack of the kiln. By moving it in and out, the pressure inside the kiln is controlled. Increased pressure decreases airflow, and decreasing pressure increases airflow.

Bisque Firing Program for Auto Kiln Controllers

Electric kilns with automatic controllers break firings down into ramps or segments of heat increase (or decrease), and the readout has abbreviations that correspond to different factors controlling the temperature rise per hour, top temperature in each segment, and thus the amount of time each ramp will take. A segment (SEGS) includes a rate (RA), a temperature (F), and a hold (HLD) setting.

Alarm and Delay can be set after you input a program. Read your manual for details.

The rate (RA) is the rate of temperature climb per hour.

The (F or C) is the temperature that a segment will fire to.

The hold (HLD) is how long the temperature will be held for that segment.

Note: These same principles can be applied to manual kilns to some degree.

Heat Transfer

Radiation: When electromagnetic waves travel through space, they transfer heat to objects they come into contact with. The sun and kiln elements produce these waves. Radiation is the primary source of heat in electric and gas kilns.

Conduction: The transfer of heat between substances that are in direct contact with each other.

Convection: Heat transfer caused by the up-and-down movement of gases and liquids. Flue gases moving up a kiln chimney are an example of convection.

Pyrometric Cones measure heat work, not a set temperature. If you fire to cone 04 at a rate of 108°F an hour, cone 04 will drop at around 1922°F (1050°C). If you fire to cone 04 at a rate of 270°F per hour, cone 04 will drop at a higher temperature of 1940°F (1060°C).

Much of the carbon sourcing information for this article comes from: The Potter's Dictionary of Materials & Techniques by Frank and Janet Hamer.

Steve Davis has been the production manager at Aardvark Clay & Supplies for 23 years and is the inventor of the Kazegama.

Bisque Program for an Automatic Kiln Controller

Controller Display	Input	Press	Comments
"STOP or IDLE"		STOP	This resets the kiln so you can program the kiln.
"STOP"		RAMP/ HOLD	This puts you into a custom program mode. These can be saved and reused.
"PROG"	1	Enter	Select a numerical program such as User Program 1.
"SEGS"	6	Enter	You'll enter 6 segment entries for ramp, temperature, and hold.
"RA1"	60	Enter	This is ramp 1, increasing 60°/hour up to 180°F, then held there for 12 hours.
"F1"	180	Enter	Water forms steam at 212°F so 180°F is a safe temperature to remove water.
"HLD1"	12.00 (hours)	Enter	The amount of hold time at this temperature varies depending on water content and thickness of the ware.
"RA2"	200	Enter	This is ramp 2, increasing 200°/hour up to 600°F.
"F2"	600	Enter	Organic carbon burns out from 300–600°F.
"HLD2"	0	Enter	No hold time is necessary for ramp 2.
"RA3"	240	Enter	This is ramp 3, increasing 240°/hour up to 1300°F.
"F3"	1300	Enter	1292°F is start of inorganic carbon burnout, which is why the ramp ends at 1300°F.
"HLD3"	0	Enter	No hold time is necessary for ramp 3.
"RA4"	60	Enter	This is ramp 4, (60°/hour up to 1650°F). The slow ramp ensures removal of inorganic carbon at this critical stage.
"F4"	1650	Enter	Inorganic carbon burns out from 1292–1652°F, so the ramp ends at 1650°F.
"HLD4"	0	Enter	No hold time is necessary for ramp 4.
"RA5"	360	Enter	This is ramp 5, increasing 360°/hour up to 1850°F.
"F5"	1850	Enter	The kiln can gain temperature quickly through this phase up to 1850°F.
"HLD5"	0	Enter	No hold time is necessary for ramp 5.
"RA6"	108	Enter	This is ramp 6, increasing 108°/hour up to 1922°F (cone 04).
"F6"	1922	Enter	Approaching the final temperature more slowly ensures all wares reach the desired bisque firing maturation.
"HLD6"	0	Enter	No hold time is necessary for ramp 6.
"ALRM"	9999	Enter	9999°F is a default temperature. You can set the kiln alarm to any temperature.
"IDLE"		START	Now the program is set, and you can start the kiln. This firing schedule takes 26 hours to complete.