

# reduction misnomer

by Ryan Coppage, PhD

Reduction firing is often not properly understood or explained. Find out what is really going on in the kiln so you can get more color depth and a more refined color palette.

## Defining the Terms

**Reduction:** The process of gaining electrons and a decrease in oxidation state/charge.

**Oxidation:** The process of losing electrons and an increase in oxidation state/charge.

**Electrons:** Negatively charged particles that contribute to the net charge of an element.

**Protons:** Positively charged particles that contribute to the net charge of an element.

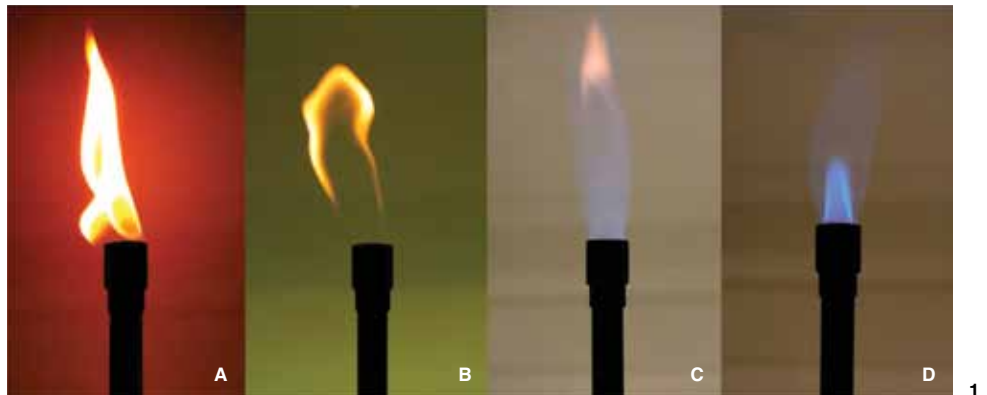
**Oxidation State:** The net charge of an atom with respect to other atoms in the molecule and the number of electrons/protons.

**Net Charge:** The number of electrons fewer (+ charge) or more (- charge) than the number of protons in an element.

## The Reduction Firing Process

Almost as a standard, the process of "reduction" is described with some degree of equivocation no matter where you go or in which ceramic setting you work. Most pottery professionals don't like to describe it, especially to a persnickety chemist. These descriptions vary from place to place, but the process of reduction is most commonly communicated as "reducing the amount of oxygen in a kiln," such that the flame/fuel searches for more oxygen and will pull said oxygen out of clay bodies, etc. While this is absolutely parallel and incidental to reduction taking place, that phenomenon is not reduction and is not responsible for the vibrant, beautiful colors that are synonymous with the firing method.

Reduction is the process of electrons being donated to a metal/element/surface through some set of reactions, while another component in the same set of reactions is oxidized (electrons lost). This is your defined set of oxidation and reduction parameters. In a gas kiln, albeit natural gas or propane, you are using some set of hydrocarbons and oxygen. Your reaction breaks down to the following for an oxidation firing using propane:



1 Four different flame qualities are present, ranging from the most fuel rich (reductive) on the left to the most oxygen rich (oxidative) on the far right with intermediates between the two.

With access to enough oxygen to efficiently burn your fuel, you are almost exclusively producing water vapor and  $\text{CO}_2$ , which will cause oxidation of your ceramic surfaces. This is the clean-burning, efficient, blue flame, which is why easy temperature gains are synonymous with oxidation atmospheres. Upon limiting the amount of oxygen access to the inside of your kiln via vents, flue control, or passive dampers, you are no longer producing purely  $\text{CO}_2$  from your fuel; you are now producing carbon monoxide (CO) and carbon black in the form of soot and char (C:H compounds in the ratio of 8:1 or so).<sup>1</sup> Your flame is bright orange (1A) and you can see smoke and soot often rolling up and out of the kiln. Conversely, a fully oxidative flame is bright blue (1D), with transitional flame compositions between the two (1B, 1C). CO and soot both deliver electrons to the surface of your pottery in the kiln. CO reacts with oxygen at the surface and forms  $\text{CO}_2$ , leaving electrons behind. Soot will flow and adhere to the surface of whatever it touches in the kiln as incredibly small, free-radical black carbon particulate.<sup>1</sup> As small carbon particulates build up on pottery surfaces, they begin to aggregate as soot and oxidize, causing a small flow of electrons into the ceramic surfaces. These processes result in the metals in your glazes gaining electrons, which means the net charge or oxidation state is reduced. Potters take advantage of this atmosphere for reducing oxidation states of metal colorants, soot production in carbon trapping, and more specialized glaze effects via soaking.



2



3

2 Specimen of the mineral malachite, with chemical formula  $\text{Cu}_2\text{CO}_3(\text{OH})_2$ . Copper has a 2+ oxidation state in this form. 3 Specimen of the mineral cuprite, with chemical formula  $\text{Cu}_2\text{O}$ . Copper has a 1+ oxidation state in this form.

## Oxidation States of Metals and Their Colors

Most commonly pursued with reduction firings are the vibrant reds of copper, the deep reds/browns/blacks of reduced iron washes, reduced iron blues in celadon/chun, and the almost electric waterfall blues of reduced rutile. These glazes all obtain their color from the metal colorants undergoing a reduction in oxidation state or charge via distance between electron orbitals. For example, your starting copper source from both copper oxide and copper carbonate has an oxidation state of  $\text{Cu}^{+2}$ , most commonly recognized as green malachite,  $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$  (2). In glaze,  $\text{Cu}^{+2}$  yields deep greens (oribe, as the ceramic world knows it), however, upon reduction, copper accepts one electron from CO/soot via a reducing flame and changes to  $\text{Cu}^{+1}$ , yielding a ruby red color that is recognizable in the mineral cuprite,  $\text{Cu}_2\text{O}$  (3). Reduced properly, a copper glaze will yield a bright to deep ruby red, but in oxidation a vibrant emerald green is maintained. If a kiln is not in reduction hard or long enough, incomplete reduction of your  $\text{Cu}^{+2}$  will result in red blushes on a copper green glaze surface.

of pin-holed mauve or tan staring at you after you open the kiln, you understand the other side of the rutile coin.

## Streamlining Firing and Glazes

By understanding the actual process of reduction and the parameters of it therein, the method of gas firing can be better tuned for reductive atmospheres, oxidation climbs, and more properly fired glazes. Associating the process of reduction with the transfer of primarily CO, soot, and thus electrons to ceramic surfaces combines the otherwise somewhat separate knowledge pools of gas firing and oxidation state metal color chemistry. Additionally, selecting glazes based on the atmosphere required for them and the oxidation state of the metal colorant needed would lead to more efficient firings, fewer glazing mistakes, and more selective use of glazes that explicitly need reduction in gas kilns.

It is most advantageous to fire the kiln up to body reduction, put the kiln into hard reduction, and then maintain a soft reduction through

the remainder of the firing. This retains the oxidation state required for gorgeously reduced glazes without wasting the extra gas needed to smoke a kiln the entire way to cone 10.

Ultimately, the metals at the surface of your glaze are effectively receptive to oxidation/reduction changes until they are cooling back down and the glaze is solidifying. Because of this, a majority of metal reduction can happen during body reduction and then a soft reductive atmosphere can be maintained for the remainder of the firing to retain those oxidation states that are characteristic with gas firing.

Greater overall reduction firing and reduction glaze awareness leads to fewer misglazed or misfired ceramic works, less

pottery smashed in the throes of anger, less wasted pounds of clay and hours of work, and cheaper, more efficient, and faster firings.

**the author** *Ryan Coppage is currently visiting chemistry faculty at the University of Richmond, Virginia. He assists with glaze formulation and mixing at the Visual Arts Center of Richmond and makes far too many pots. To learn more, visit [www.ryancoppage.com](http://www.ryancoppage.com).*

Identical white stoneware tiles dipped in Panama Red, fired in oxidation (left) and reduction (right).

**PANAMA RED**

Cone 6 Oxidation or Reduction

Dolomite	7.76 %
Gerstley Borate	10.67
Strontium Carbonate	4.17
Whiting	2.60
Ferro Frit 3110	9.70
Custer Feldspar	44.10
EPK Kaolin	2.60
Silica	15.80
	100.00 %
Add: Tin Oxide	2.62 %
Zinc Oxide	2.60 %
Copper Carbonate	1.75–2 %

Additionally, traditional red iron oxide exists as  $\text{Fe}_2\text{O}_3$  with a  $\text{Fe}^{+3}$  oxidation state. Upon being fired in reduction, iron undergoes reduction through a complicated number of precursors to  $\text{FeO}$  with a  $\text{Fe}^{+2}$  state and changes from rust red to gun metal black/brown. This same process is responsible for the blues in celadons and chuns, and for the variable, beautiful blues in rutile and ilmenite glazes. The presence of iron in rutile (up to 10%, also some niobium) is responsible for its color and must exist in its  $\text{Fe}^{+2}$  reduced state for the traditional rutile blue. If you have had the misfortune of firing rutile or celadon/chun glazes in oxidation and have been horribly disappointed to see a mess

### References:

1. Omidvarborna, H., Kumar, A. & Kim, D.-S. Recent studies on soot modeling for diesel combustion. *Renewable and Sustainable Energy Reviews*. Volume 48, pp. 635–647 (August 2015).