

Potter’s Reduction Diagrams

Written by **Howard T Sawhill**

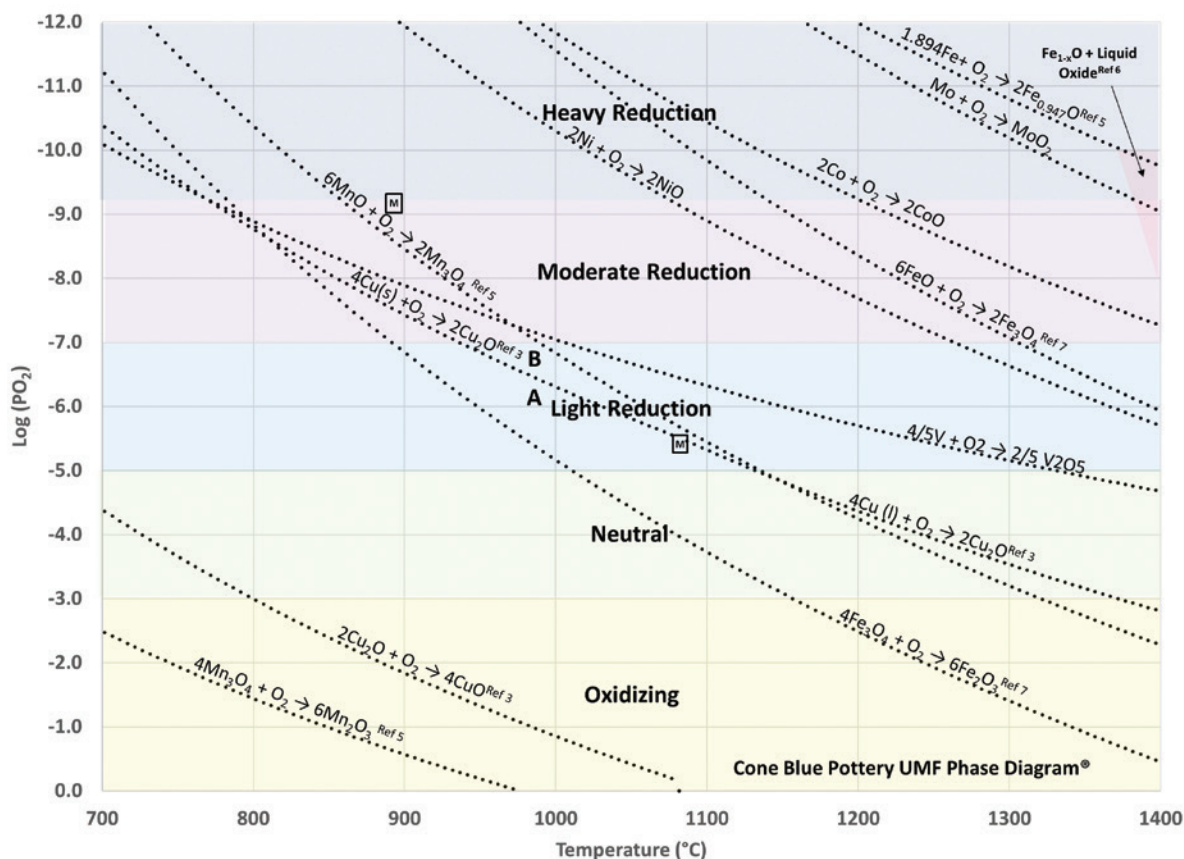
Potters have been transforming the color and texture of their pottery for thousands of years by exposing their ware to reducing environments during the kiln firing. Through experience, they’ve learned how to achieve the desired level of reduction in their kilns for their clays and glazes. Still, reduction firing results are variable – from shelf to shelf, and firing to firing. Sometimes new colors and interesting textures emerge, but as luck would have it, these happy accidents often end up being difficult to reproduce. The purpose of this article is to introduce a set of *Potter’s Reduction Diagrams* designed to help potters gain better control over ceramic oxide redox reactions (oxidation-reduction reactions) that affect color and texture in their clays and glazes.

Potters look at the iron-induced color in fired pottery (in both clay and glazes) as a means of gauging how strong the reduction was during the firing – darker colors suggesting stronger reduction. Most clays or glazes contain some amount of iron. Still, the reduction of iron oxide

is complex. First, Fe₂O₃ (Hematite – sold as “red iron oxide”) reduces to Fe₃O₄ (Magnetite – sold as “black iron oxide”), then at higher temperatures to Wüstite (FeO), and finally to metallic iron (Fe). Magnetite exhibits a range of stoichiometry in Fe₃O₄ (variation from ratio of 3Fe/4O) at high temperature, while Wüstite’s stoichiometric range is so wide it’s considered a non-stoichiometric oxide (Fe_{1-x}O)¹. Perhaps variations in stoichiometry account for some of the non-explicable colors in iron oxide-based glazes.

Much of what is known today about the science behind the reduction of ceramic oxides was developed during the iron and steel-making expansion of the 20th century. Strong reducing furnace environments ensured efficient smelting of oxide ores to produce molten metals that, with further heat treatment and alloying, were processed into different grades of industrial iron and steel. The Ellingham Diagram² was developed to describe the redox behavior of metal oxides during smelting in metallurgical processes. It shows the oxygen partial pressure

Metal Oxides and Chemical Formula	Potters purchase as	Metal atomic no. – chemical formula	Other forms available
V ₂ O ₅	Vanadium Pentoxide	Vanadium (23) V	
Cr ₂ O ₃ ¹	Chrome Oxide Green	Chromium (24) Cr	Pink Chrome Oxide ²
MnO ₂ ⁴	Manganese Dioxide	Manganese (25) Mn	Manganese Carbonate ³
Fe ₂ O ₃ / Fe ₃ O ₄	Red/Black Iron Oxide	Iron (26) Fe	Yellow Iron Oxide, Crocus Martic, Spanish Red
CoO	Cobalt Oxide	Cobalt (27) Co	Cobalt Carbonate ³
NiO	Nickel Oxide	Nickel (28) Ni	Nickel Carbonate ³
CuO/ Cu ₂ O	Black/Red Copper Oxide	Copper (29) Cu	Yellow Copper Oxide, Copper Carbonate ³
MoO ₃ ⁴	Molybdenum Trioxide	Molybdenum (4) Mo	Molybdenum Dioxide
1. Oxides with reduction curves outside the range of figures 1 and 3. 2 Potters should avoid using pink colored chromium trioxide (CrO3) and lead oxide due to their toxicity. 3 Carbonates (as well as sulfates, etc.) thermally decompose to oxides during firing. 4 Oxide thermal decomposition begins well below 700°C during firing (MnO₂ → Mn₂O₃, MoO₃ → MoO₂).			



Potter's Reduction Diagrams [are] designed to help potters gain better control over ceramic oxide redox reactions that affect color and texture in their clays and glazes.

Opposite:
Table 1.
List of metal oxides and associated metals represented in Figure 1.

Above:
Figure 1. Stability diagram for ceramic oxides – Log (PO₂) vs temperature. The area below the curve for a specific oxide reaction represents the stable region for this oxide (the reaction goes as indicated by the arrow). The area above the curve represents the unstable region (the reaction goes in the opposite direction, indicating a reduction of the oxide to a lower form or the metallic element).

(the portion of gas in the kiln which is oxygen (O₂) gas) and the temperature under which an oxide becomes unstable and begins to reduce to a lower form of the oxide (e.g. red Fe₂O₃ reducing to black Fe₃O₄), or to its elemental form (e.g. Cu₂O to Cu). A description of how these diagrams are constructed can be found in textbooks on the thermodynamics of materials³. Potters use oxygen probes to measure the oxygen partial pressure (PO₂) in a kiln. By cross-referencing PO₂ values with the curves in the Ellingham diagram, one can predict what oxides are being reduced during the firing process. The **Potter's Reduction Diagrams** that follow are aimed at simplifying the effort to make this connection.

Figure 1 shows the stability regions for common ceramic oxides of most interest to potters. Because oxygen partial pressures are very low during reduction, they are reported as log (PO₂). Data from the JANAF-NIST tables⁴ were used to generate these curves unless a different reference (e.g. refs.5-7) is indicated.

Table 1 lists the chemical formulae for ceramic oxides in Figure 1, along with the names under which they are sold to potters. Additional details about materials shown in this table can be found on the Digitalfire Corporation website⁸. Each curve in Figure 1 represents the boundary conditions of temperature and log (PO₂) between the stability region of the indicated oxide (the area below the curve) and the instability region where the oxide begins to reduce (the area above the curve). This transition accounts for the dramatic shifts in the color and texture seen in a wide range of glazes fired in reduction. For example, a kiln fired to point A in Fig. 1, which lies below the curve for 4Cu + O₂ → 2Cu₂O (the stable region for Cu₂O) results in a glaze containing Cu₂O (or CuO if allowed to re-oxidize before the glaze sealed over), producing a glaze color ranging from violet to green. A kiln fired to point B, which lies above the curve and represents the unstable region, results in a glaze containing metallic Cu, which can produce a bright red glaze.

Figure 2 shows all three of these colors in a glaze containing 1% copper carbonate and fired to cone 8 during the test firing of an oxidation kiln converted to a gas kiln⁹. This test tile demonstrates the variety of colors originating from the incorporation of Cu, Cu₂O and CuO into the glaze during the haphazard reduction cycles of this test firing.

At the high temperatures of pottery firing, these redox reactions occur rather rapidly. The consensus on the time required for the kiln a) to equilibrate after a change from oxidation to reduction and b) to complete the reduction reactions of un-sintered clay and/or fine oxide powders in the glaze, is approximately 1 hour. Larger kilns may require additional time. The reduction cycles will depend upon the sintering^{*} characteristics of the clay and glazes used. For stoneware and porcelain clays, it is common to begin the initial reduction stage once the kiln reaches around 900°C or ~cone 010.

The base glaze chemistry has a strong impact on the glaze color. The particle size of the colorant can influence the glaze texture if the colorant is incompletely solubilized during firing. An extensive range of colors is possible by mixing several oxides together¹⁰. Things get even more interesting when reduction stages are introduced. Copper particles of different sizes (formed by nucleation and growth after the glaze seals over) are thought to be responsible for the sought-after *sangre de boeuf* color.¹¹ For this to happen, copper oxide would first need to be reduced to metallic Cu (e.g. point B in Fig 1 for ~1 hour), then the furnace heated in reduction (to prevent re-oxidation of the Cu to Cu₂O or CuO) until the glaze seals over. Some studies have reported the presence of Cu₂O in ancient red copper glazes and proposed Cu₂O as an important component in their color development. Others have reported that charge transfer between O and Cu in Cu₂O particles, rather than metallic copper, is responsible for the red color¹². For potters interested in further exploration, I would recommend experimenting with firing conditions in the stability region for Cu₂O, which is the area between the two curves labeled $4\text{Cu} + \text{O}_2 \rightarrow 2\text{Cu}_2\text{O}$ and $2\text{Cu}_2\text{O} + \text{O}_2 \rightarrow 2\text{CuO}$.

Figure 3 represents the same boundary conditions between the stable and unstable regions of the oxide, this time as a function of the potter's oxygen probe values (mV) and temperature. This diagram allows potters to determine which oxides will become unstable and undergo reduction for any specific reduction firing profile. In the case of red copper reduction glazes described above, an oxygen probe value above the $(4\text{Cu} + \text{O}_2 \rightarrow 2\text{Cu}_2\text{O})$ curve (~ 500mV) will cause the copper oxide to reduce to pure Cu metal. There are two curves that pertain to Fe₂O₃. Curve ① refers to Fe₂O₃ formed from the elements (Fe and O), and curve ② represents Fe₂O₃ formed from the oxide (Fe₃O₄). Both are correct, but curve ② is more relevant to potters since it occurs well before curve ① during a reduction stage. The curve for formation of Fe₃O₄ from the elements is not included in Figure 1, but it would lie slightly above curve ①. For potters, curve ③ (Fe₃O₄ formed from the oxide FeO) is of greater interest, for this same reason. A range of colors and textures available from firing an iron containing glaze in reduction can be seen in Figure 4.

While oxygen probes are a dependable tool for firing in gas kilns, there can be a problem using them in wood kilns. The ash produced in wood firing kilns contains sticky bits of alkali carbonate that attach to the probe, causing a dry ash buildup over multiple firings that can interfere with the sensor performance, resulting in inaccurate PO₂ readings.

Potters create reducing environments by

Below:

Figure 2. This test tile exhibits a color range associated with Cu, Cu₂O and CuO in a clear glaze containing 1% copper carbonate fired to cone 8 with reduction. This was the first test firing of a kiln converted from electric to gas so the reduction stages were rather haphazard but included "heavy reduction" for short periods of time.

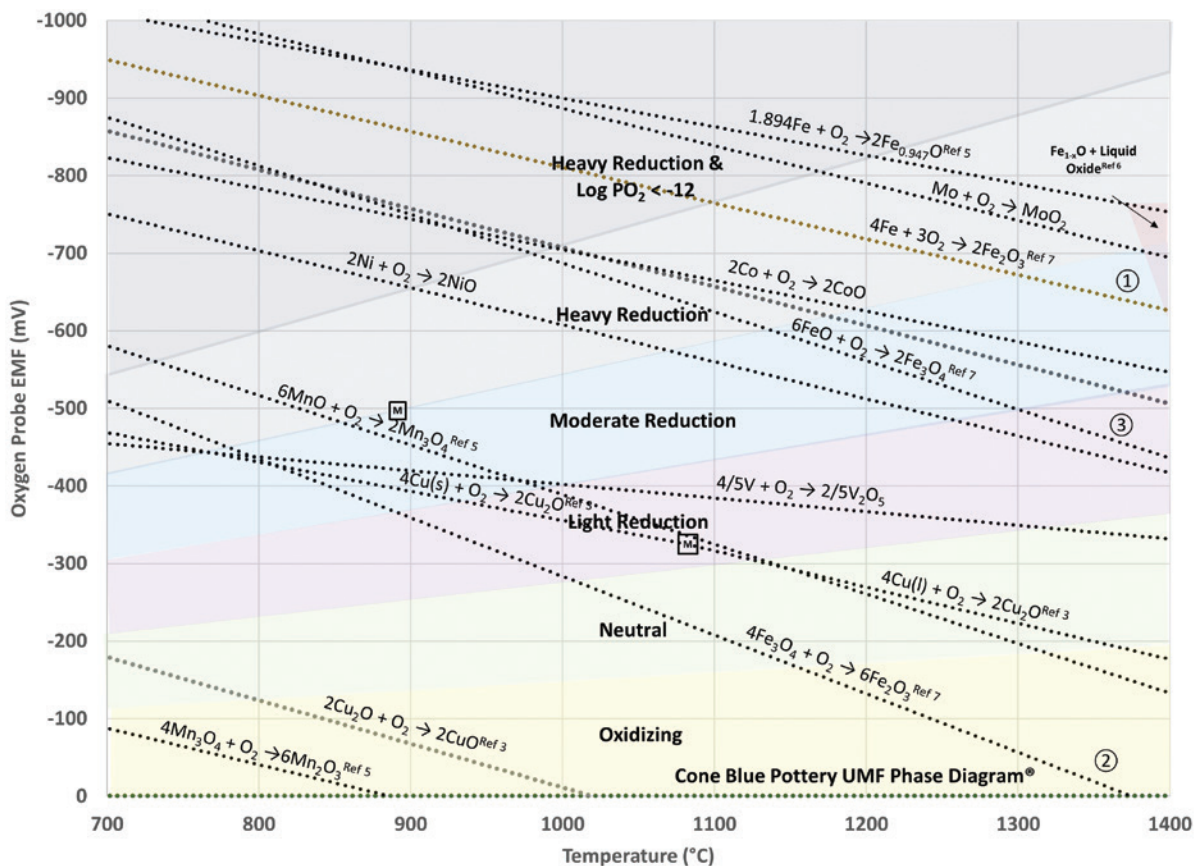
^{*} Sintering is the science of shape change, particle rearrangement, surface area reduction and densification in powder compacts at elevated temperatures. Details of different sintering mechanisms that apply to clay and glazes can be found in chapter 10 of reference 1.



Right:
Figure 4. Saturated iron red glaze on porcelain clay fired to cone 10 with reduction cycles, made by the author's father (William P. Sawhill) in 1982. Yellow ochre (a high iron clay) was used as the base glaze colorant, the bottom two inches received a black iron oxide wash and a red iron oxide containing overspray was used.



Below:
Figure 3. Stability diagram for ceramic oxides – oxygen probe readings (mV) vs temperature. The area below the curve for a specific oxide reaction represents the stable region for this oxide (the reaction goes as indicated by the arrow). The area above the curve represents the unstable region (the reaction goes in the opposite direction indicating a reduction of the oxide to a lower form or the metallic element). Probe reading will show positive numbers.



increasing the fuel/air ratio entering their kilns. The color of the flame exiting the burner reflects whether the ratio is producing an oxidative (blue) or reducing (yellow) flame. There are several ways to adjust the fuel/air ratio, based largely on the fuel and burner type. Venturi burners utilize a pressure drop inside the burner to draw in primary air for combustion. A chimney establishes a draft to pull in secondary air for complete combustion. The operation of a variety of different burners can be found in books on kiln building¹³. A common approach for establishing a reducing environment is to slowly close the damper. This reduces the draft and therefore the secondary air, increasing the fuel/air ratio. Pushing in the damper creates back pressure (positive pressure in the kiln versus the outside air), preventing air from entering through any cracks in the kiln. The result is a more uniform reduction atmosphere throughout the kiln, and therefore more stable oxygen probe readings. The presence of a flame exiting the spy holes is a sure indication of positive pressure and a reduction environment inside the kiln¹⁴. Kiln firing literature is full of tips on optimizing firing efficiency during reduction and oxidation cycles^{15, 16}.

the stoichiometric Fuel/Air ratio, $[\phi = [F/A]/[F/A]_{\text{stoich}}]$. For propane, the stoichiometric ratio is 1/23.86 on a volume basis (1 cubic ft propane/23.86 cubic ft Air). For example, a ϕ value of 1.25 represents a 20% reduction of air input ($0.8 \times 23.86 = 19.08$), thus ($\phi = [1/19.08]/[1/23.86]_{\text{stoich}} = 1.25$).

Figure 5 shows the different kiln environments resulting from changes in the Fuel/ Air ratio for a propane gas kiln. The flammability range for propane lies between the two blue lines ($\phi = 0.51$ and $\phi = 2.83$)¹⁷. The area above the green line represents the limit of the reaction $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$ before the gas becomes unstable and begins to precipitate solid carbon, resulting in smoke and soot. The curves for different equivalence values of propane/air were calculated using the water-gas shift reaction equations¹⁷ combined with the principles of simultaneous equilibria⁷ and $\text{CO}/\text{CO}_2/\text{PO}_2$ equilibrium equations³. The curves for methane $[F/A_{\text{stoich}} = 9.52]$ and natural gas $[F/A_{\text{stoich}} \sim 10]$ are similar but slightly shifted downward compared to propane. Firing a propane kiln with fuel/gas equivalence (ϕ) value 1.11 (10% less air than the stoichiometric ratio) will establish reduction conditions heavy enough to reduce

Figure 5. Kiln environments for different values of the fuel/air equivalence ratios ϕ for propane gas. Neutral environments describe the region near the stoichiometric ratio for propane where there is just enough air for the fuel to completely burn.

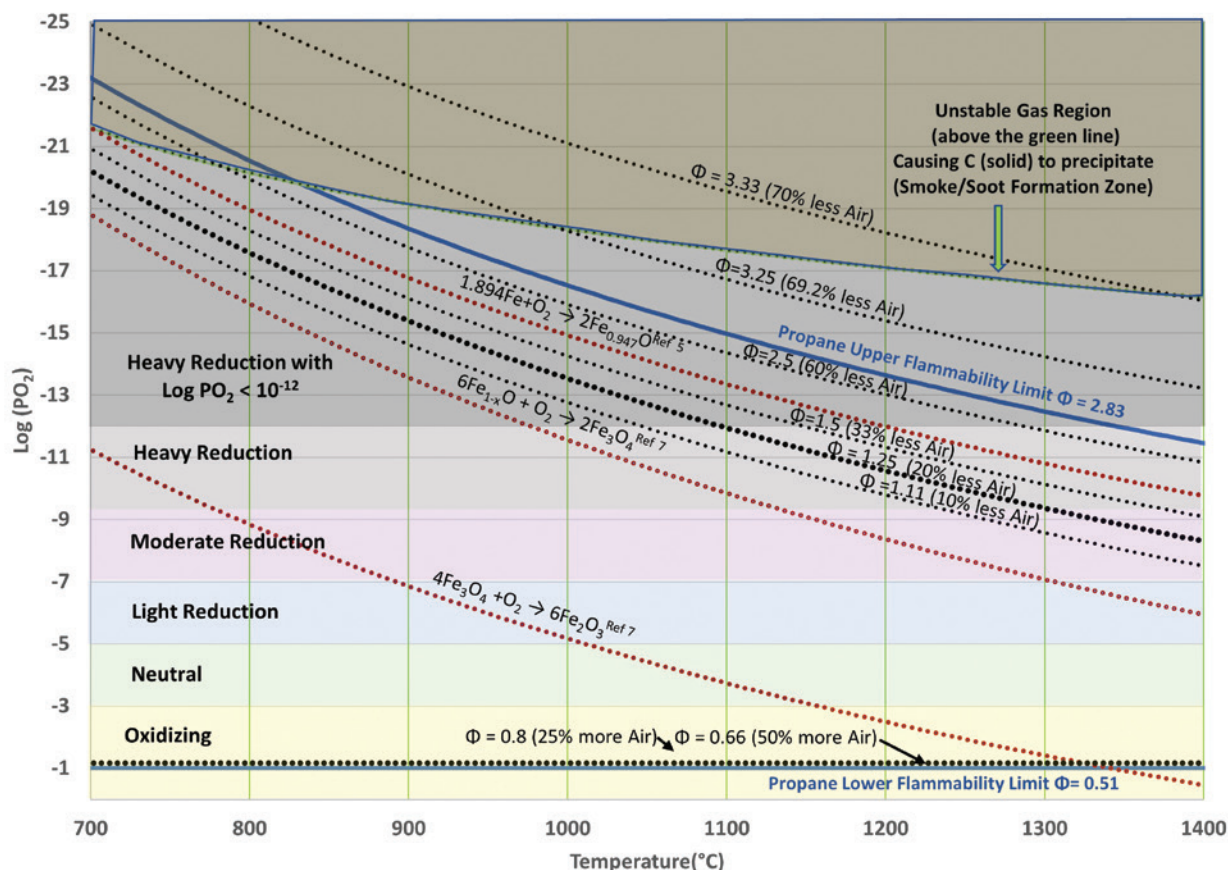
While oxygen probes are a dependable tool for firing in gas kilns, there can be a problem using them in wood kilns.

Alternatively, the gas flow can be increased or the primary air can be reduced by lowering the blower speed or air-supply line pressure. For wood burning kilns, blocking off the entrance to the firebox, closing ports, or slowly closing the damper are all techniques to reduce the amount of air available for combustion in order to create a reducing environment.

In Figures 1 and 3, “oxidizing”, “neutral” or “light/moderate/heavy reduction” are terms used to describe the different firing environments. Neutral environments describe the region where there is just enough air for the fuel to burn completely – a condition referred to as the stoichiometric ratio $(F/A)_{\text{stoich}}$. Excess fuel (fuel rich) and excess air (fuel lean) conditions lead to reducing and oxidizing environments respectively. These conditions are described using an equivalence ratio ϕ , defined as the ratio of Fuel/Air in the kiln divided by

Fe_2O_3 (red) to Fe_3O_4 (black) without reducing the oxides to pure iron. For oxidation conditions, ϕ values of 0.66 (50% more air) result in a 6.7% excess of oxygen in the kiln – more than sufficient to ensure complete burnout of clay and glaze organic matter and break down sulfide and other non-oxide compounds during the early stages of firing before the initial reduction stage.

The unpredictable nature of glaze color and texture in reducing environments is one of its charms – but sometimes it’s nice to have a bit more control, especially in cases where replicating the effects is desired. I hope that the “Potter’s Reduction Diagrams” presented in this article will help potters achieve better replication of past successes, while inspiring them to explore new possibilities of reduction colors and textures. ■



About the Author

After graduating from MIT with a PhD in Ceramics, Howard Sawhill worked 30 years with DuPont Electronics where he led research and development teams that introduced new ceramic-based products into the marketplace. In his second career, he started Cone Blue Pottery where the mainstay is research and development of ceramic glazes. He is currently working in collaboration with potters on challenging glaze issues and performing glaze studies aimed at improving the understanding of glaze performance.

Further Information

Examples of glaze research and development studies, collaborations, videos and his contact information can be found on the website www.conebluepottery.com.

Potter's Reduction Diagrams ©
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Cone Blue Pottery UMF Phase
Diagrams ®
Cone Blue Pottery, 2019.

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Endnotes

1. Barsoum, M.W., *Fundamentals of Ceramics*. McGraw-Hill series in materials science and engineering. 1997, New York: McGraw Hill. pp. 175-179 and p.136.
2. Ellingham, H.J.T.; Available from: http://web.mit.edu/2.813/www/readings/Ellingham_diagrams.pdf
3. Gaskell, D.R., *Introduction to the Thermodynamics of Materials*. 3rd ed. 1995, Washington, D.C.: Taylor & Francis. pp. 356-369.
4. JANAF-NIST. Available from: <https://janaf.nist.gov>.
5. Turkdogan, E.T., *Physical Chemistry of High Temperature Technology*. 1980, New York: Academic Press. pp. 5-24.
6. Darken, L.S. and R.W. Gurry, "The System Iron - Oxygen. II. Equilibrium and Thermodynamics of Liquid Oxide and Other Phases". *Journal of the American Chemical Society*, 1946. pp. 798-816.
7. Fegley, B. and R. Osborne, *Practical Chemical Thermodynamics for Geoscientists*. 2013, Waltham, MA: Academic Press. pp. 458-459.
8. Material. Available from: <https://digitalfire.com>.
9. YouTube Video "Converting an Electric Kiln to Gas". Available from: www.ConeBluePottery.com.
10. Chappell, J., *The Potter's Complete Book of Clay and Glazes*. Rev. ed. 1991, New York: Watson-Guption Publications. pp. 385-395.
11. Cuvelier, P.A., et al., Copper Red Glazes: a Coating with Two Families of Particles. *Applied Physics A*, 2012. 106(4). pp. 915-929.
12. Nassau, K., *The Physics and Chemistry of Color: the Fifteen Causes of Color*. Wiley series in pure and applied optics, 1983, New York: Wiley. p. 311.
13. Olsen, F.L., *The Kiln Book: Materials, Specifications, and Construction*. 2nd ed. 1983, Radnor, Pa.: Chilton Book Co. p. 192-216.
14. Finkelburg, D., Kiln Atmosphere. *Ceramics Monthly*, 2019(December). pp. 56-57.
15. Frenzel, H., Striving for Perfection: Energy Efficiency and Perfect Combustion. *Ceramics Monthly*, 2007(December). pp. 37-39.
16. Colson, F.A., *Kiln Building with Space-age Materials*. 1975, New York: Van Nostrand Reinhold.
17. Turns, S.R., *An Introduction to Combustion: Concepts and Applications*. 2nd ed. McGraw-Hill series in mechanical engineering. 2000, Boston: WCB/McGraw-Hill. p. 287.