Developing a Gas Kiln Reduction Profile

By Howard Sawhill

A common problem potters face in firing gas kilns in reduction is variability of glaze results depending on where the pieces were placed in the kiln. This results from non-uniform reduction conditions in the kiln during firing. A good way to picture the variability of reduction in your kiln is to generate a kiln reduction profile. In this article, I describe the development of a reduction profile of a Geil DL-12F gas kiln[1] using three different glazes, each color-sensitive to the level of reduction during different temperature stages of the firing. Full recipes[2] of these three glazes can be found in John Britt's book, "The Complete Guide to High-Fire Glazes"[1]. Selected details of the three glazes are shown as follows in Table 1.

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[1] Owned by Susan Filley

[2] Minspar was substituted for F4 Feldspar since it is no longer available from suppliers. EPK was the choice of Kaolin, and OM-4 was the choice for the ball clay in this same recipe.

Glaze Name	Glaze Colorants	Major Glaze Ingredients (in addition to clay and silica)	Specific Gravity
Malcolm's Carbon-Trap Shino	Iron Oxide component of Red Art Clay	Nepheline Syenite, Minspar & Soda Ash	1.25
Jeff's Flambé Red	Copper Carbonate and Tin Oxide	Custer Feldspar & Gerstley Borate	1.50
Pinnell's Blue Celadon	Yellow Iron Oxide	Custer Feldspar & Calcium Carbonate	1.60

Table 1: Properties of the three selected glazes.

Fabrication and Firing of Test Tiles: Test tiles using Standard Ceramic Supply Company Porcelain 257 clay were made by extrusion and then bisque fired to cone 05 and single dipped 4 seconds into the glaze. A set of the 3 individually glazed test tiles was placed on 8 different shelves. An oxygen sensor (Econox -HT) was located near the bottom of the flue below the damper. The Geil kiln was fired using a ~ 10-hour profile (from start to peak temperature at cone 10 / 11) with reduction starting around cone 011. Test tiles of all three glazes were fired separately in oxidation to cone 10 in an L&L JD-18X-3 kiln using the slow glaze firing cycle (8 hours from start to peak temperature). All reduction fired test tiles were refired in oxidation to cone 11 in an LDL JD-18X-3 using a fast bisque profile (8 hours from start to peak).

The Reduction Process: The kiln atmosphere (oxidation vs. reduction) is determined by the ratio of gas to air entering the kiln. The burner and damper settings determine the amount of air entering the gas kiln during firing. Highly reactive carbon monoxide (CO) is produced inside the kiln when the propane (or other fuel) lacks sufficient oxygen for complete combustion[3]. It is the reaction of CO with the transition metal oxides (used as colorants in the glaze) that causes their reduction and is responsible for subsequent color changes in the fired glaze. In this reaction an oxygen atom is transferred from the transition metal oxide to CO, thereby reducing the valence of the transition metal and converting CO to CO_2. An example is the reduction of iron oxide: $6Fe_2O_3 + 2CO \rightarrow 4F_3O_4 + 2CO_2$. In highly reducing environments when the gas/air mixture becomes sufficiently rich,[4] soot (carbon black) is produced.

Results of Malcolm's Carbon Trap Shino glaze: This glaze is the first of the three glazes to begin melting during firing. This is due to the large percentage of soda ash which begins to decompose to sodium oxide and carbon dioxide at its melting point of 851°C (~cone 013) --slightly below the onset of reduction around cone 011. Two factors make the resulting colors of this glaze sensitive to when the reduction is started relative to the melting point of soda ash: 1) Soda ash is water soluble and floats to the top of the glaze during drying, putting it in direct contact with the flame, and 2) Sodium oxide begins to vaporize to form sodium gas as the kiln heats to higher temperatures. Results of test tiles fired in oxidation and reduction are shown in Figure 1. The presence of carbon black during heavy reduction increases the decomposition rate of soda ash and adds sodium gas to the reaction products[3]. The

[3] Air contains ~ 21% oxygen by volume.
[4] At cone 011 this translates to a condition where only ~35% of the air necessary for complete combustion of unreacted propane in the kiln is present.

sodium oxide acts as a strong flux, causing carbon black to get trapped at the surface (note the dark areas on the tile to the right). The sodium gas carries iron-containing reaction products and redistributes them nearby (note the bright orange coloration below the glaze line). Uneven reduction results in less carbon trapping and a smaller amount of redistributed reaction material. No carbon black is produced in the oxidation kiln, so neither of these effects occur. The presence of the flame path in the gas kiln is pronounced with this glaze. Refiring the tile on the right to cone 11 in oxidation produces a tile similar to the middle tile.

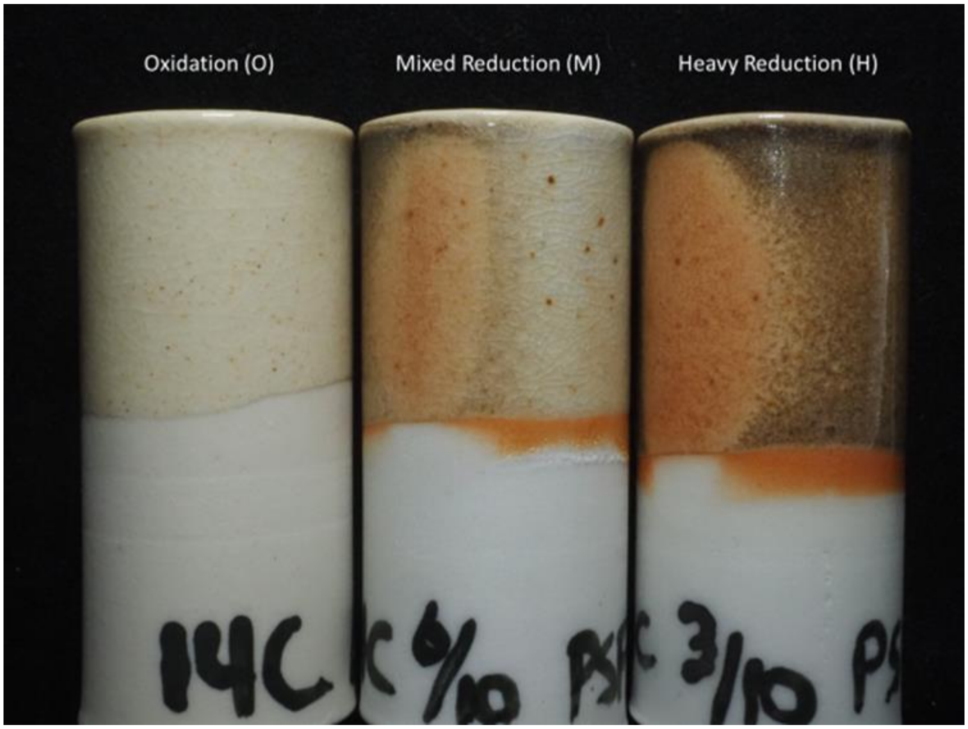

Figure 1: Fired results of Malcolm's Carbon Trap Shino glaze. O=Oxidation, M=Mixed (Uneven) Reduction, H=Heavy Reduction

Results of Jeff's Red Flambé glaze: The next of the three glazes to react during firing is Jeff's Red Flambé glaze. The Gerstley borate content and low alumina levels lower the maturation temperature of this glaze. Test tiles fired under oxidation and reduction conditions are shown in figure 2. The red color in this glaze originates from small amounts of copper carbonate and tin oxide in the glaze. The brightness of this color was originally thought to result from the scattering of colloidal metal (Cu) precipitates forming in the glass during reduction firing. More recently, it's been reported to result from a charge transfer mechanism between $O^{-2}$and Cu^{+1}in cuprous oxide (Cu_2O)[4]. Higher levels of copper carbonate additions to this glaze can shift the color significantly and introduce a degree of muddiness, suggesting that multiple color- generating mechanisms are likely present. In oxidation the glaze color is light green. Uneven reduction (M) shows evidence of both of these colors. Refiring the tile on the right in cone 11 oxidation produces a color mix similar to the tile in the middle, but with the additional light green areas in a 3/8-inch band around the top and protruding slightly through the red-colored area.

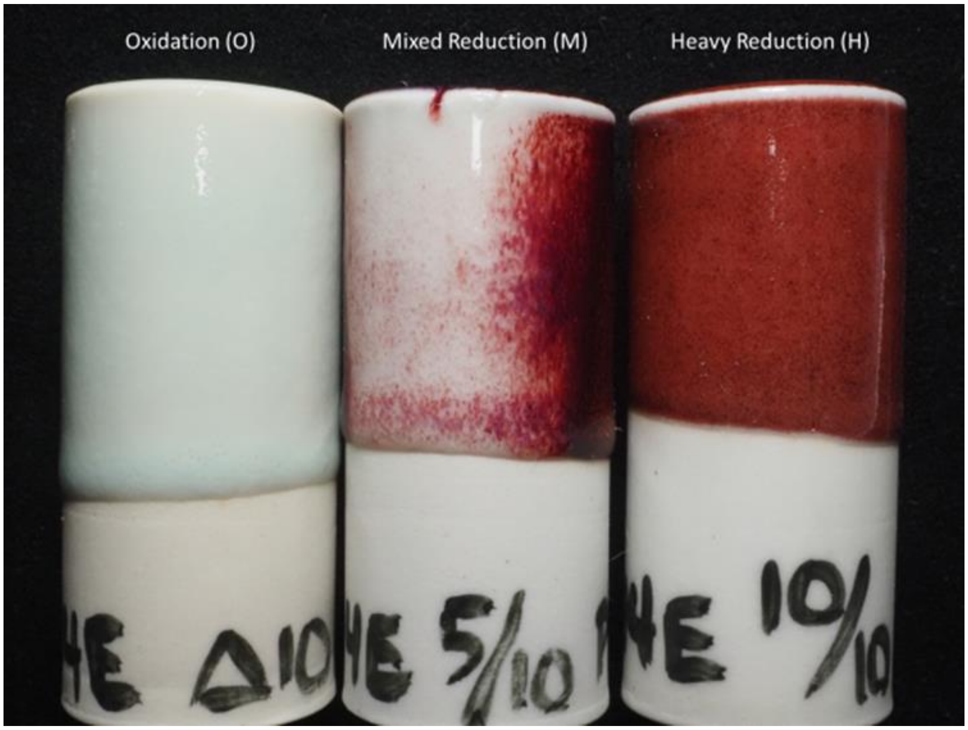

Figure 2: Results of Jeff's Red Flambé glaze. O=Oxidation, M=Mixed (Uneven) Reduction, H=Heavy Reduction

Results of Pennell's Blue Celadon glaze: This alkaline-earth feldspathic glaze has no alkali additions and is the last of these three glazes to mature. Test tiles fired in oxidation and reduction are shown in figure 3. The valence state of the iron dissolved in this celadon glaze determines the color. Small amounts of ferric iron (Fe^{+3}) in the glaze produce a pale yellow-green, while ferrous iron (Fe^{+2}) produces the blue- green color[4]. Hematite (Fe_2O_3) is the stable, ambient room temperature form of iron oxide. However, when exposed to high temperatures in air or moderate reduction conditions, it reduces to Magnetite (Fe_3O_4), which contains a mixture of valence states ($Fe^{+2}$and Fe^{+3})[2]. Upon stronger reduction, Wüstite (FeO containing Fe^{+2}) is formed, which is only stable at higher temperatures. FeO acts as a flux, causing Fe^{+2} to be incorporated into the glaze as a true solution[4]. The oxidized test tile (O) is pale yellow-green, while the heavily reduced glaze (H) exhibits a blue-green color. Uneven reduction (M) produces a color midway between these two. Refiring the test tile on the right to cone 11 in oxidation produces a slight color shift in the direction of the middle tile.

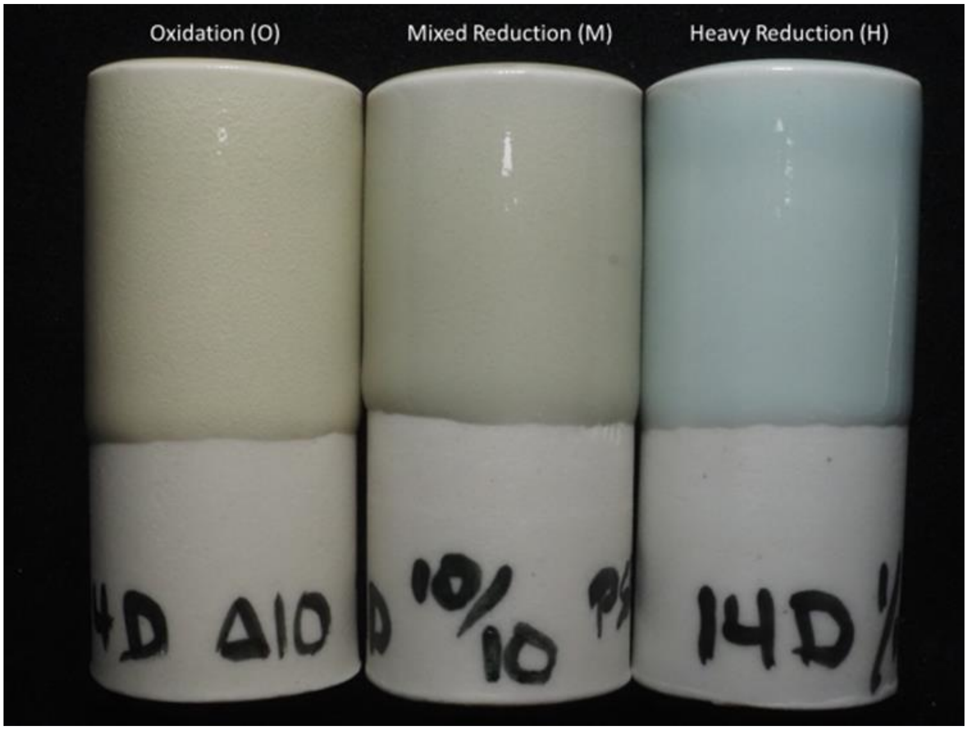

Figure 3: Results of Pinnell's Blue Celadon glaze. O=Oxidation, M=Mixed (Uneven) Reduction, H=Heavy Reduction

Behavior of the three glazes during firing: Each of these three glazes begins to mature and seal over at different temperature ranges in the firing. By cone 2, both Malcolm's Carbon Trap Shino and Jeff's Red Flambé have sealed over, but their surfaces are pitted, while Pennell's Blue Celadon remains dry with open and connected porosity. By cone 6, each glaze has sealed over, but none has completely matured. By cone 10, all three glazes have matured to yield smooth, glossy finishes. Reduction of the transition metal colorants must occur before the glaze has sealed over in order to yield the colors attributed to the reduced valence states. Once the glaze seals over, oxygen diffusion through the glaze becomes extremely slow and the colorants are effectively sealed in. After this point, converting to oxidation (even at somewhat higher temperatures) would re-oxidize only the part of the glaze nearest the top layer. This is borne out by the results for each of the three glazes after refiring in oxidation at cone 11 (similar to M/uneven reduction rather than O /Oxidation).

Kiln Reduction Profile: Results of test tiles of the three glazes fired in different locations throughout the kiln are shown in figure 4. The twelve shelves are represented by horizontal lines – six front kiln shelves on left, six back kiln shelves (near chimney) on right. The levels of reduction for each of the three glazes are noted in the following order: Shino, Flambé, Celadon. The firing produced a uniformly high level of reduction throughout the kiln, with the single exception of uneven reduction on the lowest back shelves close to the burners and the flue exit. The oxygen sensor readings showed a consistently high level of reduction[5] throughout the firing once the kiln was put in reduction.

[5] High reduction can be a subjective term. For this study, it refers specifically to the conditions under which Hematite (Fe_2O_3) is reduced to Wüstite (FeO). See Pennell's Blue Celadon glaze results.

Top of Kiln			Top of Kiln		
Front Left	**Front Center**	**Front Right**	**Back Left**	**Back Center**	**Back Right**
					H,H,H
		H,H,H			
	H,H,H				H,H,H
H,H,H		H,H,H	H,M,H		M,M,M
Bottom of Kiln			**Bottom of Kiln**		

Figure 4: Reduction profile of a Geil DL-12F Kiln firing. Firing results from different locations in the kiln are indicated in the following order: Shino, Flambé, Celadon. O=Oxidation, M=Mixed (Uneven) Reduction, H=Heavy Reduction

It's worth noting that a consistent, high level of reduction throughout the kiln is not necessarily what every potter is aiming to achieve. Also, happy accidents have been the consolation of many a poor firing. For potters aiming for improved consistency in their gas kiln reduction firings[6], I hope this study provides a useful starting point.

Acknowledgements: I would like to thank Susan Filley for her suggestions and helpful discussions during this project. Her pottery and unique glazes can be seen at www.susanfilley.com. Thanks also to John Britt for his recommendation of the three glazes used in this project. His work and his many publications on ceramic glazes can be found at www.johnbrittpottery.com.

References:

[6] A discussion of all the possible steps to reduce areas of uneven reduction is beyond the scope of this article. However, they generally involve adjustments of gas pressure, burner settings, damper positions, and kiln packing.

1. Britt, J., *The Complete Guide to High-Fire Glazes*. 2007: Lark ISBN 978-1-60059-216-4.
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3. Kim, J., Lee, HG., *Thermal and carbothermic decomposition of Na2CO3 and Li2CO3.* Metall Mater Trans B, 2001. **32**: p. 17-24.
4. Nassau, K., *The physics and chemistry of color : the fifteen causes of color* 1983, New York: Wiley.308-311, ISBN 0471867764

About the Author:

After graduating from M.I.T. with a Ph.D. in Ceramics, Howard Sawhill worked for 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, whose mainstay is research and development of ceramic glazes. He currently collaborates with potters on challenging glaze issues and performs glaze studies designed to improve the understanding of glaze behavior. Examples of his glaze research, collaborations, and videos, along with contact information, can be found at www.ConeBluePottery.com.