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**Ceramic Materials Workshop**

**Glossed Over: Durable Glazes**

**NCECA 2016: Kansas City**

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Understanding what makes ceramics durable in the kitchen is one of the most important responsibilities of the potter. If the chemistry is not rugged, food interacts with the glaze surface and absorbs material from the glaze. This concern is compounded by the popularity in firing temperatures under cone 10, which often accommodates temperature without addressing durability.  Through research and experimentation, a method to predict glaze durability performance through Unity Molecular Formula analysis has been developed, which helps artists understand their glazes and provides confidence in their quality.

In the past, the ceramics community was concerned with potentially poisoning users from materials such as lead and cadmium. These materials have been removed from the palette of the common potter, but many ceramicists are still concerned with glaze durability. A poorly made glaze is perilous, as it may appear fine to the naked eye or with simple tests, but can still be soluble in common acids and bases. Whereas a well-designed glaze is safe and in fact one of the most durable man-made materials.

Glazes have two common enemies, pH and water. pH refers to the alkalinity or acidity of a materials. Water is often referred to as “The great solvent” as with enough time it will dissolve almost anything. The alkaline soaps we use are exceptionally caustic and destructive to poor quality glazes. Soap and hot, sprayed water come together in the dishwasher to make a destructive pairing. Yet acid, generally in the form of vinegar (acetic acid) or lemon juice (citric acid) is what most ceramicists fear. The lemon test is a common way to test glaze durability; you place a slice of lemon on a piece of glazed ware overnight and see if it changes the color and finish of the ware.

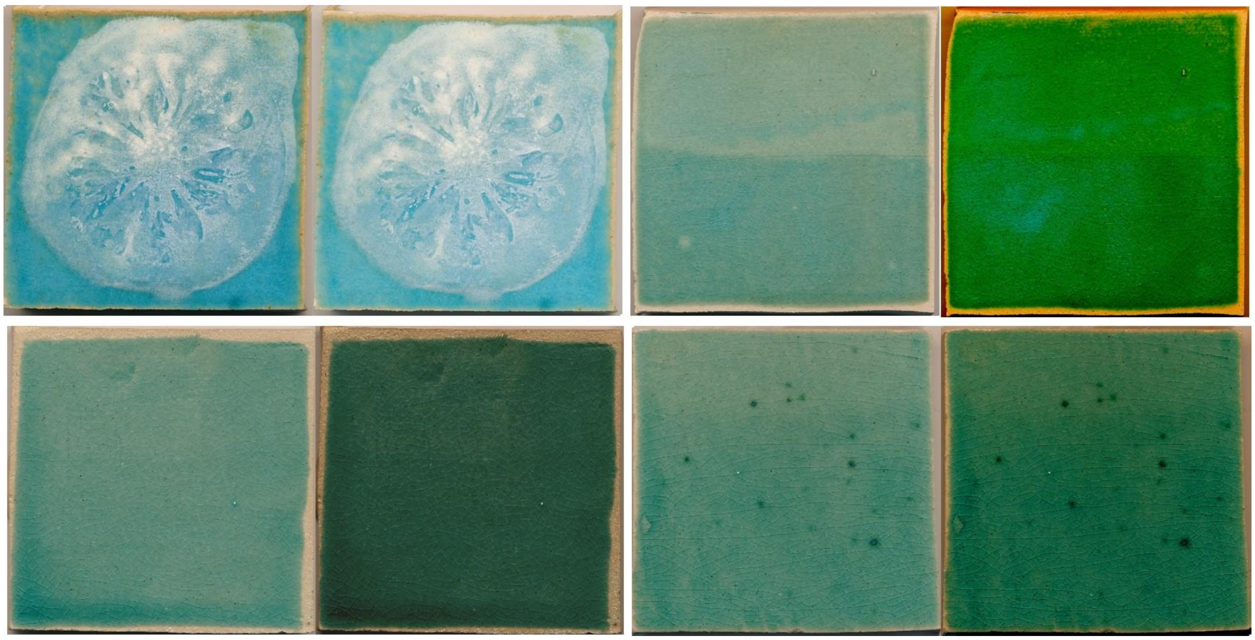

*Figure 1. Above is an image of various non-durable cone 04 glazes exposed to the lemon test. On the left of each pair are the original samples, post-test. On the right are the same samples, with the color and saturation adjusted to make the acid etching more visible.*

The lemon test is not conclusive because naked-eye observations are subjective. The lemon test identifies only the poorest of glazes. The danger is in glazes that pass (or appear to pass) the lemon test but fail in common real-world conditions.

Many believe that a glossy glaze is safe, but this is not the case. Glossy glazes are just as susceptible to degradation as matte, but are harder to see with the naked eye. Figure 1 shows several glazes subjected to the lemon test. Some of the glazes failed obviously, some failed in a subtle way, and some appear to have passed. All these samples failed the Unity Molecular

Formula (U.M.F.) testing described below, which means they will fail in actual use. Basic understanding of glaze chemistry is a much more powerful and effective tool than visual observation.

The U.M.F. not only allows us to understand important concepts like matte, gloss, and many types of glaze flaws, but also lets us specify firing temperature. Arguably, the U.M.F. allows us assess the potential durability of glazes simply from an analysis of the formula, long before glaze ever meets food.

**The Background.**

This research is a continuation of work documented in the 2012 NCECA Journal[i], wherein glaze durability was examined in cone 10 and cone 6 glazes. Previous work by R.T. Stull[ii], continued by W. Carty, B. Quinlan[iii], and myself[iv], show that glazes with a 7:1 $SiO_2$: $Al_2O_3$ ratio and a flux ratio of 0.3 $R_2O$:0.7 RO will be glossy. The 2012 work determined that a 0.3 $R_2O$:07 RO flux ratio provides a solid durability footing at either temperature, although at cone 6 a supplement of boron is required for acceptable performance**.** It also demonstrated that increasing $R_2O$ amounts from the standard flux ratio (0.3 $R_2O$:0.7 RO) results in lower temperature melting than cone 10 – but also results in a glossy but chemically weak glaze. The tests explored here examine the role of fluxes and boron as applied to cone 04 glazes to determine how various glaze compositions withstand regular use.

We can use boron, altered flux ratios and/or reduced glass former volume to lower effective melt temperature. Examining existing cone 04 formulas may lead one to believe that a high $R_2O$ level is primarily what is needed to melt at cone 04. In fact, except for certain special circumstances, it is the boron supplement that is required to achieve melt for most low temperature glazes. The question then becomes, do the glaze strengthening properties of boron overcome the weakening caused by the overabundance of alkaline metal fluxes or reduced glass formers?

**The Experiment.**

| Map | | Boron | | | | | |
|---|---|---|---|---|---|---|---|
| $R_2O$ | RO | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 | 0.55 |
| 0.85 | 0.15 | ● | * | * | * | * | * |
| 0.7 | 0.3 | - | ● | ● | ● | ● | x |
| 0.5 | 0.5 | - | ● | ● | ● | ● | x |
| 0.3 | 0.7 | - | - | ● | ● | ● | ● |
| 0.1 | 0.9 | - | - | ● | ● | ● | x |

*Table 1: Test Map. Samples marked with a dot (●) were tested, blue dots were best quality samples. Stars (*) were chemically impossible to compose. Dashes (-) were generated, but abandoned as they failed to reach a sufficient melt. Samples marked with an (x) were consider redundant and not created.*

The grid of glaze formulas in Table 1 represent 0.1 (U.M.F) ascending amounts of boron, contrasted with various flux ratios of 0.85 $R_2O$:0.15 RO, 0.7 $R_2O$:0.3 RO, 0.5 $R_2O$: 0.5 RO, 0.3 $R_2O$: 0.7 RO, and 0.1 $R_2O$: 0.9 RO, Each test has a set silica level of 2.1 and an alumina level of 0.3, for a 7:1 Si:Al ratio. The sample marked with a large blue circle is the established standard rugged cone 04 glaze, composed of 90% Frit 3124 10% EPK. This glaze has long been known to be one of, if not the best performing cone 04 gloss glaze with 2.8 $SiO_2$, 0.38 $Al_2O_3$ for a ratio of 7.46:1.

The samples were batched with EPK, Nepheline Syenite, Whiting, Soda Ash, Flint, Frit 3124, Gerstley Borate and Cadycal. Samples were applied by spray except in situations where the Soda Ash content was too high, which clogged the spray gun (those samples were brushed). Samples were applied to 5x5” flat, bisque tiles composed of Higby’s low fire white body and fired to cone 04.

After firing, samples were tested with a glossmeter (M&A Instruments-ETB-0833), to determine the quality of the glaze’s natural finish. Measurements were made at 20°, 60°, and 85° in each corner of the tile as well as the center. The highest and lowest readings from each sample was recorded. The samples were then run through a dishwasher (Frigidaire FPHD2491KFO) on the “Power Plus-Hi Temp Wash” setting for 64 cycles with one “Finish Powerball All in 1” detergent tablet per cycle. Samples positions were changed randomly every five wash cycles. Glossmeter readings were taken at 1, 2, 4, 8, 16, 32, 50, and 64 cycles. The change in gloss was then calculated by the percent of degradation from the initial unwashed samples to 64 wash cycle samples.

**The Results**

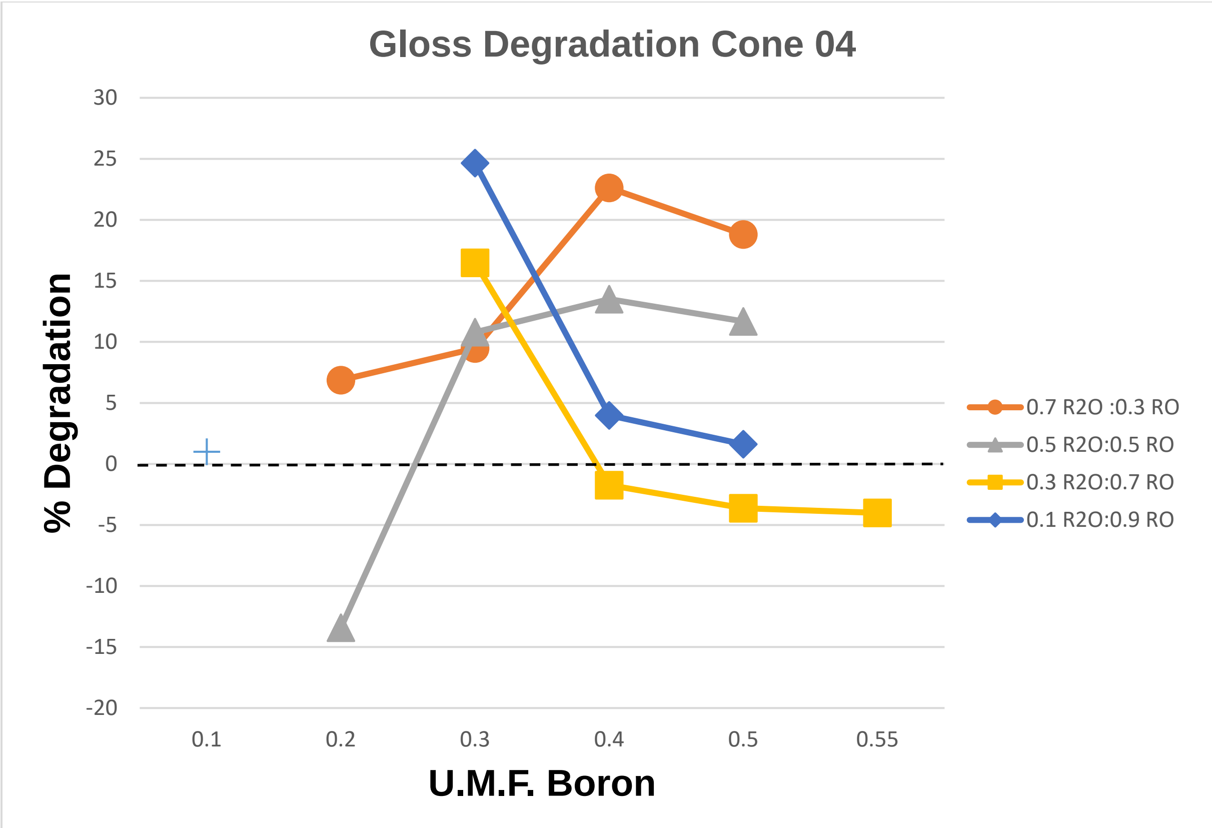


*Figure 2. Documenting the washed degradation of several glazes based on boron and flux variation.*

Table 1 indicates that a boron level of 0.3 is the absolute lower limit for a sufficiently glossy glaze, (having an initial gloss meter average over 45). This applies only to the 0.5 $R_2O$: 0.5 RO flux ratio. At lower levels, $R_2O$ alone provided insufficient fluxing power at cone 04. The problem is that this particular glaze suffers from a gloss degradation of 10.79% after 64 cycles. In fact all glazes tested with a 0.5 $R_2O$: 0.5 RO flux ratio suffer from poor dishwasher performance as can be seen in Figure 2. The three 0.5 $R_2O$: 0.5 RO glazes in the acceptable gloss range, with boron content ranging from 0.3-0.5, have an average degradation of 11.99% after 64 cycles. All the 0.5 $R_2O$: 0.5 RO also failed to show substantial or any wear with the lemon test, as seen in the two lower sets in figure 1 (0.3 and 0.5 boron respectively) which suffered from 10.79% and 11.68% dishwasher degradation.

Thus a glaze may appear sufficiently glossy but not be of high physical quality. This confirms the result seen in the 2012 cone 6 glazes, in which 0.5 $R_2O$: 0.5 RO glazes have high quality results based on initial appearance and ability to melt at lower temperatures, but suffer in long-term durability. The addition of boron fortifies a glaze somewhat as they suffer less degradation than 0.5 $R_2O$:0.5 RO glazes without boron, fired to cone 6. Those glazes had an average degradation of 18.2%. Thus the quality of glazes is not dependent on any specific temperature for durability. Chemistry is the only relevant factor.

Additionally, it is possible to lower temperature by reducing total glass former volume, although this method also adversely effects glaze durability. Several glazes with 0.2 $Al_2O_3$ levels were tested and although they were glossier than their comparative glazes with 0.3 $Al_2O_3$, their degradation was 58.9% worse in the dishwasher than equivalent glazes with higher total glass former volume.

The best result in this series of testing is the 0.3 $R_2O$:07 RO series. These glazes are the best performers seen in any tests at any temperature. This series did not begin to mature into quality glazes until a 0.4 boron content was reached. Below that level, the glazes were still dry and under-fired.

With adequate boron content, these glazes had an average degradation of -2.82%. They actually became slightly glossier than their initial reading after 64 cycles. This negative value can be attributed to the dishwasher providing a post-firing cleaning. 0.3 $R_2O$:07 RO glazes at cone 04 are more durable than our best cone 10 glazes without boron, (2.8% degradation) or cone 6 with boron (1.7% degradation). Glazes with a 0.3 $R_2O$:0.7 RO flux ratio plus boron have a better average initial gloss (58.7) and no degradation. Compared to glazes with a 0.5 $R_2O$:0.5 RO ratio plus boron (48.9) and suffered from dishwasher degradation.

This series also produced a surprising result. Previous research into the relationships between fluxes, boron, and temperature showed that glaze with a 0.1 $R_2O$:0.9 RO flux ratio suffered from wash degradation. Yet in this series 0.1 $R_2O$:0.9 RO was surprisingly robust. The glazes themselves have an average baseline gloss of 68.8, higher even than 0.3 $R_2O$:0.7 RO. The degradation levels showed adequate performance, with an average of 2.8%. This value may be misleading since a boron level of 0.5 had only 1.62% degradation, while the 0.4 boron level was a still low at 3.98%. But the curve and slope of this series matches 0.3 $R_2O$:0.7 RO almost perfectly. This result will be explored in future research, along with the effects of altering the silica /alumina ratio and the role of colorants such as copper.

**The Conclusion**

This testing series displayed clear trends relating to composition and temperature; confirming and expanding the understandings determined in the 2012 experiments. The main conclusion is that the primary factor in glaze weakness is an overabundance of $R_2O$ fluxes. Glazes with the ideal flux ratio (0.3 $R_2O$:0.7 RO) perform exceptionally well. This ratio, when combined with boron to reduce the temperature from cone 10 glazes, performs with flying colors, displaying virtually no physical wear. Using the boron levels set in the 2012 research (roughly 0.15 for cone 6 and 0.5 for cone 04) we can generate chemically durable glazes at all relevant temperatures.

All in all this research confirms previous findings: 0.3 $R_2O$:0.7 RO is the ideal flux ratio for all functional glazes and provides a universal standard for all glazes at any temperature. Hopefully helping ceramicists view their glaze palette with confidence, knowing that the performance of their glazes is at the highest possible level, and their work is the best and safest it can be.

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[i] M. Katz, "Mid-Temperature Glazes"; *2012 NCECA Journal*. 58-60 (2012).

[ii] R. T. Stull, "Influences of Variable Silica and Alumina on Porcelain Glazes of Constant RO", *Transactions of the American Ceramic Society*, **XVI**, 62-70 (1914).

[iii] B. Quinlan, "The Unity Molecular Formula Approach to Glaze Development"; *M.S. Thesis. Alfred University, Alfred, NY,* (2002).

[iv] M. Katz, "New Understanding of Glaze Composition"; *2004 NCECA Journal*. 65-69 (2004).