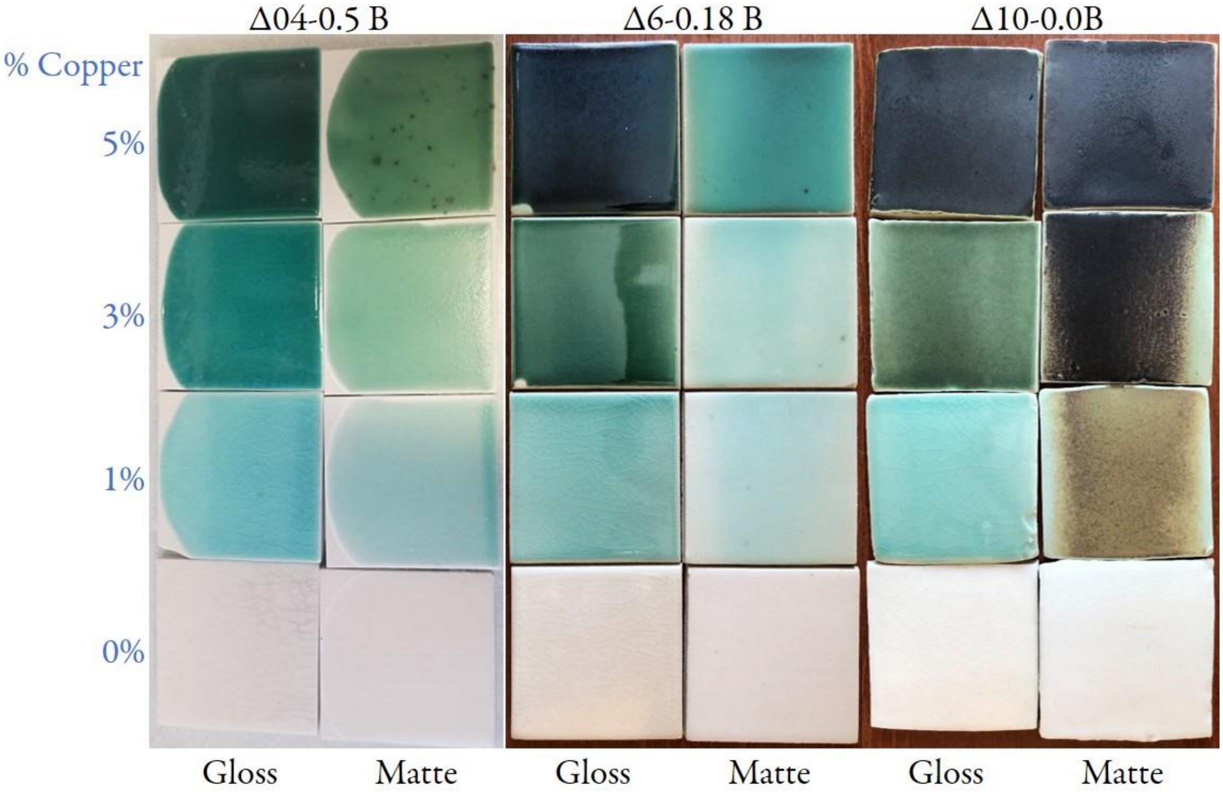
Copper Leaching and Glaze Durability

Peter Berg with Matthew Katz



The Introduction

The functional potter has to worry about issues of material toxicity in functional work. The interaction of glaze materials and food are always a concern, as everyone wants to make the safest work possible for their users. The most pressing concern is not the materials used in the glaze, but rather what material is potentially leached out from the glaze? Laboratory leach testing is the best possible answer, as it provides a definitive answer to potential toxicity of glazes. Many artists do not or cannot test, or use unreliable testing home methods to test their glazes, so the question becomes, what are the relevant concerns with glazes and toxicity? One material of common concern is copper. Most books, references, and conversations on the internet, declare that copper is a toxic material. We wanted to find out what is the role of copper in glaze toxicity and the health effects therein?

The most common studio test for glaze quality is the so called “lemon test”. A potter will place an acidic material, such as a lemon slice, vinegar, or tomato sauce on a glaze and leave it overnight to see if it makes any marked effect on the color, tone, or texture of the glaze. These tests suffer from an inherent flaw, which is the assumption that any glaze failure would be visibly obvious. This is a problem as glaze failure and potential toxicity exist on the microscopic level and cannot be detected by visual observation. This topic was address by Matthew Katz at NCECA 2016[i]. In that work, Katz showed that most glazes will fail tests for glaze durability, with no visual evidence of failure.

Katz' research had an interesting side note. In his examination of glaze durability, he was able to correlate composition of the glaze to physical durability. He found that there was a direct correlation between the Unity Molecular Formula (U.M.F.) flux ratio of a glaze and its ability to withstand physical wear. This question became central to this research. Can we correlate physical disability to chemical durability? So, to say is it possible to predict if a glaze will leach, based purely on the underlying chemistry of the glaze?

Additionally, the question remains, “What is acceptable” when it comes to leaching levels for our glazes? What should we be looking for in glaze testing, both in the tests themselves and in the results. We worked with toxicologist Sarah Urfer, to examine that question.

The Background

Poor durability of glazes can be attributed to a condition called ion exchange. In this process, hydrogen present in the acids in food and base in soaps can displace the alkali metal (lithium, sodium, potassium) in the glaze.[ii] This process can be restricted by having an ideal flux ratio of 0.3 R_2O 0.7: RO via unity molecular formula in glazes at all temperatures, as defined by Katz.[iii]

Based on this principle, we created a series of glaze formulas, designed to have exceptionally robust durability performance. We created matte and gloss formulas designed for maximum strength at the common ceramic temperatures of Cone 04, 6, and 10. All six glazes have an ideal flux ratio of 0.3 R_2O: 0.7: RO and a silica to alumina ratio of 7:1 for gloss and 4.5:1 for matte. Glazes for cone 04 and 6, also had the addition of 0.5 Boron and 0.15, respectively, these numbers were derived by previous work by Katz[iv]. Each composition was then made with additions of copper carbonate at 0%, 1%, 3%, and 5%, making for 24 tiles total.

The glazes were formulated using varying percentages of only Nepheline Syenite, Whiting, Frit 3124, Gerstley Borate, Silica, and EPK. The chemistry of each glaze was made such that there was an adequate amount of boron for the dictated firing range, a normalized flux ratio of 0.3 R_2O to 0.7 RO fluxes, and appropriate levels of silica and alumina which will dictate whether a glaze is matte or glossy. You will find the actual formulas used, at the end of this report.

The Experiment

Samples were applied by spray, to a flat tile and fired in an oxidized atmosphere to their prescribed temperatures. Samples were then washed twice with dish soap and hot water, based on the work by Dr. William Carty on the volatilization of copper and leach testing[v]. Samples were then sent to Lucideon Laboratories for a copper leach test.

For leach testing, the surface of the prepared tile samples, a wall is built using polymer clay to form a cavity to hold a 4% concentration of acetic acid made by diluting 99% pure Glacial Acetic Acid. The cavity is then filled with the diluted acid and covered with an opaque glass or polymer tile to reduce interference from light.

After a duration of 24 hours, the opaque plate is removed from the surface of the tile, and the Acetic Acid is transferred to a glass holding vessel and brought to be measured by atomic flame absorption spectroscopy. The device is calibrated using a known quantity of copper in dilute acid as a control.

The Results

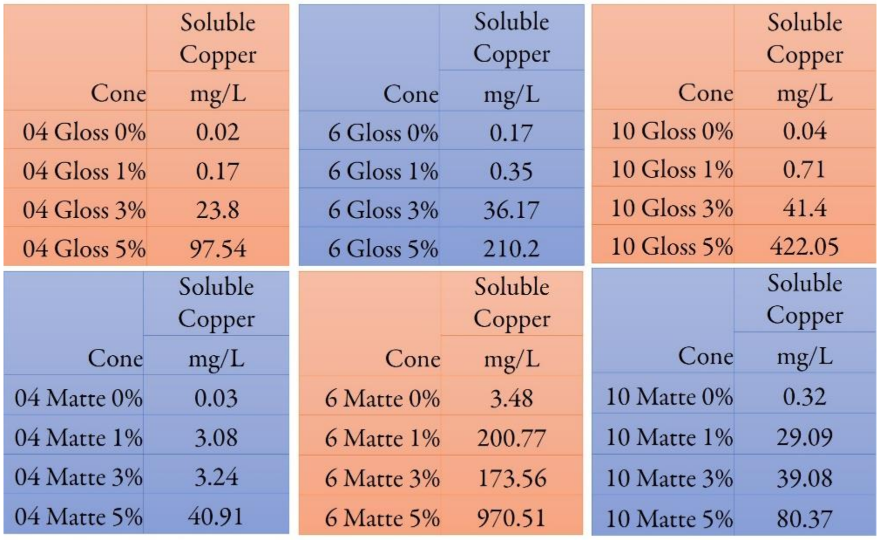
Initial leach testing was conducted with ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectroscopy). The results of that test were that all of our samples had zero copper release. This means that the theory of high quality glazes, (0.3 R_2O :0.7 RO) restricting copper release holds true.

Additionally the ICP-AES is a newer standard of testing than that available to most artists. The common testing method available for American ceramists Is (Atomic Absorption Spectroscopy). The issue for AAS testing is that it is no longer considered adequate or accurate enough testing for the water testing industry (the basis for testing procedures). ICP-AES is a superior testing standard, but even ICP-AES is not an adequate standard.

The current standard for leach testing is ICP-MS (Inductively Coupled Plasma-Mass Spectroscopy) because of this, we tested our sample with ICP-MS.

The question remains, what are acceptable copper release standards? The F.D.A. list 2mg of copper per day as a micronutrient. The E.P.A. lists the allowable concentration of copper in drinking water as 1.3 mg/L, the National Academy of Sciences considers 3.7 liters of water intake to be average for an adult male, leading to a potential acceptable copper dose of 4.81 mg/day, from regular consumption. But water quality standards are not the same as acceptable consumption standards, they are simply the absolutely allowable limits.

From an excess standard, studies by The Center for Disease Control found that that rats are able to process from 180-550 mg of copper per kilogram of body weight per day with no negative effects. Whereas, they develop serious illnesses such as chronic hepatitis and liver problems at doses greater than 550 mg Cu/kg of body weight/day[vi].



Cone	Soluble Copper mg/L
04 Gloss 0%	0.02
04 Gloss 1%	0.17
04 Gloss 3%	23.8
04 Gloss 5%	97.54

Cone	Soluble Copper mg/L
6 Gloss 0%	0.17
6 Gloss 1%	0.35
6 Gloss 3%	36.17
6 Gloss 5%	210.2

Cone	Soluble Copper mg/L
10 Gloss 0%	0.04
10 Gloss 1%	0.71
10 Gloss 3%	41.4
10 Gloss 5%	422.05

Cone	Soluble Copper mg/L
04 Matte 0%	0.03
04 Matte 1%	3.08
04 Matte 3%	3.24
04 Matte 5%	40.91

Cone	Soluble Copper mg/L
6 Matte 0%	3.48
6 Matte 1%	200.77
6 Matte 3%	173.56
6 Matte 5%	970.51

Cone	Soluble Copper mg/L
10 Matte 0%	0.32
10 Matte 1%	29.09
10 Matte 3%	39.08
10 Matte 5%	80.37

Above are the results of our samples from ICP-MS testing. The tests show several interesting trends. First, these number are pointless without context, which we will explore below.

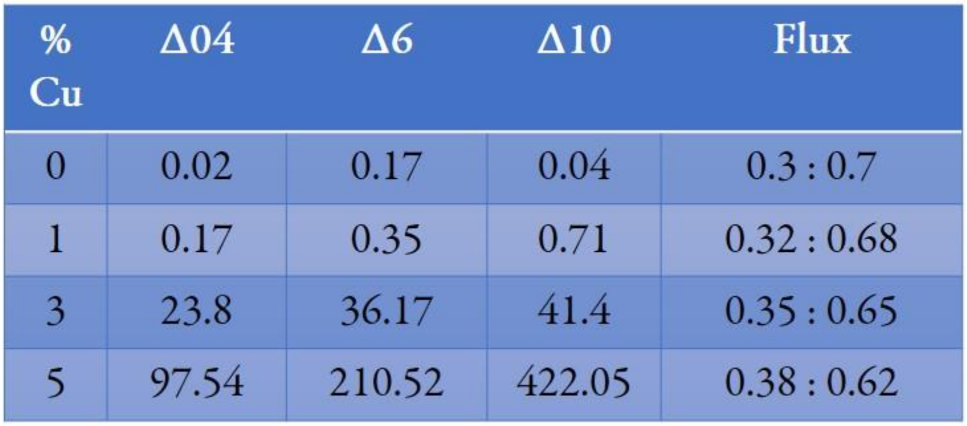
Second, Cone 04 glaze are more durable than Cone 6, which are more durable than Cone 10. This result is consistent with the results found by Katz in his presentations at NCECA 2012 and 2016.[iii, iv] This is because the addition of boron, to lower the melting temperature of the glaze, results in a more durable glaze, independent of temperature.

Third, matte glazes are more durable than equivalent gloss glazes. This is not something that has been tested for, or documented before, but we are comfortable with the concept, but more testing must be done to verify the result.

There are two major anomalies in the testing. The first is the data from Cone 6 matte test, Theses test are substantially divergent from the trends of all the other tests. Because of this we believe that there was an error in the testing procedures. The test must be performed again, to verify the data, but as the other five sets follow consistent trends, we believe this set to be in error. Although this set is possibly anomalous, we will use this data as a “worst case scenario” in the analysis below.

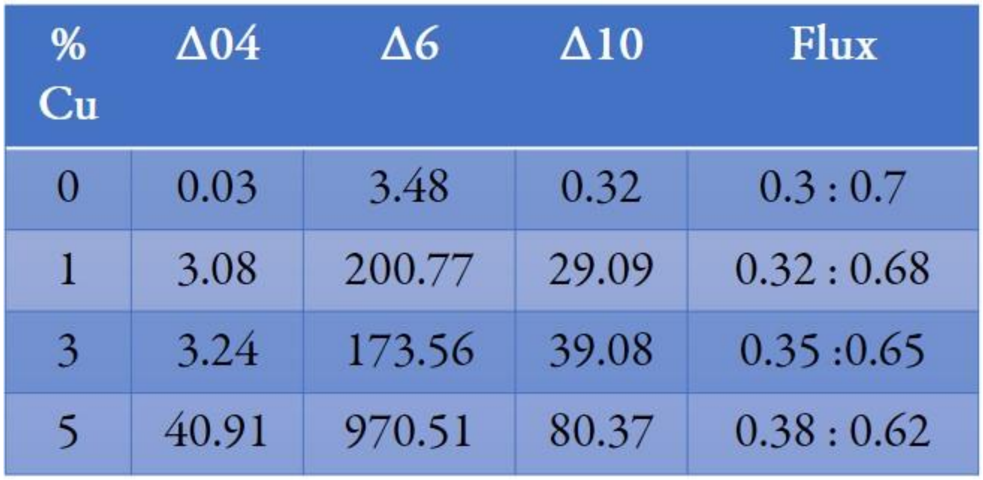
It can be noted that the samples with 0% copper additions still result in detectable copper. This is because copper, volatilizes in the firing and becomes a vapor that will deposit itself on other surfaces in the kiln. As the 0% sample were fired with the other samples containing copper, that the volatilized copper contaminated the non-copper containing samples.

Gloss Glazes



% Cu	Δ04	Δ6	Δ10	Flux
0	0.02	0.17	0.04	0.3 : 0.7
1	0.17	0.35	0.71	0.32 : 0.68
3	23.8	36.17	41.4	0.35 : 0.65
5	97.54	210.52	422.05	0.38 : 0.62

Matte Glazes



% Cu	Δ04	Δ6	Δ10	Flux
0	0.03	3.48	0.32	0.3 : 0.7
1	3.08	200.77	29.09	0.32 : 0.68
3	3.24	173.56	39.08	0.35 :0.65
5	40.91	970.51	80.37	0.38 : 0.62

One factor, to consider with the results for future testing. In the work by Kiara Matos "Colorants as Fluxes" [vii]. It was documented that copper functions in a glaze as an alkali metal flux. This is an important consideration as substantial amounts of copper can significantly alter a glaze's formula. By rearranging the metals release data we were able to see a correlation between flux ratios increasing as copper increases and its corresponding metals release as well as a general metals release increase as boron decreased. This discovery was made after we conducted our testing but prior to publication. This should be considered for all future work.

Sample	Sample volume (mL)	Metals Release (mg/L)
1	500	866.5
2	600	794.3
3	700	742.7
4	800	704.1
5	900	673.9
6	1000	649.9
7	1100	630.2
8	1200	613.7
9	1300	599.9
10	1400	588.0

The results in the table above is the full scope of the test results returned, showing the concentration of the copper in the acetic acid solution (mg/L) Using the formula (mg/dm^2 = Concentration * Volume / Surface Area) we were able to extrapolate the metals release based on a variety of volumes of liquid to represent different vessel sizes. While the results for the Cone 6 Matte were very likely a statistical anomaly, the values were used as an absolute worst case scenario. The below table contains the results from that extrapolation

Sample	Sample Volume (mL)	Metals Release (mg/L)	Litres/ Max Exposure (L)	Max Metals / day (mg)	Actual Metal/kg of weight (mg)	H_2O consumed to max exposure	Hypo-natremia Limits
1	500	866.5	43.28	3,206	47.0	39.6	11.5
2	600	794.3	47.21	2,938	43.1	43.5	15.5
3	700	742.7	50.49	2,748	40.3	46.8	18.8
4	800	704.1	53.26	2,604	38.2	49.5	21.5
5	900	673.9	55.64	2,493	36.6	51.9	23.9
6	1000	649.9	57.70	2,404	35.2	54.0	26.0
7	1100	630.2	59.50	2,331	34.1	55.8	27.8
8	1200	613.7	61.10	2,271	33.3	57.4	29.4
9	1300	599.9	62.51	2,219	32.6	58.8	30.8
10	1400	588.0	63.78	2,175	31.9	60.0	32.0

It was discovered that the small surface area samples we had sent, represented the worst case scenario, i.e. Highest concentrations. The ratio between the volume of liquid held, and the available surface area of the piece dictates the metals release. As volume increases, the metals release will decrease to lower levels. These levels were used in reference to the CDC's toxicity limits for).

Copper toxicity comes from chronic exposure to copper. Under normal conditions, the body and process and expel copper, but excess exposure over a period of time will result in decreased liver function and possible eventual Hepatitis. The Center for Disease Control has documented that that the limit for copper toxicity is 550mg of copper per kilogram of body weight per day[viii]. This translates to a 150lb (68kg) person, being able to consume up to 35,750 mg of copper per day, without suffering chronic effects.

It is important to place these values in context of pottery exposure, to establish how much liquid one would have to drink to begin to suffer from the effects of copper toxicity. The first question is how much actual copper is in, say a mug? Based on an application gram weight of 0.5 grams per square inch (industrial standard), and a surface area od 37.36 square inches for a 3'x'3.25" cylindrical mug. A 5% copper mug would be normalized to 4.76% of the composition, and that copper carbonate is only 64.4% copper (the remained is CO_2) The glaze application for the mug would only have 590.4 mg of copper, total. That also assumes that the liquid from that leaching would extract 100% of the available copper, which is only realistic for the absolute poorest glazes. Even so it will still only equate to the one day expose for a one pound creature. A 150lb (68kg) person would need to drink 39.6 liters of copper contaminated water from our worst performing sample (Cone 6, Matte at 5% copper carbonate) to approach chronic toxicity exposure for a single day. For reference, the average human male drinks 3.7 liters of liquid, total in a day[ix].

Let us suspend our disbelief and assume that water will leach these values of metal. In reality, a health condition called hyponatremia (aka Water Poisoning) would set in well in advance of even nearing the required amount of water. At first the body would start to get slow and sluggish, and concentration would waver early on into the experiment. As the subject continues to drink, seizures would start to take place leading to eventual coma, and possible death. This is all before actually reaching any level of copper intake that would result in negative toxicological effects.

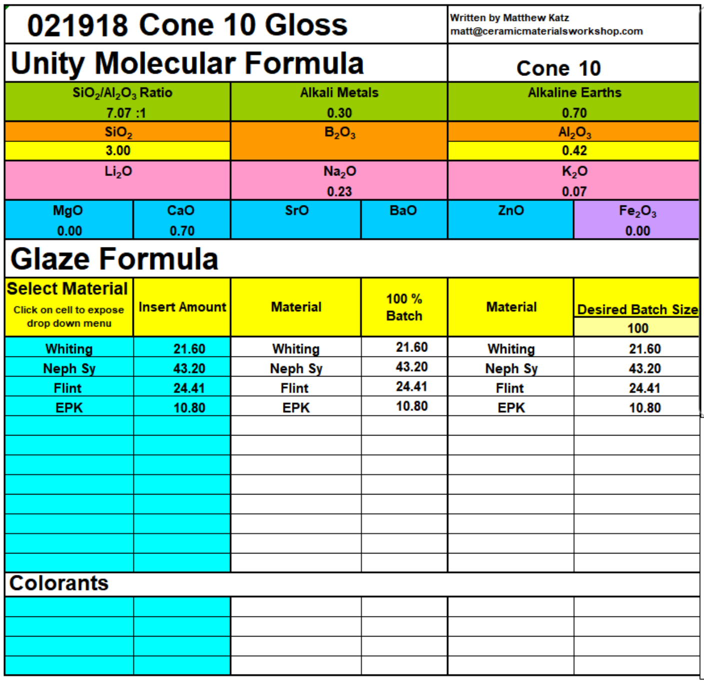
The Conclusion

Toxicologists have an adage from Paracelsus “The dose makes the poison”. In reality, there are zero American or European Union standards for copper release in food ware, is not something that is considered or monitored, and the specific standards of copper toxicity are nebulous. From our testing, we have found nothing of concern in the leaching behavior of copper containing glazes.

Our testing shows that all glazes containing copper, or even fired in a kiln containing copper glazes, will have copper release. The act of release in and of itself is not a problem, our consumption of food and drink is a constant exposure various chemical compounds. From cookware, pipes, ground water contamination, holding vessels, utensils, and our food itself, all contain contaminating elements.

Context for our materials will always be the relevant factor when considering toxicity. Glazes should be designed and fired for maximum durability and quality at all times.

Glaze Formulae



021918 Cone 10 Gloss

Written by Matthew Katz
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Unity Molecular Formula

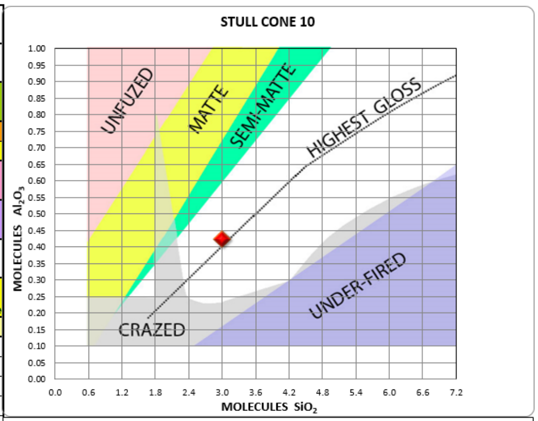
Cone 10

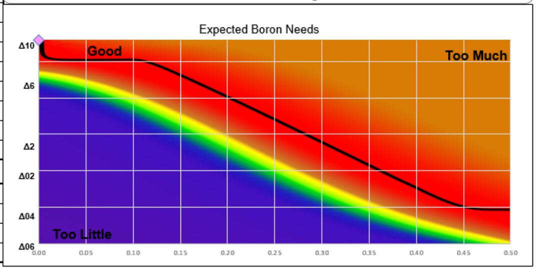
SiO$_2$/Al$_2$O$_3$ Ratio		Alkali Metals		Alkaline Earths	
7.07 :1		0.30		0.70	
SiO$_2$		B$_2$O$_3$		Al$_2$O$_3$	
3.00				0.42	
Li$_2$O		Na$_2$O		K$_2$O	
		0.23		0.07	
MgO	CaO	SrO	BaO	ZnO	Fe$_2$O$_3$
0.00	0.70				0.00

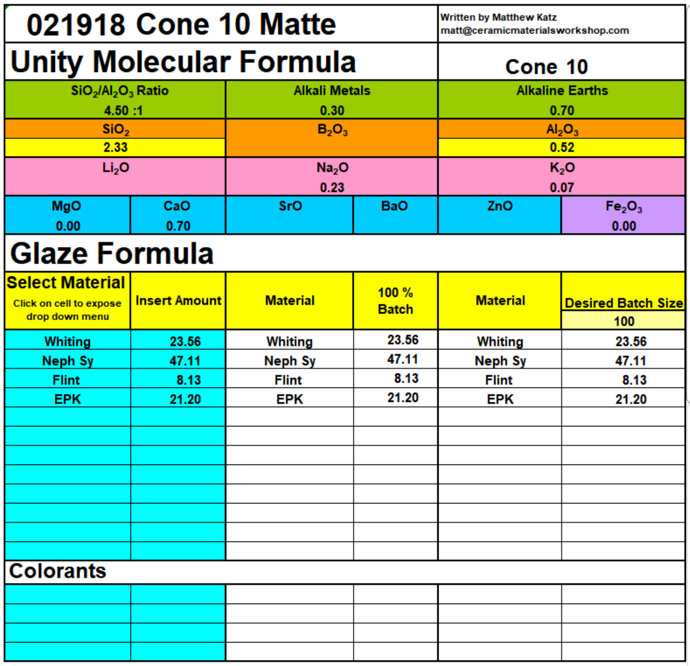
Glaze Formula

Select Material Click on cell to expose drop down menu	Insert Amount	Material	100 % Batch	Material	Desired Batch Size 100
Whiting	21.60	Whiting	21.60	Whiting	21.60
Neph Sy	43.20	Neph Sy	43.20	Neph Sy	43.20
Flint	24.41	Flint	24.41	Flint	24.41
EPK	10.80	EPK	10.80	EPK	10.80

Colorants







021918 Cone 10 Matte

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Unity Molecular Formula

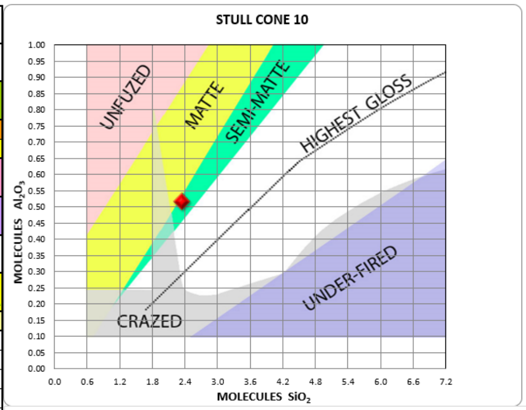
Cone 10

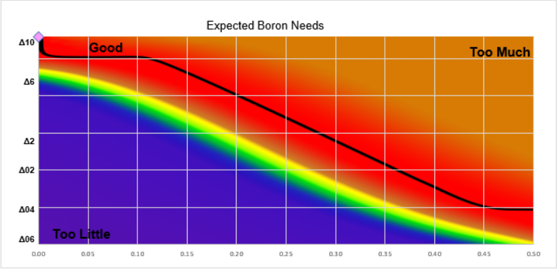
SiO$_2$/Al$_2$O$_3$ Ratio		Alkali Metals		Alkaline Earths	
4.50 :1		0.30		0.70	
SiO$_2$		B$_2$O$_3$		Al$_2$O$_3$	
2.33				0.52	
Li$_2$O		Na$_2$O		K$_2$O	
		0.23		0.07	
MgO	CaO	SrO	BaO	ZnO	Fe$_2$O$_3$
0.00	0.70				0.00

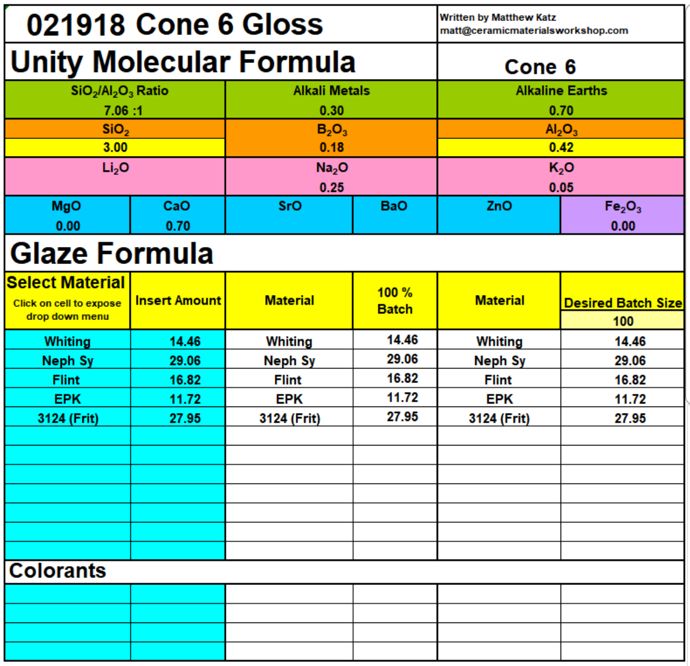
Glaze Formula

Select Material Click on cell to expose drop down menu	Insert Amount	Material	100 % Batch	Material	Desired Batch Size 100
Whiting	23.56	Whiting	23.56	Whiting	23.56
Neph Sy	47.11	Neph Sy	47.11	Neph Sy	47.11
Flint	8.13	Flint	8.13	Flint	8.13
EPK	21.20	EPK	21.20	EPK	21.20

Colorants







021918 Cone 6 Gloss

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Unity Molecular Formula

Cone 6

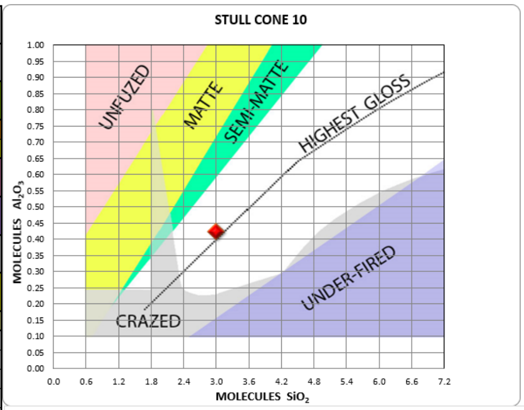
SiO_2/Al_2O_3 Ratio	Alkali Metals	Alkaline Earths
7.06 :1	0.30	0.70
SiO_2	B_2O_3	Al_2O_3
3.00	0.18	0.42
Li_2O	Na_2O	K_2O
	0.25	0.05

MgO	CaO	SrO	BaO	ZnO	Fe_2O_3
0.00	0.70				0.00

Glaze Formula

Select Material Click on cell to expose drop down menu	Insert Amount	Material	100 % Batch	Material	Desired Batch Size 100
Whiting	14.46	Whiting	14.46	Whiting	14.46
Neph Sy	29.06	Neph Sy	29.06	Neph Sy	29.06
Flint	16.82	Flint	16.82	Flint	16.82
EPK	11.72	EPK	11.72	EPK	11.72
3124 (Frit)	27.95	3124 (Frit)	27.95	3124 (Frit)	27.95

Colorants



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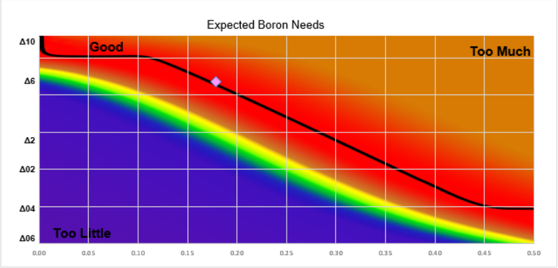
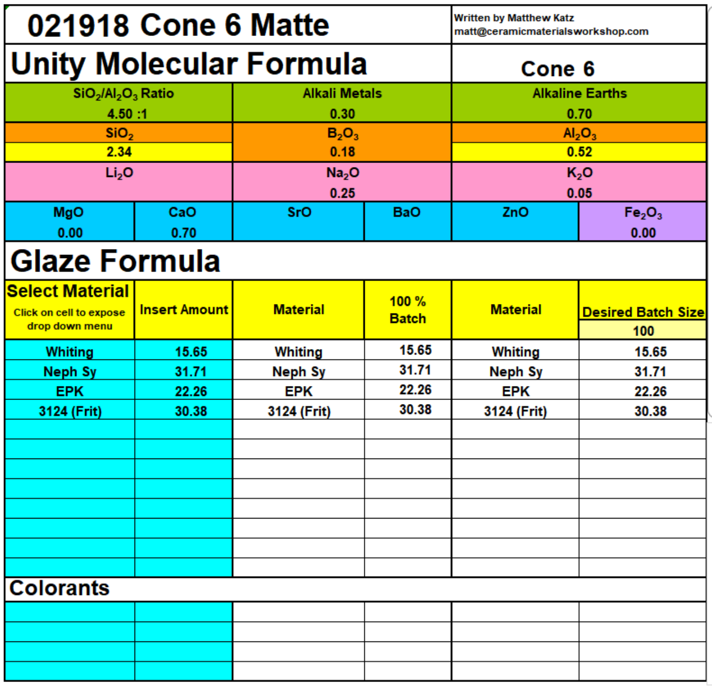


Expected Boron Needs



021918 Cone 6 Matte

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Unity Molecular Formula

Cone 6

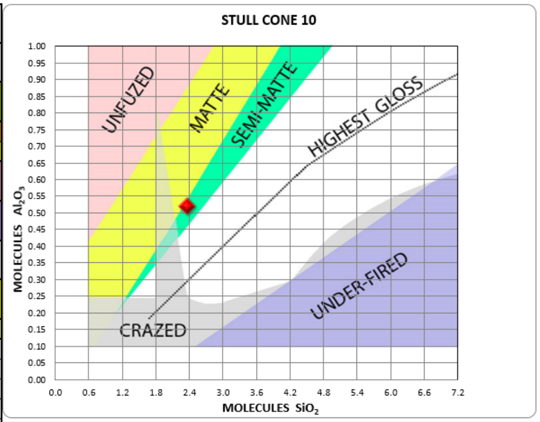
SiO_2/Al_2O_3 Ratio	Alkali Metals	Alkaline Earths
4.50 :1	0.30	0.70
SiO_2	B_2O_3	Al_2O_3
2.34	0.18	0.52
Li_2O	Na_2O	K_2O
	0.25	0.05

MgO	CaO	SrO	BaO	ZnO	Fe_2O_3
0.00	0.70				0.00

Glaze Formula

Select Material Click on cell to expose drop down menu	Insert Amount	Material	100 % Batch	Material	Desired Batch Size 100
Whiting	15.65	Whiting	15.65	Whiting	15.65
Neph Sy	31.71	Neph Sy	31.71	Neph Sy	31.71
EPK	22.26	EPK	22.26	EPK	22.26
3124 (Frit)	30.38	3124 (Frit)	30.38	3124 (Frit)	30.38

Colorants



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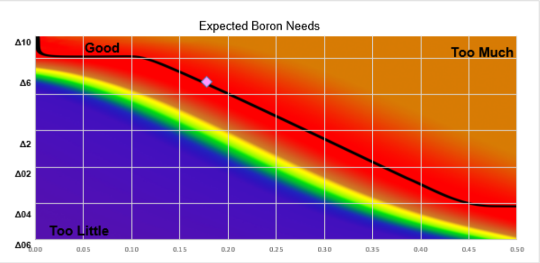
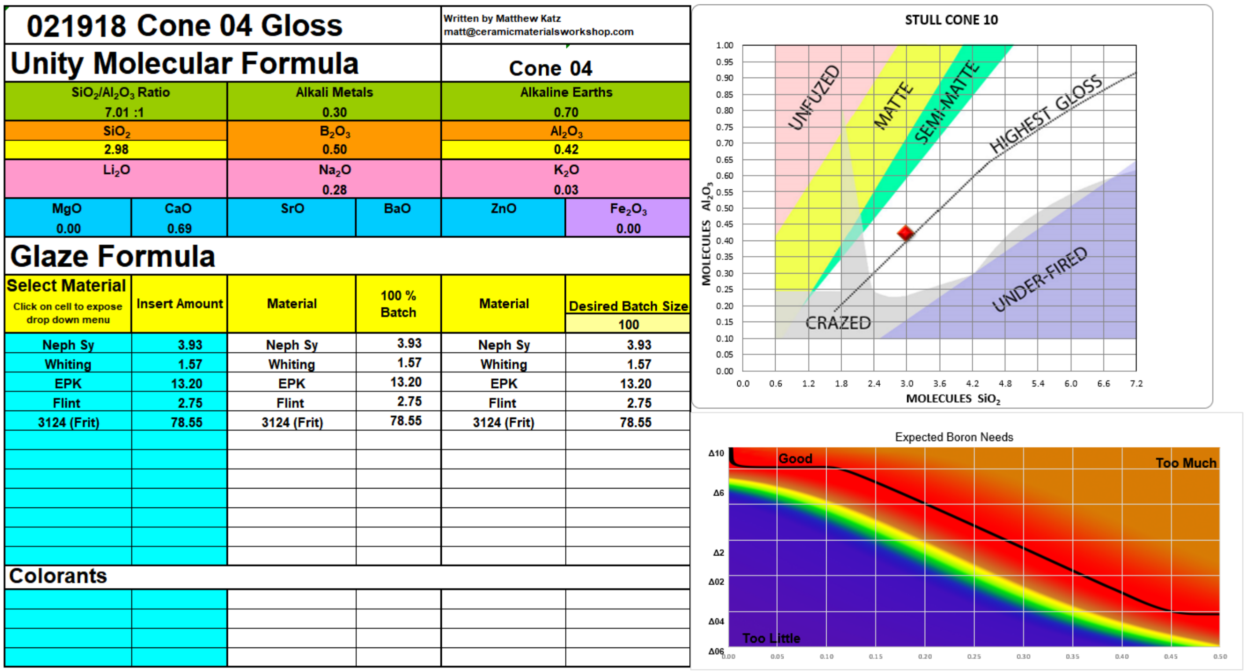


Expected Boron Needs



021918 Cone 04 Gloss

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Unity Molecular Formula

Cone 04

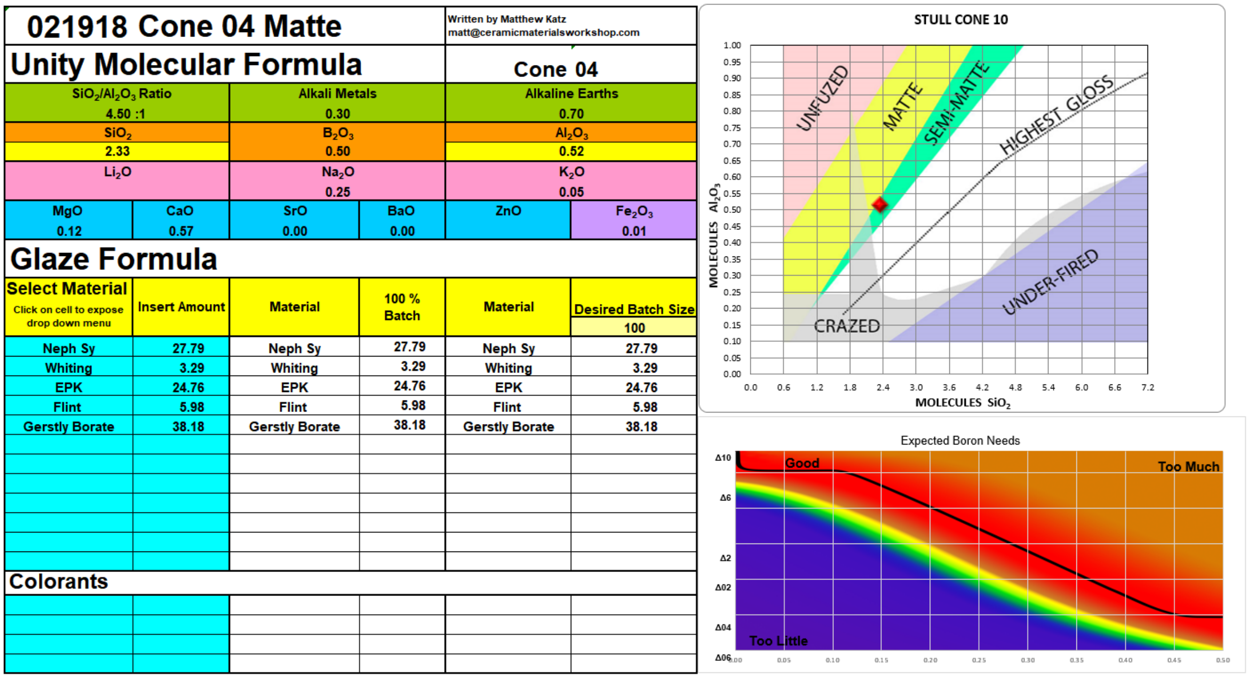
SiO_2/Al_2O_3 Ratio	Alkali Metals	Alkaline Earths
7.01 :1	0.30	0.70
SiO_2	B_2O_3	Al_2O_3
2.98	0.50	0.42
Li_2O	Na_2O	K_2O
	0.28	0.03

MgO	CaO	SrO	BaO	ZnO	Fe_2O_3
0.00	0.69				0.00

Glaze Formula

Select Material Click on cell to expose drop down menu	Insert Amount	Material	100 % Batch	Material	Desired Batch Size 100
Neph Sy	3.93	Neph Sy	3.93	Neph Sy	3.93
Whiting	1.57	Whiting	1.57	Whiting	1.57
EPK	13.20	EPK	13.20	EPK	13.20
Flint	2.75	Flint	2.75	Flint	2.75
3124 (Frit)	78.55	3124 (Frit)	78.55	3124 (Frit)	78.55

Colorants



021918 Cone 04 Matte

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Unity Molecular Formula

Cone 04

SiO_2/Al_2O_3 Ratio	Alkali Metals	Alkaline Earths
4.50 :1	0.30	0.70
SiO_2	B_2O_3	Al_2O_3
2.33	0.50	0.52
Li_2O	Na_2O	K_2O
	0.25	0.05

MgO	CaO	SrO	BaO	ZnO	Fe_2O_3
0.12	0.57	0.00	0.00		0.01

Glaze Formula

Select Material Click on cell to expose drop down menu	Insert Amount	Material	100 % Batch	Material	Desired Batch Size 100
Neph Sy	27.79	Neph Sy	27.79	Neph Sy	27.79
Whiting	3.29	Whiting	3.29	Whiting	3.29
EPK	24.76	EPK	24.76	EPK	24.76
Flint	5.98	Flint	5.98	Flint	5.98
Gerstly Borate	38.18	Gerstly Borate	38.18	Gerstly Borate	38.18

Colorants

End Notes

[i] Matthew Katz, "Glossed Over: Durable Glazes," NCECA Journal, vol. 37 (2016)

[ii] Eppler & Eppler, Glazes and Glass Coatings, pg 254

[iii] Matthew Katz, "Glossed Over: Durable Glazes," NCECA Journal, vol. 37 (2016

[iv] Matthew Katz, "Mid-Temperature Glaze Science," NCECA Journal, vol. 33 (2012)

[v] William M. Carty and Hyojin Lee, "An Overview of Glaze and Glazing Safety" NCECA Journal, vol. 35 (2014)

[vi] www.atsdr.cdc.gov/toxprofiles/tp132-c2.pdf

[vii] NCECA Journal 2018

[viii] www.atsdr.cdc.gov/toxprofiles/tp132-c2.pdf

[ix] www.nationalacademies.org/hmd/Reports/2004/Dietary-Reference-Intakes-Water-Potassium-Sodium-Chloride-and-Sulfate.aspx