Glaze Stability to Acidic Foods and Basic Cleansing Agents
A Review of the Literature

a study in progress by John Hesselberth

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Introduction

There is a strong belief in many parts of the current community of potters that certain criteria must be met in order for ceramic glazes to be stable or durable in use. By stability and durability, I am specifically referring to (1) the ability of glazes to withstand attack by weak acids and bases such as would be encountered in foods (orange juice, tomato sauce, vinegar, etc.) or in dishwasher detergents and (2) properties that affect the glaze's appearance in use such as resistance to being marked by metal utensils, abrasion resistance, chipping resistance, etc. These properties are important, both to assure no changes in the color or surface character of the glaze in use as well as to minimize the release of any glaze components into food served or stored in ceramic vessels. This study of the literature was undertaken to try to understand the quantity and quality of the underlying research that supported these beliefs with a specific emphasis on chemical stability of glazes.

Release of lead and cadmium, of course, have been regulated for many years and all potters who use these materials must test their pots to assure that release of these heavy metals meets the applicable government laws and regulations. Potters use other materials, however, whose release on exposure to weak acids or bases could result in unsatisfactory performance of the pot or, perhaps, health problems to people who might ingest these glaze components. Among the materials of concern are colorants such as cobalt oxide, copper oxide, chrome oxide and nickel oxide and other glaze components such as barium oxide and lithium oxide.

The criteria that many potters have been using to assess the stability of glazes are called "limit formulas". These are ranges of the various oxides used in glazes expressed in the standard Seger Empirical Formula format (now more commonly called the unity formula). If a glaze is within the specified ranges it is thought to be stable. This study is as an effort to try to understand how well limit formulas might predict stability and, specifically, the leaching of coloring metal oxides from a matured glaze. This task of searching the literature for this subject was complicated by the fact that most research on glazes was done from the late 1800s to about 1950. Relatively little of significance has been done in the last 40-50 years as the focus of ceramic research shifted from glass and pottery glazes to electronic, space and health applications.

The Early Years: The Search for Basic Understanding

Herman A. Seger[1] the father of modern glaze chemistry in my opinion, defined the currently used method to describe a glaze by its various chemical components, i.e. the unity formula. In conjunction with his development of the unity formula Seger developed, in the late 1880s, what might be called the first "limit formulas". He expressed the <u>outside limits of composition for glazes in actual use at the time</u>. These were:

Earthenware and fine French faience: RO = 1.0, SiO_2 = 1.5 - 3.0

German and English Whitewares: RO = 1.0, Al_2O_3 = 0.1 - 0.4, SiO_2 = 2.5 - 4.5

Porcelain: RO = 1.0, Al_2O_3 = 0.5 - 1.25, SiO_2 = 5.0 - 12.5

Seger also began to develop some rules for adjusting such things as maturing temperature and level of crazing. He was also an advocate of eliminating lead oxide as a glaze material and suggested the use of barium in place of lead. However he also developed and proposed a lead free glaze containing alkalis (**Note:** for the purposes of this article I will use the term alkali to denote those alkali metals commonly used by potters: lithium, sodium and potassium), lime, alumina, boron and silica and developed "limits" for it. In his paper titled "Glazes Free from Lead,"[2] he also began to establish limits for the individual oxides within the RO component of the glaze. For example, when summarizing his work on alkali-lime glazes, he pointed out:

> "Collecting the results of this investigation, it is seen that the use of alkali-lime glazes is confined to much more narrow limits than the application of lead glazes, and that much more care is necessary in their preparation in order that their composition may correspond to definite conditions.... The proportions permissible lie here between a content of 0.2 equivalent potash or soda to 0.8 equivalent of lime, and 0.6 equivalent potash or soda to 0.4 equivalent of lime."

It is interesting to note that Parmalee and Harman[3] reported, in the 3rd edition of Ceramic Glazes published in 1973, that:

> "The limits of the molecular equivalents of the alumina and of the silica for useful glazes were stated by Herman Seger many years ago, and no important change has been proposed, excepting that the field has been extended..."

The scientific literature for the next several decades expanded on, refined, challenged and verified these statements and rules of Seger's. Most workers in the field, however, focused on whether or not a given composition resulted in a vitreous fired glaze having minimal defects (the terms "good glass" or "good glaze" appear more than once in the literature without further definition of what those terms mean). When the subject of chemical stability or durability is addressed in the literature, it is apparent that the issue of lead--either making sure it was insoluble or eliminating it--was the driving force behind much of the work that was done between, say, 1890 and 1950. While lead had been recognized as a serious problem for more than a hundred years prior to this time, society had not yet been galvanized to address it.

One of the most interesting references I found in this entire search was a short (130 page) book by William J. Furnival[4] titled Researches of Leadless Glazes published in 1898. He writes of the situation in England and starts by chiding those who would not share their results on leadless glazes with him "notwithstanding the humanitarian considerations of the case," and later in the book goes on to name them. In total, it is one of the most impassioned pleas I have ever read about any subject and he devotes many pages to describing the terrible problems that lead causes. Allow me to digress

just briefly to give a short example of his writing:

> "D. Prendergast mentions 432 cases of lead-poisoning occurring in the earthenware and china manufacture during the year 1896, of which 382 were from potteries....Mr. Bertram Wilson, in the Hanley Labour Church report on lead poisoning, refers to inquests upon the bodies of two young boys, fourteen and fifteen years old, who had worked in the dipping house only six and twelve months....Of 156 cases reported to them, twelve resulted in total blindness, two of these being paralyzed and insane, three of them died since having been reported...."

The research that Furnival reports on, however, shows that the efforts to replace lead in England's potteries are purely empirical and at a very early stage with the exception of porcelain glazes. There is nothing in this document that would indicate that there was any relationship between glaze durability and limit formulas. In fact the Seger Empirical Formula is not even mentioned.

Other examples that illustrate the growing awareness of the lead issue were in a discussion on "leadless glazes" [5] in 1899 where E. Orton, Jr. made the point that the U. S. Commissioner of Labor was getting concerned about lead and S. Gresbeek pointed out that the Germans already use leadless glazes whenever possible. Also in 1899 the British Government published regulations which state that no glaze which contains lead shall be regarded as satisfying the requirement as to insolubility which yields to a dilute solution of HCl more than 4% of the dry weight of the soluble lead compound. It is interesting to note that, at this time, galena was considered to be a "safe" form of lead and was exempt from the regulation.

Much of the research work done during this era was documented in abstract form by Koenig and Earhart[6] (a reference book well worth owning if you are a student of glaze technology). There were literally dozens of articles published that have some relevance to the general subject of limit formulas and/or glaze durability. While it is not feasible to discuss all of them here, I will comment on quite a few which, in my opinion, were the more important and which will give a flavor for the nature of the research being done prior to 1950.

One of the earliest attempts to verify Seger's work was published by Binns[7] in 1900. Binns started with a glaze composition at the minimum of the whiteware limits, as stated by Seger, and fired it to Cone 3. He stated that it was "dull...no resemblance to a glaze". He then reduced the silica to 1.3 and found it to be a "good glaze...but inclined to run off the ware". Binns then systematically increased both the alumina and the silica while preserving the ratio of RO + R_2O_3 to SiO_2. He found an optimum at 0.26 Al_2O_3 and 1.78 SiO_2. Binns considered this to be outside of Seger's limits for whiteware glazes. Fickes[8], in 1901, tried to resolve Binns' challenge by saying that "the differences between the statements of these two writers may be due to variation in conditions which they have not stated" and went on to say "...the limits shown in plates I, II, and III represent the correct limits within which will be found all the good glazes...".

It is important to reemphasize that, in all the work done during the era, good glazes were apparently determined by one or more of the following: 1) appearance (did it "mature", i.e. was it vitreous), 2) did it stay on the pot and 3) was it free from defects like

crazing, pinholing, shivering and crawling.

Other workers in this same time period explored niche areas that were of interest to each of them. For example Cannan[9] in 1901 explored Seger's thoughts on barium and considered it to be the least promising of all the potential fluxes. He described the resulting glazes as scummy and worthless. Hull[10] explored limits for chromium-tin pink glazes. Purdy[11] defined limits for Bristol glazes. Binns[12], in a 1903 paper on mat glazes, seems to be the first, or one of the first, to recognize that mixtures of several fluxes usually gave better results than depending on only one or two fluxes.

In 1907, Purdy and Fox[13], tried to establish "oxygen ratio" (the ratio of the molar equivalents of oxygen supplied by silica + boron to the molar equivalents supplied by alumina + fluxes) as an important factor to consider in the formulation of glazes. In this writer's opinion, their points are not well made and a bit convoluted (it was as if someone had done a body of work which didn't show much and was trying to make the best of it). In any case, oxygen ratio shows up several more times in the literature and then seems to disappear from mention. In addition to oxygen ratio, though, this paper focuses on the role of boron and makes the point that it should be treated along with alumina rather than with silica as Seger proposed. Specifically, they say that B_2O_3 and Al_2O_3 operate alike in counteracting devitrification.

In 1910, Binns[14] and Singer[15] wrestled directly with the question of the role of boron in glazes and how it should be treated in the glaze formula. They both come down firmly on the side of Purdy and Fox that it should be treated with alumina and make several points in support of this conclusion, e.g. the substitution of an equivalent amount of B_2O_3 for Al_2O_3 in mat glazes does not change the character of the glaze, but merely reduces the melting point. This is, perhaps, the first successful challenge to something of substance that Seger wrote about glazes in the 25+ years since Seger's work.

One of the first relevant references to the subject of retention of coloring oxides in glazes was authored by Ramsden[16][17] in 1905-1908. Ramsden studied the solubilities of NiO, MnO_2, Cr_2O_3, Fe_2O_3 and CuO in glazes with the objective of understanding: 1) color effects produced by variations in the glaze formula, 2) influence of temperature on color, 3) whether and under what conditions any reduction of content of the coloring oxide could be made while maintaining the finished color, 4) what volatilization of oxide (if any) took place and 5) effects produced by large excesses of oxide. While he did not look specifically at whether or not the metals could be extracted from glazes, the understanding he gained on how much metals a glaze would "hold" would seem to be related. He also began to gain some understanding of what one could do to increase the solubility of a given metal in a glaze. For example, in leadless glazes one can raise the solubility of nickel by 1) increasing boron within certain limits, 2) adding approximately 0.5% tin, or 3) lowering alumina to the point just above where devitrification occurs.

In 1916, Parmalee and Williams[18] defined limits for leadless C7-9 glazes intended for sanitary ware. Within the RO group they set limits of 0.4-0.6 for K_2O, 0.0-0.3 for ZnO and 0.4-0.6 for CaO. They also determined that alumina should be 0.5-0.6 and silica 3.0-4.0. They note that these limits are within those proposed by Seger. Their criteria were ones of appearance and defects, e.g. "Those glazes higher in calcium were dull

and those having more that 0.3 zinc oxide were likely to blister."

Sortwell [19] [20] published 2 papers in 1921 that looked extensively at limits for glazes from Cone 10-16. He held CaO at 0.7 and K_2O at 0.3. A sampling of his results are that, at Cone 10, bright glazes are obtained between 0.3-0.7 alumina and 3.0-5.3 silica; semi-mat glazes are obtained from 0.3 alumina with 4.4-6.0 silica and 0.6-0.9 alumina with 3.0-7.2 silica; mat glazes are obtained from 0.3-0.4 alumina with 6.0-8.4 silica and 0.9-1.25 alumina with 4.9-8.9 silica. Achieving maturity of the glaze was the criteria on which he set the limits.

As an example of related work that was going on during this time period, Parmalee and Lyon[21] in 1934 established limits for frits. Here the criteria were well defined. First, the melted frit at 1100 degrees C. had to flow through an opening of 0.5 cm. in diameter at a minimum rate of 1 drop per second. Second, the melt must not cause excessive corrosion of the smelter lining. Pretty straight forward! The limits established which met both criteria were:

Fluxes (Total = 1.0)	Stabilizers	Glass Formers
Na_2O: 0.3-0.7	Al_2O_3: 0.0-0.1	SiO_2: 1.0-3.0
CaO: 0.7-0.3	B_2O_3: 0.5-1.5	

The Years of Practical Application: Learning to Control or Eliminate Lead

During the 1930s there was a distinct shift in the character of the research that related to limit formulas and stability of the resulting glazes. Prior to this time, the primary criteria for setting limits was whether or not the resulting mixture formed "good glass" mostly determined by visual examination of the glaze. In the 1930s the terms "durability", "chemical durability" and "stability in the presence of acids and bases" appear much more in titles of journal articles as well as in the body of the articles themselves. Apparently society had finally demanded that lead be brought under control. The overwhelming focus of this interest on chemical durability was with respect to the solubility or insolubility of lead in both frits and glazes. Even articles that mentioned other metals usually did so in the context of examining the effect of that metal on the amount of lead which was extractable.

During this period there were also parallel attempts to develop limits for leadless glazes that extended down to earthenware temperatures. While some of this work began to quantify the "durability" of the glaze, chemical durability was only mentioned occasionally because there was no lead to be worried about. Rather, where durability was examined it was usually things like metal marking or abrasion resistance. Examples of both of the above areas, including some where chemical durability of leadless glazes is explicitly addressed, follow.

Both Koenig[22] and Rieke and Mields[23] tried to learn how to make the lead-containing frits insoluble. Koenig learned that boric oxide has a particularly strong effect on increasing the solubility of lead from a frit and recommended that boron be introduced into a glaze via a second lead-free frit. He also noted that the alkalis increased lead's

solubility but not nearly to the degree that boric oxide did. Alumina, silica, calcium oxide, zinc oxide, barium oxide and zirconium oxide, on the other hand, decreased the solubility of lead. Rieke and Mields studied two 3-component systems (Na_2O-PbO-SiO_2 and K_2O-PbO-SiO_2) in great detail and were able to find compositional regions where lead solubility was very low.

Mellor[24] published an extensive study on the effects of both acids and bases on the durability of lead-containing glazes. While he did not publish limits in the usual format, he gave enough guidance and data that they probably could be constructed. For example he pointed out that, as a rough kind of rule, glazes become more durable by increasing the complexity of the composition, e.g. two bases are better than one, three are better than two, etc. He also noted that durability increases with increasing alkali content up to a point; however when alkali content exceeds 0.5 the glaze becomes very dangerous. Mellor also incorporated knowledge from previous workers such as Peddle, Einenlohr and Diehl and Thorpe into his study and notes that boric oxide has a deleterious effect unless silica level is unusually high. Lastly, he points out that it is general knowledge that the "harder" the firing of a glaze the less likely it is to be attacked in service.

In the area of leadless glazes, Horak and Sharp[25] showed in 1935 that when ZrO_2 was progressively substituted for alumina in a borosilicate glass that the chemical durability improved. In 1939, Richardson[26] found that using lithium carbonate to replace more soluble alkalis in glazes fired between cones 07 and 05 permitted increases in the amounts of alumina, calcium and silica. The result was a more stable glaze that still had sufficient alkalinity to produce vivid copper blues and other typically alkaline colors. Another relevant paper to the current question during this time period was written by Geller and Creamer[27] in 1939. They studied a variety of colored glazes to determine whether they constituted a health hazard because lead or other toxic metals that might be dissolved from them. The results indicated that glazes of only one color (tangerine from uranium oxide) constituted a health hazard. They were initially concerned about a copper-containing glaze also; however they determined that the high solubility of the copper was only a surface condition and would disappear if the glaze were subjected to an acid wash before use. Geller and Creamer, however, did not try to determine limits for acceptable levels of leaching. They only tested specific glazes that were in commercial use.

Danielson and Van Gordon[28] came the closest to establishing limit formulas for leadless earthenware glazes in 1950. They concluded, after an extensive series of tests that the best glazes (note that they held alkalis, boric oxide and zirconium constant so their limit formula is not complete) were obtained at:

Cone	Fluxes (Total = 1.0)	Stabilizers	Glass Formers
4	CaO: 0.25-0.35	Al_2O_3: 0.21-0.25	SiO_2: 2.1-3.0
	MgO: 0.05	B_2O_3: 0.193	ZrO_2: 0.138
	BaO: 0.0-0.1		
	Alkalis: 0.2		
	ZnO: 0.3-0.5		

They went on to describe areas of bright and mat glazes. Criteria they used for establishing the above limits are only partially described, but include pinholing and crazing propensity.

In 1949, Orlowski and Marquis[29] were searching for satisfactory glazes for dinnerware at Cones 4-6. They reported that the best leadless glazes have equaled or bettered the resistance of the lead glaze to crazing, impact, chipping and scratching. No mention was made of chemical durability. They partially developed limits by saying that 1) zinc oxide can be used up to 0.3 equivalents, 2) magnesium oxide can be used up to 0.15 equivalents, 3) alkalis should not exceed 0.28 equivalents (crazing) and 4) boric oxide cannot exceed 0.35 equivalents (blistering, surface softening and effect on color)

In 1950, Kock, Harman and O'Bannon[30] examined glaze hardness by the Knoop indentation test and glaze durability by reflux boiling for 6 hours in 3% sodium carbonate solution. They also looked at sand blast resistance and glaze fit. They did this work for 54 glaze compositions fired at Cone 5. They determined that the best chemical durability was obtained with 0.25-0.35 alumina and 2.7-2.8 silica as well as with 0.38-0.42 alumina and 3.2-3.8 silica. Beryllium oxide hurt chemical durability while calcium oxide and magnesium oxide improved it.

The last work I will describe in this section was done in 1975 by Richard Eppler[31]. Eppler takes quite a different approach in defining a "Figure of Merit" which is based on the acid resistance of the oxides in the glaze. The Figure of Merit is calculated by summing the empirical formula concentrations of those constituents which improve the acid resistance and dividing by the square root of the empirical formula concentrations of those constituents which deteriorate the acid resistance. In his original article, Eppler said that when the Figure of Merit was greater than 2.05, the lead release of the glaze would likely be acceptable; when it was less than 1.80, the lead release would probably be unacceptable. With the changing limits of acceptability of lead release in recent years, he has revised these numbers to 2.48 and 2.30 respectively. Eppler's list of oxides that should be in the numerator (increase acid resistance) includes Al_2O_3, SiO_2, TiO_2, ZrO_2 and SnO_4. Those oxides in the denominator (decrease acid resistance) include Na_2O, K_2O, Li_2O, BaO, SrO, CaO, MgO, PbO, ZnO, CdO, B_2O_3, P_2O_5 and F.

In calculating the Figure of Merit, the concentrations of each oxide must be multiplied by the number of molecules of cation it contains (e.g. Al_2O_3 concentration must be multiplied by 2). It should be noted that Eppler's Figure of Merit is a purely empirical correlation with no theoretical underpinning. Therefore, trying to extend it or extrapolate

it would be unwise. Nonetheless, it would be interesting to see if a similar type of Figure of Merit could be developed for other metals such as copper, cobalt, nickel or manganese.

The Years of Consolidating and Summarizing

While the level of research on pottery glazes diminished significantly after World War II, several professors in the general field of ceramics began publishing books which summarized, and in some cases, extended the work of the early workers. Included in several of these books are limit formulas of varying levels of detail. While most of these limits are similar, the authors usually do not state the source of the work done to generate the limit formulas. It is as if they have arisen out of the mist of generations of glaze research--and they probably have. More than likely most of these limit formulas were synthesized from an examination of previous workers data adjusted by the author's personal data, experiences and biases. This would seem to make sense given that the literature articles discussed in the preceding section each give only a piece of the picture. Examples are given below. Note that I am only giving examples for leadless glazes; I have no interest in lead-containing glazes. I have also focused on glazes used on stoneware and porcelain but in at least one case show limits for earthenware to help me make a point. Also, I have consistently listed B2O3 with the stabilizers unless the author makes a specific point that he believes it belongs elsewhere.

F. H. Norton[32] in his 1952 book titled Elements of Ceramics does not give limit formulas in the now-common tabular form; however he gives a graphical presentation that shows the composition ranges for lead-containing and leadless glazes from Cones 016 - 16. While the scale of the graph does not allow accurate translation to a table, it does give a nice way to present the whole domain of glazes in a single picture. Cardew[33], in Pioneer Pottery, shows exactly the same chart (with credit to Norton) with the caution that it "is only a general guide to the standard glazes used in industry; there are many good glazes which depart widely, for one reason or another, from the proportions given."

Green[34], in his book Pottery Glazes published in 1963, shows the following limits (he also calls them "usual ratios"):

Cone	Fluxes (Total = 1.0)	Stabilizers	Glass Formers
3	CaO: 0.3-0.6	Al_2O_3: 0.20-0.35	SiO_2: 2.5-3.5
	MgO: 0.1-0.2	B_2O_3: 0.3-0.5	
	BaO: 0.1-0.3		
	Alkalis: 0.2-0.5		
	ZnO: 0.1-0.25		

Cone	Fluxes (Total = 1.0)	Stabilizers	Glass Formers
9	CaO: 0.35-0.7	Al_2O_3: 0.3-0.7	SiO_2: 3.0-5.0
	MgO: 0.1-0.35	B_2O_3: 0.15-0.3	
	BaO: 0.1-0.3		
	Alkalis: 0.2-0.5		
	ZnO: 0.15-0.35		

In another book, Green[35] gives perhaps the best illustration of how limit formulas can be derived. For example, he will give a list of "typical zinc glaze recipes", also showing their calculated unity formulas. He then plots all of those unity formula numbers on a composition graph. The outer limits of the range of composition found for each oxide become the "limits" for that oxide. While other authors are not as explicit about their techniques, I suspect most have used a very similar technique while sometimes limiting the recipes they used to those having a specific set of criteria important to them at the time.

Rhodes[36], in Clay and Glazes for the Potter in the 3rd edition published in 1973 gives similar, but slightly different limit formulas as shown below. Again, no source is given. Rhodes simply says the formulas represent "the maximum and minimum amount of each oxide which is likely to occur in a glaze of a given maturing temperature." Nelson[37], in the 4th edition of Ceramics: A Potter's Handbook uses identically the same limit formulas calling them "a helpful guide". Nelson does not give a source either.

Cone	Fluxes (Total = 1.0)	Stabilizers	Glass Formers
2-5	CaO: 0.2-0.5	Al_2O_3: 0.20-0.28	SiO_2: 2.0-3.0
	B_2O_3: 0.3-0.6		
	BaO: 0.1-0.25		
	Alkalis: 0.1-0.25		
	ZnO: 0.1-0.25		

Cone	Fluxes (Total = 1.0)	Stabilizers	Glass Formers
8-12	CaO: 0.4-0.7	Al_2O_3: 0.3-0.5	SiO_2: 3.0-5.0
	MgO: 0.0-0.35	B_2O_3: 0.1-0.3	
	BaO: 0.0-0.3		
	Alkalis: 0.2-0.4		
	ZnO: 0.0-0.3		

Taylor and Bull[38], in their 1986 book titled Ceramics Glaze Technology, give only one example of a limit formula for strontium-fluxed glazes that mature at 1150-1180° C. This book does, however, contain one of the two most complete discussions of chemical resistance of glazes that I have found. An entire chapter is devoted to the subject. It is well referenced with many literature citations that, for the most part, I have not included in the sections above since they are so well summarized by Taylor and Bull. I must make the point, however, that while they discuss the subject of chemical resistance of glazes at length, they do not once try to link compositions within limit formulas to good chemical resistance. Rather they try to give mechanistic understanding and qualitative directional guidance on how to improve chemical resistance of glazes. For example they note that:

   1. "Soft" glazes that mature at low temperature are often high in alkali and are more subject to attack. Release rates for these soft glazes can be improved by inclusion of one or more divalent or polyvalent elements such as Ca, Ba, Zn, Al, Zr or Ti.

   2. Multiple component glazes are normally very resistant to attack except when substantial amounts of silicon are replaced by potassium.

   3. Acid resistant glazes can be formulated by basing the compositions on very high silica contents.

   4. Low amounts of boric oxide can improve chemical resistance of a glaze; high amounts hurt chemical resistance. No numbers are given.

   5. Alumina is known to increase the alkali resistance of silicate-structured glazes.

   6. Physical effects can also be important. For example, highly glossed smooth glazes are more resistant that immature glazes; if phase separation has occurred the alkali rich phase will be attacked first; glazes with micro cracks offer, to any reagent, an enormous surface area which will enhance its attack.

   7. Copper with lead is a particularly bad combination, generally giving rise to lead release above the statutory limits.

   8. Copper in leadless glazes is one of the more difficult coloring oxides to contain. Release levels of 2-20 parts per million are typical. It is known that 10 ppm of copper in orange juice can give it a bitter, unpalatable taste.

The other reference that gives a good discussion of the chemical resistance of glasses is A. Paul's Chemistry of Glasses[39] first published in 1982 and revised in 1990. Paul also devotes an entire chapter to "Chemical Durability of Glass" which gets right down into the physical chemistry and thermodynamics of what is happening when glasses are attacked by aqueous solutions (either acidic or basic). Some of the practical points Paul makes are:

   1. Attack on a glass structure usually starts by dissolving of the alkalis. Generally the rate of extraction decreases when almost any divalent oxide replaces alkalis.

2. Addition of lime to a alkali-silicate glass is known to increase durability; however more that 10 mole % does not have additional benefit.

3. Al_2O_3 increases the alkaline durability of glass.

4. Of all the oxides, addition of ZrO_2 is known to increase the durability of silicate glasses the most. Even as little as 2% increase both the alkaline and the acid durability significantly.

While all of this is potentially directionally helpful, I must point out that no data nor even any qualitative statements are included with respect to retaining colorant transition metals or metal oxides like cobalt, copper, chrome, nickel or iron in glasses. So, for example, would adding zirconium oxide help make copper less leachable? I don't think anyone knows; I certainly have not been able to find it in the published literature.

It has been said by a number of current practitioners in the field that Cooper and Royle[40] make the case for treating boron as a flux and include boron in unity when calculating the unity formula. Indeed, they do talk about the fluxing properties of boron and even list it with the fluxes in the limits they give on page 91. There is no statement, however, that they included boron in unity when they calculate unity formulas and, in fact, examples they give for frits in Chapter 8 show boron with silica and clearly not included in unity. Examples of the Cooper and Royle limits are:

Temperature	Fluxes (Total = 1.0)	Stabilizers	Glass Formers
1200 C	CaO: 0.0-0.55	Al_2O_3: 0.275-0.65	SiO_2: 2.4-4.7
	MgO: 0.0-0.325		B_2O_3: 0.0-0.35
	BaO: 0.0-0.4		
	Alkalis: 0.0-0.375		
	ZnO: 0.0-0.3		

Temperature	Fluxes (Total = 1.0)	Stabilizers	Glass Formers
1275 C	CaO: 0.0-0.7	Al_2O_3: 0.45-0.825	SiO_2: 3.5-6.4
	MgO: 0.0-0.34		B_2O_3: 0.0-0.23
	BaO: 0.0-0.475		
	Alkalis: 0.0-0.3		
	ZnO: 0.0-0.36		

An additional piece of evidence supporting my belief that Cooper and Royle did not mean for boron to be included in unity is supplied by Green[41] in his 1980 book titled Pottery Glazing Basics. While this book has much of the same material as his 1963

book, it is shorter (for example he no longer has the chapter that describes how to use a slide rule) and has been updated in some respects. With respect to limit formulas Green gives, in Table 6, a list of the "maximum amount of common fluxes present in glazes". The numbers are identical to those given by Cooper and Royle in the stoneware range. However, Green's table extends down to earthenware temperatures and there he shows boron numbers as high as 2.0 at 900 degrees C. Clearly boron was not in unity with a limit of anything over 1.0. It would appear extremely likely that the original source for both Green's and Cooper and Royle's limit formulas is the same; however that source is not identified in either book. Examples of the leadless earthenware flux limits given by Green are:

Temperature	Fluxes
900 C	CaO: 0.0-0.15
	MgO: 0.0-0.225
	BaO: --
	Alkalis: 0.0-0.675
	ZnO: --
	B_2O_3: 0.0-2.0

Temperature	Fluxes
1000 C	CaO: 0.0-0.25
	MgO: 0.0-0.28
	BaO: 0.0-0.24
	Alkalis: 0.0-0.575
	ZnO: 0.0-0.14
	B_2O_3: 0.0-1.4

McKee[42], in his 1987 book titled Ceramics Handbook, gives 3 sets of limit formulas for low, mid and high firing temperatures. He cautions that the proportions listed are only guidelines. His high fire limits are:

Cone	Fluxes (Total = 1.0)	Stabilizers	Glass Formers
5-12	CaO: 0.0-0.5	Al_2O_3: 0.25-0.45	SiO_2: 2.5-4.5
	MgO: 0.0-0.4	B_2O_3: 0.10-0.4	
	BaO: 0.0-0.8		

Alkalis: 0.0-0.4

ZnO: 0.0-0.5

SrO: 0.0-0.8

Li_2O: 0.0-0.4

Richard Zakin[43], in his 1990 book titled Ceramics: Mastering the Craft, gives one of the most extensive sets of limit tables which he attributes to Professor Robert Schmitz of the School for American Craftsmen at the Rochester Institute of Technology. As of this writing, I have not located Professor Schmitz's original work to be able to understand the criteria on which the limit formulas were established. He had retired by the time I tried to reach him and, although I was given his retirement home phone number, I was never able to reach him. Zakin also points out the dilemma about boron and suggests that it be considered "almost the same as the fluxes in the RO column." Examples of these Zakin/Schmitz limits are:

Cone	Fluxes (Total = 1.0)	Stabilizers	Glass Formers
3-5	CaO: 0.05-0.4	Al_2O_3: 0.28-0.4	SiO_2: 2.0-3.0
Mat	MgO: 0.0-0.35	B_2O_3: 0.0-0.2	
	BaO: 0.0-0.35		
	Alkalis: 0.05-0.25		
	ZnO: 0.0-0.25		
	SrO: 0.0-0.4		
	Li_2O: 0.0-0.05		

Cone	Fluxes (Total = 1.0)	Stabilizers	Glass Formers
8-10	CaO: 0.2-0.7	Al_2O_3: 0.3-0.5	SiO_2: 2.5-4.0
Satin	MgO: 0.0-0.2	B_2O_3: 0.0-0.2	
	BaO: 0.0-0.2		
	Alkalis: 0.05-0.3		
	ZnO: 0.0-0.3		
	SrO: 0.0-0.7		
	Li_2O: 0.0-0.1		

In Recent Years

While there has been little, if any, additional basic research done on limit formulas, in the years from 1980-2000 a serious attempt has been made to make glaze calculation and use of limit formulas a more doable task. Several computer programs have been written which eliminate the tedious manual calculations involved:

Some of the better known programs which are available are:

GlazeMaster™ written by John Hesselberth (Windows or Macintosh)

HyperGlaze written by Richard Burkett (Windows or Macintosh)

Insight written by Tony Hansen (Windows or Macintosh)

Matrix written by Lawrence Ewing (Windows only)

All of the above programs have limit formulas of one kind or another built into them-- mostly from one of the textbooks referenced above. Matrix has one set I have not previously seen. The original source is Monash University in Melbourne, Australia; although attempts by the author of Matrix, Lawrence Ewing, to learn more about the origination of these limit numbers were not successful.

HyperGlaze also shows some very specialized limit formulas that Richard Burkett has derived over the years by calculating the unity formulas from known glaze recipes that work. Examples are cone 10 Shino, cone 10 Temmoku and cone 6 Lithium Mat limits. Burkett shows more than 25 of these specialized limit formulas within the HyperGlaze program.

An excellent review article on these and other glaze calculation programs was written in 1998 by Malmgren[44]; however, it is now out-of-date as all the programs have been improved and GlazeMaster did not exist when that review was written.

In 1999 research was started by the author of this article specifically directed at trying to understand what factors were important to keeping glaze components from leaching into food or drink. The results of that work were published in *Mastering Cone 6 Glazes*[45] in 2002. I focused my attention on leaching of copper oxide (usually supplied to a glaze as copper carbonate) because it seemed most difficult of all the commonly used colorant oxides to keep in a glaze. I derived 4 "rules" for making stable glazes as follows:

1. The glaze must have enough silica--at least 2.5 and preferably greater than 3.0.

2. The glaze must have enough alumina--0.25-0.45 at cone 6. Higher levels are probably OK if Rule 3 is met.

3. The glaze must be thoroughly melted in firing. This means the type and amounts of fluxes + boron must be sufficient for the cone.

4. The glaze cannot be overloaded with colorants. The amount allowable varies with the colorant. As an example I have not yet seen a glaze that will hold more than about 5% copper carbonate, while 10-15% of red iron oxide does not usually result in significant leaching if the above 3 rules are followed.

Notice in the above there is no mention of flux limits as long as the glaze gets thoroughly melted. So, for example, I have made very stable glazes at a calcium oxide level as high as 0.85--well outside the limits proposed by any of the authors referenced above. I have also made very unstable glazes that are within the limits proposed by those authors. I also find it very encouraging that my results as expressed in the first two rules are consistent, if not identical, with those reported by Kock, Harman and O'Bannon in 1950

Summary and Conclusions

So where does this leave us with respect to using limit formulas to predict whether or not metal oxides will leach from a glaze? In a word, it is my belief that they don't. If data exists to show that glazes within the limit formulas will resist leaching of metals by acids and bases, this author has not found it. For the most part limit formulas have been assembled by visually examining hundreds of glaze samples and determining which make "good glass", i.e. which compositions have vitrified at the cone tested while having minimum or no defects such as crazing, pinholing, etc. Some researchers have also included other tests such as abrasion or chipping resistance. No one that I have found has included chemical resistance criteria when they defined limit formulas for leadless glazes. My own work, referenced directly above, shows that silica and alumina levels are important to leaching but that individual flux levels are not or, perhaps, are of secondary importance. Further, the silica and alumina levels I found necessary are at the upper end of the ranges quoted by most earlier workers.

It must also be noted that most authors of the books cited above state very clearly that their limit formulas should only be used as a guide and that good glazes may well exist outside of the limits. What they do not say is that bad glazes (from the viewpoint of resistance to leaching of colorants by weak acids) are readily found within the limits they proposed.

There are a few gaps in time where I was not able to search and, of course, I just may have overlooked a key article. If anyone knows of data or information I have missed please let me know. This is still a "work in progress" and I am very open to modifying it as/if I find more information.

In the meantime, I will contend that the only way to know if a specific glaze formula is

resistant to attack by acids or bases is stay within the 4 rules listed above and even then one should follow by testing it or having it tested. There are 3 specific tests I would recommend:

1. The most practical way to test for resistance to attack by bases is to put a glazed pot in the back of your dishwasher and leave it there for repeated cycles. After a month examine its appearance vs. a control that has not been in the dishwasher. Repeat for at least 3 months. If it hasn't changed color and the surface hasn't dulled after that period of time it is probably dishwasher safe and reasonably resistant to attack by weak bases. A more rigorous and accelerated test is had by simmering a sample for 6 hours in a 5% sodium carbonate solution. This is similar to the ASTM used by the ceramics manufacturing industry.

2. Fill a cup part way with vinegar and leave it for 72 hours. Rinse it, dry it, and examine carefully for color fading. If it has visibly faded, the glaze is very unstable and should not be used on functional work. If the color has not faded but the sheen has changed it is of very questionable stability. Please note that this test will tell you if your glaze is totally unsatisfactory; it will not tell you if it is satisfactory. I have recently had a glaze sample that passed a 24 hour vinegar test but still released over 40 ppm copper when tested by Alfred Analytical Lab--that is a very high level!

I have to be very direct here and say that, in my strong opinion, any glaze that does not pass these first two tests should not be used on functional pottery unless it is on a surface that never sees food and/or on a pot that will not be put in a dishwasher. Not only would you be selling a shoddy product that is not suitable for its intended use and ruining your reputation, you are potentially giving potters everywhere a bad name. Maybe on a vase that might only get used a few times a year it would be OK, but on a mug or a pitcher or a plate---no way.

3. Have the glaze tested quantitatively for metals extraction by a professional lab like the Brandywine Science Center (www.bsclab.com). While I have done this for all of my glazes meant for food contact, it is particularly important to do if the glaze contains copper and/or is fired at low temperatures. The question you will have here is what do the results mean? How much leaching is too much for the glaze to be considered to be food safe? That too, is a question for which, at present, there is no definitive answer. But food safety is only one part of the question. The other is suitability for use. A glaze that fades after a year of two of regular use is, in my opinion, clearly unsuitable for that use.

In the meantime we are left with an uncomfortable level of uncertainty about whether a specific glaze formula might cause problems in use and we will each have to use our own judgment. We do have the comfort, however, in knowing that there is no known, documented case of release of metals, other than lead, from a commercially produced glazed surface having harmed anyone[46]. It is more likely that our concern is one of durability in use rather than potentially causing health problems but, given the lack of

data, you just don't know. With that in mind, I think it behooves each of us to minimize the level of extractable metals in our glazes consistent with our aesthetic goals which are what give us a saleable product. This can be done in several ways: 1) we can learn how to formulate glazes with a minimum level of extractables, 2) we can limit ourselves to glaze materials with no known toxicity issues or 3) we can use liner glazes having no known toxicity questions on food contact surfaces, particularly those exposed to liquids or in which liquids are likely to be stored.

Please Email comments, corrections, suggested additions, etc. to

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Revision Notes:

Revision 1 on 2/14/99: Added the article by Eppler thanks to the reference provided by E. J. Pawlicki of Pemco. Significantly rewrote the paragraph on Cooper and Royle and added the 1980 reference by David Green. Added the section on computer glaze calculation programs.

Revision 2 on 3/13/99: Added 1979 Green reference and made minor changes to the section on glaze calculation.

Revision 3 on 5/28/00: Numerous minor changes and corrections in preparation for publishing in Adobe Acrobat file format.

Revision 4 of March 2008: Added GlazeMaster as an available glaze calculation program. Also added a section noting the research I have done since the initial publication of this article. Changed the results and conclusions as a result of the preceding sentence.

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