FRIT COMPOSITION EFFECTS ON COLOR DEVELOPMENT WITH ZIRCON PIGMENT IN SINGLE FAST-FIRE TILE GLAZES

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ABSTRACT

The effects of frit composition on the fired microstructure and color of fast-fire ceramic tile glazes with zircon-vanadium (Zr-V) blue pigment was studied. Statistical empirical models were developed to quantify the significant effects of ZrO_2, ZnO, SrO and the Al_2O_3/alkali ratio.

Frits with ZrO_2 yielded glazes with both the best color strength and high-temperature stability. Fritted ZnO enhanced zircon crystallization from the frit and produced very stable opaque coatings. Replacement of ZnO with SrO in these formulas prevented zircon from forming and resulted in transparent glazes with strong and relatively stable color. Uniquely light yet high-chroma blue color was produced by adjusting the ZnO and Al_2O_3/alkali ratio to cause precipitation of spherical zircon particles which were close in diameter to the wavelength of blue light.

All experimental frits without ZrO_2 exhibited significant Zr-V dissolution and crystallization of Ca-based silicates during firing, resulting in poor color strength and stability, and low gloss and whiteness.

1. INTRODUCTION

Color control is becoming increasingly important in the industrial production of ceramic glazes. Color incompatibility between products advertised to have the same appearance is currently the largest customer complaint in the U.S. ceramic tile market. Color inconsistencies also burden manufacturing with higher reject levels, lower productivity and increased product inventories which are required to accommodate multiple color shades per item.

Color control has become more difficult due to complicated new products which require multiple layers of colored coatings. The continual effort to reformulate glazes with lower cost materials has also caused problems due to a lack of understanding of formulation effects on color development. In addition, the rapid evolution of firing technology has resulted in glaze color variations by causing many factories to fire the same product with different types of kilns and cycles during the transition. There is a great interest in the ceramics industry in developing more robust glaze formulations which yield consistent colors over a wide range of processing conditions.

Multi-oxide silicate glass frits are the predominant materials in single fast-fire ceramic tile glazes[1-5], and zircon doped pigments are the most commonly used colorants in the U.S. tile industry. Frits for opaque glazes contain zirconia (ZrO_2), which at high temperatures combines with SiO_2 to precipitate opacifying zircon particles[4,5]. It is the customary industrial practice to exclude ZrO_2 from frits for transparent glazes due to the belief that zircon will crystallize. However, excluding ZrO_2 or keeping it at very low levels (<2%) increases zircon pigment solubility and results in poor color stability. Although high-temperature interactions between frit oxides and zircon pigments determine the fired color, they have not been well understood.

The main purpose of this study was to determine the effects of individual frit oxides on the fired color strength and high-temperature stability of glazes colored with zircon pigment. Other objectives were to develop statistical empirical models which quantify the effects of significant oxides, and to relate the fired glaze microstructure to the resulting color. Special emphasis was placed on comparing compositions with (1) ZrO_2 versus no ZrO_2, (2) low versus high alkali levels, and (3) SrO versus ZnO as the secondary flux. Since the EPA classifies ZnO as a regulated material in the US, there is an increasing interest in replacing it with another RO group oxide.

2. MATERIALS AND EXPERIMENTAL PROCEDURE

Compositions of the eight experimental frits studied (A-H) are listed in Table 1.

The frits were designed to encompass a range of oxides normally utilized for fast-fire tile glossy glazes. They were smelted in the laboratory and ball milled to a mean particle diameter of 20-28 μm. No crystalline phases were detected in the powders with x-ray diffraction (XRD) scans. Main differences in the compositions shown in Table 1 are that A-D contain ZrO_2 (≈8 wt. %),

Table 1. Experimental Frit Compositions

	(Molar Equivalents Normalized to Total Oxides = 1.0)							
Oxide	A	B	C	D	E	F	G	H
SiO_2	0.613	0.556	0.618	0.569	0.586	0.541	0.599	0.555
ZrO_2	0.044	0.043	0.044	0.044	0	0	0	0
ZnO	0.098	0.098	0	0	0.094	0.096	0	0
SrO	0	0	0.078	0.079	0	0	0.076	0.077
Al_2O_3	0.026	0.026	0.026	0.027	0.050	0.051	0.051	0.052
* Alkali	0.043	0.088	0.045	0.090	0.044	0.083	0.042	0.084
** Other RO	0.129	0.128	0.130	0.132	0.180	0.183	0.184	0.188
B_2O_3	0.058	0.058	0.058	0.059	0.046	0.047	0.047	0.043

* = $K_2O + Na_2O$ ** = CaO + MgO

[1] SACMI LABS, *From Technology Through Machinery to Kilns for Sacmi Tile,* Sacmi R&D Lab Publication, Imola, Italy (1986).
[2] R. TOZZI, *Glazes for Fast-Firing,* Assiceram Italian Ceramic Society, Rimini, Italy (1986).
[3] J. ENRIQUE, J. AMOROS AND A. MORENO, *Evolution of Ceramic Tile Glazes,* pp. 357-370 in Science of Whitewares. Edited by V. HENKES, G. ONODA AND B. CARTY, American Ceramic Society, Westerville, OH (1996).
[4] T. BARSON, *Frit: the Engineered Material,* Ceram. Eng. Sci. Proc., 18 [2] 28-36 (1997).

while E-H have no ZrO_2; A, B, E and F incorporate ZnO but no SrO, while C, D, G and H replace the ZnO with SrO; and A, C, E, and G have a relatively low alkali level, where the level is high in B, D, F and H.

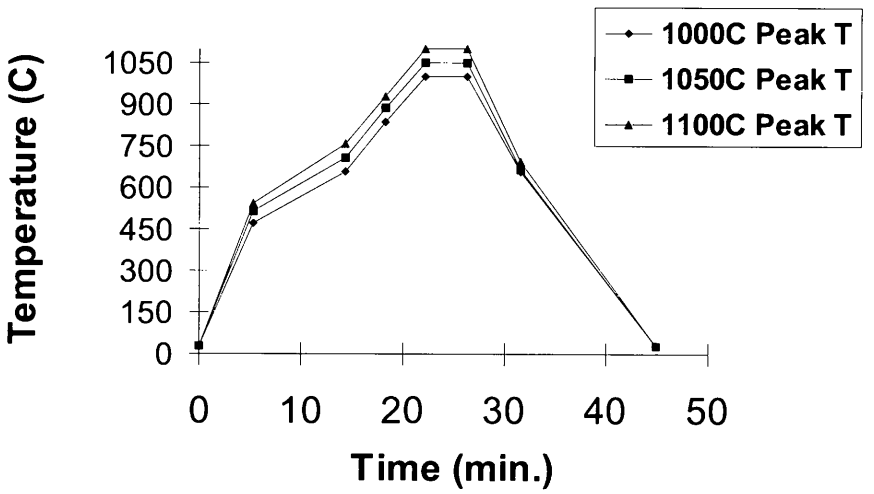


Figure 1. Firing cycles employed.

Glaze formulations consisted by dry weight of 95.5% frit, 2.0% zircon-vanadium (Zr-V) blue pigment (≈8.9 μm mean particle diameter) and 2.5% bentonite. For each coating, a 1.75 sp.gr. mixture of materials and water was sprayed onto 2"X6" wall tile body substrate at a constant volume of 2.70cm³. Samples were fired in an industrial pilot roller kiln with a heating rate above 700°C of 43°C/min., a 4-minute hold at the peak temperature, and a rapid cooling rate of approximately 200°C/min, as shown in Figure 1. Three different peak temperatures of 1000°C, 1050°C and 1100°C were tested in order to determine color stability over a wide range of firing conditions.

A fired glaze's color strength was quantified by its Kubelka-Munk pigment absorption factor (K/S), calculated from spectral reflectance curves:[6-8]

$$K/S = (1-R_{min})^2 / 2R_{min} \qquad (1)$$

where K is the absorption constant, S is the scattering constant and R_{min} is the spectral reflectance at the wavelength where minimum reflectance or maximum absorption of light by the pigment occurs. The R_{min} values were measured using a spectrophotometer with 10^3 cd/m² luminance, a D65 light source, 2° angular subtense and the specular component excluded.

The color stability of a glaze formula was taken as the inverse of the color difference (ΔE*) caused by a 50°C increase in peak firing temperature from 1050°C to 1100°C. Using the CIE L*a*b* color space, where L*= lightness, a* = +redness/-greenness and b*= +yellowness/-blueness, the color difference is given by:

$$\Delta E^*_{(1050\text{ to }1100°C)} = [\,(L^*_{1100} - L^*_{1050})^2 + (a^*_{1100} - a^*_{1050})^2 + (b^*_{1100} - b^*_{1050})^2\,]^{0.5} \qquad (2)$$

where $\Delta E^* \geq 1.0$ is visible by the human eye. L*, a* and b* values were derived from the same spectral reflectance curves used to calculate K/S values.

[6] D. Eppler and R. Eppler, *Analyzing the Color of Reddish Glazes,* Ceram. Eng. Sci. Proc., 17 [1] 77-87 (1996).
[7] D. Eppler and R. Eppler, *The Relative Stability of Ceramic Pigments,* Ceram. Eng. Sci. Proc., 18 [2] 139-149 (1997).
[8] R. Blonski, *The Effect of Zircon Dissolution and Reprecipitation on the Color Development of Glazes,* Ceram. Eng. Sci. Proc., 14 [1-2] 176-189 (1993).
[9] D. Montgomery, *Design and Analysis of Experiments,* 4th Ed., Chpt. 13, John Wiley & Sons, New York (1997).
[10] R. Blonski, *Higher-Chroma Zircon Colors for Glaze Applications,* Ceram. Eng. Sci. Proc., 15 [1] 266-280 (1994).
[11] R. Blonski, *The Effect of Zircon Dissolution on the Color Stability of Glazes,* Ceram. Eng. Sci. Proc., 15 [1] 249-265 (1994).

From the experimental results, multiple regression techniques[9] were applied to develop statistical empirical models for predicting color strength (K/S) and stability ($1/\Delta E^*$) based on the frit oxide composition.

Fired coatings were also examined using XRD techniques (CuKα, 0.02° 2θ steps, 2s/step) to qualitatively identify phases that crystallized during firing and to measure the quantity of zircon present. Zircon content was determined by comparing a coating's integrated area under the zircon [312] reflection peak (53.5° 2θ) to a standard curve derived from unfired samples with known weight percentages of zircon. Previous studies found that the mixed index [312] diffraction line can be reliably used to determine the concentration of zircon in glazes.[8,10,11] In frits A-D, both zircon pigment and zircon precipitates from the frit could be present in fired coatings. A graphical method was employed to estimate how much of the zircon was pigment. Since K/S →0 as Zr-V content→0, positive x-axis intercepts on plots of K/S from fired coatings versus Zr-V content in the unfired coatings (x-axis) estimate quantities of dissolved Zr-V. For this analysis, additional glazes were prepared from frits A-D with 0.5%, 2.0% and 5.0% Zr-V, and processed using the preceding methods.

Scanning electron microscope (SEM) micrographs were generated to view crystalline phases. Energy dispersive x-ray spectroscopy (EDS) was applied to perform a semi-quantitative analysis of elements present in non-zirconium crystalline phases that were difficult to identify.

3. RESULTS AND DISCUSSION

3.1.- SPECTRAL REFLECTANCE CURVES

Spectral reflectance curves from the unfired materials (Fig. 2) show that R_{min} for the Zr-V pigment is at 640 nm. The unfired frit powders have uniform reflectance across the visible spectrum and appear white, while the bentonite and engobe substrate reflect more long wavelength light and appear yellowish in color. The yellowish engobe color could lessen the Zr-V blue strength in non-opaque glazes. The average reflectance from the unfired glazes is a weighted composite of the individual raw materials.

Reflectance curves for each glaze fired to 1000°C (Fig. 3) and 1100°C (Fig. 4) illustrate changes in optical properties resulting from the increase in peak firing temperature.

Legends on the figures are listed in order from lowest to highest color strength, which is inversely proportional to the reflectance at 640 nm. At either firing temperature, frits C and D, which included both ZrO_2 and SrO, but no ZnO, yielded the highest color strength. The lowest change in reflectance values and thus the highest color stability resulted from frits A and B, which included ZrO_2 and ZnO, but no SrO. The greatest changes in reflectance values, indicative of the lowest color stability, occurred with frits F and H, which contained no ZrO_2 and had a relatively high alkali level. From 1000°C to 1100°C, reflectance values from F and H shifted upwards and towards larger wavelengths, which indicates both Zr-V dissolution and crystallization of other species.

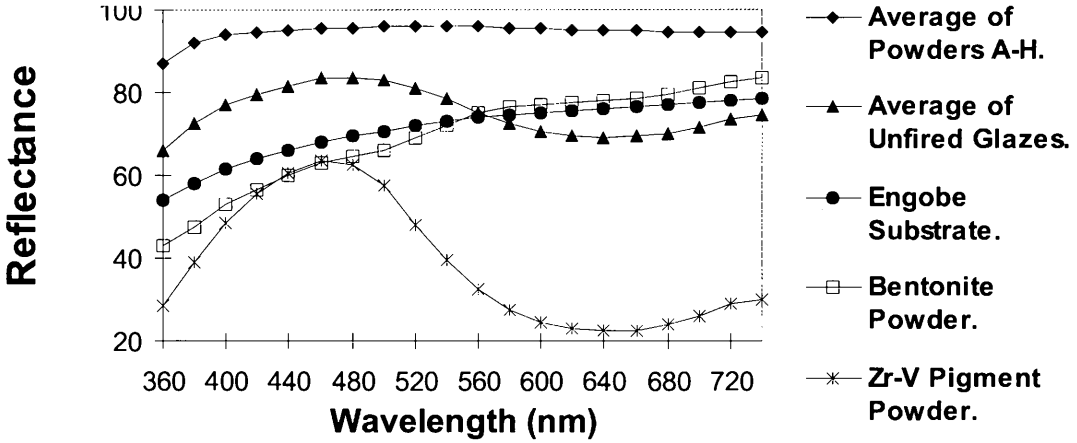


Figure 2. Reflectance curves from unfired individual batch materials.

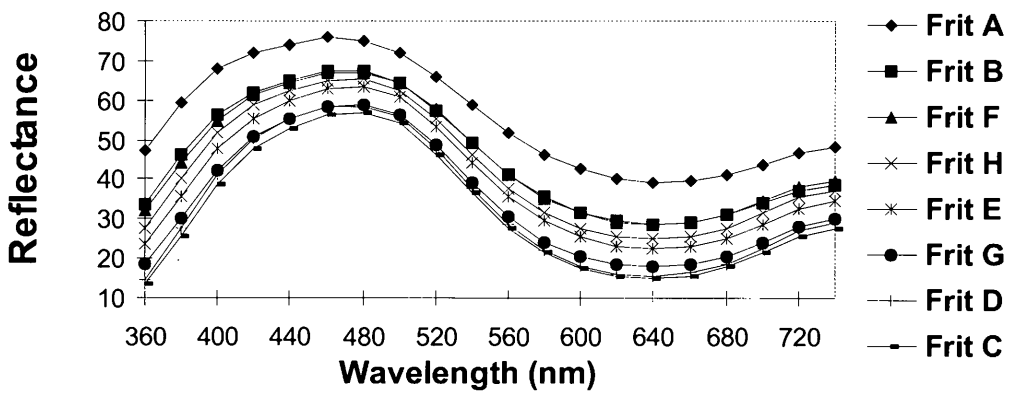


Figure 3. Reflectance curves from glazes fired to 1000°C.

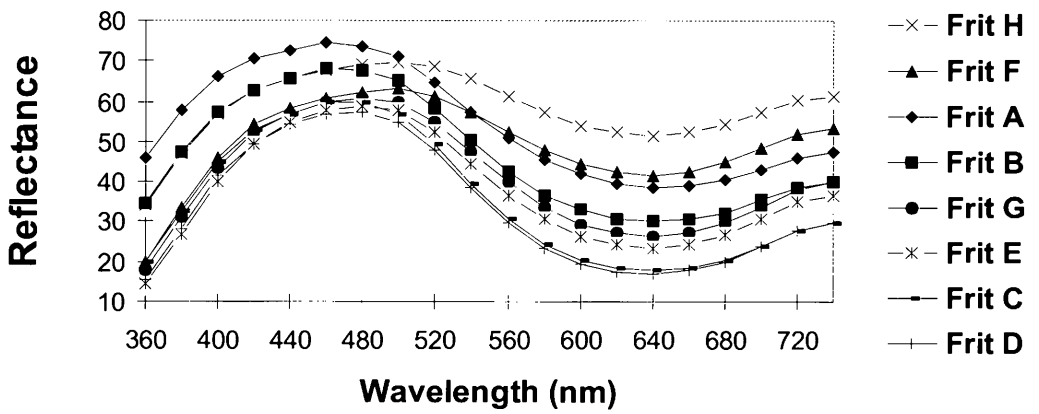


Figure 4.Reflectance curves from glazes fired to 1100°C.

3.2.- STATISTICAL ANALYSIS OF FRIT OXIDES EFFECTS ON COLOR VALUES

From the experimental results, the following statistical models were developed for predicting fired color values as a function of the frit composition for glazes batched with 2% Zr-V:

$$K/S = 1.9 - 1.4(ZrO_2) + 24.2(SrO) + 30.4(SrOxZrO_2) - 22.7E\text{-}3(SrOxT) - 3.6(Al_2O_3/alkali) + 2.6(Al_2O_3/alkali)^2 \quad (3)$$

$$(R^2 = 0.95)$$

$$\Delta E^*_{1050\ to\ 1100oC} = 5.0 - 76.0(ZrO_2) + 15.7(SrO) - 49.3(SrOxZrO_2) + 26.8(Al_2O_3/alkali) - 22.5(Al_2O_3/alkali)^2 \quad (4)$$

$$(R^2 = 0.98)$$

where oxides are in molar equivalents. Only oxides listed in equations (3) and (4) were found to be statistically significant ($t > 2.0$ for 95% conf. level) within the particular experimental range tested, although it should be noted that autocorrelations existed between the CaO and Al_2O_3 levels (+) and the alkali and SiO_2 levels (-).

The statistically adjusted oxide effects are shown graphically in figures 5 and 6, with the model standard error as error bars. Data for the plots were generated by inputting the range of composition tested for an individual oxide into the models while holding the others at their average levels. The resulting plots uncover the true, unconfounded effects of individual oxides based on model interpolations.

Figures 5 and 6 illustrate that increases in ZrO_2 raised color strength (K/S) in the presence of SrO but lowered K/S when ZnO replaced SrO (5(a)). Higher ZrO_2 improved color stability (lower ΔE^*) in all cases (6(a)). Higher SrO is shown to have significantly raised K/S only when ZrO_2 was present and had little effect without ZrO_2 (5(b)). However, the overall color stability was lowered with increasing SrO (6(b)). The nonlinear effect of the Al_2O_3/alkali ratio is such that with higher ratios, color strength (5(c)) and stability (6(c)) were lowered in frits with ZrO_2, but the reverse occurred in frits without ZrO_2.

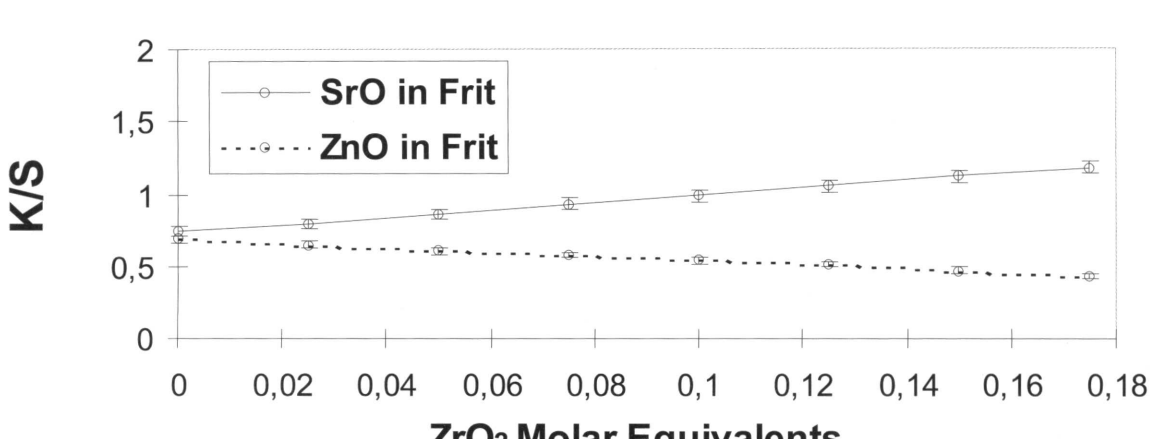
From the color measurements, statistical analysis and inspection of fired tiles, it was confirmed that the highest color strength was achieved with high levels of fritted ZrO_2 and SrO in systems without ZnO. However, replacing SrO with ZnO in otherwise the same compositions resulted in low color strength, high opacity and the best stability. Overall, frits without ZrO_2 yielded poor strength and stability which tended to improve somewhat with higher Al_2O_3/alkali levels. Now an effort was made to find a physical basis for the results.

3.3.- FIRED MICROSTRUCTURE ANALYSIS: XRD, SEM & EDS

Figure 7 displays the weight percent zircon in glazes batched with the eight experimental frits (A-H) and fired to 1000°C and 1100°C. Under each frit label are the oxides found to be significant by the statistical analysis. In frits A-D, zircon could precipitate from the frit in addition to the 2% Zr-V pigment from the batch. In E-H, only a maximum of 2% zircon from the pigment could be detected.

In A, which contained ZrO_2, ZnO and an Al_2O_3/alkali ratio of 0.6, nearly all of the fritted ZrO_2 precipitated to form zircon. This frit produced the most opaque and stable glazes. In B, which was nearly the same formula as A except that the Al_2O_3/alkali ratio was lowered, much less zircon formed, even though the melt viscosity was lower. Further XRD analysis revealed that crystalline ZrO_2 monoclinic and tetragonal phases formed by 1000°C in B due to the lower viscosity. Although these phases weren't detected in samples fired to 1100°C, zircon formation at lower temperatures from crystalline ZrO_2 would be

slower than directly from the melt. Thus, in the higher viscosity medium (frit A), more zircon formed because ZrO_2 wasn't tied up in crystalline phases at low temperatures. No Zr-V dissolution was observed in A or B.



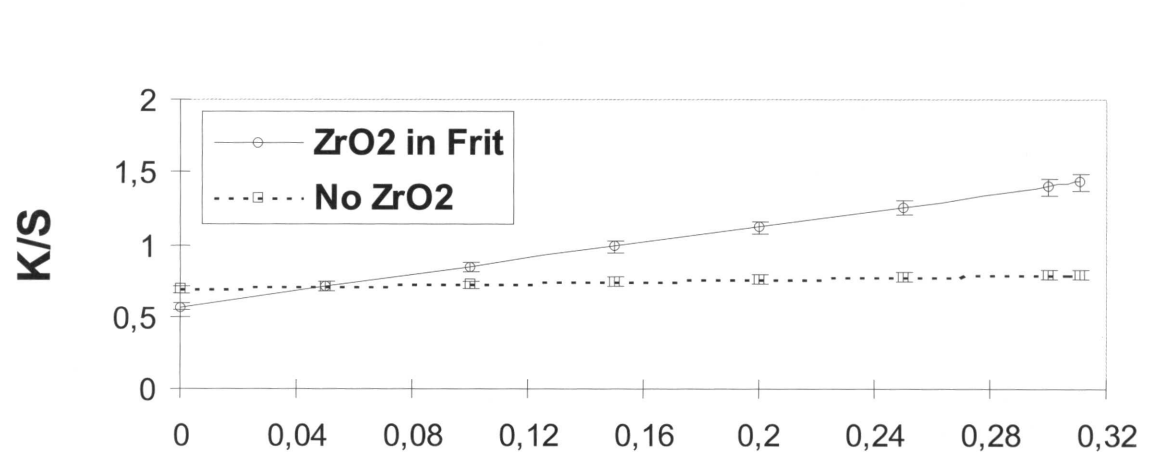
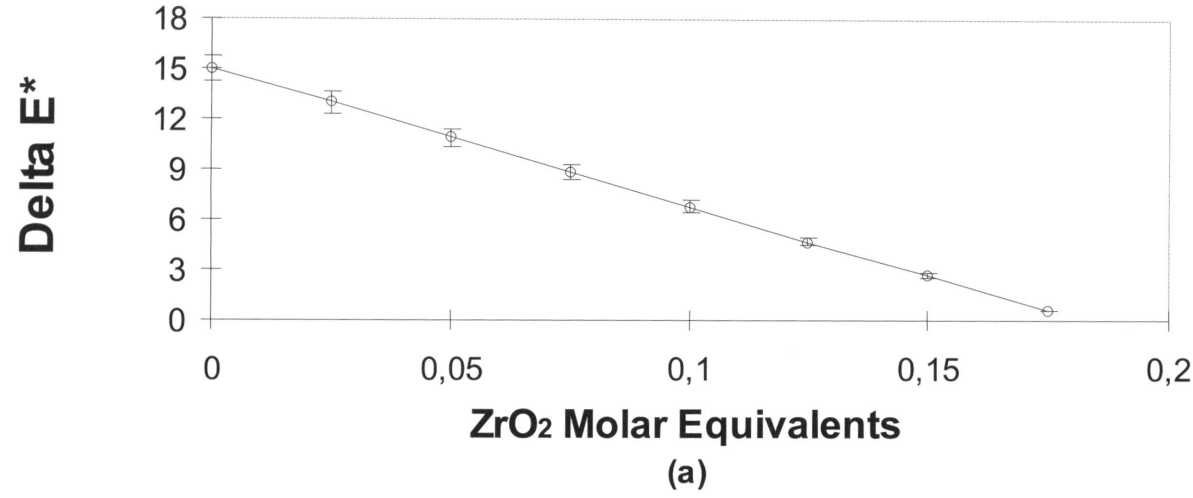
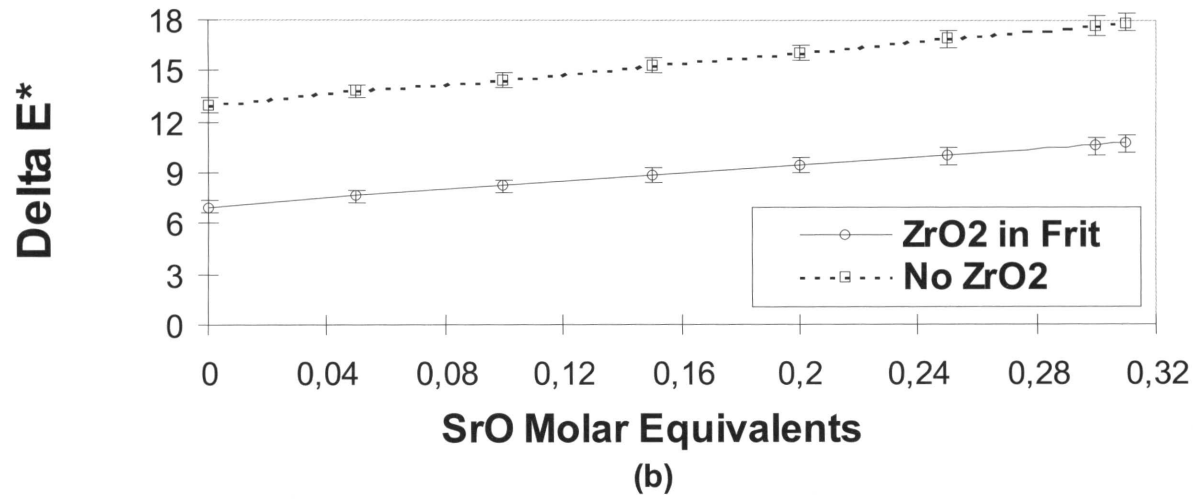


Figure 5. *Statistically adjusted effects of (a) ZrO_2, (b) SrO and (c) Al_2O_3/alkali ratio on the glaze color strength (K/S).*





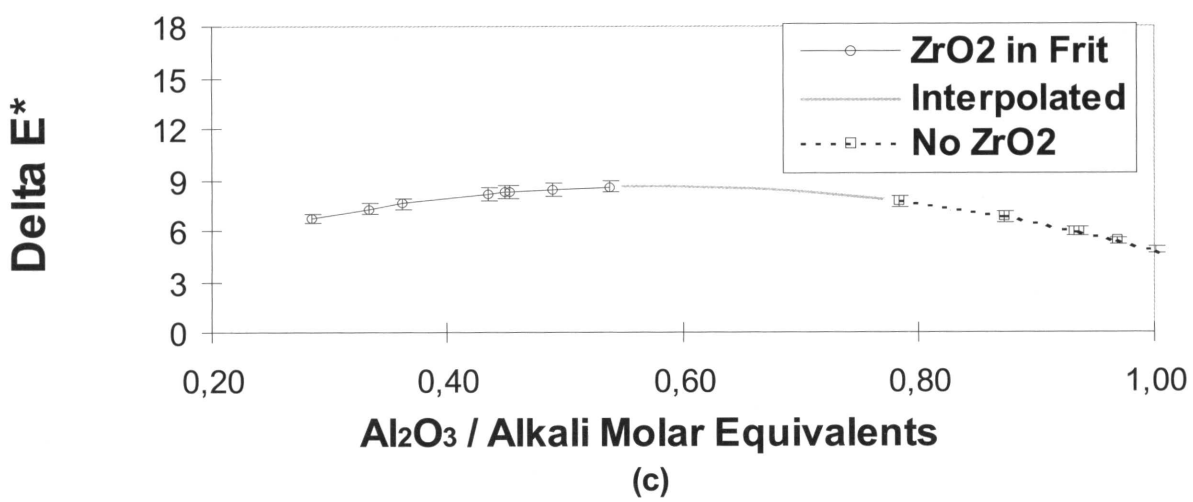


Figure 6. Statistically adjusted effects of (a) ZrO_2, (b) SrO and (c) Al_2O_3/alkali ratio on the glaze color change from 1050°C to 1100°C (ΔE^*).

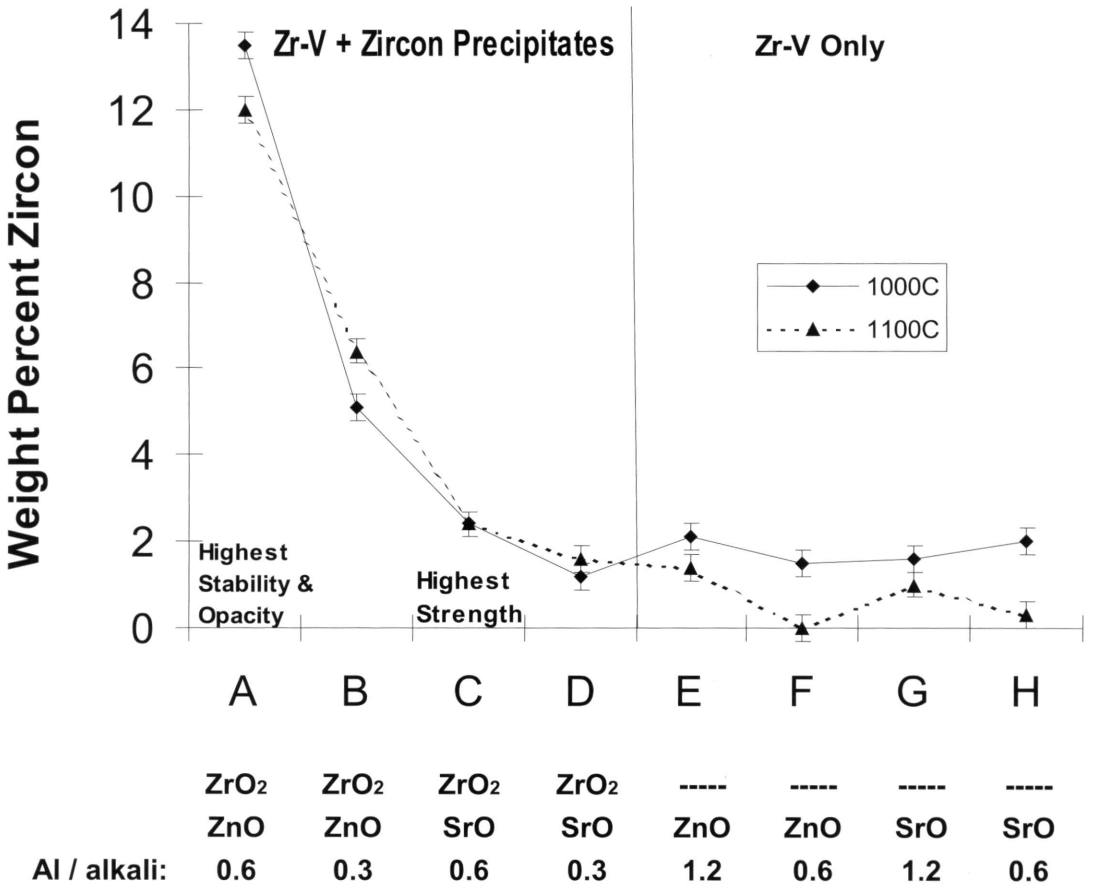
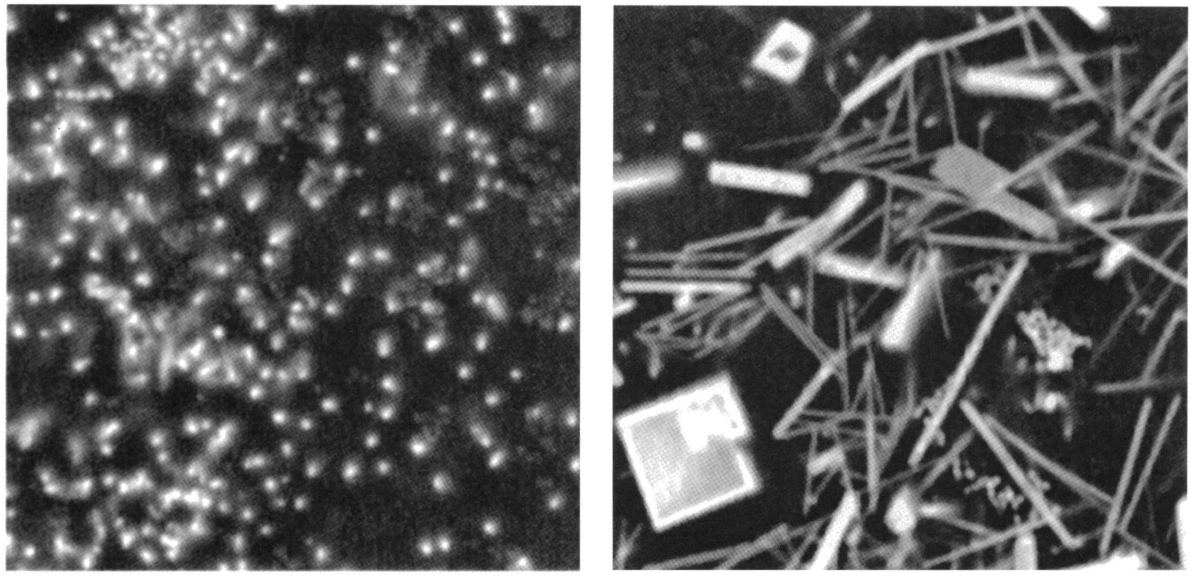


Figure 7. *Zircon content in fired glazes originally batched with 2 wt. % Zr-V. (Lines are drawn as guides to the eye)*

The Al_2O_3/alkali ratio in A and B also effected the morphology of zircon precipitates. The SEM micrographs in Figure 8 illustrate that small, spherical particles (8(a)) formed in the high viscosity medium provided by frit A, where a lower ratio and correspondingly lower viscosity in B (8(b)) produced fibrous zircon. The result was a superior scattering of light, opacification and whiteness in glazes made with frit A.

Overall in both A and B, XRD and SEM analyses showed that zircon crystallization occurred rapidly below 1000°C and was nearly complete by this temperature. Correspondingly, variations in peak temperature had little effect on crystal formation and the resulting fired optical properties. Thus, frits A and B yielded the most stable color.

In C and D, where SrO replaced ZnO in formulas otherwise the same as A and B, no zircon crystallized. The SrO substitution completely prevented zircon from precipitating and resulted in transparent glazes with the highest color strength. Compared to traditional transparent frits which contain no ZrO_2, C and D also yielded relatively good stability because the fritted ZrO_2 lowered zircon pigment solubility. A physical basis for SrO preventing zircon crystallization could be related to its effect on the melt viscosity. Further experimentation revealed that when SrO replaces ZnO, the slope on the viscosity versus temperature curve increases without appreciable changing the glass softening temperature (Ts). A high viscosity near Ts and a viscosity which increases rapidly below Ts would result in fewer nucleation sites and lower crystallization. This could especially influence zircon formation, which occurs rapidly at relatively low temperatures (~ 900-1000°C) during the firing cycle.



(a) (b)

Figure 8. *Zircon precipitates in glazes batched with* ***(a)*** *frit A, Al_2O_3/alkali ratio = 0.6; and (b) frit B, Al_2O_3/alkali ratio = 0.3. Displayed are glazes fired to 1100°C; SEM magnification X4000. All particles shown are zircon which precipitated from the frit during firing, except for the large square particle in* ***(b)****, which is Zr-V pigment with a lower side length of 4 μm.*

As shown in Figure 7, all experimental frits without ZrO_2 (E-H) exhibited significant zircon pigment dissolution during firing. Simultaneous pigment dissolution and crystallization of different species increased with higher peak temperatures and lower Al_2O_3/alkali ratios. In E and F, which contained ZnO but no SrO, diopside and hardystonite crystallized. In G and H where SrO replaced the ZnO, wollastonite and a $SrCa_2Si_3O_9$ phase formed. The pronounced Zr-V dissolution and crystallization in these glazes resulted in very poor color strength and stability.

3.4.- ZIRCON PRECIPITATE MORPHOLOGY EFFECTS ON GLAZE COLOR

Figure 9 compares the influences of Zr-V blue pigment and zircon precipitate contents on the fired color. Higher Zr-V levels caused simultaneous proportional decreases in lightness (L*) and increases in blueness (-b*). The linear changes occurred with approximately the same magnitude in uniform L*a*b* color space. However, zircon precipitation from the frit effected L* and b* to different degrees. A change in crystalline zircon from a low content of fibers (frit B) to a high content of spheres (frit A) altered the blueness to a lesser degree (higher slope on plot) than the lightness. In glazes made with frit A, many of the spherical crystals were 0.4-0.5 mm in diameter. Scattering of blue light (0.4-0.5 μm wavelength) would be enhanced by spherical particles of this size, especially with zircon's high index of refraction, and would partially reduce the blue color loss from zircon's whitening effect.

The relationship between L* and b* for 96 different fired glazes batched with 0% to 5% Zr-V, and prepared with the range of frit compositions and firing temperatures previously tested, is shown in Figure 10. Data points above the second order polynomial regression curve represent glazes with a higher than expected lightness value for a given blueness. These data points are from coatings that precipitated 0.4-0.5 mm spherical zircon, which tended to preserve the blueness (-b*) at high L* values.

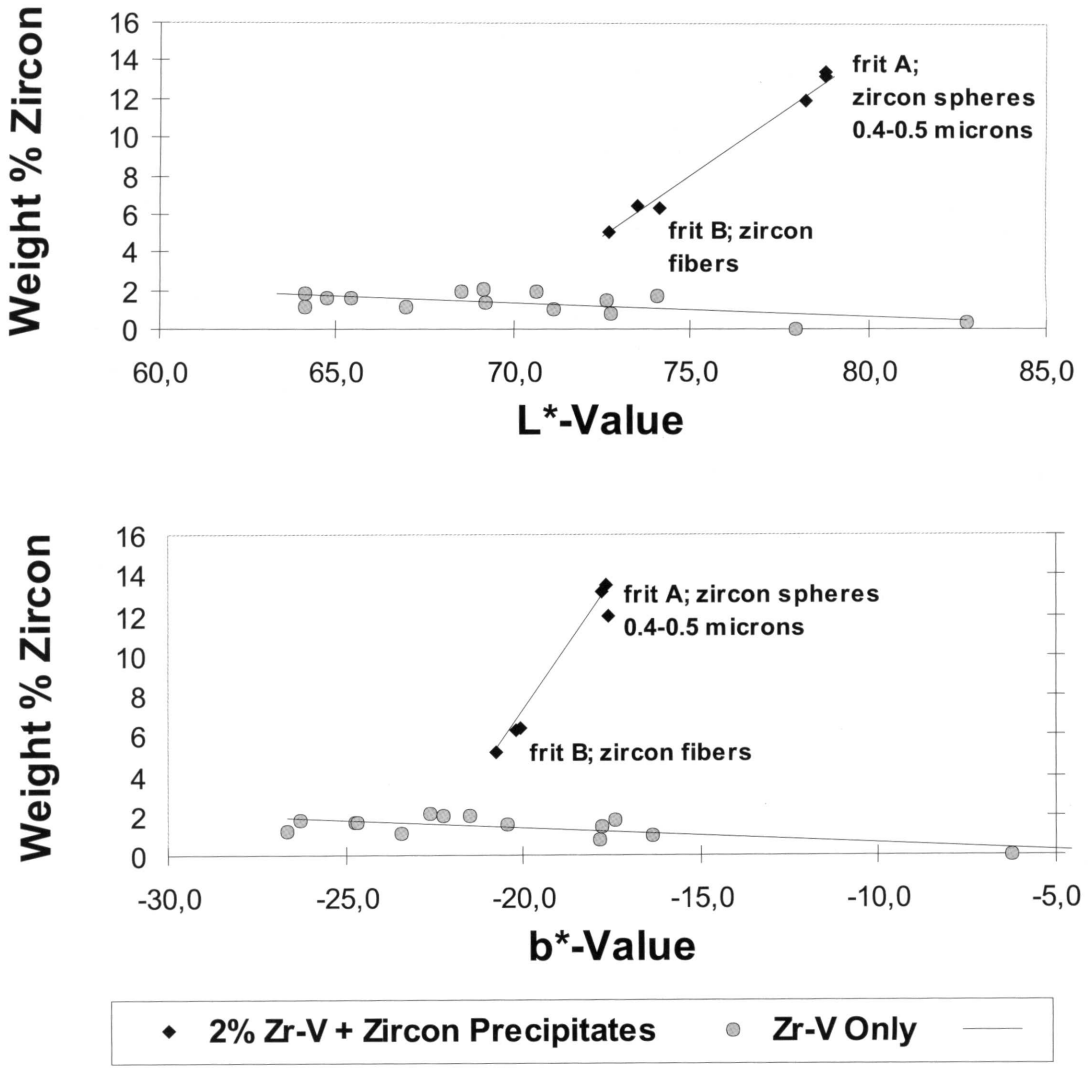


Figure 9. Weight percent Zr-V and zircon precipitate vs. lightness (L) and blueness (b*).*

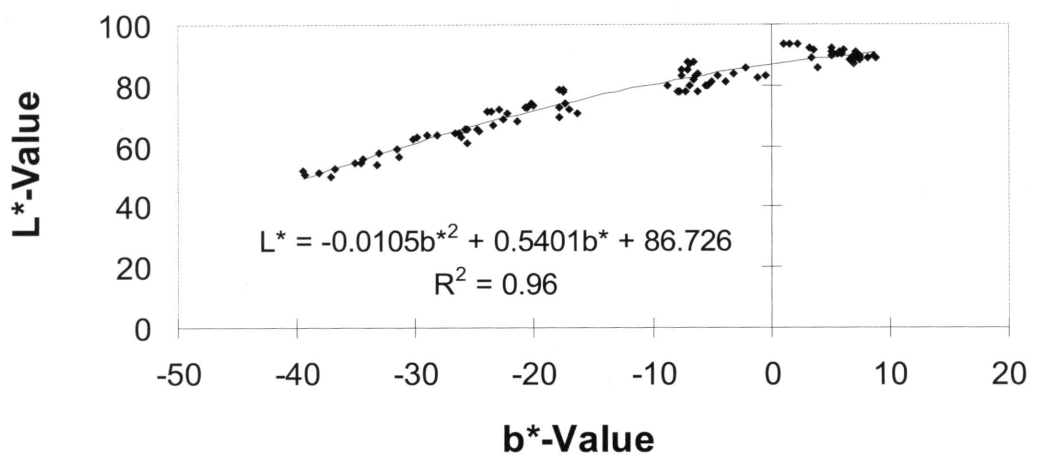


Figure 10. Relationship between lightness (L) and blueness (-b*) for 96 fired glazes batched with 0% to 5% Zr-V blue pigment, and prepared with the range of frit compositions and firing temperatures tested.*

4. CONCLUSIONS & FUTURE WORK

Optimum color strength and stability were achieved for both opaque and transparent glazes with frits which incorporated a high level of ZrO_2. The quantity, size and morphology of opacifying zircon that precipitated from the frit during firing were mainly dependent upon the ZrO_2, ZnO, SrO and Al_2O_3/alkali levels.

Experimental frits with ZrO_2 formed consistent microstructures, color and gloss over a 100°C peak temperature range. These frits provided for a low zircon pigment solubility and rapid, low temperature crystallization of only zirconium based species. Fritted ZnO enhanced zircon crystallization and tended to produce very opaque coatings, while replacing ZnO with SrO in the same frits prevented zircon from precipitating and resulted in relatively stable transparent glazes. The coatings with SrO exhibited the highest color strength and deviated from the customary industrial practice of excluding ZrO_2 from frits for transparent glazes. Although raising the Al_2O_3/alkali ratio increases the melt viscosity, it resulted in a greater quantity of zircon crystallizing, more spherical precipitates and superior opacification. Unique light yet high-chroma blue color was produced with Zr-V pigment by crystallizing 0.4–0.5 mm zircon particles in the fired glaze through control of ZnO and Al_2O_3/alkali levels. Particles of this size and refractive index tend to enhance the scattering of 400-500 nm blue light while increasing the lightness.

Overall, frits without ZrO_2 exhibited significant crystallization of Ca-based silicates and pigment dissolution, both of which increased over the 100°C peak temperature range and resulted in poor color and gloss stability. Increasing the Al_2O_3: alkali ratio somewhat improved color stability with these frits.

Future work should be performed with a wider range of frit oxide compositions and firing profiles. Other zircon pigments and matte glazes should also be tested. In addition, experiments should be conducted to determine the effects of SrO and other oxides on the melt viscosity and resulting quantity and morphology of zircon precipitates.