

GLAZES THERMAL EXPANSION

Description

The way to deal with crazing or shivering is to understand what thermal expansion is, how it relates to the chemistry to the glaze and practical ways to calculate it. There is a rich mans and poor mans way to fit glazes.

Article

Almost any fired ceramic object experiences expansion as it is heated and contraction as it is cooled. A typical piece of functional ware is a two-part system in that body and glaze possess independent expansion characteristics. However the glaze is fixed to the underlying body and is therefore obliged to conform to the body's thermally induced size changes. Stresses are thus part of what we could call a 'glaze-body marriage'.

To succeed a marriage needs two important things:

- **Compatibility:** In a body/glaze 'marriage' they must have compatible expansion curves. Key fact to remember is that fired ceramic is strong under compression but very weak under tension. If a glaze is stretched onto the body at any time (even as a result of contraction due to quick surface cooling) it will likely form a network of cracks to relieve the stress. This is why having a glaze under slight compression is good.
- **Firmly bonded:** In most cases a significant reaction layer or interface does bond them together. This buffer forms as the liquid glaze melt attacks the body, penetrating into it and forming intermediate compositions layered against the body. The temperature, soaking, cooling rate, glaze and body chemistry, and material particle sizes all affect the development of the intermediate zones. On one extreme earthenware will have a poor interface while on the other high temperature slow fired porcelain will have a highly developed one. Fritted glazes will typically be more reactive and produce a better interface.

Crazing (the fired glaze forms a network of crack lines) and shivering (the fired glaze flakes off at rims and edges) are among the most common problems glaze technicians have to deal with. Many manufacturers and individual potters suffer serious loss of product strength and compromised hygienic properties because of these. Unfortunately some do not even realize it.

Glazes that have a higher expansion than the body by implication also contract more on cooling. This puts the glaze under tension, stretching it, sort of a "size 6 mug in a size 5 glaze" situation. If you would like to demonstrate some dramatic crazing, mix nepheline syenite and water and apply a thick layer to a test piece made from a typical cone 10 clay body and fire. Tension can also occur where a normally compatible glaze is subjected to stretching by a moisture absorbing and expanding body (e.g. water reacts with alkaline or alkaline earths remaining uncombined in under fired bodies). However I will assume that your clay body is either vitreous or contains additives to prevent this.

Shivering is the opposite, a "size 6 mug in a size 7 glaze" situation where areas of the glaze unable to 'hang on' can actually flake off the fired ware. If you would like to see some pretty dramatic shivering, make a body composed of ball clay and silica 50:50 and apply a typical cone 10 low-feldspar glaze.

There are plenty of common misconceptions about how to deal with crazing problems, most tend to attack the symptoms instead of the real cause, thermal expansion mismatch. It is not difficult to create a glaze:body marriage that survives the initial contraction test of cooling slowly in the kiln. The real trial is achieving a 'working fit' that ensures the glaze is under the correct amount of compression over the entire range of heat/cool cycles it will experience during many years use. You must create a two-part system that achieves a degree of compression in the glaze that is within the "interfacial layer's" ability to hold it comfortably over a long time. Thus, compressive stress actually becomes a contributing factor to the ability of the 'marriage' to stand up under thermal attack during use.

Expensive Way to Fit Glazes

If you can afford an instrument called a **dilatometer**, then you can take a much broader view of thermal expansion. This device is the standard instrument used to measure thermal expansion of small test samples from room temperature to set point (for glazes) or an arbitrary temperature (for bodies). It is basically a small furnace in which a small bar made from the glaze or body is heated. The bar is positioned in a refractory tube against which a sensitive push-rod measuring probe rests (newer designs use lasers). Length changes during a fixed-rate heat-up from room temperature to the softening point of the glaze are recorded and plotted as a 'dilatometric curve'.

Visualize a reversal of the dilatometric heat-up curve: On cooling, a molten glass solidifies at its "set point". From here, it is capable of accepting differential stress from the body to which it is attached. The total thermal expansion could be considered as the percentage increase in length of the bar at its 'set point'. However glazes have different set points so a more useful standard has evolved: divide the total expansion by the number of degrees taken to produce it (since the curve is often fairly linear over the range this value is reliable). This produces a figure that represents the change in length per °C. By the time the mathematics are finished, the result for ceramics is a value in the 10^{-6} decimal range. Thus an expansion of '7.0' is really 7.0×10^{-6} in/in/°C (the length units are obviously arbitrary, it could be cm/cm/°C if you like).

As already stated, the ideal glaze should have a slightly lower expansion than the body to put it under some compression. It is thus not difficult to imagine a technician superimposing the curves for variations of a glaze on top of the one for the body to find one whose curve tracks a little lower than the body. How much lower? That would be determined by that companies experience with the type of glaze and body they use.

Cheap Way to Fit Glazes

An interesting point is that although a dilatometer provides a graphic view of the history of thermal expansion for a glaze and body, the technician still has to decide what the proper spatial relationship between body and glaze curves should be. How do they do this? Other kinds of tests. They must subject ware to extreme thermal stresses and mechanical tests to try to induce crazing. Over the years a history of these test results and a record of how ware stands up over time produces the body of knowledge that enables them say where the line for a glaze should be in relation to a specific body. From that point on new glazes can be brought on line based on dilatometric testing without the need for all the other tests.

It may have already struck you that you can fit a glaze just fine without the use of a dilatometer. Industrial tests for glaze fit are not nearly as complicated as most people might think. While dilatometric curves of body and glaze are nice to have, isn't it the "acid-test" of subjecting the body-glaze 'marriage' to stress that tells the real story? Typically, multiple specimens of glazed ware are repeatedly subjected to an atmosphere of steam at high pressure, heated in air or boiling water, and then quenched in ice water. It is important to standardize the test. Make sure that the ware is thoroughly heated and cooled throughout on each cycle and examined closely to record results. Some have been able to translate the failure point in their tests to the expected failure rate in the field. For bodies with an absorption, it is also important to realize that body expansion can occur if, and when, water is absorbed. So in the above tests, an important element is long exposure to heat and being sure the ware is thoroughly and completely cooled (some people will put ware in a freezer overnight to take it well below the temperature of ice water). Many have standardized on a 5 minute cycle ice-water boiling-water test.

A second valuable test is fired strength. The idea is to glaze and fire a sample bar of the body, then break multiple specimens in a device that records the necessary force for each. Calculations and subsequent averaging yield a strength figure that can be compared with the unglazed body's strength. In this way, you can create a profile comparing strength with formulation changes designed to vary the expansion of the glaze. While achieving a high strength is good, it is important that a glaze not be under too much compression, this might produce stronger ware out of the kiln but under continued use it may eventually fail.

Another interesting observation you can make is a fracture test. Make a thin-walled vessel of the clay (as close to spherical as possible) and glaze it on the inside and fire. Then drop it on a concrete floor (cover your eyes). If the glaze is under compression the piece will almost explode into dozens of pieces, often with a popping sound (glazed edges of shards will be razor-sharp). If the glaze is crazing the piece should break with a dead thud into many pieces with some grainy material produced by disintegration along break lines (because of craze-induced weakness). A vitreous piece with a fitted glaze should be strong and break into only a few pieces. Glazed edges on shards should follow the contour of the crack as if the body and glaze were one.

Using Calculation to Fit a Glaze

It might seem logical that we measure the thermal expansion of each of the materials used in a glaze recipe and then calculate the expansion additively based on the percentage of each. However such an approach is completely wrong. The problem with calculating glaze expansion from the expansions of the raw materials is that those expansions are a product of the mineralogy and crystal structure of the material (or should I say: 'of the material particles') rather than its chemistry. The classic example of this is carbon. Graphite is a soft lubricating powder, diamond is the hardest material known. They have the same chemistry but different mineralogy. In ceramics the classic example is silica powder. It has a very high thermal expansion, particles of quartz are literally the 'kings of thermal expansion'. Fused silica (melted and then quickly solidified before it can crystallize) is the lowest (or one of the lowest) expansion ceramic materials known! How is that possible? Because quartz is a crystal, fused silica is a glass. Yet they have exactly the same chemistry! This story can be repeated for almost any other raw ceramic material, they are almost all crystalline. Most materials are mixtures of minerals and even mixtures of different forms of the same mineral (and others).

A fired glaze is a glass, it is not crystalline. Thus its expansion is a theoretical product of the contributions of the oxides that its chemistry enumerates. Each recipe material contributes one or more oxides, the same oxide can be contributed from a number of materials in the recipe (SiO_2 for example). Thus calculating a glaze's expansion additively from the percentage of each oxide is practical (although there are caveats as you will see later). INSIGHT knows the expansion of each of the oxides (expansions of ceramic oxides, especially the common ones, are well known) and calculates the expansion of the glaze as a whole from the formula. Thus expansion is a formula level property.

We must be aware of the limitations of this to employ it effectively. First, it is not possible to calculate a glaze's absolute coefficient of thermal expansion accurately. Various mathematical techniques have been employed that produce good results within certain systems, but there is no universal method that works everywhere. Remember also that dilatometers have their own absolute vs. relative interpretation problems and a glaze on a piece of ware might not exhibit the same thermal expansion as a test specimen (for a variety of reasons).

The simple additive method of calculating expansion is the most common and has proven quite workable. Why? Different authorities disagree on absolute expansion but they generally agree comparatively. Also the differences between oxide expansions are so profound that calculations unquestionably give direction. So remember: Calculations produce relative, not absolute thermal expansion values. But isn't that what we need? If a glaze is crazing then we need to take its expansion downward. Do we need an absolute number to represent the expansion of the glaze and clay? No. This is why calculated expansion is effective, oxides that increase or decrease it are well known. This is similar to driving with a broken speedometer and judging your speed according to surrounding traffic. Little old ladies are likely driving below the limit, teenage men likely above. Different roads are like different clay bodies.

How much should you adjust expansion value to fix a crazing problem? If a glaze is crazing soon after a piece is fired this is an indicator of a serious, not a minor problem. Thus, if the expansion of the crazing glaze calculates to 7.5, then try to move it to 7.0. After stress testing, then move it more or less.

Establishing Calculated Expansion Targets for Your Clay Bodies

Anyone who has done a lot of calculations on recipes they have tested on their own clay bodies soon learns to predict whether or not new ones will craze. However, remember that calculations are relative within 'systems', although a dolomite matte may need to calculate to 7.0 to fit your body don't expect a highly fluid zinc lithia crystalline to work at the same calculated value.

Consider an example of a silky matte cone 10 glaze.

Silky Matte

CUSTER FELDSPAR..... 33.0

DOLOMITE..... 23.0

EPK KAOLIN..... 22.0

SILICA..... 22.0

FORMULA & ANALYSIS

*CaO .41 8.33%

*MgO .41 5.90%

*K₂O .12 3.97%

*Na₂O .05 1.16%

*Fe₂O₃ .00 .23%

*TiO₂ .00 .09%

*P₂O₅ .00 .05%

Al₂O₃ .44 16.25%

SiO₂ 2.98 64.02%

COST/KG .23

RATIO 6.70

EXPAN 6.45

The company using it has found it to be successful with an ironware brown body at *cone 10* reduction. Not only does it not craze but it considerably strengthens the ware. This is important because such bodies are usually fairly weak (iron bodies develop their characteristic warm color as a function of stopping the firing short of vitrification). A glaze that fits poorly on such a clay can cut its strength quite dramatically whereas one that fits well can significantly increase strength. In the case of this company, they were producing ware that was tougher than others who used a stronger clay body but with a poorly fitted glaze. In fact, the strength difference in the ware was so great that simply breaking a mug of each made it obvious which was stronger.

Since this glaze is known to function well, the calculated expansion of any other glaze using the same or a similar material suite can be compared and fairly reliable fit predictions can be made.

Although a dilatometer-equipped factory technician correlates strength and thermal stressing glaze fit tests to actual measured expansions, you can correlate to calculated numbers. This method is not quite as precise but it is more flexible in that it allows prediction of fit without having to make fired samples and measure them. Predictions become increasingly accurate with time and experience.

How expansion is calculated?

As already noted, it has been shown that thermal expansion is considered an additive property (with the limitations noted). This means that a knowledge of the expansion values of a glaze's constituent oxides makes it possible to calculate the expansion of the glaze as a whole by simple addition. The equation for a glazes calculated expansion, G, is:

$$G = E_a \times P_a + E_b \times P_b + E_c \times P_c \text{ etc.}$$

Where a, b, and c are oxides, E is the oxide expansion and P is the proportion of oxide in the glaze. For example, if a glaze consists of 50% oxide A, which has an expansion of 5, and 50% oxide B, which has an expansion of 10, then the expansion is:

$$(.50 \times 5) + (.50 \times 10) = 7.5$$

Remember, this is only an approximate way to deduce a glaze's expansion since other factors (especially interactions) besides the oxide make-up are involved. The issue is further clouded by the fact that basic expansion data from different authorities can vary, use different units, and be intended for use with molar formulas or percentage analyses. There is, thus, the challenge of either averaging the data or accepting the set one feels is more applicable or credible. In actual practice, I have found this to be less of an impact than expected since there is good agreement on the oxides that typical comprise 90% of the glaze (e.g. the huge expansion contributions of Na₂O and K₂O, moderate CaO, low MgO, Al₂O₃, SiO₂, B₂O₃).

There are, of course, irregularities not yet accounted for. One interesting exercise is to page through the frits in DOS FORESIGHT and compare calculated expansion figures with the physical expansion values shown for many of them. For most the correlation is good, but for some there is a considerable discrepancy (B and Li containing frits are examples, this is understandable since these two oxides are known to have non-linear response to proportion). Like the drug industry, we must also consider interactions between oxides, this is not well understood.

The Art Glass Industry: An interesting parallel

The importance of knowing expansion is paramount to glass artists who cool their thick pieces in minutes instead of hours. Pieces of glass of different colors and chemistry are routinely joined and they must be expansion compatible to cool without cracking. The supply chain considers thermal expansion a fundamental piece of information that should never be separated from a glass or glass mix. 90-compatible, for example, refers to soda glass that has an expansion of 90×10^{-7} . Built in stresses that cause failure over time are a great concern also and glass artists use hot/cold tests and special instruments to identify and deal with them. Ceramic artists can take a good lesson from this.

Thermal Expansion Numbers Provided with Frits

Frit companies normally publish expansion numbers with their frits. These may be derived by measurement in a dilatometer or by calculation. Various frit companies have different ways of calculating (usually involving the standard additive process with exceptions). Ferro, likely pretty typical, calculates coefficient in degrees C using Hall factors if available and M & H factors otherwise. The numbers are the COE $\times 10^{-6}$. When they measure the thermal expansion of glazes or frits in the laboratory they log the expansion change between 0-450 degrees C using a 3 degree C per minute heating rate.