THE FORMULATION OF CERAMIC GLAZE USING SODA-LIME SILICA GLASS

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Abstract
The properties of soda-lime silica glass greatly determine the characteristics of the glaze formed when used as cullet in formulating a ceramics glaze. Meanwhile this practice is found common among ceramist and potters making self made glaze in Nigeria. The availability of waste soda lime silica glass has made it readily available for use when using cullet as an optional means of glaze formation. Many of the elements making up soda lime container glass are the same as those used in glaze formulations, although in somewhat different proportions. This Best Practice describes some of the issues involved with using recycled soda lime silica glass as a constituent of ceramic glaze formulation. Although the exact content of soda lime container glasses vary somewhat by manufacturer, color, and container application. This paper therefore discuss the availability and operation of this particular type of waste glasses for formulating a ceramics glaze with the understanding of soda ash as the major flux which has a relatively high thermal expansion and poor resistance to heat.

Introduction
In the last four decades, intense research work has gone into ceramic glaze development aimed at a better knowledge and understanding of glaze materials and their properties, therefore widening the art of glaze making and application. Fournier (1976) define glaze as a sort of glass differing from window-glass and glass ware in its lower thermal expansion and higher alumina content, which increases its viscosity and help it to adhere to the body. Parmelle (1973) also described glaze as a mixture of complex silicates and borates which is applied on ceramic products before heat treatment to produce the glossy-smooth or matty finish as desired. This therefore means that without silica, there will be no glass or glaze.

In theory of glass structure, silica is regarded as the network former while the fluxing oxides (elements of lower valences) as network modifier because they break the silicon-oxygen bond and therefore lowering the melting temperature of Silica. In practice, glasses containing only potash or soda and silica, can be made to melt as low as 780°c (with potash) or 850°c (with soda) but they become soluble in water and therefore useless as glasses or glazes. Limestone was later discovered to be insoluble in water if it replaces some part of the potash or soda. This is because the calcium atom, though about the same size as potassium and sodium can make a stronger bond with the oxygen atoms giving it a quarter-charge and also increase the melting point making the result insoluble in water. (Carty, 2002) explains that this combination is called soda-lime silica glass which forms the basis of common glass till date.

Generally glass makers like their melt to be fairly fluid, so it can be manipulated and they therefore use only a small quantity of alumina in the batch but ceramist need a viscous melt to prevent the glaze from trickling off the surface of their pots and they consequently use much more of it. Glaze properties and firing range depends on the type of flux used in lowering melting point of the silicate used. This is due to the component of alkaline fluxes and alkaline earth fluxes used in the

glaze and glass batches. Fluxes generally perform different functions in ceramic glazes. For example alkaline fluxes are soluble in water if not fritted, and if used directly affects glaze wares.

These fluxes are normally used in corrected proportion during glass production for producing glass of different properties, and in order to understand the rudiment of these fluxes and the kind of glass produce from such fluxes which will be the properties of the cullet used therefore creating effect on the glaze batch, further explanations gives a better view.

Components of Soda Lime Silica Glass and their Fluxing Properties

Alkaline fluxes

The alkaline are elements that react vigorously with cold water to liberate hydrogen gas and form alkali (Ababio 1990) the alkaline elements are mainly group 1 element which act as a strong flux in ceramics glazes, they increase fluidity of the molten glaze and have important influences upon development of colour, they increase the refractive index of the melt, and also increase the brilliancy, they have influence upon the thermal expansion, and also have a direct bearing on crazing.

The oxides of alkaline elements dissolve in water to form a very strong alkali which serves as basis of their solubility in ceramic glazes. According to Parmelle (1973) the alkaline element used by the ceramist also by the glass manufacturer are compounds of Sodium, Potassium, and Lithium, these are widely distributed in nature, chiefly as water-insoluble compounds or associated with other bases in complex insoluble silicates. The chlorides, carbonates, and nitrates of these elements occur naturally e.g (soda ash, borax, pearl ash) or prepared industrially are readily soluble and must be incorporated in frits to permit their use in the usual glaze slip.

Examples of Alkaline Fluxes used for making Soda Lime Silica Glass

Soda ash (sodium tri-oxo-carbonate (iv)) which exists in three states

a) Anhydrous (Na_2CO_3)
b) Monohydrates ($Na_2CO_3 .H_2O$)
c) Decahydrates ($Na_2CO_3 . 10H_2O$) commonly called washing soda

Soda ash as described by Reindl (2003) can be had in ample quantity and at a relatively high degree of purity for a low price. Soda ash is made industrially by the Solvay process with the use of ammonia gas. It's chiefly used by potters just because it's the main source of sodium for the ceramist with the exception of borax.

Alkaline Earth Fluxes

The alkaline earth elements according to Ababio (1990) are elements of group 2 in the periodic table; they include magnesium, calcium, barium, strontium. The oxides of alkaline earth element are reactive but less so than the alkaline element. Their ionization energy decreases as we go down the group, resulting in a corresponding increase in the reactivity of the elements from magnesium to barium. Calcium compound is a major flux in cullet and it's a constituent of all kinds of glazes. Calcium oxide contributes properties to mature glazes like.

a) Increase the hardness (resistance to abrasion)
b) Increase the resistance to weathering and the solvent action of water, and to dilute solution of the ordinary inorganic acids.
c) Increases the tensile strength
d) Lowers the coefficient of thermal expansion greatly as compared with the action of the alkalies.

Alkaline Fluxes and Crazing in Ceramic Glazes

Alkaline fluxes tend to exhibit the properties of high expansion and contraction during firing, Gregory (1992) explains that crazing is greatly associated with tension during cooling. Tension might develop when glaze contracts more than clay body. This means that there is difference in the co-efficient of expansion of materials of the body and glaze. Similarly rapid cooling of wares after a firing may cause wares to craze due to the thermal shock on the wares.

The following list shows the diminishing order of expansion as given by
Cooper & Derek (1978)

High Expansion Sodium Na
Potassium K

Calcium	Ca
Barium	Ba
Titanium	Ti
Antimony	Sb
Lithium	Li
Zinc	Zn
Magnesium	Mg
Zirconium	Zr
Tin	Sn
Aluminium	Al
Silicon	Si
Low expansion Boron	B

A glaze with a high proportion of sodium will tend to give a crazed surface and this can be changed by the substitution of part of the sodium for a flux with less high expansion, such as lithium David (2005). Alternatively, the addition of a small amount of boron, found in colemanite or calcium borate will also reduce crazing, because of its low expansion, it will be able to counteract much of the expansion effect of the sodium and render a non-crazed glaze.

Soda-Lime-Silica Glass

Soda-lime glass, also called soda-lime-silica glass, is the most prevalent type of glass, used for windowpanes, and glass containers (bottles and jars) for beverages, food, and some commodity items. Glass bake ware is often made of tempered soda-lime glass.
Soda-lime glass is prepared by melting the raw materials, such as sodium carbonate (soda), lime, dolomite, silicon dioxide (silica), aluminium oxide (alumina), and small quantities of fining agents (e.g., sodium sulfate, sodium chloride)

Soda Lime glass is the most common type of glass; representing 80% of all commercial glass. Soda lime glass is extremely important in our day to day lives because, it's used for windows, jars, jugs, and everyday drinking glass. Soda-lime Silica glass can be prepared by melting the raw materials, such as soda, lime, silica, alumina, and small quantities of fining agents in a glass furnace at temperatures locally up to 1675°C on a bed of molten tin, this method gives the sheet uniform thickness and very flat surfaces. Soda-lime glass is the base material for most clear, colored and patterned glass types Stotzel (1997). Green and brown bottles are obtained from raw materials containing iron oxide. Relatively inexpensive minerals such as trona, sand, and feldspar are used instead of pure chemicals. The mix of raw materials is termed batch.

Soda and lime are usually the principal flux used in forming glass, such materials can be use to form glazes for the ceramist. Glass cullet and are abundantly available as a waste materials all over the world, and the materials silica, soda and lime are very much abundant and cheap, and as a result glass can be made in great quantity and at low cost. Rhodes (1981) informs that in making glass, silica is usually used in form of white sand, soda is added as soda ash and lime is gotten from lime stone. Rhodes further explain that colours is obtained by adding metallic oxides such as iron-oxide manganese dioxide or cobalt, which eventually lower the melting point of glass.

All of these materials earlier mentioned are needed to form ceramics glazes which are already composed as one into glass cullet, where as cullet are cheaply available as waste or disposed resources, this therefore will reduces the stress of ceramist in seeking for materials to form glazes, thereby giving the opportunity of turning waste to wealth within the environment. Soda-lime glass is divided technically into glass used for windows, called float glass or flat glass, and glass for containers, called container glass. Both types differ in the application, production method (float process for windows, blowing and pressing for containers), and chemical composition (information below). Float glass has a higher magnesium oxide and sodium oxide content as compared to container glass, and a lower silica, calcium oxide, and aluminium oxide content. From this follows a slightly higher quality of container glass concerning the chemical durability against water, which is required especially for storage of beverages and food.

Experimentation

In order to understand the chemical analysis and the material composition of Soda Lime Silica Glass "SLSG", X-Ray Florescence was carried out on fritted and Non-Fritted Brown, Green and Clear White waste glasses. With the aim of composing glazes using SLSG as

a raw material supplying SiO_2, Soda Ash, and Calcium Oxide to the glaze.

Percentage Analysis of Non Fritted Soda Lime Silica Glass

SiO_2	70.00%
Al_2O_3	2.00%
K_2O	1.00%
Na_2O	14.00%
MgO	1.50%
CaO	9.00%
B_2O_3	2.50%

Results and Discussion

- From the results of the analysis carried out, it was obvious the soda lime silica glass has almost the same percentage of Silica with Potash Feldspar.
- It was also pertinent from the analysis that using SLSG as a major flux in composing a ceramic glaze may be a wrong approach as it has a very high percentage of Silica compare to the flux it's used for.
- On entering data analysis of soda lime silica glass to the glaze calculation software, SLSG was seen as a raw material supplying Silica, Calcium and Sodium to the glaze composition not as a material supplying Soda.
- Soda lime silica glass can be best used a raw material for composing a stoneware glaze rather than a flux that produces glaze defects likes Crazing and Running.
- Soda lime silica silica glass could also can be best used in composing a slip glaze

Conclusion

A cullet glaze is not a special glaze type. Many glazes could be reformulated to use cullet of Soda lime Silica Glass which is the most common type of glass seen as waste within the environment. Sodium is the main flux in soda lime silica glass and calcium is added to stabilize the Oxygen-Silica bond so as to make it non soluble in water. Sodium has the highest expansion of all the fluxes, therefore a glaze is likely to craze if it uses a high percentage of Soda Lime Silica Glass. Cullet of SLSG adds silica, Sodium, some calcium and maybe some magnesium to the glaze. The most valuable use for soda lime silica glass will be in slip glazes since these types of glazes have a high percentage of clay, meanwhile SLSG supplies sodium flux that is also low in alumina, since the clay already supplies a lot of alumina. Cullet fills the bill. Feldspar is an easier and cheaper choice if the extra alumina it adds to the mix is not a problem.



Results after Reduction Firing at 1200°c

Table 1: XRF Analysis of Fritted Soda Lime Silica Glass

Material	Composition		
	Green Bottle	**White Bottle**	**Brown Bottle**
SiO_2	71.520	72.120	69.250
TiO_2	0.085	0.082	0.08
Al_2O_3	1.890	1.890	1.970
Fe_2O_3	0.350	0.032	0.375
CaO	10.450	10.320	10.250
MgO	1.020	1.020	2.500
K_2O	0.214	0.215	0.190
Na_2O	13.570	13.850	12.560
Cr_2O_3	0.250	0.000	0.005
BaO	0.074	0.076	0.070
ZrO_2	0.024	0.023	0.022

Source: Central Research Laboratory FUTA

Molecular Formula of Clear Soda Lime Silica Glass

K_2O	0.0257	Al_2O_3	0.0475	SiO_2	2.8652
Na_2O	0.5082	B_2O_3	0.1047		
CaO	0.3459				
MgO	0.1202				

Table 2: Material Composition of Potash Feldspar

Material **Potash Feldspar**	**Composition**
SiO_2	66.250
TiO_2	0.20
Al_2O_3	17.70
Fe_2O_3	0.575
CaO	-
MgO	-
K_2O	0.190
Na_2O	14.560
Cr_2O_3	0.017
BaO	0.050
ZrO_2	-

Source: Raw Materials Research and Development Council

Table 3: Glaze compositions derived from Material Analysis of Soda Lime Silica Glass using Glaze calculation software Insight.

	Composition 1 in %	Composition 2 in %
White SLSG	30.31	-
Green SLSG	-	9.56
Potash Feldspar	5.84	39.96
Soda Felspar	13.77	20.02
Magnesium Carbonate	14.54	0.54
Ball Clay	18.82	27.67
Quartz	16.71	2.23

Source: Glaze Calculator Software

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