A Study of the Accessible Approach to Replace the Reservoir Silt Glaze with New Formula

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Abstract. The author engaged in the research work of utilizing Shihmen Reservoir silt to make ceramic glazes. It was shown to be specific and feasible. But due to the different accumulation of layers or batches, it has more instability. The author had ever been three times to collect silt in different sedimentation pond, and was confirmed its chemical composition to be have obvious differences by instrumental analysis. If you used a direct replacement, you could find significant differences in appearance when silt content above 20 %. The "seger's formula" of ceramic glaze was used as the theoretical basis for the composition, and then calculated by Excel's Solver tool. It was always made the similar effect with original if you gave proper constraints and the substitution principle.

Keywords: Ceramic arts · Reservoir silt · Glaze · Seger formula · Programming solver

1 Introduction

The author engaged in the research work of utilizing Shihmen Reservoir silt to make ceramic glazes. It was shown to be specific and feasible [1]:

a. Reservoir silt glaze is classified in the category of natural silt glaze, which involves more variety of trace elements and people generally consider it as a support to the performances of the glaze color and texture. According to practical results, we find that even though the Shihmen Silt Glaze production carries a smooth surface, it still preserves a reserved, implicit sheen and possesses a fine variation effect.
b. From present observation of the experimental results, the combination of the reservoir silt with feldspar, limestone, rice husk ash, and a few other materials, can create a diversity of tone, sheen, and crystalline effects for a quality glaze. And through the manipulation of the atmosphere in the kiln, whether by oxidation firing or reduction firing, we can retrieve more variation for the glaze to perform full extent.

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c. Based on experiment statistics, the maturation temperature of the glaze, which mainly contains reservoir silt, has quit a large range (from 40–50 °C or higher), therefore, uneven temperature within the kiln seldom becomes a cause for failure.
d. On the aspect of material preparation, to employ the reservoir silt to the ceramic industry can almost leave out traditional process of water tossing, the screening procedure only needs to eliminate a small portion of sand grains. According to practical executing experiences, the Shihmen Reservoir silt has more than 95 % of the content that can be taken into good account, moreover, the preparation procedures are not as complicated. If mass production is possible to achieve, the prime cost of the silt will be much more efficient to the economy benefit.
e. As for the succeeding glazes, with the formulas, which uses the similar modern raw material that relates to the calculation of the "Seger Method", we can find the conclusion where the Shihmen Reservoir Silt Glaze can reduce the needs of diverse raw materials, furthermore, making significant impact on narrowing down the time and labor cost.

But due to the different accumulation of layers or batches, it has more instability. The author had ever been three times to collect silt in different sedimentation pond, and was confirmed its chemical composition to be have obvious differences by instrumental analysis. If you used a direct replacement, you could find significant differences in appearance when silt content above 20 %.

2 Research Purpose

The ultimate goal of this research is to find an effective model that can more accurately and efficiently to solve the replacement of raw materials. Its purpose and its importance as follows:

a. provide the most efficient and economical means to achieve the task when the ceramics industry faced the instability of raw materials.
b. Contemporary ceramics have more stringent requirements for the glaze. This study hopes that through more detailed means to effectively recover the desired glaze forms.
c. the instability of reservoir silt component is the main question that it used in ceramic glazes. Problem solving can provide users with a higher degree of trust and for the use of reservoir silt have substantial positive environmentally friendly benefits.

3 Literature Review

3.1 Glaze Formula

Ceramic glazes are mixtures of oxides: silicon (SiO_2), aluminum (Al_2O_3) and other easy to melt oxides (mainly PbO, K_2O, CaO, Na_2O).

These oxides are positioned in the form of suspension in the surface of the already baked clay and during firing they melt (due to chemical changes). When dry, they create the glassy permanent coat.

The most common oxides that consist the synthesis of the ceramic glaze (baked or not) are: SiO_2, Al_2O_3, B_2O_3, Na_2O, K_2O, CaO, MgO, PbO. These are imported in the not baked glaze with the form of raw materials. These materials, available in the market, are mostly clays and frits. Mixing the aforementioned oxides we have a specific glaze. This mix requires specific quantities from each material, different for different baking temperatures. These quantities in percentages are the recipe of a specific glaze [2].

Glazes are expressed in several different forms:

a. recipe: a list of actual materials and weights, used directly to make the glaze.
b. Molecular formula: shows the relative proportion of molecules of flux, alumina and silica in the glaze. Must be converted to recipe to make the glaze.
c. chemical analysis: shows the percentage of oxides in the glaze. Also known as ultimate composition.
d. Seger formula: a special molecular formula, which makes it easier to compare glazes. It is also known as the "empirical formula" [3].

3.2 Seger Formula

A German ceramist, Hermann Seger (1839–1893), developed Seger cones for measuring temperatures in kilns. He also proposed writing the composition of glazes according to the number of different oxides in the glaze instead of listing the raw materials used in the glaze.

The oxides used in glazes are divided into three groups according to the way the oxides work in the glaze.

a. fluxes: This group of oxides functions as melter, and fluxes are also called basic oxides or bases. They are written RO or R_2O, where R represents any atom and O represents oxygen. So all the fluxes are a combination of one or two element atoms and one oxygen atom.
b. stabilizers: These work as stiffeners in the melted glaze to prevent it from running too much. They are considered neutral oxides and are writen as R_2O_3 or two atoms of some element combined with three oxygen atoms.
c. glass formers: These form the noncrystalline structure of the glaze. They are called acidic oxides and are written as RO_2 or one element atom combined with two oxygen atoms [3].

Above three groups can be represented by a formula: $RO \cdot xR_2O_3 \cdot yRO_2$. (x and y are the representatives for the mole ratio of R_2O_3 and RO_2.)

3.3 Benefits of Using Seger Formula

The main usefulness of the Seger formula is that it presents glazes in a way that is easy to compare. It is used for:

a. originating new glazes: Glazes with desired characteristics of color, mattress etc. can first be written as Seger formulas, selecting oxides that are known to produce the effects.
b. comparing glaze recipes: It is difficult to look at two recipes and see how they are different. If they are converted into Seger formulas, the differences can easily be seen.
c. modifying glazes: Glazes that change character, have problems etc. can be analyzed as Seger formulas, and directions for testing decided.
d. substituting materials: If a material is no longer available, other materials can be substituted by working out the quantities in the Seger formula [3].

Regarding the fourth function aforementioned: Other materials can be substituted by working out the quantities in the Seger formula, which has been reported by other studies [4–8].

3.4 Problems in the Practical Application of the Seger Formula

According to Yu and Hu (1999), the Seger formula has a considerable deficiency and limitation when it is used to express glaze. Specifically, only when the glaze has a neutral oxide of $A1_2O_3$ and an acidic oxide of SiO_2 can the Seger formula reflect the actual composition and properties of the glaze. When the glaze contains Fe_2O_3, Cr_2O_3, B_2O_3, TiO_2, and ZrO_2, the result produced using the Seger formula becomes complex and contains substantial errors [9].

Regarding the glaze characteristics and the numerical relationship involved in its expression, Lee (2006) reported that the numerical values and ratios (e.g., x, y, 1:y, and x:y) for predicting glaze quality and transparency by using the Seger formula were inconsistent among various studies [10].

These two studies show that despite the numerous advantages of the Seger formula, a substantial difference existed in the results obtained by previous studies because of various complex factors including glaze composition and firing conditions.

3.5 Optimal Algorithm in Glaze Recipe

Numerous software have been developed to solve problems related to ceramic calculation and databases, including Insight, GlazeChem, The Glaze Calculator, Matrix, Clayart, and GlazeMaster. These glaze calculation software and management systems provide convenient solutions to convert the chemical composition of glazes into glaze material recipes.

Some studies have proposed calculation solutions based on computer software [2, 11–18]. In particular, the office software Excel has been used for optimization calculations, and it is regarded as simple and easy and allows users to flexibly set constraints.

Both existing software and relevant studies have provided effective calculation models for converting the chemical composition of glazes into material recipes of glazes. However, whether the data obtained from calculations can be directly applied has not been clearly verified.

4 Research Methods

According to the research purpose, an experimental study was conducted to demonstrate the appearance difference in the pottery glazes produced using the new and original glaze formulas under the same firing condition. The degree of differences was observed based on the items, which are melting degree, liquidity, glossiness, shrinkage degree, transparency, crack degree, crystallinity, color, and texture, to evaluate the accuracy that can be achieved by the Seger formula used for material replacement. Figure 1 illustrates the experimental procedures and objectives.

a. The chemical composition of the used materials was remeasured to effectively concentrate on the research objectives. The selected clay carriers were identical, which were placed in the same kiln to control the firing conditions and exclude irrelevant factors.
b. To enable the recipes of the materials to approximate the numerical values constituting the Seger formula for the original glaze formula, the function of Solver in Excel was used for optimal computation. The aim of this study was to verify the accuracy of the firing results after material replacement; therefore, the factor of cost

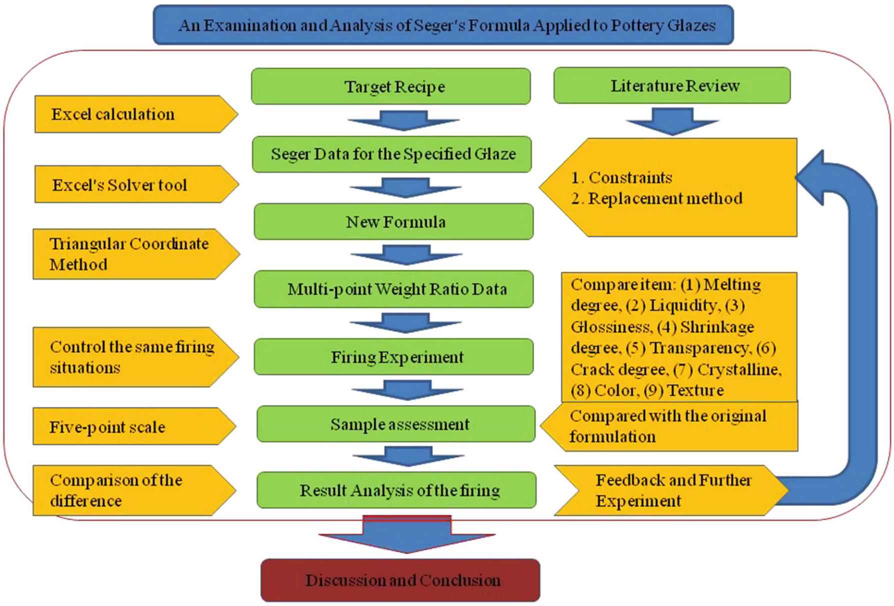


Fig. 1. Experimental procedures and objectives

(which was typically the primary consideration in previous studies) was not considered. The value differences in various oxides were summed, and the minimum value was adopted as the objective function value. Moreover, the literature was reviewed to examine the influence of x, y, 1:y, and x:y on the firing result, to set the constraints, and to enable the values in the new glaze formula to approximate that in the original glaze formula according to the theories of the Seger formula.

c. To extend the experimental points for glaze formulas, the calculated material recipes were used as the reference points for the triangular coordinate method, which was employed to perform the extended experiment based on multipoint weight ratio data, to determine the optimal glaze recipe.
d. When determining the accuracy of the firing results, the fired specimens produced using the original glaze formula were adopted as the standard samples for comparison with those produced using the new formula. The comparison was conducted based on the aforementioned items (e.g., melting degree and liquidity). To objectively determine the differences, three experts were invited to conduct the comparison by using a five-point scale. Therefore, the application of the Seger formula to the recipes of ceramic glazes can be evaluated quantitatively in terms of the result accuracy.

5 Implementation Process

5.1 Target Recipe

The primary objective of this study was to solve the replacement problem of varying batches of silt for the reservoir silt glaze. Therefore, particular glaze formulas were used as verification specimens (Table 1), the number and characteristics of which are as follows:

a. da112: This type of glaze has an excellent purple-gold color. Numerous gold and silver spots are scattered on the glaze surface, which are crystal metal oxide plates suspended in the glaze layer. They can reflect light and are thus shiny. The glaze is distinctive, similar to the natural aventurine.

Table 1. Experimental glaze formulas used in this study

Image						
No.	da112	da138	db100	dc113	rc105	rb149
Temperature	1270℃	1270℃	1290℃	1280℃	1290℃	1270℃
Atmosphere	RF	RF	OF	OF	OF	RF
Silt	50%	20%	65%	60%	80%	10%

b. da138: The color of this type of glaze is derived from iron oxide and is categorized as a temmoku glaze that features transparency. The glaze exhibits layered characteristics because of the changes in its thickness.
c. db100: This type of glaze possesses iron oxide crystals and therefore is characterized by a splashed luster. The firing result is substantially related to the content of iron oxide and the heating curve.
d. dc113: This type of glaze is black, expressing warmth and thickness. Applying underglaze iron painting can produce a decorative effect of rust color, which is a distinctive feature of the ceramics in the Song dynasty.
e. rc105: The glaze also contains crystals that produce the splashed luster effect. However, because of the melting degree and viscosity, the splashes are relatively blurred.
f. rb149: Because the content level of iron oxide in celadon should be low, the quantity of slit used in celadon is also low (only 10 %). The firing condition of the glaze is stable; the finished product is similar to the Longquan celadon in Southern Song.

5.2 Optimal Algorithm

Excel is one of the most common word processing software in MS Office. It has the function of a programming solver that can be easily used to perform optimal computations, and the constraints can be set flexibly. Therefore, this study performed optimal computations by using programming solver.

The objective function value is a key factor influencing the result of optimal computations. Lu (2007) used the objective function value to compute the lowest cost and target value of the recipe was set as the constraint [15]. Other studies on optimal computations for glazes have mostly adopted lowest cost as the objective function value. Only Wang et al. [14] provided three objective function values, which are: (a) the minimum value of the total material costs, (b) minimum value of the sum of the absolute differences between the calculated and theoretical values, and (c) maximum value of the benefit-cost ratio. In the ceramics industry, the material cost for glazes, in general, accounts for only a small proportion of the total cost. Therefore, the minimum value of the sum of the absolute differences between the calculated and theoretical values proposed by Wang et al. [14] was used as the objective function value in this study to achieve a satisfactory result.

Regarding the calculated composition value, previous studies have typically used the weight percentage of the recipe as the calculation basis. However, the interaction among the elements in glaze composition involves atoms and molecules. Therefore, the mole ratio in the Seger formula should be used to produce efficient calculation results. The minimum value of the sum of the absolute difference in mole values between the target and recipe was thus used as the objective function value in this study.

The constraints were set as follows:

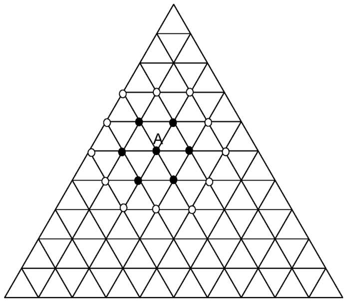


Fig. 2. Triangular coordinate method

a. Constraint 1: The glaze formulas that can be directly applied were expressed using the weight percentage of the materials. Therefore, the calculated content was set to 100.
b. Constraint 2: The weight of the used materials is included in this constraint. For example, corresponding constraints can be set for conditions where 2 % of kaolin should be used as the material for adhesion and suspension, or the amount of phosphoric acid cannot be excessively high. Because this study aimed to use reservoir silt to produce a ceramic glaze, the amount of reservoir silt was also constrained. Furthermore, this study excluded certain materials that had unstable supply or excessively high prices and set their values to 0.
c. Constraint 3: The number of material types was set. In general, using too few varieties of materials may result in the poor stability of glazes, whereas using excessively large varieties of materials may increase the time and cost of glaze compounding. Thus, the number of varieties of materials was typically less than 10.
d. Constraints 4 and 5: The absolute values of the differences in SiO_2/Al_2O_3 and RO/(RO+R_2O) were set. Specifically, the absolute value of the differences in SiO_2/Al_2O_3 was set to less than 0.5, and that of the differences in RO/(RO+R_2O) was set to less than 0.05. The relative ratio of SiO_2/Al_2O_3 to RO/(RO+R_2O) was approximately 10:1. During the calculation, the values can be lower, such as 0.1 and 0.01, and can also be increased if a satisfactory result cannot be obtained. However, other constraints should be modified if the values are increased to 0.5 and 0.05 and no solution is obtained.

5.3 Triangular Coordinate Method

To effectively achieve the objective of original material replacement, the calculated weight ratios of the materials were used as reference points. The triangular coordinate method was adopted to perform the extended experiment based on the multipoint weight ratio data to determine the optimal glaze recipe (Figs. 1 and 2). When this method is employed, a target glaze type can be effectively realized and some unexpected findings can also be derived (Fig. 3).

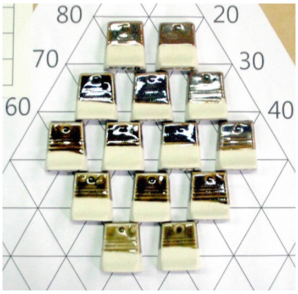


Fig. 3. Example of the triangular coordinate experiment

5.4 Replacement Method

According to the research objective, this study adopted three material replacement methods, which are: (a) replacing all materials using the Seger method, (b) replacing silt using the Seger method, and (c) replacing silt based on partial proportion. This study sought to verify whether any difference existed between the results produced by methods (1) and (2), as well as the influence of types of materials on the firing result.

6 Discussion and Conclusion

6.1 Replacement of All Materials Using Seger Method

This method was used for determining the optimal glaze recipe for replacement and for understanding the range and capability of the application of the Seger formula. Most researchers of glaze studies have agreed that the Seger formula is the most comprehensive expression among all the glaze expressions, even though it cannot be directly applied. In the Seger formula, emphasis is placed on the chemical composition of glazes; other factors such as the crystal structure of various materials are not considered. Therefore, the question as to whether the Seger formula can effectively express the final result of glazes is still open.

After firing, three experts evaluated the glaze specimens. Specifically, the following items were evaluated and scored using a five-point scale: melting degree, liquidity, glossiness, shrinkage degree, transparency, crack degree, crystallinity, color, and texture. The evaluation results are summarized as follows:

a. The firing results of the experimental glaze formula and original glaze formula were substantially different. Only a limited number of experimental glaze formulas obtained an average score higher than 4.75, indicating that the material replacement problem cannot be successfully solved using the Seger formula.
b. As the objective function value increased, the difference between the firing results and that produced using the original glaze formula also increased. Typically, the objective function value should be less than 0.2 to produce a firing result similar to the original result. This underscores the relevance of the Seger formula in glaze research.

c. Among the nine items, the results of the crack degree and transparency were most satisfactory. However, this finding is not conclusive or definite because the crack degree and transparency of the black glaze cannot be easily discerned. The specimens also showed satisfactory performance on melting degree and liquidity. Only a slight difference existed between the firing results and that of the original glaze formula regarding reducing atmosphere. In comparison, a superior performance on crystallinity, color, or texture was the most difficult to achieve. The reservoir silt glaze contains a high proportion of iron, and the iron oxide is highly sensitive to the fluxing capability and crystallization. Therefore, the success of the firing results is highly dependent on the effects of crystallinity, color, and texture.

6.2 Replacement of Silt Using the Seger Method

In this method, the replacement calculation was performed only on the Seger formula of silt. The advantage of this method is that the possible influence of the material molecular structure can be minimized because most of the materials retain the original recipes. However, an accurate replacement value with a low objective function value cannot be easily obtained using this method. The accuracy of the obtained solution was lower than that of the solution achieved by the previous method regarding the chemical composition.

After firing, the three experts evaluated the specimens. The evaluation results are summarized as follows:

a. The firing results produced using this method were superior to that produced using the first method, indicating that the molecular structure of materials is a crucial factor that should be considered in addition to the chemical composition.
b. Regarding the firing results, da138 showed optimal performance; regardless the firing atmosphere, the average scores for all the items were greater than 4.77. This superior performance may be because the original silt content in da138 was only 20 %. Except for dc113, the scores of all the other glaze specimens were greater than 4.75; only a slight modification was required to acquire the replacement recipe similar to the original recipe. The major problem of the dc113 specimen is its color. However, the replacement recipe was still obtained after slightly adjusting the content level of iron oxide.
c. Among three types of silt (i.e., silt from the Sun Moon Lake Reservoir [SMLR] and two types of silt from the Shihmen Reservoir), the replacement effect of the Shihmen Reservoir silt was superior to that of the SMLR silt. This may be primarily because the objective functional value for the replacement recipe of the SMLR silt was considerably higher than that for the replacement recipes of the two types of Shihmen Reservoir silt.
d. The evaluation results of the glaze specimens were similar to those of the specimens in the previous method. The performance on melting degree, liquidity, and glossiness significantly increased than in the first method. A superior performance on crystallinity, color, or texture was most difficult to achieve, which is actually a feature of glazes with high iron content.

6.3 Replacement of Silt Based on Partial Proportion

In our previous study, we replaced entire silt content with previous three types of silt and discovered that the glaze containing less than 20 % of silt generated an effect similar to the original effect. This method can be applied to factory manufacturing processes; that is, when new silt has been produced and old silt is still not depleted, the two materials can be combined to continue producing the same glaze color.

The three experts evaluated the glaze specimens after the firing process. The evaluation results are summarized as follows:

a. Most glaze specimens showed satisfactory firing results, indicating that replacing silt based on partial proportion is a simple and easy replacement method.
b. The firing result was substantially consistent with the properties of the glazes. For example, both the optimal computation and method of partial replacement produced the lowest effect on dc113, indicating that this type of glaze is highly sensitive to numerous factors that influence its firing result.
c. The differences in the composition among various types of silt significantly influence the firing result. The proportion of silt for replacement should be determined through experiments. The experimental result indicated that applying the partial replacement method to the same reservoir silt can produce a relatively high success rate.

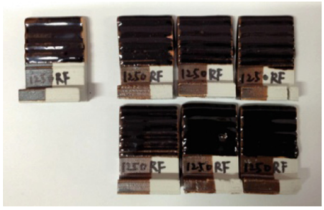
6.4 Promotion and Employment Values

The discontinued production or import of raw materials often causes troubles for the industries of ceramic production and art. In particular, because the ceramic production industry typically involves a large amount of production, it may face the pressure of costs and actively search for cheap alternative materials. Thus, how to replace the original materials with new materials in a short time and achieve a similar glaze effect is a crucial topic for ceramic production.

This study demonstrated that when the glaze materials are no longer available because of unavoidable factors and should be replaced by other materials, systematic and standardized procedures can be used to generate similar recipes. Most of the recipes can be subsequently modified through experiments to become new recipes that can produce an effect similar to the original effect. While the systematic procedures can be easily implemented, the modification should be performed by experienced experts and still involves certain factors. As numerous uncertainties are involved in the material sources, a feasible and effective method indeed allows the silt glaze to be further developed (Table 2).

The application of the silt glaze is considerably more difficult than that of the commercial glaze, primarily because of the complex influence of the iron oxide. Silt glaze contains a large amount of iron oxide, which contributes additional factors that may influence firing atmosphere, crystalline, color, and texture. Compared with the silt glaze, the ceramic glaze in mass production has relatively simple requirements for glaze characteristics such as color and texture. Therefore, the proposed method can be

Table 2. Comparison of firing results between old and new recipes

No.	Firing results		No.	Firing results	
	Target	New Formula		Target	New Formula
da138 1285℃ OF			da138 1250℃ RF		

applied to the task of material replacement for general glazes, and the problem of unstable material sources frequently faced by the ceramics industry can be solved.

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