Available online at www.sciencedirect.com
ScienceDirect
Journal of the European Ceramic Society 27 (2007) 1697–1701
www.elsevier.com/locate/jeurceramsoc

Limit molecular formulas and target formulas determination for feldspar porcelain glazes

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Abstract

The paper is with a view to glazes designed for industrial glost fast firing of feldspar porcelain. In this case, limit "molecular" formulas have to assure a transparent glaze obtaining, for glost fast firing (10 °C/min, 5 h from cold to cold) at maximum temperature, in range between 1360 and 1390 °C, what is realised through the entire "molecular" formulas balancing. There were settled limit "molecular" formulas and guidelines for feldspar porcelain glazes, starting from a relative large number of working recipes developed by feldspar porcelain industry, each oxide range has been rationalised. Target formulas reveal oxides categories and variation range of each oxide to produce a transparent feldspar porcelain glaze.

Keyword: Porcelain; Mechanical properties; Thermal expansion; Al_2O_3; Glaze

1. Introduction

Most of glaze users have taken into account the assessment and circumscription of conditions, that make a given composition to became a vitrified glaze, with a minimum of defects (the term of good glaze often given in literature without any additional definition concerning its meaning).

Starting with the 1980s years of 20th century, there were made many studies in the field of calculation of molecular formulas and usage of their variation range and many mathematical programs have been developed to minimize the volume of calculations.[1,2]

These specialized programs for glaze calculations allow transformation of a fabrication recipe into a molecular formula, as well as the calculation of related glaze properties. At the same time, there were developed programs for calculation of glaze recipes starting from the molecular formula.[3–7] All those programs have their own data bases, regarding both oxide composition and price of raw materials and, the limit molecular formula of glazes designed for different temperatures of that treatment. Some of the most available programs for glaze calculations are: GLAS[3], HyperGlaze[4], INSIGHT[5], Matrix[6], CeramDat.[7]

Present paper, as suggested by its title, deals with determination of molecular limit formulas used for preparation of transparent glazes intended to fast firing of hard feldspar porcelain (10 °C) min, 5 h from cold to cold, for a maximums temperature ranging between 1360 and 1390 °C and that is accomplished through balancing of whole molecular formula: network formers/acid oxides (RO_2; R_2O_5), network modifiers/basic oxides (R_2O; RO) and network stabilizers/amphoteric oxides (R_2O_3).

2. Conditions, criteria and procedures for determination of molecular formula, of their limits and characteristic properties

The principle of establishing the molecular formulas for glazes is given by their framing in the phase diagrams within the limits imposed by previous experimental determinations. The assessed selection criteria were to frame the glaze compositions for feldspar porcelain within the system leucite–anortite–silica corresponding to the primary crystallization field of anortite.[8]

The conditions imposed refer to heat treatment of glazes and is aimed at reducing of ratio temperature/heat treatment duration and increasing of softening temperature of glaze.[8,9]

When discussing the assignment of limit intervals, it is referred to basic functional glazes having a maxim heat treatment temperature 1360–1390 °C, and that are transparent,

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0955-2219/$ – see front matter © 2006 Published by Elsevier Ltd.
doi:10.1016/j.jeurceramsoc.2006.04.160

Table 1
"Molecular" formulas of glazes

Glaze code	Molar ratio, SiO_2:Al_2O_3	Molar equivalents calculated according to Seger's rules					Basic oxides (%)	Amphoteric oxides (%)	Acid oxides (%)
		Al_2O_3	Σ RO_2	Σ R_2O_3	Σ R_2O	Σ RO			
G1	8.32	0.57	4.75	0.58	0.11	0.89	15.8	9.16	75.04
G2	7.89	0.62	4.87	0.63	0.11	0.89	15.34	9.82	74.85
G3	7.91	0.63	4.99	0.64	0.18	0.82	15.06	9.79	75.15
G4	7.9	0.82	6.5	0.84	0.13	0.87	12	9.96	78.03
G5	7.76	0.83	6.46	0.85	0.16	0.84	12.05	10.12	77.83
G6	8.33	0.63	5.27	0.64	0.12	0.88	14.25	10.56	75.18
G7	10.01	0.49	4.9	0.5	0.09	0.91	15.65	7.67	76.68
G8	8.12	0.57	4.64	0.57	0.12	0.88	16.1	9.18	74.72
G9	9.66	0.62	6.01	0.62	0.21	0.79	13.11	8.13	78.77
G10	10.59	0.46	4.87	0.47	0.28	0.72	15.77	7.41	76.81
G11	8.3	0.57	4.71	0.57	0.11	0.89	15.95	9.09	74.96
G12	8.19	0.59	4.84	0.59	0.17	0.82	15.55	9.18	75.27
G13	9.96	0.5	4.94	0.5	0.13	0.87	15.53	7.76	76.71
G14	8.14	0.68	5.57	0.68	0.14	0.85	13.79	9.38	76.83
G15	9.83	0.49	4.85	0.49	0.12	0.87	15.75	7.72	76.54
G16	9.35	0.61	5.71	0.62	0.1	0.9	13.66	8.33	78.01
G17	8.49	0.61	5.19	0.61	0.16	0.84	14.71	8.97	76.32
G18	14.83	0.37	5.48	0.37	0.08	0.92	14.6	5.4	80
G19	15.24	0.31	4.75	0.31	0.16	0.84	16.5	5.12	78.38
G20	18.48	0.24	4.37	0.24	0.22	0.78	18.12	4.26	77.62
G21	13.38	0.44	5.86	0.44	0.09	0.91	13.7	6.03	80.27
G22	9.64	0.63	6.09	0.64	0.22	0.78	12.95	8.16	78.89
G23	10.37	0.48	5.03	0.49	0.27	0.73	15.36	7.37	77.27
G24	10.53	0.51	5.33	0.52	0.29	0.7	14.62	7.46	77.92
G25	11.97	0.41	4.92	0.42	0.29	0.71	15.8	6.48	77.73
G26	9.08	0.5	4.57	0.5	0.22	0.78	16.47	8.24	75.29
G27	8.8	0.78	6.87	0.79	0.39	0.62	11.56	9.02	79.42
G28	10.67	0.54	5.74	0.55	0.15	0.85	13.74	7.42	78.85
G29	8.4	0.62	5.18	0.63	0.14	0.86	14.71	9.12	76.18
G30	7.59	0.62	4.69	0.63	0.1	0.9	15.85	9.83	74.33

stabile in time, durable, free of surface defects, not releasing toxic substances in contact with food. There were selected and studied 30 "molecular" formulas for some functional glazes used for feldspar porcelain (Table 1).

Limit molecular formulas represent a tool and allow possible valid explanations for the defects due the composition and that become visible only after the heat treatment of the glazes. The establishing of limit "molecular" formulas of glazes represents an important step in optimization of glaze properties as, in this way, can be isolated a certain mechanism for producing certain effects of glaze surface that become, then, reproducible.

In Fig. 1 it is shown a compositional ternary oxide diagram and there are emphasized the compositions of the glazes G1–G30.

The position of different compositions of the glazes, within the diagram, offers useful information about glaze properties. Also the stating of optimization process will be done by considering the points of known composition inside the diagram, typical for industrial functional glazes.[10,11]

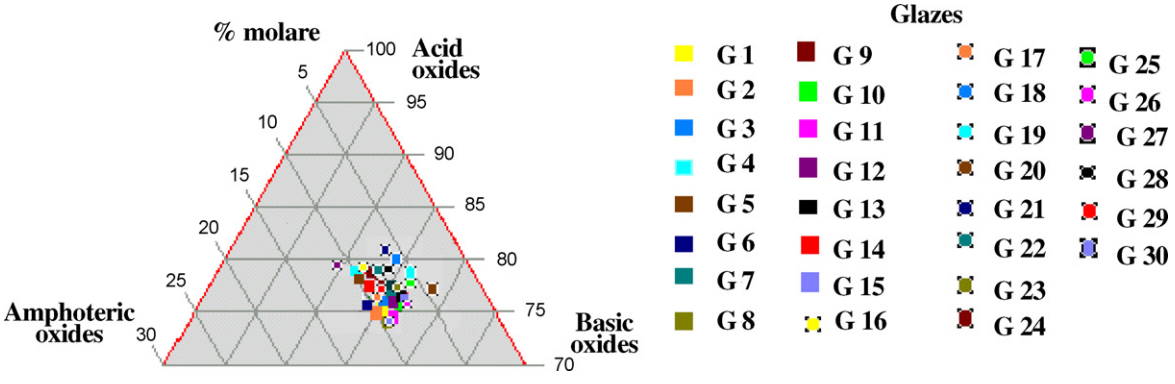

Fig. 1. The compositional domain of the studied glazes represented in a ternary diagram: acid oxides–amphoteric oxides–basic oxides.

Table 2
Characteristics and specific coefficients used for glaze preparation

Oxide	Molar weight	Winkelmann and Scott partial coefficients	Dietzel partial coefficients	Lengersdorff flux factors	Winkelmann and Scott coefficients, E_i	Appen coefficients
Na_2O	62	333.3	0.7	0.88	7	1.590
K_2O	94.2	283.3	0.7	0.88	3	1.575
MgO	40.3	3.3	6.6	0.54	3	1.610
CaO	56.1	166.7	4.8	0.58	–	1.730
ZnO	81.4	60	4.7	0.6	10	1.710
BaO	153.3	100	3.7	0.6	3	1.880
Al_2O_3	102	166.7	6.2	0.32	13	1.520
Fe_2O_3	159.7	133.3	–	0.7	–	–
B_2O_3	69.6	3.3	0.8	1	2.5	1.470
SiO_2	60.1	26.7	3.4	0.38	7	1.459
TiO_2	79.9	136.7	4.1	0.38	–	2.080
P_2O_5	141.5	66.7	–	–	7	–

The definitive properties of the glazes are, as follows:

- The temperature of heat treatment (FT): Lengersdorff[12] has developed a procedure used for calculation of an approximate heat treatment temperature, in independence of the so-called flux factor. For its calculation we can use the relation:

$$F = \frac{\sum S_i f_i}{\sum S_j f_j} \times 100, \quad (1)$$

where F is the flux factor; $S_1,\ldots, S_i$ represent the molar fraction of the oxides having the value of Lengersdorff factor $f_i > 0.4$ and $S_{i+1},\ldots, S_j$ are the molar fraction of the oxides with $f_i < 0.4$ (see Table 2).

Then, the temperature of heat treatment can be estimated using the formula:

$$\mathrm{FT} = \frac{(161.21789 - F)}{0.10252}, \quad (2)$$

with F the flux factor calculated with Eq. (1), FT the temperature of heat treatment (°C), and the numerical values are constants as determined by Lengersdorff with experimental data.

- Coefficient of thermal expansion: Winkelmann and Schott (α_{WS}) that can be calculated using the additive formula:

$$\alpha_{WS} = \sum a_i \alpha_i, \quad (3)$$

with a_1, $a_2,\ldots, a_n$ represents the weight fractions of each oxide component within the glaze and $\alpha_1, \alpha_2,\ldots, \alpha_n$, the coefficients of Winkelmann and Schott for thermal expansion of each component oxide (Table 2).

- Surface tension (σ_{G900}) is considered as an additive function based on the formula:

$$\sigma_{G900} = \sum a_i \sigma_i, \quad (4)$$

where σ_{G900} is the partial surface tension at 900 °C, of the oxides as given by Dietzel (Dietzel factors—see Table 2)[3] and a_i is the weight percentage of each oxide component of the glaze.

- Young's modulus (E) is also calculated using an additive formula:

$$E = \sum a_i E_i, \quad (5)$$

with E the elasticity modulus; a_i the weight fraction of each oxide component and E_i are the Winkelmann and Schott coefficients for each oxide component (see Table 2).[3]

Table 3
Values of different properties for glazes G1–G30

Glaze code	FT (°C)	α (10^{-6} K^{-1})	σ_{900} (10^3 N/m)	E (10^4 MN/m^2)	n
G1	1377	5.59	395.14	7.116	1.489
G2	1383	5.64	397.31	7.178	1.494
G3	1386	4.65	391.91	7.283	1.492
G4	1434	5.44	392.59	7.348	1.482
G5	1431	5.55	391.65	7.371	1.482
G6	1396	5.44	381.44	7.206	1.439
G7	1381	5.41	390.09	6.926	1.491
G8	1373	5.68	397.14	7.142	1.497
G9	1412	5.32	384.51	7.241	1.497
G10	1358	5.64	372.63	7.023	1.495
G11	1376	5.61	396.83	7.136	1.496
G12	1376	5.75	389.85	7.099	1.496
G13	1380	5.59	386.91	6.921	1.496
G14	1405	5.66	391.65	7.199	1.493
G15	1377	5.59	387.57	6.918	1.496
G16	1409	5.57	387.82	7.024	1.494
G17	1389	5.71	388.57	7.094	1.494
G18	1399	5.06	380.04	6.828	1.496
G19	1365	5.1	377.38	6.775	1.495
G20	1340	4.98	370.44	6.655	1.493
G21	1415	4.84	383.01	6.911	1.491
G22	1413	5.4	381.39	7.149	1.488
G23	1367	5.84	373.69	7.011	1.493
G24	1378	5.86	371.91	6.962	1.491
G25	1359	5.65	369.38	6.997	1.493
G26	1353	5.96	381.87	7.095	1.498
G27	1421	6.02	372.37	7.233	1.488
G28	1407	5.33	383.54	7.01	1.492
G29	1391	5.69	391.49	7.146	1.493
G30	1376	5.9	398.69	7.138	1.496

Table 4
Compositional limits for glazes having a heat treatment temperature of 1358–1391 °C

	Molar ratio, SiO_2/Al_2O_3	Basic oxides	Amphoteric oxides (%)	Acid oxides (%)	Al_2O_3	Σ RO_2	Σ R_2O_3	Σ R_2O	Σ RO
Minimum	7.59	14.62	5.12	74.33	0.31	4.69	0.31	0.09	0.7
Maximum	15.24	16.50	9.83	78.38	0.63	5.33	0.64	0.29	0.91

- Refraction coefficient (n) is calculated additively, as

$$n = \sum a_i n_i, \quad (6)$$

where n_i are the specific coefficients determined by Appen (Table 2) and a_i represents the weight fraction of the ith oxide component.[3]

Table 5
Limits of calculated properties of glazes for a heat treatment temperature of 1360–1390 °C

	α (10^{-6} K^{-1})	σ_{900} (10^3 N/m)	E (10^4 MN/m^2)	n
Minimum	4.65	369.38	6.655	1.44
Maximum	6.02	398.69	7.371	1.50

3. Results and discussions

3.1. Rationalization of limit formulas of oxides from "molecular" formulas

Calculation of "molecular" formulas for a large number of recipes taken from industrial practice does not guarantee the limit formulas, if after than a rationalization of the variation domain for each of the oxides used in these "formulas" is done. This rationalization is performed based on glaze properties. In this way, a guide for balancing glaze properties is set-up through the effects of oxides upon the properties.

The values of calculated properties according to relations from Section 2, for the 30 functional glazes are given in Table 3.

Fractional glazes should contain adequate proportions of SiO_2 and Al_2O_3 to form a layer of glass, stable from chemical viewpoint and appropriate mechanical strength. Instability of functional glazes, generally, is due to inobservance of the lower limit of those oxides proportion.[5]

By applying the selection criterion—temperature of heat treatment to range between 1360 and 1390 °C, as calculated according to relations (1) and (2), the glazes G4–G6, G9, G14, G16, G18, G20–G22 and G26–G28 are remained from the potential dist of glazes to be used.

The limit formulas of the selected glazes are presented in Table 4.

The limit of variation of "molecular" formula represents the compositional domains having the most probable optimal compositions for the studied glazes.

A detailed analysis of the elected glazes composition emphasized the limits of oxides concentration variation, namely for basic oxides (14.62–16.5%), for acid oxides (74.33–78.38%) as well as the molar ratio SiO_2/Al_2O_3 (7.59–15.24), necessary to obtain glazes within the mentioned temperature range for heat treatment.

The increasing of temperature of heat treatment for the studied glazes is generally achieved by decreasing the proportion of basic oxides correlated with the increase of the amount of amphoteric oxides and decreasing the concentration of acid oxides, as well. Since the basic oxides act as strong fluxing agents in the range 1360–1390 °C, the most obvious correlation is given by the compositional range of basic oxides, namely 14.62–16.5%.

When the increase of the amount of amphoteric oxides, especially Al_2O_3 is done on the expense of decreasing basic oxides, the action of the amphoteric oxides is to strongly increase the melting temperature (glaze 29 compared with glaze 26, the proportion of acid oxides being very close—Tables 1 and 3); such a finding is correlated with the phase equilibrium system of compositional field of the glazes for feldspar porcelain.

The calculated properties of the glaze having a heat treatment temperature ranging within 1360–1390 °C are given in Table 5.

When the concentration increase of the amphoteric oxides is based on the decrease of acid oxides amount, the action of amphoteric oxides is to strongly increase the surface tension and therefore to reduce the ability to dissolve of glazes; for the glaze 11, with 74.96% acid oxides, the calculated value for the surface tension is the highest among all the values for the selected glazes.

On the contrary, in the case G25, G19 and G23 glazes—having the lowest content of amphoteric oxides, one can notice a relevant decrease of the surface tension and a corresponding ability of dissolution (Table 4).

The increase of the content of basic oxides accompanied by the increase of heat treatment temperature leads to a higher surface tension and mechanical strength.

4. Conclusions

The study performed in present work emphasizes the interest for determining the "molecular" formulas and corresponding limit formulas for glazes designed for feldspar porcelain. There are given relevant information for design and preparation of glazes.

The main conclusions are briefly the following:

- concentration of basic oxides for glazes heat treated between 1358 and 1391 °C ranges as 14.62–16.5%;

- concentration of acid oxides for the same glazes ranges as 74.33–78.38%;
- the molar ratio SiO_2/Al_2O_3 for glazes to be fired at 1358–1391 °C ranges between 7.59 and 15.24;
- increase of the amount of amphoteric oxides, especially of Al_2O_3, when decreasing the content of basic oxides leads to strong increase of melting temperature;
- increase of concentration of amphoteric oxides on the expense of decreasing concentration of acid oxides induces a strong increase of the surface tension and lower ability of dissolution of glazes;
- decrease of concentration of basic oxides, accompanied by an increase of firing temperature leads generally to an increase of surface tension and of mechanical strength of glazes, as well;
- all these findings are correlated directly with the phase equilibrium of the studied compositional systems.

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