Calculation of the Glaze Recipe for Porcelain Feldspar Products Based on their Molecular Formula Rationalization

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Any change of the raw material sources for glazes, economically, ecologically motivated, and also from the glaze quality point of view, is conditioned by the molecular formula rationalization and by the variation limits of the molecular formula, respectively. The proper glaze compositions are placed within their limit variation intervals with optimized processing and utilization properties. For this purpose, the rationalization criteria and procedures of molecular formulas are summarized in the present paper, as well as the results referring to their rationalization obtained in the authors' previous work. Thus, one starts from a base of raw materials that are selected, usable and also accessible for the design and producing of the glazes. On these bases the groundwork and the design equation for the glaze recipes are developed, exemplified for a single glaze. For an easy access to results, computer programs are used for an easy access to results.

Keywords: glaze; molecular formula; limit molecular formula; glaze recipe

The quality of the vitrified glazes depends essentially on their oxide composition and on that of the precursor raw material mixture, respectively. The optimization of the precursor mixtures composition is made from the point of view of the economic accessibility of the raw materials that are used, able to produce the necessary oxides for obtaining potential and testable properties, corresponding to high quality products, economically suitable and technologically compatible [1-7]. As a consequence, any change of recipe for the raw materials used in glaze producing has to be based on their molecular formula being included within the demands determined by the nature of the ceramic holder and on the applied heat treatment when producing the ceramic products.

In this paper, the ceramic support of the glaze is the hard feldspar porcelain, and thus it is necessary to ensure obtaining a clear glaze and a rapid heat treatment (10°C/minute), with maximum temperature within 1360-1390°C. The rationalization of the glaze molecular formulas is absolutely necessary, namely by establishing (determining) their limits. These limits are previously assessed for as great a number as possible of glazes, selected from the industrial practice – their own or from other sources [1,7-13].

The calculation of the glaze recipe for hard feldspar porcelain is fundamentally made by the rationalization of the molecular formula in agreement with their important properties [1,2,6-8,14-17].

The experimental and calculation part

Rationalization procedures and criteria of the molecular formulas

<u>Criteria</u>

In compositions, the glazes for the feldspar porcelain are within the oxide polycomponent system SiO_2 (MO_2)–R_2O_3–M_2O–MO (the important oxides are: SiO_2, Al_2O_3, Na_2O_3, K_2O, MgO, CaO) [1,3,7,8]. As a result, the polycomponent domain in which the glazes have to be located can be circumscribed by using a comprehensive ternary diagram: basic oxides – amphoteric oxides – acid oxides frequently M_2O, MO–Al_2O_3–SiO_2 respectively. The principle of determining the molecular formulas of glazes is represented by including them in the phase diagrams within the limits imposed by previous calculations and by experimental determinations; the Seger molecular formula of the glazes could be thus suggested and established by computation.

<u>Procedures</u>

The transformation of the oxide percent weight composition of glazes into Seger formula, takes place by passing through the following calculation route.

The calculation starts by evaluating the molar factor (n_i) for each component oxide, using the following relationship:

$$n_i = \frac{\%\ weight\ oxide}{MG_i}, \qquad (1)$$

in which MG_i is the molecular weight of each oxide (i).

As was shown, the oxides of the glazes are divided, according to the phase diagram in which they are located, in basic oxides (M2O;MO), amphoteric oxides (R_2O_3) and acid oxides (MO_2, M_2O_3, M_2O_5). The sum of the basic oxide factors is considered equal to one unit (1.0). **A** correction factor is then calculated, representing the inverse of the n_i factors sum of the basic oxides:

$$k = \frac{1}{n_1 + n_2 + ... + n_n}, \qquad (2)$$

where $n_1+n_2+…n_n$ represents the sum of the n_i mole factors of the basic oxides.

Using the k factor the coefficient in moles (m_i) is calculated for each of the oxides: basic, amphoteric and acid, by the equation:

$$m_i = k \cdot n_{i(j)} \quad , \qquad (3)$$

For basic oxides $\Sigma m_i = 1$ and for the others $\Sigma m_i \neq 1$. The presentation of results, with the three separate groups of oxides is made according to the following scheme:

$$1\begin{cases} RO \\ R_2O \end{cases} \cdot m_i\ R_2O_3 \cdot m_j \begin{cases} RO_2(SiO_2) \\ R_2O_5 \\ R_2O_3(B_2O_3) \end{cases} ; \qquad (4)$$

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Glaze Symbol	FT [°C]	Oxides, % mol.			Oxizi, % wt			Molar ratio $SiO_2:Al_2O_3$
		Basic oxides	Amphoteric oxides	Acid oxides	Basic oxides	Amphoteric oxides	Acid oxides	
G_1	1377	15.8	9.16	75.04	13.24	15.0	71.76	8.32
G_2	1383	15.34	9.82	74.85	13.11	15.53	71.36	7.89
G_3	1386	15.06	9.79	75.15	14.52	15.39	70.09	7.91
G_7	1381	15.65	7.67	76.68	13.52	12.86	73.62	10.01
G_8	1373	16.1	9.18	74.72	13.60	15.00	71.40	8.12
G_{10}	1358	15.77	7.41	76.81	15.77	11.82	72.41	10.59
G_{11}	1376	15.95	9.09	74.96	13.45	14.77	71.78	8.3
G_{12}	1376	15.55	9.18	75.27	14.13	14.80	71.07	8.19
G_{13}	1380	15.53	7.76	76.71	14.00	12.62	73.38	9.96
G_{15}	1377	15.75	7.72	76.54	14.18	12.75	73.07	9.83
G_{17}	1389	14.71	8.97	76.32	13.36	14.54	72.10	8.49
G_{19}	1365	16.5	5.12	78.38	14.72	8.54	76.74	15.24
G_{23}	1367	15.36	7.37	77.27	15.12	12.10	72.78	10.37
G_{24}	1378	14.62	7.46	77.92	14.22	12.06	73.72	10.53
G_{25}	1359	15.8	6.48	77.73	15.91	10.61	73.48	11.97
G_{29}	1391	14.71	9.12	76.18	12.92	14.81	72.27	8.4
G_{30}	1376	15.85	9.83	74.33	13.62	15.98	70.40	7.59

Table 1
COMPOSITION AND THERMAL TREATMENT TEMPERATURES FOR MELTING

Limits	Molar ratio SiO_2/Al_2O_3	Basic Oxides % mol.	Amphoteric Oxides % mol.	Acid Oxides % mol.	Limit interval of variation of molecular formulas				
					Al_2O_3	ΣRO_2	ΣR_2O_3	ΣR_2O	ΣRO
Minim	7.59	14.62	5.12	74.33	0.31	4.69	0.31	0.09	0.7
Maxim	15.24	16.50	9.83	78.38	0.63	5.33	0.64	0.29	0.91

Table 2
COMPOSITION LIMITS FOR THE GLAZES WITH THERMAL TREATMENT TEMPERATURE WITHIN 1358 - 1391°C

This is the expression of the Seger molecular "formula".

The rationalization of the molecular formulas presumes establishing of their limits. For this purpose, in previous works [1,7], a relatively high number of glazes were selected (30), their composition (weight percentage) was verified and validated by a solid and credible industrial practice [1,7]. The large number of selected glazes selected does not yet guarantee the satisfactory limit interval establishment of the molecular formulas. Only their rationalization, by determining the variation limits for each oxide ratio, that make up these formulas, will give the right answer in agreement with the glaze properties in use. Balancing of the defining properties is necessary by means of the effects of all component oxides upon them. The resulted limit intervals of variation of the molecular formulas are the compositional domains in which the optimum compositions of the studied glazes will be most probably placed.

Applying this to the presented case, the priority criterion of selection – the temperature of the thermal treatment (fusion) (FT), approximately between 1360° – 1390°C, the number of rationalized glazes is limited to 17 (table 1). The variation of the structural limits for the selected glazes is presented in table 2 [7]. Their value corresponds to the composition domains, in which their composites are placed, to which the optimal properties glazes match – of processing and by material (thermal expansion - α; surface stress - σ_{900}; elastic modulus – E; refraction coefficient – n; viscosity - η. On this ground, in previous works [1,7,8], the number of glaze related compositions compatible with carrying out the performances, was further restrained.

Manufacturing recipes for glaze: raw material and computation method

Raw materials

The oxide weight composition of the materials forming the raw material base, when designing the domestic feldspar porcelain glaze used, is presented in table 3. In view of identifying the minerals present in the used raw material, further investigations were effected by X-ray diffraction [1,7] or other sources of information were applied to: [17-19]. The raw material diffraction samples used for glaze manufacture are set out in figures 1-7.

The computation method for the glaze recipes

Any change in raw material sources for the glaze, economically, ecologically and qualitatively motivated must be in accordance with the rationalization of the molecular formulas, with the results referring to the determining properties the glazes should have, depending on their utilization, respectively. As already specified, the molecular compositions of the glaze have to be placed within the variation limit of the molecular formulas corresponding to this goal. In computing the glaze recipes the conversion of the molecular formulas is necessary, in the adequate percentage and gravimetric expression, using the equation:

$$p_{i,j} = \frac{m_{i,j} MG_{i,j}}{m_1 MG_1 + m_2 MG_2 + ... + m_n MG_n} \cdot 100, \qquad (5)$$

where $p_{i,j}$ is the weight percentage ratio of each component oxide of the glaze, considered in its Seger formula; $m_{i,j}$ - the molar coefficient of each component oxide of the glaze, considered in its Seger formula; $MG_{i,j}$ - molecular weight of each component oxide of the glaze, considered in its Seger formula.

The calculation of the raw material recipe in weight percentage ratios, for producing glazes suitable for the considered feldspar porcelains, is exemplified, in particular for one of the 17 glazes, included in table 1 (selected by the priority criterion of the fusion heat treatment, which is between 1360 - 1390°C). The glaze used for exemplification of the raw material recipe calculus is that with G_{25} symbol, the oxide composition of which is presented in table 4, as a result of its molar percentage value conversion (by rationalizing its molecular formula), in weight percentage composition, in compliance with the data of table 1.

Table 3
GRAVIMETRIC OXIDE COMPOSITION OF THE RAW MATERIAL BASIS FOR THE GLAZE'S DESIGN USED

No.	Raw material	Oxide weight composition [%]									
		Na_2O	K_2O	MgO	CaO	ZnO	Al_2O_3	Fe_2O_3	SiO_2	TiO_2	PC
1	Feldspar AKW 930 L	2.70	11.10	0.02	0.55	0	18.35	0.05	66.85	0.03	0.35
2	Feldspar AKW 900 L	0.85	14.65	0.01	0.5	0	17.83	0.04	65.88	0.04	0.20
3	Feldspar Capus FC	4.5	3.6	0.3	0.5	0	12.8	0.25	77.73	0.02	0.30
4	Wollastonite Casiflux A	0.05	0.05	0.80	45.50	0	0.30	0.20	51.60	0	1.50
5	Sand Vetovo	0.01	0.01	0.05	0.05	0	0.28	0.03	99.30	0.10	0.25
6	Marble Simeria	0	0	0.10	54.50	0	0.20	0.06	0.05	0	43.64
7	Dolomite Harghita	0	0	21.00	30.50	0	0.05	0.08	0.05	0	47.42
8	Calcined Alumina EX 35	0.3	0	0	0.03	0	99.5	0.03	0.09	0.05	0
9	Calcined kaolin AKW AS45	0.10	1.30	0.10	0.20	0	42.4	0.4	55.10	0.40	0
10	Kaolin AKW BZ	0.01	0.22	0.20	0.30	0	32.5	0.35	54.00	0.12	12.30
11	Zinc Oxide	0	0	0	0	99.5	0	0	0	0	0

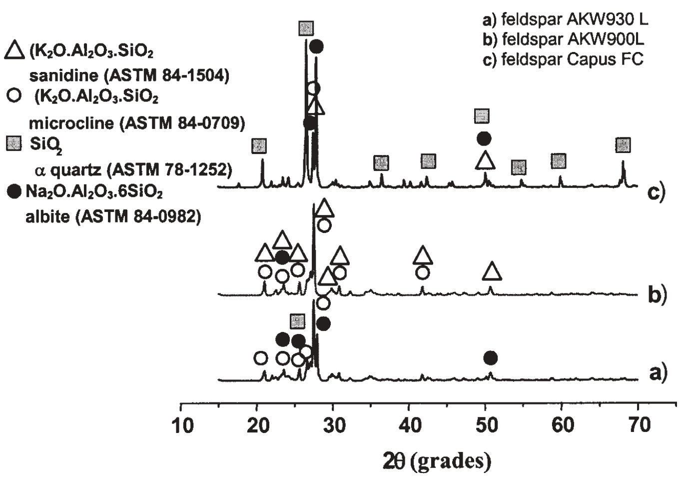

Fig. 1. Diffraction pattern of feldspar AKW 900L, feldspar Capu° FC

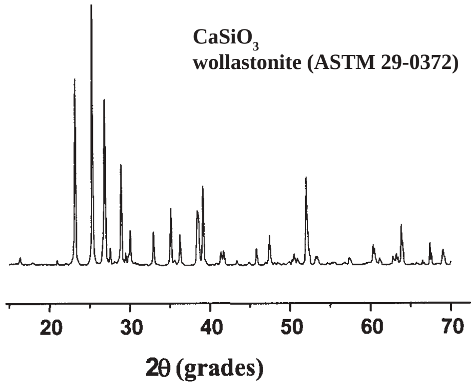

Fig. 2. Diffraction pattern for wollastonite Casiflux A

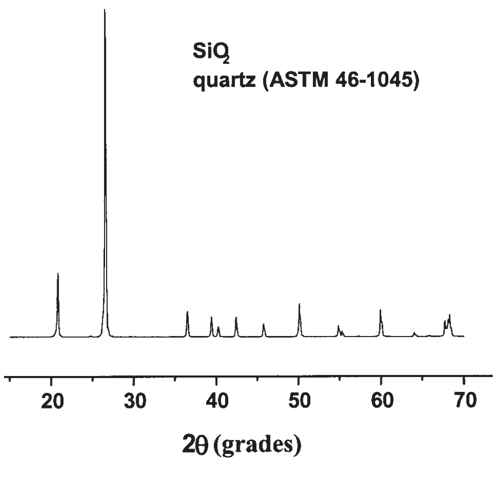

Fig. 3. Diffraction pattern for Sand Vetovo

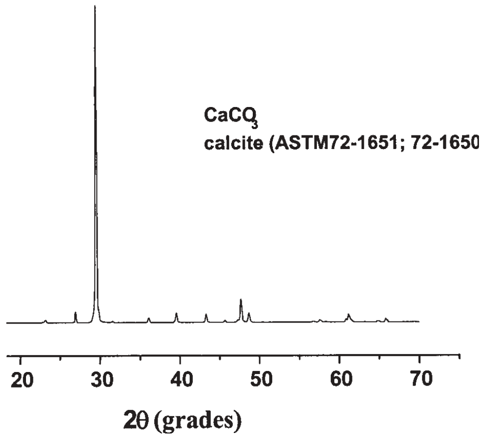

Fig. 4. Diffraction pattern for marble Simeria

The calculation of the raw material recipe is made by a balance equation of glaze constituent oxides, supplied by the selected raw materials. For this purpose, symbols of the used raw materials are established (selected in this view) and also the proportion in which they are to be used. So, the following symbols were used for the selected and used raw materials: NV - Vetovo sand; MS - Simeria marble; DH - Harghita dolomite, AKW 900L - feldspar AKW 900L; FC - Cãpus feldspar; CC - calcinated kaolin AKW AS 45; CBZ - AKW BZ kaolin; ZnO – zinc oxide. For the unknown value, which is calculated for the ratios of raw materials (constituents of the glaze recipes), the following symbols were used: p – for % NV; t – for % MS; u – for % DH; v - for % AKW 900L; w – for % FC; x – for %CC; y – for %CBZ; z – for % ZnO (the raw material gravimetric oxide composition, used for producing G_{25} glaze which was given in table 3; in this case, wollastonit Casiflax A– position 4, AKW 930L feldspar – position 1 and calcinated alumina EX 35 – position 8 were not used), from table 3.

Results and discussions

The calculation of the manufacturing recipe is based on balance equations of the glaze constituent oxides and the use of an equal number of raw materials as supply for these oxides, for the present case 8(eight) in number. As a consequence the equations (6)-(13) are obtained, out of which G_{25} glaze manufacturing recipe is deduced. There were also taken into account the roasting losses – PC, only for the raw materials with PC > 10% gravimetric:

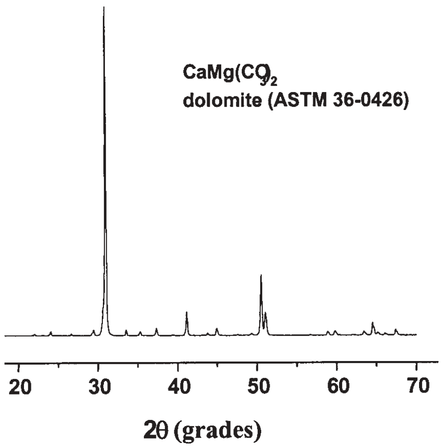

Fig. 5. Diffraction pattern for dolomite Volslobeni (Harghita)

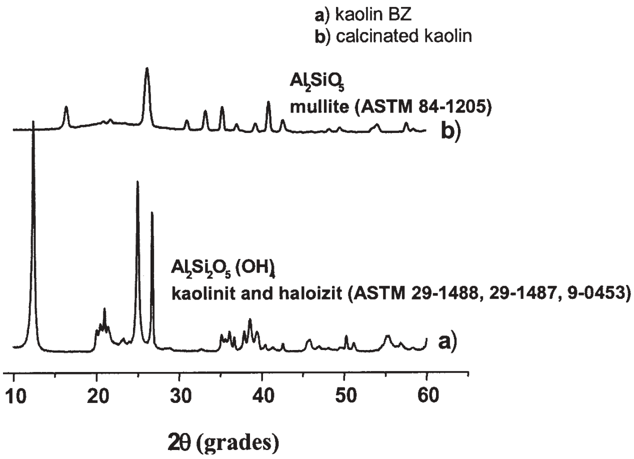

Fig. 7. Diffraction pattern for kaolin AKW BZ and calcinated kaolin AKW AS 45

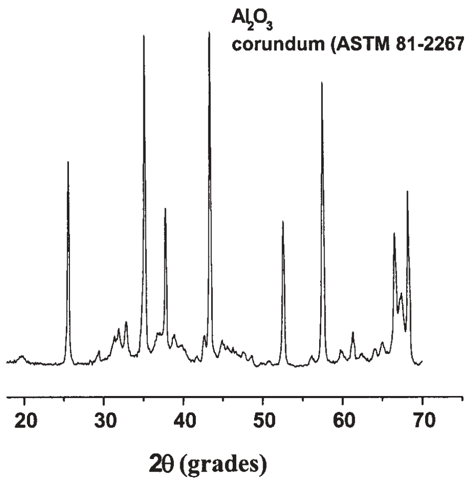

Fig. 6. Diffraction pattern for calcinated alumina Ex35

- $\%Na_2O=\%Na_2O{\cdot}p+\%Na_2O{\cdot}v+\%Na_2O{\cdot}w+\%Na_2O{\cdot}x+\%Na_2O{\cdot}100/(1-PC_{(CBZ)}){\cdot}y$ (6)

  $\%Na_2O = 0.01{\cdot}p+0.85{\cdot}v+4.50{\cdot}w+0.10{\cdot}x+0.0114\%{\cdot}y =1.68$ (6')

- $\%K_2O=\%K_2O{\cdot}p+\%K_2O{\cdot}v+\%K_2O{\cdot}w+\% K_2O{\cdot}x+\%K_2O{\cdot}100/(1-PC){\cdot}y$ (7)

  $\%K_2O = 0.01{\cdot}p+14.65{\cdot}v+3.6{\cdot}w+1.3{\cdot}x+0.251{\cdot}y=5.06$ (7')

- $\%MgO = \%MgO{\cdot}p + \%MgO{\cdot}PC_t/(100-PC_t){\cdot}t + \%MgO{\cdot}PC_u/(100-PC_u)u + \%MgO{\cdot}v +\%MgO{\cdot}w + \%MgO{\cdot}x + \%MgO{\cdot} PC_y/(100-PC_y)y$ (8)

  $\%MgO = 0.05{\cdot}p + 0.10{\cdot}PC_t/(100-PC_t){\cdot}t + 21{\cdot}PC_u/(100-PC_u)u + 0.01{\cdot}v + 0.30{\cdot}w + 0.10{\cdot}x + 0.20{\cdot}PC_y/(100-PC_y)y = 2.20$ (8')

in which PC_t = 43.64, PC_u = 47.42 °i PC_y = 12.30;

- $\% CaO = \% CaO{\cdot}p + \% CaO{\cdot}PC_t/(100-PC_t){\cdot}t +\% CaO{\cdot}PC_u/(100-PC_u){\cdot}u + \% CaO{\cdot} v + \% CaO{\cdot}w + \% CaO{\cdot}x +\% CaO{\cdot}PC_y/(100-PC_y)y$ (9)

  $\% CaO = 0.05{\cdot}p + 54.5{\cdot} PC_t/(100-PC_t){\cdot}t + 30.50{\cdot}PC_u/(100-PC_u){\cdot}u + 0.50{\cdot} v + 0.50{\cdot}w + 0.20 {\cdot}x +0.30{\cdot} PC_y/(100-PC_y)y = 5.43;$ (9')

in which PC_t, PC_u, PC_y are the terms for the same symbols used in equation (8), therefore the same value.

- $\% ZnO = \% ZnO {\cdot}z$ (10)

Table 4
OXIDE COMPOSITION OF THE GLAZE G25 IN GRAVIMETRIC %

OXIDES	NA_2O	K_2O	MGO	CAO	AL_2O_3	FE_2O_3	SIO_2	ZNO
% wt. composition	1,08	5,06	2,20	5,43	10,41	0,20	73,48	2,14

Table 5
RECIPE FOR THE MANUFACTURING OF G25 GLAZE

Raw material	Proportion of calculated raw material	
	Symbol	% wt.
Sand Vetovo	p	33.00
Marble Simeria	t	4.00
Dolomite Harghita	u	11.00
Feldspar AKW 900L	v	27.70
Feldspar Capus FC	w	17.10
Calcinated kaolin AKW AS 45	x	2.20
Kaolin AKW BZ	y	4.00
Zinc oxide	z	1.00

in which, because the Zinc oxide used is practically pure chemically, the relationship (10) becomes:

$$\% ZnO = 2,14 \% weight; \qquad (10')$$

- $$\% Al_2O_3 = \% Al_2O_3 \cdot p + \% Al_2O_3 \cdot PC_t/(100-PC_t) \cdot t + \% Al_2O_3 \cdot PC_u/(100-PC_u) \cdot u + \% Al_2O_3 \cdot v + \% Al_2O_3 \cdot w + \% Al_2O_3 \cdot x + \% Al_2O_3 \cdot PC_y/(100-PC_y) y \qquad (11)$$

$$\% Al_2O_3 = 0.28 \cdot p + 0.20 \cdot PC_t/(100-PC_t) \cdot t + 0.05 \cdot PC_u/(100-PC_u) \cdot u + 17.83 \cdot v + 12.80 \cdot w + 42.80 \cdot x + 32.50 \cdot PC_y/(100-PC_y) y = 10.41; \qquad (11')$$

In which PC_t, PC_u, PC_y have the significance of the same symbols used in equation (8)

- $$\% Fe_2O_3 = \% Fe_2O_3 \cdot p + \% Fe_2O_3 \cdot PC_t/(100-PC_t) \cdot t + \% Fe_2O_3 \cdot PC_u/(100-PC_u) \cdot u + \% Fe_2O_3 \cdot v + \% Fe_2O_3 \cdot w + \% Fe_2O_3 \cdot x + \% Fe_2O_3 \cdot PC_y/(100-PC_y) y \qquad (12)$$

$$\% Fe_2O_3 = 0.03 \cdot p + 0.06 \cdot PC_t/(100-PC_t) \cdot t + 0.08 \cdot PC_u/(100-PC_u) \cdot u + 0.04 \cdot v + 0.25 \cdot w + 0.40 \cdot x + 0.35 \cdot PC_y/(100-PC_y) y = 0.20\%; \qquad (12')$$

in which PC_t, PC_u, PC_y have the significance of the same symbols used in equation (8)

- $$\% SiO_2 = \% SiO_2 \cdot p + \% SiO_2 \cdot PC_t/(100-PC_t) \cdot t + \% SiO_2 \cdot PC_u/(100-PC_u) \cdot u + \% SiO_2 \cdot v + \% SiO_2 \cdot w + \% SiO_2 \cdot x + \% SiO_2 \cdot PC_y/(100-PC_y) y \qquad (13)$$

$$\% SiO_2 = 99.30 \cdot p + 0.05 \cdot PC_t/(100-PC_t) \cdot t + 0.05 \cdot PC_u/(100-PC_u) \cdot u + 65.88 \cdot v + 77.73 \cdot w + 55.10 \cdot x + 54.00 \cdot PC_y/(100-PC_y) y = 73.42\%; \qquad (13')$$

From the equation system (6)-(13), the manufacturing recipe is deduced for the glaze G_{25}-table 5.

Conclusions

The design of new glazes is economically, ecologically motivated as well as by their performing quality.

The priority selection criterion, from an important group of used and industrially validated glazes, is the temperature of thermal treatment (melting), together with their ceramic base (1360 – 1390°C).

The calculation of the new glazes is conditioned and sustained by the rationalization of the molecular formulas, establishing their variation limits.

The intervals of the variation limits of the molecular formulas represent the place of the optimal compatible compositions with the glaze properties determined by the effects of each component oxide.

As a result there are also deducted the limits of defining properties of the glazes.

The calculation of the glaze recipe is made on the basis of the rationalization of the molecular formula and by establishing the corresponding value limits of the glaze defining properties. This calculation is made using the balance equations of the constituent oxides of the glazes, supplied by new, selected raw materials.

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