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Optimization of wastes content in ceramic tiles using statistical design of mixture experiments

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Abstract

Mineral extraction and processing industries have been cited as sources of environmental contamination and pollution. The inclusion of wastes into productive cycles represents an alternative form of restoration, which is interesting from both environmental and economic standpoints. In this work, the development of ceramic tile formulations containing kaolin processing and granite sawing wastes was investigated using the statistical design of mixture experiments methodology. Ten formulations using the raw materials, red clay, kaolin processing and granite sawing wastes, were selected and used in the mixture design. Test specimens were fired and characterized to determine their water absorption, linear firing shrinkage and modulus of rupture. Regression models were calculated, correlating the properties with the composition. The significance and validity of the models were confirmed by statistical analysis and verification experiments. The regression models were used to optimize the waste content in ceramic compositions. The results showed that formulations containing up to 62% of waste could be used in the production of ceramic tiles.

Keywords: Traditional ceramics; Recycling; Waste materials; Design of mixture experiments

1. Introduction

Economic and demographic growth demands increasingly high indices of industrial activity, which implies two major environmental problems. First, it ultimately feeds on natural non-renewable resources that are becoming scarce and will be sooner or later depleted; and second, it produces increasing amounts of waste materials, which are more and more difficult to dispose of.[1]

Around the world, millions of tons of inorganic wastes are produced every day. Traditionally, these wastes have been disposed of in landfills and often dumped directly into ecosystems without adequate treatment. However, possible reuse or recycling alternatives should be investigated and implemented.[2–4]

The inclusion of wastes into alternative productive cycles may represent an alternative form of reclamation, which is interesting from the environmental and economic standpoints. Restoration and recycling is the best environmental solution to save raw materials and to reduce the amount of industrial wastes discarded.[5–7] Thus, the search for new recycling technologies is of high technological, economic and environmental interest.[8]

In this regard, interesting opportunities are found in the traditional ceramics industry, particularly the sector devoted to the fabrication of building products. Natural raw materials used in the fabrication of clay-based ceramic products show a wide range of compositional variations and the resulting products are very heterogeneous. Therefore, such products can tolerate further compositional fluctuations and raw material changes, allowing different types of wastes to be incorporated into ceramic tiles and bricks.[1,9,10]

Kaolin is an important raw material in various industrial sectors. However the kaolin mining and processing industry produces large amounts of waste. The kaolin industry, which processes primary kaolin, produces two types of wastes. The first type derives from the first processing step (separation of sand from ore). The second type of waste results from the second processing step, which consists of wet sieving to separate the finer fraction and purify the kaolin.

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The granite processing industry also generates large amounts of wastes worldwide. Granite sawing waste contains feldspar, quartz and mica as major constituents and metallic dust and lime (used as abrasive and lubricant, respectively) as residual materials. Various studies[9,11–15] have demonstrated the viability of using granite sawing waste in the production of ceramic tiles. However, to the best of our knowledge, no study has investigated the potential use of granite waste in combination with kaolin processing waste to produce ceramic tiles.

The current optimization procedure for developing ceramic compositions using waste materials consists of an experimental rather than a comprehensive approach. In general, the approach involves selecting and testing a first trial batch, evaluating the results, and then adjusting the mixture's proportions and testing further mixtures until the required properties are achieved. The conventional method of optimization is time consuming and does not allow the global optimum to be detected, particularly due to interactions among the variables. In contrast, statistical design methods are rigorous techniques both to achieve desired properties and to establish an optimized mixture for a given constraint, while minimizing the number of trials.[16,17]

In the development and manufacture of ceramics using waste materials the properties of fired bodies are determined basically by the combination of raw materials and process parameters. When the processing conditions are kept constant, a number of properties of dried and fired bodies are determined principally by the combination (or mixture) of raw materials.[18] That is the basic assumption in the statistical design of mixture experiments to obtain a response surface using mathematical and statistical techniques.[19,20] To this end, it is necessary first to select the appropriate mixtures from which the response surface might be calculated. With the response surface in hand, a prediction of the property value can then be obtained for any mixture, based on changes in the proportions of its components.[18,21].

This methodology has found important applications in various areas and is becoming popular in the field of glasses and ceramics.[18,21–25] In every reported case, the methodology has led to greater efficiency and confidence in the results obtained[21] and has simultaneously optimized the content of raw materials with a minimum of experiments.

Statistical experimental design methodology is an established and proven methodology,[19,20] but few researchers[23,26] have reported using this technique to research and develop ceramics using waste materials. Thus, this work aimed to optimize ceramic tile formulations containing kaolin processing and granite sawing wastes using the statistical design of mixture experiments methodology.

2. Experimental procedure

The kaolin waste utilized was obtained from the second kaolin processing step, while granite waste came from the sawing process during granite processing. The wastes were dried at 110 °C, dry milled and sieved through a 150-μm mesh sieve. The other raw material used in this research was commercial red clay (Cerâmica Espírito Santo, Brazil). Table 1 presents the chemical composition of the raw materials, determined by wet process.

Physical and chemical characterizations of kaolin processing waste and granite sawing waste are described elsewhere[10,27] (the granite waste is identified by the label "Fuji"). According to those reports, kaolin waste is composed of kaolinite ($Al_2Si_2O_5(OH)_4$), mica ($KAl_2(Si_3Al)O_{10}(OH)_2$) and quartz ($SiO_2$) and has a particle size distribution with a mean value of 54 μm and a D_{50} of 58 μm, a D_{10} of about 5 μm and a D_{90} of about 135 μm. Granite sawing waste is composed of quartz, mica, calcite ($CaCO_3$), potassium feldspar ($KAlSi_3O_8$) and sodium feldspar ($NaAlSi_3O_8$) and has a particle size distribution with a mean value of 24.5 μm and a D_{50} of 26.0 μm, a D_{10} of about 2.0 μm and a D_{90} of about 60.0 μm.

A {3,2} centroid simplex-lattice design, augmented with interior points, was used to define the mixtures of raw materials to be investigated. Mixtures with the selected compositions were processed as follows: wet mixing/milling (using ball mill), drying, de-agglomeration (by gently grinding in a mortar), moisturizing (6.5 wt.%, dry basis) and granulation. Test specimens (50 mm × 20 mm × 5 mm), were obtained by uniaxial pressing under 27 MPa and fast sintering in a laboratory furnace at 1000, 1100 and 1150 °C for 5 min, at a heating rate of 36 °C/min. Four independent batches (replications) of each composition were prepared and processed.

The water absorption (WA) was determined using the Archimedes liquid displacement method by immersion in water for 24 h. The linear firing shrinkage (LFS) was determined by the difference in the length of the test specimen before and after firing. The modulus of rupture (MR) was determined in a three-point-bending test, with a 0.5 mm/min cross-head.

The results of the four replications were used to calculate the coefficients of the regression equations iteratively until statistically relevant models and response surfaces were obtained, relating the WA, LFS and MR with the proportions of raw materials. The calculations were carried out with Statistica 6.0 (StatSoft Inc., 2001) software.

The resulting statistical analysis involves fitting of mathematical equations to the experimental results (i.e., water absorption, linear firing shrinkage and modulus of rupture) to get the entire

Table 1
Chemical composition[a] (wt.%) of the wastes and commercial raw material used

Material	SiO_2	Al_2O_3	Fe_2O_3	K_2O	TiO_2	CaO	Na_2O	LOI[b]
Granite waste	62.87	14.48	6.59	3.78	–	6.28	3.52	2.28
Kaolin waste	52.68	33.57	0.93	5.72	0.12	–	0.08	6.75
Red clay	53.49	22.25	11.15	3.87	1.44	2.66	–	5.12

[a] Determined by wet chemical analysis.
[b] Loss on ignition.

Table 2
Compositions of the design mixtures created by the augmented {3,2} simplex

Raw material (wt.%)	Design mixture									
	M_1	M_2	M_3	M_4	M_5	M_6	M_7	M_8	M_9	M_{10}
Red clay	100.0	0.0	0.0	50.0	50.0	0.0	33.3	66.6	16.6	16.6
Granite waste	0.0	100.0	0.0	50.0	0.0	50.0	33.3	16.6	66.6	16.6
Kaolin waste	0.0	0.0	100.0	0.0	50.0	50.0	33.3	16.6	16.6	66.6

Table 3
Water absorption, linear firing shrinkage and modulus of rupture measured in the 10 simplex mixtures

Design mixture	Temperature—1000 °C			Temperature—1100 °C			Temperature—1150 °C		
	WA (%)	LFS (%)	MR (MPa)	WA (%)	LFS (%)	MR (MPa)	WA (%)	LFS (%)	MR (MPa)
Replication 1									
M1	9.47	3.19	10.84	3.83	7.63	22.08	1.31	7.59	30.49
M2	28.91	−1.78	1.30	1.41	13.44	50.00	0.42	14.21	45.60
M3	20.82	−1.61	0.43	19.96	−0.81	1.70	18.85	0.31	3.03
M4	16.09	0.43	6.21	6.47	5.40	20.37	1.28	7.31	34.11
M5	14.18	−0.02	3.81	9.65	1.66	8.78	7.26	3.36	12.46
M6	26.82	−1.45	1.30	17.62	2.64	9.59	1.35	10.06	29.15
M7	16.49	0.33	5.60	9.00	3.85	16.12	1.36	7.36	28.15
M8	14.16	1.15	10.37	4.62	5.95	28.16	0.86	6.57	29.46
M9	21.31	−0.51	2.70	8.23	5.91	19.77	0.31	9.47	42.40
M10	16.95	−0.43	2.52	13.21	1.38	10.11	7.21	4.15	13.80
Replication 2									
M1	10.26	3.00	10.88	4.19	7.56	23.33	1.64	7.81	26.56
M2	28.04	−1.98	1.32	0.85	13.80	49.00	0.85	14.23	46.05
M3	20.80	−1.25	0.47	19.89	−0.91	1.87	19.75	−0.48	3.09
M4	15.18	0.76	6.88	6.16	6.11	22.26	0.42	7.82	44.00
M5	12.71	0.03	4.09	9.92	1.66	8.66	5.93	3.24	13.20
M6	25.23	−1.30	1.09	18.04	2.42	9.01	1.88	9.98	27.10
M7	16.02	−0.20	5.33	9.35	3.72	15.44	1.26	7.67	26.01
M8	13.11	1.56	9.72	4.93	6.52	25.96	1.18	7.28	30.00
M9	20.50	−0.59	2.57	6.05	6.29	21.09	0.64	9.42	43.21
M10	16.79	−0.48	2.66	12.95	1.38	10.06	6.41	3.92	16.45
Replication 3									
M1	10.12	3.34	9.94	3.18	7.81	20.04	1.86	7.94	29.91
M2	29.01	−1.88	1.23	1.32	13.70	50.64	0.62	14.03	48.88
M3	20.87	−1.80	0.44	19.96	−0.53	1.70	17.46	0.16	3.18
M4	15.35	0.38	6.64	6.87	5.71	19.90	1.05	7.59	35.00
M5	15.71	0.08	3.43	9.97	1.73	9.11	5.90	3.33	13.88
M6	26.64	−1.35	1.02	16.67	2.92	9.54	2.09	10.33	26.33
M7	16.33	0.16	5.24	8.52	3.89	15.39	1.05	7.48	23.78
M8	12.82	1.05	9.07	4.82	6.55	28.38	1.61	7.02	28.00
M9	23.25	−0.40	2.28	6.92	5.67	20.18	0.94	9.91	40.87
M10	16.92	−0.61	2.62	13.15	1.40	10.45	6.53	3.95	17.46
Replication 4									
M1	11.05	3.21	11.85	3.85	7.58	21.39	2.31	7.84	28.06
M2	28.77	−1.71	1.26	1.22	13.98	49.75	0.00	13.57	47.75
M3	21.01	−1.35	0.35	19.68	−0.77	1.54	18.42	−0.12	2.67
M4	15.18	0.53	6.54	6.65	5.40	21.58	0.53	7.18	40.61
M5	13.92	−0.05	4.68	10.67	1.88	8.77	6.88	3.08	13.49
M6	26.34	−1.43	0.99	16.67	2.60	9.48	1.73	10.31	20.62
M7	17.85	−0.18	5.37	8.31	4.02	14.84	1.47	7.59	24.94
M8	13.23	1.32	10.03	5.69	6.13	22.77	1.39	6.52	28.88
M9	20.04	−0.36	2.50	7.72	6.21	20.07	0.94	9.60	40.87
M10	16.91	−0.44	2.77	12.96	1.45	9.90	7.18	4.12	14.95

Table 4
Analysis of variance for significance of regression models[a]

Property	Temperature (°C)	Regression model	SSR	d.f.	MSR	SSE	d.f.	MSE	F test	p value	R^2 (%)
WA[b]	1000	Special cubic	10.344	1	10.3438	42.1697	33	1.2779	8.0946	0.0076	96.61
WA[b]	1100	Full cubic	4.018	2	2.0090	14.7977	31	0.4773	4.2088	0.0241	98.83
WA[b]	1150	Quadratic	251.460	3	83.8200	13.5802	34	0.3994	209.8549	<0.0001	98.82
LFS[c]	1000	Special cubic	0.717	1	0.7168	1.4268	33	0.0432	16.5794	0.0002	98.23
LFS[c]	1100	Full cubic	11.174	2	5.5870	2.2199	31	0.0717	78.0214	<0.0001	99.63
LFS[c]	1150	Quadratic	68.450	3	22.8166	8.0364	34	0.2364	96.5317	<0.0001	98.56
MR[d]	1000	Special cubic	8.8610	1	8.8610	20.6642	33	0.6262	14.1507	0.0007	95.73
MR[d]	1100	Full cubic	408.948	2	204.474	81.3820	31	2.6252	77.8885	<0.0001	98.74
MR[d]	1150	Linear	6514.033	2	3257.017	265.1378	37	7.1659	454.5170	<0.0001	96.09

[a] SSR: regression sum of squares; d.f.: degrees of freedom; MSR: regression mean squares; SSE: error sum of squares; MSE: error mean squares; R^2: coefficient of multiple determination.
[b] Water absorption.
[c] Linear firing shrinkage.
[d] Modulus of rupture.

response surface, and validation of the model through an analysis of variance.

3. Results and discussion

The compositions of the 10 mixtures (M_i, $i = 1, 2, \ldots, 10$) are listed in Table 2. Table 3 presents the measured values of water absorption (WA), linear firing shrinkage (LFS) and modulus of rupture (MR) of the fired test specimens.

Based on the data obtained (Table 3), regression equations were designed for the properties analyzed at each temperature, at a 5% level of significance. Eqs. (1)–(9) depict the behavior of the properties under study as a function of the proportions of raw materials (waste content). These equations were found to be the most statistically adequate (5% level of significance). These equations are referred to the raw materials used, and C, G and K represent the fractions of clay, granite waste and kaolin waste, respectively.

$$\mathrm{WA}_{1000\,^\circ\mathrm{C}} = 10.69C + 28.54G + 20.36K - 15.36CG - 5.75CK - 51.59CGK \quad (1)$$

$$\mathrm{WA}_{1100\,^\circ\mathrm{C}} = 3.66C + 1.10G + 19.77K + 15.85CG - 7.45CK + 26.45GK - 111.53CGK - 13.41CG(C-G) + 14.70CK(C-K) \quad (2)$$

$$\mathrm{WA}_{1150\,^\circ\mathrm{C}} = 1.71C + 0.80G + 18.45K - 15.99CK - 31.48GK \quad (3)$$

$$\mathrm{LFS}_{1000\,^\circ\mathrm{C}} = 3.12C - 1.79G - 1.44K - 3.32CK + 1.36GK + 13.58CGK \quad (4)$$

$$\mathrm{LFS}_{1100\,^\circ\mathrm{C}} = 7.67C + 13.76G - 0.72K - 19.98CG - 6.71CK - 15.24GK + 51.89CGK + 24.73CG(C-G) \quad (5)$$

$$\mathrm{LFS}_{1150\,^\circ\mathrm{C}} = 7.97C + 13.75G - 13.12CG + 12.69GK \quad (6)$$

$$\mathrm{MR}_{1000\,^\circ\mathrm{C}} = 11.35C + 0.91G - 5.67CK + 47.75CGK \quad (7)$$

$$\mathrm{MR}_{1100\,^\circ\mathrm{C}} = 21.95C + 50.09G + 1.94K - 58.03CG - 10.52CK - 64.50GK + 209.40CGK + 153.46CG(C-G) \quad (8)$$

$$\mathrm{MR}_{1100\,^\circ\mathrm{C}} = 28.60C + 49.24G + 2.74K \quad (9)$$

Table 4 lists the main statistical properties of the regressions obtained with the analysis of variance, using the nomenclature

Table 5
Composition of checkpoint mixtures and corresponding measured and predicted values of water absorption, linear firing shrinkage and modulus of rupture

Temperature (°C)	Composition (wt.%)			Predicted values			Measured values		
	Clay	Granite waste	Kaolin waste	WA[a]	LFS[b]	MR[c]	WA[a]	LFS[b]	MR[c]
1000	10	45	45	21.08	−0.79	2.26	21.35	−0.75	2.88
1100	10	45	45	13.22	3.01	11.29	11.99	3.37	13.95
1150	10	45	45	1.62	8.97	26.25	2.58	9.37	30.11
1000	55	10	35	12.92	0.71	6.17	12.84	0.58	8.66
1100	55	10	35	7.50	4.03	18.11	7.78	3.39	17.83
1150	55	10	35	3.15	5.49	21.61	3.10	5.41	23.19

[a] Water absorption.
[b] Linear firing shrinkage.
[c] Modulus of rupture.

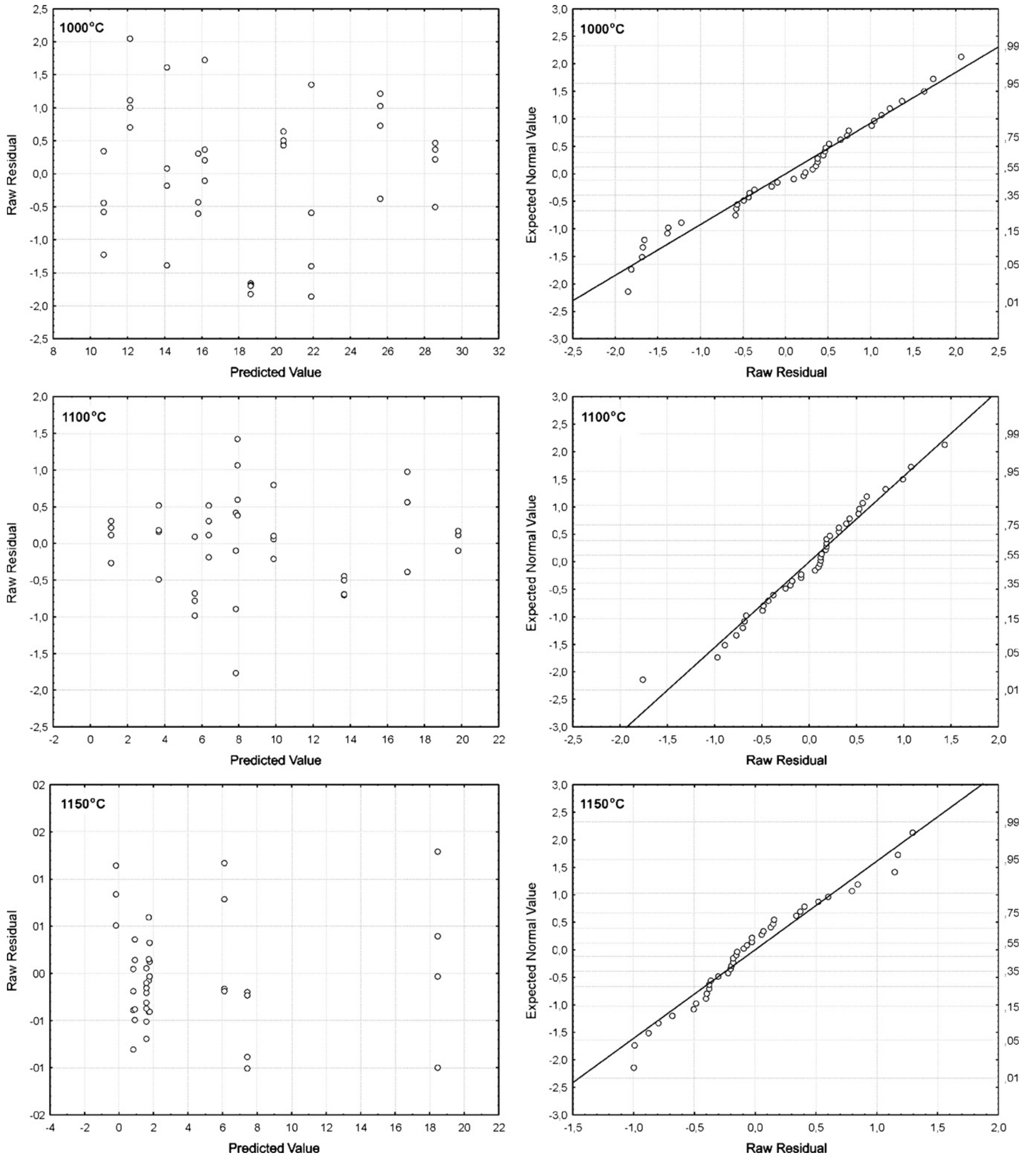

Fig. 1. Water absorption raw residuals vs. predicted values and normal probability curve for water absorption residuals after firing at 1000, 1100 and 1150 °C.

commonly reported in the literature.[19,20] As can be seen, all the regression models (Eqs. (1)–(9)) used here are statistically significant at the required level (p value below the significance level) and present little variability (high coefficients of multiple determination). The coefficients of multiple determination indicate the percentage of variation in the response that is explained by the deliberate variation in the factors (raw materials fractions) in the course of the experiment.[28]

The significance of the derived models can also be evaluated by comparing the F test value and the F value tabulated in Fisher–Snedecor distribution.[19,20] The regression is considered statistically significant, i.e., the fluctuations due to

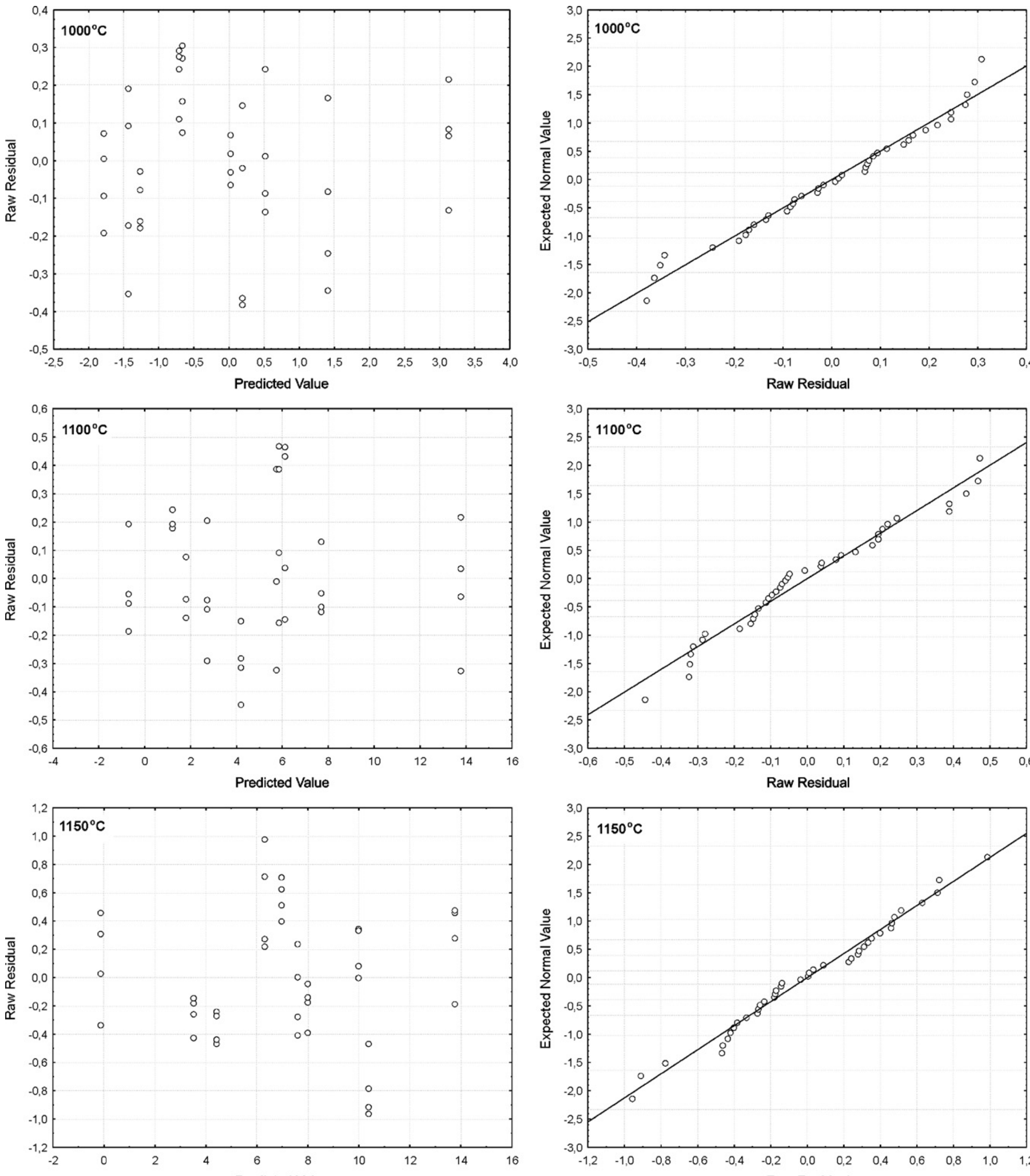

Fig. 2. Linear firing shrinkage raw residuals vs. predicted values and normal probability curve for linear firing shrinkage residuals after firing at 1000, 1100 and 1150 °C.

the independent variables are mostly explained by the model, if the F values are higher than the tabulated values (at the required level of significance). All the F values presented in Table 4 are more than fivefold higher than the tabulated values.

To evaluate the adequateness of the regression models, the analysis of the residuals is also required. Figs. 1–3 plot the properties (WA, LFS and MR) raw residuals vs. predicted values and normal probability curves for properties residuals after firing at 1000, 1100 and 1150 °C. The raw residual is the difference between the experimentally determined value and the calculated estimate.[21] The plots of raw residuals vs. predicted values (Figs. 1–3) show that the error values can be considered randomly distributed around a zero mean

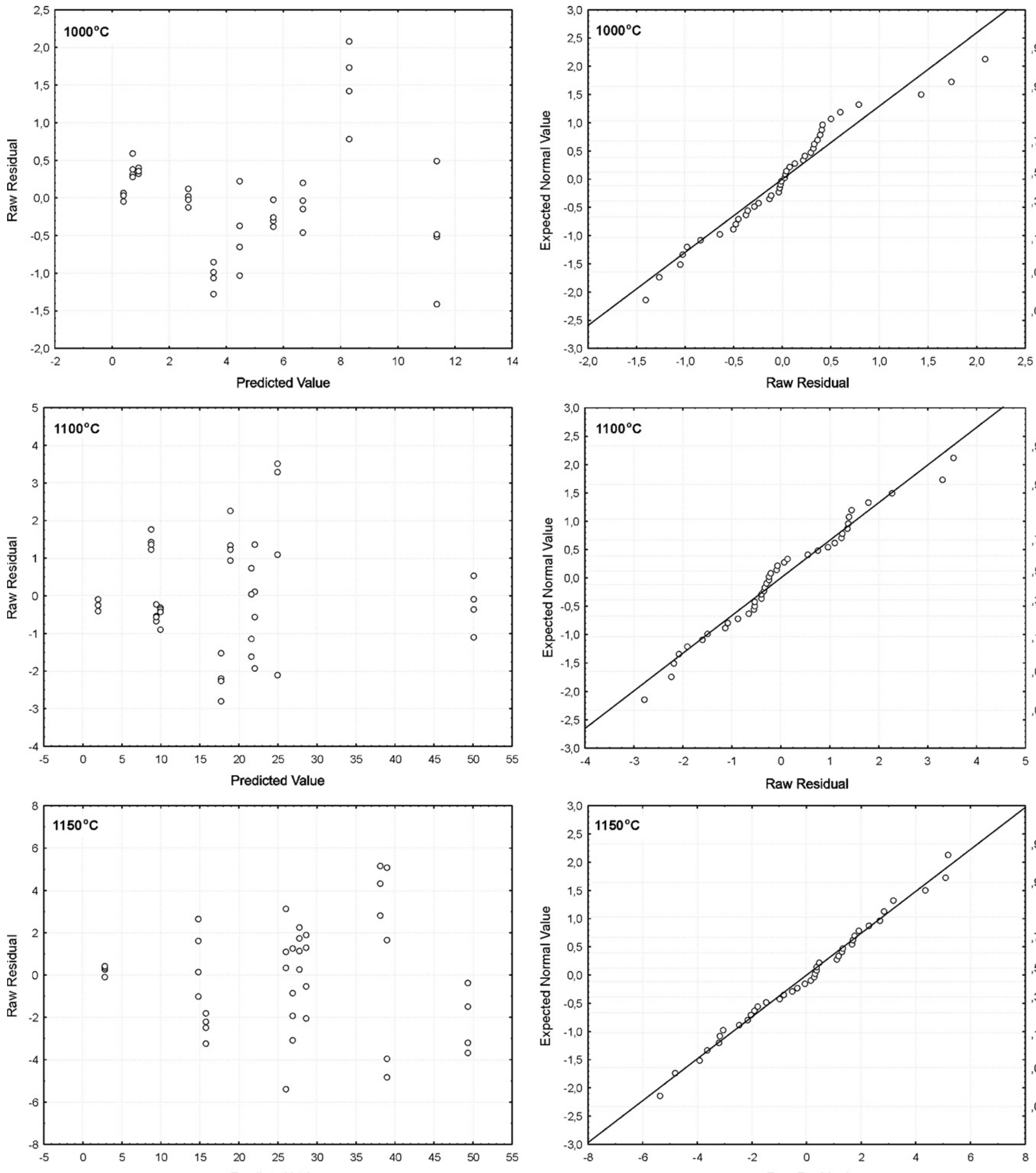

Fig. 3. Modulus of rupture raw residuals vs. predicted values and normal probability curve for modulus of rupture residuals after firing at 1000, 1100 and 1150 °C.

value (i.e., they are uncorrelated), which suggests a common constant variance for all property values at the three temperatures.

According to Figs. 1–3, straight lines can be considered to correlate the expected normal values and the raw residuals for all the property values at the three temperatures, which indicates that the distribution of residuals is normal. Thus, Table 4 and Figs. 1–3 suggest that the regression model equations are adequate to predict the behavior of the properties of the fired ceramic bodies to a very high degree of confidence.

To counter-check the statistical models, test specimens of the compositions M_{11} (10 wt.% clay, 45 wt.% granite waste, 45 wt.% kaolin waste) and M_{12} (55 wt.% clay, 10 wt.% gran-

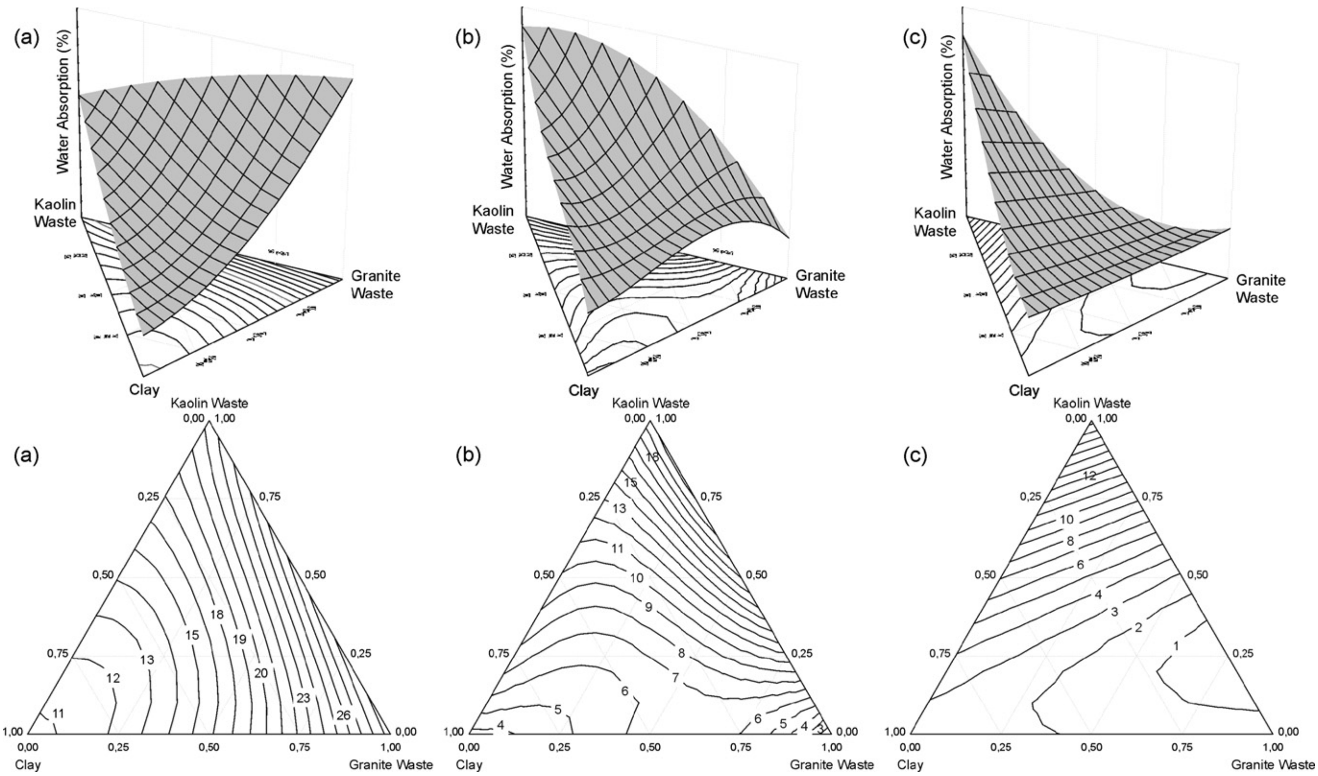

Fig. 4. Response surface plots and their projections onto the composition triangle for water absorption after firing at (a) 1000, (b) 1100, and (c) 1150 °C.

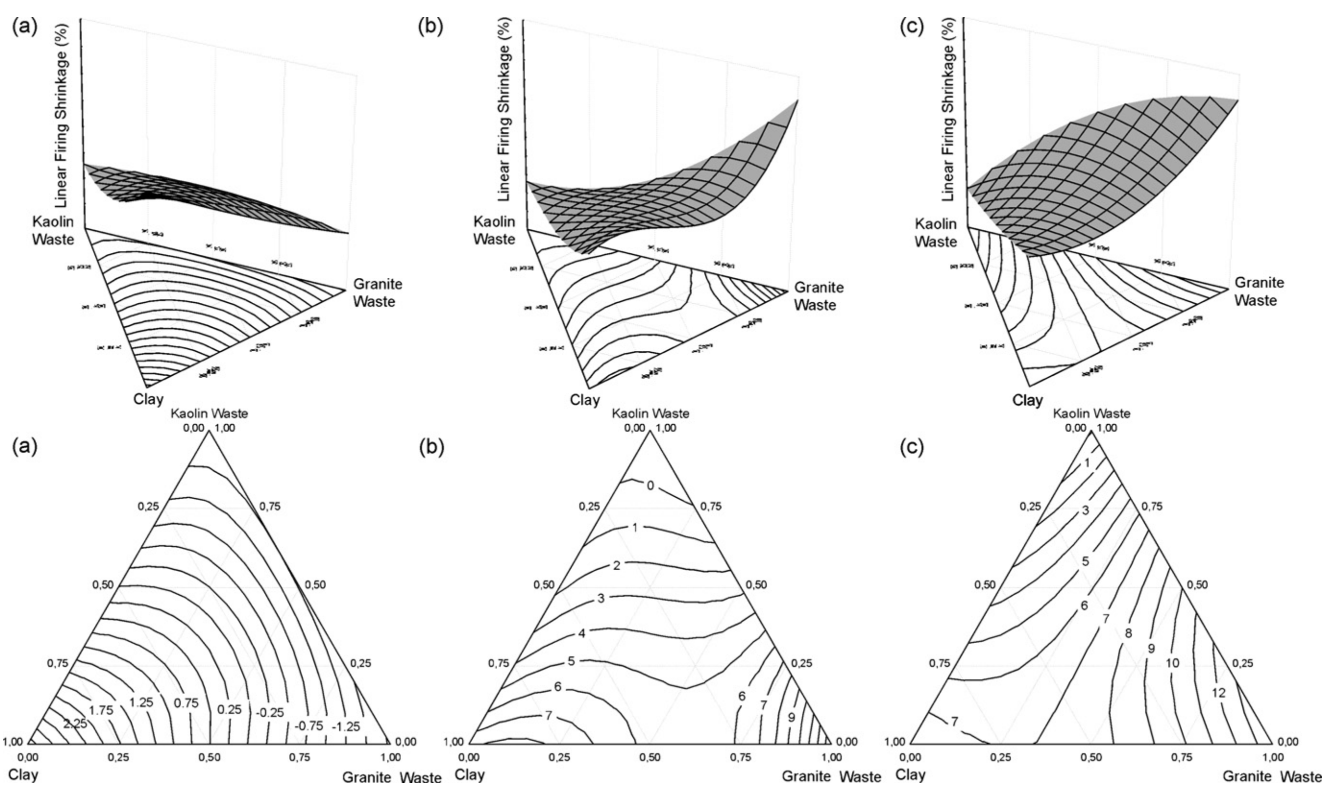

Fig. 5. Response surface plots and their projections onto the composition triangle for linear firing shrinkage after firing at (a) 1000, (b) 1100, and (c) 1150 °C.

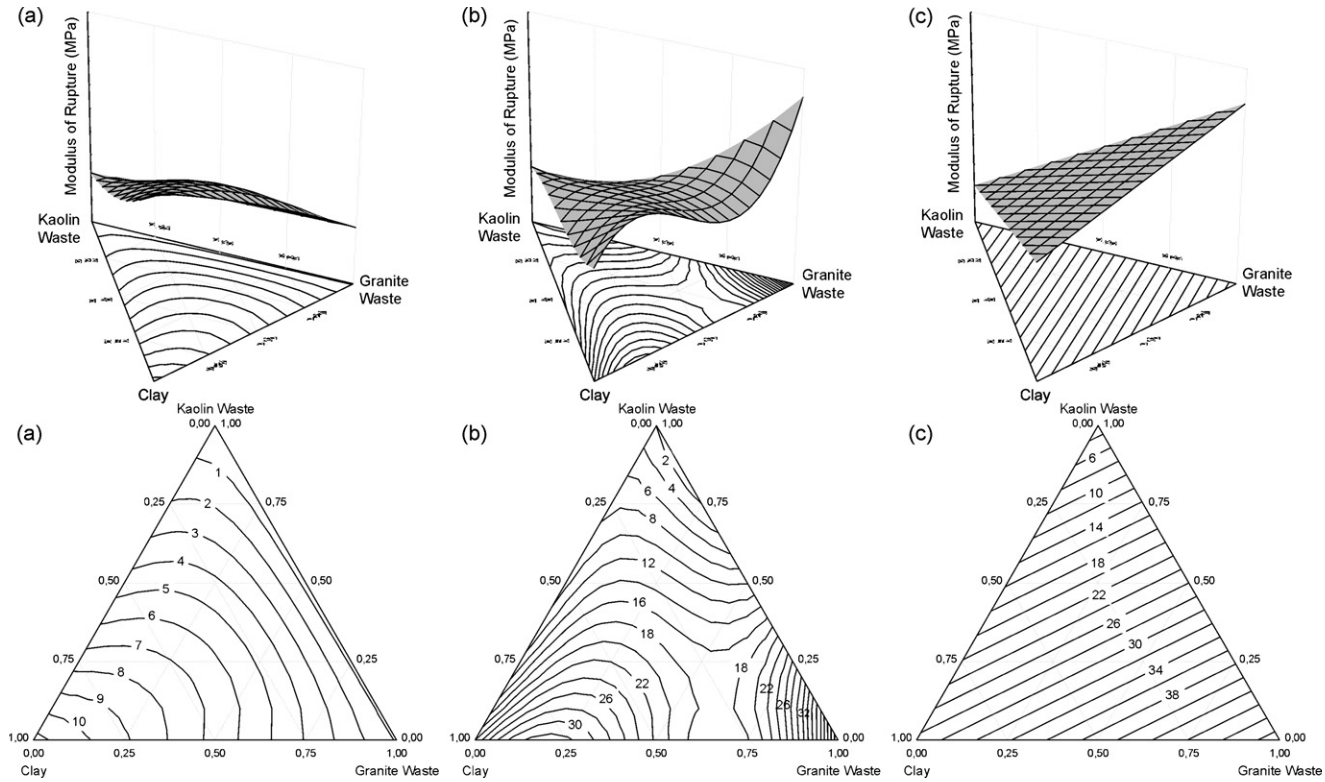

Fig. 6. Response surface plots and their projections onto the composition triangle for modulus of rupture after firing at (a) 1000, (b) 1100, and (c) 1150 °C.

ite waste, 35 wt.% kaolin waste) were prepared (as described in Section 2) and their WA, LFS and MR were predicted using the models and were measured experimentally. Table 5 shows the results obtained, indicating that errors of the predicted values are low, thus confirming the validation of the calculated models.

The mathematical equations (1)–(9), which describe the change and evolution of the properties as a function of composition (wastes and clay contents), are expressed in their canonical form as low degree polynomials, but the most statistically adequate model varied according to the analyzed property and the firing temperature. In general, the properties of the bodies fired at 1000 °C (in this study) were expressed by special cubic models, while the properties of the bodies fired at 1100 and 1150 °C (in this study) were expressed, respectively, by full cubic and quadratic models.

Comparing the values and signs of the coefficients of the models in Eqs. (1)–(3) it can be deduced that the most synergistic interaction after firing at 1000 and 1100 °C is that occurring between the three components, which contributes to reduce the WA. After firing at 1150 °C, the binary mixtures of clay–kaolin waste and granite waste–kaolin waste act synergistically on the WA.

From Eqs. (4)–(6), it can be deduced that the most synergistic interaction in the reduction of the LFS varied according to the firing temperature. After firing at 1000 °C the clay–kaolin waste mixtures displayed the highest interaction in the reduction of the LFS, while after firing at 1100 °C all the binary mixtures acted synergistically on the LFS. On the other hand, after firing at 1150 °C, only the clay–granite waste mixtures contributed to the reduction of the LFS.

The most synergistic interaction affecting the MR after firing at 1000 and 1100 °C (Eqs. (7) and (8)) was the one occurring among the three components, but the binary mixtures acted antagonistically. After firing at 1150 °C, each component alone had synergistic effect on MR, as described by the linear regression model (Eq. (9)).

Figs. 4–6 show the calculated response surface plots and their projections onto the composition triangle (as constant property contours—contour plot) for the WA, LFS and MR, respectively. The 3D surface plot is the graphical representation of Eqs. (1)–(9) and allows for easy and rapid predictive estimates over the entire composition range under investigation. Fig. 4 shows that WA increases with the waste content when the material is fired at 1000 °C and that the component that leads to the highest WA after firing at 1000 °C is the granite waste. However, the bodies with high amounts of granite waste present low WA after firing at 1100 and 1150 °C. On the other hand, the kaolin waste is the component that leads to the highest WA after firing at 1100 and 1150 °C. Fig. 4 also shows that the amount of kaolin waste in formulations can be increased when firing at 1150 °C up to about 50% without causing a sharp increase in water absorption, by using an appropriate combination of clay and granite waste fractions.

An analysis of Fig. 5 indicates that kaolin waste reduces the LFS at all the analyzed temperatures and that granite waste increases the LFS when the material is fired at 1100 and 1150 °C. This finding suggests the kaolin waste can be used to control

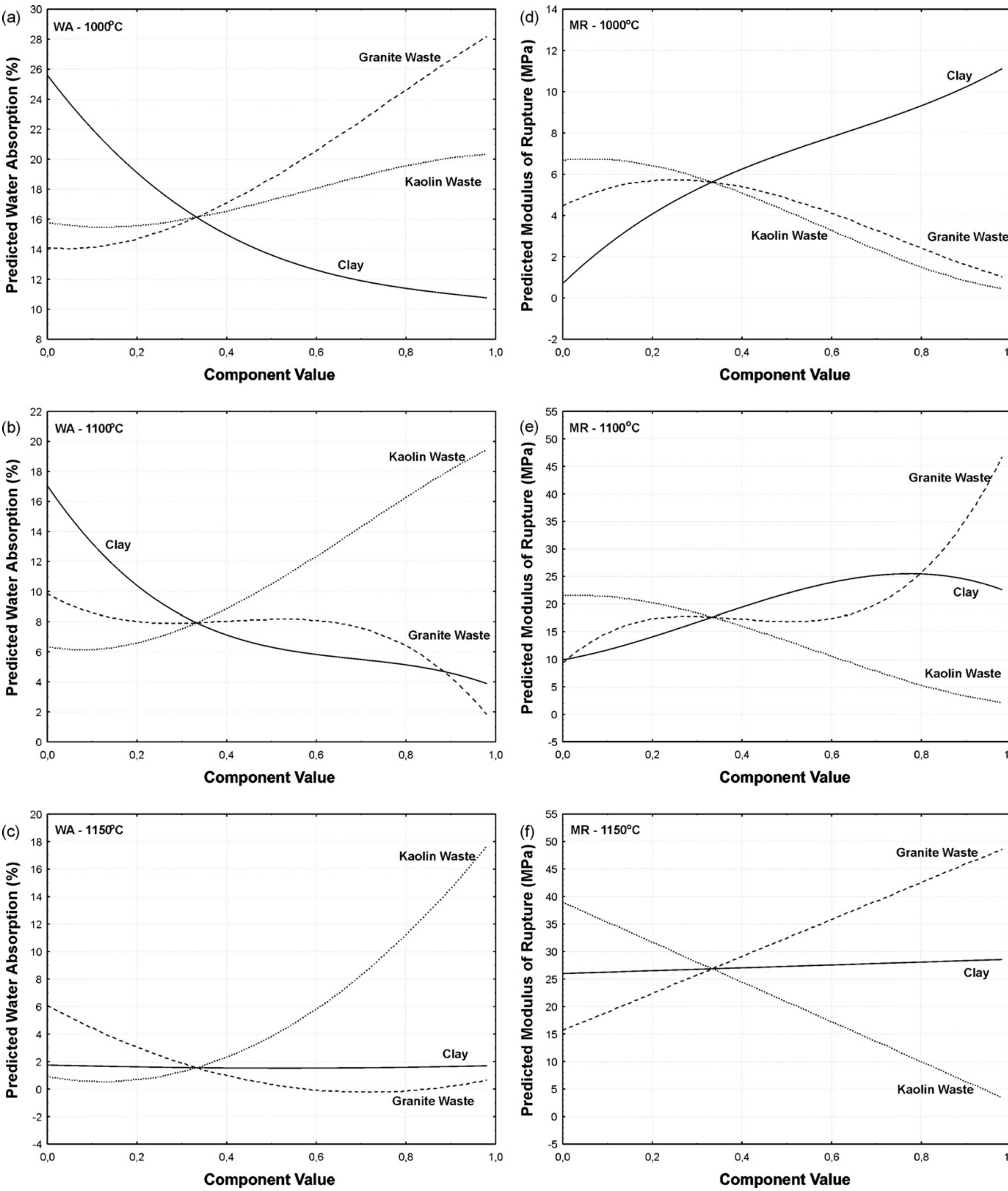

Fig. 7. Predicted properties trace plots: water absorption after firing at (a) 1000, (b) 1100 and (c) 1150 °C; modulus of rupture after firing at (d) 1000, (e) 1100 and (f) 1150 °C.

the firing shrinkage of the bodies, improving their dimensional stability during processing.

It is interesting to note that the highest MR values after firing at 1100 and 1150 °C corresponded to compositions with a high granite waste content, but that these compositions presented the lowest MR values after firing at 1000 °C (Fig. 6).

Another way of visualizing the effect that changes in composition might have on the WA and MR and improve the

Table 6
Optimized compositions and corresponding measured and predicted values of water absorption, linear firing shrinkage and modulus of rupture

Temperature (°C)	Composition (wt.%)			Predicted values			Measured values		
	Clay	Granite waste	Kaolin waste	WA[a]	LFS[b]	MR[c]	WA[a]	LFS[b]	MR[c]
1000	37.5	62.5	0.0	18.24	0.06	3.84	19.01	0.15	1.69
1100	37.5	62.5	0.0	6.56	5.34	16.94	6.33	4.25	15.50
1150	37.5	62.5	0.0	1.14	8.50	41.50	0.26	9.94	45.45
1000	37.5	50.0	12.5	16.46	0.35	5.38	15.42	0.39	7.52
1100	37.5	50.0	12.5	6.54	5.29	19,12	6.60	4.26	20.71
1150	37.5	50.0	12.5	0.63	8.20	35.69	1.20	6.48	32.51

[a] Water absorption.
[b] Linear firing shrinkage.
[c] Modulus of rupture.

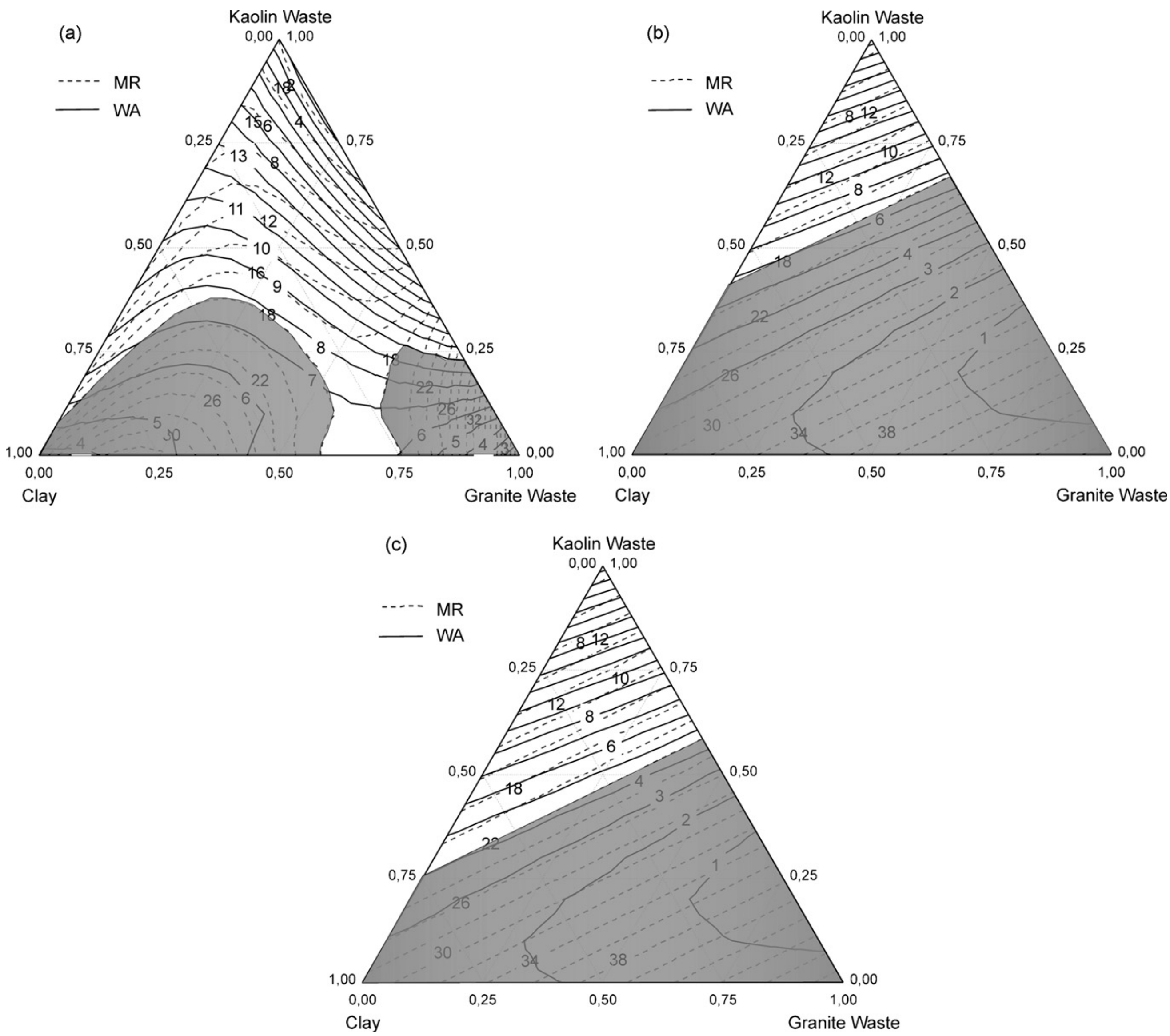

Fig. 8. Intersections of the water absorption and modulus of rupture response surfaces, with the shaded areas of the compositions with (a) water absorption ≤ 10% and modulus of rupture ≥ 18 MPa after firing at 1100 °C, (b) water absorption ≤ 10% and modulus of rupture ≥ 18 MPa after firing at 1150 °C, and (c) water absorption ≤ 6% and modulus of rupture ≥ 22 MPa after firing at 1150 °C.

interpretation of the statistical results is through the use of response trace plots. The response trace is a plot of the estimated property values as the composition moves away from a reference point, along lines that go through one of the triangle apexes (i.e., it is a vertical section through the property prism in which the fraction of one of the components is changed while the proportion between the other two is kept constant). In this way, the effect of each raw material on those properties can be best visualized.[18] Fig. 7 shows the WA and MR trace plots. The reference composition used in the trace plots was the simplex centroid, which corresponds to 33.3 clay, 33.3 granite waste, and 33.3 kaolin waste.

Fig. 7 shows that the increase in the WA with the wastes content after firing at 1000 °C is most pronounced when the amount of wastes is higher than 30% and that the increase in the clay content decreases the WA. Fig. 7 also shows that increasing granite waste and clay contents contributes to lower WA after firing at 1100 and 1150 °C.

Fig. 7 indicates that there is a composition range of low wastes content (20–30 wt.%) in which the MR is mildly influenced by the increase in wastes content after firing at 1000 °C. Wastes contents above ≈30% contribute to decrease the MR. The MR increases with the granite waste content and decrease with the kaolin waste content after firing at 1100 and 1150 °C. The clay increases the MR when the material is fired at 1100 °C, but the clay content presents mildly influence on the MR after firing at 1150 °C.

Based on Figs. 4–6 and their intersections, mixtures were selected maximizing the waste content and achieving the desired properties. The raw materials examined here are normally used in ceramic tile production. Hence, based on the Brazilian standard (ABNT 13813),[29] which specifies limits for WA and MR, several formulations with a large amount of waste can be obtained using the intersection of the WA and MR response surface according to the technical and standards requirements. For example, Fig. 8 shows the intersection of Figs. 4 and 6 and highlights the areas in the compositions where WA ≤ 10% and MR ≥ 18 MPa when firing at 1100 and 1150 °C and WA ≤ 6% and MR ≥ 22 MPa when firing at 1150 °C.

As an example of the suitability of the response surfaces intersection methodology to produce the desired formulations, maximizing the waste content and producing tiles with the desired technological characteristics, the compositions M_{13} (37.5% clay, 62.5% granite waste) and M_{14} (37.5% clay, 50.0% granite waste, 12.5% kaolin waste) were prepared (as described in Section 2). Table 6 shows the results obtained and the predicted values. The composition M_{14} was prepared to have 6% < WA < 10%, LFS < 6%, and MR > 18 MPa after firing at 1100 °C and the composition M_{13} was prepared to have WA < 3%, LFS < 10%, and MR > 30 MPa after firing at 1150 °C.[25,30,31] The results highlight that the statistical design of mixture experiments methodology can be successfully used to optimize tile formulations containing high amount of wastes. In terms of Brazilian standard (ABNT 13813),[29] the fired bodies of the composition M_{13} can be classified as BIb after firing at 1150 °C, while composition M_{14} can be classified as BIIb and BIb after firing at 1100 and 1150 °C, respectively.

4. Conclusions

The statistical design of mixture experiments and response surface methodologies proved to be powerful tools for planning and analyzing experiments to ascertain the influence of waste materials content on the technological properties of ceramic bodies and to optimize ceramic formulations containing large amounts of waste materials. The calculated regression models were found to be statistically significant at the required level and presented little variability. These regression models can be used to select the optimal wastes content to produce ceramic bodies with specific properties.

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