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Ceramics International 39 (2013) 6277–6285

CERAMICS INTERNATIONAL

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Sensitivity analysis of mathematical models for final product properties: Link to DTG curve

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Received 3 January 2013; received in revised form 19 January 2013; accepted 20 January 2013
Available online 1 February 2013

Abstract

Compressive strength and water absorption of fired heavy clay products varies with firing temperatures, but not entirely according to linear function, as it is mostly reported in literature. Also, differential thermo-gravimetric curve shows many turnovers in all the samples tested, within observed temperature range (820–920 °C). The aim of this research was to find a cause for such behaviour. Except derivative weight (*DW*), compressive strength (*CS*) and water absorption (*WA*) are chosen as outputs that represent properties of the fired samples. These parameters can be calculated using second order polynomial models (SOPs), on the basis of content of major oxides and firing temperature, as shown in our previous research. Sensitivity analysis was used as the effective approach in testing changes observed in the SOP outputs, due to the variation of content of major oxides for +1% or −1% of their nominal value. This study reveals in more detail the most significant influence of inputs (SiO_2, Al_2O_3, Fe_2O_3 and CaO content) over the outputs (*DW*, *CS* and *WA*) in every observed firing temperature. Addition or lowering of content of major oxides can both increase and decrease all the observed outputs, as revealed using sensitivity analysis.

Keywords: Heavy clay products; Properties variation; Differential thermo-gravimetry; Second order polynomial model; Sensitivity analysis

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1. Introduction

Highly heterogeneous nature of the raw materials used to produce heavy clay bricks influences final clay brick properties. Complexity of these natural occurring systems is proved by an extensive research towards better understanding of the materials themselves, as well as the behaviour of the final products [1–5]. Polynomial models are appropriate in investigating the effect of chemical composition and firing temperature on the final laboratory samples properties [1,2]. It is shown that the most important parameters influencing compressive strength (*CS*) and water absorption (*WA*), in the 820–1100 °C range, are firing temperature, CaO and SiO_2 contents. Also, content of other major oxides (Al_2O_3, Fe_2O_3, MgO, Na_2O, K_2O, and TiO_2) shows significant influence on *CS* and *WA* [1]. In this research, influences of content of major oxides are studied at certain firing temperatures within the range 820–920 °C, thus providing more sophisticated results. Sensitivity analysis was used for SOP output testing, by changing one input variable at a time, for +1% or −1% of its nominal value, while all the other variables were fixed to their baseline values. Input variables effects were calculated with reference to the same central point in the input space, thus increasing the comparability of the results obtained [6].

Thermal analysis is often used to detect changes in physical parameters, as the function of temperature in different materials. In ceramics, this technique is used for the initial characterisation of the components, study of the firing processes, mineralogical composition analysis and determination of the fired ceramic material properties. Thermal analysis methods are well established in the science of clay and related industrial implementation, as a good technique for studying complex mineral structures

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http://dx.doi.org/10.1016/j.ceramint.2013.01.049

and materials of poor crystallinity [7–10]. Changes in the mass of a sample can be detected by using thermogravimetric (TG) analysis. Since endothermic and exothermic mass loss transformation may simultaneously occur during thermal analysis, the derivative of the TG curve (DTG) is used as more indicative to several decomposition steps in clays. DTG curve shows changes in the TG slope that may not be obvious from the TG curve. As DTG curves represent the total mass loss rate (first derivative of TG data) during reactions, they allow a better evaluation of the simultaneous transformations from the respective peaks, by giving more sensitivity to small weight changes [11,12].

Since compressive strength and water absorption of final heavy clay products varied with firing temperatures and did not change its values entirely according to linear function, as it is mostly reported in the literature for the firing temperatures between 800 and 1000 °C [13–18], this research, based on sensitivity analysis, aims to reveal the reasons for such behaviour. Derivative weight also varied, so the idea was to use it in the analysis in order to obtain more detailed information.

2. Materials and methods

2.1. Samples and experimental procedure

The data used in this research were obtained experimentally. A batch containing 23 heavy clays was used to prepare laboratory blocks and cubes, according to the procedure described in our previous research [1–3]. These samples were taken in Serbia and signed according to the sampling regions in Serbia: North (N1–N7), Central (C1–C8) and South (S1–S8). The usual standard procedure for preparing raw materials involves drying at 105 ± 5 °C, shredding on laboratory vehicular mill, and then, after moistening, grinding the sample at laboratory roller mill with 3 mm, and later 1 mm differential gap [19].

All the samples were dried and fired under the same regime (1.4 °C/min until 610 °C, and later 2.5 °C/min until the final temperature). Final firing temperatures were 820, 850, 870, 900 and 920 °C. Chemical content of major oxides was determined using classical silicate analysis [3].

Compressive strength (*CS*) and water absorption (*WA*) were determined following the usual laboratory methods, as described previously [3].

Derivative weight (*DW*) is determined by simultaneous thermal analysis using SDT Q600 device (TA Instruments) with platinum/platinum–rhodium thermocouple. The temperature of the air-dried samples was increased from room temperature to 920 °C. The sample mass was about 10 mg, and the samples were weighed in platinum pans. A small amount of samples allowed better resolution of the peaks and faster heating [20]. The dynamic experiments were carried out under nitrogen atmosphere with the heating rate of 20 °C/min.

2.2. Mathematical tools

On the basis of our previous conclusions [1,2], naturally occurring materials which are acceptable for use in heavy clay industry show non-linear relationship with final product properties. These relationships are best described through second order polynomial models (SOPs). Second order polynomial model was used to find the relationships between input variables: the content of major oxides (SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, Na_2O, K_2O, MnO and TiO_2) and firing temperature (in the range of 820–920 °C), as independent parameters, and newly introduced *DW* as an output parameter. SOPs for other tested parameters (*CSB*, *CSC*, *WAT*, *WAB* and *WAC*) were published in our previous paper [1], and used in further analysis presented in this research. Regression analysis for the SOP models was performed using StatSoft Statistica for Windows (version 10). The models were obtained for each dependent variable, where factors were rejected when their significance level was less then $p < 0.05$, with 95% confidence limit.

On the basis of developed SOP models [1], sensitivity analysis is conducted in order to define the influence of content of major oxides on the observed outputs in the selected firing temperatures range more precisely. While all the inputs individually varied for $+1$ or -1% of their nominal values, SOP models were used to predict the outputs.

3. Results and discussion

3.1. Chemical composition and technological characteristics

The content of major oxides is given in Table 1. Every sample was tested at 5 firing temperatures, and this is how $23 \times 5 = 115$ individual specimens were obtained. The post-hoc Tukey's HSD tests were evaluated for comparison between oxides content in the samples, and statistically significant differences were established in all the samples, significant at $p < 0.05$ level. The heavy clays analysed present typical composition with high and varying amounts of quartz and carbonates. Since SiO_2, Al_2O_3 and Fe_2O_3 build clay minerals [21], according to their content in the samples tested, it was expected that the N6, S1, C1, S6, S8, C2, S4 were the most plastic samples, and that the N5, N4, N7, N2 and N3 contained the lowest content of clay minerals. Sensitivity analysis (Section 3.3.) describes the differences between the samples in more detail.

Compressive strength (*CS*) and water absorption (*WA*) of laboratory samples were chosen as outputs to be observed in this study, jointly with derivative weight (*DW*), all obtained in the range of 820–920 °C. Fig. 1 presents determined variation of experimental results with firing temperature. It can be seen that products often showed better characteristics at lower firing temperatures. Cubes showed much higher *CS* values then blocks, because they contained no voids and have lower surface area.

Table 1
Chemical composition of raw materials used.

Sample		SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	MnO	TiO_2
1–5	N1	50.58 ± 0.60^{bcd}	13.22 ± 0.50^{bcd}	5.79 ± 0.39^{cde}	7.61 ± 0.26^{h}	4.38 ± 0.22^{i}	1.35 ± 0.03^{gh}	3.46 ± 0.14^{jk}	0.15 ± 0.01^{i}	0.01 ± 0.00^{a}
6–10	N2	47.23 ± 1.16^{b}	10.53 ± 0.61^{a}	4.01 ± 0.3^{a}	11.53 ± 0.46^{j}	6.00 ± 0.25^{k}	1.58 ± 0.05^{i}	3.08 ± 0.14^{fghi}	0.01 ± 0.00^{ab}	0.55 ± 0.02^{b}
11–15	N3	40.32 ± 1.14^{a}	14.44 ± 0.57^{de}	4.18 ± 0.14^{a}	13.11 ± 0.52^{k}	4.35 ± 0.15^{hi}	1.18 ± 0.05^{efg}	2.99 ± 0.19^{efgh}	0.03 ± 0.00^{c}	0.57 ± 0.02^{b}
16–20	N4	39.78 ± 1.58^{a}	12.14 ± 0.88^{abc}	4.66 ± 0.16^{ab}	14.11 ± 0.87^{l}	5.19 ± 0.17^{j}	0.79 ± 0.02^{d}	3.32 ± 0.13^{hij}	0.01 ± 0.00^{ab}	0.01 ± 0.00^{a}
21–25	C1	65.48 ± 2.34^{ij}	15.14 ± 0.98^{de}	5.27 ± 0.36^{bc}	1.58 ± 0.06^{ab}	1.39 ± 0.04^{b}	0.42 ± 0.01^{b}	2.50 ± 0.06^{abcd}	0.14 ± 0.00^{h}	0.86 ± 0.04^{cde}
26–30	C2	66.21 ± 3.49^{ij}	15.23 ± 0.66^{de}	5.28 ± 0.18^{bc}	0.90 ± 0.04^{a}	1.18 ± 0.09^{b}	0.64 ± 0.02^{cd}	2.69 ± 0.11^{cde}	0.14 ± 0.00^{h}	0.87 ± 0.02^{de}
31–35	S1	60.99 ± 1.87^{ghij}	14.75 ± 0.65^{de}	6.11 ± 0.24^{def}	1.68 ± 0.08^{ab}	1.33 ± 0.04^{b}	1.22 ± 0.03^{fg}	3.69 ± 0.16^{k}	0.00 ± 0.00^{a}	1.00 ± 0.03^{ghij}
36–40	S2	66.56 ± 2.81^{j}	13.84 ± 0.88^{cd}	5.42 ± 0.09^{bcd}	1.52 ± 0.06^{ab}	0.36 ± 0.02^{a}	1.20 ± 0.05^{fg}	2.51 ± 0.08^{abcd}	0.04 ± 0.00^{d}	1.09 ± 0.03^{klm}
41–45	S3	63.23 ± 3.67^{hij}	13.69 ± 0.64^{cd}	6.64 ± 0.34^{fgh}	2.20 ± 0.07^{b}	0.12 ± 0.00^{a}	1.46 ± 0.06^{hi}	3.41 ± 0.06^{ijk}	0.02 ± 0.00^{b}	0.96 ± 0.01^{fghi}
46–50	S4	58.38 ± 1.60^{efgh}	16.45 ± 0.68^{e}	7.23 ± 0.19^{hij}	1.69 ± 0.01^{ab}	0.12 ± 0.00^{a}	1.18 ± 0.01^{efg}	2.51 ± 0.14^{abcd}	0.04 ± 0.00^{d}	1.06 ± 0.03^{jklm}
51–55	C3	55.27 ± 1.11^{cdefg}	15.02 ± 0.48^{de}	7.85 ± 0.20^{jk}	3.45 ± 0.11^{c}	3.42 ± 0.20^{f}	1.50 ± 0.05^{hi}	3.19 ± 0.08^{ghij}	0.01 ± 0.00^{ab}	1.15 ± 0.03^{m}
56–60	C4	57.69 ± 2.60^{efgh}	14.72 ± 0.94^{de}	7.68 ± 0.15^{ijk}	3.31 ± 0.06^{c}	2.97 ± 0.01^{e}	2.41 ± 0.13^{j}	2.41 ± 0.11^{abc}	0.01 ± 0.00^{ab}	1.13 ± 0.05^{lm}
61–65	C5	55.69 ± 0.79^{cdefg}	14.81 ± 0.42^{de}	7.30 ± 0.36^{hij}	3.63 ± 0.06^{cd}	$2.97 \pm 0.06\ ^{e}$	2.26 ± 0.09^{j}	2.81 ± 0.09^{def}	0.01 ± 0.00^{ab}	1.04 ± 0.04^{ijkl}
66–70	C6	53.95 ± 2.05^{cdef}	14.91 ± 0.84^{de}	8.26 ± 0.19^{k}	3.48 ± 0.05^{c}	3.93 ± 0.11^{g}	2.26 ± 0.07^{j}	2.41 ± 0.14^{abc}	0.01 ± 0.00^{ab}	1.08 ± 0.05^{jklm}
71–75	C7	55.99 ± 1.12^{defg}	14.82 ± 0.17^{de}	7.04 ± 0.32^{ghi}	3.79 ± 0.14^{cde}	3.08 ± 0.12^{ef}	1.02 ± 0.05^{e}	2.50 ± 0.03^{abcd}	0.01 ± 0.00^{ab}	0.89 ± 0.04^{def}
76–80	C8	53.70 ± 2.55^{cde}	14.13 ± 0.51^{cd}	6.94 ± 0.21^{ghi}	4.63 ± 0.08^{ef}	4.15 ± 0.08^{ghi}	1.14 ± 0.05^{ef}	2.41 ± 0.09^{abc}	0.01 ± 0.00^{ab}	0.87 ± 0.03^{def}
81–85	N5	53.91 ± 1.46^{cdef}	11.30 ± 0.66^{ab}	5.42 ± 0.18^{bcd}	9.65 ± 0.70^{i}	2.43 ± 0.10^{d}	0.72 ± 0.05^{cd}	2.93 ± 0.19^{efg}	0.14 ± 0.00^{h}	0.77 ± 0.01^{c}
86–90	N6	60.15 ± 1.16^{fghi}	15.26 ± 0.56^{de}	5.89 ± 0.07^{cdef}	1.59 ± 0.04^{ab}	1.51 ± 0.05^{b}	0.57 ± 0.02^{bc}	2.42 ± 0.09^{abc}	0.07 ± 0.00^{e}	0.81 ± 0.04^{cd}
91–95	S5	58.14 ± 1.57^{efgh}	14.53 ± 0.61^{de}	6.43 ± 0.19^{efg}	4.51 ± 0.18^{def}	1.90 ± 0.05^{c}	1.34 ± 0.09^{gh}	2.19 ± 0.10^{a}	0.11 ± 0.00^{g}	0.90 ± 0.02^{def}
96–100	S6	57.00 ± 1.40^{efgh}	15.17 ± 0.77^{de}	6.58 ± 0.36^{fgh}	4.99 ± 0.21^{fg}	2.11 ± 0.05^{cd}	1.09 ± 0.07^{ef}	2.32 ± 0.12^{ab}	0.07 ± 0.00^{ef}	0.95 ± 0.03^{efgh}
101–105	S7	58.14 ± 1.83^{efgh}	14.88 ± 0.19^{de}	6.58 ± 0.17^{fgh}	5.47 ± 0.23^{fg}	2.11 ± 0.08^{cd}	1.12 ± 0.08^{ef}	2.19 ± 0.05^{a}	0.08 ± 0.01^{ef}	0.93 ± 0.04^{efg}
106–110	S8	57.85 ± 2.34^{efgh}	15.18 ± 0.34^{de}	6.53 ± 0.27^{efgh}	5.73 ± 0.24^{g}	2.23 ± 0.08^{cd}	1.26 ± 0.04^{fg}	2.67 ± 0.06^{bcde}	0.08 ± 0.00^{f}	1.03 ± 0.04^{hijk}
111–115	N7	49.58 ± 2.11^{bc}	13.50 ± 0.67^{cd}	4.06 ± 0.20^{a}	11.77 ± 0.57^{j}	3.99 ± 0.20^{gh}	0.01 ± 0.00^{a}	2.26 ± 0.14^{a}	0.01 ± 0.00^{ab}	0.01 ± 0.00^{a}

$^{a–m}$Values with the same letter, written in superscript are not statistically different at the $p < 0.05$ level, 95% confidence limit, according to post-hoc Tukey's HSD test.

Blocks are made of thin walls and water penetrates the mass better, and therefore they are better sintered, which is also proved by a bit lower *WA* [20].

SOP models [1] revealed that most significant influence showed CaO and SiO_2. Calcite is an intense flux, especially when highly dispersed, and can in part form calcium-silicates, in reaction with clay minerals, but it also strongly influences the development of porosity, if larger grains are present (> 1 mm) and, as a consequence, physical and mechanical properties [1,3,22]. Therefore, all raw materials tested in this work are ground below 1 mm. SiO_2 is present in heavy clay systems mostly in its free form. Quartz melts with the temperature and can improve densification to a certain extent, but larger grains can lower the strength of the ceramic body [1,3,14]. Fine-grained sand, with particle size in the range of 10–30 μm improves the mechanical strength (provides full densification), but its presence as quartzite in the form of pebbles or fragments of terrace origin is undesirable. Quartz sand, especially the one of coarse grit, adversely affects the mechanical properties, due to the susceptibility to micro-cracks formation due to the quartz allotropic transformation at the temperature of around 573 °C (increase in volume of about 2%). The β–α change occurs readily on cooling. Coarser sand induces greater porosity and water absorption values. Although quartz is not stable above 870 °C, changes occur so slowly that bricks fired above 1000 °C usually still contain α quartz when examined cold [2,16,23].

The simplest explicable behaviour is observed in the case of the N2, N3, N5 and N7 samples, all of loess nature [2]: they contained low SiO_2, Al_2O_3 and Fe_2O_3, and high CaO content. Low clay minerals and high calcite content influenced low *CS* and high *WA*. The N4 sample was also of loess nature with more calcite and higher SiO_2 and Fe_2O_3 contents, compared to the N2, N3 and N7, but less Al_2O_3. *WA* was high, but lower than in N7, N2 and N3. *CS* was among the highest in the tested group of samples. Most probably fine-grained calcite left more pores after burning, but a part of it also reacted with clay minerals and gained better sintered matrix [2]. The N6 sample, the most plastic one, had the lowest *WA* (low CaO content), and the highest *CS* of the remaining samples [14,21]. The N1 sample contained average clay minerals and calcite content, so fired products properties gained also middle values. The C8 and C7 samples had almost twice as lower *CSB* and twice as higher *WAB*, then the N6. CaO content was also almost twice as high in these samples. N4 showed similar *CS* values, but almost twice as lower *WA*, then C8 and C7.This again confirms fine grained calcite in the N4 sample. These conclusions are enhanced by sensitivity analysis, presented in Section 3.3.

The rest of the samples showed combined effects of content of major oxides, which made the analysis more complex. For example, the S1 sample had high content of SiO_2, Al_2O_3, and Fe_2O_3, and low content of CaO, which gave average values of *CS* and *WA*.

Low percentage of SiO_2 caused low *CS* in most of the products, but in the case of samples with higher quartz content, conclusions drawn are more sophisticated, since there are higher quantities of larger grains, that lower the

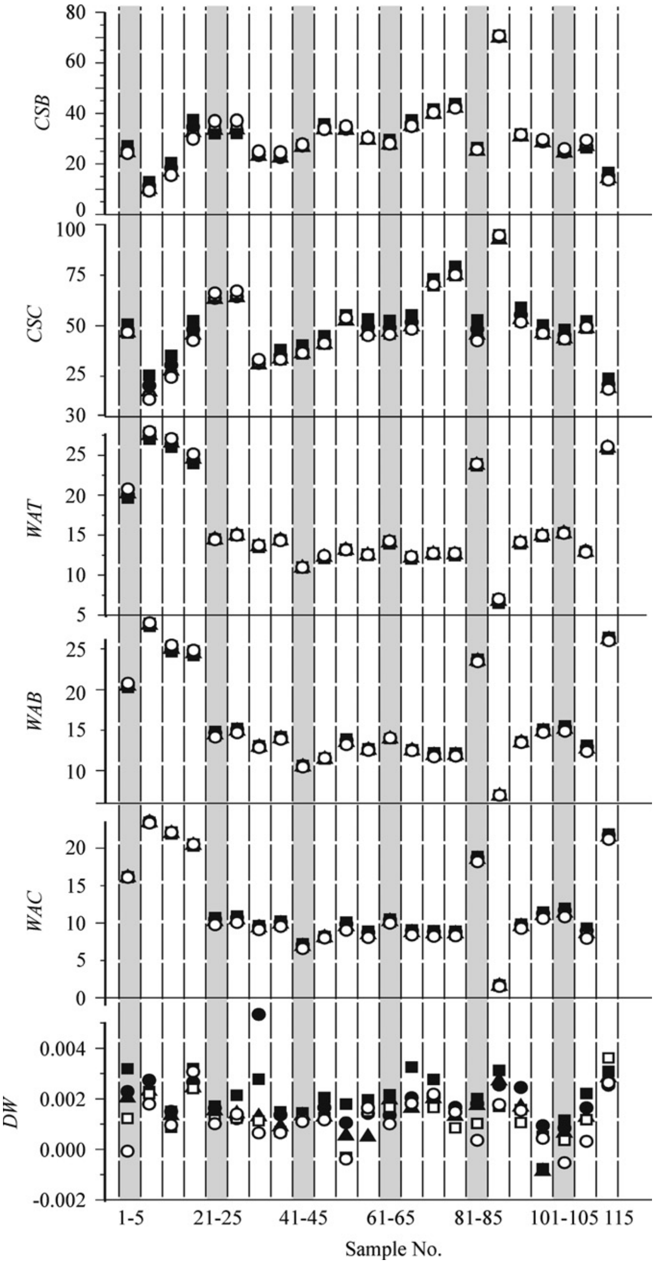

Fig. 1. Technological characteristics of the samples observed: ■—820 °C, ●—850 °C, ▲—870 °C, □—900 °C, and ○—920 °C.

strength of the material. The highest SiO_2 content is observed in S2, C2, C1, S3, S1, and N6.

The highest *CS* values are determined, surprisingly, in the case of the cubes fired at 820 °C. The exceptions are noticed in the C1, C2 and S1 samples, where *CSC* at 920 °C was the highest because of low calcite and relatively high SiO_2 and Al_2O_3 content. According to SOP model [1], except firing temperature, the most influential to *CS* are CaO and SiO_2 contents. High calcite content makes greater difference in final product properties, because it decomposes in a wide range of temperatures, starting below 650 °C (polycrystalline form) to nearly 850 °C (monocrystalline calcite). Finer particle sized calcite decomposes at lower temperatures [24]. This implies that larger grains decompose at higher temperatures, thus lowering compressive strength by making the matrix more loose and not well sintered (micro-cracks) [15]. The lowest *WAC* values are found in the samples fired at 920 °C, except for N3 and N4. These samples contain the highest content of calcite, which partially decomposes and some pores are left closed, thus reducing *WA*. Also, the temperature is more affective to samples that contain more carbonates [2]. The lowest *WA* values are generally found, besides N6, in the S3, S4 and C4 samples.

Laboratory blocks were more sensitive to raw material composition: besides C1, C2 and S1, also S2, S6, S7 and S8 showed higher *CS* values at 920 then at 820 °C. The same behaviour, but to a lesser extent, is observed in the C3 and N6 samples. The exception from conclusion that low calcium content causes expected products behaviour (*CS* increasing with temperature) is observed in the S6, S7 and S8 samples. They contained 5% and 6% of CaO, but also high Fe_2O_3 content (about 7%). The reason could be finer grained calcite that is present, as it is usually the case in South Serbia samples [24], but also a low relation of clay content to CaO content, the parameter which should be analysed in future research. *WAB* increased with temperature only in the case of N1, N2, N3, N4, S4 and S5 samples. It is obvious that *CS* and *WA* did not behave in the same manner and did not always follow each other, as mostly reported in literature [13–18].

The N6, C8 and C7 samples were generally the best sintered (the highest *CS*), and N7 and N2 were the weakest. The samples behaved similar according to *WA*, where the highest values are observed in the N2 (23.4–28.2%), N7 (21.2–26.4%), and the lowest in the N6 (1.5–7.0%) sample. The cubes absorbed less water than the blocks (lowest values at 920 °C). Hollow blocks sintered very well since their walls are thin, which allowed all the reactions to take place [3]. This is not the case with solid products such as laboratory cubes and tiles.

DW decreased in all samples when 820 and 920 °C are compared, and the observed difference was the most drastic in the samples N1, S1 and C3, and then in the S8, N5, C6, N6, S4 and C5, respectively, which pointed mostly to the larger calcite grains in these samples. DTG curves showed constant decrease of *DW* with higher firing temperature in the case of N1, C1, S2, S4, C3, N5, S7 and S8. In most of the samples, there are exceptions at certain temperatures (increase), but with general decrease tendency. It means that reactions that involve loss of weight take place mostly at lower temperatures [18], especially with smaller calcite grains and their similar size [14]. If there are larger grains, DTG curves can show exceptions from continual decrease in *DW*. Endothermic and exothermic reactions in this temperature range can be caused by destruction, crystallisation, redox reaction and the reaction in the solid phase [20]. It is concluded that *DW* behaved differently from other product parameters.

From the research presented, it is obvious that content of major oxides and final products properties are in a complex connexion, and do not simply follow each other, so further analysis needs to be conducted.

3.2. Derivative weight SOP model

Table 2 shows the ANOVA calculation for the *DW* variable, revealing the major influences of input variables, and regression coefficients for non/linear SOP model of *DW*. The effect of each variable is quantified by its sum of squares. Very good coefficient of determination and statistically insignificant error term in ANOVA analysis confirms the validity of the model compared to experimental results. Compared to our previous results [1], compressive strength and water absorption are more susceptible to changes in content of major oxides and firing temperature than *DW*. This means that minor changes occurred because the initial values of DW parameter are low themselves.

Main influential parameters were temperature related terms, and the greatest impact was observed in the linear term of temperature. The next great influence observed, combined with firing temperature, was K_2O content. Actually, in this temperature range, densification occurs, with the help of fluxes, K_2O in the first place. The rest of the fluxes content (Fe_2O_3, Na_2O, CaO and Fe_2O_3) multiplied by firing temperature also showed statistically significant impact on *DW*. It is interesting that MgO showed a bit higher effect than CaO content, which was not the case with *CS* and *WA* SOP models. It may be presumed that dolomite, although expected to finish decomposition before 800 °C [25], decomposed more slowly than calcite, thus influencing the whole system within tested firing range. Since CaO showed significant influence on *DW*, it proved that the matrix still contained coarser calcite grains in the tested firing range [24]. SiO_2 showed non-significant effect on *DW* because it slowly melts in the selected firing range (820–920 °C), starting at 870 °C, which cannot be detected using DTG analysis [10,20]. Additionally, the quantity of silica that forms clay minerals is much lower than quartz content, so it was not detected as significant for the tested parameter in SOP model. Significant combined impacts of firing temperature and Fe_2O_3, TiO_2 and Al_2O_3 correspond to clay minerals transformations during thermal treatment. Knowing that MnO content increases during weathering of feldspars [26], and that the tested raw materials almost always contain plagioclases [14], the significant influence of Temp x MnO parameter could be linked to decomposition of feldspars alone or associated clay minerals.

3.3. Sensitivity analysis

In this work, one-factor-at-a-time (OFAT) sensitivity analysis method, as one of the simplest and most common approaches, was used to access the output variables changes when one input varies for +1% or −1% of its nominal value, while other inputs keep their baseline values. Sensitivity of observed output variables was measured at the outputs of developed SOP models. However, due to its simplicity, this approach does not fully explore the input space, since it does not take into account the simultaneous variation of input variables, and it cannot detect the presence of interactions between input variables [6,27].

Figs. 2 and 3 show changes in the technological characteristics of the products, when input variables vary individually for +1 % and −1 % from their nominal values. Firing temperature was excluded from analysis, in order to test SOP models within concrete values within the tested range 820–920 °C. Changes in technological characteristics were observed only when one input variable was changed for +1% or −1% of its nominal value, while others inputs maintained their original values. The greatest observed influence with 1% addition of inputs on outputs (*CS*, *WA* and *DW*) showed SiO_2, Al_2O_3, and then CaO. Addition and decrease of these oxides content can negatively or positively affect all the outputs, depending on the original form they are found in the raw sample. With −1% inputs variation, situation is slightly different; influence is significant and decreased in the following order: SiO_2, Al_2O_3, CaO and Fe_2O_3. Since the Fe_2O_3 content above 5% presents high sinterable heavy clays [22], its content affects the product quality. This characteristic is reflected in the ability of the alkaline and alkaline–earth elements oxides, along with iron oxides, to promote liquid phase formation and development [16]. In this regard, greater problem arises when there is iron deficiency in the presented systems. All individual variations of content of major oxides at least, although significantly, influenced *DW*. The highest influence is observed in *CSB* and *CSC*. The lower influence of certain oxide content variation means its less individual effect on the final product characteristics. Generally, in all the cases, higher changes in outputs are caused by lowering oxides quantity. The SOP models [1] could not show this kind of differences.

Very high responses are observed in the case of *CSC* and *CSB*, when SiO_2 content was lowered for 1% of the original nominal values. The samples N2, N7 and N3 showed the largest positive change, because they contained high calcite and quartz content, also with large grains, which influenced mechanical characteristics. For example, the N2 sample showed *CSC* 4–8% and *CSB* 5–7.2% higher values, than experimentally observed (the values increased with firing temperature). These samples also positively responded to decrease in Al_2O_3 and CaO contents, in the case of which, *CSB* was much more sensitive. The N2 sample *CSB* increased for 1.1–1.5% and 0.9–1.2%, when Al_2O_3 and CaO contents decreased for 1%, respectively (values increased with temperature). This is due to low clay minerals and high calcite content in these samples. Sensitivity analysis confirmed the previous conclusion that high calcite content induces more changes with temperature, since the spots on Figs. 2 and 3 were

Table 2
Analysis of variance for *DW* output variables.

Term	*dF*	*DW*	
		Sum of squares	Regression coefficient
Temp. (linear)	1	3.65E-04[*]	$(2.61 \pm 0.97) \cdot 10^{-5}$[*]
Temp. (quad.)	1	7.73E-09[ns]	–
Temp × SiO_2	1	2.25E-10[ns]	–
Temp. × Al_2O_3	1	2.93E-07[*]	$(-9.56 \pm 1.60)\ 10^{-7}$[*]
Temp. × Fe_2O_3	1	9.84E-07[*]	$(-2.03 \pm 0.19)\ 10^{-6}$[*]
Temp. × CaO	1	4.42E-07[*]	$(9.53 \pm 1.30)\ 10^{-7}$[*]
Temp. × MgO	1	1.48E-06[*]	$(-2.10 \pm 0.16) \cdot 10^{-7}$[*]
Temp. × Na_2O	1	7.53E-07[*]	$(3.09 \pm 0.32)\ 10^{-6}$[*]
Temp. × K_2O	1	1.79E-05[*]	$(-1.49 \pm 0.03) \cdot 10^{-5}$[*]
Temp. × MnO	1	4.78E-06[*]	$(-6.20 \pm 0.26) \cdot 10^{-5}$[*]
Temp. × TiO_2	1	3.32E-07[*]	$(-4.05 \pm 0.64) \cdot 10^{-6}$[*]
Error	609	5.04E-06	
Coefficient of determination	r^2	0.99857	

[**] Significant at $p < 0.10$ level.
[*] Significant at $p < 0.05$ level,
[ns] Not significant, *dF*—degrees of freedom.

mostly apart. This is why loess clays require special processing line with a cleaner machine, and grinding in degrees to grade below 0.5 mm [2]. *WA* showed changes among the lowest, compared to all the other tested samples. In the case of *WAT* and *WAB* the sensitivity was also decreased in the order −1% SiO_2, Al_2O_3 and then CaO. Because of their thickness, cubes behave differently from other samples: quartz influences *CS* extremely negatively, but does not change *WA* much. It obviously does not change open porosity, but forms micro-cracks and lowers *CS*. *WAC* was not influenced by SiO_2 fluctuations, but was sensitive to Al_2O_3 and CaO contents decrease. The samples N5 and N4 behaved similarly, but less sensitive to oxides content induced changes, with the most variation in *CS* values. In the case of N4 sample, *CSB* and *CSC* were equally sensitive (responses about 2%), and in the N5 sample *CSC* was again more susceptible. The N1 sample showed greater changes in *CSB*, then in *CSC*, with slower increase with firing temperature then in the rest of loess samples. Since it contained more clay minerals and less calcite, the changes observed are less intensive. It also contained more fine-grained quartz, since the responses were similar at 870 and 920 °C.

Sensitivity analysis proved that the main influence on final product properties is owed to quartz. Loess clays generally contain fine-grained quartz [28], but tested samples also had larger particles which decreased compressive strength. Significant influence on *CS*, after quartz, belongs to calcite. The presence of carbonates in loess clays (North Serbia) in the form of larger concretions and "loess dolls" is common. Large calcite particles remain in the form of CaO after firing [2].

The most distinctive North Serbia sample was N6, since the oxides content fluctuations influenced more *WA* than *CS*. Raw materials rich in clay minerals showed greater changes in quantity of open pores, thus influencing *WA*. Although the matrix is better sintered then in other samples, porosity is also improved, so *CS* is not changed as well. The influence to all responses respectivelly decreases when SiO_2, Al_2O_3, CaO and Fe_2O_3 contents are lowered. When SiO_2 content is decreased, *CS* increases for about 1% from experimentally observed values, remaining almost constant in the tested firing range. It can be concluded that this sample also contains coarse quartz grains [16]. The greatest changes are found in *WAC* values, especially at 870 and 920 °C, when quartz melts [2,16]. *WAT* is decreased for −2.9 to −2.7% (increases with temperature), and is not as much influenced by quartz melting. Although Al_2O_3 content decrease showed positive impact on mechanical properties, the values were low (about 0.10–0.15%). This implies that sensitivity analysis can be used to determine which sample contains more clay minerals on the basis of observed responses. Since Al_2O_3 in heavy clays can be in the form of illite, $(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$, or feldspar, for example $KAlSi_3O_8$, the responses should be negative when clay minerals (illite) content is lowered [29].

The samples S1, S2 and S3 showed the next largest positive contribution in *CS* values (about 2.5–3%), while decreasing SiO_2 content. Al_2O_3 content decrease also improved *CS*, but a bit more than in the case of N6 sample, since it contains the highest content of clay minerals. Sensitivity analysis showed non-linear changes for the S1, S2 and S3 in *CS* with temperature, increase at 820 and 850 °C, and decrease at 870, 900 and 920 °C in CSB values. Finer calcite grains improve *CSB* in higher temperatures, while coarser quartz lowers it. CSC values showed the opposite trend, since calcite leaves more closed pores in laboratory cubes that in blocks. According to Al_2O_3 content decrease affect, clay minerals content

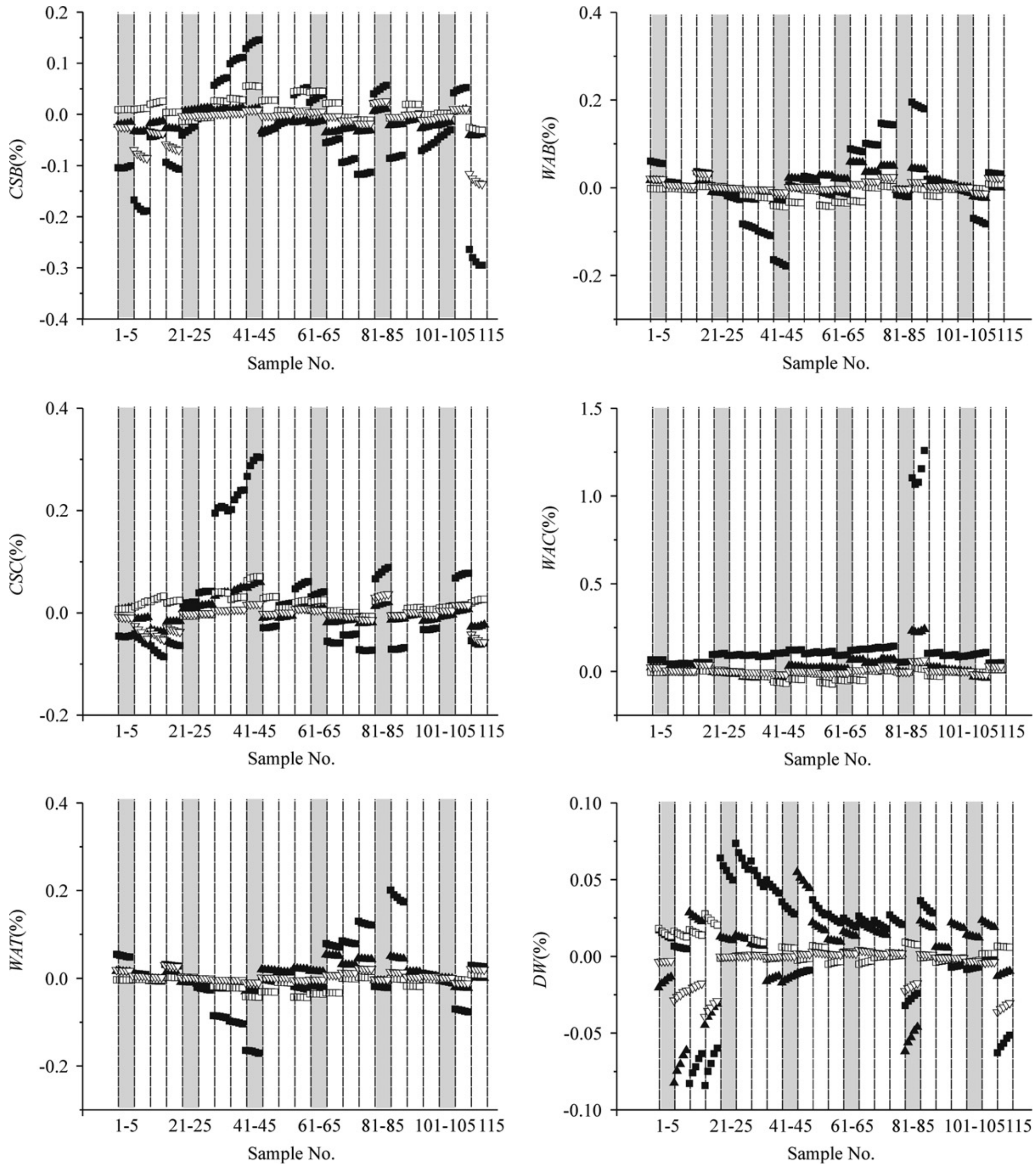

Fig. 2. Changes in technological characteristics of products, when input variables vary +1% ■—SiO_2, ▲—Al_2O_3, □—Fe_2O_3, Δ—CaO.

decreased in order S1, S2 and S3, which could not be seen clearly from the chemical analysis, although it could be expected that S1 had the highest content of potassium-feldspar, according to K_2O content. *WA* changed also significantly, but less then *CS* (decreased for about 1.4–2%). CaO and Fe_2O_3 content influenced mechanical characteristics when lowered, but to a small extent, the most S3 sample *WAC* values. The samples S3, S2 and S1 respectively showed the largest positive contribution in *CS* values, while increasing SiO_2 content, gaining greater affect with firing temperature. The S2 sample contained the highest content of SiO_2, also S3 among the highest, and it is mainly fine grained, according to sensitivity analysis. The samples S4–S8 also showed significant responses to oxide contents fluctuations, especially in the case of decreased SiO_2 content and changes in *CS*. The influence on *CSB* and *CSC* decreased in the order: S7, S8, S6 and S5. The same order is found when CaO content decrease is concerned. These four samples had the lowest Al_2O_3/CaO coefficients, above all other South Serbia samples, and the most proper behaviour with firing temperature. The S4 sample showed *CSC* changes among the highest, and *CSB* the lowest. S4 was also the least sensitive to CaO content, while Al_2O_3/CaO coefficient was the highest.

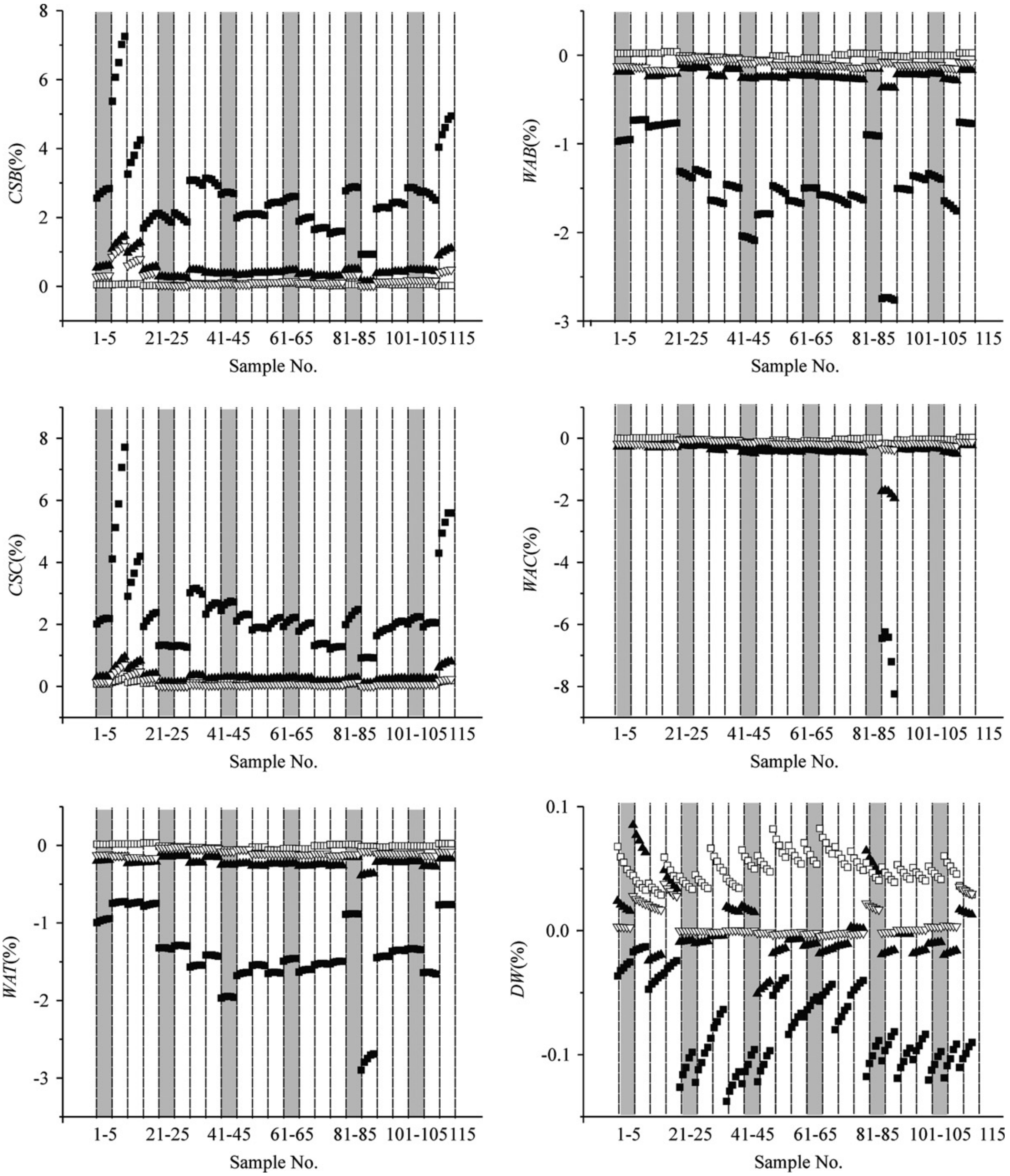

Fig. 3. Changes in technological characteristics of products, when input variables vary −1% ■—SiO_2, ▲—Al_2O_3, □—Fe_2O_3, Δ—CaO.

WAT and *WAB* values of the samples from Central Serbia were positively influenced by positive changes in SiO_2 content. Increasing of Al_2O_3 content also caused an increase of *WAT* and *WAB* values. *WAT* and *WAB* were negatively influenced by negative changes in SiO_2 content. Decreasing of Al_2O_3 content caused *WAT* and *WAB* to decrease its value. *WAC* did not almost change at all with $\pm 1\%$ oxides content variations. The C1, C2 and C3 reacted similarly in sensitivity analysis, the highest changes observed in *CSB* (about 2.1%) and *CSC* (about 1.3%, for C3 1.8%), when SiO_2 content is lowered. Sensitivity to CaO changes was the least in the case of samples with the lowest Al_2O_3/CaO values—in C2, C1, C4 and C3. C7 and C8 were also similar samples, with the lowest sensitivity to oxides contents. In all the samples from C1–C8 groups, the highest temperature difference responses are observed in *WAB* values.

DW was mostly influenced by SiO_2, Al_2O_3, Fe_2O_3 or CaO negative content change, respectively. SiO_2 negative change showed mainly positive impact on *DW* values. The highest influence is observed in N4, N7, N2, N3 and N5, all low quality loess raw materials. Strongest influence of Al_2O_3 content change is noticed in the samples N4, N3, N2, N7 and N1. *DW* in both cases decreased with temperature. Since the greatest impact is observed in the North Serbia samples, which contained highest calcite content and lowest Al_2O_3/CaO values it is again confirmed that large quartz grains were mostly present in these samples and that calcite grains did not completely decompose before 820 °C.

4. Conclusions

The intention of the presented research was to find the relationships between chemical composition of raw materials to compressive strength, water absorption and derivative weight as gained from DTG analysis in various laboratory heavy clay products. Experimental research showed that all the tested output parameters in the observed firing temperature range (820–920 °C) behaved differently, meaning that they did not decrease or increase by the same rules. Second order polynomial models developed before for CS and WA, and newly introduced for DW, were tested for sensitivity of responses by variation of content of major oxides for $+1$ and -1% of their nominal values. The analysis revealed in more detail the changes in products behaviour in every observed firing temperature. Although calcite induces greater changes in behaviour of individual samples with firing temperature, at the actual temperatures, quartz and feldspar or illite content induce grater changes.

Acknowledgements

The authors are grateful to the Serbian Ministry of Science and Technological Development for the financial support of this investigation included in the projects III450080 and TR 31055, project cycle 2011–2014.

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