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What to expect from heavy clay?

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Abstract

The need of testing the quality of brickclay arises in all brick factories, with the opening of new deposits. The analyses are both time and economically consuming, so the aim of this study was to shorten the procedure using the already known data. This study was focused on determining the usability of heavy clays, when only the raw material major elements chemical composition is determined. The effects of chemical composition, firing temperature, and several shape formats of laboratory samples on the final properties were investigated. Chemical composition of major elements was determined on the basis of classical silicate analysis. Firing was conducted in an oxidizing atmosphere, while maintaining all other experimental conditions constant, except the final temperature. Principal component analysis (PCA) was used to determinate groups of samples according to similarity of chemical composition. Prediction of compressive strength (*CS*) and water absorption (*WA*) was done by developing five artificial neural networks (ANN). The average regression coefficients r^2 were used to explore the confidence level of the models. Developed models were able to predict *CS* and *WA* in a wide range of chemical composition and temperature treatment data, and the highest average r^2 of 0.923 for *CS* was obtained, while r^2 for *WA* was 0.958. The wide range of processing variables was considered in the model formulation, and its easy implementation in a spreadsheet using a set of equations makes it very useful and practical for *CS* and *WA* prediction. As it is known from literature, all the parameters entered this analysis are dependent on each other, but their mutual relationship was not quantified yet. Most importantly—the developed neural networks can be used on a global scale.

Keywords: Heavy clay; Neural networks; Prediction

1. Introduction

Heavy clays have been widely used as the main raw materials in the brick making industry due to their specific properties. When exploring heavy clay deposits, compressive strength (*CS*) and water absorption (*WA*) are important parameters for testing at different temperatures. Mineral transformations are mainly influenced by chemical and mineralogical composition of the heavy clay, grain-size distribution, maximum heating temperature, heating rate, duration of firing, and kiln atmosphere of the original clay influence mineral transformations. Knowledge of the chemical composition of heavy clays is essential when exploring suitable compositions required for brick production [1–5].

Finding the cause-effect relationship between characteristics of heavy clay and final products is a topic that have been occupying researchers for many years. Numerous works have been published on this subject till now [1–3,5,6], but only a few of them describe the use of statistical analysis [2,7]. The effects of mineralogical and physical properties of raw materials on the thermal conductivity of fired clays are determined by multiple linear regressions [8]. Statistical analysis of chemical data establishes a classification of industrial clays on the basis of descriptive statistics, cluster analysis, analysis of variance (ANOVA), and correlation between pairs of elements [2]. Influence of firing temperature on mechanical properties of roofing tiles is tested by regression [9,10]. Neural networks

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using Matlab program are used in prediction of compressive strength [11] and water absorption [12] of geopolymers.

Artificial neural network (ANN) models have recently gained momentum in process modeling and control. ANN models are recognized as a good tool for dynamics modeling because they does not require parameters of physical models, have the of finding solutions to problems from sets of experimental data, and are capable of handling complex systems with nonlinearities and interactions between decision variables [1–3,5,7,13].

Raw materials characteristics and processing parameters exert influence on microstructure and final properties of ceramics [1,5] and one of the ways to find the manner in which these are associated is statistical analysis, which can contribute to optimization of the use of new clay deposits in different countries. This study was focused on usability of 83 representative heavy clays from Serbian heavy clay deposits. The purpose of this work was to investigate the effect of chemical composition and firing temperature (input parameters) on *CS* and *WA* of laboratory samples (outputs), using ANN prediction models, due to the complexity of the heavy clay system. The performance of ANNs was compared to multiple linear regression (MLR) models. PCA was used to evaluate the quality of tested heavy clays. The study gives an overall picture of quality of the Serbian heavy clay from different regions.

This paper presents a first-of-a-kind analysis, and shows that the ANN model can efficiently and accurately predict the final behavior of laboratory products with variable firing temperatures, using the results of chemical analysis.

2. Materials and methods

2.1. Raw materials and samples

The tested samples of 83 heavy clay were collected at three regions: North (first 39 samples), Central (next 24 samples) and South Serbia (last 19 samples). These clays are representative raw materials which reflect the similarities and differences in quality, as well as their possible application. After being collected, all samples were oven-dried at 105 °C until constant mass and then milled, following the normal practice in ceramic laboratories. To simulate industrial pressing conditions, clays were moistened by hand, mixed sufficiently and milled to 2 mm until homogeneous mass with about 20–30% of moist was obtained, according to EN standard [14]. Moist heavy clays were left to rest for 24 h in sealed nylon bags. The shaping process was done following the usual procedure [5] and using laboratory vacuum extruder (*Händle*). Laboratory samples were produced in the form of tiles ($120 \times 50 \times 14\ mm^3$), hollow bricks with vertical voids ($55.3 \times 36 \times 36\ mm^3$) and cubes ($30 \times 30 \times 30\ mm^3$). Dimensions of laboratory hollow bricks proportionally correspond to industrial bricks.

Shaped samples has been dried in the air, and later in a laboratory dryer at 105 ± 5 °C to a constant mass [5]. Extrusion and drying behavior of green products could be considered satisfactory, as the produced samples obtained the green strength required to ensure safe handling in the subsequent fabrication steps. Firing step was done in the oxygen atmosphere furnace with computer-controlled regime. Average heating speed was 1.4 °C/min until 610 °C, and later 2.5 °C/min until the final given temperature was reached, at which the samples were treated for 2 h. Applied regime had been slightly slower then reported [5]. All tested samples were fired under the same regime in order to have comparable results. Final firing temperatures were 800 °C, 820 °C, 850 °C, 870 °C, 900 °C, 930 °C, 950 °C, 1050 °C and 1100 °C, and the samples were furnace-cooled to room temperature. All fired samples contained no black cores that could remain as a result of incomplete oxidation of carbon.

2.2. Chemical and technological features

Three representative samples of about 100 g were previously dried at 60 °C and then used to determine their chemical composition by classical silicate analysis. Thow the method is old (firstly described in literature in 1938) and time consuming, it is still used today and is the standard against which other methods are measured. In this analysis, sample was melted in a furnace with sodium carbonate addition. Dry matter is then redissolved with 10 vol% HCl. After filtering, silica precipitates were fired to constant weight and later volatilized using HF and small amount of H_2SO_4, and the remaining precipitate loss in weight during firing represented the amount of silica in the sample. The filtrate was heated to near boiling point and 1:1 NH_4OH until pH 6.6–6.7 is added. Other major oxides are then determined by deposition and dissolution processes, which are explained in detail in the literature [15]. The loss on ignition (LOI) was calculated as weight difference measured between room temperature and 1000 °C. *WA* of heavy clay tiles, block and cubes was evaluated in fired clay pieces by soaking them in distilled water for 24 h, according to standard procedure [5].

CS was determined in laboratory hydraulic press Alfred Amsler, CHD, with measuring range of 100/200/500/1000 kN and resolution of 0.1/0.2/0.5/1 kN. Three specimens for each combination of sample shape (blocks and cubes) and firing temperature were tested. The samples were flattened to ensure that the surfaces were parallel. *CS* is then tested on single samples (without mortar usage), with bottom area of 0.002 m^2 for blocks and 0.0009 m^2 for cubes, and a loading rate of 0.6 kN/s. The strength results reported were the average of three specimens with a variation of no more than 10%.

2.3. Principal component analysis (PCA)

Principal component analysis (PCA) is a mathematical procedure used as a central tool in exploratory data analysis [16]. This multivariate technique groups the data transformed into orthogonal components that are linear combinations of the original variables. PCA is done by

eigenvalue decomposition of a data correlation matrix [17]. This transformation is defined in such a way that the first component has the largest possible variance. The analysis is used to achieve maximum separation among clusters of parameters [16]. Using PCA, clay composition can be identified and their geographic distributions determined. This approach, evidencing of spatial relationship, enabled a differentiation between soil samples originating from different areas.

2.4. Artificial neural network modeling

StatSoft Statistica program (version 10) was used to randomly divide collected data into three groups: training (60%), cross validation (20%) and testing data (20%). The cross validation data set was used to test the performance of the network while training was in progress, as an indicator of level of generalization and time at which the network has begun to over train. Testing data set was used to examine the network generalization capability. To improve the behavior of the ANN, both input and output data were normalized to gain values in the range of 0–1 [13].

The artificial neural networks (ANNs) are one of the most powerful computer modeling techniques, based on statistical approach, currently being used in many fields of engineering to simulate the complex relationships which are difficult to describe with physical models [15]. In this article, a multilayer perceptron model (MLP) that consists of three layers (input, hidden and output) was evaluated. This architecture is called *feed forward* because inputs propagate through layers in a forward progression. Such a model is the most common, flexible and general-purpose kind of ANN. These architectures are used in prediction, and have been proven quite capable of approximating nonlinear functions [13], giving the reason for choosing it in this study.

A trial and error procedure is necessary to perform before modeling, until a good network behavior was obtained, as well as to choose the number of hidden layers, and the number of processing elements (also called "neurons") in hidden layer(s). The use of just one layer is advisable, because more layers exacerbates the problem of local minima. The network has been trained with Levenberg–Marquardt algorithm due to its high accuracy in similar function approximation [13]. Numbers of neurons in the input and the output layers are determined by the number of corresponding variables, respectively. In order to find an optimal architecture, different number of neurons in hidden layer were taken into consideration [13] and the sum of squares error for each network was calculated, as StatSoft Statistica's default. In this study, the number of hidden neurons varied from 6–13 in developed networks, with 16 inputs and 6 outputs, bound with 138–292 weight coefficients depending on the number of hidden neurons.

A neural network tries to find a function which, when given the inputs, produces the outputs. The information passes between layers through a transfer or "activation" function is a typically nonlinear function for hidden layers and linear for the output layer. Most common nonlinear activation functions are logistic sigmoid and hyperbolic tangent functions (also exponential, sine, softmax, Gausian *etc.*). In most applications, hyperbolic tangent function behaved better compared to other functions [13].

Coefficients associated with the hidden layer (both weights and biases) are grouped in matrices W_1 and B_1. Similarly, coefficients associated with the output layer are grouped in matrices W_2 and B_2. If Y is the matrix of the output variables, f_1 and f_2 are transfer functions in the hidden and output layers, respectively, and X is the matrix of input variables. The neural network can be represented by using matrix notation, as follows [18].

$$Y = f_1(W_2 f_2(W_1 X + B_1) + B_2 \quad (1)$$

The neural network developing is often an iterative process, where design-train-test cycles multiple times [13]. Weights are determined during the training phase which updates them using optimization procedures to minimize the error function between network and experimental outputs. The modified delta rule is an improvement to the delta rule algorithm used to speed up and stabilize convergence. As the iteration termination criterion, the sum of squares (*SOS*) between the experimental and the network predicted values was used. As soon as the cross-validation *SOS* starts to increase, the training phase is terminated; otherwise, training phase ends after a fixed number of epochs or training cycles.

The training phase started, after ANN architecture had been defined. The training process has been repeated several times in order to get the best performance of the ANN, due to a high degree of variability. The accepted successful training was achieved when learning and cross-validation curves (vs. epochs) approached zero. Testing was carried out with the best weights stored during the training step; correlation coefficient r^2 and *SOS* were used as parameters to check the performance of the ANN.

The ANN model can be implemented using an algebraic system of equations, to predict compressive strength of blocks (*CSB*) and cubes (*CSC*), and water absorption of tiles (*WAT*), blocks (*WAB*), and cubes (*CSC*) at different temperatures and with different chemical composition, by substituting corresponding weights and coefficients matrices in Eq. (1). This step can be also easily achieved by some spreadsheet calculus (Microsoft Excel, for instance). Neural networks were further tested including sensitivity analysis, while determining whether and under what circumstances the combination of obtained model and the expected actual training data might result in an ill-conditioned system [13].

3. Results and discussion

3.1. Chemical composition

The 83 heavy clays samples showed the expected typical chemical compositions (Fig. 1a), rich in silica and aluminum, with satisfying content of potash, minor contents of

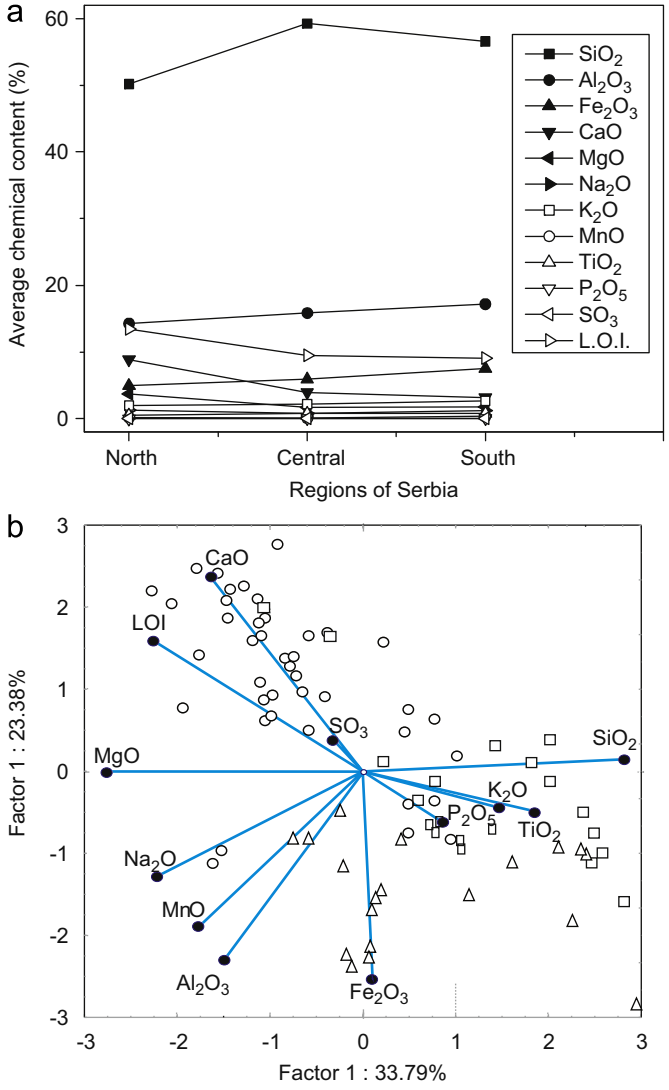

Fig. 1. Chemical composition of heavy clays from Serbia: (a) Determination of chemical composition by classical silicate analysis; (b) Clay composition by geographic origin–PCA (Regions of Serbia: ○–North, □–Central, –South).

sulfur, titan and phosphorus, accompanied by a relatively significant amount of iron oxides. Harmful constituents that can cause efflorescence, such as sulfur compounds, were not detected in most of the samples [19–21].

The PCA, applied to the given data set, had shown a differentiation between the heavy clay samples according to their geographic origin and was used as a tool in exploratory data analysis to characterize and differentiate neural network input parameters (Fig. 1b).

The amount of SiO_2 varied in the broad range (27.4–66.4%), but, in most of the samples, it was very high (around 50%). The highest mean value of silica was observed in Central Serbia region. The Al_2O_3 content was also high (10.2–20.1%), with the highest mean value in South Serbia, which indicates that the highest clay content can be expected in that area. The sinterability of clay to a great extent depends on Al_2O_3. The higher its content, the better the sinterability of the material is [1]. Tested heavy clays mainly contain silica and aluminum oxides, which shows the dominant presence of quartz in the first place, and then also of clay minerals. Quotient between the molar fractions of SiO_2 and Al_2O_3 conditions the existence of free SiO_2 (present as quartz). From the given compositional characterization (Fig. 1a), observed mean quotient is 6.3, with the highest free quartz content in North Serbia. These heavy clays represent raw materials with relatively low phyllosilicates, and high free quartz content [2]. The presence of quartz prevented cracking, shrinking and warping, and provided uniform shape to the bricks [7].

Relatively high amount of Fe_2O_3 (3.0–8.0%, and about even 13% at two South Serbia localities) classifies these samples as acceptable for use in rough ceramics. This amount is the highest observed mean value in South Serbia and that indicates that the red color of products will be the most intense. The content above 5% presents high sinterable heavy clays [1].

Most of the samples showed high relative amounts of alkaline oxides. They are present in all the regions in similar quantities (mean value 3.5%). Na_2O and K_2O in reaction with silica, aluminum and iron oxides present in clay, promote the liquid phase formation that facilitates densification, and thus explaining why samples sinter at relatively low temperatures [1,22].

The amount of earth-alkaline oxides (CaO and MgO) gained maximums of about 14% per each, indicating much higher content of carbonates in North Serbia compared to the other regions. The organogenic nature of calcite in loess contributes to the formation of a local reducing medium in firing, affecting the transition of Fe^{3+} to Fe^{2+} and facilitates sintering at relatively lower temperatures [1]. The presence of moderate amounts of carbonates in Central and South Serbia (around 5%) permits manufacture of light clay building products with good mechanical properties. In this, 28 of tested 83 samples belong to calcerous clays, with CaO content $>6\%$ [7]. CaO content below 6 mass% reduces probability of scum deposition and likelihood of lime "popcorns" on the surface of bricks appearance [5]. These phenomena occurred in the most of samples from North Serbia, because of their highest carbonates content value, but was observed in some samples from Central and South Serbia. PC analysis showed grouping of MgO, CaO and LOI, which means that LOI depends mainly of carbonates content.

LOI value indicates the amount of volatile matter that would be released during firing. The LOI was in the range of 6.8–19.9%, and can be, besides carbonates, attributed to the presence of clay minerals, hydroxides and organic matter [2,3,5]. The highest LOI mean value was observed in samples from North Serbia, due to their highest carbonates content (Fig. 1). The presence of carbonates in loess in the form of large concretions and "loess dolls" is common. Such material requires special processing line with a cleaner and multiple grinding in degrees of granularity below 0.5 mm [23].

3.2. Fired samples—water absorption and compressive strength

Final properties of ceramic materials highly depend on the raw clay composition and firing temperature [1]. Heating causes a series of transformations in clay and accompanying minerals (dehydration, oxidation, dehydroxylation, decomposition and formation of new phases, vitrification, etc), that generally improve the mechanical strength of ceramic products. The temperature at which such changes occur depend on various factors, such as chemical and mineralogical composition of heavy clay, temperature and duration of heating, *etc*. [7]. The results show only a few of all firing temperatures used, due to the visibility of behavior trend (800 °C, 900 °C, 1000 °C and 1100 °C), which is closely related to densification of the clay matrix (Fig. 2).

Cubes showed much higher *CS* values then blocks because they are voidless and have lower surface area. Blocks are better sintered because their walls are thin, and the water better penetrates into the mass, which can be seen on the basis of a bit lower *WA*. The results indicated that increasing the sintering temperature decreased the *WA*, while increasing *CS*, as reported in literature [3]. Behavior of laboratory hollow blocks and cubes was the same: the highest *WA* and the lowest *CS* values were observed in case of samples from Central Serbia in all firing temperatures. The reason was the highest SiO_2 content in samples from Central Serbia, as it melts and fills pores up while being heating. Other parameters also influence final properties to a great extent [1], which was also proven by statistcal analysis presented in this work.

High porosity and *WA*, with the lowest *CS*, have been observed in North Serbia samples, due to their loess origin, meaning the highest carbonate content and LOI value. The samples that were most influenced by CaO, MgO and LOI were sampled at north part of the country, according to PCA. Highly dispersed carbonates are intense fluxes due to the formation of lowmelting eutectics, in particular, with silica [1]. This fluxing effect of carbonates (even when they are present in significant amounts) was intensively manifested at 1100 °C in samples from North Serbia. The presence of alkaline components makes this ceramic material gain required properties, even if fired between 800 °C and 1000 °C, when carbonates strongly influence development of porosity and, as a consequence, physical and mechanical properties [1]. The lower *WA* and higher *CS* values that occured in all the samples after sintering at the higher temperatures suggest that high temperature liquid phases occurred, which contributed to convergence of pores and decrease in the pore volume [3].

3.3. Artificial neural networks development

The *MLR* models gave r^2 values in the range of 0.66–0.83. Observed behavior trend of heavy clays is in a non-linear manner [1–3,5], which justified the usage of neural networks. ANN was utilized in performing computations, which

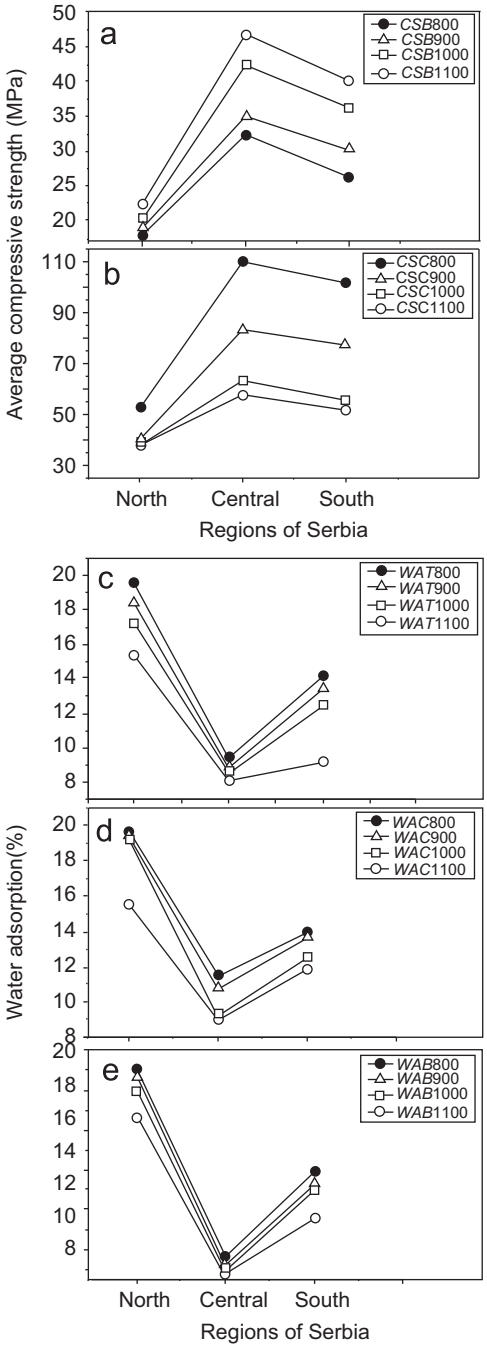

Fig. 2. Compressive strength and water absorption of fired samples.

included different neurons joined to other neurons with synaptic weights to simulate the human brain [24]. In most function approximation problems, one hidden layer is sufficient to approximate continuous functions. In the present paper, ANN was employed to approach the objective function, which is an intensive nonlinear and non-smoothing. Determination of the appropriate number of hidden layers and number of hidden neurons in each layer is one of the most critical tasks in ANN design [13].

Prior to training the neural network, all input parameters were normalized (linearly scaled) to a range of 0–1, which is

standard practice to make the network's learning task easier. A test was conducted to decide the best ANN configuration. According to the Lachtermacher and Fuller's suggestion, the neuron number is in the range of 4–12. The number of neurons in a hidden layer depends on the complexity of the relationship between inputs and outputs. As this relationship becomes more complex, more neurons should be added [13].

The optimum number of hidden neurons was chosen upon minimizing the difference between predicted ANN values and desired outputs, using r^2 during testing as performance indicator. Testing was done with 6–13 hidden neurons (Table 1). Used MLPs are marked according to StatSoft Statistica's notation, MLP (multi-layer perceptron) followed by number of inputs, number of neurons in the hidden layer, and the number of outputs. Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm, implemented in StatSoft Statistica's evaluation routine, was used for ANN modeling. The optimal number of neurons in the hidden layer was 6 (Network no. 3), when obtaining high values of r^2 and also low values of SOS, according to the Score (middle r^2 of every network) presented in the table. A greater number of neurons increased the structure complexity and did not improve the network behavior, as published previously [13]. The goodness of fit, between experimental measurements and model calculated outputs, represented as ANN performance (sum of r^2 between measured and calculated *CSB*, *CSC*, *WAT*, *WAB* and *WAC* for each ANN) are presented with significant effect ($p < 0.05$) of all output variables, and best network performance for every parameter is highlighted (Table 1).

The SOS between measured and calculated *CSB*, *CSC*, *WAT*, *WAB* and *WAC*, during training, testing and validation steps, are shown in Table 2. BFGS (or Quasi-Newton) is used as a well-known, second order ANN training algorithm with very fast convergence, and SOS is used as error function during networks training.

3.4. Simulation and optimization of ANNs

Process outputs (*CSB*, *CSC*, *WAT*, *WAB* and *WAC*) can be calculated using matrices W_1 and B_1, and matrices W_2 and B_2 (Eq. (1)), which represent system incorporating coefficients associated with the hidden layer (both weights and biases). Output variables are calculated by applying transfer functions f_1 and f_2 (Table 1) in the hidden and output layers, respectively, onto the matrix of input variables X using Eq. (1). The algebraic system of equations can be easily evaluated in a spreadsheet (i.e. Microsoft Excel) to predict *CSB*, *CSC*, *WAT*, *WAB* and *WAC* of bricks regarding chemical composition and temperature.

ANN models were used to simulate experimental measurements. Normalized *CSB*, *CSC*, *WAT*, *WAB* and *WAC* model prediction performance (Fig. 3) showed simulated curves compared to experimental data, for all 5 tested neural networks. The networks were able to predict all process outputs for a broad range of the process variables reasonably well, so all the models were proved as acceptable. The best performed model (MLP 13-6-5) did not work very well at some extreme conditions (Fig. 4). For example, experimental *WAC* (targets) and predicted values (outputs) differed to the highest degree at the left and right corner of the diagram. This happened probably because *WAC* showed very low values at these conditions. The predicted values were, however, very close to the desired values in most cases, although *CSB* and *CSC* prediction was not as good as that for *WAT*, *WAB* and *WAC* in terms of r^2 value. *SOS*s obtained with ANN

Table 1
Effect of the number of hidden neurons on r^2 during testing.

No.	Network name	Hidden activation function	Output activation function	*CSB*	*CSC*	*WAT*	*WAB*	*WAC*	*SCORE*
1	MLP 13-12-5	Logistic	Logistic	0.894	**0.906**	0.899	0.929	0.924	0.910
2	MLP 13-8-5	Logistic	Tanh	0.880	0.831	**0.933**	**0.974**	**0.970**	0.918
3	MLP 13-6-5	Logistic	Identity	0.905	0.855	0.926	0.958	0.962	**0.921**
4	MLP 13-13-5	Exponential	Exponential	**0.923**	0.887	0.923	0.938	0.931	0.920
5	MLP 13-13-5	Logistic	Tanh	0.898	0.820	0.883	0.925	0.916	0.888

Table 2
Summary of developed ANNs.

No.	Network name	Training error	Testing error	Validation error	Training algorithm	Error function
1	MLP 13-12-5	0.019	0.025	0.034	BFGS 38	SOS
2	MLP 13-8-5	0.011	0.021	0.022	BFGS 112	SOS
3	MLP 13-6-5	0.014	0.021	0.028	BFGS 99	SOS
4	MLP 13-13-5	0.009	0.022	0.043	BFGS 168	SOS
5	MLP 13-13-5	0.024	0.029	0.035	BFGS 35	SOS

models were of the same order of magnitude as experimental errors for *CSB*, *CSC*, *WAT*, *WAB* and *WAC*.

The mean and the standard deviation (SD) of residuals had been also analyzed. The mean of residuals were 0.00 for *CSB*; −0.05 for *CSC*; 0.00 for *WAT*, 0.10 for *WAB* and 0.00 for *WAC*, while SD was 0.07 for *CSB*; 0.11 for *CSC*; 0.08 for *WAT*, 0.33 for *WAB* and 0.06 for *WAC*. These results showed a good approximation to a normal distribution around zero with a probability of 95% (2 · SD) to find residuals below −0.22 and −0.19 for *CSB*; −0.29 and −0.22 for *CSC*; −0.23 and −0.19 for *WAT*, −0.62 and −0.81 for *WAB*, and −0.30 and −0.24 for *WAC*. ANN model showed good generalization ability for the range of experimental values (*CSB*, *CSC*, *WAT*, *WAB*, and *WAC*). r^2 values in *MLR* model (not presented in this work) were lower than those associated with the ANN model (Table 1). This agrees with other authors conclusions [25]. Although ANN models were more complex (138–292 weights-bias outputs models, for five ANNs) than linear regression models (13 weights-bias for outputs), ANN models performed better then *MLR* because of the high nonlinearity of the developed system. The ANN model allows an extrapolation, by extending the range of process parameters (inputs), but this model was not compared with experimental values beyond the range of variables used in its development due to the nature of tested raw materials.

3.5. Sensitivity analysis

Sensitivity analysis is a general technique from the field of decision theory for studying the effects of the uncertainties in model's parameters. Neural networks can perform an approximation to a solution partially noisy and partially imprecise data, so sensitivity analysis is necessary to check if the neural network could behave erroneously [13,26,27]. In order to assess the effect of each change in the output due to the change in the input, a sensitivity analysis was performed, and according to the results, ANNs were improved to show the best results. The greater the effect observed in the output, the greater the sensitivity presented with respect to the input [24].

The white noise signals were incorporated by adding or substracting a Gaussian error of $SD = 5\%$ and zero mean with 98% probability [25], i.e. 2241 · SD to each input variable. The white noise was normally distributed and had a constant intensity and frequency. It was used to test the model sensitivity and measurement errors. Due to the large number of combinations (13 input variables) a screening experimental design [26] was used for testing the best performance developed ANN model (MLP 13-6-5, Table 1).

A 13-factor, screening design with all inputs as the independent variables, were selected for the study [26]. For this input variables number, at least 27 assays are to be made [28]. The inputs possible coded values are −1 and +1 for negative and positive white noise incorporating, and 0 for unchanged experimental values. The final developed design with 27 combinations was in diagonal form (Table 3). The first design contains codes instead of

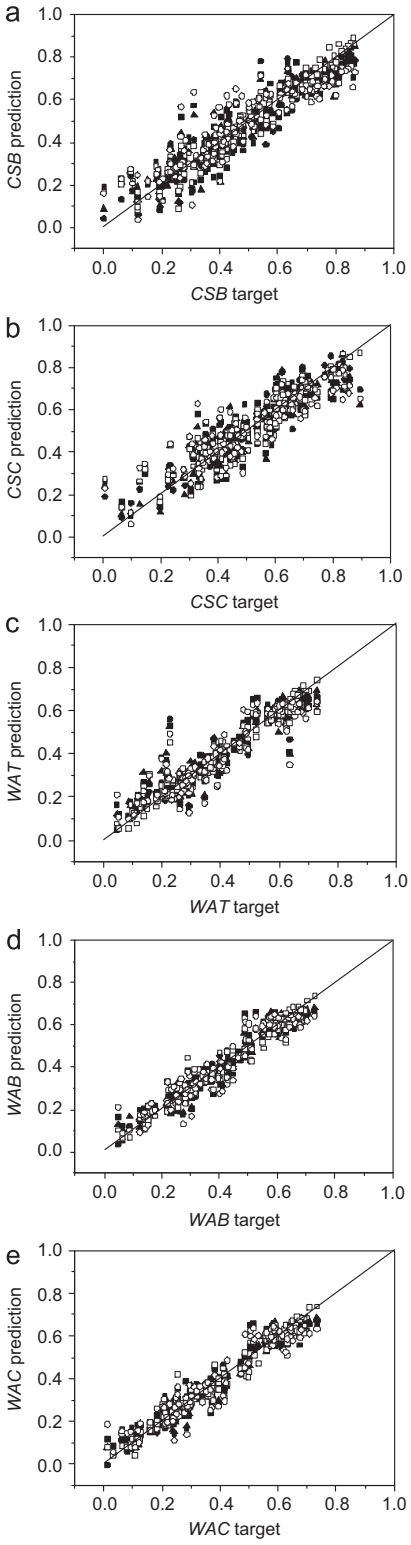

Fig. 3. Normalized *CSB*, *CSC*, *WAT*, *WAB* and *WAC* model prediction performance for: (a) MLP 13-13-5 (■), (b) MLP 13-12-5(●), (c) MLP 13-8-5 (▲), (d) MLP 13-8-5 (▼) and (e) MLP 13-8-5 (♦). Black colored signs—validation, white colored signs—train, black–white colored signs—test.

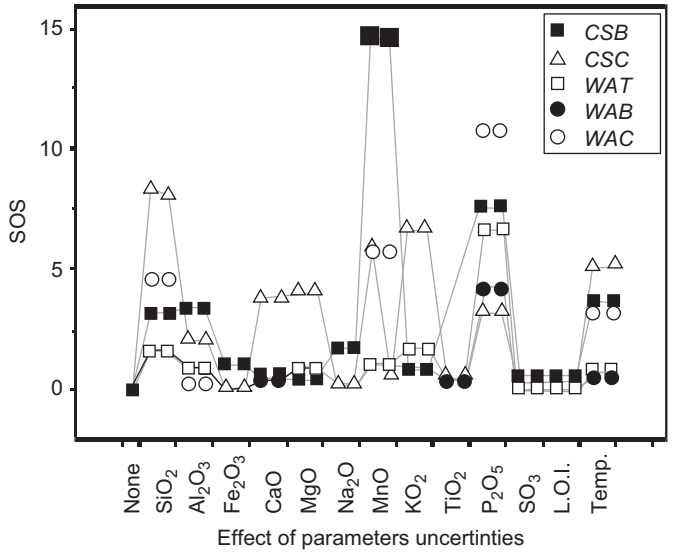

Fig. 4. Sensitivity analyses for *CSB*, *CSC*, *WAT*, *WAB* and *WAC*.

Table 3
Custom experimental design for sensitivity analysis.

Assay no.	SiO_2	Al_2O_3	Fe_2O_3	CaO	....	LOI	Temp.
1	0	0	0	0	....	0	0
2–3	±1	0	0	0	....	0	0
4–5	0	±1	0	0	....	0	0
6–7	0	0	±1	0	....	0	0
....	....	....	....	....	....	....	....
22–23	0	0	0	0	....	0	0
24–25	0	0	0	0	....	±1	0
26–27	0	0	0	0	....	0	±1

real observed values (base case), and every next two models present the effect of one input parameter with applying noise in the range of $\pm SD$. That is how each input parameter was tested to show the level of influence on outputs. The complete database (83 points from Fig. 1) was used, for a total of $83 \times 27 = 2241$ cases.

The influence of the input variables over the outputs, by calculated SOS values for all 27 designs, was presented graphically (Fig. 4). Obtained SOS values corresponded to level of experimental errors, and showed the significance of inputs influence on outputs. *CSB* and *CSC* had been most affected by Al_2O_3 and Na_2O content, and firing temperature. Statistically significant impact of CaO, MgO and MnO content was also observed, on both *CSB* and *CSC*. P_2O_5 content gained notable influence for *CSC*, but this result could not be taken without a doubt. Actually, this oxide was not present in the most of the samples, and zero values are not calculated by the program. The most effective impact on *WAT*, *WAB* and *WAC* could be observed by Al_2O_3, CaO and SiO_2 content. High influence of MnO content was observable for *WAC* and *WAB*. Temperature had not been proven to be very significant for *CSB* and *CSC*, which could not be the truth. The reason was that not all the samples were fired in all mentioned temperatures; it depended on the raw material nature (carbonates content). This is why the database contained a lack of samples fired in the extreme temperatures within a used range, which influenced neural network sensitivity. In addition, as neural networks (Table 1) and sensitivity (Fig. 3) showed, higher experimental errors were found for *CS*, where the problem was in preparation of samples for testing (Fig. 4).

4. Conclusions

This paper showed the relationship between the initial properties of representative 83 heavy clay samples and the characteristics of laboratory species fired at different temperatures (800 °C, 820 °C, 850 °C, 870 °C, 900 °C, 930 °C, 950 °C, 1050 °C and 1100 °C). Heavy clay was sampled at North, Central and South Serbia, and analyses presented gave a picture of its quality when used in brick industry in these regions. Clays were characterized by means of chemical and technological analysis, where parameters used in statistical analysis were divided into input and output variables. Input variables were chemical content and firing temperature, while output variables were compressive strength of laboratory blocks (*CSB*) and cubes (*CSC*), and water absorption of tiles (*WAT*), blocks (*WAB*) and cubes (*WAC*).

ANN-based model was developed for prediction of output variables for a wide range of input variables. Obtained model was able to successfully predict experimental output parameters. The model is easy to be implemented for design of bricks of desired quality and could be effectively used for predictive modeling and optimization of firing temperature. As compared to multiple regression models, ANN models yielded a much better fit of experimental data.

Taking into account that a considerable amount and wide variety of data had been used used in the present work to obtain the ANN model, and considering that this model proved to be capable to achieve a sufficiently good representation, it is expected to be very useful in practice. This way, a non-destructive technique for final laboratory brick properties determination is developed, based only on chemical analysis tests. The neural networks, developed for the first time, can be used on a global scale, but also improved with the database growth.

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References

[1] A.V. Kornilov, Reasons for the different effects of calcareous clays on strength properties of ceramics, Glass and Ceramics 62 (2005) 391–393.

[2] S. Meseguer, T. Sanfeliu, M.M. Jordan, Classification and statistical analysis of mine spoils chemical composition from Oliete basin (Teruel, NE Spain), Environmental Geology 56 (2009) 1461–1466.
[3] S.M. Awadh, H.H. Abudllah, Mineralogical, geochemical, and geotechnical evaluation of Al-Sowera soil for the building brick industry in Iraq, Arabian Journal of Geosciences 4 (2011) 413–419.
[4] J.G. Ten, M.J. Orts, A. Saburit, G. Silva, Thermal coductivity of traditional ceramics. Part I: influence of bulk density and firing temperature, Ceramics International 36 (2010) 1951–1959.
[5] N. Koukouzas, C. Ketikidis, G. Itskos, X. Spiliotis, V. Karayannis, G. Papapolymerou, Synthesis of CFB-coal fly ash clay bricks and their characterization, Waste and Biomass Valorization 2 (2011) 87–94.
[6] X. Cheng, S. Ke, Q. Wang, H. Wang, A. Shui, P. Liu, Fabrication of anorthite-based ceramic using mineral raw materials, Ceramics International 38 (2012) 3227–3235.
[7] C. Manoharan, P. Sutharsan, S. Dhanapandian, R. Venkatachalapathy, R.M. Asanulla, Analysis of temperature effect on ceramic brick production from alluvial deposits, Tamilnadu, India, Applied Clay Science 54 (2011) 20–25.
[8] M.L. Gualtieri, A.F. Gualtieri, S. Gagliardi, P. Ruffini, R. Ferrari, M. Hanuskova, Thermal conductivity of fired clays: effects of mineralogical and physical properties of the raw materials, Applied Clay Science 49 (2010) 269–275.
[9] L. Sidjanin, J. Ranogajec, D. Rajnovic, E. Molnar, Influence of firing temperature on mechanical properties on roofing tiles, Materials and Design 28 (2007) 941–947.
[10] V. Ducman, A.S. Škapin, M. Radeka, J. Ranogajec, Frost resistance of clay roofing tiles: case study, Ceramics International 37 (2011) 85–91.
[11] A. Nazari, G. Khalaj, Prediction compressive strength of lightweight geopolymers by ANFIS 38 (2012) 4501–4510.
[12] A. Nazari, Fuzzy logic for prediction water absorption of lightweight geopolymers produced from waste materials, Ceramics International 38 (2012) 4729–4736.
[13] B.J. Taylor, Methods and Procedures for the Verification and Validation of Artificial Neural Networks., Springer Science+Business Media, Inc., USA, 2006.
[14] EN 771-1:2010 Specification for Masonry Units—Part 1: Clay Masonry Units.
[15] S.L. Rettig, J.W. Marinenko, H.N. Khoury, B.F. Jones, Comparison of rapid methods for chemical analysis of milligram samples of ultrafine clays, Clays and Clay Minerals 31 (1983) 440–446.
[16] S. Dragović, A. Onjia, Classification of soil samples according to their geographic origin using gamma-ray spectrometry and principal component analysis, Journal of Environmental Radioactivity 89 (2006) 150–158.
[17] H. Abdi, L.J. Williams, Principal component analysis, Wiley Interdisciplinary Reviews Computational Statistics 2 (2010) 433–459.
[18] T. Kollo, D. Rosen, Advanced Multivariate Statistics with Matrices, Springer, Netherland, http://dx.doi.org/10.1007/1-4020-3419-9.
[19] M. Dondi, G. Guarini, M. Raimondo, C. Zanelli, D.D. Fabbriche, A. Agostini, Recycling the insoluble residue from titania slag dissolution (tionite) in clay bricks, Ceramics International 36 (2010) 2461–2467.
[20] E. Furlani, G. Tonello, E. Aneggi, S. Maschio, Preparation and characterization of sintered ceramics made with spent foundary olivine sand and clay, Ceramics International 38 (2012) 2619–2625.
[21] L.C.S. Herek, C.E. Hori, M.H.M. Reis, N.D. Mora, C.R.G. Tavares, R. Bergamasco, Characterization of ceramic bricks incorporated with textile laundrz sludge, Ceramics International 38 (2012) 951–959.
[22] A. Andrews, J. Adam, S.K.Y. Gawu, Development of fireclay aluminosilicate refractory from lithomargic clay deposits, Ceramics International (2012), http://dx.doi.org/10.1016/j.ceramint.2012.06.091.
[23] Z. Radojević, Z. Lalić, R. Vasić, A. Mitrović, Brick raw materials quality in Serbia and the influence for the products quality and to the production technology—loess sediments, Izgradnja 59 (2005) 45–49.
[24] J.J. Montano, A. Palmer, Numeric sensitivity analysis applied to feedforward neural networks, Neural Computing and Applications 12 (2003) 119–125, http://dx.doi.org/10.1007/s00521-003-0377-9.
[25] S.S. Sablani, A. Kacimov, J. Pret, A.S. Mujumdar, A. Campo, Non-iterative estimation of heat transfer coefficients using artificial neural network models, International Journal of Heat and Mass Transfer 48 (2005) 665–679.
[26] G.E.P. Box, D.W. Behnken, Some new three level designs for the study of quantitative variables, Technometrics 2 (1960) 455–475.
[27] S. Özgen, A. Yildiz, Apllication of Box–Behnken design to modeling the effect of smectite content on swelling to hydrocyclone processing of bentonites with various geologic properties, Clays and Clay Minerals 58 (2010) 431–448.
[28] S.W. Cheng, C.F.J. Wu, Factor screening and response surface exploration, Statistica Sinica 11 (2001) 553–604.