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EFFECT OF CHALK THERMAL TREATMENT MODE ON ITS STRENGTH

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Natural chalk is characterized by a fine-grained structure. The processing of chalk in conditions traditional for calcium carbonate baking is accompanied by its almost destruction and the formation of a huge amount of dust. The paper presents strength characteristics of chalk and chalky stone baking obtained with different temperature-time conditions of heating the raw material to a temperature of 450-600 °C. The uniaxial compression method was used to determine the strength depending on variable factors. Based on the experimental data, a model was constructed that determines the dependence of chalk strength on time and heating temperature. In the temperature range of 450-600 °C, the strength of chalk stone increases with increasing temperature and decreases with the increasing heating rate. In the process of isothermal heating, several factors will immediately affect the strength of a chalky stone: the formation and growth of calcite crystals, the evaporation of water, and the agglomeration of calcite grains. With an increase in the heating temperature from 450 to 600 °C, the average size of the crystals significantly increases and crystals with an estimated size of more than 4 microns are detected. An increase in the size of crystals is associated with an increase in their growth rate. The agglomeration of grains occurs at a temperature of 600 °C.
Keywords: chalk; baking; calcium oxide; tensile strength; lime

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Introduction. Industrial calcium oxide (quicklime), as a rule, is a product of limestone burning at a temperature of 900-1100 °C and is used in various fields: in ferrous and nonferrous metallurgy, in pulp and paper production, in obtaining building and finishing materials, fertilizers, rubber and plastic products, etc. [3, 5, 8].

The baking process is carried out mainly in rotary and shaft furnaces, which imposes certain requirements on the mechanical strength of the calcined material throughout the process. It is due to the need for stable operation of the furnace unit and its dust removal system and with the achievement of the minimum energy consumption.

The starting material for lime production could be natural chalk – friable white rock of sedimentary origin, consisting mainly of amorphous calcium carbonate and inclusions of fine crystalline calcite and aragonite. However, chalk is characterized by a fine-grained structure, and its processing in industrial furnace units is accompanied by almost destruction and the formation of huge amounts of dust, which requires expensive filtering equipment to capture [6, 9, 12, 14-16, 19].

As shown in the previous papers [7, 11], you can set the characteristics of the resulting chalky stone already at low-temperature heating in the temperature range of 450-600 °C. In this temperature range, the processes of structural relaxation of amorphous calcium carbonate occur, accompanied by the formation and growth of calcite grains, which has a significant impact on the strength of the chalk stone. Also, the strength is influenced by the porosity, humidity, grain size of calcite, and their relationship to each other.

The problem of using chalk to produce quicklime was previously proposed to be solved with the help of special additives: coke or anthracite [1, 2] and alkali metal salts [13]. However, this technology was not implemented due to low efficiency and contamination of the final product. As a result, chalk is not used to produce quicklime.

The purpose of this paper is to study the effect of temperature-time heating on the strength of a chalkstone obtained at a temperature of 450-600 °C, and the selection of conditions for obtaining a durable chalk stone as a result of such baking.

Experimental part. For the experiments, we used chalk from Lebedinsky mining and processing plant (LMPP). It is characterized by high porosity (up to 50 %) and calcium carbonate content (up to 99 %).

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The composition of LMPP chalk is the following (% by weight): $CaCO_3 \geq 98.0$; $MgO \leq 0.1$; $SiO_2 \leq 1.0$; $P \leq 0.05$; $S \leq 0.01$.

To determine the effect of temperature-time heating regimes on the strength of chalky stone, the Box-Wilson method was used with the full factorial experiment (FFE) plan. Chalk strength depends on three selected factors: heating time t_h, heating temperature T and annealing time t_{an}. Factors varied in the following intervals: $x_1 = t_h = 30\text{-}120$ min; $x_2 = t_{an} = 30\text{-}120$ min; $T = x_3 = 450\text{-}600$ °C.

After the transition to coded variables by the formula

$$\bar{x}_i = \frac{x_i - x_0}{\Delta x_i}, \qquad (1)$$

Table 1

The matrix of planning experiments to determine the effect of temperature-time regimes of heating chalk on the strength of chalkstone

№ s/n	In coded variables			In natural variables		
	$\bar{x}_1$	$\bar{x}_2$	$\bar{x}_3$	t_h, min	t_{an}, min	T, °C
1	+	+	+	120	120	600
2	+	–	+	120	30	600
3	–	+	+	30	120	600
4	–	–	+	30	30	600
5	+	+	–	120	120	450
6	+	–	–	120	30	450
7	–	+	–	30	120	450
8	–	–	–	30	30	450
9	0	0	0	75	75	525

where i – factor counter; $\bar{x}_i$ – coded i-th factor; x_i – the natural value of the i-th factor; $x_{i0} = \frac{x_{i\max} + x_{i\min}}{2}$ – the center of the experiment for the selected factor; Δx_i – the variation interval of the i-th factor, the planning matrix was built (Table 1).

Cubic samples with an average edge length of 50 mm were made from chalk using a circular saw and files of different coarseness density.

The samples were heated in a laboratory muffle electric furnace SKV 10/13 V. The heating mode was set using the PT200-02 temperature controller. The device has two programmable sections – warming and holding – where we can program the following parameters: temperature accuracy, warming and holding time. Heating to a predetermined temperature is carried out linearly with an absolute measurement error of ± 6 ° C.

The compressive strength of the specimens was determined on a hydraulic machine of the R-10 type. The load was measured using a traditional torsion force meter with a measurement error of 49 N.

A raster electron microscope SUPRA 55VP-25-78 was used to estimate particle sizes after thermal heating.

X-ray phase analysis was performed using a Bruker D8 Advance X-ray diffractometer with a vertical Θ-Θ-goniometer on a β-filtered $Cu_{K\alpha}$-radiation (λ = 1.5418 Å, Ni-filter), and a diffraction pattern was recorded by a LynxEye detector (capture angle of 3.2°) produced by Bruker with a scanning step of 0.02° at 2Θ and a signal accumulation time of 0.7 s/step. Operation modes of the tube are $U = 40$ kV, $I = 40$ mA. The survey was carried out with the Bragg-Brentano method by focusing during sample rotation (30 rpm) in the holder plane in the angle range 2Θ = 20-80°.

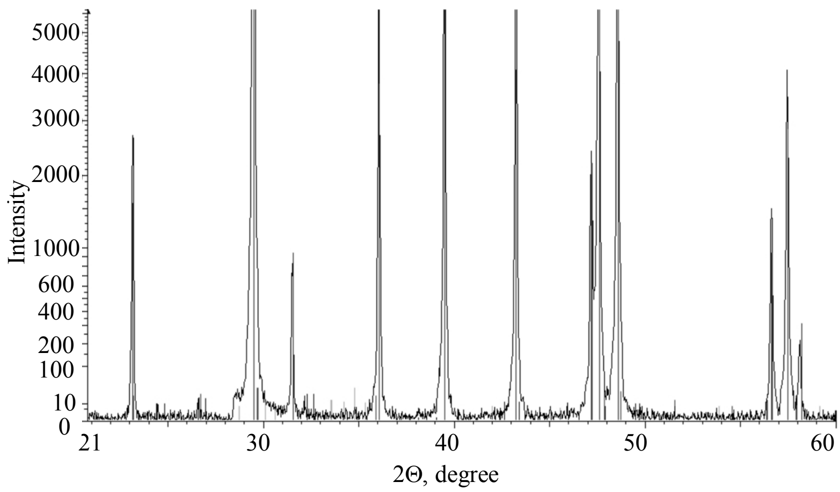

Fig.1. The results of X-ray phase analysis of chalky stone after thermal heating up to 600 °C, heating time 30-120 min

Results and discussion. X-ray analysis data (Fig.1) showed that under the experimental con-

Table 2

Technological map of experiments to determine the compressive strength and measurement results σ^{e}_{comp} and intermediate calculations using a mathematical model

Nr. of experiments	$\bar{x}_1$	$\bar{x}_2$	$\bar{x}_3$	σ^{e}_{comp}	σ^{calc}_{comp}	ε, %
3	+	+	+	7.62±0.56	7.39	3.1
3	+	–	+	5.09±1.83	4.79	6.0
4	–	+	+	6.68±0.43	6.62	0.9
3	–	–	+	4.01±0.40	4.02	0.2
3	+	+	–	4.17±0.47	3.85	7.6
4	+	–	–	4.32±0.16	4.42	2.3
3	–	+	–	3.40±0.05	3.26	4.3
3	–	–	–	4.05±0.78	3.65	9.8
5	0	0	0	3.59±0.24	4.77	32.9

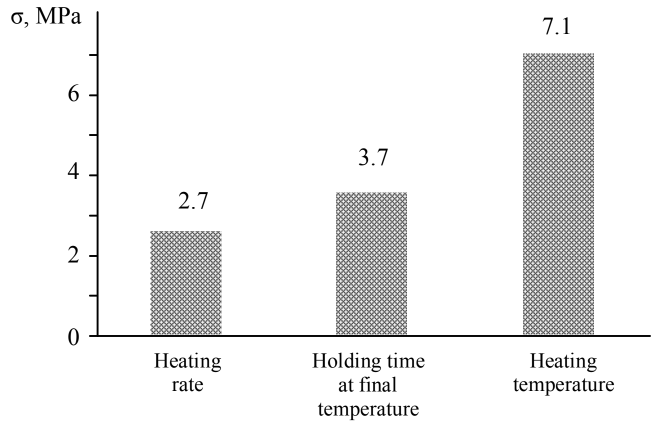

Fig.2. Ranking chart based on experimental data processing

ditions, regardless of the heating time, the basis of the chalky stone before and after heat treatment to 600 °C is calcite crystals (up to 99.7 %). Other polymorphic modifications of calcium carbonate were not detected in the studied temperature range.

The results of determining the compressive strength of the samples subjected to heat treatment according to the experiment plan (Table 1) were entered into the test chart of the experiments (Table 2), which corresponds to the orthogonal full factorial experiment of the first order and allows you to build a linear or incomplete quadratic model, check its adequacy and rank factors.

To rank the factors, we calculated the significance ranking $R = \Delta M \cdot \Delta N$, where ΔM is the difference of medians of the experimental values of the response function; ΔN is the sum of the number of outliers for each factor.

The calculated values of the significance ranking for the first, second and third factors are respectively equal: $R_1 = 2.7$, $R_2 = 3.73$; $R_3 = 7.12$. The ranking chart represents the factors according to significance increase: the heating temperature has the greatest effect on the strength of the chalk stone, the lowest is the heating rate (Fig.2).

For the calculation we selected incomplete quadratic model of the following form:

$$\sigma^{calc}_{comp} = b_0 + b_1 t_h + b_2 t_{an} + b_3 T + b_{23} t_{an} T . \qquad (2)$$

After the transition to coded variables, the model takes the form

$$\sigma^{calc}_{comp} = b'_0 + b'_1 \overline{x_1} + b'_2 \overline{x_2} + b'_3 \overline{x_3} + b'_{23} \overline{x_2 x_3} . \qquad (3)$$

The selection of this model is explained by the fact that the strength values calculated according to the model have an error relative to the experimental values within the engineering accuracy (10 %). Also, this model is adequate with a reliability of 95 %, as evidenced by the calculated value of the Fisher ratio. The choice of the pair interaction effect b_{23} and b'_{23}, respectively, as the only significant one is since such a model is the simplest among other models [10] meeting the condition of accuracy and reliability.

In the result of the calculation of the b'_0 coefficient according to the formula

$$b'_0 = \sum_{i=1}^{N} \sigma^{e}_{comp\,i} \Big/ N$$

and the b'_i coefficients according to the formula

$$b'_i = \sum_{i=1}^{N} \sigma^{e}_{comp\,i} \cdot \overline{x_i} \Big/ \sum_{i=1}^{N} \left(\overline{x_i}\right)^2$$

we have

$$\sigma_{\text{comp}}^{\text{calc}} = 4.77 + 0.38\overline{x_1} + 0.55\overline{x_2} + 0.93\overline{x_3} + 0.75\overline{x_2}\,\overline{x_3}\,, \tag{4}$$

where

$$\bar{x}_1 = (t_{\text{h}} - 75)/45; \quad \bar{x}_2 = (t_{\text{an}} - 75)/45; \quad \bar{x}_3 = (T - 525)/75.$$

The results of calculating the value $\sigma_{\text{comp}}^{\text{calc}}$ of the model (4) are given in Table 2.

Fisher ratio can be determined by the formula

$$F_{\text{calc}}(f_1, f_2) = \frac{S_{\text{ad}}^2(f_1)}{S_{\text{rep}}^2(f_2)} = \frac{\frac{1}{f_1}\sum_{i=1}^{N}\left(\sigma_{\text{comp}\,i}^{\text{calc}} - \sigma_{\text{comp}\,i}^{\text{e}}\right)^2}{\frac{1}{f_2}\sum_{i=1}^{N_0}\left(\sigma_{\text{comp}\,i}^{\text{e}} - \sigma_{\text{comp m}}^{\text{e}}\right)^2}, \tag{5}$$

where N – the total number of experiments at different points; N_0 – number of repetitions; f_1 – the number of degrees of freedom in calculating the variance of the model adequacy; $f_1 = N–q$, q – the number of coefficients in the model; f_2 – the number of degrees of freedom in calculating the dispersion of repeatability, $f_2 = N_0–1$. As a result, the calculated value of the Fisher ratio is

$$F_{\text{calc}}(4.3) = 6{,}1. \tag{6}$$

For reliability ($\alpha = 0.95$, $f_1 = 4$ and $f_2 = 3$), the table value of the Fisher ratio is $F_{\text{tabl}} = 9.1$. Comparison of the calculated value of the Fisher ratio with the table value indicates the adequacy of the linear model (4) with the reliability of 95 %.

The maximum relative error of 32.9 % does not correspond to the accuracy of engineering calculations, but since the model is adequate and the relative error for other experiments does not exceed 10 %, this model can be used to determine the influence of factors on the response function σ_{comp}.

When writing a model in natural variables

$$\sigma_{\text{comp}}^{\text{calc}} = 5.4 + 0.009t_{\text{h}} - 0.104t_{\text{an}} - 0.004T + 0.0002t_{\text{an}}T\,. \tag{7}$$

The model allows determining the influence of each of the factors on the strength of the chalk stone.

Since the heating of chalk is carried out at a constant speed, the heating time $t_{\text{h}} = T/v$, where v is the heating rate, substituting t_{h} into the model and equating the heating time to zero, we obtain the dependence of the strength of the chalk stone on the temperature at different heating rates (Fig.3).

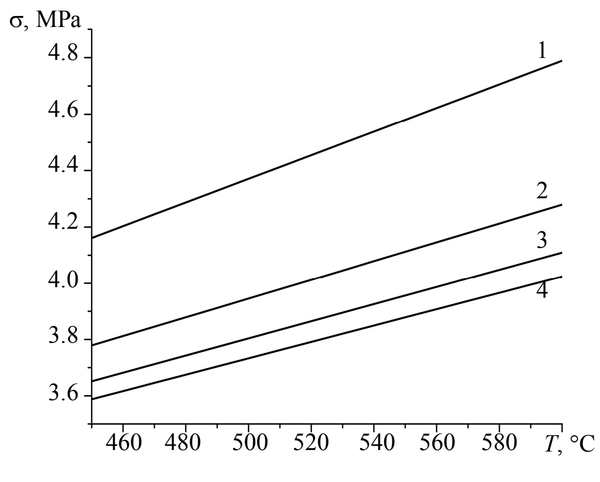

Fig.3. The dependence of the strength of the chalk stone from the heating temperature at different heating rates (heating time 30 min)

1 – 5 °C/min; 2 – 10 °C/min; 3 – 15 °C/min; 4 – 20 °C/min

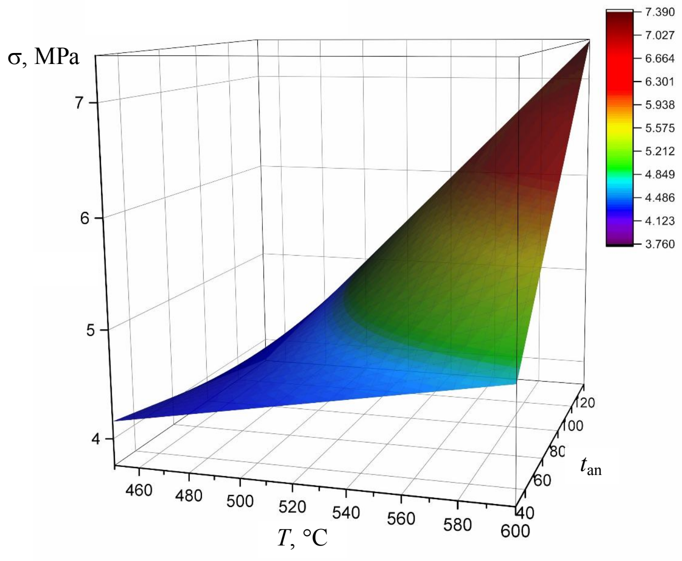

Fig.4. Graph of the strength of the chalk stone on the temperature and heating time. Heating rate 5 °C/min

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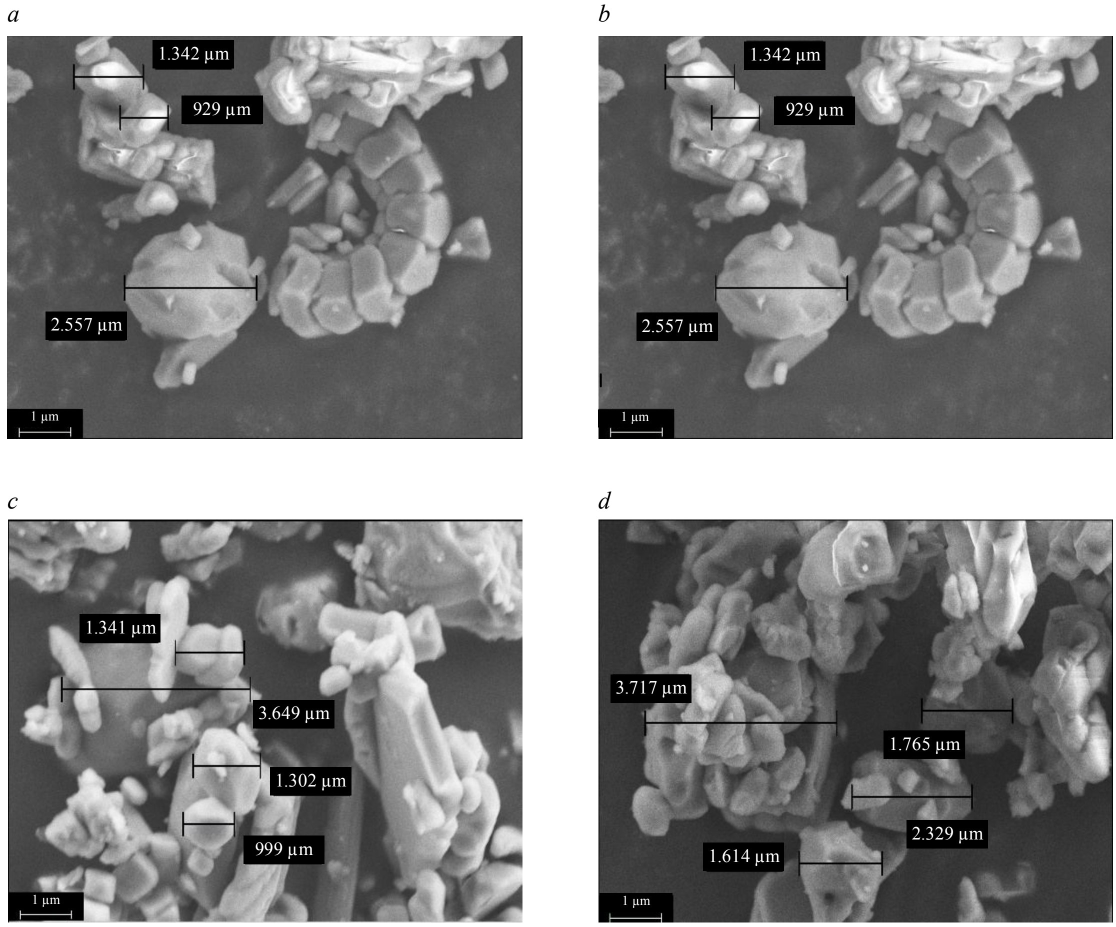

Fig.5. SEM images of samples of chalky stone obtained at different heating times, calcining times, heating temperatures, respectively: *a* – 120 min, 30 min, 450 °C; *b* – 120 min, 120 min, 450 °C; *c* – 120 min, 30 min, 600 °C; *d* – 120 min, 120 min, 600 °C

From Fig.3 it follows that with an increase in the heating rate, the strength of the chalk stone decreases, the temperature of the crystallization point increases. In this case, the time after which the same heating temperature will be reached at high heating rates is less.

Accordingly, the proportion of crystallized amorphous calcium carbonate will be less, which will affect the strength characteristics. Also, with an increase in the heating rate, processes of intense evaporation of water occur, accompanied by the destruction of the microstructure and a decrease in the strength of the chalk. The figure also shows that with an increase in the heating temperature, the strength of the chalk stone increases. The increase in strength is due to a decrease in porosity due to the growth of calcite crystals.

Figure 4 shows the dependence of the chalk stone strength on the temperature and heating time. It can be seen from the figure that over the entire range of temperatures and annealing times, the strength increases.

Perhaps in the process of isothermal heating, several factors will immediately affect the strength of a chalky stone: the formation and growth of calcite crystals, the evaporation of water, and the agglomeration of calcite grains. Hardening will be achieved due to the high growth rates of calcite and their agglomeration.

Figure 5 shows the SEM images of a chalkstone after heating under various conditions.

At a temperature of 450 °C (Fig.5, *a, b*), as a result of an increase in the heating time from 30 to 120 min, the grains increase by ~ 100 nm. With an increase in the heating temperature from 450 to 600 °C, the average size of the crystals significantly increases, crystals with an estimated size of more than 4 μm are detected (Fig.5, *d*). An increase in crystal size is associated with an increase in growth rate. From Fig.5, *c*, *d* it can be concluded that, at a temperature of 600 °C, the grains agglomerate.

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Conclusions

By laboratory studies on chalk baking with varying heating time in the range of 30÷120 min, final heating temperature from 450 to 600 °C and heating rate, a mathematical model was constructed depending on the compressive strength of chalk stone from three selected factors. The model has the following form:

$$\sigma_{\mathrm{comp}}^{\mathrm{calc}} = 5.4 + 0.009 t_{\mathrm{h}} + 0.104 t_{\mathrm{an}} + 0.004 T + 0.0002 t_{\mathrm{an}} T \, .$$

Based on the model and SEM images of the chalk stone, obtained after heating under different conditions, conclusions were made about the influence of each of the factors on the strength characteristics of the chalk stone:

- as the heating rate increases, the strength of the chalk stone decreases;
- with increasing heating temperature, the strength of the chalk stone increases;
- with increasing heating time, the strength of the chalk stone increases.

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