

doi: 10.18720/MCE.83.6

Strength and phase composition of autoclaved material: an approximation

Взаимосвязь прочности и фазового состава автоклавированного материала

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Key words: autoclaved building materials; lime-fly ash mixtures; Na_2SO_4 addition; phase composition; strength of the stone; interrelationships

Ключевые слова: автоклавные строительные материалы; известково-золяные смеси; добавка Na_2SO_4 ; фазовый состав; прочность камня; взаимосвязи

Abstract. The purpose of this work was to identify the relationship between the phase composition and strength of autoclaved pressed stone from a mixture of lime and ash of CHP in the presence of Na_2SO_4 . From these mixtures are made such building materials as silicate brick and blocks from autoclaved cellular concrete. The phase analysis of the autoclaved samples was carried out by X-ray and thermal methods. It was found that the mixtures studied after autoclaving for 8; 50 and 100 hours at 0.8 MPa isotherm with no addition or with 1 and 2% Na_2SO_4 is represented by gel-like phase C-A-S-H, aluminum substituted tobermorite, hydrogarnet katoite. Adding of 1 and 2% Na_2SO_4 makes no qualitative change in phase composition, but significantly redistribute the phase composition and increase the rate of phase formation. Thus 2 % Na_2SO_4 contributes to a substantial increase in the synthesis of Al-tobermorite, but reduces the C-A-S-H phase formation. Katoite hydrogarnet content remains unchanged. The degree of hydration of the composition with 2% Na_2SO_4 for 8 hours of autoclaving is the same as for 100 hours of treatment without an additive. This increases the strength of the material by 1.65 times with the same 8 hour steaming time. Strength of the stone is always directly proportional to the content of a gel C-A-S-H phase. Its content is proportional to the number of Al-tobermorite in non-additional mixtures, but does not correspond to the content of tobermorite in compositions with addition of 2 % Na_2SO_4 . Keywords: autoclaved building materials, lime-fly ash mixtures, Na_2SO_4 addition, phase composition, strength of the stone, interrelationships.

Аннотация. Целью данной работы было выявить связь между фазовым составом и прочностью автоклавного прессованного камня из смеси извести и золы ТЭЦ в присутствии Na_2SO_4 . Из подобных смесей изготавливаются такие строительные материалы как силикатный кирпич и блоки из автоклавного ячеистого бетона. Фазовый анализ автоклавированных образцов проводили рентгенофазовым и термическими методами. Было обнаружено, что смеси, изученные после автоклавирования при 8; 50 и 100 часов при изотерме 0,8 МПа без добавления или с 1 и 2% Na_2SO_4 содержат гелевидную фазу C-A-S-H, алюминий замещенный тоберморит, гидрогранат катоит. Добавление 1 и 2% Na_2SO_4 не приводит к качественному изменению фазового состава, но значительно перераспределяют фазовый состав и увеличивает скорость фазообразования. Таким образом, 2% Na_2SO_4 способствует существенному увеличению содержания Al-тоберморита, но уменьшает образование фазы C-A-S-H. Содержание гидрограната остается неизменным. Степень гидратации композиции с 2% Na_2SO_4 за 8 часов автоклавирования такая же как за 100 часов обработки без добавки. Это увеличивает прочность материала в 1,65 раза при одинаковом 8 часовом времени запаривания. Прочность камня всегда прямо пропорциональна содержанию гелевидной фазы C-A-S-H. Её содержание пропорционально содержанию Al-тоберморита в смесях без добавки, но не соответствует содержанию тоберморита в композициях с добавлением 2% Na_2SO_4 . Ключевые слова: автоклавные строительные материалы, известково-золяные смеси, добавка Na_2SO_4 , фазовый состав, прочность камня, взаимосвязи.

1. Introduction

The object of research in this paper is to reveal the relationship between the strength of autoclaved stone based on the lime-ash mixture and its phase composition.

The phase composition of hydrates of autoclave stone on the basis of lime and aluminosilicate raw materials still provokes discussions, not to mention the interrelation between the components of the phase composition and its strength. At the same time, numerous silicate brick plants are used as the main component or as an additive to the ash class F of the CHP.

The main law of the strength formation of silicate autoclaved materials have been discussed since the beginning of the 50s of the 20th century, when G.L. Kalouzek had found its direct dependence on the quantity of generated 11.3 angstrom tobermorite [1]. Then H.F.W. Taylor objected Kalouzek, noting that the strength of any material is a function of its density, and, for autoclaved materials, it also depends on presence of gel phase in them. The effect of a gel phase on the strength had been previously mentioned in the works of P.I. Bozhenov for whom Taylor referred. However, both P.I. Bozhenov, and Taylor have not reported quantitative relationships in those years. It was only 1977, when Taylor published the article [2] proving a direct link of strength of lime-silica material with a number of C-S-H gel being formed. Taylor stated a brief review of these issues in the last lifetime edition of "Chemistry of cement" [3], also specifying differences in opinion on this issue, particularly in the extent beneficial to crystallize a gel phase.

When using various aluminosilicate materials, including it in the form of CHP ash of the aluminosilicate composition, as well as Portland cements the silica component, phase formation of autoclave materials becomes more complicated. Even the qualitative composition of the phases had caused discussions. It was only in the 2000s, when the publications of A.S. Ray in conjunction with D.S. Klimesch [4] were issued, and as well of Japanese researchers [5] and others [6, 7], which allowed to interpret and quantify unambiguously the phases being formed in such systems. The issue of the interrelation of the phase composition and strength of autoclave stone composed of lime-aluminosilicate raw materials remained open. Because synthetic tobermorites and their Al- and Fe-substituted forms easily synthesized under saturated steam or in hydrothermal conditions at temperatures from 80 to 225 °C from a wide range starting materials, including various following mixtures: lime, zeolites, quartz, gibbsite, cement, clays, sodium silicate, ashes, cullet, trachyte and others [1, 8–19]. And the presence of a gel-like phase of the C-A-S-H type in these syntheses was often not paid attention. At the same time, publications on the features of the structure of the tobermorites and their analogs, the synthesis of minerals and their ion-exchange properties, do not give an answer to the question of the regularities in the formation of the strength of the stone on their basis [20–28].

Therefore, the purpose of this study was to establish such a relationship between the phase composition and strength for such an aluminosilicate raw material as ash.

For this, it was necessary to establish a reliable quantitative composition of phases of autoclave stone composed of aluminosilicate raw materials on the basis of the CHP ash, to use an addition that promotes redistribution of the main phases in order to disclose interrelations between the phase composition and strength of stone.

It follows from [5, 26] that the addition of Al_2O_3 or SO_3 in lime-silica autoclave composition accelerates crystallization of C-S-H gel phase and formation of larger amount of tobermorite. Furthermore, it is known that the presence of alkali in autoclave synthesis significantly accelerates the hydrate formation [29]. By definition, alumina is present in the aluminosilicate raw material. Therefore, Na_2SO_4 was selected as an activator additive. Sodium sulphate contains the required group of SO_3 , and alkaline, released in hydrothermal reactions, will accelerate the synthesis and crystallization of hydrated phases. The possibility of such processes due to the high real defectness tobermorite structure [20, 30–37].

The relevance of this study is that, for aluminosilicate raw materials, the relationship between strength and phase composition for autoclave materials has not yet been established. At the same time, such aluminosilicate materials as CHP ashes are widely used in the technology of autoclave materials.

The purpose of this study is to establish a relationship between the strength and phase composition of autoclave material based on lime and aluminosilicate ash from CHP.

To achieve the goal it is necessary to solve the following tasks:

- investigate the strength and phase composition of lime-ash material in a wide range of phase composition changes;

- to increase the range of changes in the phase composition and strength of the stone, apply the method of prolonged autoclave treatment and intensification of the processes by the Na_2SO_4 additive-activator;
- to establish the relationship between the phase composition of lime-ash and its strength.

2. Materials and Methods

In experiment, was used electrostatic precipitator ash provided by burning coal (coal ash – CA) of Kuznetsk Basin brand G at Novosibirsk CHP-5 with the composition of unburned coal of 3.29 % (Table 1, recalculated on ignited product). Ash particles range from 1.5 to 250 μm with an average diameter of 70.5 μm (determined in an equipment SALD-2101 Laser Diffraction Particle Size Analyzer – SHIMADZU, Japan). Calcium lime contained about 92 % of active CaO and MgO and, by main indicators, was consistent with first grade lime according to Russian standards. In some mixtures, it was used curing activator of Na_2SO_4 with 98 % content of the main substance.

Table 1. Chemical composition of ash provided by Novosibirsk CHP-5

Material	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Total
CHP-5 ash	61.87	23.73	5.0	4.38	1.29	0.33	99.98

The ash was mixed with powdered lime with Blaine specific surface area of about 6.000 cm^2/g with a ratio of 20 % basing on active CaO and MgO. In some mixtures with tempering water, Na_2SO_4 was added as hardening activator in an amount of 1 or 2% by weight. The raw material mixture was moistened, sealed in plastic containers and ensilaged at 60 $^\circ\text{C}$ for 2 hours to full lime hydration. After that, from that mass, it was formed cylinder samples of diameter and height of 50 mm at specific pressing pressure of 20 MPa, which were treated in an autoclave at 0.8 MPa with isothermal exposure of 8, 50 and 100 hours correspondingly. Samples strength tests were produced after their drying at 100 $^\circ\text{C}$ to constant mass. Six samples for test was chosen to ensure measurement error of not more than 3-5%. Some samples were taken out of those ones for analysis by methods of X-ray diffraction (XRD) and thermal analysis, including differential and thermal analysis (DTA), differential thermogravimetric analysis (DTG), and thermogravimetric analysis (TG). The X-ray diffraction analysis was performed on a DRON-3 (Russia) with $\text{CuK}\alpha$ radiation at tube voltage of 40 kV and current of 25 A. The thermal analysis at rate of 10 deg/min was conducted using an equipment Netzsch STA 449C (Germany) in a closed crucible and helium flow to create not-oxidative environment and eliminate the effects of burning coal residues in the ash.

3. Results and Discussions

Figure 1 shows that with increasing isothermal hold up time from 8 to 100 hours, strength of lime-ash compositions without additional of Na_2SO_4 is steadily increasing from 20 to 45.5 MPa. When injected with 1 and 2% Na_2SO_4 , there is an inflection in strength at 50 hours of autoclaving, or composition strength decrease in proportion to additions at isotherm of 100 hours. At this, the samples with the addition of 2% sodium sulphate gain the main strength after the first 8 hours of heat treatment in the autoclave and then there is no substantial increase observed. Compared with the addition-free composition, the addition of 1 and 2% of sodium sulfate increases strength by 1.3 and 1.6 times respectively at isotherm autoclaving of 8 hours.

These data require an interpretation. For this it is necessary to determine the phase composition of stone.

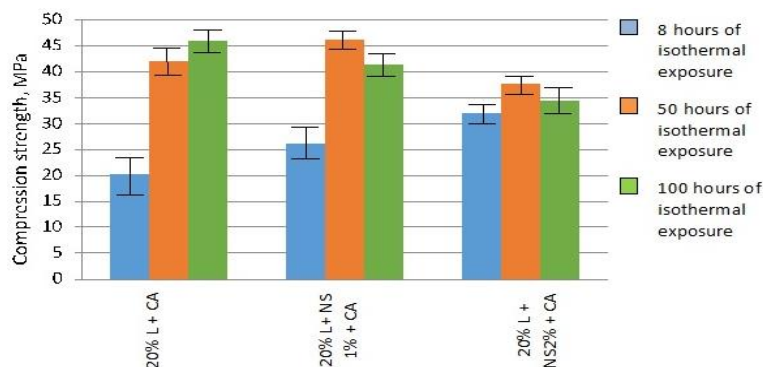


Figure 1. Strength of lime-ash samples autoclaved at pressure of 0.8 MPa depending on time of isothermal exposure and addition of Na_2SO_4 . Notice: L – lime, NS – Na_2SO_4 , CA – coal ash

The composition of the formed hydrothermal synthesis products in the addition-free mixture according to XRF (Figure 2) is presented by the following main phases: 8 hours isotherm (X-ray pattern1) - residual portlandite $\text{Ca}(\text{OH})_2$ (4.91; 2.63; 1.80), the residual quartz ash of SiO_2 (4.27; 3.35; 2.28; 1.80), synthesized tobermorite (11.48; 5.41; 3.08; 2.98; 2.79), calcite (3.04; 2.28; 1.93). In addition to these phases, there are reflections of hydrogarnets: katoite – 5.10; 2.79; 2.28; 1.67, and ferrous hydrogarnet – 3.08; 2.74; 1.62. Probably, the presence of C-S-H phases (I and II) - peaks are 3.07 and 2.80, but reflections for these phases are absent at small angles (12.5 and 9.80×10^{-10} m). Increasing the isotherm up to 100 hours in the addition-free composition (X-ray pattern2), we observe portlandite disappearance, the proportion of silica is reduced, the proportion of tobermorite is increased, but not all peak intensities of tobermorite change proportionally - the peak of 5.41 decreases, the one of 2.98 remains unchanged, and the peaks of 11.60 and 3.08 increase. Instead of the 2.79 peak, the peak of 2.76 appears. The significant deviation of 11-angstrom peak of 11.30 to 11.60×10^{-10} m should be noted. The peaks of katoite transform to reflections of ferrous hydrogarnet – 5.045; 3.08; 2.755; 1.62-1.63, although certain sources attribute the peak of 2.76 as well to katoite. Besides of 1.1 nm of tobermorite and perhaps xonotlite (3.07-3.08; 2.83; 2.70), there are no peaks of other calcium hydrosilicates.

In the presence of 1% Na_2SO_4 activator for 8 hours of treatment (X-ray pattern3), there is an intermediate phase composition reached compared with 8 and 100 hours without additive composition except of a significant increase in the peak of 2.76. It can be referred to katoite or ferrous hydrogarnet. 100 hour exposure in the presence of 2% Na_2SO_4 (X-ray pattern4) differs only slightly from the 100 hour exposure in a system without the activator, except of even larger decrease of quartz proportion and outlined supplements.

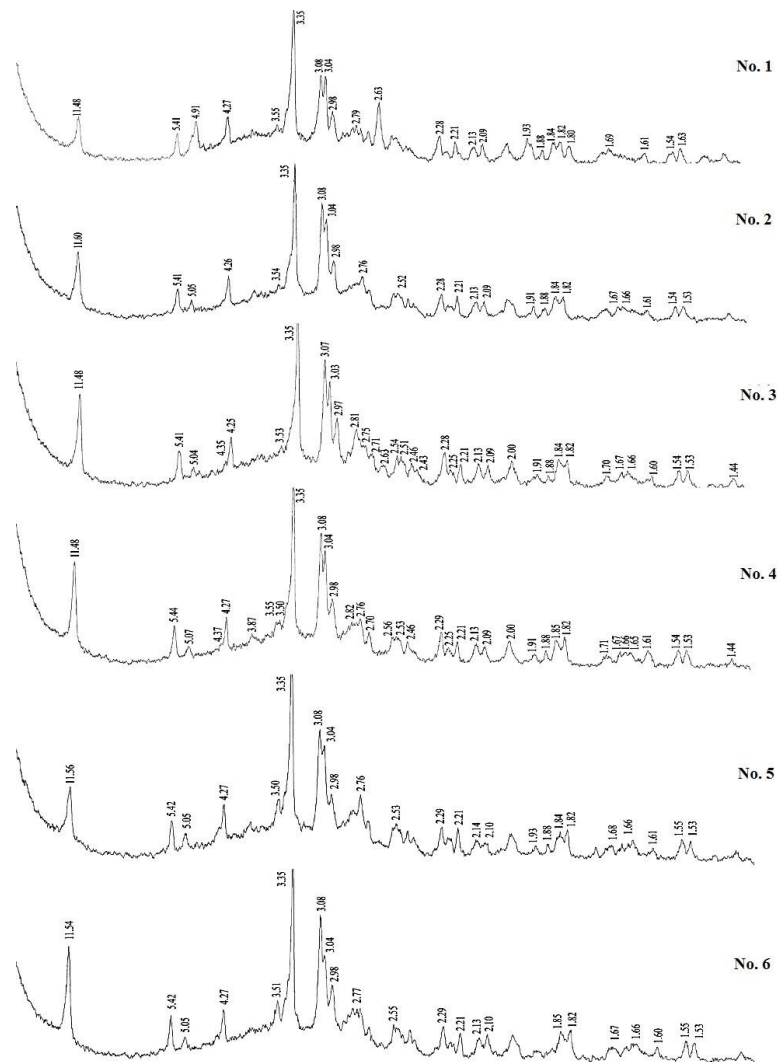


Figure 2. X-ray patterns of lime-ash stone of the 20 % lime, 80 % ash mixture, at: No. 1 – 8 h of isothermal exposure; No. 2 – at 100 h of isothermal exposure; No. 3 – 8 h of isothermal exposure with additive injection of 1% Na_2SO_4 ; No. 4 – 100 h of isothermal exposure with additive injection of 1% Na_2SO_4 ; No. 5 – 8 h of isothermal exposure with additive injection of 2% Na_2SO_4 ; No. 6 – 100 h of isothermal exposure with additive injection of 2% Na_2SO_4 .

Analysis of the mixture thermogram based on the ash of Novosibirsk CHP-5 at 8 hours of isothermal exposure (Figure 3) shows the effect of weight loss (DTG curve at approximately 95 °C, which is associated with removal of moisture adsorption. There we see presence of hydrogarnets that are noted with little effect at 373 °C. A large weight loss at 447 °C corresponds to residual portlandite $\text{Ca}(\text{OH})_2$. In the 700–780 °C interval, there occurs decomposition of calcium hydrosilicates, calcite, and probably, of C-A-S-H phase, dehydration of which is accompanied by a pronounced effect at 741 °C. H.F.W. Taylor also attributed this effect to amorphous hydrosilicate phase [2]. Tobermorite phase having significant deviations of XRD reflections from 11.3, represents aluminum substituted tobermorite with other impurities and thus loses weight at 180 °C, being much smaller than 240 °C [4].

At increasing the isothermal exposure to 100 hours, a differential curve of weight loss, DTG (Figure 4), represents a significant increase in endothermic effect at 86 °C and the disappearance of residual portlandite $\text{Ca}(\text{OH})_2$ because of the formation of hydrate phases large number being a result of hydrothermal synthesis. For this, as additional evidence, the large weight loss may serve as evidence which is associated with the removal of moisture adsorption and with loss of water by the gel phase. Weight loss effect by hydrogarnet at 381 °C is registered. The weight loss at effects of 185 and 727 °C increases up to 2.4 %.

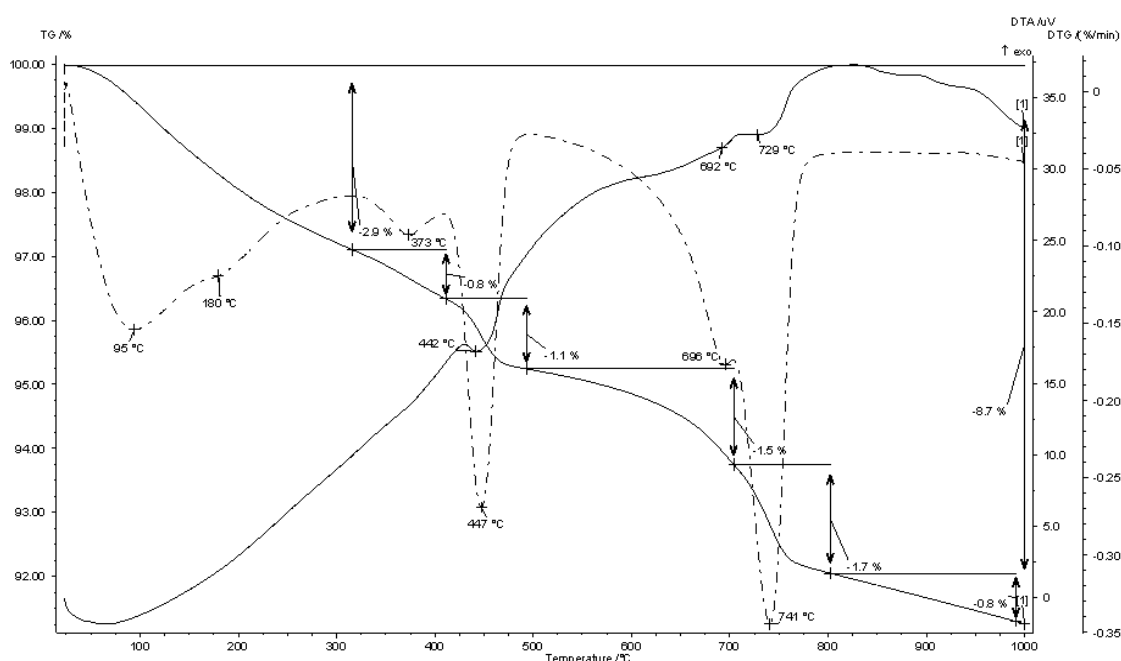


Figure 3. Thermogram of products of autoclave treatment basing on Novosibirsk CHP-5 ash at 20 % of lime at 8 hours of isothermal exposure

The thermogram of samples hydration products on the basis of Novosibirsk CHP-5 ash at 20 % of lime, with 8 hours of isothermal exposure with additional injection of 2% Na_2SO_4 (Figure 5) differs only slightly from the thermogram being addition-free of lime-ash mixture at 100 hours of isothermal exposure that indicates the activation of hydrothermal synthesis in the presence of sodium sulfate. However, with the activator additive, the proportion of C-A-S-H phase gets reduced, if judging by the weight loss at 727 °C endothermic effect.

Estimation of interrelation between strength of the stone with its composition of hydrate phases variety (Table 2) shows that it increases in proportion to the main XRD reflection of Al-tobermorite ($11.5 \times 10^{-10} \text{m}$), to increase in weight loss both at the temperature range 180 °C (tobermorite) and at 730 °C (gel C-A-S-H) that indicates the correct classifying of that effects to hydrated phases. This pattern holds true for both addition-free and Na_2SO_4 -activator systems.

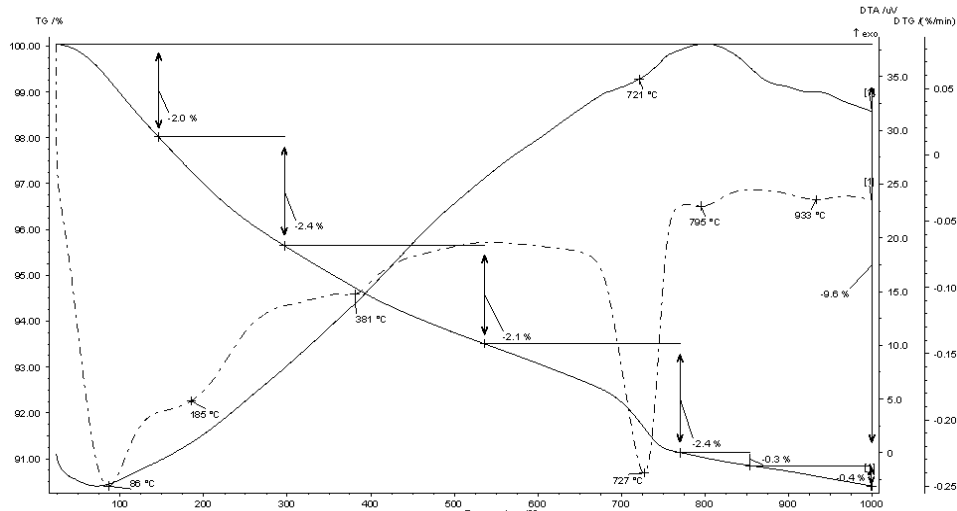


Figure 4. Thermogram of hydration products samples basing on Novosibirsk CHP-5 ash with 20 % of lime at 100 hours of isothermal exposure

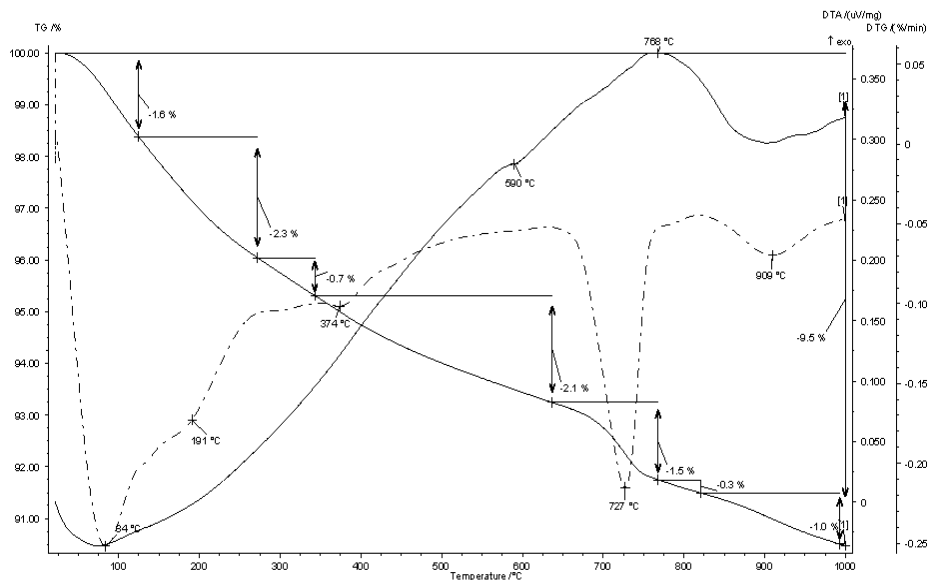


Figure 5. Thermogram of hydration products samples basing on Novosibirsk CHP-5 ash with 20 % of lime at 8 hours of isothermal exposure with additional injection of 2% Na₂SO₄.

Table 2 Strength and quantitative characteristics of phase contents in stone

Mass composition	Isotherm of autoclaving, h	Stone strength, MPa	Peak intensity 11.5×10^{-10} tobermorite (XRD) length, mm	Weight loss DTG at 165-190, °C, % tobermorite	Weight loss DTG at 373-381, °C, % hydrogarnet katoite	Weight loss DTG at 439-447, °C, % CA(OH) ₂	Weight loss DTG at 725-735 °C, % gel C-A-S-H
Base composition	8	20	48	1.5	0.8	1.1	1.7
Base composition	100	46	77	2.4	1.0	--	2.4
Base composition + 1% Na ₂ SO ₄	8	26	96	2.3	0.8	0.4	2.0
Base composition + 1% Na ₂ SO ₄	100	41	107	2.7	1.0	--	2.6
Base composition + 2% Na ₂ SO ₄	8	31	60	2.3	0.9	--	1.5
Base composition + 2% Na ₂ SO ₄	100	34	112	2.9	1.0	--	1.5

Note: base composition – 20% of lime + 80% of coal ash

Quantitative phase composition of autoclave stone, after its recalculation on corresponding compounds, is shown in Figure 6.

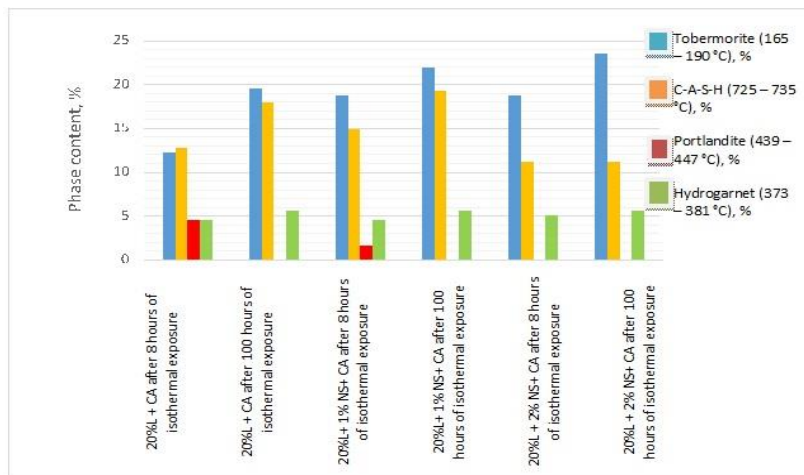


Figure 6. Quantitative phase composition of autoclave stone made of lime and ash.
 Notice: L – lime, NS – Na₂SO₄, CA – coal ash

The interrelation between strength and phase composition of the stone of the studied compositions is shown in Figures 7–9 from which is obvious that the strength of Na₂SO₄-free compositions is directly proportional to the content of both the Al-tobermorite and gel phase of C-A-S-H (Figure 7). This interrelation becomes less pronounced, but still maintained at 1% of sodium sulfate (Figure 8). However, with addition of 2% Na₂SO₄ (Figure 9), this relationship is not observed anymore. At this, a considerable increase in Al-tobermorite in this composition according to both the data of XRD and DTG does not correspond completely to a slight increase in stone’s strength. However, a small amount of C-A-S-H phase here fully agrees with the same slight increase in strength.

Thus, the strength of the autoclave stone made of lime-ash mixtures always proportional to the content of gel C-A-S-H phase. At the same time, the content of the latter can be or can be absolutely not proportional to the amount of Al-tobermorite. It is typical that initiating the synthesis of Al-tobermorite with the Na₂SO₄-addition, its crystallization is carried out at the expense of C-A-S-H phase. The content of katoite hydrogarnet remains practically unchanged at the 5–6% level.

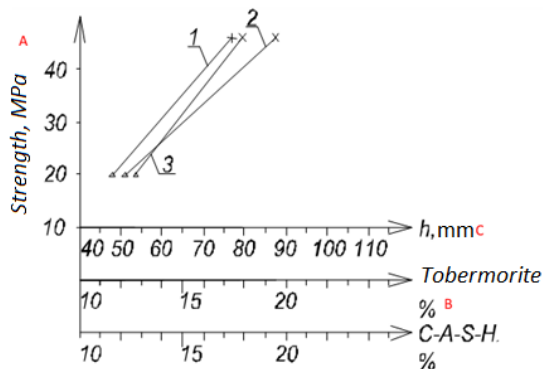


Figure 7. Correlation of lime-ash stone strength with its phase composition.
 1 – Change in the intensity of the peak of aluminum substituted tobermorite according to the X-ray data; 2 – Change in content of aluminum substituted tobermorite according to the DTG data; 3 – Change in content of C-A-S-H according to the DTG data.

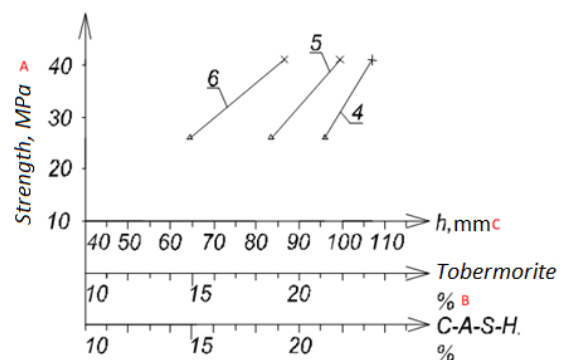


Figure 8. Correlation of lime-ash stone strength with its phase composition at addition of 1% Na₂SO₄. 4 – Change in the intensity of the peak of aluminum substituted tobermorite according to the X-ray data; 5 – change in content of aluminum substituted tobermorite according to the DTG data; 6 – change in content of C-A-S-H according to the DTG data. Note: Δ – 8 hours of isothermal exposure; x – 100 hours of isothermal exposure

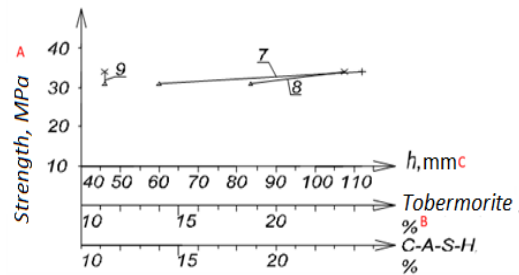


Figure 9. Correlation of lime-ash stone strength with its phase composition at addition of 2% Na_2SO_4 . 7 – Change in the intensity of the peak of aluminum substituted tobermorite according to the X-ray data; 8 – change in content of aluminum substituted tobermorite according to the DTG data; 9 – change in content of C-A-S-H according to the DTG data

The results obtained conforms with the most recent publications [5–7] reporting the formation of the phase composition in the autoclave stone basing on lime-quartz and cement-aluminosilicate compositions with additions of alumina or sulphate-containing materials.

Thus, the results obtained on the strength of the stone (Figure 1) are well explained by the findings of its phase composition. When there is no addition of sodium sulfate, the strength is proportional to the content of Al-tobermorite and gel C-A-S-H content. By adding of sodium sulfate, the rate crystallization of Al-tobermorite is increased and it replaces C-A-S-H phase. The more complete this substitution occurs, the less the strength of the stone. This can be explained by the high specific surface area of the particles of the solid phase of the C-A-S-H gel, which "glue" the composite. It is known that the specific surface area phase C-S-H is 250–300 m^2/g .

However, the same rock strength is proportional to its density. Therefore, the larger the hydration products, the higher the density of the stone and greater its strength. For this reason, the strength of the stone through autoclaving 8 hours with admixture of sodium sulfate higher than without additives. Total weight loss of the composition without additives, after 8 hours of autoclaving was 8.7 % (Figure 3), and with the addition of sodium sulfate – 9.5% (Figure 5).

4. Conclusions

1. The strength of autoclaved stone based on lime and aluminosilicate ash of CHP increases in proportion to the duration of hydrothermal treatment. The amount of Al-tobomorite and the gel phase of C-A-S-H in the stone also increases in proportion. The hydrogarnet katoite plays a subordinate role and its quantity in the stone remains constant – 4–6 %.

2. Activation of hydrothermal synthesis in stone with the addition of Na_2SO_4 substantially redistributes the phase composition. The gel phase of C-A-S-H is significantly reduced by the crystallization of Al- tobermorite. The content of katoite remains constant. At the same time, it should be taken into account that when the hydration process is carried out, the C-A-S-H phase in tobermorite is activated, injected with alkaline sulphates, the total amount of hydrates is increased, which leads to the compaction of the stone increase its strength.

3. The strength of autoclave stone basing on aluminosilicate fly ash and lime is always proportional to the content of the C-A-S-H phase irrespectively to the content of tobermorite.

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