THE ROLE OF GYPSUM IN PORTLANDITE STONE STRUCTURE FORMATION

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Abstract. The hydration of calcium oxide has been examined in the presence of SO_4^{2-}. The conditions, under which portlandite stone with the best physico-mechanical properties was formed, have been determined. The hardening conditions affect the phase composition and microstructure of portlandite stone with a bihydrated gypsum. The mechanism of CaO hardening has been determined in the presence of SO_4^{2-} ions.

Keywords: quicklime, portlandite, hydration hardening, activated gypsum.

1. Introduction

During non-autoclaved insulating aerated concrete production the structure of cement stone is formed at high water/cement ratio (0.5–0.9). Such crystal phases as etringite and portlandite have a significant influence on the concrete strength, especially at the early stages of hardening.

Portlandite is an important component of cement stone. The role of portlandite during C_3S hardening is described in [1, 2]. The authors assumed that $Ca(OH)_2$ layers are incorporated between the packs of tobermorite phases and thus the solid solution is formed. M. Sanytskyi and L. Shpynova [3, 4] present calcium hydroxide as a matrix to form calcium hydrosilicates of various basicity. The structure of hydrated compounds is formed due to isomorphic substitution and introduction of $(OH)_4^{4-}$ groups onto $[SiO_4]^{4-}$ tetrahedron.

Portlandite is a positive factor to form crystal framework of cement stone. During the first period of C_3S interaction the C_3SH_x primary hydrate is formed, which is $Ca(OH)_2$ according to [5]. $[SiO_4]^{4-}$ groups are placed in its

tetrahedral pores. The portlandite crystals growth on the cement surface, as well as in the pores provides the formation of cement stone primary structure. Then $[SiO_4]^{4-}$ tetrahedra condensation in the solid phase, $Ca(OH)_2$ leaching and its crystallization in the pores as portlandite occur.

The important elements of alite stone crystal structure are hexagonal lamellar crystals of portlandite influencing construction and technical properties of cement. Portlandite content in cement stone at the age of 360 days is 18–20 % (to calculate for CaO). At leaching (for example, during filtration of water through concrete) the $Ca(OH)_2$ content decreases and stone strength becomes low. Thus, the decrease in $Ca(OH)_2$ amount by 15–30 % (relative to the total content) decreases the strength by 40–50 % [6].

Gypsum is also an important component of Portlandcement. It is well-known that gypsum affects setting [7]. Since cement without gypsum has a short setting time and bad physico-mechanical properties, it cannot be used for construction works. The lack of gypsum results in small amount of formed etringite and hence, low mechanical strength. At the same time, the excess of gypsum leads to the expansion and destroys the structure because the secondary etringite is formed [8].

In the presence of gypsum in a liquid state the colloidal particles of $Ca(OH)_2$ transform into crystal portlandite in the form of hexagonal laminae. The gypsum concentration of 0.2 mol per 100 mol of water at 298 K is the most optimum condition of the process [9]. The greatest amount of portlandite is formed in the cement stone with gypsum optimal content and the best physico-mechanical characteristics. The optimum content of gypsum is when it is possible to obtain $C_3A \cdot CaSo_4 \cdot 12H_2O$.

There is a directly proportional dependence between gypsum content, portlandite amount and stone physico-chemical properties. At gypsum optimum content the greatest amount of portlandite is observed and the

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cement stone is of maximum strength [10]. The increase in gypsum content decreases a number of micropores of 50–200 µm size. The reason is the formation of the enhanced amount of etringite and portlandite crystallization as large hexagonal laminae.

So, the aim of the present work is to establish the role of gypsum while forming portlandite stone structure at high water content and high concentration of Ca^{2+} ions in the liquid phase, that is usual for the production of non-autoclaved aerated concrete.

2. Experimental

To obtain the compositions we used quicklime and gypsum plaster. The quicklime properties are given in Table 1. Activated gypsum in a suspension form was obtained *via* rapid mixing of gypsum plaster at water/gypsum ratio of 2.0 for 30 min. As a result of hydration the colloid system of bihydrated gypsum was formed.

The chemical composition of lime, Portlandcement and binding compositions were determined using the chemical analysis and X-ray spectroscopy (ARL 9800 XP spectrometer).

The phase state of hydration products was determined using XRD analysis. The samples were analyzed by DRON-3.0 diffractometer using CuK_α radiation of BSV-1 tube. DTA analysis was used for investigations of the starting and resulting compounds in the systems: CaO–chemical additive and CaO–Portlandcement–activated gypsum. Derivatogramms were recorded using Paulik-Paulik-Erdey derivatograph Q-1500 D.

The morphology and habitus of resulting products were studied using the electron microscopy (JEM-100CX II microscope). Petrographic analysis (MIN-8 microscope) was used to determine the crystal form, pleochroism, cleavage and refractive index.

The physico-mechanical properties of the composites were determined using cubic samples of 2×2×2 cm. The effect of additives on the lime paste yield was determined in liters per 1 kg of quicklime during wet liming of 200 g of grinded quicklime.

The size of hydrated lime particles was determined by measuring the rate of lime sedimentation and lime continuous weighing.

3. Results and Discussion

The important factor affecting the physico-mechanical properties of the cement stone is the presence of electrolyte, namely SO_4^{2-} ions, in the pores. We studied the interference of gypsum plaster and quicklime on their hydration. Fig. 1 shows the effect of lime content on the setting time of gypsum plaster. The increase in quicklime content till 30.0 wt % considerably influences the structure formation. Further increase in CaO content sharply reduces a setting time. While using hydrated lime the beginning of gypsum setting is delayed.

The introduction of quicklime to the composition (Table 2) increases the stone strength. Moreover, the maximum strength is observed at CaO content of 30.0 wt % that coincides with a maximum value of setting beginning. While using hydrated lime we observe the linear dependence of strength decrease with the increase in lime content in the composition. Thus, the increase in early strength of the composition based on quicklime is provided by CaO hydration hardening. The joint use of quicklime and gypsum provides the increase in strength and coefficient of stone softening till 0.73–0.80.

Table 1

Construction and technical properties of quicklime

Index	Lime	
	Low-active lime	Medium-active lime
CaO total content, wt %	91.1	95.6
MgO content, wt %	1.7	0.9
Insoluble additives, wt %	5.1	0.9
CO_2 content, wt %	0.9	1.7
H_2O content, wt %	1.2	0.9
Total, wt %	100.0	100.0
Free CaO_{theor}, wt %	86.4	90.8
$CaCO_3$ content, wt %	2.0	3.8
$Ca(OH)_2$ content, wt %	4.8	3.6
Time for achieving hydration degree of 80 % (EN 459), min	5.0	3.0

Physico-mechanical properties of lime-gypsum stone

| Binder composition, wt %			Water/Solid	Compression strength, MPa after days			Softening coefficient
Quicklime	Hydrated lime	Gypsum G-5		1	7	28	
–	–	100	0.65	5.10	5.82	6.21	0.45
5	–	95	0.62	5.56	6.75	7.01	0.56
10	–	90	0.53	6.84	7.98	8.02	0.65
20	–	80	0.50	7.35	8.87	9.22	0.73
30	–	70	0.51	8.56	9.21	10.28	0.80
40	–	60	0.62	8.98	7.45	6.43	0.65
–	5	95	0.60	4.56	5.01	5.23	0.56
–	10	90	0.59	4.21	4.55	4.60	0.60
–	20	80	0.66	4.02	4.20	4.55	0.62
–	30	70	0.70	3.78	3.80	3.85	0.55
–	40	60	0.73	3.20	3.54	3.56	0.51
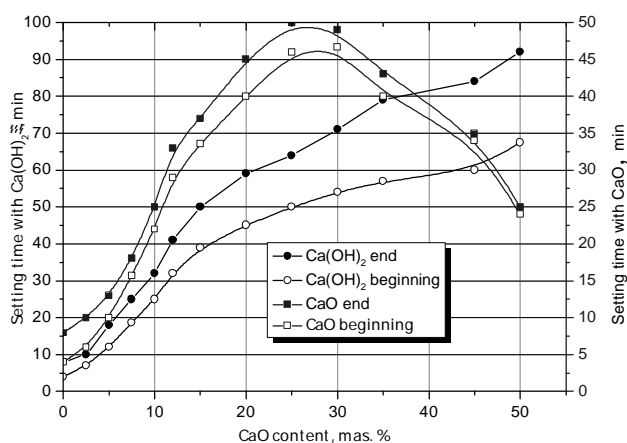
Fig. 1. CaO content *vs*. setting time of gypsum

The effect of CaO hydration hardening on physico-mechanical properties of lime-gypsum stone is confirmed by the experiments under different hardening conditions. So, at the hardening under air-dry conditions (relative humidity is 70 %) the maximum stone strength is achieved at quicklime content of 25.0 wt %. At samples storage over water the optimum lime content is 35.0 wt %. Stone strength in water is 12.8 MPa after 7 days (quicklime content is 42.0 wt %). Thus, in the presence of gypsum the conditions for CaO hydration hardening are formed providing the increase in stone strength by 2.5 times compared with the strength of gypsum without additives. Such conditions are possible only in the presence of a great amount of liquid phase provided by the samples hardening in water.

We determined by the experiments that bihydrated gypsum changes the liming parameters. At gypsum content of 50 wt % the time for achieving maximum liming temperature increases from 2 to 35 min and the maximum temperature decreases from 378 to 338 K. The gypsum effect is connected with the physico-chemical processes occurred on CaO surface. In the presence of sulfate-ions the bad-soluble sulfate layer is formed followed by the change of ξ-potential value, the decrease of water access rate and retardation of hydration reaction.

The phase composition of the hydration products was determined using different methods of physico-chemical analysis. Thermal analysis data (Fig. 2a) show that after 1 day of hardening there are endoeffects at 428 and 445 K, corresponding to water separation from $CaSO_4 \cdot 2H_2O$, and at 762 K – corresponding to portlandite decomposition. Endoeffect at 1065 K is caused by calcite decomposition, one part of which is formed at stone carbonization and the other part is a component of quicklime. After 180 days of hydration we observe the shift of portlandite decomposition temperature to 765 K (Fig. 2b) due to the perfect structure and growth of $Ca(OH)_2$ crystals during hydration hardening. Constant weight losses at 763–768 K reveal the absence of lime-gypsum stone carbonization.

Using SEM method we additionally obtained data concerning the structure of lime-gypsum stone under normal conditions of hardening. At the early stages of hardening (Figs. 3a and 3b) we observe a great number of $CaSO_4 \cdot 2H_2O$ needle-shaped crystals covered by the formed portlandite. There is a small amount of unreacted CaO grains which touch each other (Fig. 3c). The stone pores are filled with larger crystals of gypsum, between which porltandite hexagonal plates of 3–5 μm size are located (Fig. 3d).

During long-term hardening (180 days) in the presence of liquid phase the bihydrated gypsum is recrystallized and parallel oriented aggregates are formed (Fig. 4a), which are combined into fern-shaped configurations (Fig. 4b). This provides the increase of mechanical strength.
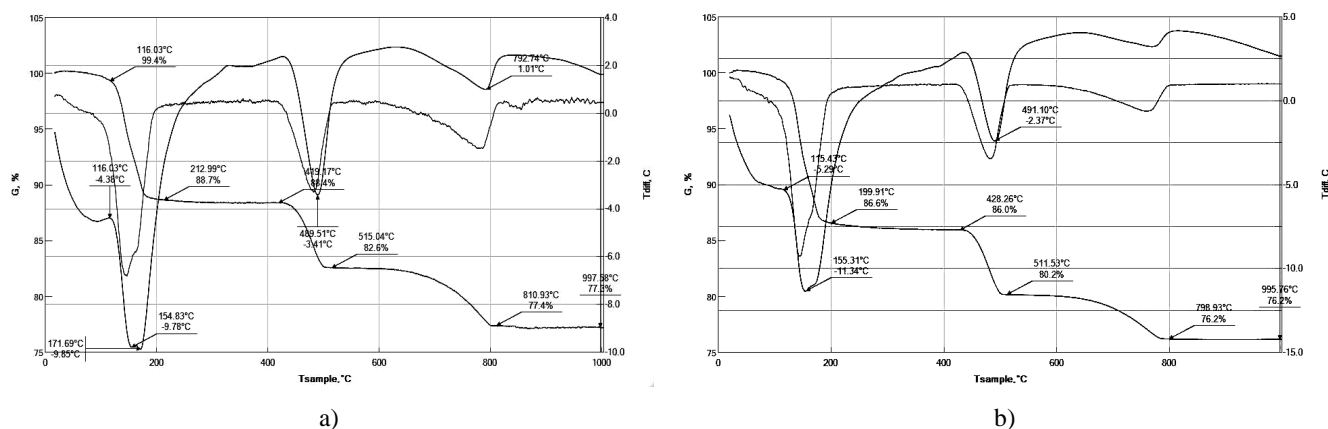
a)

b)

Fig. 2. Derivatogramms of lime-gypsum stone after 1 (a) and 180 (b) days of hydration
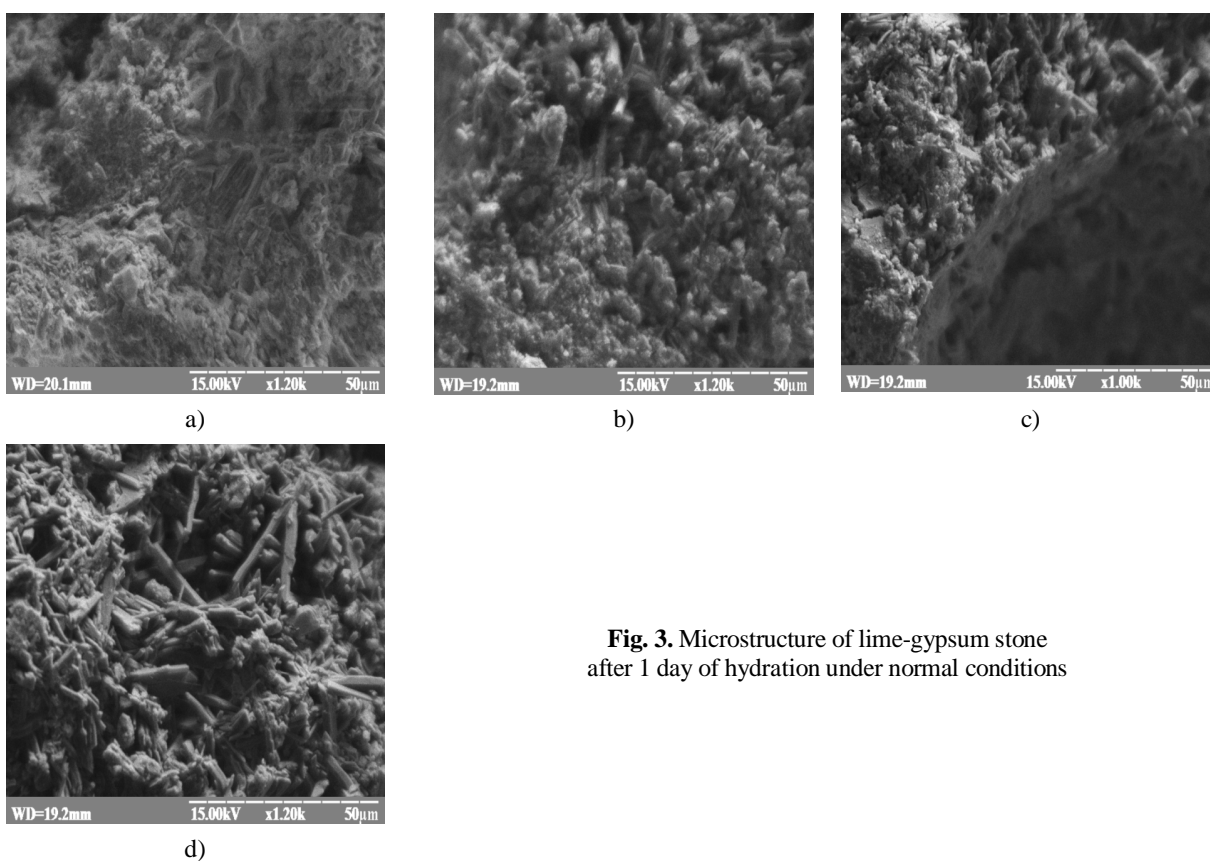

a)

b)

c)

d)

Fig. 3. Microstructure of lime-gypsum stone
after 1 day of hydration under normal conditions

The increase of reflexes intensity (001) was determined by XRD analysis in the solution with SO_4^{2-} anions. The change of diffraction maxima intensity is explained by the effect of SO_4^{2-} anions on habitus formation and morphology of $Ca(OH)_2$ crystal phase.

According to the data of electron microprobe analysis (Fig. 4d) the CaO concentration on the surface of $CaSO_4 \cdot 2H_2O$ crystals is 44.2 %. According to stoichiometry this value is equal to 35.1 % indicating portlandite localization on the surface of gypsum as a thin layer composed of hexagonal crystals.

To determine the character of SO_4^{2-} anions effect we analyzed portlandite obtained *via* hydration in distilled water and 1% H_2SO_4 by means of IR-spectroscopy (Figs. 5 and 6).

There are great differences within the range of OH-groups stretching vibration (3000–3800 cm^{-1}). Neat portlandite (Fig. 5) is characterized by clear band typical of O–H bond at 3607 cm^{-1} and wide band at 3538–2950 cm^{-1}. The presence of SO_4^{2-} groups changes the spectrum view. For the main band the frequency value shifts toward the area of short waves (from 3 607 to
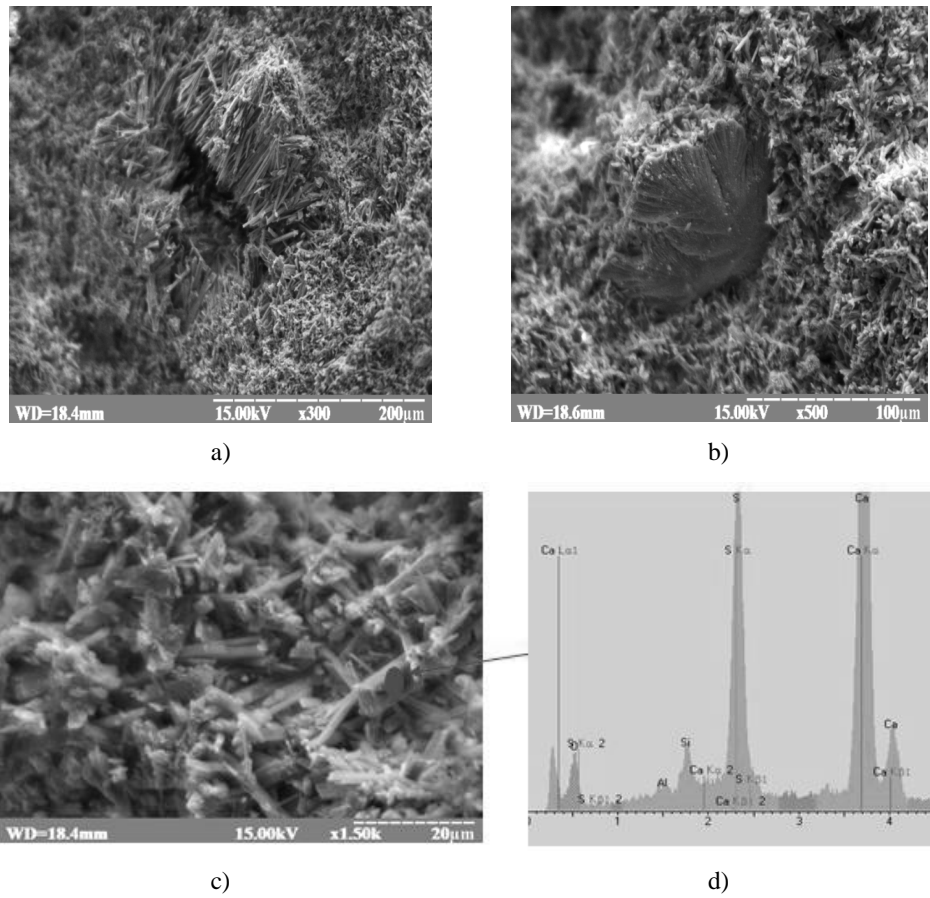
a)

b)

c)

d)

Fig. 4. Microstructure (a-c) and EMPA analysis (d) of lime-gypsum stone after 180 days of hydration

a)

b)

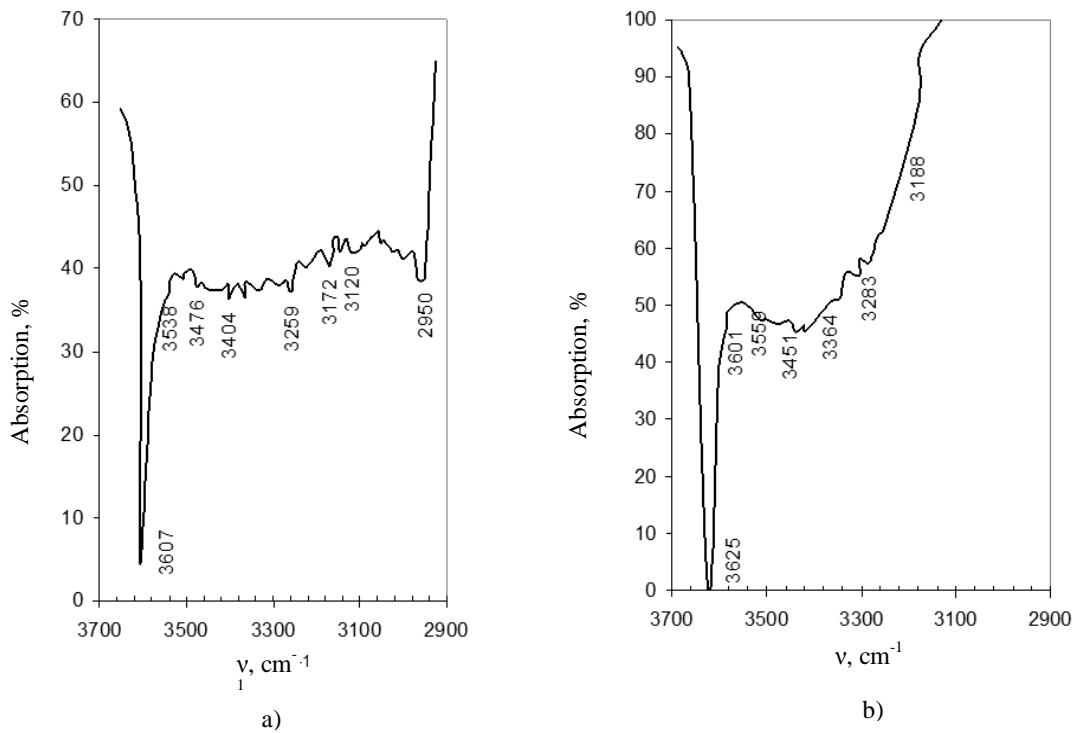**Fig. 5.** IR-spectra of OH group in CaO: without additives after 1 day of hydration (a) and with 1 mol % H_2SO_4 (b)
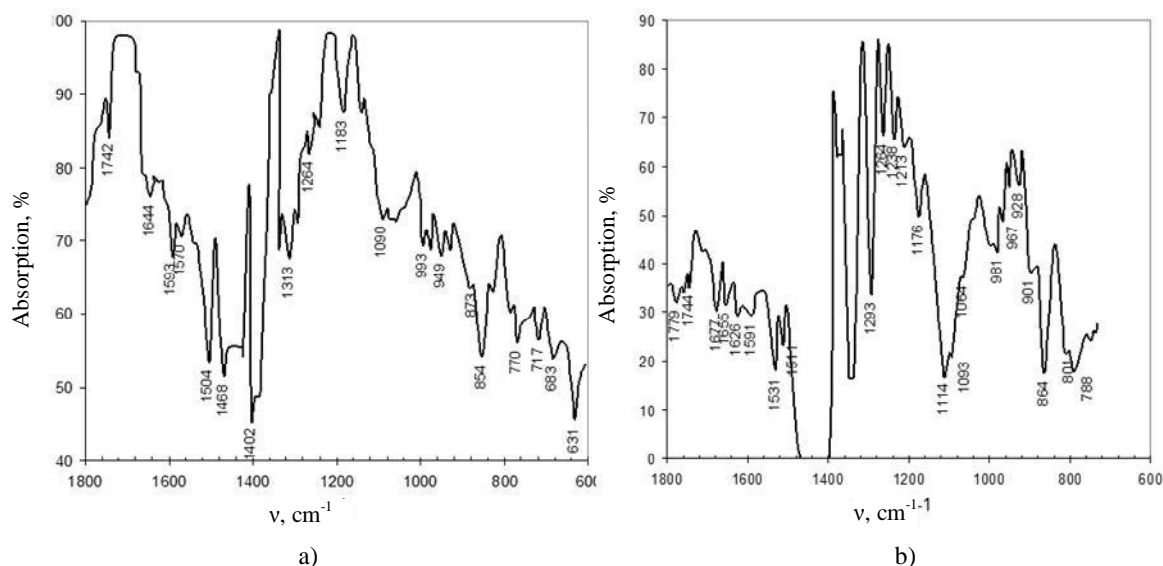
a)   b)

Fig. 6. IR-spectra of CaO without additives after 1 day of hydration (a) and with 1 mol % H_2SO_4 (b)

3625 cm^{-1}); the wide band becomes more narrow and smooth. The structure of crystal, nature of anion and force of formed H-bonds influence the stretching vibrations. The increase in vibrations frequency for the samples with sulfate acid indicates the formation of strong hydrogen bonds of $H_2O\ldots SO_4^{2-}$ type.

Stretching and deformation vibrations of CO_3^{2-} anion are observed at 1468, 1090, 854 and 717 cm^{-1} (Fig. 6). There is a wide band within 1064–1114 cm^{-1} typical of SO_4-group stretching vibrations.

Thus, in lime-gypsum binding agents with the increased amount of CaO the stone strength and water resistance increase due to the lime hydration hardening and formation of portlandite perfect crystals.

4. Conclusions

We vindicated the possibility of strong portlandite stone obtaining *via* regulation of hydration hardening in the compositions consisting of quick lime and bihydrated gypsum. The gypsum optimum content depends on hardening conditions. Thus, under dry air conditions the maximum strength of 13.0 MPa is achieved while using 25 wt % CaO, that is 2.5 time higher than the strength of gypsum without additives.

SEM analysis confirms the change of portlandite crystals form and size in the presence of gypsum. At the beginning of hardening the great amount of $Ca(OH)_2$ is a sponge mass located between needle-shape crystals of $CaSO_4 \cdot 2H_2O$. After 90 days portlanide crystals transform into hexagonal plates (3–5 μm) which fill the space between bihydrated gypsum crystals.

Different conditions of portlandite crystallization change the crystals morphology and affect physico-mechanical characteristics of portlandite stone.

The developed methods of CaO hydration harde-ning may be used in binding compositions based on Port-landcement to produce non-autoclaved insulating aerated concrete which is hardened under high water content.

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ПРО РОЛЬ ГІПСУ У ФОРМУВАННІ СТРУКТУРИ ПОРТЛАНДИТОВОГО КАМЕНЮ

Анотація. Досліджено процеси гідратації кальцію окси-ду у присутності йонів SO_4^{2-} та встановлено умови, за яких ут-ворюється портландитовий камінь з максимальними фізико-механічними показниками. Отримані дані із впливу умов тверд-нення на фазовий склад та мікроструктуру портландитового каменю з додатками гіпсу двогідрату. Встановлений механізм гідратаційного твердення CaO у присутності йонів SO_4^{2-}.

Ключові слова: негашене вапно, портландит, гідра-таційне твердення, активований гіпс.