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Effect of Previously Slacked Lime on Properties of Autoclave Composite Binders

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Abstract: It is found highly exothermic reactions occur at temperatures up to 190°C when slacking of highly active lime with water-solid ratio close to the theoretical value. At this moment lime slacking with water as well as with vapor is observed. Heat from slaking can affect the dehydration of gypsum dihydrate to prepare highly soluble [beta]- modification of hemihydrate gypsum and the maximum amount of fine particles. Ultra dispersed slaking products intensively react in autoclave composite binder systems with improving of strength properties. X-ray diffraction (XRD) and differential thermal analysis (DTA) increasing of the number of products of hydrothermal synthesis of crystalline 11Å-tobermorite, hydrated calcium sulfosilicate $Ca_3Si(SO_4)_2(OH)_6 \bullet 9H_2O$ and amorphous C-S-H structures. Additional crystalline formations completely cover the quartz particles by fibrous-diverse coat and amorphous growths provide extra compaction of crystalline composite block with the structure reinforcing.

Key words: lime slacking · Hydrated calcium sulfosilicate · Autoclave · Ultra dispersed particles · Tobermorite and gypsum.

INTRODUCTION

When production of autoclave silicate materials with compact and cellular structure fine dispersed lime -siliceous composition of different composition are used as the binder. The quality of the applied binder used and the conditions of component interaction at all stages of the production process depend on the performance properties of the final product. In most cases, the rate and completeness of lime slaking are significantly affects the chemical interaction of the components during hardening process. Numerous of studies [1-5] are devoted to increasing of reactivity of the lime and study of its interaction with the crystal in the autoclave conditions. It is known that the products obtained with lime slaking differ in dispersity and reactivity depending on condition of lime slaking [6-9]. These properties are especially important when interaction of sand-lime binder in an autoclave with the decreasing solubility of $Ca(OH)_2$ at higher temperatures. Dispersity of initial components significantly impacts on the rate of hydration and the binder hardening, as well as the synthesis and rate of crystallization of high-strength hydrated calcium silicate (HCS) in the system $CaO-SiO_2-H_2O$ in autoclave conditions [10-13]. Changing of synthesis conditions affects the phase composition of obtained HCS by, that determines the physical and mechanical properties of the final product, allows controlling technological processes and reducing energy consumption when production of autoclave construction products [14-16].

Technique: Changing of the binder dispersity was investigated using the sedimentation analysis [17].

Lime was previously slacked in the Dewar flask. The required quantity of water for slacking was varied from the theoretical value 0,32 to 0,80. The samples of mixed binder were wetted till plastic consistency and autoclaved at 183 °C in following regime: the rise buildup of steam pressure up to 10 bar for 2 h, exposure at working pressure for 6 h, step-down of steam pressure for 2 hours.

X-ray diffraction analysis of the samples was carried out at a DRON-4 with using of Cu- anode radiation (Ni- filter to attenuate [beta]- radiation components). Scanning interval was 0,05°, the measurement of the intensity in the scanning points was 1s.

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The microstructure of the samples was studied with a high-resolution scanning electron microscope (SEM) "Hitachi S- 800".

Differential thermal analysis was carried out on derivatograph 3431 Q- 1500 with following shooting: the rate of rise was 15°C / min, the sensitivity of the balance was 100 mg, the sensitivity of the DTA - 0,25 mV, the sensitivity of DTG - 0,5 mV.

The compressive strength test of samples of autoclaved composite binder was accomplished according to GOST 8462-85 [18].

MATERIAS AND MATERIALS

Chemical composition of quartz sand is characterized is following (by wt. %): SiO_2 - 92,4, Al_2O_3 - 2,36, Fe_2O_3 - 0,77, CaO - 1.88, MgO - 0,2, SO_3 - 0,05, LOI - 1,95. The content of clay, silt and dust particles is 6,5 %. The average grain size of sand composition by module size is 0,65. The sand was ground up to a specific surface of 250-300 m^2/kg. Content of CaO + MgO in the lime is at least 70 %, MgO content isno more than 5 %. Lime activity is 92.2 %. Lime was milled up to specific surface of 400 m^2/kg at least. Gypsum dihydrate is characterized by the following composition by weight. %: $CaSO_4 \bullet 2H_2O$ - 92,91; SO_3 - 43,21; LOI - 19,44. Portland cement CEM I 42,5 N of PJSC " Belgorod cement " (Russia).

The Study of Lime Slaking Dynamics and Properties of the Lime Slaking Products: According to classical hydration reaction: $CaO + H_2O = Ca(OH)_2 + 65$ kJ / mol the theoretical water requirement for lime slacking is 0,32. Studies were performed with different water-solid ratio (W/S): 0,32; 0,48; 0,64; 0,80. When the lime slaking with classical water amount (0,32) the highest slaking temperature (up to 196 °C) is observed. When increasing of water amounts the slaking temperature is reduced (Table 1). Change of water amount for lime slacking also influent on rate and dispersity of slacking products.

High temperature obtained when the slaking can be used for initiation of dihydrate gypsum decomposition to formation of β[beta]-modification of hemihydrate gypsum by following reaction:

$$CaSO_4 \bullet 2H_2O \; CaSO_4 \bullet 0{,}5 \; 1{,}5 \; H_2O + H_2O$$

Highly exothermic reactions are take place at temperature up to 190 ° C when slaking of highly active lime with water-solid ratio close to the theoretical value (0,32) and with presence of mineral additive and the presence of a mineral additive. At this moment, besides water slacking, the steam slacking also is also accomplished, providing formation of maximum of dispersed particles. Changing of water requirement for the slaking and the SO_4^{2-} -ions concentration into disperse medium effect rate and temperature of the slacking, as well as dispersity of slacking products.

Optimal production conditions for high reactive lime slacking at are followings: W/S=0,48 with introduction of 0,25 % of gypsum dihydrate and at 163 ° C, 80,8% of ultra dispersed particles (up to 30 μm) (Table 1).

It should be noted that the slacking products contain a lot of fine dispersed particles to 10 micrometers, including ultra dispersed particles, which not aggregate as they are in saturated lime mixture that leads to saving their dimensions and reactivity. During the slaking process at W/S=0,64 and 0,80 fine particles of $Ca(OH)_2$ recrystallized into larger ones, that is reflected in the binder dispersity. The presence of gypsum dihydrate as additives and its transition to a semi-aquatic modification also effects changes in and temperature of the slaking. Hemihydrate gypsum in highly exothermic conditions of the slacking has a higher dispersity than with calcium hydroxide, resulting in a changing in pH value of the solution concentration and rate reduction of $Ca(OH)_2$-crystals growth.

Effect of Products Slaking on the Strength Characteristics of the Composite Binder: Activity of the highly active lime slacking products with gypsum as additive was studied for compositions of autoclave binders at followings conditions: high degree of exothermic process, high dispersity W/S=0,48 (Table 1). The ratio of components in the binder was chosen for compact and cellular products. Strength test for Autoclave binder was carried out for samples of 20 × 20 × 20 mm. Maximum strength of free-additive binder reached at W/S = 0,8 is 38,0 MPa. Adding of the slaking products with gypsum additive into composite binder affects the mechanism of structure formation, acting to strength enhancement. The optimum concentration of gypsum dihydrate additive is 0.15 wt. % for all compositions of binder. Further increasing of the additive concentration causes a decrease in strength values.

Activated lime has significant influence on binder compositions for cellular concrete containing cement. Presence of gypsum additive in cement provides greatest strength value of 50 MPa when introduction of the lime slacking products and 0,15 % of dihydrate gypsum additive (composition 11, Table 1).

Table 1: Changing the properties of the products slaking

No	Content of gypsum dihydrate, %	Maximum temperature of lime slacking, °C	Period of reaching of maximum slacking temperature, min	Particle distribution, wt. %		
				Less 10 µm	Less 30	More 30 µm
W/S = 0,32 (classical water requirement)						
1	-	196	5	26,5	70,2	29,8
2	0,05	190	4,5	33,2	77,5	26,5
3	0,15	191	4,5	35,4	78,7	26,7
4	0,25	191	4,5	33,2	79,5	20,5
5	0,75	196	4,5	32,6	76,0	24,0
W/S = 0,48 (classical water requirement, improving in 1,5 times)						
6	-	164	4,5	30,7	74,3	25,7
7	0,05	170	4,5	41,9	78,4	21,6
8	0,15	163	4,5	40,5	79,9	21,1
9	0,25	163	4,5	38,3	80,8	19,2
10	0,75	182	4,5	37,7	76,9	23,1
W/S = 0,64 (classical water requirement, improving in 2 times)						
11	-	160	3,2	29,3	72,2	27,8
12	0,05	168	3,5	35,9	78,3	21,7
13	0,15	158	3,5	37,8	77,9	22,1
14	0,25	158	3,5	36,5	78,5	21,5
15	0,75	159	3,5	29,4	74,8	25,2
W/S = 0,80 (classical water requirement, improving in 2,5 times)						
17	0,05	148	4,5	27,5	59,4	40,6
18	0,15	146	4	26,8	59,7	40,3
19	0,25	138	4	24,6	57,6	42,4
20	0,75	138	4	29,4	55,7	44,3

Table 2: Strength of the mixed binder samples

The binder composition			Number of composition	Gypsum dihydrate additive, wt. % of lime	Yield compressive strength, MPa
Lime	Quartz Sand	Cement			
1	1	-	1	0	38,0
			2	0,05	47,0
			3	0,15	44,6
			4	0,25	43,8
1	3,2	-	5	0	29,0
			6	0,05	39.0
			7	0,15	36,0
			8	0,25	35,0
1	3,2	0,8	9	0	27,0
			10	0,05	42,0
			11	0,15	50,0
			12	0,25	38,0

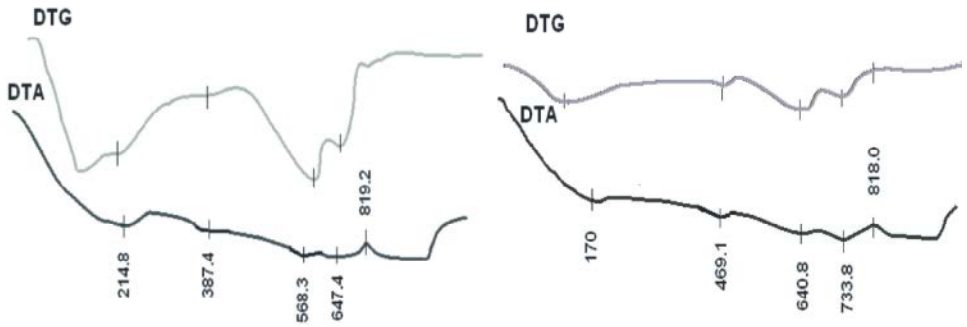

Fig. 1: Thermograms for composite binder: a - composition # 9 (Table 2); b - composition # 11 (Table 2).

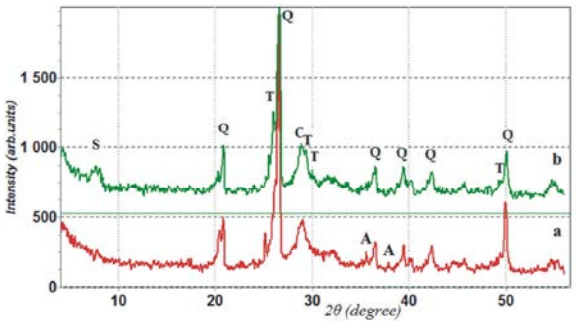

Fig. 2: X-ray diagram of autoclave composite binder: a - composition # 9 (Table 2); b - composition # 11 (Table 2). Q - Quartz; C - $CaCO_3$; T - 11Å-tobermorite; S - $Ca_3Si(SO_4)_2(OH)_6 \cdot 9H_2O$, A - α C_2SH.

Study of the Phase Composition of Autoclaved Composite Binder: The phase analysis was carried out on samples with a maximum strength values in comparison with non additive composition (compositions # 9, 11, Table 2).

On the DTA curves endothermic effects at 170-214 °C is attributed to of low-basic calcium hydrosilicates, where batch dehydration is observed in the temperature ranges of 570-650 °C and 725-750 °C with a further crystallization at 818-819 °C (Fig. 1).

The gypsum hemihydrate resulting when lime slacking, has a high solubility in comparison to dihydrate (solubility of 8 and 2 g/l respectively equivalent to $CaSO_4$), promoting to increasing of ionic strength of the solution and increasing the concentration of SO_4^{2-}-ions in the liquid phase. In combination with high dispersed particles of $Ca(OH)_2$ they have a positive effect on the solubility and the interaction of the initial components, activating the hydration process of all components of the mineral composite binder. As a result, supersaturations appearing in the liquid phase with respect to the hydrated phases accelerate the crystallization of HSCs at the earlier stages of hardening with the increase of their crystallization degree at autoclave treatment. It is confirmed by the slight mass loss in range of 120-215 °C and 550-650 °C (Fig. 1 b).

In Figure 2b the results of XRD analysis for autoclaved binder reflect increasing of quartz solubility due to the decreasing of diffraction reflexes of SiO_2, that proves its interaction with $Ca(OH)_2$ in the HSC. Previously lime slacking with the gypsum additive allows the most effective usage the lime hydration properties including reducing the solubility at higher autoclaving temperatures. The fine dispersed $Ca(OH)_2$ particles obtained are reactive to SiO_2in hydrothermal processes

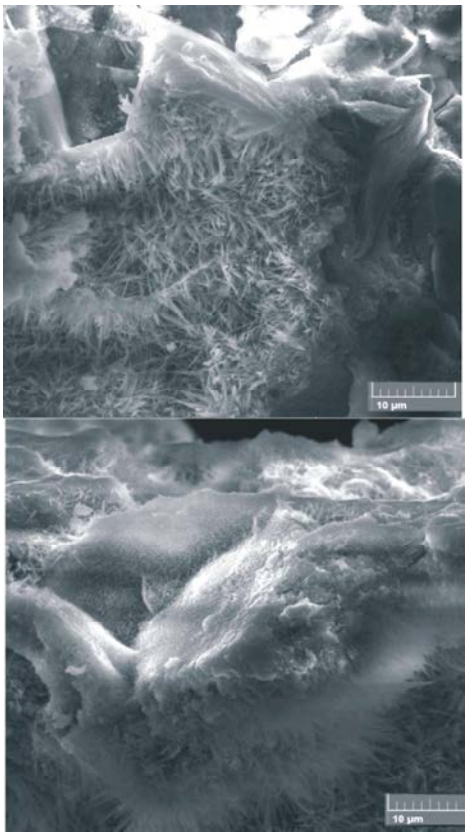

Fig. 3: Microstructure of the autoclave composite binder: a - composition # 9 (Table 2); b - composition # 11 (Table 2).

and as a result, the number of crystalline low-basic calcium silicate phases - 11Å- tobermorite is increased. The diffraction reflections of this one are fixed at the XRD (Fig. 2 b). Expansion of background in the reflection angle range of 30-35° indicates the formation of the amorphous structure of the gel C-S-H (I).

A positive aspect is the reduction of the number of highly basic orthosilicate phase of α C_2SH, which by XRF data is dominated in the binder without the gypsum admixture (Fig. 2 a) and confirmed by the endothermic effect at a temperature of 387 °C according to the DTA data (Fig. 1 a).

According to the results of XRD data in Figure 2 b in the samples with gypsum additives when the lime slacking a new formations of hydrated calcium sulfosilicate $Ca_3Si(SO_4)_2(OH)_6 \bullet 9H_2O$, are appeared, that is confirmed by endothermic effect at 470 °C on the basis of DTA data (Fig. 1 b).

Figure 3 shows the microstructure of surface of the quartz plates at various conditions of the phase formation. In the composite binder based on activated lime the

concentration of new growths increases. In this case a composite structure forms, consisting of lamellar and acicular crystals and amorphous formations. Low-basic HSCs hydrated calcium sulfosilicates form compact diverse columnar layer around quartz particles, forming micro-reinforcing frame. Amorphous formations initiate a contact area expansion between the crystals and the reduction of the pore volume in the structure of the binder matrix (Fig. 3 b), helping to improve the mechanical strength of the lime stone.

CONCLUSION

When production of silicate autoclave products the performance properties of the final products depend on the quality of the binder used and the conditions of components interaction at all stages of the production process. In most cases, the rate and completeness of lime slacking mainly effect the chemical interaction of the components during t he process of the binder. These properties are especially important in the interaction of sand-lime binder in an autoclave with the decreasing solubility of $Ca(OH)_2$ at higher temperatures. In this article is found that change the amount of water for highly active lime slacking we can change the temperature, the rate of the process and dispersity of the slacking products. Application of gypsum dihydrate additive when high-temperature slaking influences the solubility of $Ca(OH)_2$ giving fine dispersed particles. The resulted $Ca(OH)_2$ particles save dispersity, as they are in saturated alkaline solutions, avoiding their aggregation. The resulting gypsum hemihydrate when the lime slacking has a high solubility in comparison with the gypsum dihydrate, increasing the concentration of SO_4^{2-}-ions in liquid phase in combination with fine dispersed particles of $Ca(OH)_2$ intensifies the interaction of the initial components leading to phase composition change of the binder. It is advisable to use the products obtained when slaking of lime with the gypsum additive in composite binder. It allows the most effective utilization of its hydration properties that leads to a considerable increasing in the strength values of final products.

Summary: During the slaking process at W/S=0,64-0,80 the highly exothermic reaction at temperatures in range of 160-190 °C. The slacking heat can affect the dehydration of gypsum dihydrate to form fine dispersed particles of β- modification of gypsum hemihydrate and $Ca(OH)_2$.

The best parameters of lime slacking are followings: W/S = 0,48 and the additive content is 0,15 wt. %. In this case 40 % of the particles are in a highly dispersed state up to 10μm, including the nanoscale range. The resulting highly dispersed slacking products are highly reactive, effecting intensification the components interaction mechanisms when hydration and autoclave treatment with increasing amounts of silicate. The phase composition is represented by high-strength low-basic tobermorite-like GSC, hydrated calcium sulfosilicates $Ca_3Si(SO_4)_2(OH)_6 \bullet 9H_2O$, as well as amorphous growths. The phases obtained completely cover quartz particles with amorphous shell and crystals with diverse columnar structure providing micro-reinforcement of composite matrix. It allows increasing the strength of the composite binder by 85 %.

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