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THE USE OF GRANULATED MODIFIED LIME FOR EXPANSIVE CEMENT WITH HIGH-ENERGY SELF-TENSION

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Abstract. The article examines the features of hardening and structurization processes of cement with high-energy self-tension. The physical-chemical methods of the research confirm that the use of the granulated expanding additive leads not only to an increase in expansion but also proves to form zones with different hydrated phases around granule.

Keywords: granulation**,** expansion strength, phase structure, thermal analysis, microstructure.

1. Introduction

Ever since the invention of cement, its use for manufacturing of concrete and reinforced concrete constructions has been accompanied by the difficulties concerning reduction of product size, knows as shrinkage [1].

Portland cement as well as other kinds of cement, *e.g.* alumina cement, is known to form crystal and colloid hydrated compounds during the hydration process. During air hardening newly formed colloid compounds tend to dry out and tighten, which is accompanied by the cement stone shrinkage.

Use of fillers in concrete manufacturing reduces the size of the concrete shrinkage, but does not reduce the cement shrinkage. In consequence, big stretching pressures take place in the cement stone that fills the space between sand grains, resulting in the occurrence of microcracks. Such internal disruptions cause cracks in big concrete massifs through which atmospheric agents, water and other aggressive liquids can penetrate inside. According to the researches, the shrinkage process depends on the type of the cement being used, the subtlety of its grinding, water-cement ratio, filler grain content and cement endurance conditions [2].

Among the new kinds of cement (developed over the last 50 years) expansive and non-shrinking cements have attracted a large scientific interest and received the practical value [3].

Non-shrinking cements have a small expansion potential and are used for the prevention or reduction of crack formation during the concrete shrinkage process. They are characterized by early-age uniform expansion that compensates the following shrinkage or slightly exceeds it. Expansive cements have a larger amount of expansion energy in comparison with the non-shrinking ones. Strained cements, known to have a larger amount of expansion energy (not less than 2 MPa) are able to put pressure on an armature and press concrete without damaging its internal connections.

According to the latest published data on manufacturing conditions of expansive and strained cements plaster, lime, alumina cement, and other components are used as the additives [1]. The use of gypsum additive as the expansion filler is known to cause the expansion accompanied by the creation of ettringite [4]. At adding CaO or MgO together with water into the reactionary environment, the expansion occurs as a result of changing of its volume [5].

Manufacturing of known expansive cements is performed under industrial conditions and in most cases provides compatible roasting or grinding of components, which makes the final product more expensive. That is why an expansion additive that could be added directly on a building site is highly required. In order to study and research the structurization processes of these expansive systems it is necessary to understand the nature of expansion and the factors influencing it.

The paper is aimed at researching the occurrence of the hydrated hardening processes by using granulated quicklime as a component of expansive cements with high-energy self-tension.

2. Experimental

Portland cement PC II/ A-S 400, I class granulated quicklime and saccharose as a lime slacking retarding agent were used to obtain expansive compositions.

The granulation of ground lime was done with the help of a manual press model P-125 under the pressure of 40 MPa in a form of tablets with the diameter d = 8mm and the height h = 4 mm. The lime granules were heated in a SNOL – 3.5, 3.53.5/3 – IZ laboratory drying cabinets in the temperature range of 400–410 K during 60–70 min.

Such physical-chemical methods of research as complex differential-thermal, X-ray phase and thermo-gravimetric analyses were employed to study the structure formation processes.

The X-ray analysis of the samples was carried out according to the method of powder on a DRON-2.0 diffractometer and CuK_{α} radiation. The thermal analysis was aimed at determining the temperatures by which changes in physical conditions of the samples or in their chemical compositions can be observed. The thermograms have been recorded on a model Q-1500 D derivatograph of Paulic-Paulic-Erdey system. The composition samples have been analyzed in a dynamic regime and in air atmosphere at the speed of heating of 5 °/min. The mass of the substance was 500 mg, the sensitivity by DTA scale was equal to 250 uV, and by the TG scale – 100 mg. In order to carry out the X-ray phase and thermal analyses the composition samples after dehydration have been crushed in an agate mortar until they fully penetrate through the sieve No.008.

The research of the microstructure of the cement stone has been done with the help of MBS-9 optical microscope and PEMMA-102-02 scanning electron microscope.

The expansive composition has been placed into a special cylinder-like form consisting of separate rings to determine the expansion strength. The granules were distributed evenly in the volume and were covered with the cement dough of normal density. The form filled with a solution has been placed on a stand with a rigidly anchored dynamometer and initial indicators have been marked off. The dynamometer has been read for seven days. As a result, the change in the expansion strength over a period of time has been collected.

3. Results and Discussion

According to the previous researchers, in order to get the composition with high-energy self-tension (Fig. 1) the content of a ground modified (heated with saccharose) lime must be not less than 25 % under even distribution inside the volume and limitation of expansion. The expansion strength of more than 2.3 MPa is reached. The further growth of the expanding additive amount up to 30 % almost doubles the expansion strength (4.3 MPa), while up to 40 % leads to the destruction of the composition.

The use of the additive in the form of a granulated modified lime equivalent to 30 % of cement mass caused the increase in the expansion strength up to 14 MPa on the seventh day of hardening.

The rough scheme of the expansion is shown in Fig. 2.

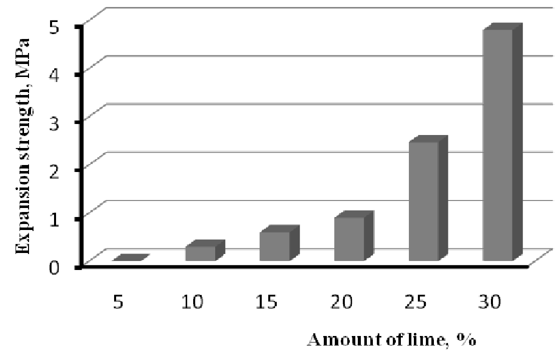

Fig. 1. The impact of the amount of lime on the expansion strength of the composition on the seventh day of its hardening under compressed conditions

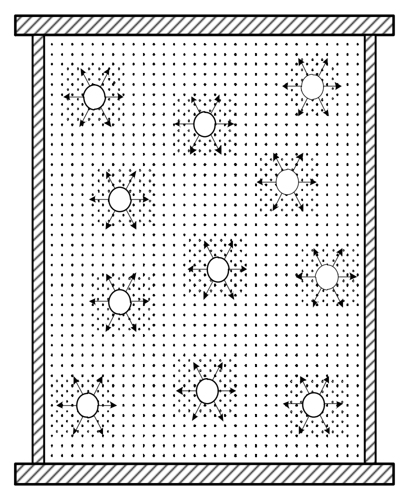

Fig. 2. Expansion mechanism at adding of the granulated lime to the composition

Fig. 3. Optical microscopy for the splinter of the expansive composition hardened seven days under compressed conditions

Moreover, the electron microscopy of the intermediate and the main zones was used additionally in the work. Fig. 4 shows the results of the electron microscopy of both zones. It can be observed that the larger thickness and the existence of smaller-sized pores are characteristic of the intermediate zone.

The analysis of the cement stone structure hydrated for seven days under compressed conditions reveals the intensity of the structure formation processes. The microstructure is presented by a large number of hydrated formations. Cube- and prism-like crystals are observed in the intermediate zone. Some prisms are vividly faceted and others are in the process of formation.

Some quantities of flakes in the form of underformed hexagonal plates, corresponding to portlandite, as well as skeleton growth forms, which can be referred to hydrated new formations, are observed in the main zone.

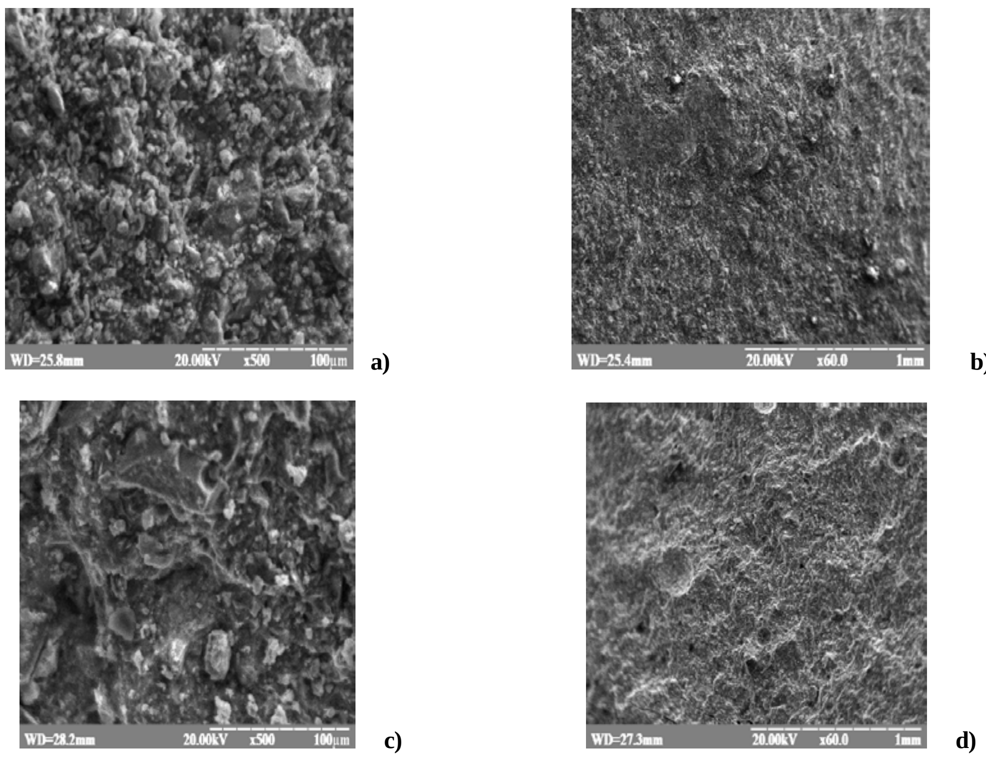

Fig. 4. Electron microscopy of cement stone samples hardened for seven days under compressed conditions: intermediate zone (a, b) and main zone (c, d)

The X-ray phase analysis of the samples hardened for seven days (Fig. 5) has been conducted to study the phase content of the hydration products of the cement stone in the main and intermediate zones. The research showed that the content of the hydrated compounds in the main zone is bigger in comparison to the main one. The larger intensity of portlandite and ettringite peaks seen on a diffractogram of the intermediate zone sample, and the occurrence of new peaks corresponding to the main high-hydro-aluminates C_2AH_8 and C_3AH_6 proves this. According to the data obtained from the X-ray phase analysis, these peaks are absent in the main zone sample. Thus, the presence of free CaO under compressed conditions changes qualitative and quantitative hydration products content of the Portland cement stone.

Thermal analysis data (Fig. 6) confirm the results of the X-ray phase analysis. The loss of the mass samples occurs during four stages and is accompanied by the occurrence of endoeffects on the DTA curves.

The decrease of mass within low the temperatures range of 290–410 K can be explained by the allocation of excess physical moisture and partially chemically connected water. Low basic hydrosilicates of the group CSH(II), which are present in both samples, lose hydrated water in this interval. The loss of the samples mass within the temperature range of 400–600 K corresponds to the continuation of step dehydration of hydrosilicates, ettringite and the beginning of the dissolution of low basic hydroaluminate CAH_{10}, that is in the intermediate and main zones. The samples of the intermediate zone are marked by the larger loss of mass in this interval, which can be explained by larger CAH_{10} content in it. The decrease of mass within the temperature range of 580–720 K is explained by the final dissolution of hydrosilicates and hydroaluminate of the group CAH_{10}, and by the beginning of the dissolution of high basic hydroaluminates C_2AH_8 and C_3AH_6 being in zone near the CaO granule. The sample 1 is characterized by the larger loss of mass within the mentioned temperature interval, which is explained by the larger high basic hydroaluminate content. The decrease of the samples mass within the temperature interval of 710–820 K corresponds to the final dehydratation of the high basic hydroaluminates and portlandite contained in the sample 1, as well as by the decomposition of portlandite present in the sample 2. The sample of the intermediate zone is characterized by the larger loss of mass in comparison to the main zone sample, which is explained by the larger $Ca(OH)_2$ content formed as a result of the dehydration of the CaO granule.

Thus, based of the thermal analysis data of the samples 1 and 2 the conclusion can be drawn that the intermediate zone sample is characterized by the larger hydrated phases content. That is confirmed by more intensive loss of the sample mass during its heating within all temperature intervals and by the occurrence of deeper endoeffects accompanying dissolution process of hydration products of the sample.

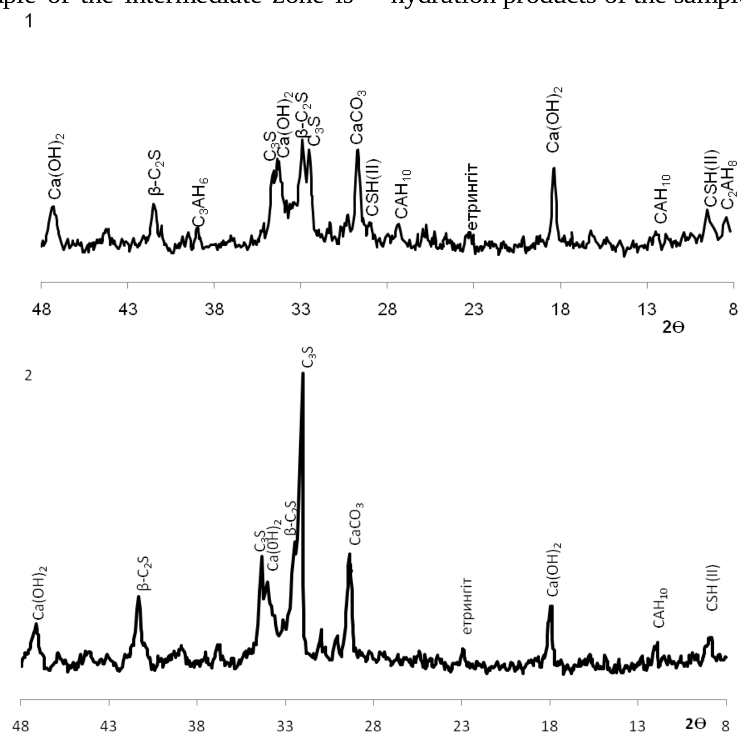

Fig. 5. Diffractograms of cement stone hardened for 7 days under compressed conditions

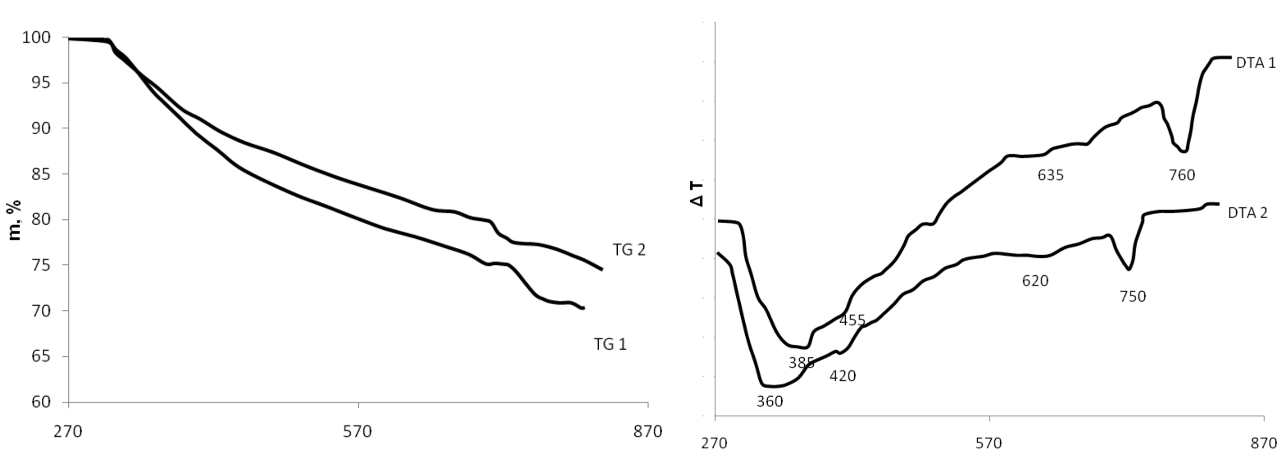

Fig. 6. Thermograms of cement stone hardened seven days under compressed conditions: intermediate zone (1) and main zone (2)

The quantitative hydration products content obtained from the thermal analysis data is shown in Table 1.

Table 1

Complex thermogravimetric and differential thermal analysis data on Portland cement stone with the additive of 30 % granulated modified lime hardened for seven days

No.	Zone	Temperature range, K	Loss of mass (Δm), %	Endoeffect, T_{max}, K
1	Intermediate	290–400	2.25	370
		400–580	2.5	invisible
		580–720	1.125	invisible
		720–820	1	760
	Total losses	290–820	6.875	–
2	Main	290–410	2	360
		410–600	2	invisible
		600–710	0.75	invisible
		710–820	0.75	750
	Total losses	290–820	5.5	–

4. Conclusions

It was determined that by adding of the granulated modified lime to the cement composition the expansion strength in the hardening process increases in comparison with the cement composition consisting of ground modified CaO. The results of the research have established that the intermediate zone characterized by larger content of hydrated phases than the main zone of the composition is formed near the modified lime granule. These hydrated new formations predetermine the formation of a strong carcass which allows to maintain large expansion strengths of the cement structure without causing destructions of the material. The use of the granulated modified lime as a supplement material of the cement composition enables to get cements with predicted expansion value, which can be regulated (according to the purpose) directly on a building site.

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ВИКОРИСТАННЯ ГРАНУЛЬОВАНОГО МОДИФІКОВАНОГО ВАПНА ДЛЯ РОЗШИРНИХ ЦЕМЕНТІВ З ВИСОКОЮ ЕНЕРГІЄЮ САМОНАПРУЖЕННЯ

Анотація. *У роботі досліджено особливості процесів тверднення і структуроутворення цементів з високою енергією самонапруження. Використання гранульованого розширного додатку призводить не тільки до збільшення зусилля розширення, але й до виникнення навколо гранули зон, які відрізняються вмістом гідратних фаз, що підтверджується фізико-хімічними методами дослідження.*

Ключові слова: *розширний додаток, гранулювання, зусилля розширення, фазовий склад, термічний аналіз, мікроструктура.*