Development of non-shrinkable cement based on local raw materials

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Abstract. With an analysis of world practice in the production of non-shrinkable and expandable cement mortars and structures, the basic methods for their preparation are revealed. The main directions of their production are established based on the use of special expanding cements developed by various authors. An analysis of the above mentioned methods revealed that for the Republic of Armenia the most accessible method is the development of a special additive and its introduction into conventional Portland cement.

Investigating the mineral base of the RA, a special additive was developed on the base of dust absorbed from exhaust gases of cement plants furnaces, by which it is possible to obtain non-shrinkable and expandable cements. Different ratios are determined at 800-1100 °C.

The study revealed that at a ratio of 40:60 and 45:55 (gypsum: dust), the additive obtained at 1000 °C contains a sufficient amount of ettringite, the main mineral for expansion. The expansion effects of the developed additives were studied, its optimal ratio corresponding to 10 percent by mass of cement was established.

Introduction

In order to increase the life span of structures and buildings, new materials with high construction and technical properties are needed, which are characterized by different features depending on the operating conditions.

Taking into account the fact that in the mentioned structures the main binding material is the ordinary Portland cement, which has a number of positive properties, but has low corrosion resistance, but in dry air conditions the reinforcement structural processes can lead to shrinkage and reduce the merging of junction units, which contribute the longevity of cementitious compositions.

In order to exclude these undesirable phenomena, special types of Portland cement has been developed, which unlike the usual ones, does not shrink during expansion, but on the contrary - expands.

Among them, cement composites and concrete are of particular importance, which is mainly used for the production of ordinary Portland cement. However, the mentioned cement having a number of positive properties is characterized by low corrosion resistance as well as undesirable deformation processes, in particular compression, which results in formation of microcracks in concrete, decrease in strength, and reduction of monolithic features of the structure unit.

Non-shrinkable, expandable cements are the same types of cements, various methods of which have been developed by a number of authors [1-6]. The use of such cements also reduce the gas and water permeability of the concrete. By studying the nature, composition and the possibilities of each method...
and taking into consideration the possibilities of the Republic of Armenia, we have come to conclusion that the most affordable and effective method is the development of a special additive and its introduction into a conventional Portland cement, which artificially modifies the mineral composition of the cement stone, resulting in ettringite formation - \((3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 31\text{H}_2\text{O})\), which is the main expanding additive in the cement.

**Materials and methods**

The main goal of this research is to find materials suitable for the development of special expanding additives, containing carbonate and sulfate.

Investigating the mineral base of the country and the existing production waste, a special additive was developed on the base of dust absorbed from exhaust gases of cement plants furnaces, by which it is possible to obtain non-shrinkable and expandable cements [7]:

However, taking into consideration the fact that the clay gypsum does not have a stable mineral composition, a new, more stable sulfate-containing component was found, which is Parakar mine of gypsum with an average chemical composition shown in Table 1.

**Table 1.** The average chemical composition of Parakar mine of gypsum

| Oxide content, % | SiO\textsubscript{2} | Al\textsubscript{2}O\textsubscript{3} | Fe\textsubscript{2}O\textsubscript{3} | CaO | MgO | SO\textsubscript{3} | R\textsubscript{2}O | Ignition curve |
|------------------|----------------|----------------|----------------|-------|------|-------------|--------|--------------|
| 15.90            | 3.10           | 2.31           | 25.04          | 3.98  | 33.63| 1.19        | 12.23  |

On the base of the selected materials, a number of raw mixtures have been developed, the calculation data of which show that the cementitious powder-gypsum compositions with a weight ratio of 40:60 and 45:55 are more favorable.

Considering the fact that the phase structure of the sulfate-containing cement clinker differs from that of the conventional Portland cement, the modular characteristics of the cake and the mineral composition calculated by calcium sulphosilicate \(2(\text{C}_2\text{S})\text{CaSO}_4\) and calcium sulfoaluminate \(3(\text{CA})\text{CaSO}_4\), which determines the mineral composition [8], saturation coefficient (KH) and introduces a new understanding about gypsum saturation (CH\text{SO}_3) for aluminates and silicates.

\[
\% \ 2 (\text{C}_2\text{S})\text{CaSO}_4 = 4\text{SiO}_2,
\]

\[
\% \ 3 (\text{CA})\text{CaSO}_4 = 1.96(\text{Al}_2\text{O}_3-0.64\text{Fe}_2\text{O}_3),
\]

\[
\% \ \text{C}_4\text{AF} = 3.035 \ \text{Fe}_2\text{O}_3
\]

\[
KH = \frac{C_0 - 0.55A_0 - 1.05F_0 - 0.75(SO_3)_0}{1.867S_0},
\]

\[
CH_{SO_3} = \frac{(SO_3)_0 - 0.261A_0 + 0.166F_0}{0.667S_0},
\]

Where, \(C_0\), \(F_0\), \((SO_3)_0\) and \(S_0\) are accordingly the contents of \(\text{CaO}\), \(\text{Al}_2\text{O}_3\), \(\text{Fe}_2\text{O}_3\), \(\text{SO}_3\) and \(\text{SiO}_2\) in the raw mixture.

The calculated modular characteristics and phase composition are presented in Table 2.

**Table 2.** Calculation modular characteristics and phase composition of the additive

| Additive composition | Saturation coefficient, (KN) | CH\text{SO}_3 | Mineral composition, % |
|----------------------|-----------------------------|------------|----------------------|
| 2(\text{C}_2\text{S})\text{CaSO}_4 | 3(\text{CA})\text{CaSO}_4 | \(\text{C}_4\text{AF}\) |
Cement dust - 40
Gypsum - 60

Cement dust - 45
Gypsum - 55

| Cement dust-40 | 0.45 | 2.0 | 71.16 | 10.29 | 8.37 |
| Cement dust-45 | 0.54 | 1.84 | 70.00 | 10.19 | 8.47 |

Analysis of the calculation data revealed that an excess quantity of CaSO₄ should remain in the first amount of cement powder and gypsum cake, which according to [1] is favorable for increasing the stability of 3 (CA) CaSO₄ mixture. At the same time, taking into consideration that some quantity of calcium oxide in the cement powder is present in free state, and the other part is present in the pre-heated calcium carbonate mixture, so it can be assumed that the raw materials based on cement-gypsum mixture must have high reaction ability.

Specimens of 2.5 ± 0.5 cm in diameter and 3.0 ± 0.5 cm in height are prepared for special expanding additives, which have been calcined to 800–1100°C.

The mineral composition of the obtained cakes have been studied petrographically, which proves that at a temperature of 1000 °C a sufficient amount of calcium sulphoaluminate is formed, which numerical value is close to the cake obtained at 1100 °C, hence the optimum temperature of calcination is 1000 °C. The resulting cakes were crushed to the value of the specific surface area of the cement.

The expence of the additive is of 5.8 and 10 percent by weight of cement. 2x2x2 cm cubes are prepared from the obtained mixture, where the linear dimension change was determined during 1; 3; 7 and 28 days of hardening with the help of indicator with accuracy of 0.001 mm.

The values of changes in linear sizes are determined by the following formula:

$$\Delta \ell = \frac{\ell_1 - \ell}{\ell} \cdot 100\%$$

Where - $\Delta \ell$ is the linear change (shrinkage and expansion),

$\ell_1$ - is the newly formed specimen size,

$\ell$ - is the specimen size tested at specified age,

| Table 3. Deformation change in cement |
|--------------------------------------|
| Linear deformation, %               |
| Ege, day                            |
| 1 | 3 | 7 | 28 |
| 0.10 | 0.17 | 0.24 | 0.20 |
| 0.09 | 0.17 | 0.27 | 0.22 |
| 0.12 | 0.18 | 0.30 | 0.25 |

The table below presents the average values of compression for three samples. Investigation of the change in the linear size of the cubes has shown that the maximum expansion rate is observed when 10 percent by mass of the additive is introduced, and the data are presented in Table 3.

Investigation of the data presented in the Table proved, that the maximum expansion of the system is observed at 3-7 days of hardening due to the intensive formation of ettringite, which corresponds the data obtained by a number of scientists, in particular [3,9].
The mentioned phenomenon is explained by the fact that in the first three days, when the cement-water system has sufficient plasticity, the formation of ettringite does not contribute to the expansion of the system, and after 7 days when the system begins to gain rigidity, especially at 28 days and over, the growing crystals of ettringite have a negative effect, because they can weaken the bonds between previously formed new particles and also decompose the hardened system.

**Summary**

The results of the research and the data obtained convincingly prove that expandable and non-shrinkable cements can be obtained by the introduction of a special additive developed on the base of Parakar gypsum and dust absorbed from exhaust gases of cement plants furnaces into Portland cement composition.

**References**

[1] Meta P K, Polivka M 1976 *Expanding cements* (Tr. VI Inter. Congress on Cement Chemistry, Moscow) 3 158-172.

[2] Kuzel H, Pollmann H 1991 *Hydration of and C3A in the presence of Ca(OH)2, CaSO4 and CaCO3* (Cement and Concrete Research) 21 885-895.

[3] Kravchenko I V, Bershtein V L 1978 *Studies of the processes of formation of ettringite in systems with calcium aluminates of various basicities in order to improve the quality of cement* (Brief Abstracts at the V All-Union Scientific and Technical Meeting on Chemistry and Cement Technology. M. SICement) 96-97.

[4] Kutateladze K S, Gabadadze T G, Nergadze N G 1976 *Alunite non-shrinking, expanding and tensile cements* (Tr. VI International Congr. in cement chemistry, Moscow, Stroyizdat) 3 189-191.

[5] Krivoborodov Yu R, Samchenko S V 1991 *Physical and chemical properties of sulfonated clinkers* (VNIIESM, Analytical review, ser. 1., Cement industry) p. 55.

[6] Bajkova A I, Kuznetsova T V 1996 *Chemistry of cement* (Moscow, Mir) p. 560.

[7] Chilingaryan N V, Meymaryan A S 2016 *Parakar mine gypsum for synthesis of a special expanding additives* (Proceedings of NUACA) 4 (63) pp. 92-96.

[8] Paschenko A A 1978 *New cement* (Kiev, Budivelnik) pp. 189-192.

[9] Gabadadze T D 1978 *Mechanism of cement expansion* (Abs. NA Georgia, SSR, Chemistry) 4 (4) 121-125.

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