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Production of expansive additive to portland cement

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Abstract

The expansive additive was produced from sulfate–calcium component and aluminate clinker, containing 60% Al_2O_3. The sulfate–calcium component is prepared by flue gas desulphurization gypsum and calcareous raw material mixture burning. The ground sulfate component, mixed with ground aluminate clinker transforms into the effective expansive addition to portland cement. The following main phases were present in this expansive material: anhydrite, calcium oxide and monocalcium aluminate.

The expansive substance was added to CEM I 42.5 cement as 7 and 12% addition. The mixtures were subjected to the hydration process; the expansion was measured as a function of varying conditions. The linear changes, as well as the compressive/flexural strength were determined after 1, 3, 7 and 28 days. The initial and final setting time was also measured.

The cement with 7% (by weight) expansive additive is a shrinkage-less material, while the mixture with 12% (by weight) expansive additive is an expansive binder.

The samples were examined by XRD and SEM-EDS.

Keyword: Hydration

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1. Introduction

The portland cement based concretes reveal natural volume changes—usually it is shrinkage, being the consequence of water consumption and gel-like product densification on hydration process. This is a significant disadvantage of concrete production and use. Shrinkage can be the reason of cracks and reduced water impermeability; further on the freezing/thawing resistance decrease. The specific properties of shrinkage-less and expansive cements give the possibility to produce concretes in which the shrinkage is compensated or even the volume increase takes place.[1]

In every hydrating cement, including portland cements, the two reciprocal processes of shrinkage and expansion take place simultaneously, but with different rate and intensity. In the expansive cement the volume changes attributed to the volume augmentation are significantly higher than the reduction of volume resulting from shrinkage. The difference gives results in expansion. Depending on the relation between these two volume changes one can distinguish the following materials: shrinkage-less cement, low-expansive cement, expansive cement (medium expansion) and expansive cement—self-prestressing (high expansion).[2]

According to the ASTM C 845-96[3] standard, the classification of expansive cements covers the three following groups: K, M and S. Expansive cement K is produced from anhydrous calcium sulfoaluminate ($4CaO{\cdot}3Al_2O_3{\cdot}SO_3$), calcium sulfate, and uncombined calcium oxide. Expansive cement M is produced from calcium aluminate cement and calcium sulfate. Expansive cement S is produced from tricalcium aluminate (C_3A) and calcium sulfate.

The production of expansive cement having precisely defined properties is based upon the standard mentioned above.

The application of expansive additives subsequently mixed with portland cement is another solution. Due to the controlled amount of additive the expansive cements with assumed expansion or shrinkage-less ones can be produced. This method can be used in the production of shrinkage-less or expansive concrete directly in the construction-site. The expansive additives with calcium sulfoaluminate (C_4A_3S), anhydrite and calcium oxide are produced in Japan, USA and Great Britain.[4,5]

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The expansive additives show so-called sulfate expansion. The commonly accepted theory links this "sulfate expansion" with the formation of ettringite (noted as AFt phase) as a result of topochemical reaction. There are also many other hypotheses dealing with the expansion mechanism, but they do not explain completely this phenomenon.[6]

From the practical point of view in the reaction of ettringite formation the aluminate phases are the most important: CA ($CaO\cdot Al_2O_3$) and C_4A_3S ($3CaO\cdot 3Al_2O_3\cdot CaSO_4$).[7] The synthesis of ettringite is the result of the following reactions:

$$CA + 3CaSO_4 + 2CaO + 32H_2O = C_3A \cdot 3CaSO_4\cdot 32H_2O \tag{1}$$

$$C_4A_3S + 8CaSO_4 + 6CaO + 96H_2O = 3(C_3A \cdot 3CaSO_4\cdot 32H_2O) \tag{2}$$

The degree of crystallinity, crystal size and time when the ettringite appears (as relates to the setting process) are very important as the formation of ettringite is discussed. Early ettringite formation does not bring about the volume increase; late crystallization of ettrinigite is the reason of the collapse of paste structure; at better case the strength decrease is only observed. The expansion which is equivalent to the reaction of ettringite formation should take place mainly between the 24 and 72 h after mixing with water.[1]

There is much more data relating to the ettringite formation from calcium sulfo-aluminate (C_4A_3S) than the ones dealing with the transformation of calcium mono-aluminate into ettringite phase. The mono-calcium aluminate ($CaO\cdot Al_2O_3$) expansive additive, which is the basic component of aluminate cements and sulfate–aluminate component has been the subject of long lasting investigations by the research team from the AGH-University of Mining and Metallurgy and further on patented in Poland.[8] The specific microstructure of ettringite as well as the kinetics of ettringite crystallization during the hardening of cement produced by mixing portland cement and expansive components brings about the controlled changes of volume only when the proper method of sulfate–lime expansive additive preparation is applied.

In this work the way of the production of this sulfate–lime component will be given. Then the preparation of expansive component will be presented and finally—the results for the hardened cement CEM I 42.5 mixed with 7 and 12% of expansive additive.

2. Experimental results

The flue gas desulfurization gypsum containing 45% SO_3 together with limestone containing 55% CaO were used to produce the sulfate–lime component. The ground sulfate component was mixed with ground aluminate clinker containing 60% Al_2O_3 for expansive additive. The shrinkage-less and expansive cements were produced by mixing portland cement CEM I 42.5 with 7 and 12% (by weight) of expansive mixture.

The mixture of flue gas desulfurization gypsum (66.5%) and limestone (33.5%) was dried, ground, heated at 1150 °C and subsequently cooled. The product thus obtained was ground to the 10% residue on the sieve with 4.900 sieve mesh/cm^2. The anhydrite phase together with calcium oxide were detected; their contents were 72 and 28% (by weight), respectively. In Fig. 1 the XRD pattern and in Fig. 2 the SEM-EDS picture of this sulfate–lime component are shown.

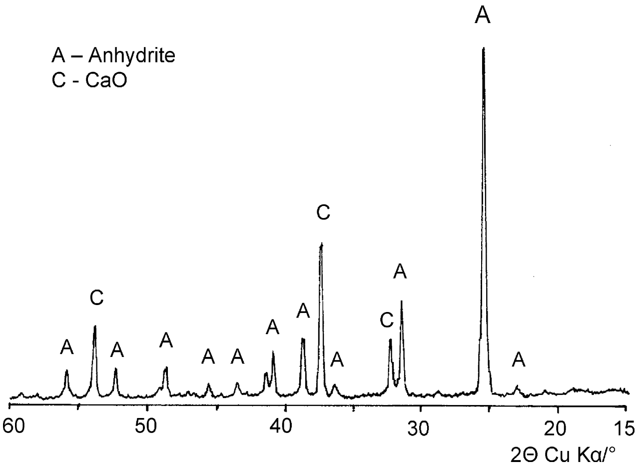

Fig. 1. The XRD pattern of sulfate–lime component.

The burnt sulfate–lime component was mixed with the ground aluminate clinker; the percentages were 78 and 22% (by weight) respectively. The specific surface of expansive additive thus produced was 2.940 cm^2/g. The grain size composition was as follows: fraction >60 mm, 15.8%; fraction 45–60 mm, 14.9; fraction <45 mm, 69.3%.

The XRD pattern of expansive additive is shown in Fig. 3.

The paste produced from expansive additive mixed with water at water to cement ratio $w/c = 0.3$ were cast to the 40 mm × 40 mm × 160 mm standard moulds and stored in humid air for 6 h. After this the bars were put out and measured using the Graf Kaufman testing device. Further on the samples were stored in different conditions: in saturated $Ca(OH)_2$ water solution, in chambers at different relative humidity (RH)—98 and 55%, respectively, at temperature 21 °C. After 1 day maturing the dimensions of the bars increased significantly, so that the further expansion determinations by Graf Kaufman device became impossible. Therefore the length of the bars was measured using the electronic slide caliper.

The bars store in saturated $Ca(OH)_2$ water solution collapsed first, the samples stored in air of 98% RH—after 2 days, while those kept at 55% RH reached the expansion on the level of 25% after 10 days. The phase composition of the pastes was studied by XRD method.

The results of linear expansion measurements, given in % are shown in Fig. 4.

The SEM-EDS studies, as well as the observations under the classic optical microscope of expansive additive hydrated bar stored in $Ca(OH)_2$ water solution were carried out. In Fig. 5 the SEM-EDS results are presented.

In order to produce the shrinkage-less and expansive cement the portland cement CEM I 42.5 from Górażdże cement plant in Poland was used. The phase composition of this cement was

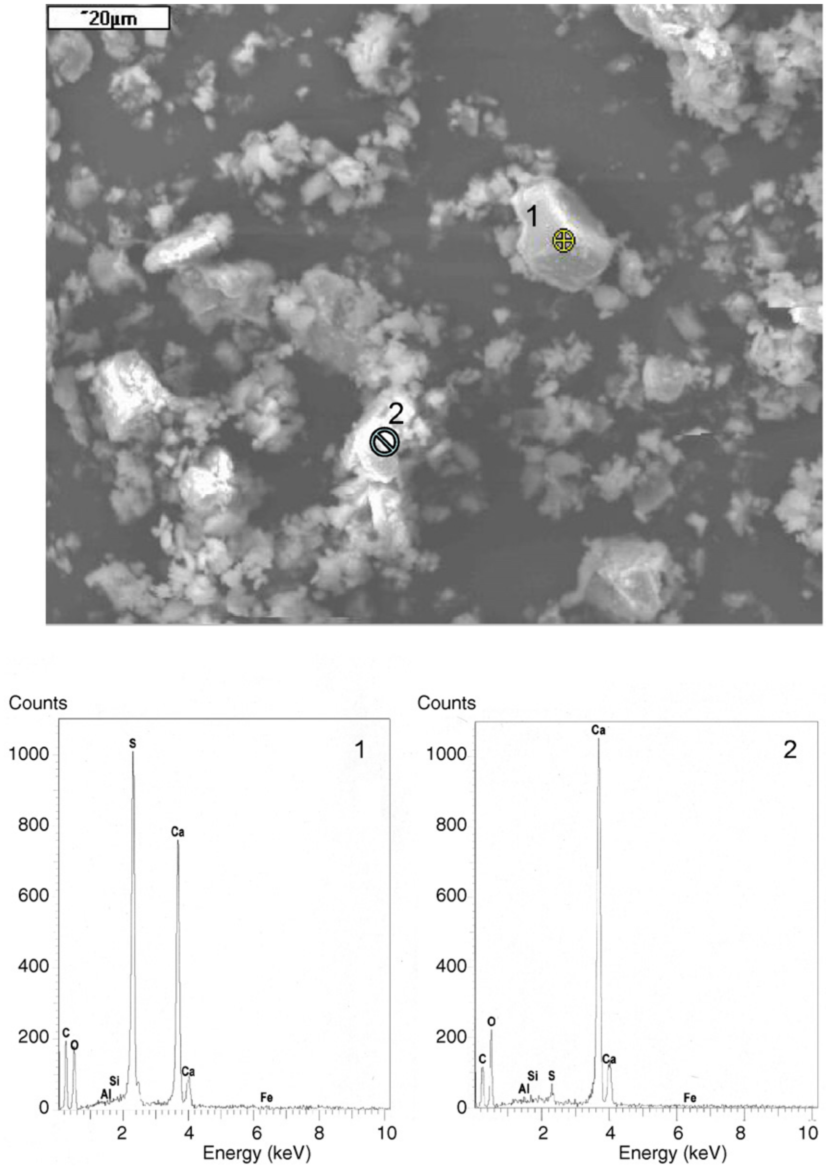

Fig. 2. SEM-EDS of sulfate–lime component. (1) Anhydrite, (2) CaO.

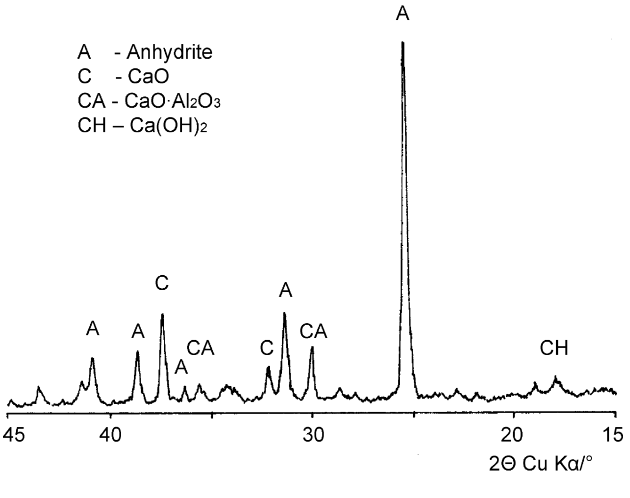

Fig. 3. XRD pattern of expansive additive.

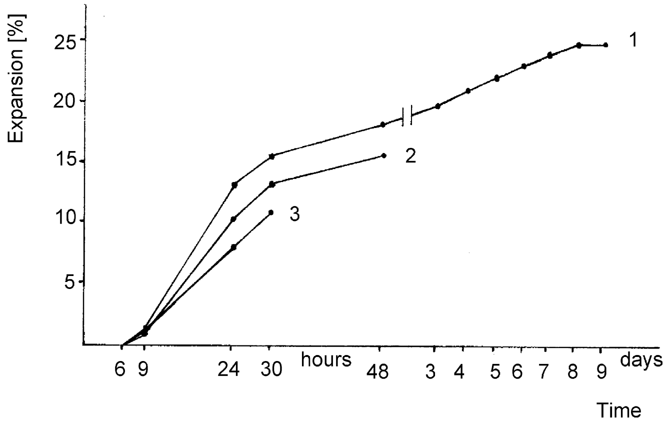

Fig. 4. Linear changes (in %) of pastes produced from expansive additive vs. time, as a function of curing conditions. (1) Sample stored in air of 55% RH; (2) sample stored in air of 98% RH; (3) sample stored in saturated $Ca(OH)_2$ water solution.

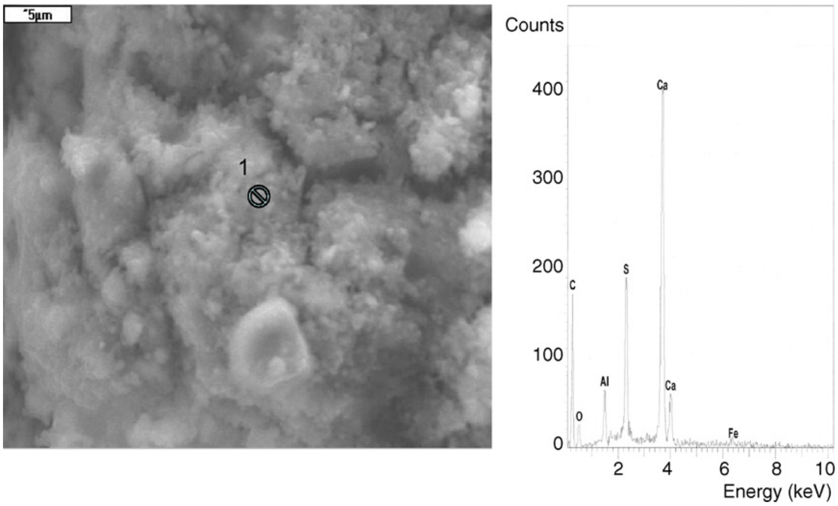

Fig. 5. SEM-EDS of expansive additive hydrated sample stored in $Ca(OH)_2$ water solution. (1) Ettryngite.

Table 1
Compressive/flexural strength and linear changes of standard cement mortars

Parameter	At age (days)			
	1	3	7	28
Compressive strength (MPa)	25.48	43.53	46.85	57.33
Flexural strength (MPa)	4.62	6.54	6.80	7.40
Shrinkage (mm/m)	−0.062	−0.077	−0.050	−0.130

as follows: C_3S, 66.50%; C_2S, 9.76%; C_3A, 9.17% and C_4AF, 7.88%. Initial setting time was 3 h 15 min and final setting time was 4 h 30 min, respectively; the specific surface—3.375 cm^2/g (Blaine method). In Table 1 the compressive and flexural strength of standard cement mortar is given, together with the linear changes (shrinkage), as determined by Graf Kaufman testing device.

The shrinkage-less and expansive cements produced by mixing portland cement CEM I 42.5 with 7 and 12% (by weight) of expansive mixture were subsequently tested with aim to characterize their physical properties and strength. Further on the XRD and SEM-EDS examinations of pastes after 1, 3, 7 and 28 days hydration were carried out.

Initial setting time for the cement with 7% (by weight) of expansive additive was 1 h 55 min and final setting time was 4 h 55 min, respectively. Initial setting time for the cement admixtured with 12% (by weight) of expansive additive was 2 h 25 min and final setting time was 4 h 05 min, respectively. In Table 2 the compressive and flexural strength of standard cement mortar is given, together with the linear changes, as determined by Graf Kaufman testing device.

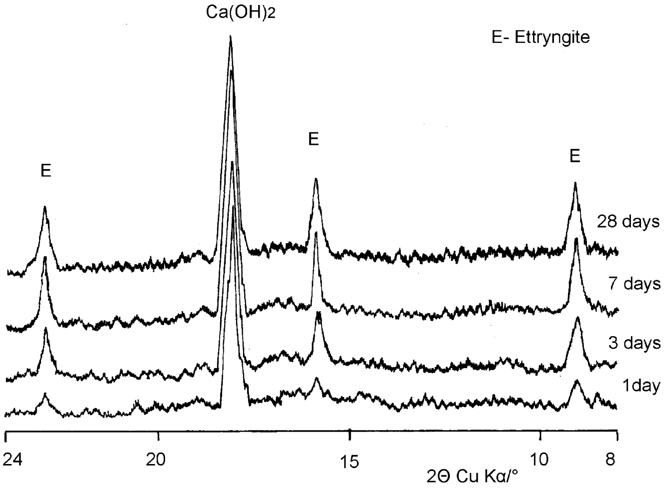

Fig. 6. XRD patterns of hydrated cement CEM I 42.5 with 12% expansive admixture after 1, 3, 7 and 28 days hydration.

The cements thus produced were subjected to the hydration process at w/c ratio resulting from the standard consistency test. The pastes were examined by XRD after 1, 3, 7 and 28 days curing. As one can find from the XRD data, the heights of ettringite peaks grow between 3 and 7 days of hydration (Fig. 6).

Table 2
Compressive/flexural strength and linear changes for standard cement mortars admixtured with 7 and 12% (by weight of cement) of expansive additive

Parameter	Portland cement CEM I 42.5 + 7% expansive additive, at age (days)				Portland cement CEM I 42.5 + 12% expansive additive, at age (days)			
	1	3	7	28	1	3	7	28
Compressive strength (MPa)	25.28	43.12	42.27	60.63	29.16	41.95	41.16	59.19
Flexural strength (MPa)	4.39	4.43	5.26	7.88	4.50	4.70	4.13	6.30
Linear changes (mm/m) (free expansion)	0.724	0.901	0.940	0.934	0.737	1.946	4.481	5.193
Linear changes (in %) (free expansion)	0.072	0.090	0.094	0.093	0.073	0.195	0.448	0.519

3. Discussion

The way of the expansive additive production has been found as a result of the studies reporter in this work. This expansive addition to cement induces the formation of expansive ettringite during the reactions occurring in cement paste on hydration. This ettringite appears at a "right moment" and reveals a specific microstructure.

The preparation of sulfate–lime component is, in our opinion, one of the important parameters affecting the synthesis of expansive additive with specific properties. As the authors could find—burning of the mixture composed of the flue gas desulfurization gypsum with limestone at 1150 °C resulted in the formation of material with assumed phase composition (Fig. 1). This is the anhydrite matrix with calcium oxide built up in it (Fig. 2). The expansive components produced either from calcium aluminate cement, calcium aluminate clinker or anhydrite mixed with calcium oxide without their co-burning do not guarantee the proper microstructure and kinetics of ettringite formation. It relates particularly to their reaction with calcium mono-aluminate.

The expansive mixture produced from aluminate clinker and sulfate–lime component added at a specific ratio (see Fig. 3) and hydrated in different conditions collapsed first, as one could presume, in calcium hydroxide solution. It is shown in Fig. 5 that the hydrated expansive additive paste consists mainly of microcrystalline ettringite aggregates.

The observations under the classic optical microscope proved the hexagonal character of ettringite crystals. The birefrigence of material is relatively high—around 0.05. It reveals no differentiation as concerns the granulometric composition; the crystal size can be estimated for 0.01 mm.

The linear expansion measurements of cement mortars admixtured with 7 and 12% expansive additive were done by means of Graf Kaufman method, according to the de-moulding procedure recommended by ASTM C 806-95 standard.[9] The 40 mm × 40 mm × 160 mm standard mortars were prepared at $w/c = 0.5$. The same procedures were followed on compressive and flexural strength determination.

The expansive cements are included neither in the Polish nor in European standards. In order to classify the material (shrinkage-less or expansive), the American ASTM C 845-96[3] standard was applied. In this standard the range of linear restrained expansion value in % for expansive cement is given. These values relate to the limited expansion, as it results from the special testing machine used. However the data reported in this work were produced as free expansion ones. Therefore the calculations were done basing upon the earlier works[10] in such a way that the free expansion values in % were subjected to the one order of magnitude reduction (see Table 2).

Taking into account the linear changes data and the results of other tests one can find that in the light of relevant ASTM standard requirement cement CEM I 42.5 with 7% expansive additive is a shrinkage-less material, while the same cement with 12% expansive additive reveals the features of expansive cement.

Application of expansive additive to cement CEM I 42.5 gives no strength decrease in case both shrinkage-less and expansive product.

The examinations of hydration products seem to point the formation of expansive ettringite as a product of topochemical reaction.

4. Conclusions

1. The expansive additive of fairly good quality can be produced starting from aluminate cement based on mono-calcium aluminate and sulfate–lime component. This additive in the mixture with portland cement gives expansive or shrinkage-less material.
2. The quality of expansive additive is strongly related to the properties of sulfate–lime component.
3. The sulfate–lime component of good quality is produced by burning of flue gas desulfurization gypsum and lime-bearing raw material. As a result the anhydrite matrix with calcium oxide built up in it is produced.
4. The hydration of expansive additive as well as the hydration of cements with this additive brings about the formation of microcrystalline aggregates of hexagonal ettringite.
5. The crystallization of ettringite on hydration takes place as a topochemical process.

Acknowledgement

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