Dependence of the Structure of Cement Stone from the Dispersion of the Alumina Component

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Abstract. Usually, sulfoaluminate clinker or a mixture of aluminate clinker with calcium sulphates is used to obtain expansive cements. For these cements ettringite is an important hydration product. This paper deals with the composition and properties of solid solution of calcium aluminate. It was studied an influence of calcium aluminate on structure and properties cement phases. The properties of cements containing these phase were also studied. The investigation of hydration and properties of aluminate cements shows that ettringite and its analogies are formed thus providing expansion and compression of cement stone.

1. Introduction
The structure of the cement stone varies markedly from the composition and crystallineness degree of crystalline hydrates, which in turn is determined by such factors as the presence of impurities in the minerals, the hardening conditions, and the dispersion of the hardening system and depends mainly on the amount of hydrates and porosity [1-5].

At present, various materials have become widely used as expanding additives [6-11]. Among such additives, aluminous slag, sulfoaluminate, sulfoferrite and sulfoalumoferrite clinkers were widely used [12-16]. In this thesis, we studied the use of an additive in the form of the aluminous slag [17-20].

The study of the expanding component dispersion effect on the formation of the cement stone structure was being performed on Portland cement mixtures with an expanding component (calcium monoaluminate) of various fractions: < 28 µm, 28-45, 45-63, 63-80 and < 80 µm.

2. Material and Methods
The Portland cement clinker was ground to a specific surface of 350 m²/kg. Separately the gypsum was ground up to S = 350 m²/kg. Mixtures were prepared by mixing the components in a ratio of Portland cement clinker – 80%, expanding additive (of a certain fraction) – 10% and gypsum – 10%. The finished cements were covered with water at water/cement = 0.4, the samples were made from the cement paste, which were hardened under normal conditions for 1, 3, 7, 14 and 28 days and tested for strength and expansion. The samples were also subjected to physicochemical analysis. The degree of the samples hydration was estimated from the change in the intensity of the main analytical peak of the calcium monoaluminate mineral (CA) – (d = 0.296 nm), the degree of hydration of the portland cement clinker was estimated by alite.

The following results were obtained for the mixtures. Characteristics of the peaks of minerals are presented in Table 1.
Table 1. X-Ray characteristics of minerals

| Characteristics of minerals | Source materials | Sieve residue R0063 | Sieve residue R0045 | Undersize |
|-----------------------------|------------------|---------------------|---------------------|-----------|
| d, nm                       | 0.2959           | 0.2955              | 0.2963              | 0.2953    |
| Int                         | 373              | 370                 | 383                 | 443       |
| half-width                  | 0.29              | 0.27                | 0.33                | 0.33      |
| peak area                   | 107              | 91                  | 104                 | 121       |

3. Results and discussion

The X-ray phase analysis of the hydrated samples showed that the particles of CA fractions <28 μm and 28-45 μm are hydrated completely up to 3 days, the particles of fractions 45-63 μm - up to 7 days, the coarse fractions – up to 14 days. In these terms, reflection reflexes of the initial mineral CA are completely absent on the X-ray spectra.

The total porosity of the samples containing small fractions of CA is lower than in the samples with coarse fractions (Fig. 1). The strength of the cement stone is also higher. Cement stone containing fine CA fractions (28-45 and less than 28 μm) has a strong structure and small expansion, and the cement stone of samples with the coarse fractions (>80 μm, 63-80, 45-63) has a large expansion, which leads to decrease in strength of the samples (Fig. 2, Fig. 3).

Figure 1. Total porosity of the samples.

Electron microscope investigations of the cement stone structure showed that hydration of the fine fractions of the mineral CA results in the mud injection and intensive hydration of the fine-grained Portland cement clinker creates a dense, strong structure that combines fine crystal crystalline hydrates of ettringite and a finely dispersed and gel-like mass of calcium hydrosilicates. When hydrating the coarse and middle CA fractions, formation of large needle and prismatic ettringite crystals is observed, which create a crystalline stone skeleton.

The conducted studies show that the fineness of grinding of the expanding additive based on the aluminous slag and the granulometric composition of cement have a great influence on the formation of the cement stone structure. In this case, the dispersity of both the portland cement component and the expanding component is important.
Thus, for the expanding components of calcium aluminates, the greatest expansion effect, combined with the high strength of the stone, is due to fractions of these minerals of 45-63 μm in size. Under such conditions, the formation of large ettringite crystals in the hardening stone occurs gradually during the period when the finely ground Portland cement component, due to rapid hydration, acquires an increased strength. The crystallization of ettringite under these conditions leads to an expansion of the system.

4. Conclusion
Thus, it can be concluded that to obtain expanding cements with a large expansion effect, the expanding additives containing calcium aluminate minerals must be ground in such a way that these minerals are contained mainly in fractions of 45-63 μm. For obtaining a durable, strong cement stone, the Portland cement component must be ground to a specific surface of at least 300 m²/kg. In order to obtain an additive of the aluminous slag with CA content in fractions of less than 45 μm, it
is necessary to grind the slag to a specific surface of 400 m²/kg.

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