Abnormal Mineral Formation in Aluminate Cement Stone

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Abstract. The paper describes the results of the study on the correlation between the strength properties and the concentration of calcium aluminate hydrates during long hardening of aluminate cement in aqueous medium. It shows the abnormal nature of hydrate mineral formation in the system of hardening aluminate cement.

Keywords: Aluminate cement · Calcium aluminate hydrates

1 Introduction

The properties of any composite materials directly depend on the characteristics of their base matrix. This also fully applies to composites based on binding agents with various composition, which quality indicators are set as a result of system hardening (Strokova et al. 2015; Kozhukhova et al. 2016; Nelyubova et al. 2017; Dmitrieva et al. 2018; Shulpekova et al. 2018). In this regard the study of phase formation in such systems seems quite relevant.

Construction materials based on aluminate cements have different properties than those based on portland cement. In particular, they are characterized by a high thermal stability and resistance to acid corrosion (Kuznetsova 1986; Kuznetsova et al. 1989).

The calcium aluminate hydrates, which are formed through hardening of aluminate cement, represent the following phases: CAH_{10} , C_2AH_8 , C_3AH_6 , AH_3 (gibbsite). From this point onward the ‘cement’ notation in formulas of chemical compounds will be used ($\text{C} - \text{CaO}$, $\text{A} - \text{Al}_2\text{O}_3$, $\text{H} - \text{OH}$).

The hydrate mineral formation in aluminate cements is characterized by the dependence of C-A-H phases on temperature. At a temperature below 15 °C the main reaction-active CA phase is hydrated according to the following scheme: $\text{CA} + 10\text{H} \rightarrow \text{CAH}_{10}$. At room temperature the C-A-H is formed according to the following scheme: $2\text{CA} + 11\text{H} \rightarrow \text{C}_2\text{AH}_8 + \text{AH}_3$. At higher temperatures (above 28 °C) the metastable hydrates CAH_{10} and C_2AH_8 will transform into stable hydrate C_3AH_6 according to the following equations: $3\text{CAH}_{10} \rightarrow \text{C}_3\text{AH}_6 + 2\text{AH}_3 + 18\text{H}$ and $3\text{C}_2\text{AH}_8 \rightarrow 2\text{C}_3\text{AH}_6 + \text{AH}_3 + 9\text{H}$ (Rashid et al. 1994).

Thus, according to insights into hydration of aluminate cements, the hydrate phases during long hydration shall be presented as follows: $\text{C}_3\text{AH}_6 + \text{AH}_3$.

The paper provides the results of hydration hardening of aluminate cement with long-term exposure to aqueous medium, which contradict the above ideas.

2 Materials and Methods

The aluminate cement GTS-50 produced by JSC Pashiysky Cement and Metallurgical Plant (Perm Region, Russian Federation) was used in the study as a binding agent. Cubes with a 2 cm side are formed from cement paste (water-cement ratio equal 0.3). After hardening on the 1st day the samples were taken from a mold and placed into the desiccator with 100% air humidity. After 28 days the samples were dried in a drying cabinet at 80 °C and placed in water, from which they were taken for further study in 1, 2, 3 and 4 months.

The study methods included the compression strength test on PGM-100 MG4 press (average against three measurements) and the quantitative full-scale XRF to define potential changes in mineral composition.

The diffraction spectra of samples were obtained via the ARL X'TRA diffractometer (λ_{Cu}) in the range of diffraction angles $2\theta^\circ = 4-64$, step angle – 0.02°. The diffraction spectra were smoothened prior to treatment.

The quantitative full-scale XRF was carried out via the DDM v.1.95e software for a difference curve derivative (Solovyov 2004).

3 Results and Discussion

According to XRF, the mineral composition of GTS-50 cement is presented by the following crystal formations (wt.%): CA (28.3), CA₂ (9.2), C₁₂A₇ (1.4), akermanite-gelenite (15.6), β -C₂S (10.0), α' -C₂S (10.2), wollastonite 2M (7.6), dolomite (10.6), perovskite (7.2).

X-ray diagnostics of mineral phases in hydrated samples of aluminate cement indicated the presence of CAH₁₀, C₂AH₈, C₃AH₆, AH₃, akermanite-gelenite, β -C₂S, α' -C₂S, wollastonite 2M, dolomite and perovskite.

Due to lack of C₂AH₈ structural model, the quantitative XRF was combined with the approach suggested by Cuberos et al. (2009).

As data show (Table 1), for nearly 5 months (28 days in damp atmosphere and 4 months in water) CAH₁₀ remains the main hydrate phase. The reduction of CAH₁₀ concentration on the 2nd month in water, which correlates well with the increase of crystal gibbsite (AH₃), does not lead to the similar increase of C₃AH₆. Most likely it is caused by the formation of C₃AH₆ in its cryptocrystalline state.

The abnormal nature of hydrate mineral formation includes the increase of CAH₁₀ metastable hydrate concentration starting from the 3rd month. At the same time the temporal change of C₃AH₆ concentration coincides well with the change of compression strength of the studied samples (Fig. 1).

Table 1. Concentration of hydrate phases (wt. %)

Time in aqueous medium, months	CAH ₁₀	C ₂ AH ₈	C ₃ AH ₆	AH ₃
0	18.8	3.5	3.1	2.0
1	26.5	4.4	8.2	5.9
2	9.0	2.1	6.8	25.1
3	33.5	3.5	4.7	6.3
4	37.2	5.8	5.6	3.0

Fig. 1. Compression strength of aluminate cement stone and CAH₁₀ concentration depending on time

4 Conclusions

The paper describes the results of the study on the correlation between the strength properties and the concentration of calcium aluminate hydrates during long hardening of aluminate cement in aqueous medium. At present it is impossible to give unambiguous interpretation of the observed abnormal compositional changes of hydrate phases of hydrated aluminate cement during long hardening.

Acknowledgements. The study is carried out in the framework of the State Task of the RF Ministry of Education and Science No. 7.872.2017/4.6. Development of principles for the design of ecologically positive composite materials with prolonged bioresistance 2017–2019.

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