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Physics

RESIDUAL STRESS ON ETTRINGITE CRYSTALS IN EXPANSIVE CEMENT PASTE

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Applying the X-ray diffraction technique, we have investigated the dependence of the residual stress components on ettringite crystals in expansive cement paste depending on the content of ye'elimite admixture. The results of above stress analysis were used to analyze how the shrinkage-compensating effect and the content of ye'elimite admixture are correlated with each other.

Keywords: expansive cement paste, ye'elimite admixture, ettringite, residual stress.

Introduction. Concrete materials are composites that comprise two main constituent parts: aggregate particles and cement paste. Expansive cement paste is a constituent part of the so-called expansive or Type K shrinkage-compensating concretes [1]. In comparison to ordinary Portland cement pastes, the expansive cement pastes exhibit much lesser porosity and cracking and, as a result of these characteristics, a higher resistance against humidity penetration. Therefore, a broad variety of concrete-made constructions (floor slabs, pavements, roofs, water storage tanks, reactors, pumping stations, etc.), exploitation of which takes place in aqueous environment, are preferentially prepared with the use of above expansive concretes. The results reported in [2] provide an evidence that a low level of cracking in expansive cement pastes is achieved as a result of formation, in the cement paste matrix, of "ye'elimite-ettringite" clusters. During formation process, these clusters are capable to spread out the contacting parts of cement paste matrix and thereby to suppress the volumetric contraction of cement paste resultant from drying shrinkage. This phenomenon is called shrinkage-compensating effect and effectively lowers the risk of a high degree of cracking that could be caused by the drying shrinkage. In expansive cement pastes, strong mechanical interaction of above "ye'elimite-ettringite" clusters with cement paste matrix presumably results in a high level of the mechanical stress on Ettringite crystals. The level of this stress along with its character (tensile or compressive) could serve as a quantitative measure of the shrinkage-compensating effect and the risk of cracking in the cement paste. Measurement of the stress on Ettringite crystals, comprised in expansive cement paste, is of technological interest and may facilitate the optimization of the phase composition of such a type cement paste in terms of achieving of the shrinkage-compensating effect. Literature contains no data on such a type investigation.

In this study, by applying the X-ray diffraction (XRD) technique, we investigated the dependence of the stress components on Ettringite crystals in expansive cement paste on the content of ye'elimite admixture. The results of above stress analysis were used to analyze

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how the shrinkage-compensating effect and the content of ye'elimite admixture are correlated with each other.

Experiment and Spectral Analysis. For preparation of samples of expansive cement paste, the blends of Type II Portland cement with commercial powder of ye'elimite admixture (with particles of near-spherical shape and sizes in the range ≈0.5–2 μm) have been used. From above specified type of blends, according to a standard procedure five flat cylindrically shaped cement paste samples were prepared: without admixture, with 3, 6, 9 and 12%, relative weight contents of admixture; water-to-cement mass ratio of 0.35; diameter of 2.5 *cm* and thickness of 0.5 *cm*. Age of samples at the time of XRD measurements was of about one year, at which the mechanical stress distribution in a cement paste is stabilized. For the sake of further identification, the notations of samples in terms of the ye'elimite admixture content are specified in Table. The CuK$_\alpha$ XRD spectra were recorded on a powder diffractometer DRON-3 with Bragg–Brentano geometry in $\theta - 2\theta$ mode within a 2θ angular range 4.5–70°. The recorded XRD spectra are presented in Fig. 1.

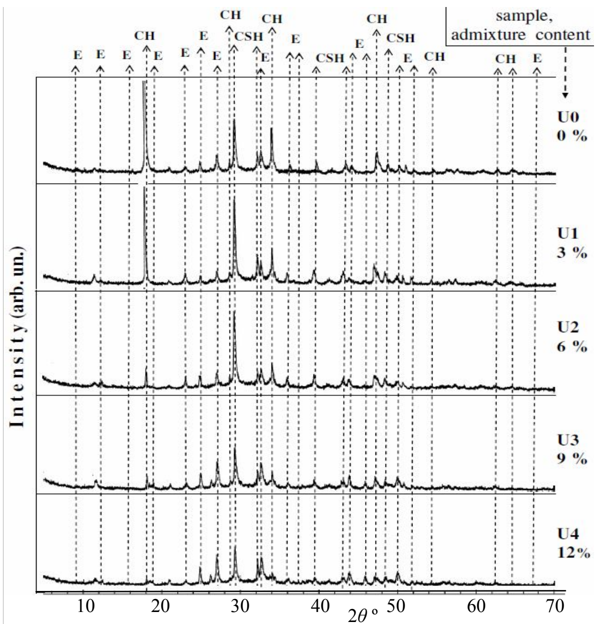

Fig. 1. The CuK$_\alpha$ XRD spectra recorded from cement paste samples. Identified diffraction peaks belong to main hydration phases: ettringite (E), calcium hydroxide (CH), and calcium-silicate-hydrate (CSH).

Sample notations, relative weight content (RWC) of ye'elimite admixture, and a and c lattice parameters of ettringite

Sample	adm. RWC, %	*a*, Å	*c*, Å
U0	0	11.242	21.450
U1	3	11.223	21.506
U2	6	11.211	21.516
U3	9	11.205	21.493
U4	12	11.204	21.488

The qualitative phase analysis and refinement of recorded XRD spectra were conducted with the use of a special computer program developed by us on the basis of the program Mathematica 5.0 (Wolfram Research) [3]. The diffraction spectra of all samples in Fig. 1 show formation of the three main constituent phases (hydration products): calcium hydroxide ($Ca(OH)_2$), Ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$), and calcium-silicate-hydrate ($(CaO)_x(SiO_2)(H_2O)_y$). The indices (not shown in Fig. 1) of reflections recorded from above indicated phases were identified according to powder diffraction JCPDS files №№ 4–733, 41–1451 and 18–1206 respectively. The crystal lattice of Ettringite is trigonal. The data determined for true (strained) a and c lattice parameters of the Ettringite along the crystallographic a- and c-axes respectively are listed in Table.

Theoretical Model and Discussion. It was established in a reliable way [2] that in such a type expansive cement pastes investigated in this study, the Ettringite phase is predominantly comprised in "ye'elimite-ettringite" clusters that are formed via heterogeneous precipitation of ordered Ettringite crystals on the surface of ye'elimite particles. The cross-section of such a type individual "ye'elimite-ettringite" cluster that is composed of a residual (partially hydrated) ye'elimite particle of a spherical shape covered with a compact near-spherical shell of Ettringite (core-shell model) is schematically shown in Fig. 2. This shell is composed of ordered Ettringite crystals that completely cover the surface of ye'elimite particle and are oriented with their crystallographic c-axis in radial directions. The mentioned crystals have a rod-like shape prolonged along the crystallographic c-axis.

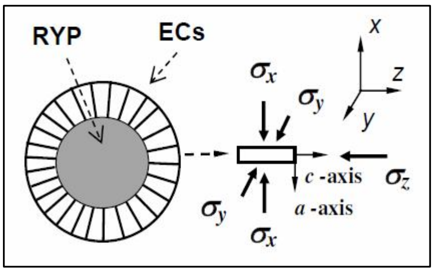

Fig. 2. Modeled "ye'elimite-ettringite" cluster composed of a residual ye'elimite particle (RYP) and a shell of ettringite crystals (ECs).

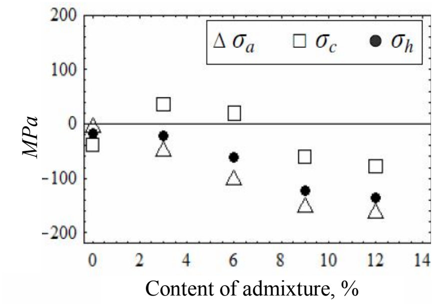

Fig. 3. Dependence of the stress components on ettringite crystals on the relative content of ye'elimite admixture.

In Fig. 2, the inset on the right-hand side shows the physical coordinate system xyz introduced for an individual Ettringite crystal comprised in the "ye'elimite-ettringite" cluster for identification of the strain and stress components (x- and z-axes are parallel to crystallographic a- and c-axes respectively). From symmetry considerations, it may be assumed that the normal stress components on ettringite crystals along the x- and y-axes are equal, $\sigma_x = \sigma_y \equiv \sigma_a$ (we introduce more convenient notation also for σ_z stress component, $\sigma_z = \sigma_c$). With the use of unstrained lattice parameters ($a_0 = 11.240\,\AA, c_0 = 21.468\,\AA$), stiffness constants of Ettringite [4], and data obtained for a and c lattice parameters (see Table), the generalized Hook's law results in dependence for stress components on Ettringite crystals presented in Fig. 3. The plots in Fig. 3 show that: (i) the compressive stress components (negative sign) are dominating for all samples and this is well expressed through the compressive mean hydrostatic stress σ_h (in our case, $\sigma_h = (2\sigma_a + \sigma_c)/3$); (ii) with increase of the admixture content (i.e. the content of "ye'elimite-ettringite" clusters), the level of stress on Ettringite crystals increases. The σ_a stress components (i.e. σ_x and σ_y components) in the "ye'elimite-ettringite" cluster are self-equilibrated (see Fig. 2). The σ_c stress component that varies in range from $+37$ to -77 *MPa* (Fig. 3) quantifies the mechanical interaction of "ye'elimite-ettringite" clusters with cement paste matrix and is more important from technological point of view (see Fig. 1).

Conclusion. In Fig. 3 the plot for stress component shows, that for samples U1 and U2 (at 3 and 6% admixture contents respectively) σ_c stress is tensile (positive sign) and, hence, no shrinkage-compensating effect (see Fig. 1) is expected at above contents of the ye'elimite admixture. For samples U3 and U4 (at 9 and 12% admixture contents respectively), the σ_c stress on Ettringite is compressive. This means that at 9 and 12% admixture contents the stress that is exerted from "ye'elimite-ettringite" clusters on cement paste matrix is tensile thereby resulting in a shrinkage-compensating effect.

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R E F E R E N C E S

1. **Mehta P.K., Monteiro P.J.M.** Concrete Microstructure, Properties and Materials. NY: McGraw-Hill, 2006.
2. **Cohen M.D.** Modeling of Expansive Cements. // Cem. Concr. Res., 1983, v. 13, p. 519–528.
3. Wolfram Research, Inc. Mathematica, Version 5.0, Wolfram Research, Inc. Champaign, IL, 2003.
4. **Speziale S., Jiang F., Mao Z., Monteiro P.J.M., Wenk H.R., Duffy T.S., Schilling F.R.** Single-Crystal Elastic Constants of Natural Ettringite. // Cem. Concr. Res., 2008, v. 38, p. 885–889.