SEM investigation of microstructures in hydration products of portland cement

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Abstract Portland cement is the one of the main ingredients in the manufacture of many building materials include concrete composites. The phase composition of hydration products is controlled by means of XRD and DTA/TG analysis. Observations of phase changes and microstructure of maturing cement pastes can also be observed using scanning electron microscopy (SEM) techniques combined with chemical analyzes in microareas (EDS analysis). Hydrating in time cement paste is composed mainly of hydrated silicates of calcium so called C-S-H-phase accompanied with a calcium hydroxide (portlandite) and hydration products of calcium aluminate i.e. ettringite. SEM analysis of changes in the morphology and microstructure of cement pastes allow to track the hydration progress observed mainly by changes in the C-S-H phase. The initial stages of hydration of this phase is characterized by radial concentration of fibers or needles, often narrowed at the ends. This fibers grow from the surface of the cement grains. The increase in the degree of C-S-H structure orientation is shown by formation of fibers lattice, sometimes three-dimensional plates so called "honeycomb", which is transformed into the form of a closely-packed, isometric grains. In addition, besides C-S-H cement phase investigation, scanning electron microscopy can also be applied to observation of the crystals formation of tobermorite, ettringite and relicts of portlandite, that often can't be detected by XRD and DTA/TG due to their small amount in mineral composition of concrete.

Key words: hydration, Portland cement, microstructure, C-S-H

1. INTRODUCTION

Knowledge of the basic chemical reactions and physical phenomena as well as microstructures of the hardened mass formed by the hydration and hydrolysis of cement is one of the basic conditions for the optimal use of cement in building materials. Predicting the cement properties on the basis of its chemical and mineral composition is essential for its use [1]. No fully define mechanism of the cement hydration and hydrolysis processes does not allow for explanation anomalies in the process of binding and hardening. Strength of hardened cement paste is a function of: mineral and chemical composition as well as has a direct impact on the structure that determines the strength of the crystalline lattice and tightness of mass. Therefore, they are needed studies of crystallizing mineral phases changes (hydration products) and observations of the reconstruction of the microstructure of maturing cement paste [2]. Method used to determine this type of phenomena may be scanning electron microscopy combined with the chemical composition analysis (SEM-EDS).

Quantitatively, the main component of the most cement paste and at the same time the most important factor affecting the strength of the hardening mass is phase denoted by the symbol C-S-H - often called phase of tobermorite-like or tobermorite because its chemical composition is similar to natural mineral - tobermorite ($5CaO \cdot 6SiO_2 \cdot 5H_2O$). This phase in general is the entire group of compounds of a hydrated calcium silicate with varying degrees of crystallization and differential alkalinity. The hydration and hardening mechanisms of cement is based on density of C-S-H gel combined with the addition of water and crystallization of ettringite and calcium hydroxide intergrowths forming and filling pores in hardening cement paste. Knowledge of the mineral composition and structure during maturation cement paste allow to predict its technical properties [3].

2. MATERIALS

The hydration process of cement pastes were observed on the basis of mortars samples prepared in accordance with PN-EN 196-1: 1996. To this aim bars about size of 40x40x160 mm were done, the composition of which was as follows: Portland cement CEM I 42.5 R (450 g), standard sand (1350 g), water (225 g). Thus formed samples were aged in water and subjected to observation of changes in the phase composition with SEM after 2, 28 and 90 days of maturing.

3. METHODS

The chemical and mineral composition of products hydration were determined by using a scanning electron microscope SEM–EDS and X-ray method. The morphological forms and the chemical composition of the main mineral components were analysing by means of a scanning electron microscope (SEM) FEI Quanta 250 FEG equipped with a system of chemical composition analysis based on energy dispersive X-ray- EDS of EDAX company [4].

The mineral composition was determined via powder X-ray diffraction (XRD) method using a Philips X'pert APD diffractometer (with a PW 3020 goniometer), Cu lamp, and a graphite monochromator. The analysis was performed within the angle range of 5–65 2 theta. Philips X'Pert Highscore software was used to process the diffraction data. The identification of mineral phases was based on the PDF-2 release 2010 database formalized by the ICDD [5].

4. RESULTS AND DISCUSSION

The hydration process of cement and development of cement paste structure can be presented in three stages, depicted in Figure 4.1[6].

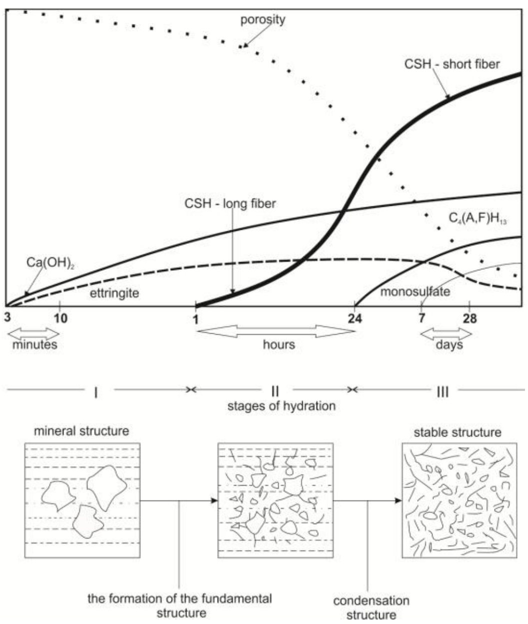


Fig. 4.1 Formation of the of hydration products and the creation of cement paste structure.

In the first stage of cement hydration the calcium hydroxide (portlandite) is separated. Its formation is a result of the hydrolysis of tricalcium (C_3S) and dicalcium (C_2S) silicates, what has a place after a few hours of mixing Portland cement with water. The resulting calcium hydroxide at solid phase of paste is present primarily in the form of portlandite. It creates massive, hexagonal crystals about size of 40 microns (Fig. 4.2), which aggregates taking the form of column (Fig. 4.3). The morphology of the resulting portlandite crystals is dependent on available free space for crystallization (w/c), the type of admixtures and additives [7]. Portlandite in hydratated paste of Portland cement is up to 25% by volume of solid phase.

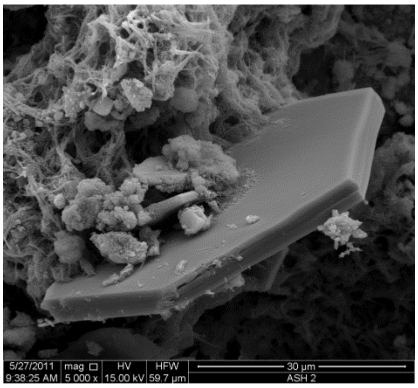


Fig.4.2 Hexagonal plate of portlandite

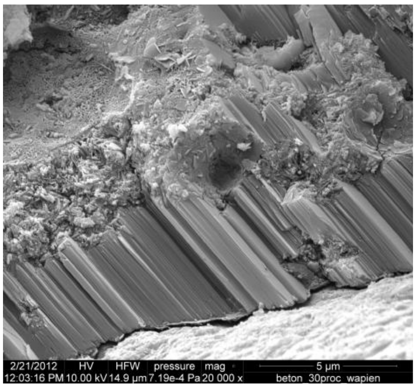


Fig.4.3 Column aggregate of portlandite

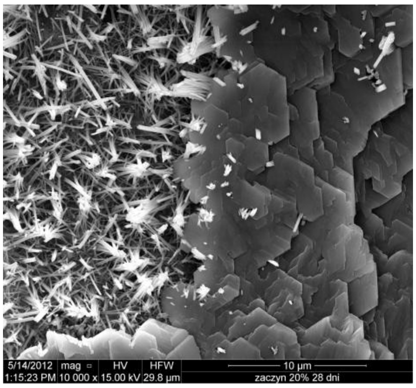


Fig.4.4 Needle form of C-S-H and plates of portlandite

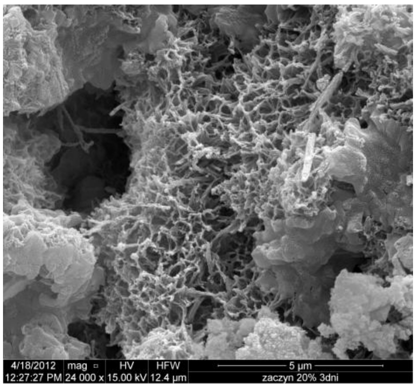
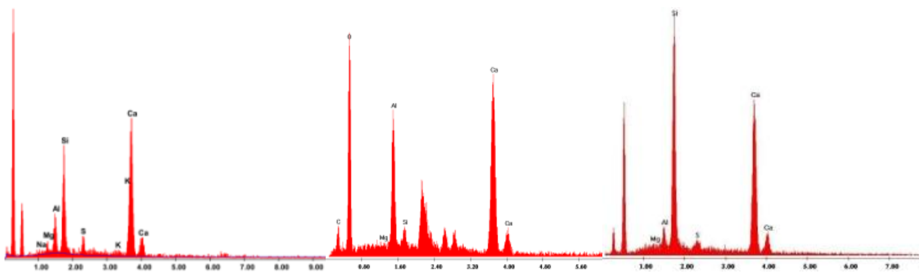


Fig.4.5 Transformations of portlandite into solid forms, and needle forms of C-S-H into "honeycomb" structure

In the second period of hydration of cement paste the first forms of hydrated calcium silicates are created. Their quantitative contents in completely hydrated paste of Portland cement is between 50-60% of the volume of all solid phases.

Proposed by Diamond [9] model of the morphological distribution of C-S-H gel in cement paste distinguish form of fiber from size of 2 microns - characteristic for the early stages of hydration (Fig. 4.4), which goes in the form of a mesh, so-called "honeycomb" (Fig. 4.5). Subsequent stages of maturing the paste constituted forms becoming more and more massive consisting of a packed and interspersed with each other thin crystals (so called foils), up to the formless and massive gel characteristic for old pastes.

In the third period of paste hydration occurs pore filling of hardening cement paste by short fibers or lamellar phases of hydrated calcium silicates. The duration of this stages is a period of several days to several months, and covers almost complete hydration of the cement. A characteristic feature of this phase is transformation of calcium aluminate trisulfate $3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32\ H_2O$ to calcium aluminate monosulfate $3CaO{\cdot}Al_2O_3{\cdot}CaSO_4{\cdot}12\ H_2O$. Ettringite crystals and AFt phases typically form an elongated crystals about circular habit similar to the needle (Figure 4.7.), while tobermorite create lamellar aggregates (Fig. 4.8). The spectra of the chemical composition of the main phase formed during the maturation of the cement paste is shown in figure 4.6.



EDS of C-S-H phase EDS of portlandite EDS of C-S-H honeycomb

Fig.4.6 Mineral phases occurring in maturing cement paste.

Scanning microscope observations also allow to identify the minerals forming the relics of clinker for example periclase that the presence in the paste in the form of large crystals unfavorably affects the stability of the structure of maturing cement pastes (Fig. 4.9). These types of mineral phases due to their trace amounts in tested samples are not recognizable by diffraction (XRD), or thermal (TG-DTA) methods.

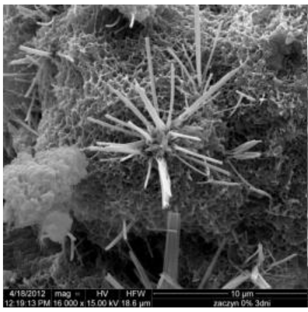


Fig.4.7Needle crystals of ettringite

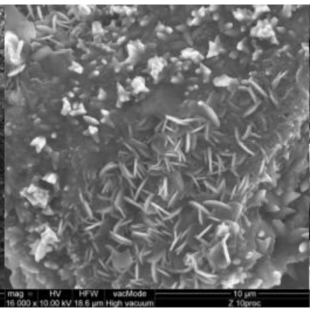


Fig.4.8 plate crystals of tobemorite

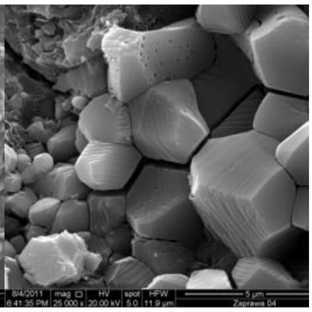


Fig.4.9 Octahedral forms of periclase

5. CONCLUSION

The presented results obtained by means of scanning electron microscopy with chemical microanalysis (SEM-EDS) indicate the practical opportunity to observe changes in the microstructure of maturing cement pastes or concrete. Based on changes in the morphology of the main phases arising during the hydration of cement paste it is possible to predict the properties of cement mortars and concretes.

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References

1. HansenT. C., Physical structure of hardened cement paste. A classical approach Materials and Structures, Volume 19, Issue 6, pp 423-436 (1986)
2. Arandigoyen M., AlvarezJ.I., Pore structure and mechanical properties of cement–lime mortars. Cement and Concrete Research Volume 37, Issue 5, Pages 767–775 (2007)
3. Kurdowski W., Chemia cementu i betonu. pp. 1-727 Wyd. PWN, (2010)
4. Wdowin M., Franus M., Panek R., Bandura L., Franus W., The conversion technology of fly ash into zeolites. Clean Technologies and Environmental Policy.16:1217-1223 (2014)
5. Franus W, Dudek K., Clay minerals and clinoptilolite of Variegated Shales Formation of the Skole Unit. Polish Fly Asch Carpathians. Geologica Carpathica, vol. 50, p. 23-24 (1999)
6. Locher R., Richartz W., Study of hydration mechanism of cement. Symp. Chem. Cement Moscow, Moscow, Russia (1974)
7. Mehta P.K., Concrete, structure, properties and materials. Englewood Cliffs, NJ, Prentice-Hall, pp. 450, (1986)
9. Diamond S., The Microstructures of cement paste in concrete, 8th ICCCC. Vol. 1 pp. 113-121, Rio de Janeiro (1986)