Effect of mixing water magnetic activation cycle on cement stone structure

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Abstract. The paper presents results of investigations of hydration processes and structure formation of the cement paste matrix mixed with water activated by magneto static field using water treatment cycle technology. It is shown that crystallization of phases occurs in the cement-water system at different rates, and phase redistribution in the structure of the cement paste matrix is described before and after magnetic activation of mixing water. Also, modeling of the cement-water system and calculations of amorphous and crystalline phases using the Rietveld refinement method before and after magnetic activation show that strength properties of the cement paste matrix depend not only on quantitative but also qualitative relationship between phases.

1. Introduction

Today, consumer’s market of cement-based concretes is one of the most attractive markets of building materials. Therefore development of functional cement-based materials is important to improve their functional performance and lowering material consumption.

Currently there is a broad range of techniques that allow purposefully controlling the structure and properties of cement systems. One of these techniques is activation of mixing water using external physical effects [1-5]. However, in spite of this perspective technique, it has not been widely developed within the concrete technology due to the absence of a safe theory that would predict the development of structureization processes in hardening cementitious systems. This work is the first to focus on fine interaction effects between water and cement including a dissolution consistency of existed and neoformed phases before and after activation; the ratio between amorphous and crystalline phases which form the structure of the cement paste matrix, etc.

This paper mainly focuses on quantification of the paste matrix phase content, detection of its structurization properties obtained from cement paste mixed with activated water using the treatment cycle technology.
2. Experimental procedure

Cement paste matrix used for this experiment was prepared from the type M 500 Portland cement-based paste mixed with water activated by a magnetostatic field with 40 mT magnetic density with the use of water treatment cycle technology. Magnetic activation included 15 and 25 cycles. Flat-surface specimens having 20×20×20 mm size were selected for this experiment.

XRD analysis was carried out by DRON-4-07 diffractometer which was modified for digital signal processing. Measurements were conducted using copper radiation (K) and Bragg-Brentano X-ray optical scheme. Specifications for the DRON-4-07 included 0.02° scanning step; 17 – 92° range for angles to be scanned.

The preliminary stage has the task to identify the structure of the cement paste matrix referring to the Crystallography Open Database (COD) [6]. Detected reference phases having high figures of merit (FOM) [4] are presented in Table 1 which also gives numbers, chemical formulas, lattice parameters, and space groups and types.

| COD number | Chemical formula | FOM | Space group and type |
|------------|------------------|-----|---------------------|
| 100-1769   | H2O2Ca           |     | P-3m, trigonal      |
| 120-0010   | O20Al7.04Ca8Fe4.96 |     | Ima2, orthorhombic |
| 900-0097   | C6O16Mg6         |     | R-3C, trigonal      |
| 900-0966   | C6O16Ca6         |     | R-3C, trigonal      |
| 900-3354   | O20Al8.93Ca8Fe3.07 |     | Ima2, orthorhombic |
| 900-8367   | O179.98Si36Ca108 |     | Cm, monoclinic      |
| 901-1411   | O64Al28Ca24      |     | I-43d, cubic        |
| 901-2682   | O24Si6Ca9        |     | Pmmm, orthorhombic  |
| 901-2792   | O16Si2Ca6        |     | P2/m, monoclinic    |

The quantitative phase analysis (QPA) of phase content by the Rietveld refinement method is used to determine intensities of each reference phase presented in Table 1 [7, 8]. As a result, the ratio between the theoretical and the experimental intensities of diffraction maxima is refined. The intensity reproducibility is detected by convergence criteria [7].

In these terms, the structural, profile, and experimental parameters involved in theoretical intensity are compared and refined using the non-linear least-square method. The QPA by the Rietveld method is carried out using the software Reflex [9]. In reference phases the following parameters are refined: spatial atom distribution in crystal lattices through redistribution of atomic relative coordinates; lattice;
reflections; zero shifts; background intensity, etc. Figures 1-3 contain plots of theoretical and experimental XRD histograms of phases and integrated intensity.

Figure 1. QPA of cement paste matrix in its original state: a) XRD histograms: 1 – theoretical, 2 – experimental, 3 – difference; b) theoretical XRD histograms of phases: 1-6\([\text{CaO}\times\text{CO}_2]\); 2 - 36\([\text{CaO}\times\text{SiO}_2]\); 3 - 6\([\text{CaO}\times4\text{SiO}_{2.5}]\); 4 - \(\text{CaO}\times\text{H}_2\text{O}\); 5 - 2\([4\text{CaO}\times\text{Al}_2\text{O}_3\times\text{Fe}_2\text{O}_3]\).

Figure 2. QPA of cement paste matrix at 15-cycle magnetic activation of mixing water: a) XRD histograms: 1 – theoretical, 2 – experimental, 3 – difference; b) theoretical XRD histograms of phases: 1 - 4\([6(\text{CaO})\times3(\text{Al}_2\text{O}_3)\times\text{AlO}]\); 2 - 6\([\text{CaO}\times\text{CO}_2]\); 3 - 36\([\text{CaO}\times\text{SiO}_2]\).
Figure 3. QPA of cement paste matrix at 25-cycle magnetic activation of mixing water: a) XRD histograms: 1 – theoretical, 2 – experimental, 3 – difference; b) theoretical XRD histograms of phases: 1 - 6[CaO×CO₂], 2 - 36[3CaO×SiO₂]; 3 - 6[CaO×4SiO₂₅], 4 - CaO×H₂O; 5 - 2[4CaO×Al₂O₃×Fe₂O₃].

As shown in Figures 1-3, experimental XRD patterns are full of both intensive and weak overlapping peaks in crystalline phases. Also, the cement paste matrix contains a large amount of the amorphous phase. The quantitative phase analysis shows the substantial convergence between integrated theoretical and experimental intensities achieved for the cement paste matrix (Figures 1-3a). Two independent convergence criteria $R_{wp}$ and $R_p$ [7, 9] obtained by different ways are calculated for the original state of the paste matrix (6.46 and 4.92%); the paste matrix at 15-cycle magnetic activation (8.51 and 6.55%); and the paste matrix at 25-cycle magnetic activation of mixing water (6.92 and 5.41%) shown in Figures 1а, 2a, and 3a respectively. The difference between theoretical and experimental values of integrated intensities is insignificant. In this work, the QPA of the cement paste matrix by the Rietveld method allows determination of phases which contribute most to the integrated intensity at refinement of the above stated parameters. The QPA results and a list of major phases in the cement paste matrix are presented in Tables 2-4.

Table 2. Properties of cement paste matrix in its original state.

| COD number | Chemical formula | Intensity (%) | FOM | Space group and type |
|------------|-----------------|---------------|-----|---------------------|
| 900-8367   | 36[3CaO×SiO₂]  | 49.64         | 3.3108 | 0.7041 | 1.8510 | Cm, monoclinic |
| 100-1769   | CaO×H₂O        | 17.02         | 0.3622 | 0.3622 | 0.4952 | P-3m1, trigonal |
| 901-2792   | 6[CaO×4SiO₂₅]  | 15.05         | 0.5489 | 0.67446 | 0.9226 | P2/m, monoclinic |
| 900-0966   | 6[CaO×CO₂]     | 10.90         | 0.4991 | 0.4991 | 1.7162 | R-3C, trigonal |
| 120-0010   | 2[4CaO×Al₂O₃×Fe₂O₃] | 5.89      | 0.5562 | 1.4517 | 0.5371 | Ima2, orthorhombic |

Table 3. Properties of cement paste matrix after 15-cycle magnetic activation of mixing water.

| COD number | Chemical formula | Intensity (%) | FOM | Space group and type |
|------------|-----------------|---------------|-----|---------------------|
| 901-1411   | 4[6CaO×3(Al₂O₃)×AlO] | 51.03 | 1.1970 | 1.1970 | 1.1970 | I-43d, cubic |
| 900-0966   | 6[CaO×CO₂]     | 25.10         | 0.4988 | 0.4988 | 1.7061 | R-3c, trigonal |
| 900-8367   | 36[3CaO×SiO₂]  | 21.61         | 3.3083 | 0.7027 | 1.8499 | Cm, monoclinic |
The QPA results show that the experimental XRD histogram of the original state of the paste matrix displays the superposition of contributions to the intensity from such phases as \(3\text{CaO} \times \text{SiO}_2\), \(\text{CaO} \times \text{H}_2\text{O}\) (calcium hydroxide), \([\text{CaO} \times 4\text{SiO}_2\times 3\text{H}_2\text{O}]\) (larnite), \([\text{CaO} \times \text{CO}_2]\) (calcite), \([\text{4CaO} \times \text{Al}_2\text{O}_3\times \text{Fe}_2\text{O}_3]\) (tetracalciumaluminoferrite). As it follows from Table 1, the integrated intensity of these phases is close to unity and equals to ~0.985 that proves rather a high accuracy of phase quantification for the cement paste matrix. After 15 cycles of magnetic activation of mixing water (Table 3), the integrated intensity in the paste matrix comprises contributions from \(6\text{CaO} \times 3(\text{Al}_2\text{O}_3)\times \text{AlO}\), \(\text{CaO} \times \text{CO}_2\), and \(3\text{CaO} \times \text{SiO}_2\) phases, while after 25 cycles (Table 4) it comprises contributions from \(3\text{CaO} \times \text{SiO}_2\), \(\text{CaO} \times 4\text{SiO}_2\times 5\), \(\text{CaO} \times \text{H}_2\text{O}\), \(\text{CaO} \times \text{CO}_2\) phases. The integrated intensity as shown in Table 4 is close to unity and equals to ~0.991. Thus, the QPA results show a high reproducibility and validity of theoretical and experimental data.

The QPA technique is used to detect parameters of the unit cell in calculating the theoretical intensity for each phase allowing for reference values. Refined phase parameters are given in Tables 2-4. Atomic relative coordinates in phase lattices are refined also, however, they are not given herein due to large data volumes.

The degree of crystallinity which coincides with the relative superposition of refined intensities in crystalline phases is described by experimental XRD histograms. It is stated that in the paste matrix the crystalline phase is 0.39 in the original state, 0.39 after 15-cycle activation, and 0.46 after 25-cycle activation of mixing water. Crystallinity grows with the increase of the number of cycles. The amorphous phase is characterized by a short-range order of atom arrangement, while translation symmetry is not observed. Diffraction patterns of amorphous phases demonstrate spread reflections of weak intensity which provide the main contribution to the background intensity.

The QPA results show that magnetic activation of mixing water has a strong effect on hardening of the paste matrix (see Tables 2-4). It is reflected, first of all, in the list of major phases of the paste matrix which are present in its original state, and secondly, in a change of their relative amount. In the original state, \(3\text{CaO} \times \text{SiO}_2\) (alite) is the major phase for the paste matrix after 25 cycles of water treatment. At the same time, after 15 cycles of water treatment, \(6\text{CaO} \times 3(\text{Al}_2\text{O}_3)\times \text{AlO}\) is the dominant intermediate phase. It is possible to assume that at 15-cycle magnetic activation the intensity of crystallization of \(3\text{CaO} \times \text{SiO}_2\) phase significantly decreases, while at 25-cycle activation it increases due to a suppression of chemical reactions which produce \(\text{CaO} \times \text{H}_2\text{O}\), \(\text{CaO} \times 4\text{SiO}_2\times 5\), and \(\text{CaO} \times \text{CO}_2\) phases. The amount decreases in the integrated intensity (see Tables 2-4). Also, one can suppose that activated water suppresses crystallization of \(4\text{CaO} \times \text{Al}_2\text{O}_3\times \text{Fe}_2\text{O}_3\) phase which is present only in the original state. The different activity of water has the different effect on crystallization of \(\text{CaO} \times \text{CO}_2\) and \(\text{CaO} \times 4\text{SiO}_2\times 5\) phases. The amount of the first phase increases after 15 cycles and decreases after 25 cycles of water activation. Crystallization of \(\text{CaO} \times 4\text{SiO}_2\times 5\) phase is completely suppressed after 15 cycles and partially suppressed after 25 cycles of water activation.

A significant redistribution of the amount of crystallized phases as well as formation of new phases in the course of the hardening process results in a variation of mechanical properties of the cement paste matrix. Data obtained on the structure of unit cells of described phases are the basis for further investigations, in particular, theoretical calculations of cell energy, elastic constants, simulation of amorphous phases with a view to predict strength properties of the cement paste matrix and their experimental testing.
3. Conclusions

The quantitative phase analysis of the cement paste matrix by the Rietveld method showed that magnetic activation of water significantly affects the structurization processes in hardening cementitious systems. First of all, it is connected with the different intensity of crystallization of different phases and, as a consequence, a formation of phases differ from the original state, and secondly, with phase redistribution. It was stated that in the paste matrix the amount of amorphous phase is rather considerable. At the same time, this amount decreased with the increase of the number of cycles of magnetic activation.

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