Phase analysis of hydrated Portland cement

Yu A Abzaev, A I Gnyrya, S V Korobkov and K S Gauss
Tomsk State University of Architecture and Building, Tomsk, Russian Federation

E-mail: korobkov_1973@mail.ru

Abstract. The paper studies the quantitative phase composition in cement paste using the Rietveld refinement method. Investigations are carried out within 0–67 h time period at 40, 50 and 70 °C. It is found that tobermorite, deliate and $mCa_nH_{20}Si_2$ are major phases in cement phase, where $m = 5$ or 3, and $n = 3$ or 1. The phase composition is determined by the contribution from estimated peak intensities to the integrated peak intensity which, in turn, is compared to the experimental diffraction patterns. The volume fractions of the studied phases are measured. It is found that the time and temperature of isothermal curing significantly affect the structure of the cement paste.

1. Introduction
In different types of concrete, the basic binding material is Portland cement. The main components of Portland cement are calcium silicates $C_3S$ and $C_2S$, aluminate $C_3A$ and ferrite $C_4AF$. Such components as calcite, calcium oxide, magnesium oxide, sodium and potassium sulphates are also present [1]. During the hydration process, various products form in Portland cement, namely: calcium–silicate–hydrate ($C–S–H$), Portlandite, ettringite, and others [2–6]. Information about the structure of solid materials in initial phases and hydration products attracts the interest of many researchers in practical applications of Portland cement and estimation of its performance characteristics and strength properties, in particular. This information includes the crystal lattice parameters, space group, grade, relative coordinates of atoms, etc. The analysis of the rapid achievement of high performance characteristics cannot be carried out without structural information. Using GEMS software it is possible to describe the chemical interaction between the solid and liquid phases in Portland cements as a thermodynamic system having the certain content of products at different stages of hydration process [2, 4, 7]. GEMS allows considering the influence of such external and internal factors as temperature and its gradients, curing time, quantification of clinker phases, water-cement ratio, mineral additives, etc. GEMS also allows predicting the quantitative content of hydration products in various conditions within longtime periods. Along with the obtained structural information on the hydration product parameters, it is possible to predict diverse performance characteristics of binding materials in concretes. It seems to be rather relevant to study the quantitative phase composition in Portland cements at different curing stages using the Rietveld refinement method and GEMS software.

The aim of this work is to identify the structure and phase composition of Portland cement using the Rietveld refinement method and curing mechanisms in terms of the hydration model proposed by Parrot and Killoh [3] detected by GEMS modelling within 0–67 h time period at 40, 50 and 70 °C.

2. Material and model approximation
The type CEM I 42.5B Portland cement was used in this experiment to determine its weight content. This type of Portland cement is manufactured at OOO ‘Topkinskii cement’, Novosibirsk, Russia [10]. Its chemical composition and the weight content are summarized in Table 1. The chemical composition allows us to obtain the mineralogical composition of Portland cement using the Bogue equations [1]. The obtained composition of major phases includes 61.06 g alite, 13.62 g belite, 12.79 g ferrite and 6.50 g aluminate per 100 g. The water-cement ratio necessary for the formation of a binding material is selected to be 0.41.

| Chemical composition | Weight content (wt.%) | Weight (g) |
|----------------------|-----------------------|------------|
| SiO₂                 | 20.49                 | C₃S        |
| Al₂O₃                | 5.06                  | C₂S        |
| Fe₂O₃                | 4.14                  | C₄AF       |
| CaO                  | 62.83                 | C₃A        |
| MgO                  | 1.75                  | Aqueous solution |
| Na₂O                 | 0.34                  | O₂         |
| K₂O                  | 0.65                  | MgO        |
| SO₃                  | 3.10                  | K₂O        |
| −                    | −                     | Na₂O       |
| −                    | −                     | SO₃        |

The X-ray diffraction (XRD) analysis was carried out by DRON-4-07 diffractometer (Russia) which was modified for digital signal processing. Measurements were conducted using copper radiation (K_α) and Bragg-Brentano X-ray optical scheme. Specifications for the DRON-4-07 included 0.02° scanning step; 14–71° range for angles to be scanned; 30 kV voltage; and 25 mA current. The phase composition in Portland cement was determined by the Rietveld refinement [11, 12]. A tobermorite-like model of the cement paste was created in accordance with the GEMS modeling results and literature information [5]. Based on the C–S–H detailed analysis, Richardson [5] presented structural information of a number of tobermorite crystal lattices which include water molecules. The primary analysis of diffraction patterns shows both overlapping reflections and non-monotonic background behavior on the dependences between the X-ray reflection and Bragg reflection angle, which indicate to the contribution from the amorphous phase to the X-ray reflection intensity (Figure 1). The Rietveld refinement utilizes alite, belite, aluminate and alumoferrite for the identification of clinker phases. These minerals are selected from the Crystallography Open Database [13]. It is interesting that the amount of aluminate and alumoferrite in Portland cement is insignificant (table 1). Also, it is important to note that we estimate the contributions of crystalline phases to the integrated intensity (Table 2). The approximation of the background pattern is addressed separately over the estimated peak intensity of the hydrated amorphous phase.

The qphase analysis (QPA) based on the Rietveld method (Table 2), shows a satisfactory agreement between the theoretical calculations and experimental findings of integrated intensities. The convergence criterion is R_wp ≈ 14% (see Figure 1, curve 3). The identified quantitative composition of clinker phases and hydration products predominates because the total phase intensity is close to unity (~98%) as can be seen from table 2.

In order to identify the amorphous hydration product within the molecular dynamics, the C–S–H crystal lattice is amorphized in the Amorphous software code, the operation of which was described in [11]. The results obtained are then used for the background approximation of the experimental XRD patterns with the Rietveld method (see Figure 2). The simulation modeling is performed in a force field, in which we consider only non-valence pair contributions, *i.e.* Coulomb interactions and van der Waals forces. For the latter case, we apply the Lennard-Jones potential.
Figure 1. Peak intensities of hydration products: 1 – experimental; 2 – integrated; 3 – difference between experimental and integrated intensities; 4 – alite phase; 5 – belite phase; 6 – Portlandite phase.

of electrostatic forces is 1.85 nm. The measurement accuracy of the van der Waals forces is 10^{-5} kcal/mole. The molecular modeling of the atom paths is performed at a room temperature, at 1 fsec time step. The initial atom velocity is selected using the Boltzmann distribution and periodic boundary conditions for elementary cells. Calculations of the atom paths are carried out in terms of the microcanonical ensemble in which the specified number of atoms, the volume and the temperature range of 10 K remain. 1000 iterations are studied. The initial conditions for calculations include the atomic density and temperature. The energy density for the amorphous mineral is calculated depending on the atomic density range of 1.5–3.5 g/cm^2 with a view to reach the optimum state, when the total energy of domain is the lowest, i.e. the convergence criterion is –142.158 kcal/mole at 3.2 g/cm^2 atomic density. Such a density determines the size of the cubic domain which concentrates atoms of the mineral of interest. As a result of this procedure, C−S–H achieves the amorphous state with the established spatial distribution of atoms with the achieved force equilibrium on them. Unlike the short-range order which is retained for amorphous oxides, the long-range order is disturbed. If the primary space group P1 is assigned to the domains, they are identified as an elementary C−S–H cell, the total structural information for which is known. Hence, for the background identification of the experimental XRD pattern, the structural factors and the integrated intensity can be calculated for C−S–H. The results of the background approximation are presented in Figure 1, the convergence criterion is \( R_{wp} \approx 1.73\% \).

Table 2. Structural phase parameters.

| Phases    | \( a, (\text{Å})^a \) | \( b, (\text{Å})^a \) | \( c, (\text{Å})^a \) | \( \alpha, (\text{degrees})^b \) | \( \beta, (\text{degrees})^b \) | \( \gamma, (\text{degrees})^b \) | Symmetry groups | Phase composition, % |
|-----------|----------------------|----------------------|----------------------|----------------------|----------------------|----------------------|---------------------|-----------------------|
| Tobermorite | 11.350               | 7.300                | 20.840               | 90.00                | 97.30                | 90.00                | C1, Triclinic        | 47.72                 |
| Amorphous  | 11.6152              | 11.6152              | 11.6152              | 90.00                | 90.00                | 90.00                | P1, Triclinic        | 0                     |
| Ettringite | 11.230               | 11.230               | 10.720               | 90.00                | 90.00                | 120.00               | P63/mcm, Hexagonal   | 37.40                 |
| Portlandite| 3.5862               | 3.5862               | 4.8801               | 90.00                | 90.00                | 120.00               | P-3m1, Trigonal      | 0.30                  |
| Alite      | 12.235               | 7.073                | 9.298                | 90.00                | 116.31               | 90.00                | C1m1, Monoclinic     | 7.96                  |
| Belite     | 5.5041               | 6.7622               | 9.3281               | 90.00                | 94.172               | 90.00                | P21/n, Monoclinic    | 5.12                  |

\(^a\) lattice parameters (1Å = 10^{-10} m).
\(^b\) lattice angles.

3. Results and discussion
Based on the results of GEMS modeling, major phases which predominate in Portland cement are identified. The experimental XRD patterns are complicated by the distribution of reflections, for which the estimated intensity peaks overlap. Therefore, the structure identification using the Rietveld refinement is divided into two stages. The first stage includes the analysis of contributions only from such hydration products as crystalline cement paste (C\(\text{--S}--\text{H})\), ettringite, C\(\text{--S}--\text{H}\) amorphous component and Portlandite. The results of the analysis of the lattice structural parameters and phase composition are given in Table 2. It is shown that the cement paste and ettringite predominate and are respectively 47.72 and 37.4 % (see Table 2, Figure 1). The difference between the theoretical calculations and experimental data on the peak intensities (Figure 1) shows a good approximation of XRD patterns. The second stage includes a study of peak intensities without hydration products as presented in Figure 2. Using the Rietveld refinement, the contributions from clinker minerals are studied. According to Table 2, the contributions from alite and belite are respectively 7.96 and 5.12 %. The difference between the peak intensities also indicates to a good approximation of XRD patterns.

![Figure 2. Peak intensities of hydration products without tobermorite and ettringite contributions:](image)

1 – experimental; 2 – integrated; 3 – difference between experimental and integrated intensities; 4 – alite phase; 5 – belite phase; 6 – Portlandite phase.

With a view to determine the stability \(\Delta E\) of major phase lattices at 0 K, the \textit{ab initio} analysis of their energy \(E\) is performed [6]. The results are summarized in Table 3.

| Phases          | Tobermorite | Amorphous | Ettringite | Alite     | Belite    | Portlandite |
|-----------------|-------------|-----------|------------|-----------|-----------|-------------|
| \(E, \text{eV}\) | -61216.54   | -65463.99 | -72504.21  | -31868.08 | -934.85   | -1911.72    |
| \(\Delta E, \text{eV}\) | -2335.69    | -2281.27  | -934.85    | -934.85   | -391.20   | -65.02      |

Energies of the studied phases, including the amorphous, are negative. Moreover, they are stable relative to the delamination into pure elements. The binding energy \(\Delta E\) reaches several hundred electron volts, that indicates their high stability. The phases stabilize during the hydration process.

Thus, the QPA performed with the Rietveld refinement allows us to determine the amount of contributions from both cement paste and ettringite hydration products and clinker minerals. Over 85% of the Portland cement composition belong to cement paste (C\(\text{--S}--\text{H}\)) ettringite. Complete structural information is obtained for all the minerals, and the phase stability is achieved. In a reliable manner, our investigations show the dominance of the short-range order C\(\text{--S}--\text{H}\) phase, the amorphous component of Portland cement.

4. Conclusions
Based on the research results it can be concluded that the behavior of the stress-strain curves includes three stages, namely: transition, elastic and plastic strain ranges. The temperature and time of isothermal curing substantially affected the intensity of strength generation in the plastic strain range. At the end of the isothermal curing, the values of the limit strength and the yield stress almost coincided. Stress-strain curves in the plastic strain range are non-monotonic, with a high density of breaks, and a catastrophic failure of specimens occurred at the end of the investigated temperature range. Within 0–67 h curing, the yield stress increased almost by an order to magnitude, and the elasticity modulus increased also. It was shown that with the growth in the curing temperature, these parameters also increase, and a more intensive strength generation was observed. The yield stress was found to be the main estimation parameter of the strength properties at different curing temperatures. After 67 h curing the strength properties of Portland cement achieved not less than 75% of the design strength values corresponding to 28-day curing.

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