1. Introduction

Cement brick relates to multiphase calcium silicate hydrate (C–H–S) of a variable phase composition. Under diverse environmental conditions, cement brick manifests the different qualitative relation between the elements. Although much published information is available concerning the analysis of the structural properties of C–H–S phases with variable phase composition, structural information is incomplete [1-19]. This information should primarily include the atoms coordinates in the lattice and the number, the unit cell size and a possible spatial redistribution of atoms in C–H–S lattices. There is almost no information in the literature about the lattice stability of different phases determined in cement brick during the hydration process. It is appropriate to quantify the phase composition of cement brick during the curing process at isothermal temperature considering the lattice stability and a possible variation in the number of atoms in the C–H–S structure.

The aim of this work is to study the structure of the hydrated Portland cement brick using the Rietveld method, to perform the quantitative analysis of its phase composition, mass fraction, and the spatial redistribution of atoms within the lattice stability interval and different time of low-temperature curing. This study also includes the identification of the crystal lattice parameters and the explanation of structural information about the different phase composition of cement brick.

2. Materials and methods

The Rietveld refinement method [11,12,20] was used to quantify the phase composition of the cement brick after the different time of its curing at 40 °C. 20×20×20 mm test cubes with a 0.38 water/cement
ratio were prepared for the experiments. The cement paste was packed in 6FK-20 steel forms matching the Russian standards.

After a 3-hour curing in air the test samples were extracted from the forms and placed into a steam-curing chamber with a 100% humidity and then cured under the atmospheric pressure during 0, 3, 6, 19, 30, 43, 54 and 67 hours. The X-ray diffraction (XRD) analysis of the test samples was carried out by DRON-4-07 diffractometer which was adapted to a digital signal processing. Measurements were conducted using copper radiation (Kα) and Bragg-Brentano X-ray optical scheme. The operating parameters for the DRON-4-07 included 0.020 scan step; 1 s scan time; 16–810 range for angles to be scanned; 30 kV voltage; and 25 mA current.

Figures (1–7) contain the X-ray intensity profiles of the experimental and theoretical results and the difference between the obtained results depending on the angle of reflectance. Theoretical calculations of the X-ray intensity are based on the superposition principle applied to the cement brick phases after the Rietveld refinement of the instrumental and profile parameters of the crystal lattices of phases [12]. Table 1 summarizes the reference structures from the Crystallography Open Database [21] used for the quantitative phase analysis (QPA) of the XRD data, chemical formulas and other lattice parameters.

Table 1. Structural parameters of the reference phases.

| Chemical formula | Number of atoms | \( a^a \) | \( b \) | \( c \) | \( \alpha^b \) | \( \beta \) | \( \gamma \) | \( V^c \) | \( E, \text{ eV} \) | Crystal symmetry and system |
|------------------|----------------|--------|----|-----|------|-----|-----|-----|-------|---------------------------|
| \( \text{Ca}_3\text{HO}_9\text{Si}_3 \) | 30 | 11.124 | 7.328 | 9.585 | 97.64 | 89.31 | 89.4 | 774.636 | -13994.022 | \( P1 \) triclinic |
| \( \text{Ca}_3\text{H}_6\text{O}_{10}\text{Si}_2 \) | 84 | 16.347 | 5.801 | 11.269 | 95.4 | 124.87 | 83.89 | 871.260 | -30749.999 | \( P1 \) triclinic |
| \( \text{Ca}_4\text{H}_2\text{O}_{13}\text{Si}_3 \) | 44 | 6.8516 | 6.962 | 12.9 | 89.97 | 98.154 | 100.7 | 598.350 | -4207.748 | \( P1 \) triclinic |
| \( \text{H}_2\text{O}_2\text{Ca} \) | 12 | 3.5956 | 3.595 | 4.908 | 90 | 90 | 120 | 54.952 | -1911.726 | \( m-3m \) trigonal |
| \( \text{Al}_2\text{Ca}_3\text{H}_{12}\text{O}_{12} \) | 263 | 12.418 | 12.418 | 12.418 | 90 | 90 | 90 | 1914.98 | -68425.534 | \( B11m \) cubic |
| \( \text{Ca}_2\text{H}_5\text{O}_{11}\text{Si}_3 \) | 94 | 6.735 | 7.385 | 22.487 | 90 | 90 | 123.25 | 935.351 | -8914.134 | \( B11m \) monoclinic |

\( ^a a, b, c \) are lattice parameters in Angstrom units (1 Å = 10^{-10} \text{ m}).

\( ^b \alpha, \beta, \gamma \) are lattice sites in degrees.

\( ^c V \) is the lattice volume, (Å).

Figure 1. Cement brick XRD patterns after 0 h curing: (a) 1 – experimental; 2 – theoretical; 3 – difference; (b) 4, 5, 6 – reference phases.
Figure 2. Cement brick XRD patterns after 3 h curing: (a) 1 – experimental; 2 – theoretical; 3 – difference; (b) 4, 5, 6 – reference phases.

Figure 3. Cement brick XRD patterns after 19 h curing: (a) 1 – experimental; 2 – theoretical; 3 – difference; (b) 4, 5, 6 – reference phases.

Figure 4. Cement brick XRD patterns after 30 h curing: (a) 1 – experimental; 2 – theoretical; 3 – difference; (b) 4, 5, 6 – reference phases.
3. Results and discussion

It should be noted that despite the number of atoms in \( \text{Ca}_6\text{H}_2\text{O}_{13}\text{Si}_3 \) and \( \text{Ca}_3\text{H}_9\text{O}_9\text{Si}_3 \) phases in particular, H atoms are absent in the reference structures. During the curing process of the cement brick or silicate hydration, H atoms should be present in the crystal lattices of these phases. Therefore, H atoms are introduced in all the reference structures given in table 1 using the TOPOS program.
package [20] with regard to the crystal symmetry of the initial phase lattices. Due to the restricted number of pages, we do not indicate here the modified reference structures with the atoms coordinates.

The results of the QPA of the XRD data are presented in table 2 which contains such parameters as different curing time, X-ray intensity ratios and mass fractions. The QPA by the Rietveld method shows a good agreement between the experimental diffraction patterns and calculated profiles. The difference $R_{wp}$ is also shown in table 2.

Table 2. Structural parameters and phase composition at 40 °C and different curing time.

| Curing time, h | Phase | $a$  | $b$  | $c$  | $\alpha^b$ | $\beta$ | $\gamma$ | $V$ | Intensity % | Mass fraction, $R_{wp}$ % | Integrated intensity % |
|---------------|-------|------|------|------|-------------|-----|-------|-----|-------------|----------------------|----------------------|
| 0             | Ca$_6$H$_2$O$_{13}$Si$_3$ | 6.884 | 6.982 | 12.900 | 89.41 | 98.75 | 100.67 | 602.216 | 46.92 | 48.33 | 8.586 | 98 |
|               | Ca$_3$H$_2$O$_9$Si$_3$    | 11.152| 7.221 | 9.588 | 96.69 | 90.02 | 88.67 | 766.809 | 51.11 | 51.68 | 7.472 | 98.2 |
| 3             | Ca$_6$H$_2$O$_{13}$Si$_3$ | 6.885 | 6.998 | 12.941 | 90.07 | 89.45 | 100.73 | 605.862 | 57.28 | 55.54 | 98 |
|               | Ca$_3$H$_2$O$_9$Si$_3$    | 11.185| 7.231 | 9.708 | 97.90 | 88.54 | 89.65 | 777.493 | 41.02 | 44.46 | 8.422 | 98.1 |
| 6             | Ca$_6$H$_2$O$_{13}$Si$_3$ | 6.879 | 6.952 | 12.905 | 89.51 | 98.89 | 100.90 | 598.687 | 51.70 | 53.76 | 9.404 | 98.1 |
|               | Ca$_3$H$_2$O$_9$Si$_3$    | 11.116| 7.297 | 9.593 | 97.43 | 89.94 | 88.53 | 771.44 | 46.42 | 46.17 | 6.601 | 93.9 |
| 19            | Ca$_6$H$_2$O$_{13}$Si$_3$ | 6.864 | 6.977 | 12.921 | 89.66 | 98.87 | 100.81 | 600.416 | 52.86 | 55.67 | 4.748 | 98.1 |
|               | Ca$_3$H$_2$O$_9$Si$_3$    | 11.179| 7.320 | 9.590 | 97.65 | 89.64 | 88.79 | 777.669 | 45.25 | 44.99 | 9.404 | 98.1 |
| 30            | Ca$_6$H$_2$O$_{13}$Si$_3$ | 6.898 | 6.993 | 12.926 | 90.04 | 89.40 | 100.68 | 606.013 | 43.54 | 42.39 | 6.601 | 93.9 |
|               | Ca$_3$H$_2$O$_9$Si$_3$    | 11.177| 7.337 | 9.623 | 97.74 | 89.67 | 88.97 | 781.94 | 50.44 | 51.66 | 7.749 | 98.2 |
| 43            | Ca$_6$H$_2$O$_{13}$Si$_3$ | 6.893 | 7.008 | 12.939 | 89.83 | 98.46 | 100.50 | 607.818 | 67.31 | 69.14 | 6.601 | 93.9 |
|               | Ca$_3$H$_2$O$_9$Si$_3$    | 11.133| 7.287 | 9.630 | 97.55 | 89.34 | 88.87 | 774.333 | 30.98 | 30.86 | 7.749 | 98.2 |
| 54            | Ca$_6$H$_2$O$_{13}$Si$_3$ | 6.828 | 6.969 | 12.947 | 90.25 | 98.42 | 100.57 | 598.866 | 53.83 | 53.41 | 8.777 | 98.5 |
|               | Ca$_3$H$_2$O$_9$Si$_3$    | 11.146| 7.315 | 9.555 | 96.99 | 90.16 | 88.74 | 773.202 | 44.72 | 46.59 | 8.777 | 98.5 |
| 67            | Ca$_6$H$_2$O$_{13}$Si$_3$ | 6.853 | 7.006 | 13.131 | 89.42 | 98.5 | 100.84 | 612.434 | 55.99 | 54.96 | 6.807 | 98.3 |
|               | Ca$_3$H$_2$O$_9$Si$_3$    | 11.181| 7.339 | 9.551 | 97.92 | 89.87 | 88.48 | 776.101 | 42.47 | 45.04 | 8.364 | 98.3 |

As can be seen from table 2, the phase composition detected with a high degree of reliability predominates, since the contribution of the integrated intensity of the diffraction peaks to the theoretical intensity exceeds 98% at each curing time. The Rietveld method used for the phase quantification shows that Ca$_6$H$_2$O$_{13}$Si$_3$ and Ca$_3$H$_2$O$_9$Si$_3$ phases predominate in cement brick, whose refined parameters and their geometric measurements are also given in table 2. The Rietveld refinement method used for the phase quantification shows that the mass fraction of major phases depends on the curing time. The lattice parameters differ from both the initial values (see table 1) and those obtained after the different curing time. According to table 2, Ca$_6$H$_2$O$_{13}$Si$_3$ phase predominates in cement brick, except for 0 and 30 h isothermal curing, when Ca$_3$H$_2$O$_9$Si$_3$ phase prevails. There is no significant exchange between the two phases with the increasing time of curing. According to table 1, the volume of the Ca$_3$H$_2$O$_9$Si$_3$ phase lattice tends to grow with the curing time due to the growth in Ca$_6$H$_2$O$_{13}$Si$_3$ phase in $b$, $c$ and $a$, $b$ planes. Intercalation of H atoms can destabilize the lattices of the reference structures.

A quantum-mechanical estimation of the lattice energy of hydrated cement brick is important for the identification of the lattice stability relative to the phase changes in Ca, O, H$_2$ and Si pure elements. *Ab initio* calculations of the lattice stability are presented in [12], and table 3 shows the results of the lattice energies of Ca$_6$H$_2$O$_{13}$Si$_3$ and Ca$_3$H$_2$O$_9$Si$_3$ phases.

Table 3. Lattice and mixing energies of Ca$_6$H$_2$O$_{13}$Si$_3$ and Ca$_3$H$_2$O$_9$Si$_3$ phases.

| Energy, $\Delta E$, eV | Phase | 0 h | 3 h | 6 h | 19 h | 30 h | 43 h | 54 h | 67 h |
|------------------------|-------|-----|-----|-----|------|------|------|------|------|
| $E_c$ Ca$_6$H$_2$O$_{13}$Si$_3$ | -23610.83 | -24013.49 | -23792.79 | -23876.18 | -23631.05 | -23952 | -25347.81 | -23935.07 |
| Ca$_3$H$_2$O$_9$Si$_3$ | -14484.44 | -14540.84 | -16445.33 | -14531.08 | -14495.21 | -14478.74 | -14392.89 | -14548.33 |
| $\Delta E$ Ca$_6$H$_2$O$_{13}$Si$_3$ | -266.336 | -668.996 | -448.303 | -531.691 | -286.559 | -607.507 | -2003.32 | -590.575 |
| Ca$_3$H$_2$O$_9$Si$_3$ | -363.61 | -420.015 | -2324.503 | -410.258 | -374.382 | -357.917 | -272.067 | -427.5 |
The negative values of the lattice energy indicate to metastability of the lattices. The lattice stability is measured by the mixing energy $\Delta E$:

$$
\Delta E = E_c - \left( \frac{n_{cO}}{8} \times E_O + \frac{n_{cH}}{4} \times E_H + \frac{n_{cCa}}{4} \times E_{Ca} + \frac{n_{cSi}}{8} \times E_{Si} \right)
$$

(1)

where $\Delta E$ is the mixing energy; $E_c$ is the lattice energy; $E_O = -3269.862$ eV; $E_H = -55.405$ eV, $E_{Ca} = -4006.140$ eV, $E_{Si} = -858.155$ eV are lattice energies of O, H, Ca, Si pure elements, respectively; 8, 4, 4, 8 are the number of atoms in lattices of the pure elements; $n_{cO} = 26$, $n_{cH} = 4$, $n_{cCa} = 12$, $n_{cSi} = 6$ are the number of atoms in Ca$_6$H$_2$O$_{13}$Si$_3$ phase lattice after the different curing time.

For Ca$_3$HO$_9$Si$_3$ phase, the numbers of atoms $n_{cO}$, $n_{cH}$, $n_{cCa}$, $n_{cSi}$ equal 18, 8, 6, 6, respectively. The lattice and mixing energies of O, H, Ca, Si elements are measured using the reference phases from COD [22]. Thus, the energies $E_O$, $E_H$, $E_{Ca}$, $E_{Si}$ equal respectively $-3269.862$, $-5.404$, $-4006.139$, $-858.155$.

According to table 3, the mixing energy of Ca$_6$H$_2$O$_{13}$Si$_3$ and Ca$_3$HO$_9$Si$_3$ phases is negative at each curing time. The energy $-\Delta E$ is the binding energy. The results show that the binding energy of Ca$_6$H$_2$O$_{13}$Si$_3$ phase tends to grow with the increasing curing time at 40 °C. The same effect is observed for Ca$_3$HO$_9$Si$_3$ phase. We can therefore assume that the major phases of the cement brick stabilize during the curing process at isothermal temperature. Therefore, a certain spatial redistribution of Ca, H, O and Si atoms is observed inside the lattice stability interval.

4. Conclusions

Summing up the results of the QPA by the Rietveld method it can be concluded with a high degree of reliability that Ca$_6$H$_2$O$_{13}$Si$_3$ and Ca$_3$HO$_9$Si$_3$ phases predominated in the cement brick at different curing time. Complete information was obtained about the phase composition detected in cement brick. It was shown that the major phases were highly stable, and the phase stabilization continued with the increasing curing time.

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