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Structural-Phase State Analysis of Calcium Mono-Aluminate

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Abstract. The paper presents results of the Rietveld refinement method in X-ray diffraction quantitative phase analysis of calcium mono-aluminate, the mineral. It has been stated that the theoretical calcium mono-aluminate CaO·Al2O3. is a high-stable phase, mixing energy of which is equal to 16214,10 eV. Ab-initio calculations and Rietveld refinement method were used to identify die structural state of CaO·Al2O3.

Introduction

The quantitative phase analysis (QPA) was carried out for calcium mono-aluminate CA contained in Portland clinker composition [1,2,4]. Calcium mono-aluminate CA can be written as a chemical formula CaO Al2O3. At the baseline, only its weight composition has been known. A complexity of crystalline structural-phase state of Portland cement is illustrated by X-ray diffraction (XRD) patterns. The XRD patterns is full of overlapping peaks in major phases which, in him, also possess a complex internal structure [2,3]. A significant fraction of Portland cement is amorphous. As for a systematic X-ray diffraction analysis of both amorphous and crystalline phases of calcium mono-aluminate, it has not vet been found in literature.

This work is a continuation of the XRD analysis of Ca [4]. It has been stated that the phase CaO·Al2O3 is the main portion of this mineral, and its contribution to the integrated intensity is about 83%. The efforts to more rigorously quantity all of the phases in calcium mono-aluminate CA taking reference phases as a basis appeared to be unsuccessful.

The aim of this work is a rigorous quantitative phase analysis method capable of quantifying the structural-phase state of calcium mono-aluminate CA. The Rietveld method with the use of both reference phase and theoretical phase CaO·Al2O3 is the foremost technique of this study. And refinement of the structural-phase state [3-5] of the mineral are also included in this analysis.

Molecular Dynamics Simulation of Amorphous and Crystalline Phases

Reference phases used in the XRI) analysis in the work [4] did not allow a rigorous identification and quantification of individual phases in calcium mono-aluminate CA. This indicates that a list of reference phases in Crystallography Open Database (COD) [6] is rather insufficient. Therefore, a simulation of a new phase based on CaO·Al2O3 is believed to be relevant. Taking into account the analysis of calcium mono-aluminate CA diffraction pattern (Fig. l). it is possible to suppose that it contains an amorphous phase [1]. This amorphous phase is characterized by a short-range order of atom arrangement while translation symmetry is not observed. The QPA of calcium mono-aluminate CA amorphous phase content allows identification of its molecular structure and angular range. These parameters show the largest contribution of the reflected X-rays to the integrated intensity (X-ray halo). The essential part of these problems was previously discussed in [4].

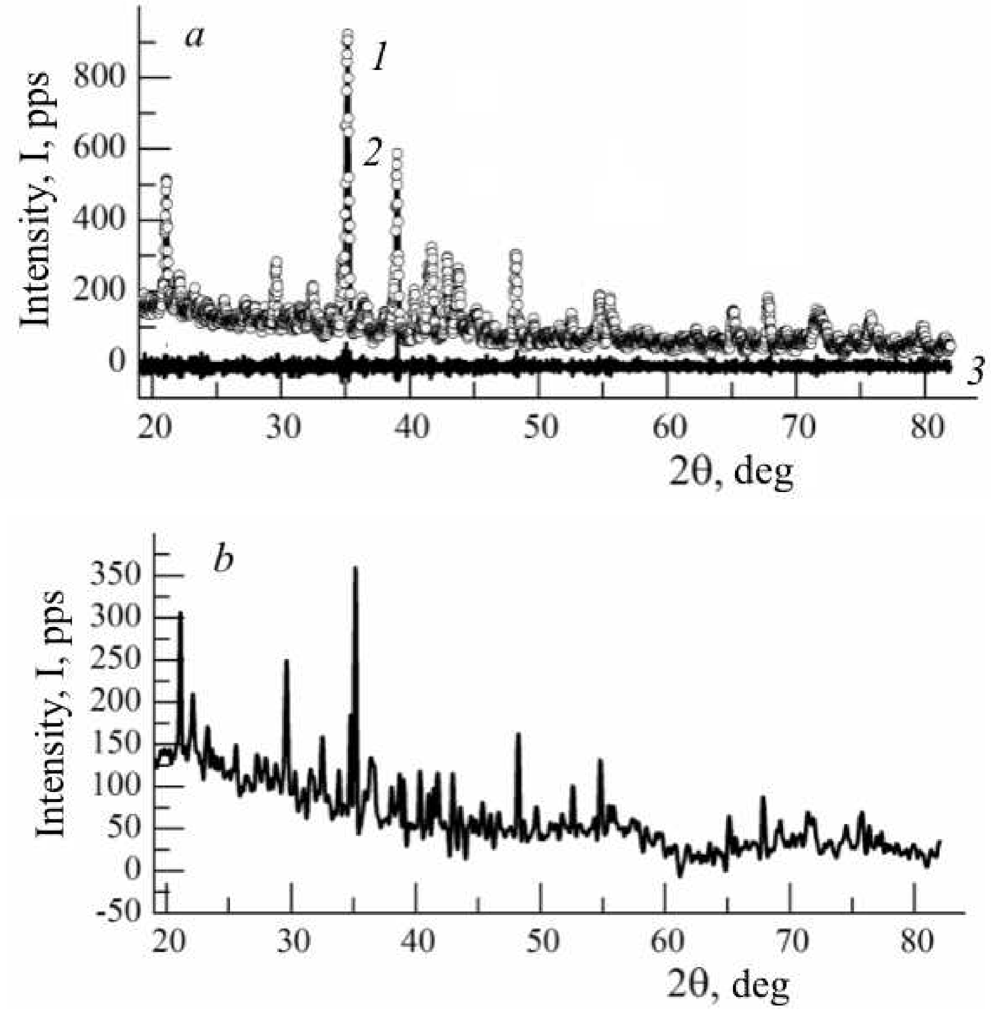

Fig. 1. XRD histograms of calcium mono-aluminate: *a* – experimental (1), theoretical (2), and the difference between experimental and theoretical values (3); *b* – phase containing amorphous and crystal structures [96-900-2487-Al6Ca4O13 (2)-Temp]

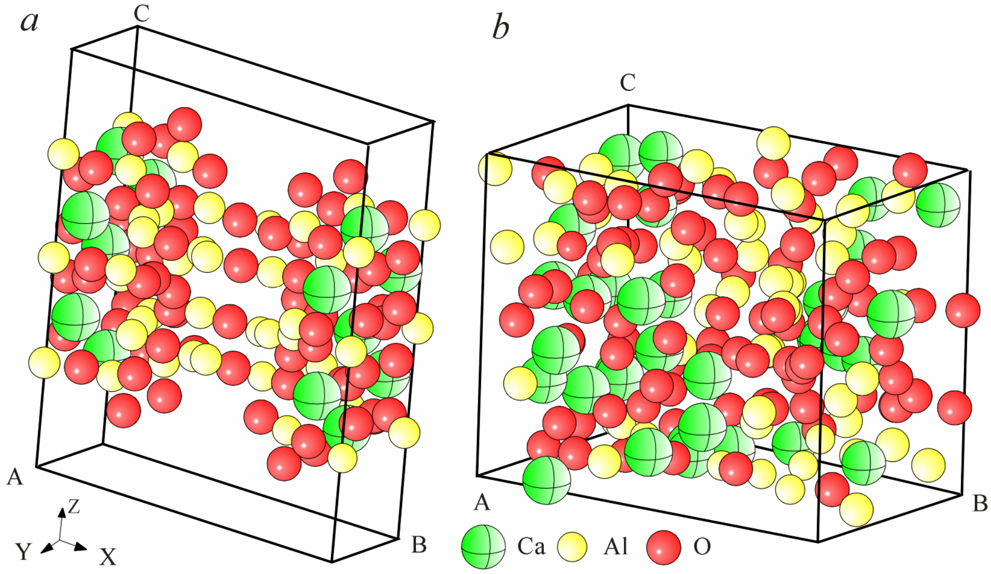

Fig. 2. 3D atom arrangement in the simulated unit cell: *a*) initial state of the unit cell; *b*) unit cell after simulation and refinement of atom arrangement using the Rietveld method. Unit cells contain 188 atoms

It is assumed that at least some fraction of the amorphous phase is converted to the microcrystalline state. In this case, the elemental composition of the phase and its structural state must be the same. XRI) analysis of calcium mono-aluminate CA has shown that the system CaOAl203 (N 96-900-2487 in COD) contributes mush to the integrated intensity [6]. The structural state of the system CaO·Al2O3 was obtained from Rietveld refinement, namely: a space group and a crystal class, the space unit parameters, and relative atomic coordinates. Shown in Figure 2 a. is the initial 3D distribution of atoms.

Simulation of CaO·Al2O3 system is represented by several sequential procedures. Calcium mono-aluminate described in works [4, 5] was used to simulate CaO·Al2O3 system the contribution of which to the integrated intensity of reflections shown in Fig. 1, is dominant.

At the first stage, molecular dynamics (MD) simulation was used to convert CaO·Al2O3 system from the initial crystal structure to the amorphous state [4,5,9]. At the same time, atom arrangement in CaO Al2O3 system leads to minimizing of its potential energy. The optimized molecule then gradually acquires crystallinity properties. It means that the crystal structure must possess parameters that meet its crystallinity properties, namely: space group and a crystal class, space unit symmetry, and relative atomic coordinates. As a result of MD simulation, the crystal structure obtained corresponds to stable state conditions.

At the second stage, the Rietveld method was used to compare the theoretical and experimental spectrums of XRD patterns. The difference between these two spectrums must be minimized.

In order to identify the amorphous phase from the initial structural state of CaO·Al2O3 system, crystallinity properties mentioned above were be removed.

However, bonding atomic radii that correspond to that of the initial crystal structure must be preserved in CaO·Al2O3 system that is represented by N 96-900-2487 from COD (Table 1). As a result of the atom arrangement optimization, it contains 188 atoms. The same number of atoms was contained in CaO·Al2O3 system in its initial state. In this study MD simulation was used for the amorphous structural state and energy calculations. Amorphous phase was simulated in a universal force field by Ewald summation method [3]. The software package described in works [4,5] was used to compute the initial velocities of the atoms from the Boltzmann distribution. It corresponded to 298°K temperature. A microcanonical ensemble was used to represent the finite atomic arrangement in the molecule. The variables of the microcanonical ensemble are quantities such as the number N of atoms in the molecule, the volume V, and the temperature T. Each of these three quantities is a constant of the NVT ensemble. Convergence in energy was equal to 2×10−5 kcal/mol. At the MD preliminary stage the total energy of molecule with different atom distribution was analyzed depending on the bulk density of interacting atoms which was chosen within the range of (1.5...3.0) g/cm2 at 0.1 g/cm2 interval The given density determined the size of the cubic

Table 1. A list of primary phases for determination of Ca content

COD numbers	a, [nm]	b, [nm]	c, [nm]	α,[deg]	β,[deg]	γ, [deg]	Space group
96-900-2487-Am	1.8703	2.0636	1.8343	97.50	94.77	96.46	P1
96-900-2487	0.5300	1.7761	2.1089	90	90	90	Pmmm
00-005-0355	0.4425	0.9465	0.3078	90	90	90	Pmmm
96-200-2889	0.8721	0.8106	1.5109	90	90.31	90.00	P2/m
96-210-2959	1.2238	1.2238	1.2238	90	90	90	I-43d
96-900-2333	0.9.218	0-9223	0.2766	90	90	90	Cmcm
96-900-2487	0.5224	1.7846	2.1230	90	90	90	Pmmm
96-900-6737	0.5012	0.5012	0.5012	90	90	90	Fm-3m
96-900-6835	3.5104	3.5104	4.6294	90	90	120	P-3m1
96-900-9681	0.4747	0.4747	1.2954	90	90	120	R-3c

box containing 188 atoms arranged in 3-dimensions. As the analysis showed, a molecule with 2.45 g/cm2 density possessed the lowest energy E = –293.423 kcal/mol. In all calculations of atomic amorphous arrangement, convergence criteria in energy were satisfied. This molecular energy is in good agreement with the optimized configuration.

At the next stage, the crystallinity properties were assigned to the simulated atom arrangement. The known bulk density of atoms determined the choice of lattice parameters. The crystal lattice was referred to the space group P1 with triclinic family. Bonding atomic radius in the lattice were retained. A theoretical 3D atom distribution with the indicated crystalline properties is the system CaO·Al2O3. The crystal lattice of the solid-state solution is given in Fig. 2, b. The obtained CaO·Al2O3 system refers to alloys which eventually have a quasi-stable state that is confirmed both by the high degree of the above convergence in energy and the negative value of molecular energy.

Ab initio calculations were performed for mixing energy to determine a phase stability of the system CaO·Al203 (96-900-2487-Am) (Table 2). The structural state of theoretical system CaO·Al2O3 completely defines the input data for energy calculations and the geometric optimization

Table 2. Mixing energy of solid-state solution of CaO·Al2O3 mineral and pure components Ca, Al, O2

Phases	Lattice energy, [eV]	Atomic numbers	*a,* [nm]	b, [nm]	c, [nm]	α,[deg]	β,[deg]	γ,[deg]	Space group
$CaOAl_2O_3$	–79037.71	188	1.8703	2.0636	1.8343	97.50	94.77	96.46	*P*1
Ca	–976.82	4	0.3980	0.3980	0.6520	90	90	120	*P6/mmm*
Al	–229.28	14	0.4050	0.4050	0.4050	90	90	90	*Pmmm*
O_2	–6238.63	56	0.6780	0.6780	0.6780	90	90	90	*Pm*-3*m*

of atomic arrangement when calculated using the software package [4]. Mixing energy can be obtained from:

$$E_m = E_t - (xE_{Ca} + yE_{O_2} + zE_{Al}), \qquad (1)$$

where Em is pie total energy of the system CaO·Al2O3; x, y, z are relative atomic numbers included in the system CaO Al2O3; ECa, Eo2, EAl are total energies of atoms Ca, Al and molecule O2. Calculations of mixing energy of the system CaO·Al2O3 and Ca, Al, O2 were carried out in the ground state (at 0°K) using the Density Functional Theory. A standard pseudo-potential of the local density approximation (LDA) was used for the system CaO·Al2O3 and Ca, Al, O atoms allowing for interchange and correlation energies of electrons. In the investigated structures, valence-electron wave functions were analyzed in a plane-wave basis set at kinetic energy cut-off 300 eV. Atomic lattices were taken from COD to calculate the total energy of pure components Ca, Al, O [6]. The solid-state solution and Ca, Al, O2 were geometrically optimized. Structural parameters corresponded to the minimum of the total lattice energy.

Calculations for mixing energy of the system CaO·Al2O3 and Ca, Al, O2 are available at Table 2. This table also shows lattice parameters and the phase space group, the number of atoms in pure component lattices and in the solid solution. Table 2 shows relative atomic numbers of pure components: x = (32/4); y = (104/56); z = (52/14). Substituting the total energy of the solid solution CaO Al2O3 and Ca, Al, O2 into (1), the mixing energy of the solid solution is given by Em=–1621410 eV. Mixing energy is significantly below zero. The negative value of molecular energy indicates that the solid solution CaO·Al2O3 is a high-stable phase. One can also suggest that low-stable CaO·Al2O3 phases can exist which have higher but negative values of mixing energy.

Experimental phases of calcium mono-aluminate CA found in COD [6] also confirm the existence of different CaO·Al2O3 clinker modifications some of which are given in Table 1. Crystal lattices of these modifications are not obligatory geometrically optimized. The existence of modifications of one and the same substance leads to the QPA complication. Structural parameters of the theoretical CaO·Al2O3 system together with the experimental one given in Table 1 were used to quantify phases of calcium mono-aluminate CA.

Quantitative Phase Analysis

Research was conducted into a phase composition of calcium mono-aluminate CA. At the baseline, information about the space group, crystal lattice parameters of CA phases, amorphous fraction, and its internal molecular structure was absent. X-ray diffraction analysis of calcium mono-aluminate CA was made on a DRON-4-07 diffractometer which was modified for digital signal processing. Measurements were conducted using copper Kα radiation and Bragg-Brentano X-ray optical scheme. Process parameters for the DRON-4-07 were set as 0.02° scanning step; 2θ angular range of 19-82° to be scanned.

Fig. 1 presents experimental and theoretical XRD patterns of calcium mono-aluminate CA. Theoretical XRD patterns were obtained on the basis of COD structural parameters [6]. Table 1 depicts primary phases for determination of calcium mono-aluminate CA content. As Fig. 1 shows experimental XRD pattern is of a complex spectrum created by crystalline compounds and the amorphous phase.

The quantitative phase analysis of calcium mono-aluminate CA was carried out using structural parameters from Table 1 and the theoretical system CaO·Al2O3. The Rietveld refinement method was used to describe the structural parameters of the systems investigated in works [2,4], [8]. As a result, the ratio between the theoretical Ith(2θ) and the experimental Iexp(2θ) intensities (Fig. 1) of diffraction maxima were refined. In these terms, the structural, profile, and experimental parameters involved in theoretical intensity have been compared and refined using the non-linear least-square method [5]. The substantial convergence between theoretical and experimental values was achieved for Ca (Fig. l, a). The reference intensity ratio was equal to RWP = 8,93% [3]. The theoretical total intensity fraction of phases given in Table 3 comes to 99,6% of the experimental XRD pattern. The unit cell parameters of CaO·Al2O3 system are depicted in Table 1. The QPA by the Rietveld method was used for parameters refinement of relative atomic coordinates in reference lattices for each phase (see Table 3). It was stated that calcium mono-aluminate CA contains CaO·Al2O3 system amounting to 97,13%. It also contains a small amount of iron oxides Fe3O4 (2,46%) and calcium oxides. The system CaO·Al2O3, as determined by the Rietveld refinement method, can be represented by different cristallographic modifications the volume fraction of which is different for

Table 3. Contributions of theoretical intensities of reference phases to the integrated intensity

N	COD numbers	Chemical formula	Intensity, [%]	Weight, [%]
1	00-005-0355	AlO(OH)	$6.11*10^{-5}$	0.38
2	96-200-2889	Al_2CaO_4	9.447	13.29
3	96-210-2959	$O_{65,8}Al_{28}Ca_{24}$	0.53	0.76
4	96-900-2333	Fe_3O_4	2.46	1.44
5	96-900-2487-Am.	$Al_6Ca_4O_{13}$	83.16	76.96
6	96-900-2487	$Al_6Ca_4O_{13}$	3.99	7.00
7	96-900-6737	4CaO	$1.84*10^{-4}$	0.17
8	96-900-6835	CaO_2	$1.32*10^{-5}$	$1.15*10^{-5}$
9	96900-9681	$6Al_2O_3$	$4.70*10^{-5}$	$7.13*10^{-5}$

each modification. It has been shown that the high-stable system CaO·Al2O3 (96-900-2487-Am) is dominant in calcium mono-aluminate CA (96-900-2487-Am, see Table 3).

Conclusions

The results of the X-ray diffraction quantitative phase analysis of calcium mono-aluminate CA were obtained using the Rietveld refinement method. The theoretical XRD pattern has shown the high value of integrated intensity relative to the experimental XRD pattern and conies to 99,6%. It has been stated that the theoretical CaO·Al2O3 system is high-stable, mixing energy of which is equal to 16214,1 eV. This system contributes mush to the integrated intensity of calcium mono-aluminate CA XRD pattern. Ab-initio calculations and the Rietveld refinement method allowed detection of the unit cell parameters and atom arrangement in CaO·Al2O3 system.

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