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CHEMICAL PROCESSES CAUSING DISSOLUTION OF CALCIUM CEMENT MINERALS
ХІМІЧНІ ПРОЦЕСИ, ЩО ЗУМОВЛЮЮТЬ РОЗЧИНЕННЯ КАЛЬЦІЄВИХ ЦЕМЕНТНИХ МІНЕРАЛІВ
ХИМИЧЕСКИЕ ПРОЦЕСССЫ, ОБУСЛАВЛИВАЮЩИЕ РАСТВОРИМОСТЬ КАЛЬЦИЕВЫХ ЦЕМЕНТНЫХ МИНЕРАЛОВ

Annotation. This paper is devoted to the usage of crystal-chemical approach for establishing nature of dissolution and driving force of hydration reactivity of calcium cement minerals on the atomistic. The progress of cement chemical reactions on a nanoscale, as well as correlation between the crystal structure of calcium minerals and their reactivity with water during hydration of cement minerals are discussed. Significant progress in this direction reached by using crystal-chemical approach based on relationship between the composition, crystal structure and properties of calcium cement minerals.
Keywords. Calcium cement minerals, crystal structure, dissolution, driving force, chemical processes.
Анотація. Розглянуто механізми розчинення в процесі гідратації кальцієвих мінералів, що базуються на даних кристалохімічного аналізу. Показано, що успіхи в розшифровці кристалічних структур основних цементних мінералів і їх гідратних фаз створюють нові можливості з точки зору кристалохімії для більш глибокої інтерпретації взаємозв'язку між структурою, розчиненням і рушійною силою процесів гідратації кальцієвих цементних мінералів.
Ключові слова. Кальцієві цементні мінерали, кристалічна структура, розчинення, рушійна сила, хімічні процеси.
Анотация. Рассмотрены механизмы растворения в процессе гидратации кальциевых минералов, основанные на данных кристалохимического анализа. Показано, что успехи в расшифровке кристаллических структур основных цементных минералов и их гидратных фаз создают новые возможности с точки зрения кристаллохимии для более глубокой интерпретации взаимосвязи между структурой, растворением и движущей силой процессов гидратации кальциевых цементных минералов.
Ключевые слова. Кальциевые цементные минералы, кристаллическая структура, растворение, движущая сила, химические процессы.

Introduction

Cement hydration involves a number of coupled chemical processes each of which occurs at a rate that is determined both by the nature of the process and by the state of the system at that instant. An important aspect of recent progress on hydration kinetics is that the proposed mechanisms have been described in increasingly quantitative terms. However, some very important questions according mechanisms of cement minerals dissolution remain almost completely unanswered. Relationships between the rates of hydration reactions and the resulting microstructure – and thus the ultimate properties – have long been accepted, although with little mechanistic understanding [1, 2]. Major findings show that dissolution of crystals preferentially occurs at specific surface sites that are characterized as having "excess surface energy". Dissolution of crystals concepts from geochemistry suggests that dissolution is directly controlled by surface reactions at reactive sites that include defects, dislocations, twinning and grain boundaries [3].

Mechanisms concerning the early hydration of alite are still a subject of controversy. However, it is generally admitted that hydration of alite, the principal phase of ordinary Portland cement, is a dissolution-precipitation process according to Le Châtelier principle. At the same time the rates of reaction of the clinker minerals are different: alite and aluminate are confirmed to be the most reactive phases with degrees of reaction of between 40 and 60% for alite and 20–80% for aluminate at 1 day [4]. Due to the mechanism of incongruent dissolution Ca^{2+} cations are dissolved from a layer of C_3S close to the surface and replaced by H^+ ions. The rate of further decomposition is governed by the diffusion of the

Ca^{2+} ions through the Ca^{2+}-dispersed boundary layer [6]. The deviations result from the protonation of the unsaturated oxygen atoms are observed due to differences of the surface of minerals. Hydration rates measured in cement pastes or in C_3S pastes are in excellent agreement with the kinetic law found for C_3S under conditions undersaturated with respect to C–S–H [6, 7].

According to thermodynamic approach, the driving force of the reactions of clinker minerals with water predetermined value of the total thermal effect of two components: the thermal effect of hydration and thermal effects of destruction and dispergation of the crystal lattice of minerals. This dispergation is mainly due to protonation of the surface layers of cement particles [8]. A. N. Plugin et al. [9] considered contacts between oppositely charged surfaces of crystalline hydrates and calcium hydrosilicates on the basis of the electroheterogeneous hardening theory. The mechanism of dissolution of Portland cement clinker minerals associated with the lateral surface electrical repulsion. However, based on differences in the kinetics of cement minerals hydration and heat generation of minerals it is necessary to identify the causes of elementary acts of their interaction and dissolution. Nowadays a study of the problems related to mechanisms of dissolution of calcium minerals on the atomistic level using crystal chemistry approach is very important. It allows to obtain a more deep knowledge in the nature of binding properties of cement minerals and establish the driving force of their dissolution processes.

The peculiarities of mechanisms of dissolution processes of cement minerals could be shown on the examples of the gypsum binders and alkaline earth metal oxides.

Therefore, it is necessary to conduct a thorough analysis of the calcium minerals based on updated decryptions of their crystal structures, which defines the position of the atoms in the unit cell - the smallest group of atoms of a crystal, fully preserving all its properties.

Experimental program

Gypsum binders $CaSO_4 \cdot 0,5H_2O$, $CaSO_4$-III, $CaSO_4$-II were obtained by $CaSO_4.2H_2O$ roasting at temperatures 170; 220; 600 °C relatively. Alkaline earth metal oxides MgO; CaO; CdO; SrO; BaO were obtained by calcination of their carbonates during carbonation. To eliminate the influence of the factor of the specific surface obtained oxides were ground to the same fineness $S=200\pm10$ m^2/kg.

To study the chemical bonds in the crystal structures of coordination polyhedron of cement minerals were calculated valence distribution efforts and the strength of individual bonds Me-O in coordination polyhedrons, as well as the balances of the valences on oxygen anions taking into account the interatomic distances were drawn up. This was done using methodology developed by Yu. Pyatenko [10], according to which the valence efforts of the cation are distributed among the surrounding anions generally not evenly, but in a certain way depending on the distance cation – anion. On the basis of the functional dependence of the "distance - valent effort" made up the local (true) balance of the valences on the oxygen anions. The crystal chemistry used for a long time the approximate balance of the valences, which was called "formal." It was based on the idea of L. Pauling (1947) on the equal distribution of the valent efforts of the cation between itself surrounding anions without any dependence on the distance cation - anion, that is not always the true. Method by Yu. Piatenko allows to reveal oxygen anions, undersaturated and oversaturated with valent efforts by cations in crystalline structure of clinker minerals. For the calculation of the distribution of valent efforts V_{ij} and strength of individual bonds in polyhedrons were used the values of interatomic distances of the crystal structures of major cement minerals C_3S, γ- and β-C_2S, C_3A, C_4AF, C_2F [11, 12].

Results and discussion

Terms and method of manufacture of gypsum binders, as well as the type of raw materials (natural gypsum or REA-gypsum) have a major influence on their size distribution from the data size analysis gypsum hemihydrate the amount of less than 1 micron fraction is about 5 wt.%. However, contribution to the development of small fractions of the specific surface is the defining (incremental coefficient specific surface kmax = 3.7 m-1.vol.%), that is much higher than the contribution of particles with a size 10-45 μm. Characteristically, the maximum differential distribution curve corresponds to the grain size of 45 μm. At the same time, the particle size of 10 microns is only 30 wt.%, but their contribution to the specific surface area exceeds 90%, the main contribution to the development of specific surface introduced particles down to 3 μm. Increased of dispersed particles of such a large extent determines their surface energy and high water demand of binders. This process of stabilization properties gypsum hemihydrate by "purposeful aging" can improve its strength characteristics due to decreasing of disintegration particles through their contact with water by topochemical mechanism [13].

Most of the work in the field of dissolution gypsum binders devoted to the study processes from a position of physical-chemical mechanics. However, these studies do not reveal the relationship between the structure of the crystal lattice of gypsum binders and their reactivity. By the kinetics of the strength growth, gypsum binders are divided into two groups: the first includes rapid-hardening hemihydrate gypsum and anhydrite III, while the second - dihydrate gypsum and anhydrite II. Determining the rate of hydration of gypsum binders with hardening age, produced by calculation from the thermograms, showed that the hydration binders of the first group proceeds readily immediately after mixing with water, whereas the anhydrite II hydrates much more slowly. The crystalline structure of hemihydrate is similar to that of gypsum dihydrate and consists of circuits of atoms of $Ca2^+$ and groups of SO_4^{2-}. Moreover, the layers consisting of them are shifted in the way that results in the formation of large space channels 0.3 nm in diameter with water molecules in them. Such structure is characterized by even greater unbalance of valences and anisotropy of chemical bonds determining its higher solubility. During the hydration of gypsum hemihydrate in water medium sulphate blocks are formed, which then form strong bonds with calcium atoms owing to their water molecules. Reactivity of gypsum binders is determined by the possibility of chemisorption of water molecules on oxygen anions, which are undersaturated valent cations efforts. Local unbalanced structure and a small anisotropy of chemical bonds in the Ca-polyhedrons in anhydrite II are responsible for their low solubility and ultimately the ability to hardening. High activity of gypsum hemihydrate and anhydrite III caused by the metastability of the structure and the presence of larger spatial channels, which may include water molecules. In this case a dissolution-precipitation occur via through-solution processes.

The mechanisms of dissolution processes of cementing materials could be shown on the examples of the most simple binders as oxides of alkaline earth metal. In this case, some hydration processes do appear to proceed by a "topochemical" mechanism, e.g. as has been suggested in the case of the hydration of reactive calcia [3]. Therefore, the influence of the crystal chemistry factors on the cement minerals reactivity should be pointed out.

In the crystal structure of calcium oxide Ca^{2+} cations takes all emptiness of the dense cubic packing of oxygen atoms without disturbing its maximum symmetry. The ratio of ionic radii of Ca^{2+} and O^{2-} (rk/ra = 0,764) must meet structural type CsCl (CN=8), but for oxides CaO, SrO, BaO is characteristic structural type NaCl (CN=6), i.e. formation of these oxides structure is primarily determined by the genetic code, giving the dense cubic packing of oxygen anions. During the hydration of calcium oxide there is a protonation of oxygen anions to form OH-groups, which are the dipole (strongly polarized anion). This requires the reconstruction of crystal structure from coordination to less symmetrical - layered CdJ2 type with coordination number 6 and 3. For CaO molar with mass 56,077 g/mol the density is 3,37 g/cm^3, and for Ca(OH)2 at the molar mass 74,09 g/mol – ρ = 2,23 g/cm^3. So with one mole of CaO with 16,64 cm^3 volume formed by hydration per mole of Ca(OH)2 volume 33,22 cm^3, that is almost twice volume growth, which largely leads to CaO self dispergation during the slaking. The formation of OH-groups, i.e. strongly polarized dipoles necessitates rearrangement of a coordination structure into a layered one which is less symmetrical. On the other hand, the interaction of quicklime with water allocated a significant amount of heat (Q=1160 kJ/kg CaO). According to calculations by V.V. Kapranov [14], this highly exothermic reaction includes a range of phenomena, including the largest contribution of making electronic transition from O2- to H^+ with formation OH-groups, i.e. the process of protonation of oxygen anions (Qp=905 kJ/kg). An important factor that influences the CaO reactivity is state surface of particles, characterized by high values of surface energy 1,31·10-4 J/cm^2 [15].

One of the main principles of binding substances is matching of curing time to the intensity of processes of interaction and structure formation. The reactivity of calcium oxide in contact with water can be reduced by a variety of technological, physical and chemical methods. The technological process development of calcium binders can be characterized by the lowering of calcium oxide reactivity. During clinker burning due to the introduction into CaO lattice of small strongly polarizing cations Si^{4+}, Al^{3+}, Fe^{3+} occurs a partial or complete binding of oxygen anions by embedded elements for which the strength of the bond increases, that limits the protonation process and determines the rate of the hydration process of binders [16]. Hydration CaO by topochemical mechanism leads to high internal stresses and

causes the destruction of stone [17].

In the water clusters due to the interaction between covalent and hydrogen bonds between the oxygen atoms and hydrogen atoms can take place migration of a proton (H^+) to the surface and inside of the crystals structure of cement minerals by the relay mechanism, leading to delocalization of protons within the cluster [11]. To fully understanding the nature of the influence of the crystal structure on hydration reactivity of cement minerals it is necessary to investigate the perspective of using the theoretical calculations and analysis of models of different structures. Hydration-active phases have a number of crystal-chemical features of the crystal lattice structure, which further contribute to structural transformation in the process protonation. A more promising proposal by H.F.W. Taylor [18] suggested that the initial step in the reaction between calcium silicate and water was the proton transfer from water molecules to the oxygen atoms in the calcium silicate. This leads to the formation of the reaction zone and depending on the amount of water in currently hydration proceeds the formation of hydrates takes place by dissolution (external product) or topochemical (inner product) mechanisms.

The theory of dissolution mechanism also was considered by K.H. Jost and B. Ziemer [19] which shows the relation between the crystal structures of calcium silicates and their reactivity against water. Early arguments that only considered the crystal structures had found that the neighboring CaOx polyhedra were joined by common vertices, edges and faces in β-C_2S; however, γ-C_2S had no shared faces (fig.1).

The high reactivity of C_3S was mainly related to the active sites around the more ionic oxygen atoms in C_3S, whereas these ionic oxygen atoms were absent in C_2S. The relationship between reactivity and polymorphic modifications of C_2S was studied [20] from the perspective of electronic structures. Active O atoms with larger charge densities are found in α'L- and β-C_2S, while they are absent in γ-C_2S. The local density of states of valence bond maximum in α'L- and β-C_2S is highly localized around active O atoms, whereas that in γ-C_2S is homogeneously dispersed. The results (Fig. 2(a), (c)) clearly showed that the higher electron density around the O atoms made the localized O atoms lose electrons easier and thus are more susceptible to electrophilic attack. These differences make the active O atoms of α'- and β-C_2S more susceptible to electrophilic attack and result in higher hydration reactivity for α'- and β-C_2S. It was reported that when anhydrous calcium silicates, such as C_3S and β-C_2S, came into contact with water, a superficial hydroxylation process takes place.

The study of the structural features of pure cement minerals and their hydrated phases helps to reveal the crystal chemical idea of the hydration process of binders. Binding
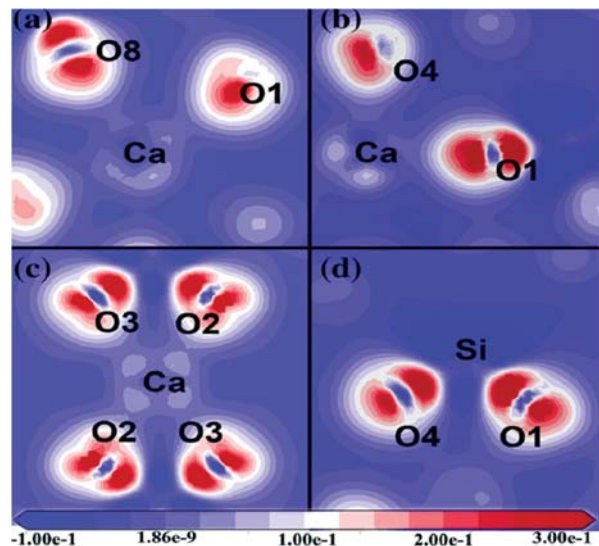

Figure 2. The calculated electron density differences (EDDs) in the cross sections parallel to the surfaces formed by three atoms, namely: (a) O1-Ca-O8 in α'L-C2S, (b) O1-Ca-O4 in β-C2S, (c) O2-Ca-O3 in γ-C2S and (d) O1-Si-O4 in β-C2S [20]

properties determined by the ability of minerals in the reaction with H2O to allow formation of the contacts caused by hydrogen bonds. This is the possibility of involving anions as donors and acceptors in the system of hydrogen bonds. It is closely related to structural factors: undersaturated valence effort of the anions, the anisotropy of the interatomic distances and most often - their combination. The reactivity of
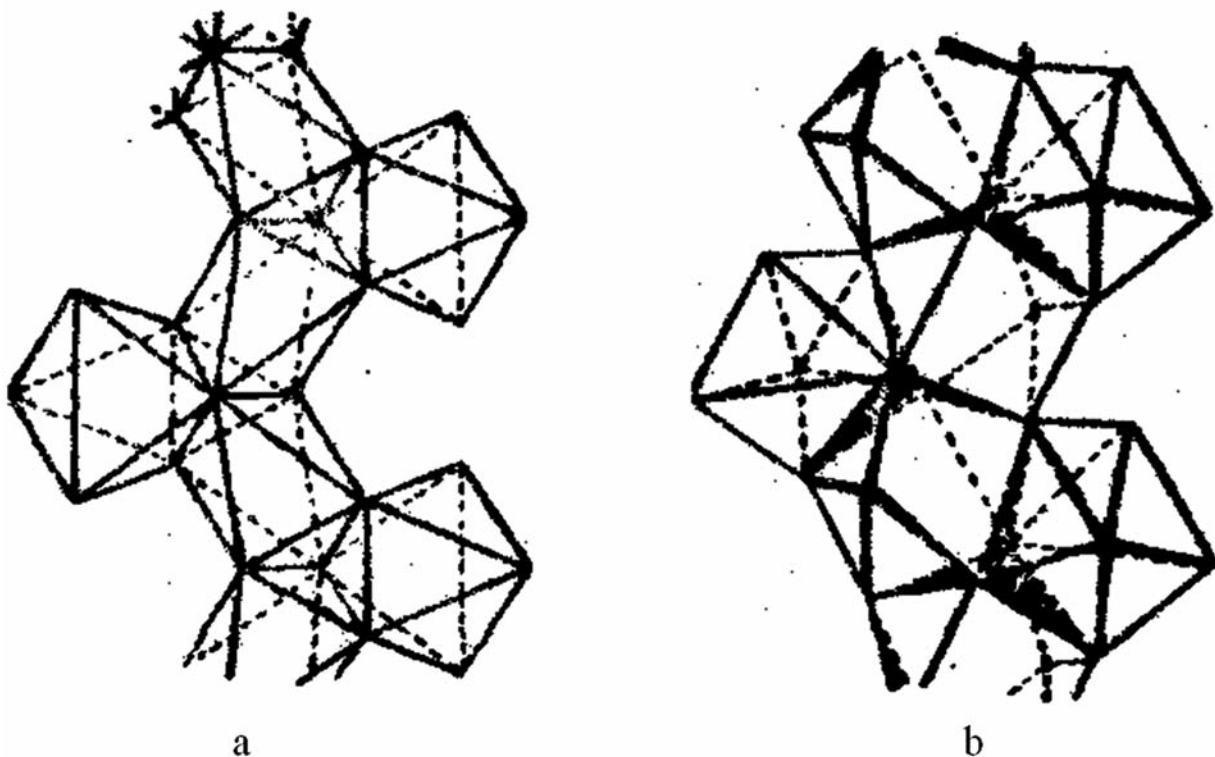

Figure 1. Fragments of Ca-polyhedra buildings in the crystal structures of dicalcium silicates γ-Ca_2SiO_4 (a) and β-Ca_2SiO_4 (b). Common faces are shaded [19]

minerals - a function of their basicity: the more Ca-polyhedron in the structure, so it is higher. The possibility of the hydration reactivity cement minerals is determined by the requirement to restructure for establishing a system of hydrogen bonds. On the example of compounds β- and γ-C₂S is particularly evident influence of the anisotropy of chemical bonds (Tab. 1) on the hydration reactivity. In the structure of γ-C₂S efforts of bonds efforts are similar (the energetic characteristics ΔE in Ca-polyhedrons vary between 18 and 37 kJ). Transition to β-C₂S increases the anisotropy of chemical bonds as in Ca(1) and Ca(2)-polyhedrons (ΔE respectively 116 and 41 kJ) and SiO₄-tetrahedrons (from 38 kJ in γ-C₂S and up to 66 kJ in β-C₂S). With an increase in the coordination number of Ca-polyhedrons β-C₂S the average energy of single bonds decreases in seven- and eight-vertex compared octahedrons on 17 and 33% respectively, and besides a minimum bonds strength of β-C₂S is 99 and 112 kJ, whereas for γ -C₂S it is equal to 172 and 169 kJ.

Crystal structure γ-C₂S is characterized by full formal oxygen saturation (Tab. 2), but local balance of valences reveals minor changes due to the saturation of oxygen anions incommensurability ribs idealized Ca-octahedrons and SiO₄-tetrahedrons (respec-

tively 0,35 and 0,26 nm). The increase in the coordination number of Ca to 7 and 8 in β-C₂S structure eliminates several local imbalances of oxygen anions, although its structure tensions grows.

The presence in C₃S = Ca₃O[SiO₄] = Ca₂[SiO₄].CaO (calcium oxymonosilicate) of fifth part of the not bonded with ion Si⁴⁺ easily protonated O²⁻ can be considered as the main reason for increasing its hydration reactivity compared with β-C₂S=Ca₂[SiO₄] (calcium monosilicate). Common edges between the Ca-polyhedra in the structures of β-C₂S and C₃S, as well as the strong anisotropy of the chemical bonds in them further accelerate the process of restructuring under the new genetic code, which is set by OH-groups (dipoles) formed by a partial protonation of undersaturated oxygen anions. This is accompanied by a rearrangement and complication of the oxygen motive as well as leaching of calcium ions with subsequent crystallization in pores in the form of portlandite. At the same time the dissolution/dissociation mechanism of calcium aluminates and aluminoferrite and their reactivity against water define two processes: protonation of all O2- and changing of aluminium's function from anion forming to cation forming.

Table 1.

Characteristic of chemical bonds in β- and γ-Ca₂SiO₄ structures

Poly-hedron	CN	Bond effort Me-0				CN	Bond effort Me-0			
		Average	min	max	Δ		Average	min	max	Δ
		β-Ca₂SiO₄					γ-Ca₂SiO₄			
Ca (1)	7	0,286	0,183	0,399	0,216	6	0,333	0,318	0,351	0,038
Ca (2)	8	0,250	0,208	0,283	0,075	6	0,333	0,312	0,381	0,069
Si	4	1,000	0,936	0,085	0,149	4	1,000	0,977	0,062	0,085

Table 2.

Local balance of valences ΣVᵢⱼ in β- and γ-Ca₂SiO₄ structures

Anions	Ratio	Ca (1)	Ca (2)	Si	Σ Vᵢⱼ	Δ	Σ'
		β-Ca₂SiO₄					
O (1)	1	0,399	0,208 0,266	1,085	1,985	-0,042	1,786
O (2)	1	0,183 0,283	0,280 0,283	1,008	2,037	0,037	2,071
O (3)	1	0,304 0,266	0,280 0,208	0,971	2,029	0,029	2,071
O (4)	1	0,237 0,328	0,263 0,212	0,936	1,976	-0,024	2,071
/Sum/	4	2,000	2,000	4,000	8,000	0,132	7,999
		γ-Ca₂SiO₄					
O (1)	1	0,332x2	0,312	1,062	2,038	0,038	2,000
O (2)	1	0,351x2	0,381	0,985	2,088	0,068	2,000
O (3)	2	0,318	0,335 0,318	0,977	1,948	-0,052	2,000
/Sum/	4	2,001	2,000	4,001	8,002	0,210	8,000

This leads to a complete destruction of the initial structure of this minerals and determine high rates of reaction and heat evolution [21]. According to the thermo-kinetic studies by A.V. Usherov-Marshak [22], for the most reactive minerals C_3S, C3A and C4AF hydration processes are accompanied by high levels of intensity and total heat generation.

So, the process, which determines the initial stages of calcium cement minerals hydration reactivity, is the protonization of anion O2-, which leads primarily to the of Ca-O bonds. It follows from this that structural changes entailed by the possibility of protonizing to the inside of the initial crystal are the driving force of cement minerals' hydration processes and determine their hydration (chemical) reactivity [23]. For the same minerals with low basicity, which do not have any hydraulic properties in pure form, hydration process determines the hydrolytic destruction of the solid phase due to the breaking of covalent bonds Si-O-Si, Si-O-Al and Al-O-Al in the alkaline solutions [24].

Hydration-active calcium cement minerals have a number of crystal chemical features of the crystal lattice structure, which further contribute to structural changes in the process protonation. This leads to the formation of the reaction zone and depending on the amount of water in currently hydration proceeds the formation of hydrates takes place by dissolution (external product) or topochemical (inner product)

mechanisms.

Conclusions

Mechanisms of dissolution in the initial stage of hydration of cement minerals certain by crystal chemical features of the crystal lattices, which determine their thermodynamic instability and the ability to interact with water. As a result of protonation of anions O2- are forming dipoles – OH-groups that require converting of structure from coordination to less symmetrical - layered. In this case, a dissolution of crystals preferentially occurs on the specific surface sites that are characterized as having "excess surface energy".

The calculations of the local (true) valence balance of crystal structures of the calcium cement minerals which take into consideration the chemical bonds anisotropy in coordination polyhedrons and local unbalance on the oxygen anions are performed. All this allows to develop the crystal chemistry factors of reactivity of calcium minerals and show their influence on the protonating processes during hydration. Just active undersaturated oxygen anions in the cement minerals' structures can be presented as proton acceptors in the process of hydration that creates conditions for passage of the dissolution process. The structural transformation caused by the possibility of protonation of active anions O2- in the inside of the initial crystal with formation OH-groups are the driving force of cement minerals' dissolution processes, which define their reactivity against water

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