

ABOUT MINERAL GENETIC ENGINEERING ELEMENTS IN LIME SLAKING PROCESS

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Practical implementation of the foundations for mineral energy engineering [1] should be better kept on monomineral lime binder. The process of lump lime slaking with water creates environment favourable for chemical reactions with high thermal dynamic indicators of alkalinity ($\text{pH} \geq 12$), high temperatures (up to 100°C and higher) and heat release ($65,5 \text{ kJ/mol}$). This environment with important thermodynamic characteristics can be called "the waste" of production as it is almost not used as secondary useful resources. Meanwhile, alkaline environment is able to transform electrically neutral particle (molecules, crystals, etc.) into active (electrically charged, amorphous). Temperature increasing is also acceleration of chemical reactions in the environment lump lime extinction. Heat release at limp slaking is a volumetric heat treatment, causing chain reaction of reactants, not from the surface inside for a long time as during the usual heat treatment of products. Ability to control these processes ideally means air binder on the basis of which low strength and water resistance concrete is received, as well as to transform it into hydraulic, more durable and water resistant.

Our task is to introduce a substance, changing thermodynamic characteristics of a system, into the system of these processes, and to obtain new formations, increasing strength and water resistance of concrete with the lime binder. Such substance does not need to be active, as environment (alkalinity, temperature, heat), into which it is introduced and which activates it, is active. Two main requirements are as follows: the substance must be highly soluble in water, and water solution must have sufficient homogeneity of its distribution, and energy of its interatomic bonds must be higher than the energy of interatomic bonds CaO (CaO is about 1062 kJ/mol) and H_2O (H-O is about 459 kJ/mol). Water solution of a chosen substance must extinguish lump lime. Silicon atom with the bond energy Si-O of 1861 kJ/mol corresponds to these requirements. It is widely spread: organosilicon liquids, aqueous solutions of sodium silicate, sodium fluorosilicate etc.

In our work we used sodium waterglass, Na_2SiO_3 , as water modifier. It gives strong alkaline medium [2] and acidified SiO_2 :

$\text{Na}_2\text{SiO}_3 + \text{H}_2\text{O} = 2\text{NaOH} + \text{SiO}_2$. Its concentration in water changes the degree of ionization (according to data of electrical resistivity) and pH medium, fig. 1a. Changing its concentration it is also possible to regulate speed of lime slaking, fig. 1b.

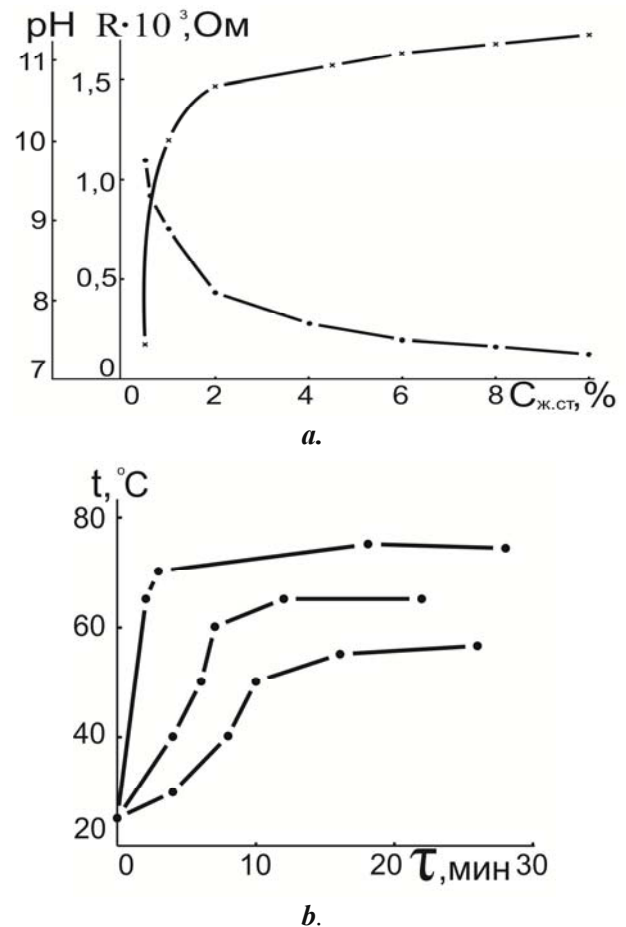


Figure 1. Influence of concentration of water solution on the values: a) pH medium (x) and its electrical resistance (•) and b) change of speed of hydration while slaking lump lime with water (the upper curve), water solution with concentration of 1% (medium) and 3% (the low curve).

Due to this fact the structure of control and studied limestones, having solidified for 4 months, was examined. Control samples were prepared on the basis of lime putty received after slaking the lump lime with water. Examined samples, as opposed to the control ones, were prepared with the use of analogue putty, but it was received by slaking

lump lime with water solution of waterglass with the concentration of 6%. Analysis of advantages and disadvantages of examined material was compared with analogue control samples. X-ray analysis was carried out with the use of diffractometer, X-ray DRON-4.0.

Quality phase analysis was carried out by comparison with tabular data about interplanar spacings and their intensity received when interpreting the diffraction patterns, fig. 2. Reliability of identification of a phase is provided by the coincidence of not less than its three the most intensive line on diffraction patterns. Diffraction patterns in the interval of angles from 5 to 65° were taken in researches. Diffraction patterns with saturated number of new forms in the range of angles rotation of 15-50° were chosen for analysis. It let us determine the kinds and quality of new forms. New forms appeared in the control samples: portlandite Ca(OH)₂ and calcite CaCO₃, fig. 2a. Moreover, the new substance, the aragonite, appears in examined samples, fig. 2b.

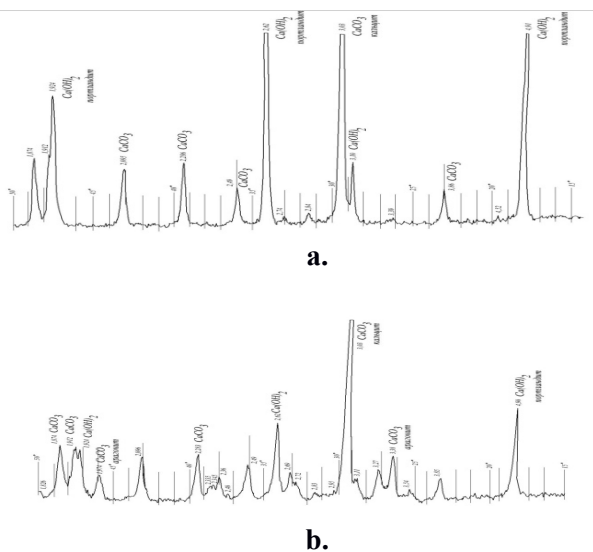


Figure 2. Diffraction patterns of new forms of a stone, prepared from a lime slaked with water (a) and water solution of waterglass (b).

Qualitative and quantitative composition of new forms as the minerals are given in Table 1. Here lime binder in the form of Ca(OH)₂ is considered as an unreacted substance, and portlandite having the chemical formula also in the

Table 1. Qualitative and quantitative composition of new forms of limestone.

Lime slaking	Kind and number of new forms			
	Calcite	Arago-nite	Portlan-dite	Ca(OH) ₂
With water	8	—	3	2
With solution	11	2	1	4

form of Ca(OH)₂, but having brucite structure of flat sheets with a dense hexagonal packing strength up to 3,5 MPa [3], is considered as solid substance. The distinguishing feature is such that modification of water with waterglass changes its ratio, namely, while slaking with water the number of portlandite is higher, and with water solution of waterglass the number of Ca(OH)₂ is higher.

The effectiveness of water modification for slaking lime is noticeable and 1,6 times higher than occurrence of calcite. But the most important thing is such that slaking of lump lime with water solution of waterglass and its further mixing with water let us obtain limestone, in which composition the new substance, aragonite, appeared. This fact corresponds to literature data[4], according to which its characteristics were determined, and, in comparison with traditional new formation, calcite, is indicated in the Table 2.

Table 2. Distinguishing features of new formations of lime binder.

Description of qualities	Calcite	Aragonite
Chemical formyla	CaCO ₃	4[CaCO ₃]
Density, g/cm ³	2,71	2,95
Firmness	2,7 – 3,2	3,5 – 4,0
Crystal structure	Cubic	Rhombic

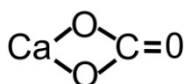
Comparing with calcite, density of aragonite is 9% higher, and firmness is 25-30% higher [4]. It is known that reducing of porosity (increasing of density) of 1% leads to increasing concrete strength of 5%. Taking into consideration the importance of these numbers, it's possible to understand the actuality of work, especially in the part of these processes control.

Quantitative difference in atomic content of crystals of calcite and aragonite causes certain changes in energy potential of interatomic bonds. Chemical formula of aragonite, including four crystals of CaCO₃, like single solid body, has separation surfaces almost 4 times smaller than the sum of separation surfaces of 4 single crystals of calcite. This advantage is to increase the density of concrete, as it is determined by the density of limestone, filler and their contact, and the contact here is on the molecular level.

Qualitative characteristics of aragonite were studied using its structural formula, which we have developed and shown in Fig. 3.

Structure of aragonite is similar to the structure of calcite. Aragonite was obtained in an environment characterized by a high degree of alkalinity, high temperature and acidic SiO₂. Due to combination of there parameters the new

calcite



aragonite

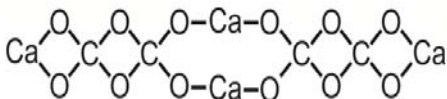


Figure 3. Structural formula of new formations.

environment appears. It is favorable for isomorphism CaCO_3 , due to which aragonite appears. Its structural formula indicates the “linking” of four crystals CaCO_3 , which confirms a hypothesis developed by us. In our researches waterglass Na_2SiO_3 with strong binding energy Si–O and increased alkaline medium, cleaves double rigid connection C=O, fig. 2, in crystals CaCO_3 , which leads to isomorphism, i.e. creation of mixed group compounds of calcite crystals.

We know that the higher the value of the interatomic bonds, the shorter the length of interatomic bonds, the denser the rigid body and the stronger it is. That is why it is important to compare thermodynamic characteristics of aragonite and calcite. The calculation of the energy of interatomic bonds of minerals of solidified lime binder is given in Table 3.

Total energy of interatomic bonds of aragonite crystals is 176 kJ/mol, i.e. 1% higher, than the one of calcite. This energy is high enough, considering that 1 g/mol of quicklime at slaking generates 65,5 kJ of heat which is sufficient for increasing of environment temperature above 100°C . Moreover, in accordance with the data of X-ray diffraction analysis total energy of interatomic bonds of all new appeared formations, having other constant parameters, is 1,9 times higher (89672 against 47014 kJ/mol) when lump lime is slaked with water solution of waterglass, not with water.

In the case of stabilization or hybridization of energy of interatomic bonds in new formations 1 bond in average has (4014:60=783,6 kJ/mol) at slaking of lime with water and (89672:123= 729 kJ/mol) at slaking with water solution of waterglass.

Thus, slaking of lump lime with water solution of active substances causes isomorphism of CaCO_3 : in our case to formation of mixed group polymorphic compounds of calcite crystals in the form of aragonite with the best physical and mechanical qualities. Structural formula of aragonite was developed. Working hypothesis was confirmed. Total energy of interatomic bonds of new formations with aragonite is 1,9 times higher than with calcite only. Secondary “raw material” in

Table 3. The calculation of the total energy of the interatomic bonds of new formations of lime binder.

Description of minerals	Interatomic bonds		Number, pcs		The total energy of bonds kJ / mol
	Kind	energy, kJ/mol	Kinds of bonds	Minerals	
Slaking of lump lime with water					
Ca(OH)_2	Ca-O	1140	2	5	11400
	H-O	459	2	5	4590
Total energy of interatomic bonds Ca(OH)_2					15990
Ca(CO)_3	Ca-O	1184	2	8	18944
	C-O	383	2	8	6128
	C=O	744	1	8	5952
Total energy of interatomic bonds of calcite					31024
Total energy of interatomic bonds of new formations					47014
Slaking of lump lime with water solution of waterglass					
Ca(OH)_2				5	15990
Ca(CO)_3				11	42658
$4[\text{Ca(CO)}_3]$	Ca-O	1184	8	2	18944
	C-O	383	16	2	12256
Total energy of interatomic bonds of aragonite					31200
Total energy of interatomic bonds of new formations					89672

the form of high heat effect of slaking lump lime and alkalinity, which medium is favourable for polymorphism of reactants, was used rationally.

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Recommended for publication: 23.04.2015.