Clinkerless Composites with Portlandite Matrix

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Abstract: The study covers the matter of technology of clinkerless composites with portlandite matrix, obtained via compaction of individual nano and microsized crystals of $Ca(OH)_2$, grown in accordance with sol-gel processing. It deals with conditions of regulation of morphologic and disperse composition, energy state of individual crystals of portlandite which are obtained in accordance with lump-lime hydration nanotechnology. The study presents the grounds for modes of contact condensation structure formation of clinkerless composites with portlandite stone matrix.

Key words: Portlandite, nano and microsized individual crystals, energy state, compaction, contact condensation structure formation, artificial portlandite stone, portlandite matrix, filler, clinkerless composite

INTRODUCTION

Now a days clinkerless composites are again in the purview of many scientists and specialists. And this can be easily understood because clinker binding materials are very energy-consuming and expensive.

Modern building industry progressed in such a way that many good clinkerless binding materials and alternative systems of solidification were "moved aside". If you study the ancestors' methods and even the experience of 40-50s of the previous century, you will be able to see that then building industry applied a quite wide range of materials based not on clinker binding substances but on clinkerless ones.

Unfortunately, the history of modern building industry development is characterized by dominating application of cement and binding materials for cementless composites are practically forgotten. A great binding substance, lime, the history of usage of which extends back over several thousands of years has not been studied as an essential researches object for a long time. Specialists have practically "resigned themselves" to the fact that lump-lime cannot lead to formation of a firm artificial stone as a result of its hydration as it happens with hydration of for instance, gypsum, cement.

Why does lime fall out of the general law of mineral binders behaviour?. This is explained by an enormous speed of lime hydration, high speed of crystallization of $Ca(OH)_2$ by a high crystallization pressure resulted thereupon and a concurrent high heat rise and accordingly, high temperatures of mixtures with vigorous

steam emission. As a result, crystals of $Ca(OH)_2$, emerging in course of hydration do not compose portlandite stone crystal aggregate due to evolving solidification system self-destruction.

Can this self-destruction of lime hydration products be overcome? Many scientists concerned themselves with this problem. Among them Bazhenov (1978), Logginov et al. (1954) and Osin et al. (1973), etc.

Osin was an active initiator of using of unslaked lime that is lump-lime and he managed to obtain portlandite stone with resistibility up to 60 MPa under the conditions of forced hydration heat removal. But this required proper additional expenses which exceeded the effect which was achieved. And thus, suggestion of Osin, having proven the real possibility of obtaining of portlandite stone, appeared to be not feasible and practically non realistic.

Over 25 years ago we took the problem of obtaining of artificial portlandite stone (Chernyshov and Potamoshneva, 1995, 1998) tried to get over the contradiction "portlandite crystals can be obtained and crystal aggregate made of them that is artificial stone cannot be".

The suggestion was that the individual portlandite crystals obtainment process would have been separated from the crystal aggregate formation process that is processes would have been "detached" in time. According to this suggestion, we needed to compact dissociated individual crystals of portlandite into a crystal aggregate using the principle of contact condensation structure formation under external mechanical pressure. As a result we succeeded in forming a stone of resistibility up to 25-30 MPa immediately after moulding

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(Chernyshov and Potamoshneva, 1999). This stone turned out to be water-resistant, having coefficient of emmoliating $\kappa_p \geq 0.85$. The latter meant that the suggested technology helped to form a crystallite structure determined by effect of physical and chemical factors not only of physical and mechanical ones.

Portlandite stone with the same properties is already regarded as a matrix which is combinable with components of calcium carbonate, silicate, aluminosilicate compositions of natural or technogenic origin (Chernyshov *et al.*, 2012; Stepanova *et al.*, 2013; Lesovik *et al.*, 2004; Lesovik, 2004; Lesovik and Klyuyev, 2012).

BASICS OF SOL-GEL TECHNOLOGY OF OBTAINMENT OF PORTLANDITE CRYSTALS AND PORTLANDITE STONE

The new technology of obtainment of artificial portlandite stone raises some questions of principle. First of all, it is necessary to provide synthesis of portlandite individual crystals with nonequilibrium energy state that is to set such technological conditions of CaO hydration and crystallization of $Ca(OH)_2$ that in course of their subsequent compaction via pressing they formed the portlandite stone specifically due to this state. The most essential thing here is the regulation of hydration kinetic parameters with solving of the problem of formation of disperse and morphologic composition of particles (crystals) $Ca(OH)_2$ that are in the utterly non equilibrium

energy state. The last requirement is the background for the fact that compacted nonequilibrium crystals of portlandite after pressing may give the firm portlandite stone as a result of contact condensation structure formation without any thermal treatment or ageing of a pressed monolith.

Generally, the concept of research using the technology of clinkerless composites on portlandite matrix includes the following "know-hows": necessity of separate formation of portlandite individual crystals from crystal aggregate formation, giving nonequilibrium state to these crystals; necessity of putting filling components mechanoactivated particles to portlandite matrix; necessity of forced compaction of mixture ingredients into a monolith with the condition of monolith (composite) contact condensation structure formation with immediate attainment of strength.

Formation of monocrystals their state and properties are in direct relationship to technological conditions of production of them. The research represents the study of >10 ways of obtainment of portlandite stone nonequilibrium state which involve variation of portlandite crystallization speed variation by means of change of concentration of solution of oxide and hydroxide of calcium via regulating value of relation water-solid, mixing modes, processes temperature conditions and allow to obtain different states of portlandite monocrystals. As a result, a range of technologic variants is substantiated and suggested (Fig. 1, 2 and Table 1-3).
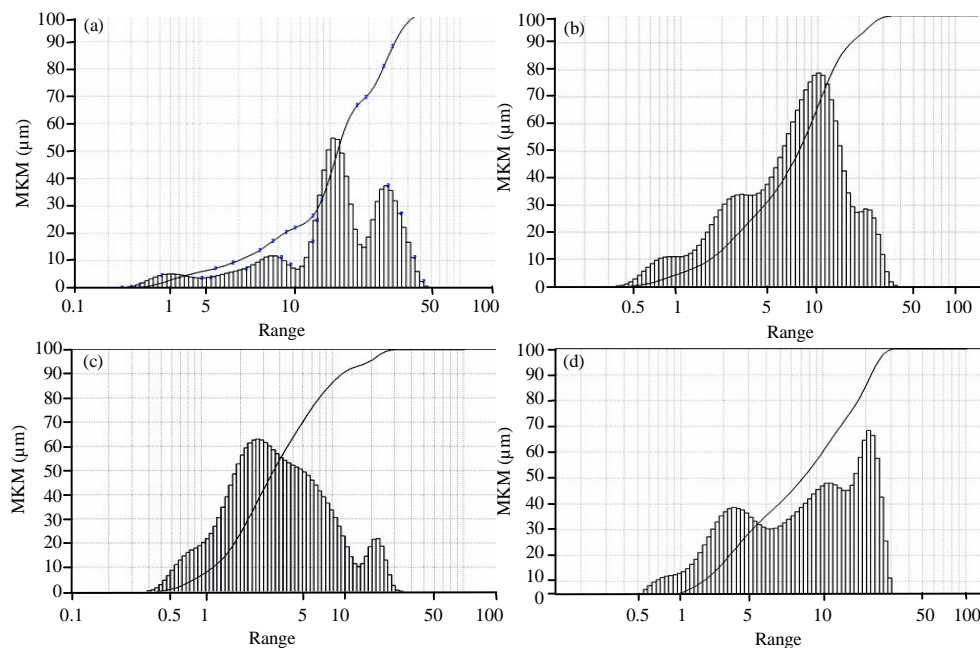

Fig. 1: Degree of dispersion of portlandite monocrystals obtained under variating of conditions of CaO lime hydration; a) I method; b) II method; III method and IV method

Taking into account "know-hows", we should speak about composites obtainment with the help of both separate and combined technology. In course of application of separate technology (A), preliminarily obtained portlandite crystals are mixed with particles which are filling composite in course of application of combined technology (B), portlandite monocrystals are formed under hydration of lump-lime mixed with particles which are filling composite. The main thing in these technologies is that filling components in mixture should be of non-equilibrium energy state. They can pass through mechanical processing-milling or through thermal treatment or through both procedures. When applying these technologies one should take into account that during compaction via pressing when internal forces of consolidation of particles of crystals $Co(OH)_2$ and particles of filler into a monolith, the pressure itself also generates non-equilibrium at points of contact of crystals and particles.

Researches which were based on experimentals set up (Table 4) for portlandite calcium carbonate and portlandite aluminosilicate composites revealed their optimal compositions and technological modes which
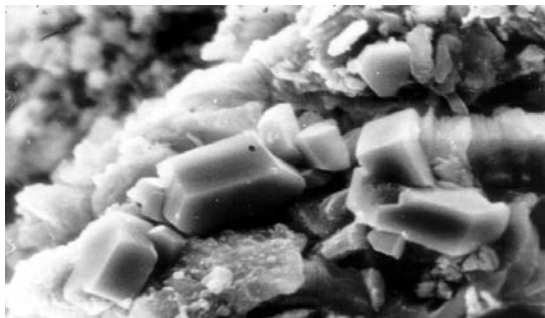

Fig. 2: Electron microphotography of portlandite stone structure (x2800)

Table 1: Dimensional specifications of portlandite monocrystals obtained in different conditions of CaO lime hydration

Method of CaO lime hydration	Mass content in percentage of fractions in relation to size (μm)						
	0-0.5	0.5-5	5-20	20-35	35-50	50-100	<5
I	2	20	43	12	23	0	22
II	0	36	44	13	7	0	36
III	0	63	30	7	0	0	63
IV	0	39	37	24	0	0	39
Range	Nanosized	Microsized	-	-	-	-	-

Table 2: Heat of wetting of portlandite individual crystals

Method of obtainment of portlandite crystals	Heat of wetting (kJ kg^{-1})
I	25.7
III	40.0
IV	28.5

were reasoned via polynomial models obtainment. Polynomial models for portlandite-calcium carbonate composite:

$$Rco_1 = 9.631 - 0.077X_1 + 2.289X_2 + 1.229X_3 - 0.325X_1X_2 - 0.225X_1X_3 - 1.625X_2X_3 - 1.536X_1^2 - 1.041X_2^2 - 0.616X_3^2, MPa$$

$$Rco_2 = 8.340 + 0.185X_1 + 1.529X_2 + 0.468X_3 - 0.150X_1X_2 - 0.325X_1X_3 + 0.075X_2X_3 - 0.721X_1^2 - 0.315X_2^2 - 0.880X_3^2, MPa$$

Here, Rco_1 is an ultimate strength under compressing of portlandite-calcium carbonate composition material with conversion chalk immediately after production; Rco_2 is an ultimate strength under compressing of portlandite-calcium carbonate composition material with flue dust immediately after production. Polynomial models for portlandite-aluminosilicate composite:

$$Rco \{I, (A), C\} = 6.68 - 1.83X_1 + 2.4X_3 - 0.52X_1^2 - 0.51X_2^2 + 0.37X_3^2 - 0.15X_1.X_2 - 1.69X_1.X_3$$

$$Rco \{I, (A), Z\} = 7.09 - 1.59X_1 + 1.05X_2 + 2.92X_3 + 1.28X_3^2 - 0.88X_1.X_3 + 0.45X_2.X_3$$

$$Rco \{II, (B), Z\} = 9.51 - 2.72X_1 + 0.33X_2 + 4.08X_3 - 1.52X_2^2 + 1.22X_3^2 - 2.36X_1.X_3$$

$$\rho_0 \{I, (A), C\} = 1612 + 62.36X_1 + 25.14X_2 + 81.01X_3 - 29.56X_3^2 - 21.25X_2X_3; MPa$$

$$\rho_0 \{I, (B), C\} = 1712 + 63.16X_1 + 24.53X_2 + 78.11X_3 - 28.36X_3^2 - 20.45X_2X_3$$

$$\rho_0 \{I, (A), Z\} = 1693.3 + 56.6X_3 + 60.22X_1^2 + 35.01X_1. X_3 - 55.3X_2.X_3$$

$$\rho_0 \{II, (B), Z\} = 1678.6 - 33.23X_1 + 70.2X_3 + 37.05X_1^2 + 24.2X_2^2 + 27.5X_1.X_2$$

Where:
I, II = Methods of obtainment of portlandite crystals
A, B = Technology variant
C = Component in the form of ground grit of ceramic bricks
Z = Component in the form of ground zeolitic tuff

Thus, it has been proved that lime should get its "historical place" among mineral binders and it should be actively worked with. That was the ground for us to launch researches in 1990 studying obtainment of a artificial portlandite stone then a composite of the portlandite-calcium carbonate type when the component mixed with portlandite was the calcium carbonate material. (Table 5 and 6). Thereafter we developed a composite of portlandite-aluminosilicate type. We proved the engineering possibility of obtainment of a brick (Fig. 3) with a mark "100" regarding strength immediately after

Table 3: Properties of portlandite stone formed with the help of compaction of portlandite stone monorystals obtained via different methods

| | Conditions of obtainment portlandite monocrystals | | |
Properties	I method	III method	IV method
Average density (kg/m³)	1330.00	1400.00	1390.00
Ultimate strength under compressing immediately after compaction (MPa)	4.00	28.10	27.40
Water absorption percentage by weight			
After 72 h	30.80	27.90	28.90
After 28 days	31.90	28.40	29.00
Coefficient of emmoliating (Ce)	0.51	0.83	0.53

Table 4: Factor space of formulation and technological conditions of obtainment of contact condensation solidification composites

Name of technology factors	Mass content of filler (%)	Humidity of raw mixture (%)	Pressure (MPa)
Code designations	X_1	X_2	X_3
Main level	50	12	80
Upper level	80	16	120
Lower level	20	8	40
Upper "star" point	91	17.5	135
Lower "star point"	9	6.5	25

Table 5: Optimum of formulation and technological conditions of obtainment of portlandite – calcium carbonate composite

Type of waste	Mass content of waste (%)	Humidity of moulding sand (%)	Pressure (MPa)	Ultimate strength under compressing (MPa)
Conversion chalk of nitro-ammophoska production	45-48	11.0-14.7	105-110	7.3-9.2
Flue dust of cement production	43-46	10.5-12.8	95-108	7.3-9.2

Table 6: Optimum of formulation and technological conditions of obtainment of portlandite-aluminosilicate composite

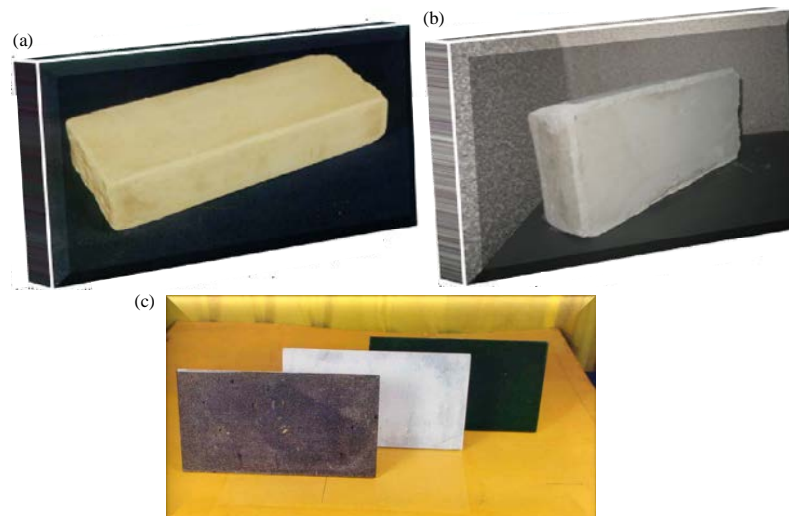| Purpose criterion	Type of aluminosilicate component	Technology variant	Component mass content	Humidity of moulding sand (%)	Pressure (MPa)	Ultimate strength under compressing immediately after moulding	Ultimate strength under compressing in 28 days after moulding
R_{max} under $\tau = 0$	Zeolitic tuff	A	28-30	10-12	100-110	≥(11÷13)	18.3
		B	28-30	10-12	100-110	≥(13÷15)	21.1
	Grit of ceramic bricks	A	30-32	10-12	110-120	≥(8÷10)	17.9
		B	30-32	10-12	110-120	≥(9÷11)	19.4
R_{min} under $\tau = 0 \geq 10$	Zeolitic tuff 23.1	A	20-25	9-11	90	≥10	
		B	20-25	9-11	90		20.0
	Grit of ceramic bricks	A	30-32	10-12	100-110		17.6
		B	30-32	10-12	100-110		16.3

Fig. 3: Test samples of products made of clinkerless composite with portlandite matrix

compaction without heat treatment. In 28 days of natural storing the brick increased its strength up to the mark "250".

CONCLUSION

We implemented sol-gel nanotechnology of obtainment of portlandite individual crystals for compaction and contact condensation synthesis of artificial portlandite stone with strength not <25-30 MPa under coefficient of emolliating not <0.8-0.85.

Artificial portlandite stone is used as a matrix for clinkerless building composites of portlandite-calcium carbonate and portlandite-aluminosilicate types with strength not <10 MPa immediately after pressing without necessity of any steam treatment. Composites of portlandite-aluminosilicate type are able to continue solidifying through time: at the age of 28 days of natural storing their strength can increase up to 20-25 MPa.

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