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STUDYING THE KINETICS OF HYDRATION STRUCTURES AND THE PHYSICO-CHEMICAL PROPERTIES OF LIME-BELITE BINDERS BASED ON MARLS DEPOSIT OF THE SOUTHERN ARALIE OF THE REPUBLIC OF KARAKALPAKSTAN

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ABSTRACT

The article presents the results of research on the study of the kinetics of hydration structures and the physicochemical properties of lime-belite binders based on marl deposits of the South Aral Sea region of the Republic of Karakalpakstan. The experimental results show that the processes of hydration of clinker and other minerals included in the binder materials, as well as hydration structure formation (HS) in these systems are interconnected. For the study, several samples were taken from two deposits, differing in the content of marls and carbonate-argillaceous parts. It turned out that the studied objects differ in the content of calcium and magnesium carbonates, the combination of silica and alumina.

The results of thermogravimetric, petrographic and IR-spectroscopic analyzes of marls at various temperatures are presented. Analysis of the chemical compositions and physicochemical properties of carbonate minerals makes it possible to choose a rational method for obtaining finished materials from them. Based on the research results, the chemical-mineralogical and dispersion compositions of natural raw materials are shown, which predetermine the possibility of their use as microfillers for marly and composite binders.

Keywords: mineral, carbonate, clay, heat treatment, hydration, structure formation, lime, additive, solution, binder, marl, silica, roasting, lime-belite binders.

INTRODUCTION

An urgent strategic step in the development of the economy of our country is the creation of new industrial zones, on the basis of which it is possible to form modern industrial facilities that ensure the production of competitive products. One of the important criteria for the development of the construction industry is the effective use of mineral resources using environmentally justified innovative technologies.

With the development of capital construction in the Republic of Uzbekistan and Karakalpakstan, the problem of creating new local building materials and changing the properties of existing compositions is most acute. With the development of capital construction in the Republic of Uzbekistan and Karakalpakstan, the problem of creating new local building materials and changing the properties of existing compositions is most acute.

A fundamentally new solution to the problem of creating lime-belite materials for the construction industry of the republic is the development of an economical, fast-hardening local binder obtained from available raw materials. In this regard, it is necessary to make fuller use of local raw materials and production waste, expand the production of various products of building materials, and focus on creating new energy-saving technological processes for obtaining new lime-belite binder building materials with desired properties. [1].

Among the mineral raw materials, carbonate rocks - lime and marl minerals are of particular interest. Marls are a fairly widespread breed, it can serve as the basis for obtaining local binders instead of relatively expensive and not available for all areas of Portland cement. It may be of particular interest to Karakalpakstan, where they use imported cement and other building materials.

Lime-belite binder (LBB) obtained by low-temperature roasting of natural marls and joint grinding of the active mineral additive with lime, as well as artificial lime-silica mixtures. LBB is a finely divided mixture of materials of the proper composition. The composition may contain aluminates, ferrites and calcium aluminoferrites, at high firing temperatures, the presence of tricalcium aluminate and even tricalcium silicate is possible. LBB consist of a raw mixture of limestone with quartz sand, tripoli and clays. Binders as a result of hardening in autoclaves used in the production of lime-sand products are obtained using mixtures consisting of 60-70% LBB and 40-30% ground quartz sand [2].

OBJECTS AND METHODS OF RESEARCH.

As a result of studies of the chemical and mineralogical compositions and some physicochemical properties of marl mineral deposits of the Republic of Karakalpakstan, marl deposits of Kungrad and Muynak were selected for further research, which belong to rocks of sedimentary origin, including carbonate (calcite, dolomite) and clayey (kaolinite, montmorillonite, hydromicas) parts with impurities of quartz, feldspars, etc. Carbonate rocks consist mainly of calcareous and marl minerals based on calcium carbonate CaCO3. Carbonate rocks are presented as chalk-like gypsum marls and brownish-gray arganogenic-detritus limestones.

Carbonate-argillaceous rocks, called marls by geologists, are quite widespread in the territory of Muynak in the southern Aral region of the Republic of Karakalpakstan. Their peculiarity is loose, clay-like structure, dark, brownish, grayish or bluish color, fine granulometric composition, rather diverse chemical and mineralogical composition; distribution directly on the surface or under the soil layer of 0.1-0.5 m, the thickness is small - from 0.4 to 2.1 m, sometimes up to 5.0 - 10.0 m [3].

The chemical and mineralogical composition of the Muynak carbonate-argillaceous rocks of explored deposits is a mixture of calcium and magnesium carbonates, silica and alumina compounds (in the form of clay particles), a certain amount of calcium sulfate in the form of gypsum, a small amount of soluble salts of sulfuric and hydrochloric acids. The content of calcium and magnesium carbonates varies widely - from 8 to 84% $CaCO_3$ and from 0 to 16% $MgCO_3$. Variations in clay impurities are also significant - from 1 to 84%.

Qualitative characteristics of Muynak carbonate-argillaceous rocks indicate the possibility of their use for the production of various binder building materials. Qualitative characteristics of Muynak carbonate-argillaceous rocks indicate the possibility of their use for the production of various binder building materials.

The issue of using carbonate-argillaceous rocks of Muynak for the needs of the industry of building materials and construction has not yet been practically resolved. Exploration work, which revealed the nature of the occurrence, structures and chemical composition of the rocks, determined the possibility of using the carbonate-argillaceous deposits of Muynak for the production of binders. Significant diversity was noted in the chemical and mineralogical composition along the strike and thickness of the occurrence of rocks of various deposits.

The Kungrad deposit of marl minerals is located in one of the central regions of the Republic of Karakalpakstan. Due to insufficient knowledge of the physical and chemical properties, the marl of this deposit is currently not being developed on a construction scale. In this connection, the study of samples of marl from the Kungradskoe deposit, obtaining materials on its basis for various purposes, is an urgent task [4].

A comprehensive study of mineral marl minerals was carried out by the methods of chemical, physical-mechanical, thermogravimetric, IR spectroscopic analysis. These analyzes are universal and by now more modern methods for studying the compositions of solid materials. A comprehensive study of mineral marl minerals was carried out by the methods of chemical, physical-mechanical, thermogravimetric, IR spectroscopic analysis. These analyzes are universal and by now more modern methods for studying the compositions of solid materials.

RESULTS AND DISCUSSION

Chemical (Table 1), thermogravimetric (Fig. 1), petrographic (Fig. 2.) and IR spectroscopic (Fig. 3) analyzes of marls were carried out.

Laboratory chemical studies of natural carbonate and gypsum minerals were carried out according to GOST 5382-91 [5]. The results of chemical analysis are shown in tables 1.

Table 1. Chemical composition of marl samples, %

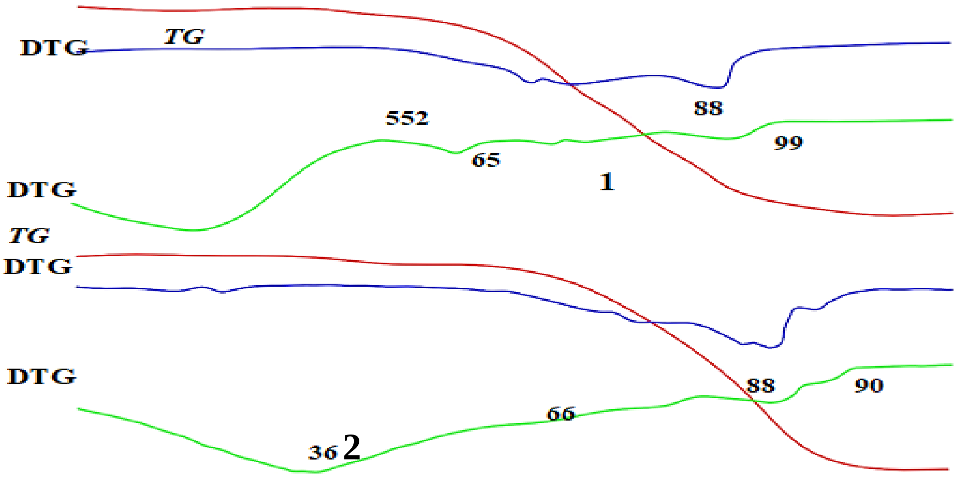
Place of birth of marl	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	p.p.	∑
Muynak	7,84	2,06	0,73	47,39	1,12	0,34	1,42	0,54	38,65	100,09
Muynak	7,50	2,08	0,83	47,28	1,16	0,21	0,93	0,50	39,52	100,01
Muynak	7,41	2,43	0,78	47,56	1,11	0,24	0,91	0,51	39,50	100,04
Kungrad	9,60	3,47	1,11	44,75	0,76	0,13	0,80	0,76	38,70	100,08
Kungrad	9,76	3,44	0,86	45,64	0,81	Сл.	0,85	0,72	37,81	99,89
Kungrad	9,71	3,41	1,19	45,20	0,81	Сл.	0,87	0,68	38,06	99,93

The chemical and physico-chemical characteristics of carbonate-clay rocks of the Republic of Karakalpakstan indicate the possibility of their use for the production of various binders of building materials: air lime, building lime, lime-belite binder, hydraulic lime and romancement, as the basis of binders for various purposes [6, 7].

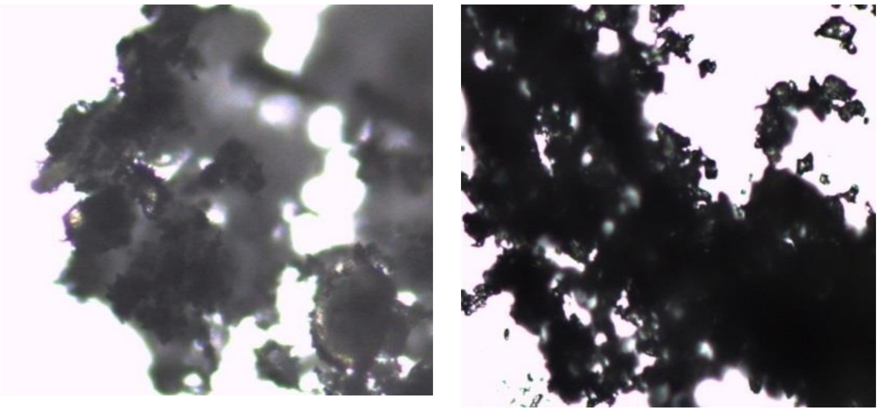
As can be seen from the chemical analysis data, the samples used in the work belong to lime marl. The chemical and mineralogical composition of marls is a mixture of calcium and magnesium carbonates, silica compounds, alumina and iron hydroxide in the composition of montmorillonite, a certain amount of calcium sulfate in the form of gypsum, a small amount of soluble salts of sulfuric and hydrochloric acids.

Derivatographic analysis (Fig. 1.) shows the endoeffect of the release of physically bound water at 300 ^{0}C from the marl of the Muynak deposit, and at 365 ^{0}C - from the marl of the Kungrad deposit; at 550-600^{0}C water of crystallization is released. The beginning of the decomposition of the carbonate part of the marl corresponds to endoeffects at 660 and 665^{0}C.

Electron microphotographs (Fig. 2.) show that calcite has an elongated rectangular shape, most often isometric in shape, forms a diamond-shaped section. Clay components are represented by flaky translucent particles of montmorillonite with a size of 0.15 microns, as well as thin isometric transparent plates of kaolinite with particle sizes of 0.15-0.2 microns. There is also a single admixture of point excretions of iron hydroxide.



Rice. Fig. 1. DTA, TG, and DTG curves for natural marls from the Muynak (1) and Kungrad (2) deposits.



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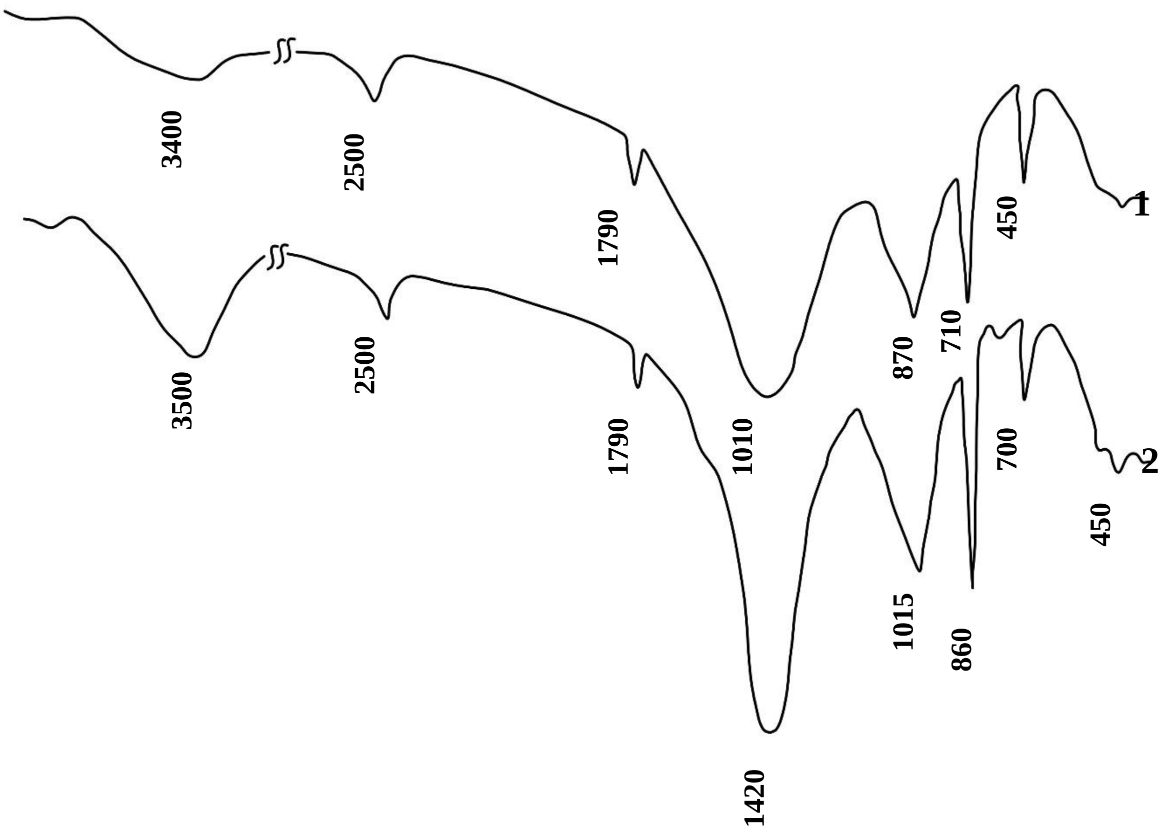
Rice. 2. Electron microscopic survey of natural marls from the Muynak (1) and Kungrad (2) deposits, x20,000 times.



Rice. Fig. 3. IR absorption spectra of marls from the Muynak (1) and Kungrad (2) deposits.

IR absorption spectra (Fig. 3.) indicate the presence of absorption bands in marl at 860-870 cm^{-1} (intense narrow band) and 1420-1430 cm^{-1} (intense wide band), due to vibrations of the CO_3^{2-} ion, which characterizes the presence of carbonate calcium. The presence of a hydroxyl group is characterized by stretching vibrations in the region of 2500-3600 cm^{-1}, and in the region of 1250-1400 cm^{-1} - deformation vibrations. The bands in the region of 1010-1015 cm^{-1} refer to the stretching vibrations of the Si-O group, and at 700 and 710 cm^{-1} - to the bending vibrations of the Al-O group.

It has been established [8] that the optimal heat treatment regimes for obtaining LBB based on the studied marls is a temperature within 1100 °C with an exposure of 60 min. Under these modes, the largest amount of free calcium oxide (52-62%) and β-dicalcium silicate-belite (30-35%) is formed in heat treatment products, in small quantities - calcium aluminates and ferrites.

The kinetics of gypsum structure can be judged from the change in the plastic strength P_m of the system, measured on a Geppler consistometer. The study of gypsum structure processes in concentrated LBB pastes makes it possible to reveal the role of the nature of the hydrated phase in the kinetics of strength formation and its creation in the emerging spatial structure.

The nature of the kinetic changes in the plastic strength of the system at a water-solid ratio W/H=0.80 (Table 2) differs from the nature of the change in the strength of the system at W/H =0,90 and 1,00. The plastic strength first increases, then, after 3 days of holding the system, it drops sharply, followed by a sharp increase again after 14 days. The nature of the kinetic changes in the plastic strength of the system at a water-solid ratio W/H =0,80 (Table 2) differs from the nature of the change in the strength of the system at W/H=0,90 and 1,00. The plastic strength first increases, then, after 3 days of holding the system, it drops sharply, followed by a sharp increase again after 14 days.

The presence of drops (W/H= 090) in the values of plastic strength Pm is apparently associated not only with the formation of different types of structures in the system - coagulation and crystallization with the transition of the first to the second, but also with different stages of formation of the crystallization structure [9].

Table 2. Kinetics of structure formation P_m, MPa, in LBB dispersions depending on the water-to-solid ratio

LBB based marl (deposits)	W/H	Change in plastic strength P_m after exposure, days					
		1	3	7	14	28	40
Muynak	0,80	16,8	19,3	16,7	13,6	19,5	27,8
Muynak	0,90	14,1	12,2	14,6	14,1	17,7	22,9
Muynak	1,00	13,4	12,0	13,9	13,4	16,5	20,1
Kungrad	0,80	16,0	19,7	17,1	15,7	20,1	30,2
Kungrad	0,90	12,2	12,6	13,6	13,5	17,6	28,3
Kungrad	1,00	11,7	11,7	14,6	13,4	16,2	23,7

During the first two stages of the formation of a crystallization structure, i.e. Accordingly, the appearance of crystalline nuclei of hydrosilicates and an increase in their number without intergrowth, as well as the formation of a crystalline intergrowth of nuclei, an increase in the strength of the system occurs, which, reaching a maximum at the transition to the third stage of formation of the structure of the formation of crystalline contacts of particles, begins to weaken due to the destruction of intergrowths and recrystallization of contacts [10]. The subsequent sharp increase in the strength of the system after a minimum is due to the formation of crystalline contacts, which give the system sufficiently high strength characteristics. This region coincides in time with the 14-day exposure of the system, which is relevant for all W/H options [11].

The fact that the minimum extreme point on the 14th day corresponds to the beginning of crystalline contacts is evidenced by the fact that the increase in strength after 14 days of exposure is sharp, since the strength parameters of crystallization structures, as a rule, always have relatively higher values for compared with coagulation structures, which is due to the nature of the forces that determine the contacts of particles in these structures [12]. It is known that the contacts of particles in the first (coagulation) structures are formed due to low-strength van der Waals forces of intermolecular interaction through thin interlayers of the dispersion medium and, therefore, have relatively low indices [13]. In crystallization structures, contacts are formed due to chemical forces with a much higher binding energy; they arise in the process of the formation of new phases from metastable supersaturated solutions, and these structures are intergrowth structures that differ from coagulation structures by several orders of magnitude in higher strength due to the formation of phase intergrowths.

Systems based on heat treatment products of marl from the Kungrad deposit at W/H =0,80 under moisture-air storage conditions have a maximum strength of about 27,9 MPa, and from the Muynak deposit – 30,1 MPa after 40 days of exposure.

In table. Figure 3 shows the results of physical studies of the dispersion based on the LBB. From the presented data, it can be seen that the water demand of the IPM obtained on the basis of the studied marls is greater than that of Portland cement or gypsum. This is due to the fact that the LBB composition, together with dicalcium silicate (β-C_2S), also contains large amounts of free calcium oxide CaO (58,24 and 50,30%), which, when hydrated with a large water demand, passes into calcium oxide hydrate .

Table 3 The results of physical studies of the LBB

LBB based on marl (deposits)	Normal density, %	Setting time, min		Specific surface, cm^2/g
		Start	the end	
Muynak	90	46	129	3200
Kungrad	90	43	142	3500

In table. 4 shows the dependence of the mechanical strength of LBB samples on the duration of hardening. It can be seen from the data in the table that both under the conditions of moisture-air and thermal-moist hardening, the mechanical strength of the samples increases with time, its greatest value occurs after 28 days.

Comparison of the strength values shows that the greatest difference in their values during compression is observed in LBB based on the marl of the Kungrad deposit, which indicates a relatively higher content of silicates, aluminates and calcium ferrites in the heat treatment products of the marl of this deposit compared to the Muynak marl.

Table 4 The results of the study of the mechanical compressive strength of LBB samples in moisture-air and thermal-moist hardening

LBB based on marl (deposit)	W/H	Compressive strength, MPa					
		moisture-air hardening, days			thermomoist hardening, days		
		3	7	28	3	7	28
Muynak	0,80	0,95	2,80	7,30	4,01	6,36	14,14
Kungrad	0,80	1,77	4,72	9,30	4,25	7,74	14,46

The initial strength of LBB is provided by the hydration of free lime and belite with the formation of the corresponding hydrates. A further very slow increase in strength (under normal conditions) is mainly due to the processes of carbonization of unbound calcium hydroxide. Therefore, with an increase in the content of the active form of SiO_2, it is possible, up to known limits, not only to intensify the hardening processes, but also to obtain a significantly higher strength of the hardened product [14].

X-ray pattern of hydrated for 28 days LBB is characterized by the presence of more intense lines of gillebrandite (0,302; 0,271; 0,260 nm), portlandite (0,486 and 0,192 nm), calcium hydrosilicate of the C-S-H type (11) (0,306 nm), as well as less intense lines of tobermorite $5CaO\ 6SiO_2 \cdot 5H_2O$ (0,251 and 0,248 nm). Lines 0,326; 0,205 nm and 0,186; 0,179 nm refer, respectively, to hydroaluminate and calcium hydroferrite. Activity, temperature and quenching time of LBB are given in table. 5.

Table 5 Activity, temperature and extinguishing time of LBB

LBB based on marl (deposits)	Extinguishing temperature, °C	extinguishing time, min	Activity, %
Muynak	44	14	70,97
Kungrad	43	15	70,22

Based on the data in table. 5, it can be assumed that LBB can be used in the production of high-strength autoclaved silicate products (cellular concrete, blocks, etc.), since the above properties of LBB correspond to the requirements for this type of product.

We also studied the influence of the method of adding sand to the original lime-belite binder. As follows from the results obtained, the ultimate compressive strength during air and wet storage of the physical and mechanical properties of LBB shows that with an increase in the amount of additives introduced (before heat treatment) of sand, the water-solid ratio decreases. This can be explained by the fact that the content of free calcium oxide decreases with the intensification of the formation of β-C_2S.

Table 6 Physical and mechanical properties of LBB

№	LBB_2 based marl	type of binder	W/H, %	Compressive strength, MPa					
				moisture-air curing			thermo-moist treatment		
				3days	7days	28days	3days	7days	28days
1	Muynak	LBB-5	0,90	0,99	2,19	9,79	1,27	3,37	12,21
2	Muynak	LBB-10	0,80	1,95	3,25	14,31	2,85	4,35	17,19
3	Muynak	LBB-20	0,80	1,35	3,19	13,37	2,95	4,37	16,48
4	Kungrad	LBB-5	0,90	1,74	3,49	13,85	1,93	5,38	16,60
5	Kungrad	LBB-10	0,80	3,38	9,39	21,11	4,19	16,76	24,40
6	Kungrad	LBB-20	0,80	1,88	5,11	19,27	1,95	9,15	21,70

The strength of the samples from the Muynak deposit is higher than the strength of the samples from the Kungrad deposit. However, by the 28th day it reaches the values of 14,29 and 21,07 MPa during moisture-air hardening, as well as 17,16 and 24,50 MPa during thermal-moist treatment, respectively, for the marls of the Muynak and Kungrad deposits. The strength of samples based on the Kungrad LBB-10 deposit after 3 days is 13,71 and 15,80%, and after 7 days – 22,60 and 44,66% of the 28 daily value, respectively, for Muynak and Kungrad marls, which gives reason classify them as slow-hardening.

As can be seen from the data in the table, the system gradually gains strength in the initial setting time, but its growth then somewhat slows down (3-7 days), the greatest strength of the system is observed by 28 days.

CONCLUSIONS

Thus, the versatile processes of GS in LBB dispersions obtained on the basis of marls of the Muynak and Kungrad deposits are characterized not only by the formation of different types of structures in the system - coagulation and crystallization - with the transition of the first to the second, but also by various stages of the formation of a crystallization structure. Based on the studies of the physicochemical and physico-mechanical properties of the considered LBB, it can be concluded that it is possible to obtain a highly effective binder for the preparation of high-strength autoclaved products.

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