

DECORATIVE DRY MORTARS ON THE BASIS OF MINERAL RESOURCES OF THE VOLGA REGION

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ABSTRACT

The possibility of using mixed-clay mineral additives of Volga region for decorative dry mortars is discussed. The effect of the clay firing temperature on the energy state of mineral additives surface as well as on the limit compressive strength of lime composite additives is shown.

KEYWORDS: Decorative Dry Mortars, Clay, Firing Temperature, Adsorption Centers, Lime Composite Strength

INTRODUCTION

For the restoration of historical buildings and structures dry building mixtures (DBM) based on lime have been widely used [1]. However, plaster on lime basis has low compressive strength, so to improve it active mineral additives are introduced into DBM.

It is proposed to get active mineral additives from mixed-clay deposits in the Volga region Vorobievsky, Kameshkirsky, Belinsky and Issinsky regions by methods of firing them at low temperatures. According to the research of Shumkov A.I. [2], clay burned at 450-650 °C is formed into monohydrate kaolinite, which is more reactive with lime than metakaolinite is. At the same time, the ability to react and the influence on the processes of interaction in the system "binder mineral additive" are explained by adsorption centers activity on the surface of the burned clay.

To reveal the distribution and concentration of acid-base centers on the surface of the clay particles, they have used indicator method of adsorption indicators with different pKa values. The research was done in Bronsted acid (pKa from 0 to 7) and basic (pKa from 7 to 13) centers, and Lewis acid (pKa > 13) centers.

The results are shown in Figure 1. These distribution curves of adsorption centers on the surface of clay in its natural state and after heat treatment at a temperature $t = 400-600$ 0C are constructed in coordinates:

$$q_{pKa} = F(pK_a), \quad (1)$$

Where q_{pKa} - the contents of active centers equivalent to the amount of adsorbed indicator of a particular acid strength - pKa.

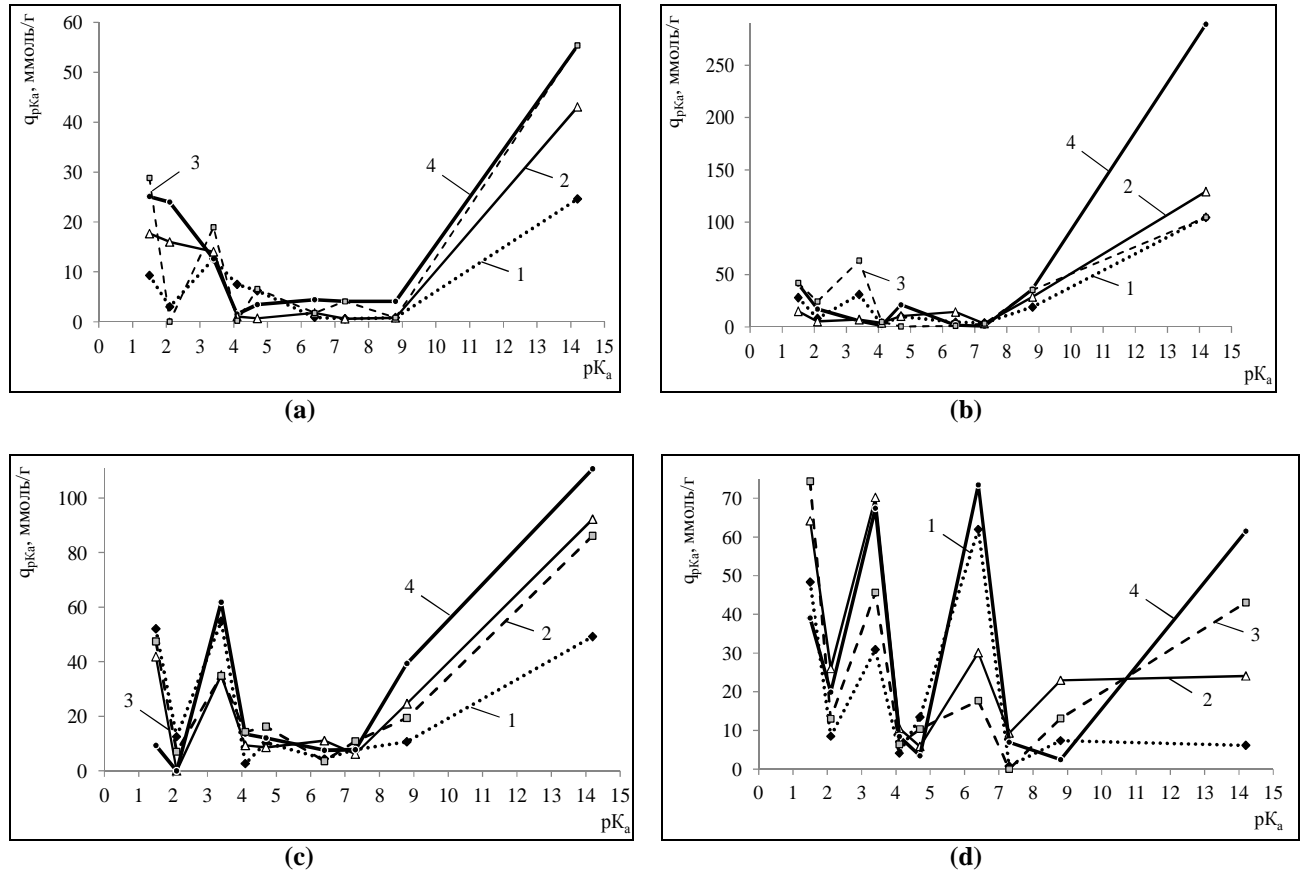


Figure 1: The Distribution of Acid-Base Centers on the Surface of Mineral Additives Produced at Different Temperatures of Clay Firing: a) Vorobyevsky Deposit: 1 - No Firing; 2 - at 500 °C; 3 - at 600 °C; 4 - at 450 °C; b) Kameshkirsky Deposit: 1 - No Firing; 2 – at 450 °C; 3 – at 600 °C; 4 - at 400°C; c) Belinsky Deposit: 1 - No Firing; 2 - at 600 °C; 3 - at 450 °C; 4 - at 500 °C d) Issinsky Deposit: 1 - No firing; 2 - at 400 °C; 3 – at 600 °C; 4 - at 500 °C.

The impact of the temperature factors has led to a change in the energy state of the surface particles of the studied clay (Figure 1). Comparison of adsorption centers distribution on the surface of materials having substantially the same chemical, mineralogical and granulometric compositions suggests that the number of Bronsted and Lewis acid centers on the surface of heat-treated clays exceeds the number of the same centers on the surface of unburned clay. From the experimental data (Figure 1) it follows that in the points of acid Bronsted (pK_a of from 0 to 7) the number of active centers on the surface of clay, calcined at 450 °C, was 71.17 mmol/g, while on the surface of unburned clay-39.54 mmol/g. In the basic Bronsted centers (pK_a of from 7 to 13) the number of active sites on the surface of the clay, calcined at the same temperature, was 8.19 mmol/g, and the surface of unburned clay-1.41 mmol/g. There is an increase of active centers number with a $pK_a > 13$, on the surface of fired clay, constituting 55.36 mmol/g, while on the surface of unburned clay-24.6 mmol/g. A similar pattern is observed when firing clays Kameshkirsky, Belinsky and Issinsky deposits (Figure 1, b-d).

According to Table 1, we can note that the multilayer aluminosilicates surface dehydration results in the formation of a large number of Lewis centers. So, before firing the clay of Kameshkirsky deposits the number of active centers in the $pK_a > 13$ was 104.57 mM/g after calcination at 400 °C it was 413.65. Lewis centers on the surface of clay give greater reactivity with a binder.

Table 1: Effect of Clay-Firing Temperature on the Clay Energy State (mmol / g) of its Surface

Deposits of Clay	Firing Temperature Clay, °C	Area of Acid-Base Centers (pK _a)			The Total Number of Active Centers, mmol/g
		0-7	7-13	>13	
Vorobievsky	Without Firing	39,14	1,41	24,60	65,55
	450	71,17	8,19	55,36	134,72
	500	51,23	1,41	43,06	95,7
	600	56,32	4,29	55,36	115,97
Kameshkirsky	Without Firing	83,50	22,73	104,57	210,8
	400	87,70	36,85	413,65	413,65
	450	55,36	55,36	129,17	216,96
	600	135,24	38,36	104,57	278,17
Belinsky	Without Firing	136,78	18,41	49,21	204,398
	450	106,03	30,80	92,26	229,09
	500	104,21	47,11	110,72	262,04
	600	123,23	110,72	86,15	218,89
Issinsky	Without Firing	167,30	8,15	6,15	181,60
	400	206,87	32,26	24,09	263,22
	500	211,75	9,43	61,51	282,69
	600	167,49	13,12	43,06	223,67

Following the experimental data (Figure 1, Table 1), we can say that the greatest total number of active centers have Kameshkirsky, Vorobievsky, Issinsky and Belinsky clay after firing at temperatures of 400 °C, respectively, 450 °C, 500 °C and 500 °C.

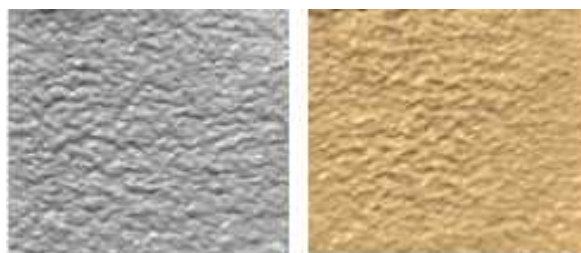
The values of lime-sand mortars strength after 28 days air-dry hardening confirm the results of research activity, distribution of acid-base centers on the surface of clay particles (Table 2). The samples were prepared on the basis of the Volga region Ukhta sand at a ratio of lime: sand = 1: 4 with addition of mineral additives in an amount of 10% by weight of lime. Water-lime ratio was at w/l = 1 4. As a binder they have used hydrated lime of 1st grade with 64-67% activity

Table 2: The Influence of the Firing Temperature on the Value of Compressive Strength R_{compress}, MPa

Deposits of Clay	Without Additive	With Addition of Unburned Clay	Clay Firing Temperature, °C				
			400	450	500	550	600
Kameshkirsky	0,84	1,22	1,75	1,70	1,69	1,63	1,58
Vorobievsky		0,95	1,28	1,67	1,55	1,52	1,5
Belinsky		1,31	1,62	1,71	2,2	1,98	1,78
Issinsky		0,95	1,45	1,57	1,68	1,64	1,58

The experimental data (Table 2) show that introduction of calcined clay into lime -sand composition increases the compressive strength after 28 days air-dry hardening depending on the firing temperature and the type of clay in 2,0-2,6 times. In case with Kameshkirsky clay the highest value of compressive strength at age 28 days of hardening is achieved by introduction of additives, burnt at 400 °C and is R_{szh}=1.75 MPa, while in the composition without these additives - 0.84 MPa. With introduction of Vorobyevsky clay, calcined at 450 °C, the strength is increased up to 1.67 MPa. Introduction of Belinsky and Issinsky clays after calcination at 500 °C increases the strength of compositions up to 2.2 and 1.68 MPa, respectively.

Introduction of dry construction mixtures of mineral additives increased compressive strength and changes the color of the finishing composition (Figure 2). Sands from Ukhtinski and Ablyazovsky fields of the Volga region have been used.



Control Formulation without Additives
Applying Composition to the Mineral Additives



Control Formulation without Additives
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Figure 2: Effect of Mineral Additives on the Color of Decorative Finishing Composition a) With Ukhtinsky Sand b) With Nizhniy Ablyazovsky Sand

In clay mixtures with sands from Ukhtinsky deposits it is recommended to use ocher clay from Vorobyevsky field as a mineral additive after calcinations at 450 °C. These clays are characterized by yellow color due to the content natural mineral ocher dye. After firing Vorobievsky clay possesses rich red color, due to which the finishing composition with addition of a mineral additive has beige color (Figure 2a). DBM based on Nizhniy Ablyazovsky sand has a matte terracotta color, which, being introduced into mineral additives based on clay from Belinsky field becomes more saturated (Figure 2b).

CONCLUSIONS

Our research has proved the efficacy of mixed clay of the Volga region fired at lower temperatures in the range 400-500 °C use in decorative DBM. The development of additives using local raw materials will reduce the cost of a decorative DBM and increase DBM decorative performance properties of coatings on their basis.

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