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INFLUENCE OF ZEOLITE ADDITIVE ON THE PROPERTIES OF PLASTER USED FOR MONUMENTAL SALTED WALLS

For the protection of walls against salt dampness various plasters and coatings are proposed. The plasters which presented the ability to transport the salt solution from the substrate, assuring the materials durability, are preferable in respect to traditional plasters such as cementplaster. The purpose of this study is to investigate the impact of natural zeolite additives in the production lime plasters meant for salted walls. This paper addresses the results of investigation of lime plaster with zeolites. The article presents the laboratory examinations of the basic physical and mechanical parameters such as absorbability, capillary absorption, density, total porosity, compressive and flexural strength. Mechanisms of the mortar modification are discussed based on the characterization results. There were used the special additives to improve properties such as hydrophobizer, methylcellulose - water-retaining additive; vinylacetate and ethylene copolymer powder, the redispersive additive for improvement of adhesion. The experimental results showed that the mortars modified by natural zeolites thank to their porous structure are distinguished for good sorption properties and can accumulate in themselves a sufficient amount of salt. Lime plasters with natural zeolites proposed in this work are fully compatible with traditional building materials, meaning that they can be used in the restoration of architectural heritage where there are problems with salts.

Key words: plaster, zeolite, compressive and flexural strength, absorbability, capillary absorption, salt.

Для захисту стін від висолоутворення використовуються різні штукатурні розчини і покриття. Штукатурки, які здатні транспортувати розчини солей з основи, забезпечуючи довговічність матеріалів, є кращими порівняно з традиційними штукатурками, такими як цементні. Мета дослідження – вивчення впливу добавки природного цеоліту в виробництві вапняних штукатурок, призначених для засолених стін. Подано результати дослідження вапняної штукатурки з добавкою цеолітів, лабораторні дослідження основних фізико-механічних параметрів, таких як сорбційна здатність, капілярне водопоглинання, густина, загальна пористість, міцність на стиск та вигин. Механізми модифікації розчину обговорюються на основі одержаних результатів. Для покращення властивостей розчинів використано спеціальні добавки, такі як гідрофобізатори, метилцелюлоза – водо утримувальна добавка; вінілацетат і порошок – кополімер етилену, редиспергувальна добавка для поліпшення адгезії. Експериментальні результати показали, що розчини, модифіковані природними цеолітами, завдяки їх пористій структурі відрізняються хорошими сорбційними властивостями і можуть накопичувати в собі достатню кількість солей. Вапняні штукатурки з добавкою природних цеолітів, запропоновані в цій роботі, повністю сумісні з традиційними будівельними матеріалами, тобто вони можуть використовуватися у реставрації архітектурної спадщини, де є проблеми з солями.

Ключові слова: штукатурка, цеоліт, міцність на стиск і вигин, сорбційна здатність, капілярне водопоглинання, сіль.

Introduction

An adequate choice of the repair plasters is crucial to succeed in a restoration process. Compatibility between the new plasters and the original components of the masonry is very desirable [1,2]. Renovations of the old moistened and saline walls must solve the problems of the presence of salts dissolved in water. It is often connected to reconstruction of the water-proof isolations and the repair of elevation together with cleaning, pointing, surface strengthening, hydrophobizing, repair or replacement of the old, destroyed plasters, etc. In renovation of the moistened and saline walls it is essential to apply suitable system of the renovation plasters which compounds are characterized by the suitable parameters that are compatible to each other.

Renovation plasters, also called WTA (ger. Wissenachaftlich – Technische Arbeitsgemeinschaft fьr Bauwerkserhaltung und Denkmalpflege – Scientific-Technical Work Group for the Maintenance and Preservation of Buildings and Monuments) are treated as complex drying and desalinating systems. These plasters are manufactured in a form of the prefabricated dry mixtures of binders, modifiers and the aggregates.

Standards for the renovation plasters are very rigorous and have been described in the German manual WTA-2-2-04 Sanierputzsysteme [3]. There have been determined the parameters which much be fulfilled by any plaster to be qualified as renovation WTA plaster.

Renovation plaster should be characterized by [4]:

- High porosity (air gaps share in the green mortar should exceed 25% and porosity of the ready mortar should exceed 40%). This enables water crystallization inside the plaster pores together with the hazardous salts without destruction of the plaster and wall structure. This causes increased frost and salt resistance.
- Diffusion resistance coefficient $\mu < 12$, which enables water vapor migration from the wall structure to the environment and quick drying, which prevents from salt and water concentration in the thin, subfacial layer of the wall.
- Suitable surface water absorptivity coefficient $w_{24} > 0.3$ kg/m^2 and depth of penetration $h < 5$ mm, which influences salt migration from the wall to the plaster surface and thus enables the limited penetration of the hazardous salts from the subsoil.
- Compressive strength β_d 1.5 ч 5 MPa and β_d / β_{bz} ratio (tensile strength during bending) < 3.

Besides the above mentioned parameters, the plasters should be characterized by high frost resistance, water resistance, salt resistance and hydrophobicity.

Characteristic feature of the renovation plasters is high porosity and the ability to cumulate water-soluble salts contained in the walls together with preventing from crystallization at the plaster surface which blocks off rainwater penetration. In general, the plasters are contained of three layers: rendering coat, priming layer and the surface layer. Rendering coat is characterized by great mechanical strength and hydrophobic parameters. It covers 50% of the wall surface and enables to increase the adherence of the priming layer. Priming is the equaling layer with great porosity and hydrophilic properties. Its aim is to accumulate water soluble salts. Final, surface layer of the renovation plaster is a porous, highly hydrophobic mortar that forms a barrier against rainwater influence. It prevents from salt cumulating layer moisturizing and thus enables evaporation of water contained in the wall by the diffusion phenomenon.

Plasters used for saline brick walls, manufactured using the traditional methods do not demonstrate constant adherence, they are crumbling and falling off the walls. A too strong repair plaster restrains movement and leads to stress that can cause failure in the original masonry [2, 5, 6]. Renovation plasters with light filling materials like perlite, polystyrene, vermiculite store great amount of salts but are not quickly destroyed. Only the plasters which use trass as a filling material are suitable for protection against moisture and salinity. Anyhow it must be mentioned here, that trass is a rock, dark and brawn in color which disturbs to obtain light colors of the plasters and to provide constant parameters of the renovation plasters.

Currently the compounds of mortars differ depending on the producer and can contain: grey and white cement, hydraulic calcium or gypsum, quartz sand, calcium and light aggregates (perlite, polystyrene, pumice, vermiculite), additives modifying their parameters and color.

Zeolites as an ennobling additive for mortar can create suitable features of the renovation plasters. Zeolite characteristics enables to obtain required porosity and diffusivity. The porous structure of the plaster with zeolite stimulates migration of water from the applied layer of plaster, what affects the hardening of plaster and its mechanical strength [7]. With their unique hollow structure, zeolites are distinguished for good sorption properties and can accumulate a sufficient amount of salt inside [8, 9].

Zeolites can increase the hydrophilic parameters of the plasters that's why they ought to be applied together with the hydrophobic additive, because one of the criteria to apply renovation plasters is high hydrophobia. It should be also underlined that costs of renovation plasters is several times greater from the traditional mineral plasters, that's why the attempts to obtain the renovation plasters using zeolites as an industrial waste can relatively decrease production costs of this type of the plasters.

The aim of this research was mineral renovation plaster (priming and facial layer) consisting of the White Portland Cement or blast-furnace cement, milled, granulated blast-furnace slag, hydrated calcium, sand, zeolite and chemical additives for plastification, strengthening, hydrophobising, aerating and stabilizing.

Experimental program

There has been designed the compound of 6 mixtures of mineral renovation plasters with high and low salinity level:

1. Mineral renovation plaster, non-colored, manufactured for walls with great salinity level. Content: White Portland Cement CEM 1 52,5 R 15.54%$_{mass}$, milled blast-furnace slag 3.45%$_{mass}$, hydrated calcium 5.00%$_{mass}$, sand with the following fractions 0 – 2mm 60.33%$_{mass}$, zeolite with the following fractions 0.5 – 2.0mm 14.76%$_{mass}$, stabilizing admixture – RETENTOR consisting of methylcellulose 0.15%$_{mass}$, powder resin based on copolymer of vinyl acetate – ethylene 0.70%$_{mass}$.

2. Mineral renovation plaster, non-colored, manufactured for walls with great salinity level. Content: White Portland Cement CEM 1 52,5 R 15.54%$_{mass}$, milled blast-furnace slag 3.45%$_{mass}$, hydrated calcium 5.00%$_{mass}$, sand with the following fractions 0 – 2mm 60.33%$_{mass}$, zeolite with the following fractions 0.5 – 2.0mm 14.76%$_{mass}$, stabilizing admixture – RETENTOR consisting of methylcellulose 0.15%$_{mass}$, powder resin based on copolymer of vinyl acetate – ethylene 0.50%$_{mass}$.

3. Mineral renovation plaster, non-colored, manufactured for walls with great salinity level. Content: White Portland Cement CEM 1 52,5 R 15.54%$_{mass}$, milled blast-furnace slag 3.45%$_{mass}$, hydrated calcium 5.00%$_{mass}$, sand with the following fractions 0 – 2mm 60.33%$_{mass}$, zeolite with the following fractions 0.5 – 2.0mm 14.76%$_{mass}$, stabilizing admixture – RETENTOR consisting of methylcellulose 0.15%$_{mass}$, powder resin based on copolymer of vinyl acetate – ethylene 0.90%$_{mass}$.

4. Mineral base plaster, non-colored, manufactured for walls with great salinity level. Content: Blast-furnace Cement CEM III 32,5 NA 15.54%$_{mass}$, gravelite 3.45%$_{mass}$, hydrated calcium 5.00%$_{mass}$, sand with the following fractions 0 – 2mm 60.33%$_{mass}$, zeolite with the following fractions 0.5 – 2.0mm 14.76%$_{mass}$, stabilizing admixture – RETENTOR consisting of methylcellulose 0.15%$_{mass}$, powder resin based on copolymer of vinyl acetate – ethylene 0.70%$_{mass}$.

5. Mineral base plaster, non-colored, manufactured for walls with great salinity level. Content: Blast-furnace Cement CEM III 32,5 NA 15.54%$_{mass}$, gravelite 3.45%$_{mass}$, hydrated calcium 5.00%$_{mass}$, sand with the following fractions 0 – 2mm 60.33%$_{mass}$, zeolite with the following fractions 0.5 – 2.0mm 14.76%$_{mass}$, stabilizing admixture –retentor consisting of methylcellulose 0.15%$_{mass}$, powder resin based on copolymer of vinyl acetate – ethylene 0.50%$_{mass}$.

6. Mineral base plaster, non-colored, manufactured for walls with great salinity level. Content: Blast-furnace Cement CEM III 32,5 NA 15.54%$_{mass}$, gravelite 3.45%$_{mass}$, hydrated calcium 5.00%$_{mass}$, sand with the following fractions 0 – 2mm 60.33%$_{mass}$, zeolite with the following fractions 0.5 – 2.0mm 14.76%$_{mass}$, stabilizing admixture – retentor consisting of methylcellulose 0.15%$_{mass}$, powder resin based on copolymer of vinyl acetate – ethylene 0.90%$_{mass}$.

Flexural strength and compressive strength

Flexural and compressive strength was determined according to the European Normative EN 1015-11 [10] using suitably 3 and 6 samples. Flexural strength was determined by the three-point weighting of the hardened mortar beams until destruction. Samples for the compressive strength determination were obtained from the previously used samples for flexural strength estimation. Research results are presented in Table 1, and the photograph from the experiment is presented at Fig. 1.

Table 1

Specification of the results of flexural and compressive strength determination

No	Force [N]	Average flexural strength β_{bz} [N/mm^2]	Force [N]	Average compressive strength β_d [N/mm^2]	β_d/β_{bz} ratio
1	740	1.736	7870	4.919	2.83
2	987.6	2.315	10868	6.792	2.93
3	1031.6	2.418	11300	7.062	2.92
4	832	1.950	6670	4.169	2.14
5	916	2.147	8653	5.408	2.52
6	621	1.455	7113	4.365	3.00

Fig. 1. Determination of flexural strength

All of the examined plasters did not exceed the required by WTA [3] $\beta_d/\ \beta_{bz}$ ratio < 3. The greatest compressive strength (7.062 N/mm^2) and the flexural strength (2.418 N/mm^2) was reached by plaster No 3 based on White Portland Cement CEM 1 52,5 R modified with powder resin based on copolymer of vinyl acetate-ethylene with the greatest resin content reaching 0.90%$_{mass}$.

The lowest compressive strength was reached by the plaster No 4 and it was 41% lower from the greatest one. The lowest flexural strength was reached by the plaster No 6 and it was 39.8% lower from the greatest one, equal to 1.455N/mm^2.

Bulk density

Densities of dried, hardened mortars were determined according to EN 1015-10 [11] normative. Volumetric density of the particular sample was determined as a quotient of dry mass and the volume covered by the saturated sample during submerging. For the experiment 6 samples were applied for each batch of mortar. Obtained results are presented in the Table 2.

Table 2

Specification of the research results of bulk density and open porosity of the plasters

Average density of the plasters, ρ [kg/m^3]					
1	2	3	4	5	6
1420	1380	1350	1430	1400	1420
Average open porosity of the plasters, P [%]					
1	2	3	4	5	6
29,5	30,0	28,2	27,5	27,4	26,6

According to the WTA 2-9-04 requirements, density of renovation plasters should not exceed 1400 kg/m^3. Only 3 of the 6 examined samples fulfilled these requirements (2,3,5). Plasters No 1, 4 and 6 not significantly (about 20 – 30 kg/m^3) exceeded the maximal density value required for renovation plasters.

Open porosity

Measurement of open porosity was conducted according to the EN 1936:2010 normative and determined using the following formula:

$$P_o = \frac{m_s - m_d}{m_s - m_h} \cdot 100\% \tag{1}$$

where: P_o – open porosity, %; m_d – mass of the dried sample, g; m_s – mass of the saturated sample in the air, g; m_h – mass of the sample submerged into the water, g.

Obtained results are presented in the Table 2. The plasters are characterized by the great open porosity which varies between 26.6 and 30.0%. It is not possible to compare open porosity to the value required by WTA instruction because both normative do not specify the value of open porosity for the renovation plasters.

Water absorption coefficient

Water absorption coefficient due to capillary uptake by the hardened mortar was determined according to the EN 1015-18 [13] normative. Research was conducted on 6 samples of each mortar. The samples shape was the rectangular prism. The experiment was conducted at the established conditions under atmospheric pressure. After drying to constant weigh, four walls of each sample were covered with epoxy resin to eliminate the influence of the external environment. Non covered walls of the samples were submerged to the depth between 5 – 10 mm for 24 hours period and the mass increase was determined. Experiment results are presented at Table 3.

Table 3

Statement of the experiment results of water absorption coefficient determination

Average water absorption coefficient C_m [kg/m^2]					
1	2	3	4	5	6
20.5	22.3	21.1	20.4	22.4	22.2

Water absorption coefficient of the renovation plasters after 24 hours of experiment should to be greater for the value of 0.3kg/m^2. All of the tested plasters are characterized by the great water absorption coefficient values, which value varied between 20.4 and 22.4 kg/m^2.

Frost resistance

Frost resistance examination was conducted using the direct method according to the method described in the Polish PN-88/B-06250 [14] normative. For the experiment there were applied 6 samples for each batch of mortar.

The samples were periodically frozen at the temperature of -18±2°C for at least 4 hours and then unfrozen in water at the temperature of 18±2°C for the period between 2 and 4 hours. Each freezing – thawing process was a single experiment cycle. There were conducted 60 cycles instead of required 25 to prove the increased frost resistance of the examined plasters. After the final cycle was finished, the beams were dried to constant weigh and weighed again to measure mass lost after the frost resistance determination. Percentage mass loss of the plasters is presented in the Table 4.

Table 4

Average percentage mass loss of the plaster samples after frost resistance determination

Average mass loss of the samples [%]					
1	2	3	4	5	6
0.50	0.03	0.01	0.80	0.03	0.01

All the analyzed renovation plasters were characterized by high frost resistance. Mass loss did not exceeded 1%, and the greatest one was observed in case of the plaster No 4 (0.80%), which was also characterized by the lowest compressive strength. The lowest, almost zero mass lost was observed at plasters No 2,3,5 and 6 both with blast-furnace slag additives and the gravelite additives. Plasters with the greatest percentage share of vinyl acetate-ethylene copolymer ($0.90\%_{mass}$) are characterized by the greatest frost resistance.

Resistance to salt crystallization

Resistance to salt crystallization was conducted according to EN12370:2001 [15] normative. For the experiment 6 samples of each batch of mortar were used. Dimensions of the samples were the following: 40x40x160mm. After drying and weighing the samples were submerged into the 14% solution of sodium sulfate decahydrate for the period of 2 hours. Then they were dried in the conditions of the progressive temperature increase until 105°C, which was achieved after 10 hours of experiment, maintaining high relative moisture at the initial stage of drying. After all, the samples were saturated with sodium sulfate again. The cycle of saturation and drying was repeated 15 times. Then the samples were stored in water for the period of 24 hours and then washed with water, dried and weighed. The obtained results are presented in percents as a relative difference of mass (loss or increase) in relation to the initial mass of the sample and the number of cycles till destruction, which meant lack of resistance to salt crystallization. Percentage mass loss of the samples after resistance to salt crystallization is presented in Table 5.

Table 5

Average percentage mass loss of the plaster after determination of resistance to salt crystallization

Average mass loss of the samples [%]					
1	2	3	4	5	6
0.20	0.02	0.01	0.50	0.07	0.15

Almost all the samples used in the examination proved good resistance to salt crystallization. Samples of the plasters No 2,3,5 and 6 during 15 cycles of experiment were not destroyed. Samples numbered as 1 and 4 are characterized by small mass loss equal 0.20 and 0.50% respectively.

Fig. 2 Condition of the plaster samples after examination on resistance to salt crystallization

Conclusions

An adequate choice of mortars and plasters is critical to the success of a restoration process. Influence of the natural zeolite fraction 0.5-2.0 mm in the amount of $14.76\%_{mass}$ on the properties of plaster is analyzed in this work. The most significant results obtained by the experimentation are as follows:

1. All examined plasters did not exceed the required by WTA $\beta_d/\ \beta_{bz}$ ratio <3. Mortars based on CEM 52,5 R Cement had greater than the required compressive strength >5 MPa, which means that it is reasonable to use lower class cements for manufacturing of the renovation plasters.

2. Copolymer of vinyl acetate (VA) - content in the mortars is also an important factor in controlling mortar properties. Mortars with the greatest polymer content obtained better strength parameters, the greatest frost resistance and the resistance to salt crystallization.

3. The plasters are characterized by high open porosity which varies between 26.6 to 30.0% and very high water absorption coefficient varying between 20.4 – 22.4 kg/m^2. This confirms good water absorptivity and accumulation of the crystallizing salts in the mortar air gaps.

4. All analyzed renovation plasters proved good frost resistance. Mass loss did not exceed 1% and in most cases was near to zero.

5. The plasters proved good resistance to salt crystallization. Only the plasters with the lowest content of copolymer of vinyl acetate (0.50%) are characterized by not big mass loss between 0.20 and 0.50%.

The zeolites additive is famous for good sorption properties, due to its unique structure, and can be used in dry mixes as a water-retaining, accumulates water with salt in walls masonry. Lime plasters with natural zeolites proposed in this work both with the additive of blast-furnace slag or the gravelite, together with the applied two types of cement – CEM I 52,5R and CEM III A 32,5 NA are suitable to the saline, moist walls and can be successfully applied as a substitute to WTA renovation plasters. They are fully compatible with traditional building materials, meaning that they can be used in the restoration of masonry walls salted.

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