

STUDY OF POLYMER-MODIFIED POWDER DRY MIX PRODUCED FROM MAGNESIA-BISHOFIT COMPOSITION WITH ADDITIVES

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1. INTRODUCTION

Today, new construction, reconstruction or renovation of buildings cannot be imagined without using dry mixes. However, having thoroughly studied technical literature and patent information extensive technology for manufacturing of dry mixes (and in particular in respect of floors) based on magnesium cement [1-3, 8-10, 7, 11] failed to be identified.

Floor construction, number of its layers, their thickness, and requirements to the basic parameters depend on application and condition of flooring underlay, as well as its application conditions, and modified dry mixes can function as the basis for any layer. When developing dry magnesia-bishofit compositions, as well as other polymineral ones, it is necessary to take into account the requirements of DSTU (State Standards of Ukraine) - PBB (Polymer-Bitumen Binders) 2.7-126:2011, as there are no regulatory documents on magnesium cement in Ukraine. Except the basic requirements, consideration should be given to the setting time of the mortar mix (at least 15 min), minimal shrinkage (widening) or its absence, absence of sedimentation (segregation), absence of cracks in the effective thickness layer.

2. RESULTS OF THE STUDIES

For the studies there was used a previously developed water-containing magnesia-bishofit composition with man-made additives and its anhydrous version for lab batching. In Table 1, except the components content, there are represented their basic specifications.

Magnesia stone, formed by curing of water-absorption mix has high strength properties $R_{manuf}(28) = 7-8$ MPa; $R_{mixcomp}(28) = 45-48$ MPa, but with relatively low water absorption ($W_{weight} = 6.3\%$) it exhibits unstable water resistance value ($F_{soft} = 0.7-0.8$). There are some problems related to microcracking in the structure of the specimens. Therefore, in order to improve physical and mechanical properties of floor elements, it was decided to add modern plasticizers and redispersible

polymer powders (RPPs) [2] in the dry mix.

After adding water to the dry mix (estimated C/T (Curing Time) = 0.22) there was defined its CS = 7.3 cm, and according to the requirements, [9] floor elements mobility must be at least 8 cm. This

Table 1. Content of the studied composition and processing properties of the components.

Specifications of the mixture components	Dimensions	Names of the components							
		Magnesium cement	Magnesium chloride	Ceramic powder	Microsilica	Phosphogypsum	Talc	Ferrous sulfate	Blast furnace slag
Content	%	41.58	25.98	15.20	4.729	3.378	3.378	3.378	3.368
Content of the dry mix (lab. batch)	kg	3.2	0.58	1.17	0.364	0.26	0.26	0.0345	0.182
True density	kg/m ³	2650	2700	2600	2340	2270	2780	4900	2600
Bulk density	kg/m ³	1250	2325	1350	300	1210	450	2500	850
Specific surface area	cm ² /g	3000	3000	2000	20000	3000	3000	3000	3000

difference can be reduced by adding plasticizers. This is important, as due to C/T, a mortar mix fails to be compacted tightly enough, and density reduction results in strength reduction. But with an increase in C/T, the concentration of polymer dispersions reduces, and without increasing the RPP content, the bond strength to various surfaces immediately drops, and the capillary water absorption significantly increases. Therefore, for

low C/T compositions the mortar mix should be sufficiently plastic, and this consistency is achieved through modification with a superplasticizer. Among a great number of them we chose Melment F10, chemical base of which is melamine formaldehyde produced by SKW (Germany), and which is recommended, inter alia, for self-leveling floors, with a proportion of 0.2...2.5% by weight of binder. This dry rapidly soluble powder is classified as an anion-active surfactant and outperforms a well-known C-3 [2, 7] by an order of magnitude. The principles of its action are based on scattering of electrostatic charges and stabilization of binder particles, which effect their dispersion and deflocculation. Thus, mortar mixes mobility is improved (Fig. 1) and water demand is considerably reduced.

As you can see in Figure 1, the optimal Melment content is 1% by weight of binder. We have obtained CS (Cone Slump) = 8.5 cm, but its further increase insignificantly improves plasticity of the soluble mixture. According to Uretskaya E.A. [8], this result is sufficient for self-leveling floor screeds.

Obtaining target plasticity and particularly water retention values requires dry building mixes modification of the so-called first-level, implemented by using cellulose ethers, as well as various types of methyl hydroxyethyl cellulose, soluble in polymer water. Dissolution time depends on the Blaine fineness of a polymer and chemical modifications of cellulose.

Results of adding Tylose SE to the magnesia-bishofit mixture with additives are given in Figure 2.

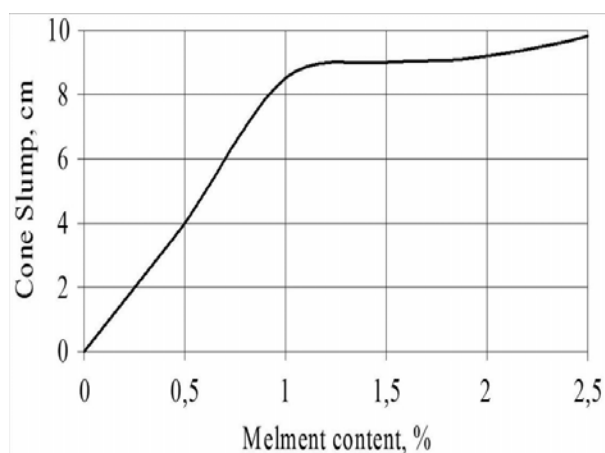


Figure 1. Magnesia-bishofit mixture mobility-to-superplasticizer content ratio.

Tylose SE additive added in the composition in the amount of 0.3%, contributes to the increase in water retention. Addition of 0.3-0.4% of additive in the mixture functions as a lubricant and increases a

shelf life of the mixture, i.e. its lifetime.

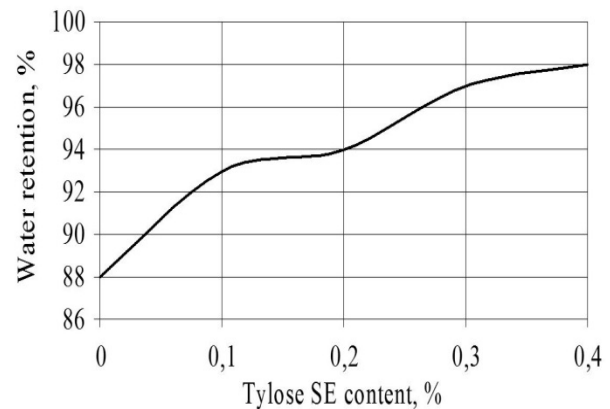


Figure 2. Water retention-to-Tylose SE content ratio.

At the same time, there was conducted a study on impact of Tylose SE on bond strength of magnesia-bishofit composite mortar to concrete base, the results of which are given in Figure 3.

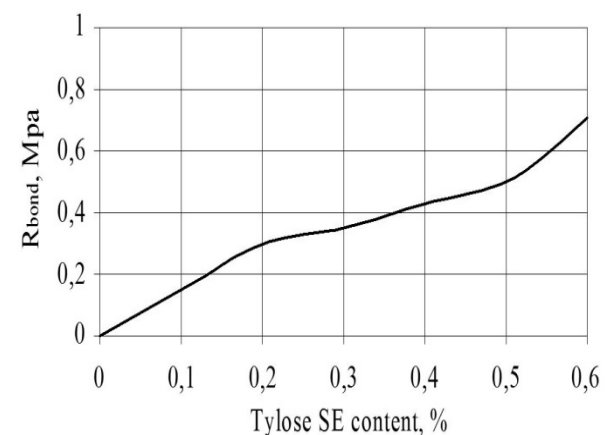


Figure 3. Bond strength of magnesia-bishofit composition with additives-to injected Tylose SE content ratio.

In Figure 3 you can see that after adding 0.3% of Tylose SE in the composition its bond strength to the concrete base was $R = 0.35$ MPa, and in order to obtain $R = 0.5$ MPa complying with the requirements for screeds [1], 0.5% of the additive is required. According to E.A. Uretskaya [8], European requirements for R_{bond} , in particular for self-leveling screeds should be $R_{\text{bond}} = 0.8$ MPa. According to DBN (State Regulations for Construction) [10], R_{bond} for self-leveling compositions (F2 (F-Flow) Group, layer thickness of 2-15 ml) is 0.5 MPa, and for F5 Group, designed for rigid base construction of polymer cement floors (R_{compr} less than 30 Mpa with layer thickness of 5-3 mm) bond strength should be at least 1 MPa. The first method of magnesia-bishofit mixtures

modification failed to give the above mentioned results, but it enabled improvement of one of the main properties of mortar mix, namely water retention - 96.3%. After adding 0.3% of Tylose SE in the dry composition (Table 1), standard specimens were made, the relevant test results are given in Table 2.

Table 2. Physical and mechanical properties of specimens made from a dry mix containing cellulose ethers.

True density ρ , g/m ³	Mean density P, kg/m ³	Porosity Po, %	Water absorption by weight, %	Water resistance factor F _{soft}	Strength properties, MPa, at 28 days			
					R _{bond}	R _{manuf}	R _{ext}	R _{compr}
2610	2040	248	56	0.081	0.35	6.3	3.2	42.4

As can be seen from Table 2, with improving water resistance some reduction in strength properties occur. This composition has low bond strength to base. Moreover, solutions designed for floor elements must not only have sufficient strength, but also permeability, low shrinkage, resistance to impact loading and other factors. Such values can be obtained through adding dispersible polymer powders in dry mixes, which is the second more complicated modification method.

In Ukraine, for floor elements experts from "Henkel Bautechnik" [6] recommend Winnapas Ri551Z and Winnapas Ri554Z RPP grades containing VC-E-VL polymers (VC-Vinyl chloride; E-Ethylene; VL-Vinyl laurate), providing dry cement base mixes with high physical and mechanical properties. Optimum Winnapas content in the mixes is 4 to 5%. RPPs manufactured by European and US companies listed here below exhibit similar properties as Winnapas: Mowilith (FRG); Celanese(FRG); Rhoximat, Rhodia (France); Elotex (Switzerland); Xinavil (Italy); DLP.Dow Chemiral (USA). Currently, two technologies are used in the production of powdered polymers: 1) by copolymerization of Vinyl acetate monomer and Ethylene (others are rarely used); 2) technology using Vinyl ether of Versatic acid. There is only one manufacturer of Versatic acid and its vinyl ethers in the world - Resolution Derformans Deodurts (RPP). During the last decade Copolymer vinyl acetate versatic dispersions (Veo

Va) were produced in the Western Europe in large volumes and are an excellent feedstock for the famous RPP Group - Mowilith, the manufacturer is Celanese (Germany). Basic properties of some representatives of this Group [5] are given in Table 3.

Table 3. Basic properties of copolymer vinyl acetate versatic dispersions.

Names of Mowilith Group RPPs	Bulk density ρ_{0nt} , kg/m ³	Mean particle size, μm	Anticaking agent content, %	Anti-foaming agent content, %	Minimum film forming temperature, t°C	pH (30% of dispersions)
Mowilith Pulver LD14 2080P Mowilith Pulver 1141P Mowilith Pulver JM 2072P	140-500	0.1 -0.5	5-15	10-15	5-25	4-12

However, even these RPPs relating to the same Group have different internal structure. Thus, Mowilith Pulver 1141 P contains Vac-E polymer (Vinyl acetate-ethylene). Mowilith Pulver LDM 2080 P contains Vac-Veb Va-A polymer (vinyl acetate- vinyl versatate-ethylene). The latter was selected as the second binder for the magnesia-bishofit composition, as it promotes improvement of bond strength and formation of a hydrophobic magnesia stone. Its working mechanism is that having a water-soluble agent when interacting with water, it restores the emulsion to its original form with the formation of a polymeric film coating all components of the mortar mix.

Minimum film forming temperature (MFFT) is a critical parameter for RPPs, because above MFFT latex particles are movable and form a film that is able to resist high mechanical stresses. The less MFFT value, the wider temperature range available for film formation. Addition of Mowilith increases shelf life of mortar mix, and air entraining effect

provides mortar with additional compressibility properties, thus facilitating application of a spreading device, and at the same time, bond strength continuously increases within the first week, and moreover, the value of 1 N/mm² can be obtained through the consumption of 1.5 to 5%. The higher Mowilith consumption, the higher tensile strength of hardened mortar, which is significantly higher than ordinary mortar strength.

In order to decide between two additives - Winnapas and Mowilith, there were conducted studies on influence of percentages of RPP additives in magnesia-bishofit composition on one of the most important parameter of floor elements, namely bond strength of coating to concrete base.

In Table 1 you can find the coating content that is a rational magnesia-bishofit composition. The curing time of coatings on the concrete specimens is 28 days in air-dry conditions, after this period 50x50x50 mm EDP (ЭДП) Grade metal plates were glued down over the coating with an epoxy adhesive. In a day bond strength value was estimated by using PSO-MG4 device [4, 11]. Test results are given in Figure 4.

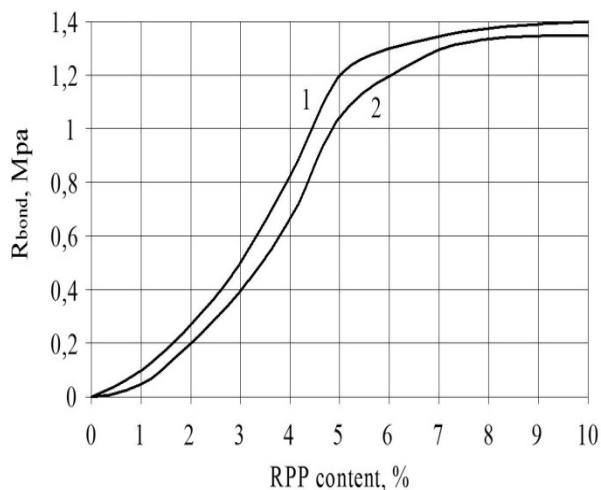


Figure 4. Bond strength (R_{bond}) of the specimens of magnesia-bishofit mortar to concrete base-to-percentage of RPP additive ratio: 1- Mowilith; 2-Winnapas.

Figure 4 shows the test results for a range of magnesia bishofit specimen mixes modified with RPPs -Mowilith Pulwer LD14 2080P and Winnapas RiS548. Inclusion of 3 to 3.5% of both RPPs in the mixtures enabled to obtain $R_{\text{bond}} = 0.5$ MPa, which complies with the DSTU requirements for screeds [3, 11]. With increasing the percentage of the additives up to 5%, R_{bond} reaches the values of 1.05 MPa to 1.2 MPa, thereby complying with the requirements for interlayers and coatings of floor elements, as well as the requirements for waterproof

flooring mixtures, $R_{\text{bond}} = 1.2$ MPa. Thus, adding 5% of RPPs in the mixture enabled to form a magnesia stone structure with more stable bond strength parameters.

Adding 5% of Mowilith improves all strength properties of the specimens (Table 4), in particular R_{bond} responsible for crack resistance of screeds, and also increases their hydrophobicity, and consequently freeze-thaw resistance. Comparative physical and mechanical properties of the screed specimens are provided in Table 4.

Table 4. Physical and mechanical properties of the screed specimens made with the use of various RPPs at 28 days.

Mortar	Grade used	Structural polymer	Strength values				Water resistance factor F_{soft}	Water absorption, %	
			RPP content, %	R_{bond}	R_{manuf}	R_{ext}			R_{compr}
Magnesia-bishofit with additives	without RPP	-	-	0.35	6.3	3.2	42.4	0.81	5.6
	Mowilith Pulwer LD14 2080P	VAC-1 VeOVa	5	1.12	9.81	6.8	45.2	0.91	3.3
	Winnapas RiS548 Z	VC-E-VL	5	1.02	9.39	6.5	44.6	0.89	3.7

As can be seen from Table 4, hardened compositions containing Mowilith, selected as an additive of the second modification level and functioning as the additional binder, have better parameters.

The shelf life of the developed composition is estimated according to paragraph 11.2.15 [9]. The shelf life of the mixture was estimated in minutes from the start of mixing the hardener and the mixture until the last test before the dissolved mixture filled the groove that was made with a stir rod. The shelf life of the mortar mix amounted to 1 hour 12 minutes, which complies with the requirements for screeds provided in Table 3 [9].

CONCLUSIONS

Through studying physical and mechanical properties of the cured magnesia-bisphofit composition specimens with added man-made powder components and 5% of modified Mowilith, it was established that high-strength is achieved through the formation of $5\text{MgO}\cdot\text{MgCl}_2\cdot 13\text{H}_2\text{O}$ and $3\text{MgO}\cdot\text{MgCl}_2\cdot 11\text{H}_2\text{O}$, and water resistance is improved not only by oxyhydrochlorides, but also by both calcium and magnesium silicate hydrates bonded by polymer binders, namely Mowilith.

Chelyabinsk: OOO (Ltd.) "SKB Stroyprobor", 2006. - p. 22- Access mode: http://www.stroypribor.ru/netcat_files/314/173/h_0ffd41bfb0974281f8f46cd3f1584b97.

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