

## Contact – Condensation Binders Containing in Polymers

MAISTRENKO Alla<sup>1, a</sup>, BERDNYK Oksana<sup>1, b\*</sup>,

AMELINA Natalia<sup>1, c</sup> and PETRIKOVA Evgenia<sup>1, d</sup> and TRIGUB Volodimir<sup>2, e</sup>

<sup>1</sup>Kyiv National University of Construction and Architecture, 31, Povitroflotskyi avenue, Ukraine, 03037

<sup>2</sup>National University of Civil Defence of Ukraine, 94, Chernyshevska str., Kharkiv, Ukraine, 61023

<sup>a</sup>maistrenko.aa@knuba.edu.ua, <sup>b</sup>berdnyk.oyu@knuba.edu.ua, <sup>c</sup>amelina.no@knuba.edu.ua, <sup>d</sup>petrykova.iem@knuba.edu.ua, <sup>e</sup>vlad.trigub.1978@gmail.com

**Keywords:** water – resistant polymer, contact-condensation binders, ecological safety, adsorption, Polivinyle acetate dispersion.

**Abstract.** The current paper focuses on the processes which bring about the formation of water – resistant polymer – containing film coatings based on contact – condensation binders. With the aid of complex physical – chemical investigations, the interactions in the polymer silicate systems and especially those which are stipulated by the structure state of silicates have been studied. These silicates are represented by highly – dispersed, amorphous or sub- microcrystalline phases. Established that, the properties of coatings, namely, increased water and atmospheric resistance, are determined by formation of chemical bonds in the system “Polyvinylacetate-calcium silicate hydrate”. Exposed the differences in the processes of structure formation, depending on the special features of the mineral components. The interaction activity of calcium silicate hydrates, to a certain extent is higher than for the unhydrous analogues of the stable crystalline structure. Presented the experimental results of the developed contact – condensation binders for composite materials based on industrial waste products, particularly, red bauxite slime. Therefore, the technological processes for production such binders are based on the methods which enable to synthesize materials with the given structural features. Hence, the present research is directed to the development of new-white and coloured painting materials.

### 1 Introduction

It is well known, that the determining property, of contact – condensation binders, consist of their capacity to form a water-resistant material either during mechanical convergence of macroparticles or spontaneous mobilization of water coupled with the conversation of the chemical constituent of the hydrated phases [1]. This group is related to the organic-mineral binders [2], whereby chemical interaction is conductive between hydrates and salts of the fatty acids in the dispersion state, with subsequent development of process under cramped conditions thus enhancing the formation of a water – resistant body. In fact, the mechanism of contact and hydrated hardening are realized in a sequence for such systems.

That's why, in order to extend the of the use of minerals, of contact - condensation binders, represented by dispersed calcium silicate hydrates of unstable crystal structure, the processes accompanying the formation of water - resistant coating films from silicate polymers, have been studied. First of all such materials have been used for the achievement and decoration building paint.

### 2. Main part

**Materials and methods.** The chemical composition of the raw materials used in order to obtain calcium silicate hydrate (CSH) is given in Table 1.

**Table 1.** Chemical composition of the raw materials

Name of material	Oxide content, [mass %]										
	LOI	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	TiO <sub>2</sub>
Lime	3.2	4.1	1.6	0.1	89.0	4.3	0.12	2.4	1.2	–	–
Quartz sand	0.08	98.76	–	0.31	0.07	–	0.11	–	–	–	–
Red bauxite slime	8.5	10.1	18.2	41.0	9.5	–	6.2	–	–	0.2	5.2

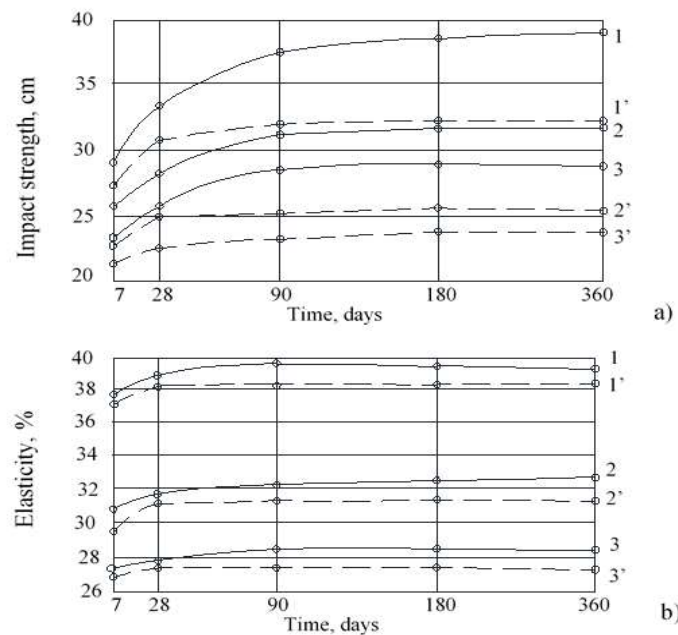
Binders are prepared by the proposed technology [3] through the use of hydrothermal treatment of lime silicate slime in a reactor at defined parameters, which provide the total execution of reactions and the synthesis of products satisfying the stoichiometry  $\text{CaO}:\text{SiO}_2=0.8\text{--}2.0$ . The evaluation of CSH with the aid of DTA, XRD methods plus surface energy values and true density, confirms it being amorphous, distinguishing it from the similar crystal possessing the same parameters [4].

The red bauxite slime by – product of aluminium production was employed as a technical raw material were obtained through in according with the technology [5], the addition of hydration activators in the form of  $\text{CaSO}_4$ ,  $\text{Na}_2\text{SO}_4$  and  $\text{CaO}$ ,  $\text{SiO}_2$  combined at the milling stage.

Polivinyl acetate dispersion (PVAD) mark DB48/5 of particle size 1–3 microns were used as water dispersed polymers. The compounds were prepared by mixing ingredients in a high - speed mixer so as to achieve compounds having viscosity of 20–30 sec. The solidification of the coating occurred under normal condition at  $18\pm 2$ .

### 3. Results and discussion

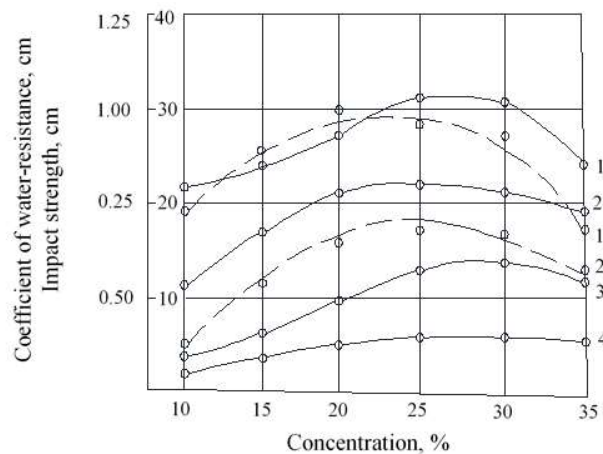
The structures formation of the polymersilicate composition with using CSH, obtained by synthesis of lime and quartz sand. Polymer – silicate materials made of CSH synthesized by lime and sand, are characterized of a general law expressing the increase in strength and elasticity at the initial period of solidification with respect to time when preserved in air as well as in water (Fig. 1).



**Fig. 1.** Kinetic curves for impact strength (a) and elasticity (b) of coatings based on CSH with basicity: 1.1' – 2.0; 2.2' – 1.5; 3.3' – 0.8

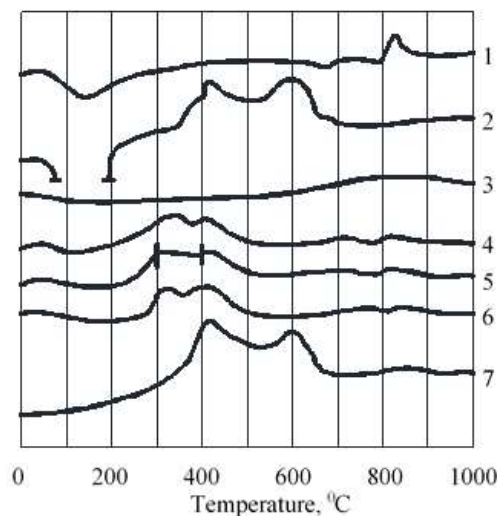
Remarks: — conservation in air; - - in water.

The comparison of strength properties of studied compounds based on lime powder, wollastonite and chalk paste that is a substance of stable and crystal structure, shows that the latter, hardening on possess impact resistance of 2–2.5 less than the polymer silicate coating basis on CSH like C-S-H(1) (Fig. 2). Besides the studied coatings based on C-S-H (1) with concentration PVAD 13–30 % have coefficient of water resistance 0.85–0.99, differing from the compared analogues. Hence, the principle differences in properties may be linked with the role of mineral components of a compound, where by active physical-chemical processes probably occur in the system containing CSH of submicrocrystalline structure, and facilitating the synthesis of strength.



**Fig. 2.** Influence of PVAD content on the coefficient of water resistance (1', 2') and impact strength of coatings (1, 2, 3, 4) based on: 1,1'. CSH C-S-H (I); 2, 2'. Wollastonite; 3. Lime powder; 4. Chalk paste

According to thermographic readings for: samples, (Fig.3, curve 4) the interaction in the system is accompanied with the appearance of complex polymer silicate phase "X", which can be assessed owing to the presence of a double exothermal effect at maximum of 325 and 420 °C, with the absence on curve 1, as well as on curve 2 of the initial components (Fig. 3). This product accumulates for 90 days (curve 5), and considered of being basic and sufficiently stable. The enlargement of the base of the total effect curve 6 in comparison with curve 4 (Fig. 3) acts as the proof. This process stabilized 90 days.



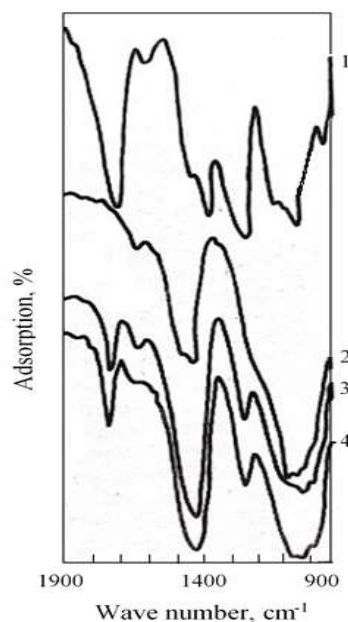
**Fig. 3.** DTA curves of coating samples based on CSH (curve 1), PVAD (curve 2), wollastonite (curve 3), CSH and PVAD with concentration of the latter – 20 %, wollastonite and PVAD (curve 7) in the age of hardening: curve 4 – 48 hours; curve 5 – 90 days; curve 6 – 360 days.

It is of necessity to note that, an alternative process in the systems containing anhydrous mineral compounds of stable crystalline structure in particular, is through the application of silica, calcite and anhydrous wollastonite. Curve 7 on the DTA charts shows that the compound based on wollastonite is characterized of an exoeffect at a temperature range of 320–650 °C and maximum at 400 and 600 °C, thus corresponding to PVAD.

Earlier investigations on compounds possessing silica and calcium carbonate have established that (3), the prolonged of unstable disintegrating phases in such systems.

Distinquishing from the above process, the presence of CSH provides an intensive and a complete interaction by accelerating the systems structure formation. The DTA data, based on specimen aged 48 hours, 90 and 360 days of hardening provides the proof. All the compounds have practically the same thermal effect, notwithstanding the significant differences in time conservation (Fig.3).

The most reactive part of PVAD molecules is considered to be the carbonyl C=O. Its presence is confirmed by absorptions band of 1700 cm<sup>-1</sup> (Fig. 4, curve 1). Besides, the C-O-C, group characterized by spectral band 1200 cm<sup>-1</sup> (Fig. 4, curve 1), is necessary for the reaction capacity. Particularly, according to changes in absorption band, which is related to these groups, we can judge the changes in the whole system. The availability of un-divided electron pairs in the oxygen atom, which takes part in the mentioned bondings stipulates it to acquire the properties of an electron-donor as well as possibility in conjunction with these of forming a donor-acceptor bond [6].



**Fig.4.** IR-spectrograms: 1.PVAD; 2.CSH as C-S-H (I); 3. Specimen of polymer silicate coatings with PVAD of concentration 20 %; 4. The same 30 %.

Calcium ion acts as the electron acceptor in the CSH with the formation of a compound [5].

Comparing the research results (6) the data given concerning the character of the processes in the system polymetacrylate (PMC) – Portland cement, whereby defined displacement, characterizing the formation of hydrogen bonding with the carbonic group are not recorded in the Infra-Red spectrometer. The Infra-Red spectroscopy (IRS) graphs of the investigated compounds (Fig. 4, curve 3, 4) record a visible displacement of 1630 cm<sup>-1</sup> of about 5 cm<sup>-1</sup> less, which is caused by the nature of the binder (compared to the cement stone impregnated with (PMC)).

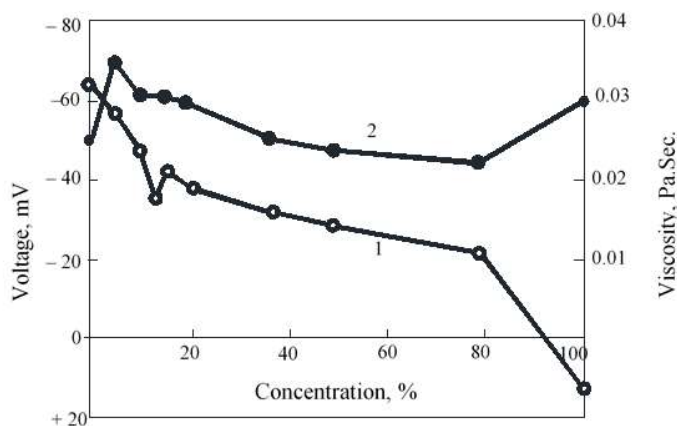
Besides, the characteristic of the donor-acceptor interaction between Ca ion and carbonyl group, evaluated by the absorption band 1530–1560 cm<sup>-1</sup> of low intensity, is known [7]. In the studied polymer silicate system it is difficult to record such a band, due to its coincidence with the vibration of the silicate group C-S-H (I) at 1420 cm<sup>-1</sup>. In this zone on the IRS graphs spectroscopy (Fig. 4, curve 3, 4) insignificant vibrations at 1550–1560 cm<sup>-1</sup>, corresponding to the formation of complicated

compounds, characterizing of donor-acceptor interaction between the calcium ion and the carbonyl group of PVAD are observed.

As shown by curves of IRS, a shift of vibrations of carbonyl group  $1700\text{ cm}^{-1}$  by  $40\text{ cm}^{-1}$ , that is  $1740\text{ cm}^{-1}$ , is obvious also for the C-O-C group  $1200\text{ cm}^{-1}$ , that is  $1240\text{ cm}^{-1}$ . The film formation process is accompanied by changes in bonds shape of the silicate components. The IRS graphs, expressed the increase in absorption band in zones of  $900\text{--}1200$ ,  $450\text{--}650\text{ cm}^{-1}$ , relating to the valency vibrations of Si-O.

As indicated by the investigations, the electrokinetic (zeta) potential (EKP) of the polymer containing dispersions of CSH can vary in wide limits, depending on the PVAD concentration (Fig. 5 curve 1). The initial CSH possesses a negative EKP ( $-64\text{ mV}$ ), which is characteristic for the majority of the natural and synthetic silicates [7] and explained by the peculiarities of the crystalline structure. Distinguishing from CSH, the PVAD in water possesses a positive EKP ( $+11\text{ mV}$ ). The difference in charge sign on the surface of the CSH and PVAD particles in the blended dispersion facilitates the interaction of particles thus providing conditions for heterocoagulation. Thus, varying the correlation of the concentrations contrary to the charged phases ought to alter the structure state of the system. Experiments show that, the addition of PVAD into CSH dispersion decreases the EKP to zero and latter attains positive values. However, isoelectrical point is attained at very high PVAD concentration –  $90\%$ .

Curve  $\eta\text{-C}$  is characterized by two sections (Fig. 5, curve 2): a rapid reduction in EKP is observed for regions with minor concentrations of PVAD, whereas after inflection when PVAD content is  $10\text{--}20\%$  a relatively gradual change in EKP with respect to rise in concentration is observed.



**Fig.5.** Dependence of EKP (curve 1) and effective viscosity (curve 2) of polymer silicate suspension upon the PVAD concentration

The appearance of the point of inflection on the curve proves of the transition of the dispersion from one structure state to the other, which is caused by the achievement of a specific correlation of the surface charges of CSH and PVAD particles. Therefore, in the same regions of PVAD concentrations ( $10\text{--}20\%$ ), the maximum value of effective viscosity of dispersions is observed (Fig. 5, curve 2). The addition of PVAD and increase in viscosity, corresponding to the strengthening of structure continues till the achievement of anisotropy on the surface charge of the CSH particle [8]. Such a state is linked with the formation of a large quantity of bridge bondings of the CSH particles and globules, corresponding to an incomplete enveloping of the CSH particles while conserving the negative charge on the surface of their sections [9].

Therefore, physical-chemical investigations on the process of structure formation of the compounds under consideration confirm that, their interaction is higher than for similar systems, containing unhydrous minerals of stable crystalline structure. To a certain extent, this character of the process of structure formation is determined by nature. That is – the state of the silicate structure based on highly dispersed amorphous or sub-microcrystalline phases [10].

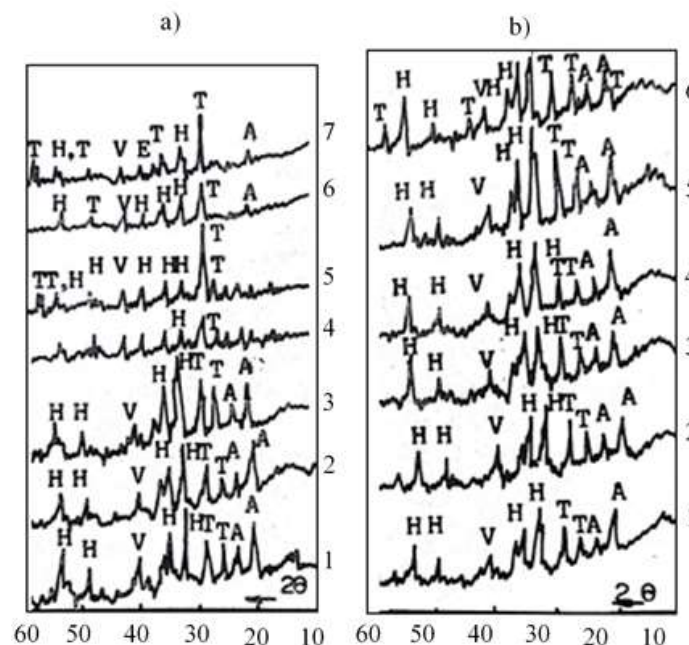
Binders based on bauxite slime. The employment of red bauxite slime for the achievement of dispersed products, leads to the formation of insignificant products during the hydration of CSH minerals (Fig. 6a, curve 2, 3). This is predetermined by the chemical-mineralogical composition of the slime, specific the presence of the hematite (Fig.6a, curve 1 with  $d=0.2696$ ;  $0.2513$ ;  $0.1843$ ;  $0.1692$ ;  $0.1452$  nm), wustite ( $d=0.221$  nm), magnetite ( $d=0.149$  nm) phases, as well as sodium aluminosilicate hydrate of constituent  $\text{Na}_2\text{O Al}_2\text{O}_3 (2.3\text{--}2.5) \text{SiO}_2 \cdot 2\text{H}_2\text{O}$  ( $d=0.74$ ;  $0.411$  nm). There is the probability of the presence of hydrogarnets with general formula  $3\text{CaO} (\text{Al}, \text{Fe})_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ , compounds possessing: titanium-like perovskite  $\text{CaO TiO}_2$ , phosphorus-like apatite  $3\text{CaO P}_2\text{O}_5 \cdot \text{H}_2\text{O}$  in the red slime, as well as complicated compounds containing titanates and silicates whose quantity (content) cannot be determined due to their sophisticated chemical constituents and insignificant presence.

Hence, the intensity of forming silicate hydrate phases in compounds based on the red slime with  $\text{CaSO}_4$ ,  $\text{Na}_2\text{SO}_4$  (2 %) additives on in their absence is not observed. Only insignificant quantities of silicate hydrate phases are present (Fig. 6b, curve 2, 3, 4, 5, 6 with  $d=0.307$ ;  $0.306$ ;  $0.302$ ;  $0.301$ ;  $0.183$  nm).

For complete bonding of ferrous compounds in the process of interactions, 2 %  $\text{TiO}_2$  was injected, taking into account the known capability of titanium dioxide to participate in the chemical reaction with ferrous. The presence of  $\text{TiO}_2$  has no influence on the formation or calcium silicate hydrates (Fig. 6a, curve 6, 7).

The investigation leading to the development of coating hydrates based on red slurry represents a unique interest, since the achieved powder contains terra-cotta color and can simultaneously perform the functions of an active ingredient as well as a colouring agent.

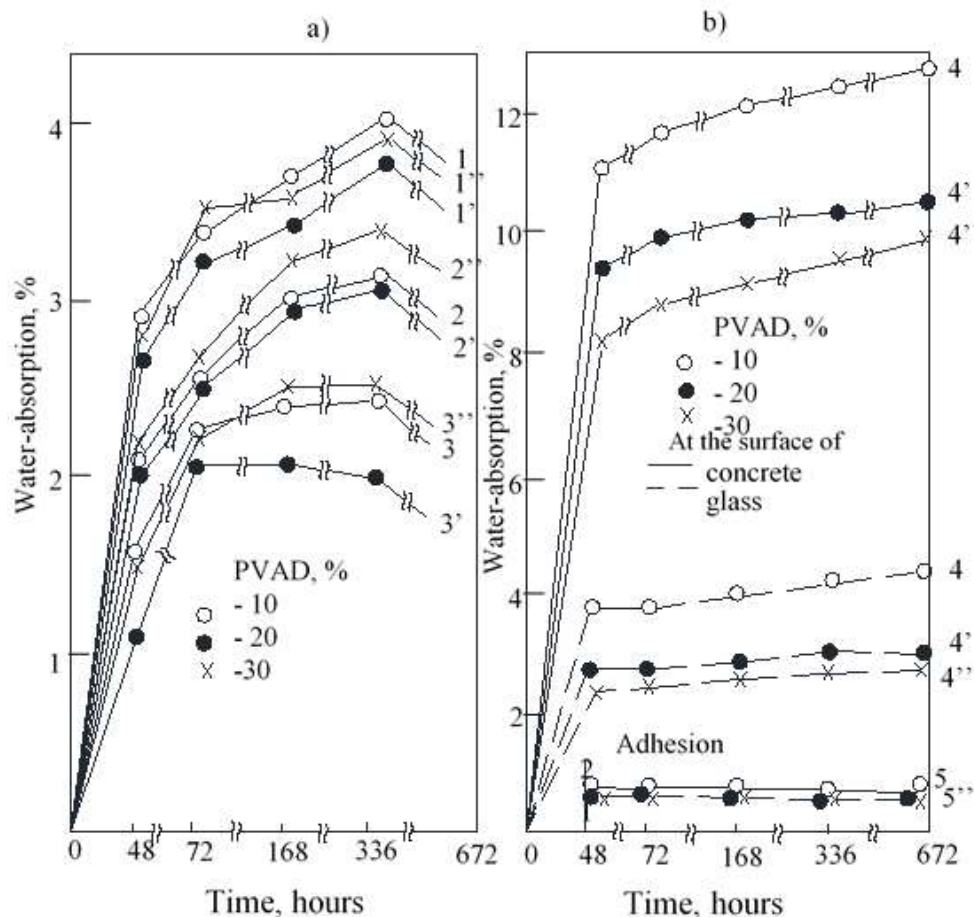
Coatings developed on the basis of red slime hydrates synthesized in the absence of additives or in the presence of  $\text{CaSO}_4$ ,  $\text{Na}_2\text{SO}_4$  and PVAD are characterized of reduced water-resistance properties. Investigation results (Fig. 7a) exhibit that, after 336 hours of water-saturation, the surface coating start to wreck, that is corrosion takes place on the film surface.



**Fig. 6.** XRD products synthesized on the basis of bauxite slurry: a). 1. Slurry-dry milling; 2. The same-wet milling; 3. The same-steam cured; 4. Mixture with 24 %  $\text{CaO}$ , 26 %  $\text{SiO}_2$  – after wet milling; 5. The same-after steam curing; 6. Vixture with 24 %  $\text{CaO}$ , 26 %  $\text{SiO}_2$  and 2 %  $\text{TiO}_2$  – after wet milling; 7. The same-after steam curing. b). 1. Mixture with 2 %  $\text{CaSO}_4$  – after wet milling; 2. The same-after steam curing; 3. The same-after autoclave treatment; 4. Mixture with 2 %  $\text{Na}_2\text{SO}_4$ -after wet milling; 5. The same-after steam curing; 6. The same-after autoclave treatment.

A-sodium aluminosilicate hydrate; H-htmatite; V-wustite; T-calcium silicate hydrate.

Through washing off, more over the washing-off occurs more intensively on the coatings developed on the basis of hydrates synthesized with the application if additives like  $\text{CaSO}_4$  and  $\text{Na}_2\text{SO}_4$ . Thus after 336 hours of water-saturation (Fig. 7a) the surface coatings suddenly reduce their water-absorption capacities. This is testified by the washing off of particles from the surface, as well as the visual observation of the surface coating destructed in the form of peelings.



**Fig. 7.** Water absorption of coatings made of red slime hydrates synthesized (a) without additives and with additives  $\text{CaSO}_4$ ,  $\text{Na}_2\text{SO}_4$ , (b) with additives  $\text{CaO}$ ,  $\text{SiO}_2$ ,  $\text{TiO}_2$ . 1, 1', 1'' – coatings based on additive free hydrates; 2, 2', 2'' – same with  $\text{CaSO}_4$  additive; 3, 3', 3'' – same with  $\text{Na}_2\text{SO}_4$  additive; 4, 4', 4'' – same with  $\text{CaO}$ ,  $\text{SiO}_2$ ,  $\text{TiO}_2$  additive; 5, 5' – adhesion of coatings based on hydrates synthesized with  $\text{CaO}$ ,  $\text{SiO}_2$ ,  $\text{TiO}_2$  additive.

It seems that, this process is linked with the availability a significant amount of phases of iron-containing compounds, which are present in the mineral powder as well as in the formed coatings, in a disintegrated state. Therefore, in order to improve the properties of surface coatings, powders synthesized with  $\text{CaO}$ ,  $\text{SiO}_2$  and  $\text{TiO}_2$  admixtures were utilized. Such powders contain mostly CSH in the form of C-S-H (I). The coatings based on such hydrates are characterized of an insignificant rise (approximately by 0.5 times) in water-absorption after 672 hours of water-saturation compared to the initial period (48 hours) (Fig. 7). Thus, samples containing 10 % PVAD have higher water-absorption properties compared to those containing 20 and 30 % PVAD (Fig. 7, curve 2, 2' and 3, 3'). Adhesion of surface coatings remains in variable.

Therefore, compiling the chemical constituents (formula) of the paint as well as the determination of the vital properties (water-resistance, adhesion) the possibility of developing decorative-protection materials based on contact-condensation systems, conforming with the required standards has been established.

#### 4. Conclusions

The physical-chemical investigation, results prove that, interaction activity of the polymer silicate composite systems is higher than that of the similar systems, containing anhydrous mineral compounds of stable crystalline structure.

Established that, the achieved coatings are characterized of being water-resistant, and this is regarded as one of the most significant properties accounting for the durability of paints as construction materials.

The mineral component in the form of contact-condensation binder can be obtained with the utilization of industrial waste products, in particular, red bauxite slime.

#### References

- [1] R.F. Runova, Bases of Technology for Silicate Materials of Contact-Condensation Hardening, Summary of Dr. Sc. Thesis, Kiev, Polytechnic Institute, 1987, 32 p.
- [2] I.V. Glukhovskiy, Organic – Mineral Binders of Contact Hardening. Summary of Phd. Thesis, Kharkov, Civil Engineering Institute, 1985, 19 p.
- [3] V.I. Rezvantsyev, P.F. Dolgaya, Thermographical Research for Structure – Formation of Emulsiomineral Mixtures, Prog. Gidrodornii, Publish, 1973, Rev.7, 121–126.
- [4] O.Yu. Berdnyk, O.V. Lastivka, A.A. Maystrenko, N.O. Amelina, Processes of structure formation and neoformation of basalt fiber in an alkaline environment. IOP Conf. Series: Materials Science and Engineering. Innovative Technology in Architecture and Design (ITAD 020). 907 012036.
- [5] V.I. Gots, O.V. Lastivka, O.Yu. Berdnyk, O.O. Tomin, P.S. Shilyuk, Corrosion resistance of polyester powder coatings using fillers of various chemical nature. Key Engineering Materials. 864 115–121.
- [6] R. Runova, V. Gots, I. Rudenko, O. Konstantynovskiy and O. Lastivka, MATEC Web of Conferences. 230 (2018) 03016.
- [7] R. Nicolas and J. Provis, Frontiers in materials. 2 (2015) 70.
- [8] O. Berdnyk, N. Amelina, E. Petrikova, A. Maystrenko, The use of self-compacting concrete with polycarboxylate additives in the production of long reinforced concrete structures. Reliability and durability of railway transport engineering structure and buildings.
- [9] V. Gots, O. Berdnyk, O. Lastivka, A. Maystrenko, N. Amelina, Corrosion of basalt fiber with titanium dioxide coating in NaOH and Ca(OH)<sub>2</sub> solutions. AIP Conf. Proc. 2490 (2023) 050010.
- [10] V. Gots, O. Lastivka, O. Berdnyk, O. Tomin and V. Mehet, Physical-Mechanical properties of powder coating in the system "Film-Forming – Crosslinking Agent". AIP Conf. Proc. 2840 (2023) 020002.