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The Role of the Law of Affinity Structures in the Construction Material Science by Performance of the Restoration Works

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Abstract: Within this research the processes of structure formation and structural optimization as well as properties of the cement stone and composite in whole during the process of hydration were studied; the construction composites with the specified properties were produced by means of the target structure formation. There was established a correlation between the porous structure of the monument under restoration and the properties of restoration composites.

Key words: Structure formation, construction composites, law of affinity structures, chemical additives, active mineral admixtures, porosity, construction-restoration materials

INTRODUCTION

Now a days preservation of many monuments is considered to be possible only after performance of restoration works. The experience in performance of such works is developing and improving continuously. One of the main requirements applicable to restoration is the maximum protection of the object originality. Replacement of the damaged pieces is the last extreme measure; preference shall be given to special reinforcement techniques. For each monument the most appropriate restoration method is selected based on the knowledge of the construction technology of the past and ability to reproduce it, if necessary to a certain approximation extent.

There are a few key restoration methods: conservation, additional arrangement of the damaged parts, replacement of the lost fragments, general preventive repair-restoration works, imitation of separate elements or parts, additional smearing works. As a rule, all of these techniques are used more or less simultaneously.

By all the variety of restoration materials including cementing agents some general requirements are applied to them. The new materials that directly contact the original monument materials shall match them in a number of parameters. They shall be near the genuine materials in terms of texture, micro and macrostructure do not change the color of the monument material, feature the comparable durability parameters including atmospheric durability, biostability be long-term stable and reliable. An important point is the compatibility of the new and old material preventing strains at the joints by accumulation of moisture and water soluble salts in the contact area. This diminishes the destructive processes and rejection of new inclusions that is usually followed by destruction of the original monument material.

So by performance of restoration works we shall be guided by the basic principle the principle of affinity structures (that is since 2014 called the law of affinity structures in the construction material science) consisting in minimization of the physic-chemical and structural differences between the adjustable matrix and rigid structure of the item under restoration in order to theoretically achieve the uniformity and homogeneity of the pore structure of the end composite (Lesovik *et al*., 2014; Lesovik and Chulkova, 2011; Lesovik, 2006; Geonics, 2012).

This will allow water migrating along capillaries of the entire composite facilitating the uniform compaction and reinforcement thereof by the new growths. Adjustment of the matrix structure is achieved by means of the principles of improving the construction material performance in order to get the homogenous uniform composite structure with uniformly distributed pores.

The objective of this study is improvement of efficiency of production of construction-restoration materials by means of managing the structure-forming processes, formation of the optimal structure and use of the restoration wastes.

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MAIN PART

During the study the processes of the structure formation and optimization of structure and properties of the cement stone and the composite in whole during the process of hydration and hardening with the use of technogenic raw materials and wastes of the restored item were analyzed; construction composites with the desired properties were designed by means of the target structure formation.

The was suggested the concept of formation of the construction composite structure on the basis of the law of affinity structures according to which all structures of construction materials may be divided into 3 levels by the pore size: nano-structure; micro-structure; macro-structure.

Formation of the capillary-porous structure with production of materials of all three levels is made possible by applying the processing techniques of fractionation, mixed grinding, modifying by additives use of the technogenic raw material, etc. and use of the components ensuring certain material porosity.

Production of the high-quality unique materials with minimal porosity is possible in case of using the durable and dense raw materials and use of the nano-dispersed fillers and chemical admixtures super plasticizers, hyper plasticizers, heavy salts for formation of porous structure at the nano-level. The adhesive strength of bonding of the new material with the old one is of the principal interest (Table 1).

The results of analysis of the adhesion strength of additional compositions used with these supports are presented in Table 1. These data show that the adhesion strength of the additional compositions containing the SP admixtures is higher than that of the admix-free composition. Higher adhesion strength was demonstrated by the compositions with SP N-1 and S-3.

Analysis of the hydration products formed in the presence of SP admixtures with the use of the XFA and DTA showed the absence of any significant changes in their phase composition (Fig. 1 and 2).

The structure of the cement stone has an influence on its strength that is in direct relationship to porosity. This is why, the cement stone depends mostly on the stone porous structure. The number and size of pores formed by the stone setting depend on the quantity of mixing water. Structural changes of the cement stone can be clearly seen in case of use of SP admixtures.

Introduction of super plasticizers to cement paste results in reduction of the overall porosity of the cement stone and redistribution of pore volume over the radii. Thus, in compositions containing SP admixtures the overall porosity is reduced as compared to the control compositions by 40-30% and is accompanied by the sharp redistribution of the pore volumes according to their dimensions. The large pores (with the radius over 103 nm) share is significantly reduced and the gel pores (with the radius <10 nm) content is increased. A denser and less porous cement stone structure is formed.

By maintenance of the W/C ratio in the compositions containing SP admixtures the overall porosity is reduced as well, however in this case disaggregating effect of SP

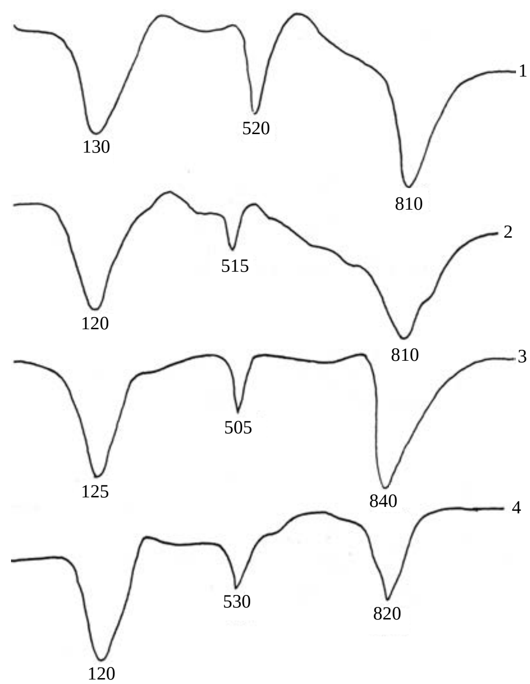

Fig. 1: DTA curves of the cement stone, low aluminate cement, S_{sp} = 300 m^2/kg; W/C = SC; 28 days of standard curing, SP concentration 0.7 wt.%; 1: without SP; 2: N-1; 3: S-3; 4: MF-AR

Table 1: Strength of the additional compositions on the basis of low aluminate cement with different materials

Admix SP	Admix quantity (wt.%)	W/C = SC (Standard Consistency)	Strength of adhesion MPa with the material at 28 days		
			Grass	Cement	Brick
-	-	0.26	0.01	0.1	>2
N-1	0.7	0.19	0.05	0.6	>4
S-3	0.7	0.20	0.05	0.6	>4
MF-AR	0.7	0.21	0.03	0.4	>4

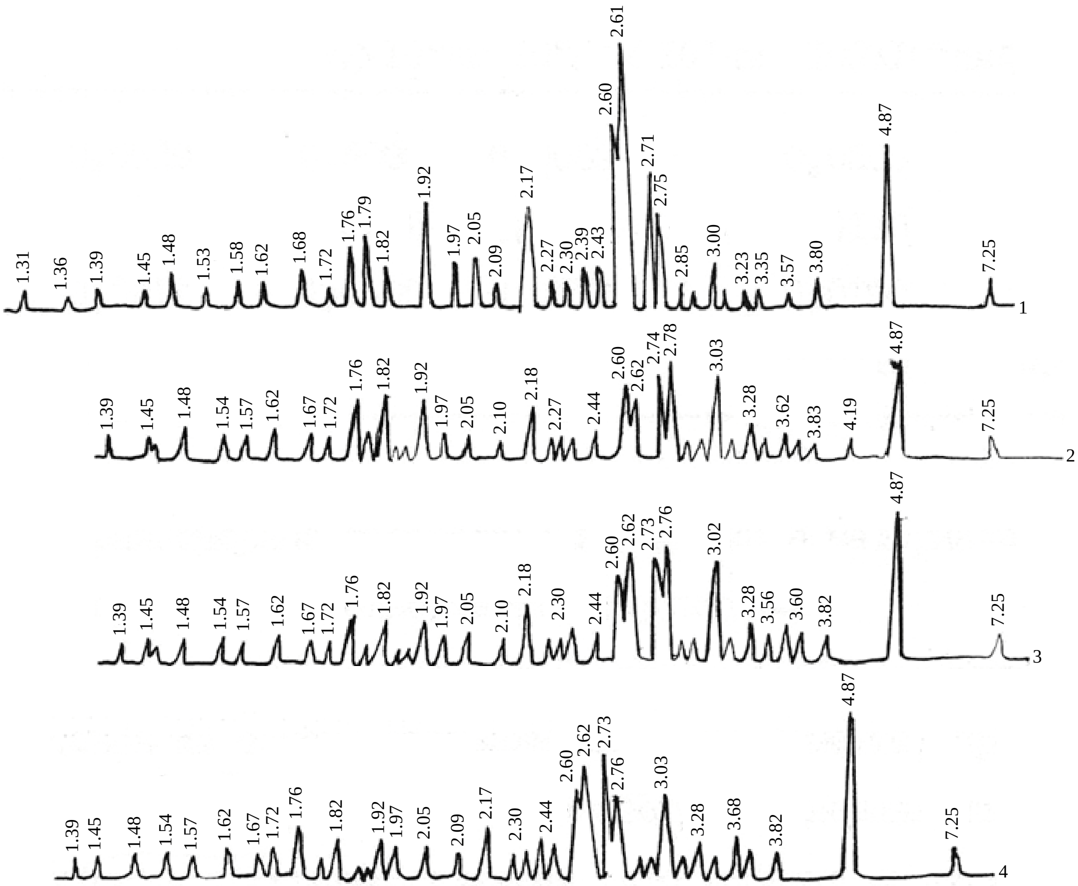

Fig. 2: Cement stone patterns, low aluminate cement, S_{sp} = 300 m^2/kg; W/P = SC; 28 days of standard curing, SP concentration 0.7% wt.; 1: without SP; 2: N-1; 3: S-3; 4: MF-AR

plays the major role. More uniform particle distribution over the material is accompanied by the increase in its structural homogeneity.

Introduction of SP allows preventing the initial cement flocculation due to adsorption and recharging of the particle surface. By adsorbing on the surface of cement particles, molecules of the SP admixes shield the intermolecular forces between solid particles, converting the cement-water suspension into a stable colloid. The water immobilized from floccule as the result of deflocculation increases the dispersion medium share which results in suspension dilution and reduction of its viscosity. The process of disaggregation (deflocculation) of the cement particles is illustrated in Fig. 3.

Thus, the SP admixes result in the reduction in the size and increase in the number of solid-phase particles featuring larger specific surface area. Under otherwise equal conditions this should be accompanied by the increased uniformity of the solid-phase particle distribution over the material structure, increased number of the twinning contacts between them and acceleration of formation of the heterogeneous disperse system structure (Chulkova, 2012).

Within this study, we attempted not only to define the change of the ξ-potential charge in the presence of SP but also to determine the value of the electro kinetic potential of cement dispersions.

In order to determine the ξ-potential, we used the Micro Electrophoresis Method. The procedure includes measurement of velocity of the charge particle moving under exposure to the electric field. It is rather difficult to measure the ξ-potential of cement particles without SP because of the extremely low particle velocity within the standard range of the field applied and by increasing the values of the potential applied electrophoretic flow becomes irregular. That is why in this case, the value of the ξ-potential of disperse particles was estimated rather approximately.

It is known that the ξ-potential value is affected by composition of mixing water this is why all the tests were

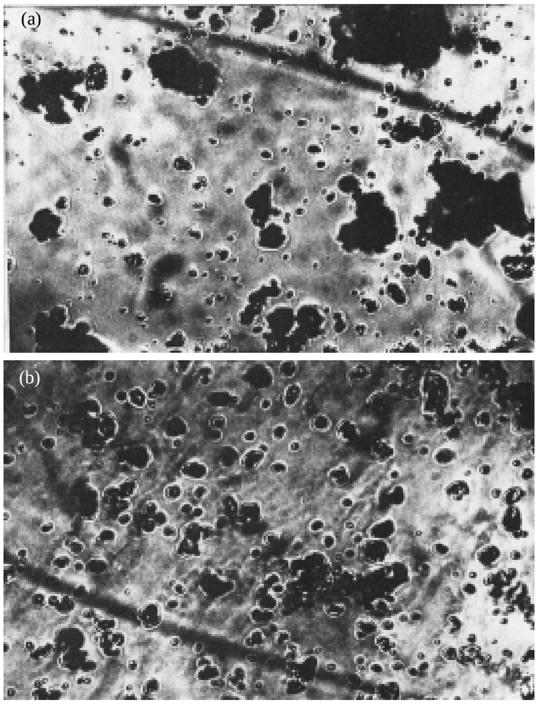

Fig. 3: Distribution of solid-phase particles in the cement-water suspensions, W/P = 10; x500: a) without SP and b) SP N-1

Table 2: Variation of the ξ-potential of different cements in the presence of SP (mV)

		Adsorption value g/100 g of adsorbent					
Cement	S_{sp} (m^2/kg)	-	N-1	N-3	S-3	MF-AR	10-03
N.-a.	300	10	-19	-24	-21	-13	-16
S.-a.	300	8	-26	-31	-32	-22	-20
V.-a.	300	8	-30	-36	-34	-26	-22

performed in distilled water. The results presented in the Table 2 show that this method of measurement of the ξ-potential value is suitable for the systems tested and is consistent with the available literature data.

Analysis of impact of SP (0.7% DS from the cement weight) on the ξ-potential value showed that in the suspensions of Portland cements the naphthalene-formaldehyde SP and SP of the "H" grade reduce the electro kinetic potential almost equally while introduction of naphthalene formaldehyde SP has a significantly weaker effect. Analysis of the results obtained allows comparing the reduction of the ξ-potential caused by SP admixes differing by the nature in the cement systems containing C_3A in the amount of from 4-10%. For all kinds of the SP tested the maximum values of ξ-potential were achieved by using high aluminate cement and the minimum by using low aluminate one.

Fig. 4a, b): Kolchak's headquarters building in Omsk

Thus, the designed compositions on the basis of ordinary cements have successfully passed experimental testing on the monument of architecture and culture of the 18th century Kolchak's headquarters building in Omsk. The building is in the excellent condition even after 14 years since restoration (Fig. 4). The experimental-restoration test reports confirmed their high efficiency. Methodological recommendations as to selection of the restoration techniques and methods of application thereof have been developed (Lesovik, 2007, 2003, 2004a, b; Yuriev, 2006; Gridchin, 2002; Lesovik *et al*., 2004, 2077; Lesovik and Klyuev, 2012; Klyuev and Lesovik, 2012; Klyuyev *et al*., 2013; Rakitchenko *et al*., 2013; Ageeva *et al*., 2014).

SUMMARY

The use of SP in the mixtures of the cement-based restoration compositions allows to directionally change their rheological, structural and physic-mechanical properties which are the result of their plasticizing, water-reducing, disaggregating and adsorption-modifying effect. Restoration compositions containing SP admixes feature increased density, reduced shrinkage strains, higher values of strength of bending, compression and adhesion to substrates of different texture.

Mineral Fillers (MF) along with imitation of the original material color through the increased water-need as well as due to the own peculiar features change the structural and strength characteristics of the restoration compositions and in fact are a tool ensuring conforming to the original material. Along with this they allow improving or maintaining at a sufficient level such properties as: adhesion to the original material, shrinkage strains, qualitative structure of the contact area, freeze-thaw resistance, softening coefficient, etc.

The use of SP in the mixtures of the cement-based restoration compositions increases the durability of the new materials under the aggressive atmospheric conditions. At the same time kinetics and value of the capillary water intake by the set material are changed substantially which may be used for optimization of humidity conditions inside the material of the restored item and if necessary for removal of salts penetrating it with the ground waters and acidic precipitations.

The SP admixes are the efficient factor of the targeted change of structure and properties of the cement-based restoration materials. The nature and extent of these changes depend on the mineral nature of cements, their dispersability as well as SP composition and volume. Through, changing of the rheological properties and water-content, through the adsorption-modifying effect SP (depending on their kind an volume) affect the parameters of the capillary-porous structure of restoration compositions, their strength and deformation properties. Such compositions feature increased density, bending and compression strength and most significantly, strength of adhesion to substrate of different texture. Their durability is increased significantly, the changes of the capillary properties allow managing the moisture transfer inside of the item under restoration.

Combination of the SP admixes with MF in the restoration compositions allows ensuring the acceptable shrinkage values (up to 1 mm m^{-1}), high adhesion strength (up to 3.6 MPa for the brick restoration materials, up to 2.8 MPa for chalkstone), sufficient freeze-thaw resistance of the material and low softening coefficient.

CONCLUSION

Ability to substantially change the capillary-porous structure allows managing the mass transfer in such material and consequently, removing excess water, salt solutions and preventing further monument destruction. Analysis of water absorption by cement-based restoration compositions showed that the ability of the target formation of their structure with the use of MF and SP allows regulating the moisture transfer process in the segments under restoration.

No phase changes were observed in the restoration compositions containing SP and MF. It was found with the use of electron microscopy and petrography that the proposed restoration compositions are similar to the restored material by their texture. The area of contact between them does not have a sharp edge; instea of it a compact homogenous structure with the uniform solid-phase distribution that almost does not differ from the adjacent segments is formed.

By the simultaneous introduction of MF and SP admixes the latter overcompensate the increase in the water-need of the restoration compositions determined by introduction of MF. By using MF and SP admixes we may get high-end restoration compositions similar to the original material (brick, chalkstone) in all basic parameters (strength, density, effective porosity and pore structure) which in its turn ensure the acceptable shrinkage values, high adhesion strength and durability of the monument material in whole.

It was shown that it is possible to directionally change the capillary-porous structure of such material and therefore manage the moisture transfer and remove the water-soluble salts from the deep layers of the original monument material which promotes to better preservation thereof.

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