The Parameters of Composite Binders of Technogenic Waste from Russian Far East

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Abstract: The paper considers the process optimization of structure of cement stone due to the use of industrial waste, which allows to increase the strength characteristics of the binders. Proposed composite binders, obtained by co-grinding of cement, hyper plasticizer, fly ash and limestone crushing screenings. The connection of the seal structure of the composite binder with increasing hydration activity of the fine fraction of the mineral filler. The increased strength characteristics developed binders provided due to their high specific surface area with mechanic and chemically activated surface layers of filler grains and cement.
Keywords: composite binders; cement; fly ash; limestone; hyper plasticizer.

1. Introduction

In terms of actual problems of modern building science issues include reducing energy producing efficient building composites, environmental improvement and optimization of the system "man-material-environment". These problems are typical for all world, including the Far Eastern region of Russia, which the priority development is one of the most important state tasks.

The construction industry is widely used as a structural material concrete on cement binder and natural aggregates. Since the Far East as a result of activity of the enterprises of the fuel and energy sector and mining industry generated large-capacity waste ash and rubble crushing screenings on the rocks, it seems necessary to optimize the processes of structure of concrete mixtures by using industrial waste. This will not only improve the strength characteristics of the binders, but also to improve the environmental situation in the region.

Foreign researchers have also made a significant contribution to the Exploration of concrete permeability. In particular S.-Y. Chung, T.-S. Han, S.-Y. Kim (South Korea) [1] studied the distribution of voids in the concrete and their effect on air permeability. Virtual models have been developed sufficiently reliable characteristics.

Chinese scientists M. Luo, C.-X. Qian, R.-Y. Li [2] have studied the self-healing concrete with special bacteria. The results showed that self-healing microbial agent may be used to achieve the purpose of self-healing concrete cracks. On the surface, cracks are formed precipitation of calcite, which provides a more dense morphology packaging.

Joint research schools of Hong Kong [3] found that the addition of limestone in the composite binder allows you to fill in the voids between the aggregate particles and thus create a more dense packing, which increases the tightness of cement stone.

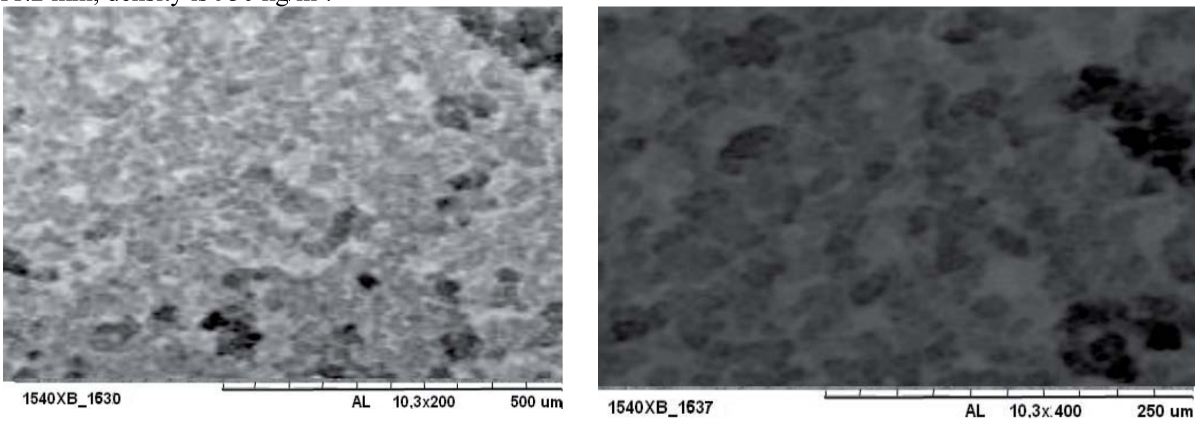
The fine-grained structure, in addition to the high homogeneity, is characterized by a decrease in specific stresses in the contact area and an increase in the adhesion between the components of the composite. Adhesion sand component increases significantly with an increase in the contact area, and an advanced surface-binding fine particles allows to intensify the process of hydration and structure, contributing to the improvement of the dynamics of growth and strength of the concrete compaction of structural composite matrix.

2. Experimental part

These conditions have been successfully used in the creation of fine-grained concrete on the basis of composite binding with screenings of crushing limestone rubble Wrangel field. To achieve this goal have been proposed composite binders, obtained by co-grinding of Portland cement, hyper plasticizer, fly ash and limestone crushing screenings. As components of fly ash used the largest thermal power plant of Primorye territory: Vladivostok TPP, Artem TPP, Primorye SPRS and Partizansk SPRS. This important factor is the possibility of dry ash selection implemented on these TPPs currently.

The use of man-made materials in the production of building materials contributes to the solution of the following main objectives: energy and resources saving; waste management; improve the environmental situation in the regions. Fly ash of thermal power plants is an effective material for the production of active mineral additives and fine.

The characteristics of the composite binder (Figure 1): The specific surface area - 600 m^2/kg (specific surface area meter indications PSH-11); particle size is 0.15-500 microns; average particle diameter is shifted to 0.65-11.2 mm; density is 930 kg/m^3.



(a) (b)

Fig. 1 General view of the composite binder (composition number 7 in Table 1): (a) × 200; (b) × 400

Developed composite binder has a reduced performance of normal consistency of cement paste – 18.3-20.5% (density cement slurry of cement CEM I 42.5N is 27.5%). The composite binders, where the proportion of cement is reduced to 50% of mineral additives, by co-milling the components, a high specific surface area of the individual components. Due to increasing the degree of poly dispersive of the grain seal space and hence viscosity concrete mix, which affects the normal density cement paste.

As part of the work was made of seven kinds of samples on the different formulations of the composite binder. In each of the formulations was added hyper plasticizer PANTARHIT PC160 Plv (FM) in an amount of 0.3%.

For controlling the composition of a sample of Portland cement CEM I 42.5 was passed Spassky cement factory. In other samples, we change the amount of cement, limestone and fly ash of two TPPs (Table 1). In the study of fly ashes Primorye SRPS and Partizansk SRPS were found exceeding the maximum permissible content of radionuclides in the waste of man-made, therefore they are not subject to fly ash use in construction.

Data of table 1 shows that the joint grinding Portland cement, hyper plasticizer, fly ash and limestone intensifies hydration process and enhances the hardening composite binding activity to 62%. Decreasing values of the normal density of the raw material mixture of the composite binder does not affect the positive nature of the dynamics of growth of physical and mechanical properties of hardening.

Table 1 Compositions and strength of composite binders

No	Cement content, by weight [%]	Fly ash content, by weight [%]		Limestone content, by weight [%]	Compressive strength, MPa		
		Vladivostok TPP	Artem TPP		3 d.	7 d.	28 d.
1	100 (without final grinding)	–	–	–	17	32.5	47.5
2	30	–	50	20	30.2	40.1	50.4
3	35	45	–	20	34.2	43.1	53.2
4	40	–	45	15	36.6	48.2	56.6
5	45	45	–	10	39.2	50.1	59.2
6	50	–	40	10	45.1	54.9	65.8
7	55	40	–	5	47.2	54.1	70.2
8	100	–	–	–	60.3	81	103.2

Note: The control formulation number 1 (without final grinding); number 2-8 compositions is milled to Ssp = 600 m^2/kg

Thus, cement paste strength binder number 7 at the age of 3 days of natural hardening of 47.2 MPa, which is 2 times the durability test samples (at a later date - by 1.4-1.6 times). In this joint grinding of components not only increases the end strength of the samples under compression, but also the strength development.

Mill ground active mineral components of the composite binder facilitate binding released during cement hydration $Ca(OH)_2$ in an additional amount of hydrosilicate tumors. The larger particles of the mineral component andsuperfine spherical ash particles act as crystallization centers and perform micro filler function, sealing the intergranular space in the cement concrete structure and reducing the number of pores and microcracks, which together reduces shrinkage strain (see., e.g. [4]) and positively affect the performance characteristics of the composite.

The additional amount of hydrate the crystalline phase contributes to filling the voids at the micro level in the crystal matrix hydrosilicates in the contact zone boundary, which increases the adhesion of the binder with filler. Thus, the structure of cement paste on the composite binder is a very dense packing of the grains in the common weight of neoplasms. These results are consistent with the published data [5, 6].

In order to optimize the particle size of the joint cement grinding was conducted hyper plasticizer, ash and limestone (composition number 7 in Table. 1) to different values of specific surface.

The results of measuring the strength of cement specimens obtained binders are shown in table 2.

Table 2 The dependence of the compressive strength [MPa] of cement samples from the specific surface area of the composite binder

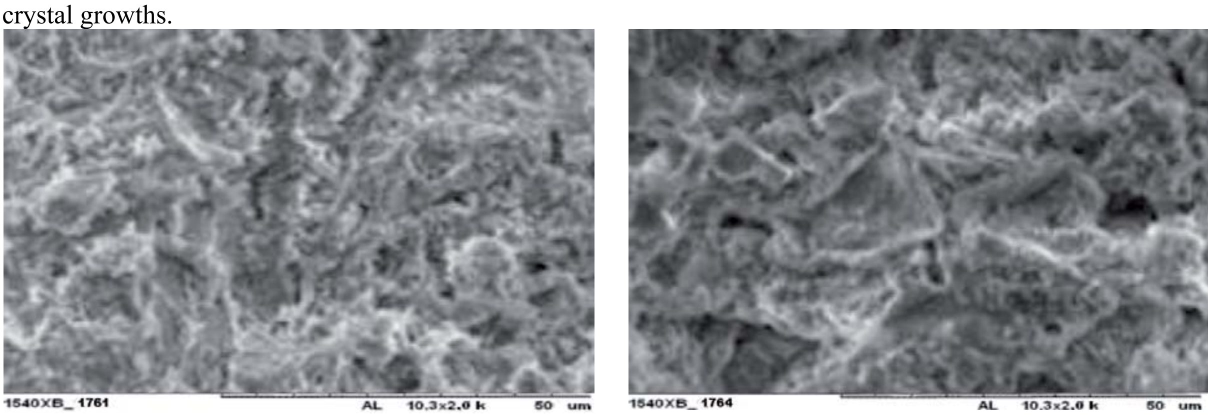
The hardening [d.]	The specific surface of the composite binder [m^2/kg]					
	500	550	600	700	800	900
3	46.1	47.4	47.2	46.0	45.6	45.5
7	50.3	54.2	54.1	49.1	48.6	48.4
28	68.1	77.3	70.2	65.8	55.0	65.0

The optimal specific binding surface is 550-600 m^2/kg. Its increase has a negative effect on the structure: binder with a surface area of over 600 m^2/kg significantly accelerates the curing of the mixture (up to 35-40 minutes, which is confirmed by experimental studies), but a quick grasp of raw prevents uniform distribution of spherical particles in the macrostructure of cement stone. Electron microscopy has allowed detect the presence of heterogeneity macrostructure and irregularly shaped cells.

The microstructure of the binder has a significant influence on the durability, strength and other characteristic properties of composite building materials, determining their period of operation in the products and designs.

The composite binders by using silica component can significantly reduce the amount of cement without reducing the physical, mechanical and technological parameters of concrete. The use of additives not only saves cement, but also accelerates the growth of tumors in a volume of the cement matrix.

Study of the microstructure was performed on samples aged 28 days with different contents of constituent components. Comparison of conventional cement stone on CEM I 42.5N (Figure 2a) with the cement stone in the composite binder (Figure 2b) showed that the structure the latter is more dense with a large number of crystal growths.



(a) (b)

Fig. 2 The microstructure of the cement stone: (a) - on CEM I 42.5N; (b) - on composite binder (composition number 7 in Table 1).

The resulting cement stone represents a microscopic heterogeneous dispersion. Cement grain has not yet come into the hydration reaction, play the role of micro filler, which are marked on the surface of the gel and crystalline growths. From the ratio of the gel-like and crystalline phases having different dispersion, morphology and physical and mechanical properties depend on the basic performance of the cement stone.

Electron microscopy showed that the introduction of the binder is formed of mineral fillers in high-density packaging structure of the composite grains of ash, clinker and limestone in the total mass of neoplasms. The microstructure of crystal formations riddled hydrosilicates, hydroaluminates, hydroferrites calcium and forming a dense array on the grains of the mineral filler (see Figure 1).

Thus the hydration of cementitious products have high adhesion [7, 8] to the silica component grains due to the large amount of crystal defects in the silica obtained by mechanical activation a composite binder. Mechanical chemical and treatment binder component allows to intensify the process of hydration of clinker minerals, it promotes the growth of tumors and the amount of cement paste strength. Sealing cementitious composite structure in comparison with a control sample of hydration associated with an increased activity of fine fractions of the mineral filler. The high specific surface mechanically activated surface layers of filler grains and cement, as well as emerging when hydrated amorphous surface membranes (about 2 microns) grains together ensure high physical and mechanical properties developed binders.

The most important task in creating a high-density concrete is a sustainable creation and optimization of the structure of the pore space. In general, it should be noted the overall reduction in porosity of modified composite waste production by more than 2 times (from 16.3% to 8%), the observed fluctuations pores of different diameter, due to the nature of their formation (table 3).

Table 2 The dependence of the compressive strength [MPa] of cement samples from the specific surface area of the composite binder

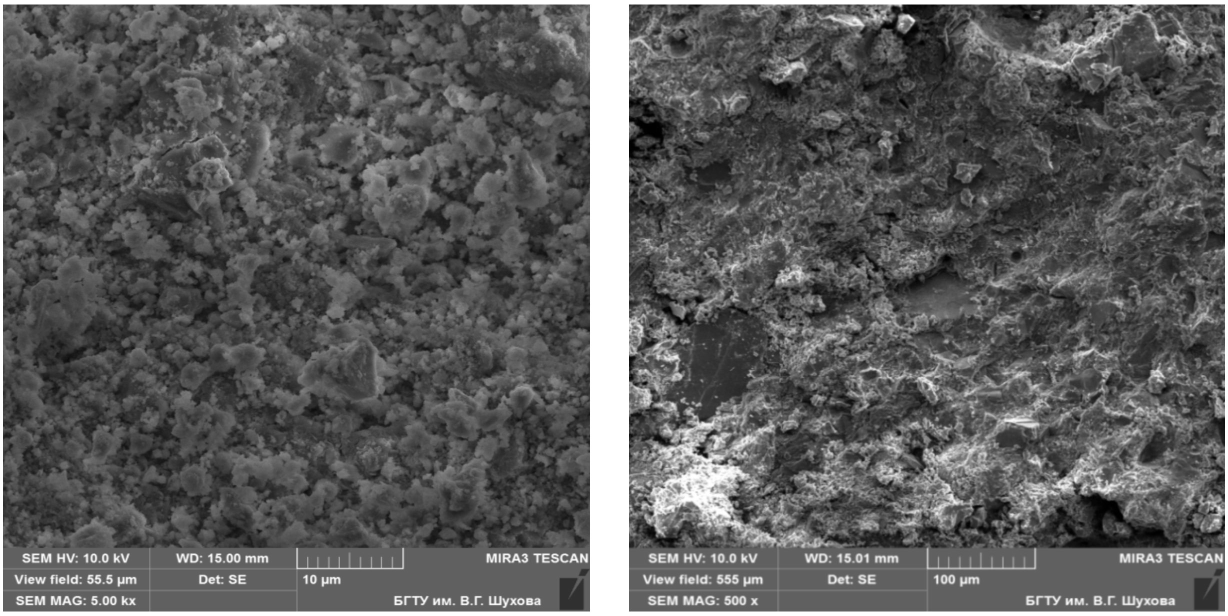
Composition according to table 1	Porosity [%]			
	technological (macroscopic level)	capillary (microscopic level / submicroscopic level	gel (supramolecular level)	total
1	1.2	4.6/2.3	8.2	16.3
2	2.6	1.7/4.5	1.6	10.4
3	1.3	1.1/5.0	3.5	10.8
4	1.4	1.9/2.3	4.4	9.6
5	3.6	1.7/2.5	1.6	9.4
6	3.2	1.1/1.0	3.5	8.8
7	1.0	0.9/1.8	4.4	8.1

3. Result and discussion

A large number of connections hydrosilicate confirmed decrease the porosity of the gel in conjunction crystalline molecularly modified composites with a maximum reduction of its more than 5 times (Table. 3). Although the maximum strength of 77.3 MPa, the optimal composition of binder (by grinding to Ssp = 550 m^2/kg), the porosity of the gel composite fell almost 2-fold. In this case, to achieve a high strength due to the influence of the complex: capillary porosity reduction due to the intensification of the processes of growth of primary crystal phases hydrosilicate, possible formation of secondary recrystallization and crystals; filling of the space at the micro, sub micro level and the structural organization of the composite in conjunction with a reduction in process porosity of 17% due to the formation of a dense packing of the grain structure at the macro level, with the participation of spherical fine components of fly ash and limestone crushing screenings.

The denser the structure of the binder composition with a lower porosity is confirmed by microstructural studies. When phase formation of a modified binder increases the amount of gel-like hydrate new formation on the surface of the filler particles (Figure 3 b), there are no visible crystals portlandite that shows a decline in its share in the total mass hydrosilicate ligament.

By varying the percentage of ash can be introduced to control the number and size of ettringite crystals, which further defines the properties of cement and concrete. The carbonates also have close contacts with cement stone, which is explained by the emergence of relations between the hydration of cement and limestone products. In the structure of the modified binder observed the growth of crystals of the needle and the "stem-like" morphology allegedly low basis hydrosilicates, there are also plate-like crystals of calcium allegedly hydrocarboaluminates (Figure 3 b). The synthesis of these compounds is the result of interaction produced during hydration of clinker minerals $Ca(OH)_2$ with active ingredients mineral ash and limestone. Growth needles contributes to reinforcement of the composite structure of nano- and micro reduction in porosity and increase strength of the composite complex.



(a) (b)

Fig. 3 The micrographs of neoplasm: (a) - cement stone without any additives; (b) - cement stone on the basis of the composite binder

4. Conclusion

The greatest effect is achieved through the synergistic effect of man-made pozzolanic additives (fly ash) and natural materials of sedimentary origin (limestone) at a content of cement - 55 wt. %, waste limestone crushing - 5 wt. % and ash - 40 wt. %. In this composite material composition of the binder it reaches the compressive strength of up to 77.3 MPa (by grinding to Ssp = 550 m^2/kg) at 45% replacement of cement by industrial waste [9, 10].

Thus, the influence of the character set of cement-fly ash-limestone composite binder, the resulting joint grinding with hyper plasticizer in vario-planetary mill, the process of structure formation. Mill ground active mineral supplements are the centers of tumors crystallization; ash particles contribute to the binding of $Ca(OH)_2$ produced during the hydration of clinker minerals, intensifying binder hydration to form needle-like crystals low basis hydrosilicates; choose from fine grains of limestone leads to the formation of calcium in the complex hydrocarboaluminates and it helps to reduce shrinkage deformation, the porosity and gas, watertight system.

Work should be continued in the direction of expanding the range of raw materials for the preparation of a composite binder in the study of the effectiveness of the use of tuff rocks of different genesis: how limestone and volcanic [11, 12].

From the standpoint of the analysis phase and structural transformations in the system «CaO-SiO_2-Al_2O_3-H_2O» further develop the theme prospects are connected with the study of the influence of the phase and dimension of heterogeneity of nanostructured composite binder, obtained on the basis of different types of mineral raw materials on the phase formation of cementitious stone [13, 14, 15].

5. References

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