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Increase in composite binder activity

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Abstract. The binder of portland cement (51-59 wt.%), fly ash of thermal power stations (36-44 wt.%), limestone crushing waste (4-9 wt.%) and dry hyper plasticizer (0.2 wt.%) has been created. It can be used in the building materials industry for production of high-strength concrete. The composite binder is obtained by co-milling of the components in vario-planetary mill to a specific surface area of 550-600 m^2/kg. The technical result is the possibility of obtaining a composite binder with significant replacement of cement with industrial waste, cost-effective and superior to portland cement for construction and technical properties, increased activity. This allows producing concrete for walling with a compressive strength of 100 MPa, while using more than 50% of industrial waste.

1. Introduction.

One of the most important tasks of our time is the reduction of energy consuming in manufacturing efficient building composites; environmental protection; the optimization of the system "man-material-environment". These problems are typical for the Far Eastern region of Russia, the priority development of which is the most important task of the state.

Building materials industry widely uses concrete on cement binder and natural aggregates as a structural material. At the same time large-capacity ash waste and rubble crushing of the rocks of different composition are formed as a result of mining industry companies and energy economy activities in the Far East.

Reengineering of concrete mixtures structure formation through the use of industrial waste seems to be necessary, which will increase strength characteristics. It will help to improve the environmental situation in the region through the use of industrial waste.

A large number of works by both Russian and foreign scientists [1-3] is devoted to the problem of increase in composite binder activity. It is known that one of the ways to improve the performance of concrete is the use of highly active additives of various composition and genesis both micro- and nanosized level, which contribute to the optimization of structure formation processes by initiating the formation of hydrated compounds. So the works carried out previously, prove effectiveness of using nanostructured silica-modifier composition as active mineral additives. Besides, capabilities of increase in composite binder activity by mechanical grinding of its components have been studied. However, with replacement of a large part of cement with production waste, there is a low strength of cement stone. It is inherent for such materials as fly ash and portland cement comprising wt. %: acidic fly ash of TPP - 30-40, bauxite and nepheline sludge - 20-30, the complex additive - 3-5, portland cement jointly milled to a surface area of 450-550 m^2/kg [4]. Thus, development of a dense structure of cement stone matrix, providing high physical and mechanical characteristics is rational. The goal of

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this is increasing strength of the cement stone, as well as obtaining high quality products on the basis of composite binding material with significant replacement of cement with industrial waste.

2. Composite binding material development

To achieve this goal, the composite binders obtained by co-grinding of portland cement, hyper plasticizer, ash and limestone in the vario-planetary mill have been used.

Fly ash of the Primorye largest thermal power plants such as Vladivostok TPP (figure 1) and Artem TPP, Primorye SRPS and Partizansk SRPS was used as a component of the composite binder. An important factor is the capacity of dry separate ash extraction that is currently implemented at these power plants.

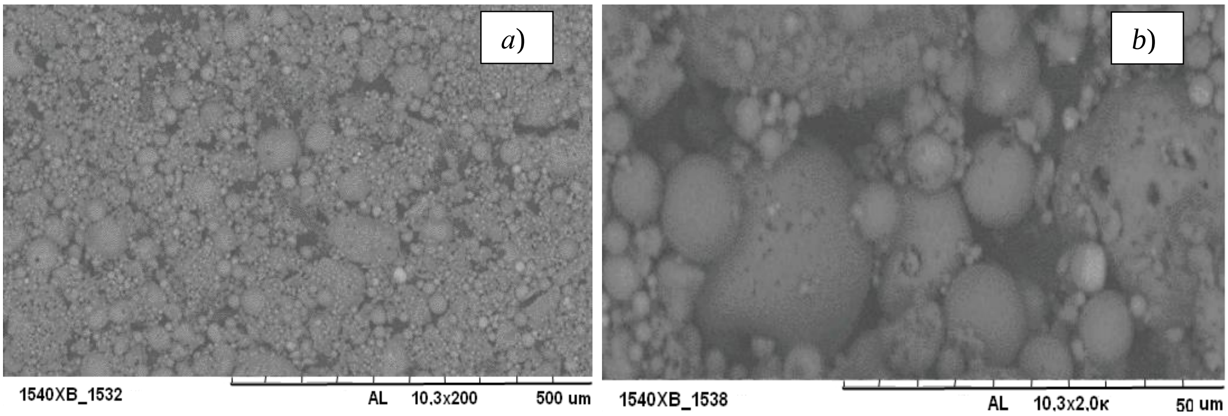

Figure 1. The general view of the Vladivostok TPP fly ash; 200x magnification (*a)* and 2000x magnification *(b)*

The use of technogenic raw materials in the manufacture of building materials contributes to the solution of the following main objectives: saving energy and raw resources; waste management; improvement of the environmental situation in the regions. Thermal power plants fly ash is an effective material for the production of active mineral and fine admixtures [5-6].

Considering the focus of research for the development and use of environmentally friendly materials, we have evaluated ash radioactivity (table 1).

Table 1. Specific effective activity of fly ash depending on the composition

Indicator	The measurement result (A), Bq / kg			
	Primorye SPRS	Vladivostok TPP	Artem TPP	Partizansk SRPS
Activity ^{40}K	496.9±101	362±89	342±68	516.9±101
Activity ^{232}Th	153.6±20.3	31.5±19.7	29.5±15.7	193.2±22.3
Activity ^{226}Ra	163.1±9.36	37.63±6.32	27.23±5.93	113.1±6.37
$A_{eff} = A_{Ra} + 1.31A_{Th} + 0.085A_K$	>398	80±30	93±20	>410

It was found that the ash of Vladivostok TPP and Artem TPP belongs to the first class of materials (A<370 Bq/kg) in accordance with GOST 30108-94 "Building materials and products. Determination of the specific effective activity of natural radionuclides" and can be used for all kinds of construction work [7-9].

Thermal studies showed that in the range of low temperatures physically bound water is removed from the ash sample. Exotherm with maximum at about 400°C indicates burnout of organic substances and endotherm at 712°C shows dissociation of calcite to CaO and CO_2, which is confirmed by X-ray diffraction (figure 2).

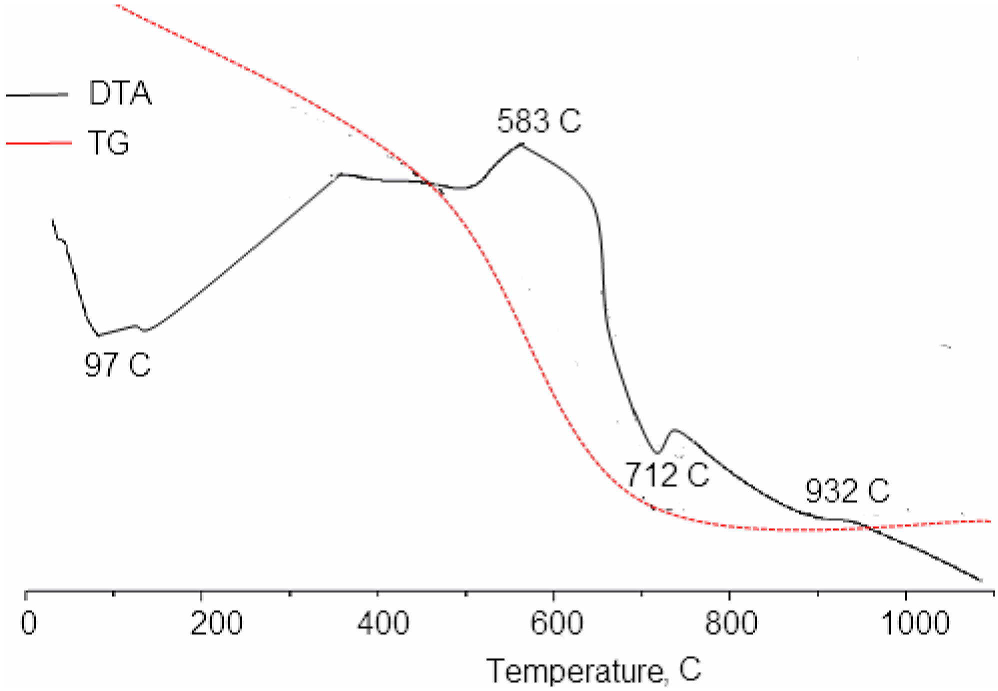

Figure 2. The results of DTA and TG of fly ash the Vladivostok TPP

Process optimization of structure formation by hydration of composite binder components creates a dense structure of the matrix, what is necessary to solve the problem of the creation composite for the production of high-strength concrete. This can be realized by co-grinding of portland cement, polyfunctional mineral admixtures and reducing the water-cement ratio of the concrete mix by using hyper plasticizer [10-12].
To reduce the water demand of concrete mix powder hyper plasticizer was selected of the six most common in the Far East market construction materials. Cement paste broke was measured with Hagermann cone. Spassky cement CEM I 42,5N was used for grout. Water-cement ratio is 0.3. Dosage plasticizer is 0.3%. Time of measurement start of Water Polution Class was recorded after the end of mixing the cement paste.
High values of WPC are achieved on binder raw mixture with hyper plasticizer PANTARHIT PC160 Plv (FM) (table 2).

Table 2. Broke of the cement paste with different hyper plasticizers

Time measurements, min	Melflux 1641 F, Germany	Melflux 5581 F, Germany	PANTARHIT PC160 Plv (FM), Russian Federation	FOX™-8H (Pwd), Russian Federation	PC-1030, China	JK-04 PPM, China
	broke, mm					
0	290	350	370	250	240	130
5	380	390	400	260	280	120
30	390	350	390	240	190	98

For further research 7 composite binder compositions have been developed. Hyper plasticizer PANTARHIT PC160 Plv (FM) was added in each of them an amount of 0.3%, the ratio of binder:

sand - 1: 3. To determine the optimal number of components in the "cement-lime-ash" system they were ground to a specific surface of 600 m^2/kg at various ratios (table 3).

Table 3. The compositions and properties of composite binders

No	Cement content, wt. %	Fly ash, wt. %		Limestone, wt. %	Compressive strength, MPa		
		Vladivostok TPP	Artem TPP		3 d	7 d.	28 d.
1	100 (without 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 milled to Ssp = 600 m^2/kg

3. Results

The positive dynamics of growth the composite binder strength under the joint influence of the fine constituents of ash, limestone crushing screenings and hyper plasticizers with the maximum increase in the activity of the binder at 62% has been achieved.

Active mineral components of the composite binder contribute to the binding of $Ca(OH)_2$ produced during cement hydration in additional amount hydrosilicate tumors. At the same time optimization of the process of structure formation is achieved by polydispersity of composite components. Highly spherical ash particles act as nucleation sites and act as a nano- and micro- filler. In conjunction with larger particles of the mineral component denser filling of intergranular spaces in cement concrete structure occurs with the reduction in the number of pores and microcracks.

This is confirmed by micrographs of cement paste on the composite binder, produced by joint grinding of clinker and industrial wastes of the Far Eastern region. Cement stone structure is a very dense packing of fine grains in the total weight of the crystalline tumors (figure 3).

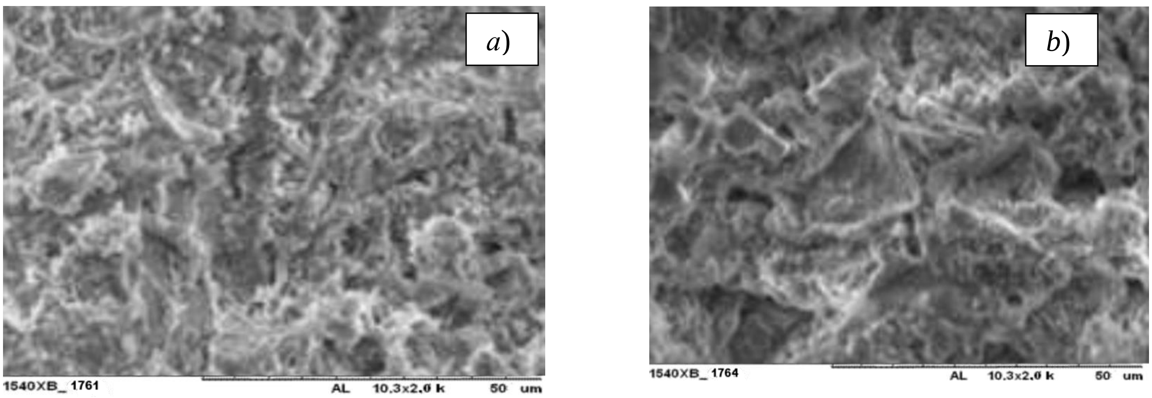

Figure 3. The cement stone microstructure: on CEM I 42.5 N *(a)* on the composite binder (composition number 7 in Table. 3) *(b)*

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An additional amount of hydrated crystalline phases contributes to filling of the voids at the micro level in the crystalline matrix of calcium hydrosilicates on the boundary of the contact area, increasing the degree of adhesion of the binder with filler.

4. Conclusion

The composite binder of portland cement (51-59 wt.%), fly ash of thermal power stations (36-44 wt.%), limestone crushing waste (9.4 wt.%) and dry hyper plasticizer (0.2 wt.%) may be used in the building materials industry for production of high-strength concrete. Binder composite is obtained by co-milling of the components in vario-planetary mill to a specific surface of 550-600 m^2/kg. The technical result is the possibility of obtaining of a composite binder with significant replacement of cement with industrial waste, cost-effective and superior to portland cement for construction and technical properties, increased activity. This allows producing concrete for walling with a compressive strength of 100 MPa, using more than 50% of industrial waste.

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