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Cements of low water demand is the flagship of composite low clinker cement binders in Russia and abroad

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Abstract. The paper provides research results on obtaining a compositional CLWD with the use of ashes from the Novo-Irkutsk Thermal Power Station and magnesites of the Savinsk deposit of the Irkutsk area. The aim of the research is to develop an effective ecological technology for producing high-quality cements. As a result of the research, the technological and physical-mechanical properties of the cement paste and cement stone were determined. The cement ND changes depending on the composition (12 to 19%), while the cement stone's strength varies from 49.5 MPa to 77.7 MPa. The CLWD strength (of different grades according to GOST 310.4) is estimated in 1 day, 28 days, and after steaming. A comparison with ordinary Portland cement was made. It is established that the CLWD 50 (has 50% of fillers) is not inferior in its physico-mechanical properties to ordinary Portland cement. A regression analysis of the influence of a number of factors on the strength of CLWD at three time periods (1 day, 28 days, and after steaming) was carried out. The regression equation was also obtained.

Last year, two new normative documents for Portland cement came into force in the Russian Federation. These are the GOST 31108-2016 (of March 1, 2017), being introduced instead of the previous version from 2003, and the GOST R 57293-2016 / EN 197-1: 2011 (of May 1, 2017) being harmonized with European standards.

The peculiarity of these documents was that they significantly increased the permissible content of mineral additives for general Portland cement. For example, now the share of blast-furnace slag in it is allowed up to 95%, and the content of clinker part is reduced to unthinkable 5%, which corresponds to the level of dosage of chemical additives!

It is obvious that today and in the near future, the modern cement industry is to follow the way of mastering the composite low clinker cements, since Portland cement production is environmentally damaging and, mainly, due to the carbon dioxide emission (about 8 tons / person) in the first technological cycle during roasting limestone [1]. A significant amount of conventional fuel (215 kg / ton) and electricity (119 kW / h) are required for the production of 1 ton of this binder, as well as considerable amounts (from 1.5 to 2.4 tons) of the raw material (limestone and clay) [2, 3].

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In European countries, the extraction of natural resources, the production of goods, their consumption, and the formation of waste are considered comprehensively, as being the links in one chain [4, 5]. It is believed that such an approach will save the environment and, in the end, reduce the formation of the greenhouse effect on the planet. As a result, laws are being adopted to motivate builders to expand the use of large-tonnage industrial waste in the production of building materials, especially in the cement industry. Therefore, the new regulatory documents that have now entered into force only emphasize the aforesaid trend.

It has been repeatedly shown that the most capacious area of industrial waste utilization is the technology of production of cements of low water demand (CLWD) [6-8]. They are able to contain up to 90% of waste without loss of quality properties. The technology is safe for the environment, less energy-intensive, and technologically simple. Since the introduction of CLWD production allows to significantly reduce carbon dioxide emissions (by 3-4 times), this technology can be attributed to the so-called "green technologies." A low indicator of the clinker capacity of these binders determines it as a resource-saving technology.

In our paper, the efficiency of a CLWD composite prepared using two types of fillers was evaluated. The first man-made ash is the demolition loss of the Novo-Irkutsk thermal power station (TPa), which, along with other fly ash, during the years of operation of the Irkutskenergo thermal power plant (TPP), accumulated about 80 million tons. Moreover, the annual growth of this waste is about 1.7 million tons. The ash consists mainly of quartz (30%), mullite (10%), sillimanite (7%), minerals of aluminosilicate structure (about 3%), and the rest is aluminosilicate glass phase (50%). The following ash properties were determined: true density – 2.33 g / cm^3, bulk density – 0.77 g / cm^3, voidness – 67%, specific surface – 279 m^2 / kg, pH 10-% solution – 12.

The second filler is the magnesite of the Savinsky magnesite deposit of the Irkutsk region, whose reserves are estimated to be about 2 billion tons, which is about 75% of all reserves of such nonmetallic minerals in Russia. Magnesites of the Savinskoye deposit contain $MgCO_3$ (92%); impurity minerals are pyrite, calcite, and talc.

As an astringent for the CLWD production, the additive Portland cement CEM I 42.5 N produced by the Ulyanovsk cement plant was used. CEM I has ND of 26%, its setting time: the beginning is of 197 min, the setting end is 287 min. The total content of high-basic calcium silicates $C_3S + C_2S = 74.5\%$, the content of $C_3A + C_4AF$ is 21%. As the superplasticizer, a concentrated solution (37%) of the polycarboxylate type "Reotech DR8500S" was used.

Since the fillers differ in hardness, the CLWD was obtained in a sequentially-separated manner by means of a vibration ball mill of CBM-3. This method consisted of the preliminary joint crushing of Portland cement, ash, superplasticizer, and their subsequent domes with magnesite.

For a comprehensive assessment of the effect of fillers on the properties of the CLWD composite and the reduction in the volume of experimental work, we used the method of mathematical planning. It was a 2-level 3-factor experiment (2^3). Factors and the range of variation are given in Table 1, the planning matrix is in Table 2. In this case, the constant factor for all compositions was a specific surface of the CLWD being equal to 5600 ± 100 cm^2 / g. The output parameter of the experiment is the compressive strength of a cement-sand mortar at the age of 1 and 28 days of normal hardening and after steaming at a standard isothermal regime at a temperature of 80°C (GOST 310.4 method).

Initially, the technological and physical-mechanical properties of the CLWD were determined, according to the planning matrix: normal density (ND), setting time, density and compressive strength of cement stone (CS) at 28 days of normal hardening (Table 3).

Table 1. Factors and range of variation.

Factors	*Factor level*			*Variation interval*
	-1	*0*	*+1*	
X_1 (brand CLWD)	30	50	70	20
X_2 (the ash content of the mixture of ash and magnesite, %)	30	50	70	20
X_3 (content of superplasticizer by dry active part from the mass of CLWD, %)	0,3	0,6	0,9	0,3

Table 2. The planning matrix.

Composition number	X_0	X_1	X_2	X_3
1	+	+	-	-
2	+	-	-	-
3	+	+	+	-
4	+	-	+	-
5	+	+	-	+
6	+	-	-	+
7	+	+	+	+
8	+	-	+	+

Table 3. Technological and physical and mechanical properties of the CLWD-cement solution.

Composition number	ND, %	Timing setting, min		CS density, g/cm^3	CS strength for compression, MPa	
		Start	End		3 days	28 days
1	19	187	317	2,08	54,8	77,7
2	19	77	322	1,94	46,5	57,6
3	19	54	277	2,00	47,9	76,6
4	16	46	307	1,96	32,9	49,5
5	17	11	24	2,23	51,9	68,3
6	15	15	21	2,20	60,4	68,0
7	13	15	23	2,15	58,2	73,5
8	12	18	26	2,23	68,0	73,8

Table 4. Technological and physical-mechanical properties of CLWD-sand solutions.

Composition number	B/C	Flowing out, mm	CLWD strength (GOST 310.4), MPa					
			after 1 day		after 28 days		after steaming	
			in bending	under compression	in bending	under compression	in bending	under compression
CEM I	0,44	110	2,4	13,1	5,6	52,1	5,1	37,5
1	0,34	109	6,4	33,0	7,3	76,2	6,2	62,7
2	0,34	120	4,2	16,7	7,1	50,8	5,9	48,5
3	0,34	120	6,3	43,4	7,5	58,7	6,75	58,4
4	0,32	130	3,2	9,0	4,7	40,7	4,6	36,7
5	0,29	123	2,1	5,8	6,7	73,0	6,4	62,1
6	0,28	130	1,7	3,5	5,9	53,6	5,5	37,5
7	0,30	112	1,7	5,0	7,5	68,8	5,35	38,5

8	0,25	116	2,3	5,8	4,7	38,5	4,9	30,4

As follows from Table 3, CLWDs have very low water requirements compared to CEM I Portland cement. This is evident from the low values of the CLWD normal density as they are not exceeding 19% (the minimum value is 12%). There was a sharp reduction in the timing of setting the cement test, which is associated with an increase in the content of the superplasticizer Reotech DR8500S.

According to the GOST 310.4, the bending and compressive strength of samples molded from a CLWD-sand solution is determined. The results are shown in Table. 4.

As can be seen from Table 4, the results obtained are correlated with the results indicated in Table 3. The water demand of CLWD-sand solutions proved to be very low (no more than 0.34) as compared to the control cement-sand mortar, prepared on the basis of CEM I (0.44). At the same time, the CLWD strength, containing 50% of the fillers, is not inferior to this Portland cement. It was found that ash most effectively manifests itself in CLWD at late stages of hardening, which is explained by its increased pozzolanic reaction. Magnesite enhances the rheological activity of the superplasticizer, reducing water requirements of the CLWD and increasing its strength.

The reliability of the presented results was obtained by calculating the confidence interval, homogeneity of the variances using the Kohren's criteria, checking the model for adequacy, taking into account the Fisher coefficients (Table 5 and Table 6).

Table 5. Values of Cochran coefficients and mean and maximum quadratic deviation based on test results.

Indicator	Strength values		
	1 day	28 days	After steaming
Max $\hat{S}^2$	1,120	4,0533	2,7911
G calculated	0,452	0,457	0,478
G tabulated	0,510	0,51	0,51
Conclusions about the homogeneity of variance	G calc.< G tabl., then the dispersion is homogeneous	G calc.< G tabl., then the dispersion is homogeneous	G calc.< G tabl., then the dispersion is homogeneous
$S^2_{\{\bar{y}\}}$	0,929	3,3275	2,19

Table 6. Values of Fisher coefficients and the model adequacy variance.

Indicator name	Strength values		
	1 day	28 days	after steaming
$S^2_{ад}$	14,356	10,050	14,222
Fobsr	15,457	3,020	6,494
Ftabl	19,250	19,250	19,250
Check the adequacy of the model	The model is adequate, because Fobsr <Ftabl	The model is adequate, because Fobsr <Ftabl	The model is adequate, because Fobsr <Ftabl
Dispersion of the regression coefficient	0,116	0,416	0,274
Quadratic error of regression coefficient	0,341	0,645	0,523
Student coefficient	4,303	4,303	4,303

Based on the results of the work, regression equations for the CLWD composite:

- On the first day of normal hardening:

$$R_1 = 14,83+6,42X_1+0,4X_2-10,05X_3+1,82X_1X_2-6,11X_1X_3-0,09X_2X_3 \quad (1)$$

- For 28 days of normal hardening:

$$R_{28} = 58,52+11,83X_1-6,48X_2+0,62X_3+0,008X_1X_2+0,73X_1X_3 +1,08X_2X_3 \quad (2)$$

- After steaming:

$$R_{prop} = 47,18+9,18X_1-5,55X_2-4,43X_3-4,43X_1X_2-1,35X_1X_3-1,77X_1X_3 \quad (3)$$

So, the desire of the world cement industry to reduce the clinker capacity can be achieved in cements of low water demand, which undoubtedly predicts this knitting for a reliable future and widespread distribution.

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