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Cement-based concretes with low water requirements

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Abstract. Highways are one of the main elements of the infrastructure and economy of any state. It is well known that the state and level of development of the country's highways directly affect the main economic indicators – the gross national product, the price level, budget revenues, the level of employment, and others. When developing multicomponent binders, as a rule, a systematic approach is used. New binders are considered complex systems consisting of subsystems or elements, each performing its functions. The elements in the system are not isolated from each other but grouped in such a way as to ensure the practicality of the entire system. It should be noted that any changes in a single element or replacing one element with another usually lead to a change in the properties of the entire system. The elements of the system are interconnected, and the more versatile the connections, the more effective the system is. The researcher's task is to correctly select the elements of the system, considering their properties and contribution to the system's overall structure. Of all types of metallurgical slags, blast furnace slags are the most widely used in the production of building materials due to their leading position in the overall balance, their ability to acquire hydraulic properties during rapid cooling, and others.

1 Introduction

Currently, there are already quite a large number of original binders developed and then tested in the factory in economic and environmental aspects. However, effective and deserving of early introduction into domestic construction binders for several objective and subjective reasons have not yet found a worthy application.

The production of highly effective binders of a new generation today is accompanied by the use of complex, from a chemical and mineral point of view, component compositions to obtain high-quality concretes of various functional purposes with improved and sometimes fundamentally new properties and certain predetermined structure." The creation of such binders is based on the principle of purposeful management of technology at all stages: the use of active components, the development of optimal formulations, the use of chemical modifiers, the use of mechanochemical activation of components, and some other

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techniques. According to this principle, a binder of low water demand (VNV) with increased content of superplasticizer C-3 was obtained using conventional Portland cement and active fillers.

The structure and properties of multicomponent binders are predetermined by choice of the necessary raw materials and their ratio, dispersion, and activity. The dispersion of binder particles can also play a negative role under certain conditions, which is why it is necessary to consider the fineness of the binder grinding every time. Currently, various additives that exclude the adhesion (flocculation) of fine particles of the binder are successfully used.

The use of additional grinding of traditional Portland cement made it possible to obtain a whole series of so-called finely ground cements.

The trend of scientific developments in the field of binders should develop and, to our satisfaction, is developing in the direction of obtaining new highly effective binders. There are all prerequisites for this: scientific schools, extensive experience in scientific developments in chemistry, physical chemistry, and the field of industrial achievements.

To improve the quality of highways, it is advisable to use the underlying layers of road clothes, which are made of concrete based on mineral-slag binders of high strength.

Thus, the development of the above research areas allows us to obtain pavement foundations with qualitatively new indicators and, ultimately, will increase the service life of asphalt concrete pavements [1-6].

The available theoretical developments could serve as an excellent scientific basis for the further development of the domestic construction industry and construction in general. Now, more than ever before, there is an urgent need for state coordination and targeted financing of scientific and practical developments in the field of creating new "breakthrough", low-energy, low- and waste-free, environmentally safe, competitively capable in domestic and foreign markets, highly efficient technologies of binders.

The activity of mineral additives, that is, the ability to bind calcium oxide hydrate in the presence of water at normal temperatures, is due to the content of substances in them that are in a chemically active form. Naturally, the nature and intensity of their interaction with lime differ depending on which chemically active substances are more in a particular mineral additive. Therefore, acidic active mineral additives are conditionally by the type of substance that determines their chemical activity and the mechanism of CaO binding.

The increased air resistance in the latter case is due to the formation of high-strength calcium hydro silicates that are more resistant to air during hardening. In addition, calcium hydroxide, which is present in a significant amount in cement stone and primarily interacts with air carbon dioxide to form calcium carbonate, contributes to additional compaction and hardening of the system. At the same time, it protects calcium hydro silicates, protecting them from premature decomposition by carbon dioxide [7-10].

The ability of slags to set and harden under certain temperature and humidity conditions during mixing with water depends on their chemical and phase composition. At normal temperatures and without activating additives, crushed slags practically cannot harden, which is explained by the absence or low content of sufficiently active phases in them under these conditions [11-14].

The only crystalline component of slags capable of hardening, albeit slowly, at normal temperature is β-two calcium silicate. Several other minerals acquire hydraulic properties only under conditions of elevated temperature and pressure, water vapor in the presence of activators.

Slag glasses interact with water much more intensively than mineral crystals. The high internal chemical energy of glass provides its increased solubility, which results in the formation of supersaturated solutions, their crystallization, and, as a consequence of the latter, the solidification and formation of artificial stone.

The hydration mechanism of slag glasses consists of the penetration of negatively charged hydrophilic ions into the glass, which violates the electrostatic equilibrium of the system and leads to the destruction of slag. Under normal conditions, hydration is prevented by forming hydrated silica films on the surface of glass particles without activating additives.

2 Objects and methods of research

Cement. The Portland cement of Standard Cement LLP PC500D0, according to Russian State Standard GOST 10178 and Portland cement 500 without additional, normal hardening, was used as a binder.

The mineralogical composition of cement is given in Table 1. Their chemical composition is presented in Table 2. The physical and technical characteristics of Portland cement, defined following Russian State Standard: GOST 310.1-76 – GOST 310.3-76, GOST 310.4-81, GOST 310.5-88, GOST 310.6-85, GOST 30515-97, and GOST 10178-85, are presented in table 3.

Mineral fillers. Until now, the production of low-water-demand cements has been limited to using only silica-containing mineral fillers; therefore, quartz sand meeting the requirements of Russian State Standard GOST 8736-93, with the largest grain size of 0.315 mm, has been adopted as a control composition. The physical and technical properties of quartz sand are given in Table 4.

As technogenic fillers, limestone crushing wastes from the Tulkubassky deposit of carbonate-containing rocks (limestones) were used in the research; mineralogical, chemical, thermal, and electron microscopic analyses of limestone are given in Tables 5-6.

Table 1. Mineralogical composition of Portland cement PC500DO

Mineral content, %			
C_3S	C_2S	C_3A	C_4AF
63.0	16.0	4.7	14.0

Table 2. Chemical composition of PC500DO Portland cement

Content of oxides, %								
SiO_2	CaO	CaO/ SiO_2	MgO	Fe_2O_3	CaO_{sb}	Al_2O_3	SO_3	R_2O
22.1	65.65	-	1.28	4.53	0.16	4.67	0.38	0.73

The Polyplast SP-1 superplasticizer was introduced during the joint grinding of cement (clinker) with a dry additive, which ensured the encapsulation of cement grains with a superplasticizer. To save the clinker component and regulate the properties of binders, the content of the mineral additive (perlite) varied. The practicality of replacing the clinker and introducing up to 30% into the binder without reducing the strength characteristics was established. The following initial composition of the composite binder was adopted: Portland cement clinker + gypsum – 70% (gypsum 5% of the clinker component), filler (silica–containing additive) - 30%, superplasticizer – 1% of the total weight of the binder.

Following TU 6-36-0204229-625-90*, the content of the active substance in C-3 in terms of dry product is not less than 69%, ash content is not more than 38%, pH = 7-9, bulk density – 400...700 g/l.

Quartz sand of the Badam deposit was used as a fine aggregate for the preparation of heavy concrete or as a seeding fraction of 0.315-1.25 mm when assessing cement activity. The properties of fine sand aggregate in its natural state are shown in Table 4.

Table 3. Physical and technical characteristics of PC500DO Portland cement

Name of indicators	Performance indicators
Specific surface area, sm^2/g	3093
Normal density (ND), %	25.6
Setting time, h-min - start - the end	 2-55 3-25
Water-cement ratio (W/C)	0.45
The average activity of the binder after 1 day of normal hardening, MPa/%: - when bending - when compressed	 2.8 14.0
The average activity of the binder after steaming, MPa/%: - when bending - when compressed	 5.1 33.3
The average activity of the binder of normal hardening, MPa/%: - when bending - when compressed	 6.1 51.8

Table 4. Physical and technical properties of quartz sand

Name of indicators	Unit of measurement	The value of the indicator	
The size module	-	2.9	
Fraction content 5...10 mm	%	1.9	
Fraction content 10...20 mm	%	0.3	
Fractional composition	%	Private balances	Full balances
2.5		23.0	22.8
1.25		14.4	37.3
0.63		15.5	52.9
0.315		35.6	88.2
0.14		11.3	99.7
<0.14		0.4	-
True density	g/sm^3	2.65	
Bulk density	g/sm^3	1.6	
Voidness	%	39.6	
The content of pulverized and clay particles	%	2.0	

Table 5. Mineralogical analysis of limestone crushing waste from quarries

№	Name of the carbonate rock quarry	Mineral composition, %				
		Calcite	Dolomite	Clay minerals	Quartz	Feldspar
1	Tulkubassky	88±7	-	8±2	3±1	< 1

Table 6. Chemical analysis of limestone crushing waste from quarries

Content of oxides, %										
SiO_2	CaO	MgO	Fe_2O_3	TiO_2	Al_2O_3	SO_3	MnO	Na_2O	K_2O	p.p.p.
5.27	51.22	0.78	0.39	0.06	1.13	<0.05	1.13	0.06	0.2	40.6

Table 7. Characteristics of quartz sand.

№	Name of the characteristic	Unit of measurement	Meaning
1	Bulk density	kg/m^3	1550…1650
2	True density	kg/m^3	2650…2750
3	The size module	-	2.7…2.9
4	The content of pulverized clay particles	%	2.5
5	Voidness	%	38…45
6	Water demand	%	5.6…8.3
7	Maximum grain size	mm	4.5
8	Fraction content (F):5 ≥ Φ ≥ 2.5 2.5 ≥ F ≥ 1.25 1.25 ≥ F ≥ 0.63 0.63 ≥ F ≥ 0.315 0.315 ≥ F ≥ 0.14 0.14 ≥ F ≥ 0.063	%	15 21 20 25 14 5
9	Natural humidity	%	5.6

Crushed stone of 5-20 mm fraction supplied from the Badamsky quarry was used as a large aggregate to prepare heavy concretes. A large aggregate's physical and technical properties are presented in Table 8.

Water - for preparing concrete and mortar mixtures, tap drinking water was used in the work, meeting the requirements of Russian State Standard GOST 23732.

Table 8. Physical and technical properties of crushed stone

№	The name of the indicator	Unit of measurement	The value of the indicator
1	Fractional composition less than 5 over 5 to 10 over 10 to 20 over 20 to 40 over 40	%	 6.0 32.6 60.0 1.4 -
2	Grade by fractionality	-	1000
3	True density	g/см^3	2.7
4	Bulk density	g/см^3	1.6
5	The content of pulverized and clay particles	%	0.6
6	Natural humidity	%	0.7

The specific surface area of the cements was determined on the device PSX-12 "NPO Khodakova". The operation of the device is based on the measurement of the specific surface of powder materials by the Kozeini-Karman method - by the air permeability and porosity of the compacted powder layer and the corresponding average mass particle sizes.

The concrete density was determined on samples of 100x100x100 mm following the methods of Russian State Standard GOST 12730.0-78 – Russian State Standard GOST 12730.4-78. The number of samples for one density value was at least 6 pieces.

Following the methods of Russian State Standards GOST 10180-90 and GOST 18105-86. The number of samples for one strength value was at least 6 pieces.

The bending and compressive strength of the 4x4x16 cm beam samples were determined on the MII-100 and UMM-10 presses according to the Russian State Standard GOST 310.4-81 method.

The compressive strength of cement stone was determined on samples with a size of 20x20x20 mm, made of cement dough of normal density according to Russian State Standard GOST 310.3-76 and sustained under normal hardening conditions (humidity 100%, ambient temperature 22-24 ^{0}C), by testing on a UMM-10 press. The number of samples for one strength value was 6 pieces.

The assessment of concrete's water absorption and porosity characteristics was determined according to Russian State Standard GOST 12730.3. The frost resistance of concrete was determined according to the Russian State Standard GOST 10060-90 method for the loss of strength and mass of samples by the accelerated method with repeated freezing and thawing in the freezer at $t = -50\ ^0$C.

The durability of 40x40x160 mm samples prepared from cements of low water demand - 1:3 sand mortar according to Russian State Standard GOST 310.4, and 20x20x20 mm cement stone samples were evaluated by evaluating their appearance (presence of cracks) and strength changes over time.

The activity of fillers was determined by the absorption of CaO from a saturated lime solution with pH = 12.15.

3 Results and their discussion

One of the main goals of all the work is to establish the possibility of replacing the general construction Portland cement with "low-water carbonate cement" in the construction market. Since silica cements of low water requirements have long proven themselves as effective binders in the production of high-strength concrete [15-19], in this regard, it is necessary to evaluate the technical effectiveness of new "carbonate" cements of low water requirements in the composition of various types of concrete and determine the properties of concrete on it.

PC500DO Portland cement was used as a binder for the control composition. For the main compositions, carbonate cement of low water demand (CNV-50) prepared based on dolomite from the Tulkubassky quarry and superplasticizer (SP) S-3 in an amount of 2% of the mass of low water demand cement (CNV-50) was used.

For grades M200, M300, which have low strength, gravel with a crushing capacity of 800 was used as a large aggregate. Crushed stone with a crushing capacity of 1200 was used for the strength of M550.

Concretes were prepared from mobile mixtures not lower than grade P4 (cone sediment $\geq$ 190 mm). The following properties of the concrete mixture and concrete were determined: workability (according to the draft of the cone), density, air intake, water separation, and strength.

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As can be seen from Table 9, the compositions of heavy concrete No. 1, No. 3... No. 8 correspond to the calculated class (grade) in strength. Only composition No. 2 does not meet the requirements for strength and water separation, which is explained by our low cement consumption and low water demand for concrete. Due to the absence of low-water cement and the small thickness of the filler coating, the friction between its grains increases, and, accordingly, the workability of the concrete mixture decreases. As a result, to achieve the required mobility, it is necessary to add an excessive amount of mixing water, which eventually separates from the concrete mixture.

The described phenomenon is also confirmed by the dependence of a decrease in the water demand of concrete on Portland cement with an increase in consumption. In this case, the thickness of the coating around the filler grains increases, and the increased workability of the concrete mixture is ensured, which does not require excessive consumption of mixing water. The described phenomenon is also confirmed by the dependence of a decrease in the water demand of concrete on Portland cement with an increase in consumption.

Table 9. Test results of heavy concrete compositions

Composition No	Cone sediment, cm	W/C	ΔB, %	Density of concrete mix, kg/m^3	Air involvement, %
M100 (B7.5)					
1	21.0	1.11	-	2250	7.1
2	19.0	1.0	10.0	2270	7.0
M200 (B15)					
3	21.0	0.68	-	2300	5.7
4	19.0	0.52	19.1	2350	6.0
M300 (B22.5)					
5	22.5	0.64	-	2310	5.5
6	21.0	0.46	28.1	2360	5.0
M550 (B40)					
7	20.0	0.44	-	2440	3.7
8	25.0	0.32	27.3	2500	3.0

Continuation of table No. 9.

Composition No	Water supply, %	Compressive strength of concrete, MPa			
		after thermo-humidity treatment	age, day		
			1	7	28
M100 (B7.5)					
1	0.4	6.0	2.4	6.8	10.5
2	3.0	5.1	2.0	5.9	8.9
M200 (B15)					
3	0.1	14.0	4.8	18.8	22.4
4	0.5	13.8	5.9	20.0	24.1
M300 (B22.5)					
5	-	17.4	7.1	21.5	30.5
6	-	19.2	11.4	24.9	32.4
M550 (B40)					
7	-	33.6	21.6	42.8	53.7
8	-	37.6	28.0	48.0	56.8

From the results obtained, the heavy concrete on the CNV-30 corresponds to the design class (grade) in strength and is characterized by water separation not exceeding the value required by Russian State Standard GOST 10181-2000 (0.8%).

Almost all concrete problems, in one way or another, are related to its cement component. A very common point of view is that due to the increased consumption of cement, high-strength concretes should have increased shrinkage [20-21]. However, there are also opposite judgments; the authors believe that the shrinkage of stronger concretes is lower due to the greater resistance of the crystalline joint to volumetric changes in the gel, lower porosity and, consequently, lower intensity of moisture exchange between concrete and the environment.

It should also be noted that to date, no relationship has been found between the shrinkage value and cement activity [21-22].

It is shown that in practical assessments, the influence of cement properties on the amount of concrete shrinkage deformations can be neglected if the mineralogical composition and fineness of cement grinding are within the usual limits. And, since low-water cement is characterized by a finer particle size distribution, shrinkage for concretes at the CNV is of great interest.

To study the properties of low-water cements with fillers of different natures (silica and carbonate), we evaluated their shrinkage deformations: contractional (chemical) and humidity (physical) shrinkage. As is known, the concrete hardening process is accompanied by changes in its volume, which reduces the operational life of reinforced concrete structures. Therefore the study of these properties is very relevant.

4 Conclusion

It has been established that for the production of low-grade concrete, it is necessary to use CNV-30, the consumption of which will be significantly higher than when using CNV-50 (CNV and the small thickness of the filler coating, the friction between its grains increases, and, accordingly, the workability of the concrete mixture decreases). At the same time, heavy concrete on low-water cement (CNV-30) corresponds to the design class (grade). 7.5 (100) in strength is characterized by a water separation not exceeding the required value of Russian State Standard GOST 10181-2000 (0.8%).

The persistence of the concrete mixture on Portland cement and carbonate cement of low hydrogen is investigated. The persistence of the concrete mixture on both Portland cement and CNV is practically the same.

The kinetics of the strength gain of concretes on low hydrogen (CNV-50) carbonate cement from the hardening conditions is investigated.

It has been found that CNV-50 accelerates the hardening process for the first time a day under normal hardening conditions and is less effective during heat treatment.

Compressive strength when using CNV-50 increased by 10% after heat and humidity treatment, 24% after normal hardening 1 day, and 10%. The acceleration of hardening for the first day is caused by a larger specific surface area of cement, accelerating the hydration process. Due to the use of CNV-50, the water demand for the mixture decreased by 35%.

The bending strength of fine-grained concrete on CNV-50 is the same as on PC500DO, both after heat and humidity treatment and after 1 day of hardening in normal humidity conditions.

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