#### CONCRETES BASED ON NANOCEMENTS USING NON METALLOFERROUS AND OFF GRADE FILLERS FROM DIFFERENT REGIONS OF RUSSIA

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My work is dedicated to one of the major problems of concrete technology: feasibility of production of high-quality, durable concrete and products based on them using significant amount of fillers (gravel, chipped stone etc.) formed during tunneling or civil engineering construction, as well as the use of different regional local non-metallic materials – chipped gravel and sand, that do not meet all the requirements of the modern state standards for concrete production.

The major part of concrete mass is usually a coarse filler - crushed stone in the form of crushed igneous, intrusive and extrusive rocks: granite, diabase, basalt, gabbro, etc., as well as sedimentary rock - limestone, dolomite, quartzite, sandstone and metamorphic rock - marble, gneiss etc.

In each production region, selection of coarse and fine fillers for concrete is defined, in addition to quality requirements and standard compliance, by how far suppliers are from production facilities; since the shipping cost may significantly increase the cost of production. Thus, in Moscow and Moscow Region for manufacture of lower grades concrete (22.5 per GOST 26633) limestone gravel is being shipped from Kaluga and Vladimir Regions; for the production of high strength concretes - crushed granite is transported from Republic of Karelia.

Research of possibility to use weak chipped gravel lacking in frost proof quality, byproducts of processing rocks, overburden rocks, local non ferrous materials plays a key role when trying to lower transportation cost of raw materials and consequentially construction cost of housing, roads, engineering objects etc.

Only in Russia hundreds of millions cubic meters of concrete is being poured every year; at that hundreds of millions tons of gravel and sand is being supplied and transported for concrete production.

Just recently, quite difficult situation encompassed construction of landmark Olympic sites and surrounding infrastructure near Sochi. Due to large-scale construction and need in high quality concrete, large amount of non-ferrous fillers were transported into the area, which was driving up the prices. Thus, the price for granite macadam in Sochi regions had reached 1500 rubles per ton (appr. 50 USD), and mortar sand price – 1300 rubles per ton (appr. 43 USD).

In Crimea region, the prices were driven up by difficulties with transportation itself, thus causing the rise in imported ballast price up to 50 USD per ton; mortar sand - up to 67 USD per ton.

The present research is dedicated to an attempt to solve problems pertained to production of high quality, high strength concretes during construction of railway and motor way combined project near Adler city and Alpika Service station (Krasnodar region near Sochi) by utilizing raw materials such as soils of mining excavation and other local non ferrous raw materials.

The main classes of cement produced by cement plants around the world recent decades range from 32.5 MPa to 52.5 MPa, with a predominance of class 42.5 with a common drawback: the quality guarantee period does not exceed 2 months. Cement professional having exhausted their resources to improve the quality of the basic construction material, reassigned this responsibility to concrete manufacturers.

Presently, the technology ensuring the quality of concrete involves variation of concrete mixtures with extensive use of considerable amounts of mineral and chemical additives, modifying concrete properties in order to achieve required parameters.

This approach significantly tightens requirements to cements (Blaine fineness, optimal mineralogy, absence of toxic impurities, compliance with short (no more than two months) shelf life); requirements to coarse fillers: high strength, low abrasion capacity, frost-resistance, cube-shape with a minimal number of stone-flag particles; requirements to fine fillers: mortar sand –certain particle size, minimal content of clay impurities.

Use of chemical additives significantly increases the cost of concrete and is often accompanied by adverse effects during actual usage of constructed objects, such as ammonia smell etc.

Our Nano cement technology made it possible to achieve high construction and technical properties of concrete without traditional approach to tighten the requirements for non-metallic components of concrete mixtures and virtually without the need for costly and often harmful chemical additives in concrete mixes.

The results of many year tests of technical properties of concrete based on Nano cements shown in (2-7). Proven increase in basic binding characteristics of Nano cements demonstrated a new prospect for the use of Portland cement production in modern high-strength concretes, when manufacturing ordinary concrete it allows for radical cost-savings and reduction in production cost.

Thus, today's compliance to requirements of GOST 8267-93 to GOST 8736-93 for crushed stone and sand for concrete production results in considerable expenses for shipping of coarse and fine fillers that meet GOST requirements.

Traditional concretes, as well as all other products based on a binder - Portland cement, include quartz sand as a mandatory component, particles of which act not only as "fine" filler but also as the reagent that enters into chemical reaction with the products of Portland cement hydration with the formation of basic minerals at the final stage which provide strength and durability to concrete - calcium hydrosilicates.

Mortar sand is characterized by the presence of very large particles of silica and siliceous minerals; major volume of particle sizes ranges from hundreds to several thousand microns; this makes the surface of reaction of sand particles and significantly smaller cement particles very small - less than 50 - 70 sq.m / kg of cement-sand mixture, while the average specific surface area of the Portland cement in Russia is 300 sq.m / kg and abroad 400 sq.m / kg.

Series of research were conducted in the workshop of ZAO IMETSTROY to produce experimental batches of different formulations of low clinker Nano cements according to technical specifications TS - 5745-067-05442286-99 with Portland cement produced at Proletaryi OAO Novoroscement and mortar sand from Maikop quarry.

Subsequent research covered testing different types of concrete made on the basis of Nano cements and byproducts of mining excavation and other non-ferrous raw materials.

Optimized concrete mixtures were used to obtain concretes according to technical specifications and conduct testing of samples in the State Unitary Enterprise GUP "NIIMosstroy" to determine construction and engineering properties of concrete and its compliance to current state standards: strength, water resistance, frost resistance and other characteristics of concrete made with non conditional materials.

One should bare in mind, that main disadvantages of products of mine excavation, overburden rocks and prevalent local non-ferrous raw materials are:

- *for macadam* - low strength and high abrasion capacity, a significant mass of stone flag particles, low frost resistance, presence of clay inclusions, uncertain mineralogical composition;

- for sands - low content of siliceous components, primarily silica, significant amount of debris and particles of detrital sediments, clay impurities, possible presence of hydrationally active minerals.

## Methods of research and testing

Analysis of the mineralogical composition of materials was carried out on DRON-3M through X-ray quantitative analysis (RCA) using an external standard -  $\alpha$  - quartz ... using cards, standard diffraction patterns and software programs to process spectra radiometric determinants.

Preparation of analyzed samples after drying included:

- selection of an average sample by cone quartering, weight up to 5 g;
- grinding in a metal mortar to a particle size  $\leq 1$  mm;
- grinding in mechanical mortar for 5 min;
- sifting through a sieve 006;
- grinding of residue in agate mortar until complete passage through sieve 006;
- mixing and homogenizing of obtained powder by multiple sifting through large 1 mm gauge sieve;
- placing the sample saturated in ethanol in a cuvette, forming working surface;

The specific surface area of dispersions determined by the standard method on the instrument PSC - 2

Density of concrete mixtures determined according to GOST 10181.2-81.

Consistency of concrete mix determined by cone slump method according to GOST 10181.1-81.

Strength parameters and concrete density determined using standard methods according to GOST 10180-90.

Water resistance of concrete samples determined according to GOST 12730.5-84.

Frost resistance according to  $GOST \ 10060.1-95 - basic$  method to determine frost resistance and according to  $GOST \ 10060.2-95 - expressed$  methods to determine frost resistance, methods 2 and 3.

## Research objective

In the present research, we have been tasked to obtain the most economical concrete on the basis of low clinker Nano cements with coarse fillers: soil from Southern Portal quarry, macadam from Kamensky quarry, sands from Volzhsky, Maikop (Maisky), Vybor-S, Titan, Alpha, August and Hromtsevsky quarries, that is local raw materials of the Krasnodar region, near Sochi.

Selection of concrete mixtures were made with the objective to produce concretes of classes 7.5 to 45 with the use of raw materials mentioned above and minimal use of Portland cement and chemical additives; aiming at parameters such as consistency of concrete mix, water and frost resistance to be within the norms of GOST standards.

#### **Coarse concrete fillers**

Two types of macadam were sampled for research with fractions of D 5 - 20 mm from Kamensky and Yuzhnyi Portal quarries of Krasnodar region. The macadam samples were tested for strength and frost resistance by express method. Fine fillers were selected from local raw materials.

Macadam from Kamesky quarry soil turned out to be limestone based on the results of quantitative and qualitative X-ray diffraction analysis. Quantative X-Ray diffraction analysis

Mineral	Particles larger than 5 mm	Particles smaller than 5 mm
Calcite	96.5	93,0
Silica, $\beta$ - SiO <sub>2</sub>	1.0	2.5
Hidrous mica	1.5	0.5
Calcium Sulfate Dihydrate	1.0	
Mullite		1.5

of fractions showed that in finer particles of the macadam content of impurity phases increases, % of weight:

Tests by known methods in salts, conducted by the State Unitary Enterprise GUP NIIMosstroy confirmed low frost resistance in both types of macadam, very little strength of macadam from Kamenskii quarry (not more than M-300) with a significant abrasion capacity.

Analyzed compositions of concrete mixtures, included: coarse filler soil of the outthrow of tunnel digging works (rail way tunnel #3 Yuzhnyi Portal in the form of macadam fractions of 5 - 20 mm with a crushing capacity of M - 300, the content of platelet and needle shaped particles - 17 wt.%; sieve #5 residue - 83.2%, content of dust and clay particles - 3.5% by weight). Low strength characteristics of the coarse filler from the outthrow of tunnel works (further herein "Yuzhny Portal Macadam") as well as the lack of frost resistance capacity were confirmed by the relevant tests conducted by the State Unitary Enterprise GUP NIIMosstroy.

Macadam from the soils of Kamensky and Yuzhny Portal quarries does not comply with standards: GOST 8267-93, GOST 26633 - 91 in grain classification; sieve residue with d = 5 mm, and also high content of dust and clay particles - 5.1% by weight (GOST allows no more than 2%), as well as frost resistance capacity, being only 25 cycles (Table 1).

Tests were conducted in accordance with GOST 8269-97 "Macadam and gravel of dense rocks, industrial waste products for construction works. The method of physical and mechanical testing".

Conclusion: based on test results for frost resistance capacity, samples of macadam from Kamensky quarry and Yuzhny Portal (the tunnel №3) meet the requirements of GOST 8267-93 "Macadam and gravel of dense rocks for construction works. Technical Specifications " (F25).

Study of mineralogy of soil from the outthrow of the tunnel #3 works – Yuzhny Portal Macadam by the method of X-ray diffraction phase quantitative analysis showed that the main mineral phase (about 80 % by weight) it contains analcime - 6 SiO2 Na2OAl2O3 2 H2O; calcite - up to 10% by weight, field spar - up to 5% by weight; and kaolinite - up to 5% by weight. The content of the main phase in the form of water-containing mineral - analcime explains low strength and, especially, low frost resistance ability.

Table 1. Test results of macadam samples by Experimental Laboratory of the State Unitar	ry
Enterprise GUP NIIMOSstroy according to the agreement №479/28/00/11.	

Samp le #.	Sample name	Fraction size, mm	Frost resistance capacity. Loss of weight in % after alternating freezing and thawing:		
			F25	F50	
80	Kamensky Macadam ZAO «Sochinerud»	10-20	5.06	17.20	
81	Yuzhny Portal Macadam rail way tunnel №3	10-20	3.53	7.60	
Requ and	irements of GOST 8267-93 «M gravel of dense rocks for cons works. Technical specification	No more than 10	No more than 5		

## Fine concrete fillers

Fine fillers were sampled from primarily local, not expensive sources. For the purpose of research sands from different quarries of Krasnodar region and the surrounding areas were taken, as well as imported from Ivanovo region: Volzhsky, Ramenskoye, Alfastroy, Avgust, Vybor S (two types) and Hromtsevsky (Ivanovo):

- sand provided by "Maikop nonmetallic company" (MSDS # 508, number 601, hygienic certification, certificate of compliance, protocol  $N_{0}$  177/8, protocol  $N_{0}$  96-1 with the attachment number 2, laboratory research protocol number 17228);

- sand of OOO "Vollzhskoe GTP №1» (Test report from 10.05.2011, MSDS# 151);
- sand of Hromtsevsky quarry (Test Report number 147, a certificate of conformity);
- sand of OOO Titan (MSDS # 170, № 171, № 163);
- sand of Vybor S quarry (Test Report number 150, MSDS # 208, a certificate of conformity);
- sand of OOO Alfa -stroy (Test Report number 151, hygienic certificate, protocol number 32-10s, Minutes of 18.11. 2010);
- sand of Avgust quarry (Test Report number 149, number 21 / A, passport # 27);

Results of sieve analysis of fine fillers are shown in Table. 2.

X-ray diffraction qualitative and quantitative analysis of the most promising local sands and widely used in construction sand from Titan quarry revealed the change of quantitative proportion of mineral phases, depending on the fineness of sand (Table 3).

As a general pattern, it can be noted that the content of silica increases in fine fillers with decrease in particle size, and vice versa, content of impurity phases increases in sands with larger particles.

These large particles are most often various detrital sediments and sedimentary rocks: plagioclase, chlorite, mica, zeolites, and calcite. The maximum content of  $\beta$  - quartz was found in construction sand from Titan and Avgust quarries.

Sand name	Grain com	Grain composetion, sieve residue % by weight							
	2.5	1.25	0.63	0.315	0.16				
Ramensky	0.5	13.5	33.0	30.5	20.0	2.5			
Titan	24.0	9.5	16.0	31.5	15.0	4.0			
Khromtsevsky	15.5	10.0	31.0	33.5	8.5	1.5			
Vybor - S	18.5	10.5	14.5	22.3	25.5	8.7			
Avgust	28.6	6.6	13.2	36.2	15.4	-			
Alfa	0.6	1.1	13.1	65.4	15.8	4.0			
Volzhsky	18.5	6.0	12.5	36.5	20.0	6.5			

Table 2. The results of sieve analysis of grain composition in studied sands

## Nano cement production

Production of pilot batches of Nano cement was carried out on the pilot cycling ball mill BM - 2 in the experimental workshop of ZAO IMETSTROY according to Technical Specifications 5745 067 05442286 0 99.

Several batches of Nano cement based on Portland cement of factory OOO Proletarian of Novoroscement and quartz sand from Ramenskoye quarry and sand from Maikop quarry.

Figure.3 BM-2 Nano cement production unit.



Produced Nano cement was packed in paper bags. Pilot batch of Nano cements of different composition was also shipped to Sochi, to the industrial base OOO SEVER STORY.

Quarry	Sample,				Phase		
	fraction size	$\begin{array}{c} Quartz \\ B-SiO_2 \\ \pm 5 \% \end{array}$	Plagioclase ± 3 %	Chlorite $\pm 2\%$	Mica ± 2 %	Zeolite ± 1 %	Calcite ± 3 %
Alfa stroy	ПАС-1 < 1,25мм	50	13	8	11	> 1	7
Alfa stroy	ПАС -2 >1,25 < 2,5 мм	40	12	11	6	> 1	6
Alfa stroy	ПАС-3 ≥2,5 мм	36	8	10	5	> 1	26
Vybor S	ПВС -1 < 1,25 мм	58	21	7	8	3	-
Vybor S	ПВС -2 > 1,25 >2,50 мм	52	20	9	4	4	-
Vybor S	ПВС-3 ≥ 2,5 мм	46	18	10	4	4	-
Avgust	ПАТ-1 < 1,25 мм	80	9	5	4	2	-
Avgust	ПАТ-2 > 1,25 >2,50 мм	68	12	9	4	3	-
Avgust	ПАТ -3 ≥ 2,5 мм	65	12	7	2	5	-
Titan	ПТ-1 < 1,25 мм	87	14	4	5	> 1	-
Titan	ПТ-2 >1,25 < 2,5 мм	85	14	6	2	> 1	-

*Table 3. Change in content of mineral phases, depending on dispersity of sands tested according to X-Ray quantitative analysis data* 

## Research results

The research allowed to determine the optimal ratio of studied fine and coarse fillers in concrete mixtures made on the basis of Nano cements.

Laboratory studies have allowed to develop optimal content of concrete mixture and concrete complying with standard requirements to quality, with the use of sub-standard non-metallic materials: from B 7.5 to B 45, with appropriate concrete workability, water resistance and resistance to frost.

For preparation of concrete mixes, Nano cements with different content of Portland cement manufactured by Novorossiysk cement plant were used, also macadam from Kamensky and Yuzhny Portal quarries, and various other sands.

Preparation of concrete mixtures was carried out in a concrete mixer BS - 4 with forced

mixing by the shaft with blades manufactured at the mechanical plant number 268, Ivanov city.

When calculating concrete mixtures, requirements of the Client were taken into account, which were to regulate concrete consistency in a large range. Concrete consistency of the mixture was determined by the standard slump cone method. The strength characteristics of concrete were determined by standard methods in accordance with technical specifications.

Standard concrete samples were made from concrete mixtures of optimal compositions to determine construction and technical properties of concrete and subsequent certification of the samples by testing laboratory of the State Unitary Enterprise GUP NIIMosstroy.

Consumption of Portland cement in optimized concrete mixtures ranged from 80 to 350 kg per cubic meter of concrete for concrete products with a wide range variation of construction and technical properties, required water and frost resistance. After removal of formwork, the samples were tested according to standard procedures and the requirements of GOST on modern testing equipment of the State Unitary Enterprise GUP NIIMosstroy (Figure 4)



Figure 4. Concrete samples being tested for tension in bending at the testing laboratory of the State Unitary Enterprise GUP NIIMosstroy

Concrete mixtures on non-conditional macadam: composition, consistency and test results, by the State Unitary Enterprise GUP NIIMosstroy

Concrete mixture № 10, composition, kg/m3

Nano cement 90 H (on Portland cement by OAO Novoroscement)	395 (355*)
Yuzhny Portal Macadam **, M-300, F-25	921
Mortar sand from Ramensky quarry	920
Water	145
Water-solid ratio	0,36
Cone slump, cm	3

\* Amount of Portland cement

\*\* Macadam of fractions 5-20 from the tunnel outthrow soil

## **Concrete mixture #1, parameters**

Material consumption per 1m <sup>3</sup> of concrete mixture, kg	Slump cone, cm	Concrete strength of normal hardening, different time periods, MPa : In denominator at compression, In nominator at bending			Concrete parameters upon testing completion		
		3 days	7 days	28	D, кg/m <sup>3</sup>	W	F
				days			
Nano cement 90H395including:907Portland cement355Ground sand40+ in concrete mixture :40Ramensky sand (Moscowregion)920Yuzhny portal macadamfrom tunnel №3 outthrow,M-300921water145	3	<u>57.6</u> <u>4.3</u>	<u>64.2</u> <u>4.6</u>	72.4	2415	16	300

## Concrete mixture № 10, composition, kg/m3:

Nano cement-90 H ( on Portland cement by OAO Novoroscement )	384 (342*)
Yuzhny portal macadam** M-300, F - 25	897
Sand of Volzhskoe quarry	897
Water	193
Water-solid ratio	0.50
Cone slump, cm	5

## Concrete mixture №10, parameters

Lah#	Density (kg/m3)	Grade based		
Euo II	3 days	7 days	28 days	resistance

	kg/m <sup>3</sup>	MPa	kg/m <sup>3</sup>	MPa	kg/m <sup>3</sup>	MPa	
105-10	2370	<u>38.4</u> <u>3.7</u>	2350	47,9	2360	53.3 5.9	W20

\* Amount of Portland cement

\*\* Macadam of fraction 5-20 from tunnel outthrow

# Concrete mixture №7, composition kg/m3:

Nano cement-50 H ( on Portland cement by OAO Novoroscement )	380 (190*)
Yuzhny portal macadam** M-300, F - 25	887
Sand of Ramensky quarry	887
Water	165
Water-solid ratio	0.43
Cone slump, cm	7

## Concrete mixture №7, parameters

	Den	Grade based						
Lab #	3	days	7	days	on water			
	kg/m <sup>3</sup>	MPa	kg/ m <sup>3</sup>	MPa	kg/m <sup>3</sup>	MPa	resistance	
00.7	2210	35.6	2245	43.0	2250	43.5	W20	
77-/	2318	3.7	2343	4.1	2350	2550	4.6	vv 20

\* Amount of Portland cement

\*\* Macadam of fraction 5-20 from tunnel outthrow

## Concrete mixture №5, composition kg/m3:

Nano cement-75 H ( on Portland cement by OAO Novoroscement )	286 (215*)
Yuzhny portal macadam** M-300, F - 25	938
Mortar sand of Volzhsky quarry	857
Water	196
Water-solid ratio	0.68
Cone slump, cm	8

## Concrete mixture №5, parameters

		Density (kg/m3), compression strength / bending strength (MPa)								
Lab #	7 days		28 days		When saturated		after F200			
	kg/m <sup>3</sup>	MPa	kg/m <sup>3</sup>	MPa	kg/m <sup>3</sup>	MPa	kg/m <sup>3</sup>	MPa		
99-5	2276	<u>19,8</u> 2,8	2300	<u>23,0</u> 2,7	2345	20,5	2300	21,2		

- \* Amount of Portland cement
- \*\* Macadam of fraction 5-20 from tunnel outthrow

## Concrete mixture №17, composition kg/m3:

Nano cement-75 H ( on Portland cement by OAO Novoroscement )	393 (298*)
Yuzhny portal macadam** M-300, F - 25	917
Mortar sand of Maykop quarry	917
Water	184
Water-solid ratio	0.46
Cone slump, cm	25

## Concrete mixture №17, parameters

	Density (kg/m3), compression strength / bending strength (MPa)								Grade	
Lah #	Lab # 3 days		7 days		28 days		When	after F, cycles		based on
Lau #							saturated			water
	kg/m <sup>3</sup>	MPa	kg/m <sup>3</sup>	MPa	kg/m <sup>3</sup>	MPa	MPa	300	400	resistance
112-17	2410	27.4	2370	41.7	2375	50.1	52 5	55.2	50.8	W20
		3.7		4.4	2070	5.2	02.0	MPa	MPa	

\* Amount of Portland cement

\*\* Macadam of fraction 5-20 from tunnel outthrow

Concrete mixture №16, composition kg/m3:

Nano cement-50 H ( on Portland cement by OAO Novoroscement )	394 (197*)
Yuzhny portal macadam** M-300, F - 25	917
Mortar sand of Maykop quarry	917
Water	193
Water-solid ratio	0.48
Cone slump, cm	9

## Concrete mixture №16, parameters

	De	G 1 1 1								
Lab #	3 d	ays	7 d	ays	28 d	lays	When saturated	afte	er F	Grade based on water
	kg/m <sup>3</sup>	MPa	kg/m <sup>3</sup>	MPa	kg/m <sup>3</sup>	MPa	MPa	300	400	Tesistance
112-16	2420	<u>12.2</u> 2.1	2360	<u>16.6</u> <u>3.2</u>	2380	<u>21.9</u> <u>4.3</u>	22.5	22.9 МПа	22.4 МПа	W6

\* Amount of Portland cement

## Concrete mixture №6, composition kg/m3:

Nano cement-50 H ( on Portland cement by OAO Novoroscement )	290 (145*)
Yuzhny portal macadam** M-300, F - 25	946
Mortar sand of Maykop quarry	866
Water	198
Water-solid ratio	0.68
Cone slump, cm	12

#### Concrete mixture №6, parameters

	Γ	Density (kg/m3), compression strength / bending strength (MPa)							
Lab #	7 da	ys	28 days		When sa	iturated	after F200		
	kg/m <sup>3</sup>	MPa	kg/m <sup>3</sup>	MPa	kg/m <sup>3</sup>	MPa	kg/m <sup>3</sup>	MPa	
99-6	2301	<u>16.2</u> 2.8	2310	<u>20.1</u> 3.0	2320	17.5	2335	18.1	

## Concrete mixture №2, composition kg/m3:

Nano cement-50 H ( on Portland cement by OAO Novoroscement )	370 (185*)
Macadam of Kamensky quarry M-600, F - 25	864
Mortar sand of Volzhsky quarry	864
Water	135
Water-solid ratio	0.36
Cone slump, cm	3

#### Concrete mixture №2, parameters

	Density (kg/m3), compression strength / bending									
т 1 //		strength (MPa)								
Lau #	3	days	7 6	lays	28 days					
	kg/m <sup>3</sup>	MPa	kg/m <sup>3</sup>	MPa	kg/m <sup>3</sup>	MPa				
97-2	2232	<u>32.9</u> 3.6	2208	<u>33.8</u> 4.4	2255	<u>45.3</u> 4.6				

\* Amount of Portland cement

Concrete mixtures 1, 5, 7, 10 and 17, include in a composition the coarse filler: macadam from the outthrow of tunnel 3 works of Yuzhny Portal quarry in the form of macadam fractions 5 - 20 mm; with a crushing capacity grade M - 300, with grains of platelet and

needle shape - 17 wt.%; residue on sieve #5 - 83.2%; dust and clay particles - 3.5 wt.%; frost resistance F - 25. The above-mentioned parameters make this macadam non compliant with the requirements of standards: GOST 8267-93, 26633-91 and 8269-97.

Low strength parameters as well as low frost resistance capacity of the macadam from the outthrow of tunnel 3 works of Yuzhny Portal quarry were confirmed by the abovementioned test results conducted by the State Unitary Enterprise GUP NIIMosstroy.

Studies of compositions of concrete mixtures based on Nano cements of various classes allowed to select ultimate compositions to achieve a given concrete strength, water resistance and frost resistance capacity.

In the course of conducted studies and tests, we were able to not only use non conditional coarse fillers to produce high-strength and high-quality concrete, but also significantly reduce consumption of Portland cement for concretes of various classes to record low values - from 355 to 145 kg per cubic meter of concrete mixtures.

For the first time in the world's concrete production practice, excellent results were obtained with the use of non conditional coarse fillers associated. This is attributed to high hydraulic activity of Nano cements, formation of cement-sand stone with dense contact even on weak grains of macadam, formation of high strength impermeable microstructure of cement stone, as evidenced by the intense maturing of concrete samples already during the initial periods of hardening, an unusually high strength, water resistance and frost resistance capacity of the new concrete on non conditional nonmetallic materials.

Only 335 kg of Portland cement modified into Nano cement, even with such non conditional in basic parameters coarse filler, without introducing costly chemical additives was sufficient enough to produce a fast hardening (80% of strength in the first three days of hardening) concrete of class B 55, with water resistance capacity of W16, frost resistance capacity over 300 cycles (concrete mixture #1; lab # 97-1 of NIIMOSstroy).

Optical microscopy analysis of the microstructure of concrete confirms the scientific substantiation of Nano cement properties. For example, Figure 8 depicts a typical photograph of the microstructure of the cleavage face of the concrete sample after mechanical testing with record-breaking results.



Figure 8. Cleavage face of concrete sample (composition  $N_21$ , Class 55) after mechanical testing. There is destruction of the material directly along macadam grains. 28 days of normal hardening.

Observation of cleavage faces of concrete samples of almost all compositions showed a very dense structure of cement stone with the high density contact zone along the border with grains of coarse filler, forming already during the initial period of hardening (Figure 10).

Research and tests results have shown that Nano cements allow to obtain high-quality cement stone and concrete on almost any mortar sand, weak, non-frost resistant macadam due to intense reaction of Nano cement material and presence in it of silica component ground to dispersion level:

 $3 \text{ CaO SiO}_2 + 3 \text{ H}_2\text{O} + \text{SiO}_2 = 2 (\text{ CaO SiO}_2 \text{ H}_2\text{O}) + \text{Ca (OH)}_2$ 

In studied concrete samples based on Nano cement, quickly gaining strength during the initial periods of hardening, much faster than conventional concrete mixtures based on Portland cement, a high-strength matrix is formed: Nano cement - quartz sand fine ground to nano levels.

This ensures formation of dense, high-strength, impervious to air and water microstructure of cement stone and concrete, which very positively effects construction and technical characteristics, and above all the strength and durability of cement stone and concrete based Nano cements.



Figure 10. Cleavage face of concrete sample composition #5 after mechanical testing. There is destruction of the material directly along macadam grains. 7 days of normal hardening.

# Concretes on coarse fillers from macadam of Kamensky quarry and fine fillers from different quarries.

Limestone macadam (according to X-Ray quantitative analysis data containing 96 wt.% of calcite) fractions 5 - 20 mm of ZAO "Sochinerud" Kamensky quarry, with a crushing capacity grade M 600 and frost resistance F 50 (according to laboratory of OOO SEVERSTORY) with the content of dust and clay particles of 5.1% (instead of 2% according to GOST) and significant content of platelet and needle-shaped grains (29 wt.%); does not meet the requirements for coarse filler for concrete according to GOST 8267-93 and GOST 26633-91.

Despite the use of non-conditional non-metallic materials, low clinker Nano cements form highdensity cement stone and water- and frost-resistant concrete (Figure 11).



Figure 11. Cleavage face of concrete sample, composition # 7 on macadam of Kamensky quarry after mechanical testing. There is destruction of the material directly along weak grains of macadam and large particles of sand. 28 days of normal hardening.

Low clinker Nano cements allow, as shown by studies and tests, to obtain all classes of concrete, including, those ones of fast hardening and high strength. In addition to provision of all necessary construction and engineering properties of concrete, the use of low clinker Nano cements reduces to a minimum Portland cement consumption per cubic meter of concrete.

Thus developed concrete mixture with composition # 2 with a decreased Portland cement content of 185 kg per cubic meter of concrete and its application in the form of Nano cement allowed to obtain high strength in the initial period of hardening: at three days of normal hardening - 32.9 MPa compressive and 3.6 MPa bending strength; at 28 days - 45,3 MPa compressive and 4.6 MPa bending strength. Consumption of Portland cement per cubic meter of concrete reduced to a record level of 145 kg (concrete mixture, composition #6 with macadam of Kamensky quarry and sand of Volzhsky quarry) having high fluidity of concrete mix consistency allowed to obtain the desired strength of concrete with a normal hardening for 28 days at 20 MPa compression strength and 3.0 MPa bending strength with frost resistance capacity over 200 cycles.

Research of concrete mix compositions with the use of very weak in strength and frost resistant capacity limestone macadam of Kamensky quarry confirmed high construction and technical properties of concrete on low clinker Nano cements of different classes. The concrete mixture composition #16 with such macadam with frost resistance capacity being in the range of 25 to 50 cycles recorded during tests at State Unitary Enterprise GUP "NIIMOSstroy, yielded in concrete of class B 15, with a given strength and frost resistance of more than 400 cycles.

Such high results for the first time in the world concrete practice were possible to achieve due to already mentioned properties of low clinker Nano cement: high rate of hardening at the initial periods, considerable strength with a record low consumption of Portland cement; high fluidity of concrete mix consistency; all this eliminates the need for chemical additives.

Despite the resistance of backward industrial science and conservatism of the Russian cement factories that do not recognize domestic achievements in science and technology, Rosstandart adopted a national preliminary standard "Portland cement, nano-modified. Technical Specifications"; this opened possibilities, (in accordance with The Order of the Federal Agency for Technical Regulation and Metrology number 561 of 16 November, 2011, on the adoption of GOST R1.16.2011 "PRELIMINARY NATIONAL STANDARDS") for wide implementation of the most outstanding achievements of cement science in the history of cement industry.

## Conclusion:

Application of Nano cements not only saves considerable amount of cement in concrete production, but also, as shown by recent studies of Moscow IMET, allows to use low cost local materials for high-quality concrete production instead of expensive imported ones: non-ferrous materials that do not meet state standard criteria, including waste products of mining and fine sands.

Implementation of production and use of Nano cements in concrete technology and construction will enable a radical revision of the existing GOST standards in the direction of maximum use of local, non conditional non-metallic fillers in construction industry with significant cost savings and reduction in transportation cost.

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