Influence of Additives-Wastes of Chemical Industry Enterprises on the Properties of Reinforced Concrete in Transport Structures

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Abstract
As a result of corrosion processes, crystals are formed inside the concrete, the growth of which leads to the occurrence of cracks and destruction of reinforced concrete transport structures. For the long-term protection of the reinforcement, low concrete permeability (dense structure) has been required. The denser the concrete, the better it resists penetration to the reinforcement of aggressive substances. In addition to the micropores, macropores can also participate in the corrosion of RCC, when defects in the form of cracks occur in the protective layer creating the effect of differential aeration. The experience of using the additive-plasticizer of coke-chemical production, which application will reduce the number of pores and capillaries, increase the strength, density, corrosion resistance of reinforced concrete is studied in the article. It has been experimentally established that the optimum amount of the additive is in the range between 0.6 ... 0.7% of the cement weight. The additive allows to save 5% of cement at achievement of the designed durability; reduces the vibration time of concrete mixture by 20 ... 30%; does not affect the quality of the concrete surface, does not lead to the bloating of temporary openings, provides the given strength and crack resistance of cement-concrete products, which allows to obtain reinforced concrete with high quality, reliability and durability.
Key words: REINFORCED CONCRETE, TRANSPORT STRUCTURES, RCC CORROSION, PLASTICIZERS, PROPERTIES, STRENGTH, CRACK RESISTANCE, DURABILITY.

Ukraine is actively involved in the global social and economic processes and joins WTO. The strategic goal is an associate membership in the European Union. Transport as an infrastructure branch should be developed at a rapid pace in order to facilitate the rapid economic and social development of the country and its participation in the international division of labor [1].

The transport and operational condition of highways is unsatisfactory: 51.1% do not meet the requirements of smoothness, 39.2% - of strength [2, 3].

On the country's main roads, non-rigid pavements with asphalt-concrete pavement prevail (97%) and only 3% of roads have cement-concrete coatings.

In unreinforced coatings, the length of the plates regardless of the initial step of the transverse joints after a few years of operation is actually 4 ... 6 m due to the formation of the through transverse cracks. Reinforcing of coatings allows us significantly increase the length of concrete slabs, and, consequently, to decrease the number of transverse seams and reduce the defects of the coating. The slab length in this case is closely related to the content of the reinforcement and at a consumption of the latter in an amount of 3 ... 5 kg /m^2 can be increased up to 10-24 m respectively. Further increase in the content of the reinforcement (up to 8 ... 12 kg / m^2) allows increasing the length of the plate up to 200 ... 400 m and turn to the seamless so-called continuously reinforced structures, the use of which fundamentally solves the issue of improving the performance and durability of cement-concrete coatings [3].

The first small sections of roads with continuously reinforced concrete coverings were built in the USA (Indiana) in 1938. Over the next twenty years (until 1953), 55 km of continuously reinforced coatings had been experimentally built in the USA and their mass construction began since 1959. By 1966, the total length of pavements of this type was 3630 km, in 1968 - 8000 km, in 1971 - 16000 km and until 1975 it had reached 35 000 km. [4, 5].

Since the 60s, continuously reinforced coatings are also used in England, Germany, Sweden, Switzerland, Australia and other countries.

Continuously reinforced bases for asphalt-concrete coatings are widely applied in some countries (the United States and Great Britain). In some cases, continuously reinforced coatings are also used as reinforcement of existing road pavement [6, 7, 8].

Combined constructions are widely used, where layers of materials of various types are combined in order to make the best use of the advantages and accomplishments of each material. The most known combinations are cement-concrete or continuously reinforced concrete in the lower layer and dense or porous bitumen concrete in the upper; low-quality cement concrete in the lower layer and small block concrete in the upper layer; cemented material in the base, a separating layer of dense bitumen concrete and a top layer of ordinary or continuously reinforced cement concrete. Each of these combined types of structures has been tested and has an economically justified field of application [9, 10].

Implementation of the concept of obtaining new types of concrete with improved performance properties is impossible without the use of complex chemical modifying additives [11, 12, 13, 14].

In Ukraine, the application of additives is regulated by DBN B.2.7-64-97 "Rules for the use of chemical additives in concretes and mortars".

Important disadvantages of reinforced concrete are the corrosion processes caused by the action of atmospheric chemical factors including aggressive components of the atmosphere and frequent frost-thaw cycles.

As a result of chemical reactions, crystals are formed inside the concrete, the growth of which leads to the appearance of cracks and destruction of concrete. Rust formed during the oxidation of steel reinforcement increases its volume and leads to fracture of concrete and exposure of reinforcement. As a result, exposed parts of the reinforcement are destroyed even more rapidly, which leads to rapid deterioration of the concrete.

Salts destroy both steel reinforcement and concrete itself. Destruction caused by calcium chloride contributes to the acceleration of corrosion of the reinforcement. Salts reacting with calcium hydrate in concrete form oxidized calcium hydrate with subsequent increase in volume.

For the long-term protection of the reinforcement, low concrete permeability (dense structure) is required. The denser the concrete, the better it resists penetration of aggressive substances to the reinforcement. In addition to the activity of micropores in the process of corrosion of the reinforcement, macropores can also take part, when in the protective layer there are defects in the form of cracks, which create the effect of differential aeration or various measures of saturation with water or with ions OH^- and CL^-.

The use of plasticizing additives will allow reducing the number of pores and capillaries, increasing the strength, density, corrosion resistance of reinforced concrete. Their application allows us to reduce the water requirement of reinforced concrete by 20 ... 30% with the provision of a given mobility of the mixture [15].

Such plasticizers include the additive "Plasticizer of coke production" (herein after PLCP), which consists of a mixture of inorganic sodium salts, lignosulfonates of technical and other components. It is a dark opaque liquid. It dissolves well in water. It is fire and explosion-proof and has low toxicity.

The use of the complex additive PLCP increases the durability of concrete and its protective properties in relation to the reinforcement.

At the first stage, the effect of the influence of the PLCP additive on steamed out reinforced concrete of the same composition, which has been adopted at the plant with the determining of the optimum amount of the additive, has been investigated. Consumption of materials per 1 m^3 of concrete is as follows: cement M 500 - 410 kg /m^3; sand - 607.5 kg / m^3; crushed stone - 1320 kg / m ^{3}; water - 139 l / m ^{3}. The results of the studies are given in Tables 1 and 2.

After previous studies, it has been found that the optimum amount of the PLCP additive is in the range between 0.6 ... 0.9% of the cement weight. To clarify the optimum amount of the additive, additional studies have been conducted on the effect of the additive in the amount of 0.6% of the cement weight on the properties of cement concrete.

From the data given in Table 2, it can be concluded that the addition of PLCP in amount of 0.6% from cement weight allows reducing cement consumption by 5% per 1 m^3 of concrete mix.

In order to test the effect of PLCP additive on the properties of cement concrete, research in the production conditions of the plant was conducted. For this purpose, the effect of the additive in the amount of 0.6%, 0.7%, 0.8% and 0.9% of the cement mass was investigated. The additive in the form of an aqueous solution of 30% concentration was injected into the concrete mixture directly into the forced-mix concrete mixer, preliminary reducing the amount of water depending on the amount of the aqueous solution. The composition of concrete per mix of concrete mixer V = 0.54 m^3 is given in Table. 3.

The effect of the additive was investigated for the time of vibration of the concrete mixture and on the compressive strength (10×10×10 cm cubes).

The objective was to get a high-quality surface of reinforced concrete; reduce the time of vibration; to reach a given strength; exclude the bloating of temporary openings. The results of the studies are given in Table 4.

Table 1. Influence of PLCP additive on compression and bending strength of steam cured concrete.

No	Amount of additive, %	H (hardness), with / CS (cone slump), mm	R_{bend} (Bending strength) MPa/%	R_{com} (Compression strength) MPa/%	W/C Water to cement ratio
1	Etalon	20.0/115.0	6.28/100.0	47.58/100.0	0.385/100.0
2	0.6	10.0/130.0	6.29/100.2	50.56/106.3	0.385/100.0
3	0.8	15.0/120.0	7.33/116.7	42.44/89.2	0.385/100.0
4	1.0	15.0/120.0	7.36/117.2	40.03/84.2	0.385/100.0
5	0.6 (-8% of cement)	22.0/111.0	6.69/106.5	46.22/97.0	0.400/104.0
6	0.6 (-10% of cement)	20.0/115.0	6.05/96.3	41.50/87.0	0.436/110.0

Table 2. Influence of PLCP additive on compression and bending strength of steam cured concrete with reduced cement consumption.

No	Amount oof additive, %	H, with /CS, mm	Cement amount kg/m3/%	W/C	R_{bend} MPa/%	R_{comp} MPa/%
1	Etalon	15.0/20	410.0/100	0.385	5.92/100.0	37.59/100.0
2	0.6	10.0/24	410.0/100	0.385	6.35/107.3	39.38/104.8
3	0.6	15.0/21	389.5/95	0.385	6.34/107.1	39.33/104.6

Table 3. Concrete composition.

No	Availability and amount of additive %/l	Amount of materials per 0.54 м^3 in kg			
		Cement	Sand	Brocken stone	Water
1	Etalon	230	340	700	54
2	PLCP – 0.6%/5	230	340	700	49
3	PLCP – 0.7%/6	230	340	700	48
4	PLCP – 0.8%/7	230	340	700	47
5	PLCP – 0.9%/8	230	340	700	46

Table 4. Effect of additives on the concrete properties.

No of composition	Presence of the opening bloating	Time of vibration, minutes, sec.	Surface quality	Compression strength MPa after steaming out
1 (etalon)	Absent	15.46	There are bugholes, pores, capillar	61.1
2 (0.6 %)	Absent	10.02	There are bugholes, pores, capillar	61.2
3 (0.7 %)	Absent	12.05	There are bugholes, pores, capillar	61.8
4 (0.8 %)	Absent	10.02	There are bugholes, pores, capillar	62.7
5 (0.9 %)	Absent	12.05	There are bugholes, pores, capillar	63.5

From Table. 4 it can be seen that there have been no bloating of temporary openings and the quality of the surface is the same as in comparison with the etalon. Vibration time has been reduced by 20 ... 30%, which will allow saving energy and improving working conditions in the shop. The strength of concretes without additives and with PLCP additive is the same. But it has been saved 0.6 ... 0.7% of cement.

Thus, it is established that the PLCP additive allows reducing the time of vibration with all other equal parameters.

In the plant conditions, samples for crack resistance at IT-316 press have been tested. Two samples have been tested without additive (cement consumption - 100%) and another two samples with PLCP additive (0.6%) with a cement consumption of 95%. The tests have shown a complete absence of cracks, i.e. requirements for crack resistance of the samples and for reducing the cement consumption by 5% (24 kg per 1 m^3 of concrete mix) are met.

The effect of PLCP additive on the physical and chemical processes that take place in the hardening concrete has been investigated by petrographic, X-ray phase and differential thermal analysis on samples that have been saturated with water (I), an aqueous solution of PLCP (0.6%) (II) and PLCP (0.9%) (III).

Petrographic analysis has been performed using a polarization microscope MZHI-6 on transparent sections of concrete samples, which hardened after steaming out for 28 days of normal hardening.

The hydrated binder without the additive consisted of non-hydrated binder and hydration products (65%), which have been mostly fine-grained scale units with a clear polarization and coarse grains (up to 30 microns) of $Ca(OH)_2$ crystals. Opaque gel has been placed unevenly (10%). Contact with the filler is sufficiently tight; the adhesion is weak with a certain number of cracks. The pores in the form of balls are closed, with a size of 5 ... 250 micron. The refractive index is 1550 ... 1557.

The hydrated binder with PLCP additive of 0.6% (II) is significantly different from the sample (I). The degree of hydration is 65 ... 70%, and the degree of crystallinity is higher. The refractive index is 1.545 ... 1.550. The size of the crystals is up to 60 ... 70 micron. Opaque gel is distributed unevenly. Pores are single, spherical. Cracks are sawn in mass of new formations and are almost beyond the zone of contact with the filler (width - 20 ... 25 micron, length up to 700 micron), they make up 10% of the binder.

In the sample (III) (0.9% of PLCP), the binding mass is more homogeneous, the amount of opaque gel (up to 30%) is more evenly distributed; the refractive index of $Ca(OH)_2$ crystals is 1.560; crystallization is higher; pores are of different shapes; cracks are single and sawn; contact with the filler is tight.

Conclusion regarding the influence of PLCP additive on the processes of cement stone hydration has been made using DTA curves and the results of X-ray structural analysis.

DTA results of specimen shown in Fig. 1 confirm that concrete filled with a solution of PLCP additive (0.6%) has a higher degree of hydration of cement clinker minerals.

Differential thermograms have been carried out using specimen made with ordinary water and on an aqueous solution of PLCP (0.6%), which have been hardened for 28 days in normal thermal and humidity conditions after steaming out.

Analyzing the thermograms (Fig. 1), it can be seen that they all have an endothermic effect in the range of 80-360 °C with a maximum of about 145 °C. At these temperatures, hydrosilicates are dehydrated, the ettringite is partially dehydrated and the crystallization water from calcium hydroaluminate is disappearing. The lowest depth (145 °C) has a maximum on thermogram 3 (concrete, with PLCP additive of 0.9%). The endothermic effect of decomposition of crystalline calcium hydroxide in the range between 550 … 650 ° C is weakly expressed (especially on thermogram 3).

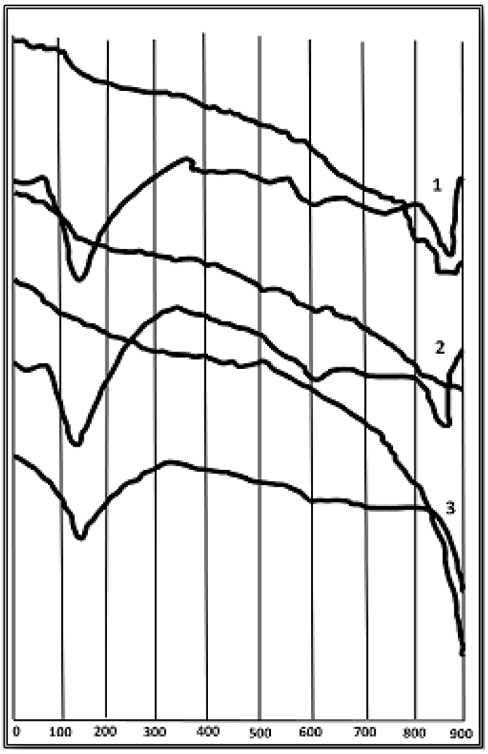

Figure. 1. Thermograms of samples of cement stone made of concrete, which has been mixed with water (I); 0.6 % PLCP (2); 0.9 % PLCP (3)

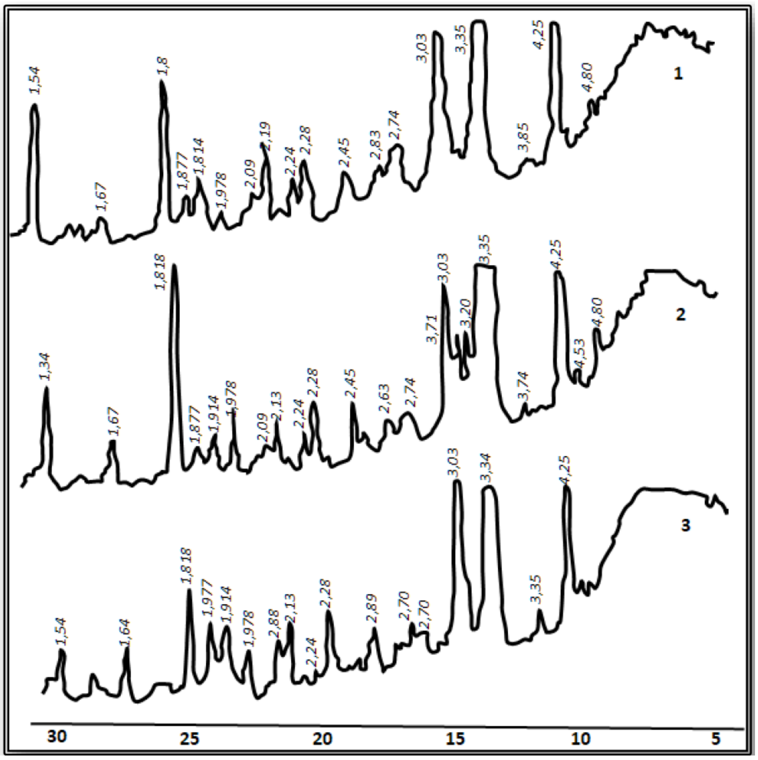

Figure. 2. X-ray pictures of samples of cement stone made of concrete, which has been mixed with water (I); 0.6 % PLCP (2); 0.9 % PLCP (3)

On thermograms 1 and 2, a third endothermic effect is shown the most clearly in the range between 800 … 900 ° C, and on thermogram 3 - in the range between 850 ... 950 ° C.

At these temperatures, hydrosilicates with low basicity are decomposed and some hydrosilicate formations are finally dehydrated. The displacement of the hydrothermal effect in the temperature range of 850 ... 950 °C on thermogram 3 indicates an increase in the degree of hydrosilicates dispersion.

X-ray patterns of the samples have been taken with URS-50 IM equipment (Cu – radiation, Ni – filter, ZMA 22 KW mode). The results of the experiments are shown in Fig. 2.

Studies have shown that samples with PLCP additive are characterized by more intense lines d=3.03 Å (Fig. 3), which indicates an increased content of low-basicity hydrosilicates (CSH). In the same sample, less amount of unbound SiO_2 has been observed (d = 1.540; d =1.818; i d =3.34 i d = 2.45 Å). The non-hydrated clinker minerals in the soluble part of the concrete have been in significantly less amount than in concrete that is filled with pure water (2.74 Å effect). The lime carbonization in concrete filled with PLCP additive of 0.9% concentration is higher than in concrete with 0.6% concentration and filled with clean water (d = = 1.877; d =2.09; d =2.28; d =3.35; d = 3.03 Å).

The results of the conducted studies (petrographic, X-ray phase and differential thermal analyzes) confirm that reinforced concrete with PLCP additive the addition is characterized by a greater degree of hydration of the cement, they have an increased amount of low-basic hydrosilicates, and a microcrystalline structure of the cement stone.

As a result of the work carried out to verify the effectiveness of PLCP additive in the technology of manufacturing of reinforced concrete samples, it has been established that the optimum amount of additive is in the range between 0.6 ... 0.7% of the weight of the cement; the additive allows to save 5% of cement at achievement of the set hardness; additive reduces the time of vibration of the concrete mixture by 20 ... 30%; the additive does not affect the quality of the concrete surface; the additive does not lead to the bloating of the temporary openings; additive provides the given strength and crack resistance of cement-concrete products ensuring their high quality, reliability and durability.

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