The use decorative concretes with the addition of highly dispersed chalk for volumetric and spatial elements of urban space

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Abstract. In recent years, the attitude to the external appearance of the urban environment and its elements has changed dramatically. Interest in new constructive solutions, style of urban space design and modern materials which improve the quality of urban space has increased. Installed that the most effective material is decorative concrete, which is used to create a variety of volumetric and spatial elements of engineering improvement, architectural and urban design. The possibility of creating decorative concrete with the addition of highly dispersed chalk and the natural pigment that is distinguished by high operational, decorative, aesthetic properties and solves environmental and economic problems has been considered in the article. The results obtained indicate the possibility of combined use of highly dispersed chalk and yellow natural pigment (ocher) to create colored concrete with high corrosion resistance, frost resistance and decorative and aesthetic properties. The relationship between the durability and corrosion resistance of the test concrete on the size and nature of the pores has been established.

1. Introduction

In recent years, changing the appearance of most cities in Ukraine that were characterized by monotony and sameness of buildings, especially residential areas, has been observed. Today, for creating an artistic expression, comfort and harmony of the urban environment, as well as an increase in the manifold and aesthetic qualities of residential areas are used various means of architectural and urban design, which are represented by stairs, ramps, fences, small architectural forms. These various means are added uniqueness, originality, originality, and scale to individual territories and as a whole the city [1, 2].

The diversity used elements of urban design are depended on the type of used building materials and products. The volumetric and spatial elements of the urban environment are exposed to various climatic factors and mechanical stress in accordance to various defects to connected with processes of maintenance are observed with their surface. These defects are caused by the influence of temperature fluctuations, air humidity, exposure to wind, precipitation and solar radiation, the presence of household and industrial impurities in the atmosphere (dust, soot, carbon black) [3].

Therefore, to create various elements of engineering improvement, architectural details, materials are used to are characterized by high-performance properties, especially weather resistance, wear resistance, mechanical resistance, durability, corrosion resistance, but at the same time have high aesthetic and decorative qualities and solve environmental and economic problems. Concrete and products of concrete are matched all these characteristics. Architectural forms made of concrete are practical, easy to install, are allowed to create a variety of textures and shapes of either complexity, and concrete is much cheaper than marble or granite. But products of concrete have one disadvantage of their color is gray and unattractive [4, 5, 6, 7].

Accordingly, decorated concretes are given wide use. According to in December 2019 report by Value Market Research, the global decorative concrete market will grow from $ 15.4 billion in 2020 to $ 20.5 billion by 2025, with a CAGR of 5.9% from 2020 to 2025 year [8]. Due to the fact that decorative concrete can be used to produce a variety of architectural products not only flat but also curved, with smooth conjugation of surfaces, the required color, and high-quality texture, to are allowed creating new
architectural elements in buildings and structures, while providing high artistic and aesthetic expressiveness such elements [8].

One of the ways are given decorative concrete sufficient brightness is developing the composition of a concrete mixture on Portland cement using pigments, but obtaining bright saturated colors such concretes are impossible because of the fact that the brightness of the pigment color is muffled by the gray color of the cement. Consequently, such concretes don’t better use to create objects of architecture and urban design. It will add greyness and uncomfortable areas. In order to avoid this effect and obtain decorative concrete with high properties, white cement is used in that case the cost of products is increased significantly, but at the same time, such concretes must retain decorative and operational characteristics during the time and contribute to the elimination of hazardous pollutants from the urban environment and be similar to natural materials, such as marble or granite [9, 10, 11].

The properties of decorative cements largely depend on the quality of the cement and the properties of the pigment. Therefore, pigments must be resistant to alkalis, sunlight and atmospheric influences, have been a high coloring power, but at the same time, a minimal effect is affected on the physical and mechanical properties of concretes. The quantity of mineral or synthetic pigments by decorative concrete should not exceed 15%, and natural pigments by decorative concrete are no more than 0.5% [12, 13]. An effective method of getting concrete, characterized by significant whiteness, with increased durability characteristics, is the use of carbonate additives, in particular, highly dispersed chalk.

Chalk is a lithological type of limestone that is a mixture of particles of organic calcite (small fragments of skeletons, or shells of mollusks), to have a negative surface charge due to the fact that the presence of free silicic acid, and small particles of chromogenic calcite and it is had positive surface charge. Against the background of the bulk (about 80%), chalk is represented by coccoliths and their parts (powdered calcite) [6, 14, 15, 16]. (Figure 1).

![Figure 1](image)

**Figure 1.** Electron microscopic image of the surface of natural chalk (Slavyansk field, Ukraine).

Accordingly, the cementation of rock is caused by both condensation and crystallization bonds between particles [15]. The microstructure of chalk is a fine-grained mass consist of particle size 0.01 mm. According to [15, 17, 18], the main part of chalk (95-98%) is represented by particles from 0.05 to 0.005 mm. The chalk has low solubility, does not form crystalline hydrates and does not interact with water, but easily disperses when dispersed. In this case, the chalk contains the cations that are part of most clinker minerals [19, 20].

The surface of the chalk in aqueous dispersions has an excess negative charge, as evidenced by the small negative value $\zeta$ potential, while the equipotential chalk point corresponds pH from 5 to 7 [7, 17]. According to [15, 19, 21] is covered with free silicic acid, so the mechanism of interaction of chalk with clinker minerals and products of their hydration is significantly different from the known mechanisms of interaction of other carbonate rocks, including limestone.

Particles of highly dispersed chalk that were added into the composition of concrete, are placed in the pores and create hydrophobic areas to prevents the movement of water into the concrete. Highly dispersed chalk doesn’t only contribute to the compaction and plasticization of the mixture, but also it is affected the formation of the phase composition of calcium hydrosilicates [13, 20, 22]. In this case,
the main products of hydration are low-basic hydrosilicates of the CSH (I) type and calcium hydrocarbosilicates that it leads to an increase in the strength and frost resistance of such compounds [23, 24]. Accordingly, the use of highly dispersed chalk in cement compositions is led to changes in the phase composition of the cement stone due to the fact that the formation of complex compounds, including CaCO$_3$ and Ca(OH)$_2$, and it also is lea to the acceleration and complete hydration of clinker minerals.

In the process of hydration, highly dispersed chalk enters into chemical interaction with aluminum-containing clinker minerals C$_3$A and C$_4$AF, cubic calcium hydroaluminate 3CaO·Al$_2$O$_3$·6H$_2$O and a complex compound calcium hydrocarboaluminate C$_5$A $\times$ CaCO$_3$$\times$11H$_2$O are formed, provided that chalk is represented by grains d <42 μm [15, 25, 26]. With larger grains of highly dispersed chalk is it formed.a small amount of cubic C$_3$AH$_6$. In the presence of highly dispersed chalk, the character of crystallization of calcium hydrosilicates can also change, namely: instead of large fibrous crystals are formed small ones with a more developed surface, also it is led to the mixing of strength characteristics and is provided an increase in frost resistance, sulfate resistance, and water resistance [26, 27, 28,29, 30].

Based on the above, it was assumed that the particle size of highly dispersed chalk is matched the size of the capillaries of the cement stone, thus a significant part of the capillary pores volume can be filled with calcite, to is poorly soluble in water, it will increase the density and it will reduce the permeability of the cement stone.

The purpose of the study is to develop a composition of color concrete with the addition of highly dispersed chalk for volumetric and spatial elements of urban space.

2. Research methods and materials

2.1. Materials

For experimental studies Portland cement was used (CEM I 42.5 N), as a coarse aggregate, granite crushed stone of Znamenivsky Quarry (Kirovogradka region), it has fractions 2.5 ÷ 5 mm and 5 ÷ 10 mm, with a density of 2590 kg / m$^3$ were used, as a fine aggregate quartz sand of the Bezlyudivsky Quarry of Kharkiv region with the size of Mk = 0.9, bulk density 1370 kg/m$^3$ were used. As an additive chalk of the Slavyansk deposit is used, pigment is used ocher, it is clay colored with iron oxides which has various shades from light yellow, golden to dark, red and even brown. In concrete, a mixture of highly dispersed chalk is introduced as a chalk suspension [5, 6, 7].

For the study, a series of samples with different percentages of highly dispersed chalk were produced that are consider at Table 1.

| Sample number | Material costs, % | W/C |
|---------------|-------------------|-----|
| 1             | 100               | 0.466 |
| 2             | 90 10             | 0.460 |
| 3             | 80 20             | 0.462 |
| 4             | 70 30             | 0.468 |
| 5             | 60 40             | 0.472 |

The degree whiteness of the cement is determined depending on the light reflectance as a percentage of the absolute scale and the grade must be at least: I - 80%, II - 75%, III - 68% [32].

The required quantity of pigment that it was introduced into the concrete mixture, is determined by the need color. An increase in the quantity of pigment to a certain level are led to an increase in the intensity color. The development of concrete mixtures for the manufacture of various volumetric and spatial elements for engineering improvement, architectural and urban design should be had high level operational and decorative characteristics.
2.2. Method for determining the density
The research of density was determined according to DSTU B V. 2.7-114-2002 [31] before testing the compressive strength. The tests were carried out on concrete samples - cubes 100×100×100 mm in relatively normal humid conditions at a temperature of (20 ± 2)°C and relative humidity of at least 95%.

The density of the samples was found by the formula (1):

$$\rho = \frac{m}{V} \cdot 1000$$  

where

$m$ - mass of samples, kg;

$V$ – volume of sample, m$^3$.

2.3. Method for the determination of corrosion resistance
To determine the corrosion resistance, an express method was used, developed by M.I. Strelkov [32] and beams 70×70 × 280 mm were made. The basis, concentration diagram of the four-component system (Na+, Mg$^{2+}$, Cl$^-$, SO$_4^{2-}$) was used proposed by M.I. Strelkov [32]. According to [32], the high aggressiveness of this system is due to the formation of compounds with a high molecular weight as a result of chemical interaction between the salts of the system: NaCl, Na$_2$SO$_4$, MgCl$_2$, MgSO$_4$, and products of hydration cement.

To increase the corrosion resistance of the cement stone, finely dispersed chalk was used as a mineral additive. Samples of cement stone were made from Portland cement without additives and with the addition, respectively, of 10, 20, 30, 40% of chalk from the total mass of cement and chalk at W/C=0.45. After solidification under normal conditions for 28 days, the samples were crushed and for the following researches, fractions of 0.14-0.315 mm were, after which a quantity such particles were placed in measuring cylinders with aggressive solutions. It was a solution to various salts. For the researches, solutions were prepared to contain salts of NaCl, Na$_2$SO$_4$, MgCl$_2$, MgSO$_4$ that are shown in Table 2.

Table 2. Compositions of an aggressive solutions.

| Liquid number | Compositions of the aggressive solutions |
|---------------|-----------------------------------------|
| 1.1           | 0.4NaCl+0.2Na$_2$SO$_4$+0.27MgCl$_2$+0.13MgSO$_4$ |
| 1.2           | 0.42NaCl+0.4Na$_2$SO$_4$+0.13MgCl$_2$+0.27MgSO$_4$ |
| 1.3           | 0.13NaCl+0.27Na$_2$SO$_4$+0.2MgCl$_2$+0.4MgSO$_4$ |
| 1.4           | 0.1NaCl+0.1Na$_2$SO$_4$+0.4MgCl$_2$+0.4MgSO$_4$ |
| 1.5           | MgCl$_2$                                  |
| 1.6           | 0.2MgCl$_2$+0.8MgSO$_4$                 |

For the research, the solutions were selected according to the results of determining the corrosion resistance by the express method.

The samples of degree stability were established by the value of the stability coefficient (Cs) as was determined by the formula (2):

$$C_s = \frac{f_{3\text{month}}}{f_{28\text{day}}}$$  

where

$f_{3\text{month}}$ – compressive strength of the sample after immersion in an aggressive solution during 3 months, MPa;

$f_{28\text{day}}$ – compressive strength of samples after 28-day hardening before immersion in an aggressive solution, MPa.

3. Results of experimental studies
According to research results, it was found that an increase in density is observed in samples № 2, №3, modified with 10% and 20% highly dispersed chalk, while there is an increase in compressive strength
for sample № 2, and for sample № 3, the strength remains the same as the control sample. The density of samples № 4 and № 5, modified with 30% and 40% highly dispersed chalk, has decreased (Figure 2).

![Figure 2. The dependence of compressive strength \( f_{cd} \) and density \( \rho_w \) concrete samples from chalk component.](image)

The research has shown that the higher the percentage of the quantity of highly dispersed chalk in concrete samples, the greater the whiteness of the sample. Sample № 5 that is modified with 40% of highly dispersed chalk has the highest whiteness, according to [32], it can be classified as grade II, wherever the light reflectance is 77%. Samples № 2 and №3, modified respectively with 20% and 30% of highly dispersed chalk, have a light reflectance of 70% and 73%, respectively, that it allows classifying as III grade. When a yellow pigment in the quantity of 0.3% had added, samples № 4 and №5 had a bright yellow color, the other samples had a saturated color (Table 3).

| Sample number | Initial compressive strength, \( f_{cd} \), MPa | Index durability of cement stone, % in an aggressive liquid \( \ell \) (liquid number) |
|---------------|-----------------------------------------------|--------------------------------------------------------------------------------|
|               |                                               | 1.1   | 1.2   | 1.3   | 1.4   | 1.5   | 1.6   |
| 1             | 41.8                                          | 72    | 78    | 62    | 85    | 76    | 67    |
| 2             | 46.6                                          | 126   | 115   | 103   | 98    | 94    | 96    |
| 3             | 41.8                                          | 123   | 99    | 98    | 85    | 85    | 93    |
| 4             | 33.5                                          | 98    | 95    | 88    | 86    | 93    | 91    |
| 5             | 25.4                                          | 86    | 91    | 76    | 78    | 87    | 86    |

The research on corrosion resistance has shown that samples № 1 and №2 modified 10% and 20% of highly dispersed chalk, are the most stable in all corrosive environments (the stability coefficient \( Cs \) is outreach 85%), while cement stone without additives is not very stable in these solutions.

4. Discussion of results obtained in the study

To a large extent, the density of concrete is determined by the strength on the adhesion of the cement stone by aggregate, that depends on the shape, roughness and surface cleanliness of aggregate grains, as well as adhesion. The corrosion resistance of concrete is depended on the phase composition of the cement stone, since the solubility and reactivity of its individual phases is differed significantly. The structure of concrete is determined the speed of penetration to aggressive ions and is removal of corrosion products, that is, the course of corrosion processes.

Since all reactions are occurred on the surface of the cement grain, so crystallization of new formations, as a rule, is occurred on the surface of the grain, gradually filling the free space between the particles of cement grains (pore space), while forming a new structure of the cement stone, which it is
represented by calcium hydrocarboaluminate, low-basic hydrosilicates. Considering that the particles of highly dispersed chalk are formed supplemental crystallization centers, accordingly, there is a change in the quantitative ratio of structure-forming and destructive factors during the synthesis the strength of cement stone and concrete. In this case, there is an increase in the number of growths of crystals of newgrowths, which increases the volume concentration of newgrowths and the density of the gel in the pore space between the particles of cement stone [6]. As the volume of capillary pores decreases, hydration products, such as calcium hydrocarbonaluminate, fill the voids between the cement particles, which is due to the structure of the chalk, increasing the packing density and leading to an increase in the sample density [6]. The appearance of calcium hydrocarboaluminate \(C_3A \times CaCO_3 \times 12H_2O\), the formation of which is due to the interaction of C3A with CaCO3 chalk, is confirmed by X-ray studies (Figure 3).

![Figure 3. Radiograph of cement stone modified with 10% highly dispersed organogenic calcite (chalk).](image)

The introduction of highly dispersed chalk, the particle size of which is in the range of from 0.54 to 2.21 μm, is helped to reduce the content of micro- and capillary pores filled with calcite, so that it is poorly soluble in water. An increase in the volume of capillary pores will increase the density of the concrete and will reduce the permeability of the cement stone. Since the volume of capillary pores usually does not exceed 40%, therefore, so that chalk is filled them, the total volume of the binder can be increased due to dispersed chalk by no more than 40%. A decrease in the number of growths is increased capillary pores, which leading to an increase in the looseness of the concrete structure and, accordingly, to a decrease in density. Therefore, in terms of capillarity, the concrete samples under research can be classified as dense.

5. Conclusions
According to the studies, carried out, it was found that highly dispersed chalk is affected growths in cement composites, which is led to a change in the phase composition of the cement stone due to the formation of complex compounds, including \(CaCO_3\) and \(Ca\ (OH)_2\), and also it will lead to the acceleration and complete hydration of clinker minerals. An increase in concrete density is allowed to improve its physical and mechanical characteristics, in particular, compressive strength, permeability, frost resistance, water resistance, corrosion resistance, that will lead to the durability of structures. The relationship between the density and permeability of the samples has been established, that it is allowed to predict the strength and deformation properties of decorative concrete, as well as crack resistance, frost resistance, and corrosion resistance during their operation.
The obtained results are showed that concrete samples with the addition of highly dispersed chalk have had a bright white color, that it allowed to use it as an alternative to white cement, the introduction of yellow ocher pigment does not reduce the physical, mechanical, operational and decorative characteristics of the samples. The dosage of the pigment is formed 0.1 to 0.3% by weight of the cement, depending on the desired color.

Due to the use of concretes modified highly dispersed chalk, and in combination with organic or natural pigments, it can be expanded the range of decorative ones that will be used to create and improve the urban and architectural environment.

References

[1] Denednyova E, Demina O, Volkova A and Krivitskaya A A 2015 Collected scientific works of Ukrainian State University of Railway Transport 152 pp 187-192
[2] Dedeneva E B, Demina O I, Stelmakh A A and Rachkovsky A V 2014 Priority areas of science and technology pp 60-64
[3] Olga Bazhenova and Maxim Kotelnikov 2018 E3S Web of Conferences 33 pp 1-6
[4] Kochevikh M O, Blazhis G R, Gonchar O A and Vyalin D 2016 Visnyk KhNTU Inzhenerni nauky pp 54-59
[5] Chepurna S M, Zhydkova T V and Chepurna M Ie 2018 Zbirnyk naukovykh prats «Suchasni tekhnolohii ta metody rozrakhunkiv u budinvytsvi» 10 pp 195-204
[6] Svitlana Chepurna, Tetiana Zhydkova and Olha Popova 2020 Trans Tech Publications Ltd (Zurich, Switzerland) pp 27-35
[7] Chepurna S, Borziak O and Zubenko S 2019 Materials Science Forum 968 pp 82-88
[8] Decorative Concrete Market by Type (Stamped Concrete, Stained Concrete, Colored Concrete, Polished Concrete, Epoxy Concrete, Concrete Overlays), Application, End-use Sector, and Region Global Forecast to 2025 https://www.marketsandmarkets.com/Market-Reports/decorative-concrete-market-189792263.html
[9] Luigi Cassar, Carmine Pepe, Giampietro Tognon, Gian Luca Guerrini and Rossano Amadelli 2003 11th Int. Congr. on the Chemistry of Cement (Durban)
[10] Mindess S, Young JF and Darwin D 2002 Concrete 2nd edn. Pearson (Upper Saddle River)
[11] Cassar L, Pepe C and Tognon Getal 2003 11th International congress on the chemistry of cement (Durban, South Africa) pp 41–11
[12] Trofimov B Ya and Kramar L Ya 2010 Vestnik of the South Ural State Univ. pp 36-38
[13] Marco L 1983 Raw materials for decorative concrete (Moscow: Stroyizdat)
[14] Arshinnikov D I and Svidersky V A 2015 Technology audit and production reserves 4 pp 7-11
[15] Gorkova M et al. 1962 Priroda prochnosti i deformatsionnye osobennosti mela i nekotoryih melopodobyh porod. (Moscow: Akademiya nauk USSR)
[16] . Kozlova V K, Manokha A M, Lykhosherstov A A and others 2012 Tsement i eho primenenie 3 pp 53-57, 60
[17] Poluektova V A, Lomachenko V A, Stolyarova Z V, Lomachenko S M and others 2014 Basic Research: Technical Sciences 9 pp 1205–1209
[18] Kuznetsova T V, Kudriashov Y V and Tymashev V V 1958 Fyzycheskaia khmyia viazhushchykh veshchestv (Hosudarstvennoe izdatelstvo literatury po stroitelstvu i arkhitekteure USSR) pp 5-16, 49-66
[19] Marushchak U, Sanitsky M, Mazurak T and Olevych Y 2016 Eastern-European Journal of Enterprise Technologies 6/6 (84) pp 50-57
[20] Sanitsky M, Kropyvnytska T and Kotiv R 2014 Advanced Materials Research 923 pp 42-47
[21] Kriwenko P V, Sanitsky M, Kropyvnytska T and Kotiv R 2014 Advanced Materials Research 897 pp 45-48
[22] Ustinova A A, Potapova E N and Konyshkina A Yu 2017 Advances in chemistry and chemical technology XXXI (3) pp 114-116
[23] Marushchak U, Sanytsky M, Sydor N and Braichenko S 2018 MATEC Web of Conferences 230 03012
[24] Kononova O V and Cherepov V D 2013 Sovremennye problemy nauki i obrazovaniya: Tekhnycheskiye nauky 1 pp 227-234
[25] Samchenko S V and Makarov E M 2013 Tekhnyka i tekhnolohiya silikatov 3 pp 27-29
[26] Matschei T, Lothenbach B and Glasser F P 2007 Elsevier Magazine: Cement and Concrete Research 7 (4) pp 551–558
[27] Mchedlov-Petrosian O P and Olhynskyi A H 1971 Eksperimental’noe issledovanie mineraloobrazovaniya (Nauka)
[28] Loshak V V, Cherkasov S V and Vlasov V V 2011 Sci. Bull. Of Voronezh State Arch. and Constr. Univ. pp 3-4, 61-66
[29] Guziy S and Terenchuk S 2016 Science Rise vol. 9 2 (26) pp 49-54
[30] Borziak O S, Chepurna S M, Plugin A A, Zavalniy O V and Dudin O A 2019 IOP Conference Series: Materials Science and Engineering (MSE) 708 pp 1-5
[31] DSTU B V. 2.7- 114 – 2002. 2002 Budivelnii materialy. Sumishi betonni. Metody vyprobuvan (State standard of Ukraine, Kyiv)
[32] Strelkov M Y and Zaslavskyi Y N 1987 Uskorenniaia otsenka ahressynosti k betonu vodnykh rastvorov s uchetom mnohokomponentnosti ykh sostava (Lenynhrad, PromstroinyYproekt)
[33] HOST 965-89. 1990 Portland cements, white. Specifications (Moscow: Stroyizdat)