Features of the structure formation processes and synthesis of strength for Portland cement compositions modified with nanocarbonate additives

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Abstract. The work shows the results of studying the features of the structure formation process when nano-carbonate additives of different physical states are added to Portland cement and the establishment of the appropriate technology for their introduction, which provides the best conditions for the synthesis of artificial stone. It was found that the introduction of nanocarbonate additives in the form of dispersion provides better kinetics of the cement stone strength gain, and the effect of the introduction of dispersion exceeds the effect of the introduction of powder on 7th day by (43 ... 48)% , on 28th day - (27… 30)% and 365th day by (25… 29)%. The using of the dispersion is more economically efficient, while preventing the aggregation of particles provides a directed synthesis of crystal-chemically similar compounds. The nanocarbonate additive acts as a substrate for the directional formation of hydrosilicate phases, providing microreinforcement and the formation of a more homogeneous and improved structure of artificial stone at both nano- and micro-levels.

1. Introduction

According to the US Geological Survey for 2020, global cement production has reached about 5 billion tons and is expected to grow from year to year. Moreover, large increases in cement production are expected in some developing countries, such as China and India [1]. Given the above, it becomes clear why in the production of cement and concrete are increasingly using various mineral additives, including carbonates.

It is confirmed that the use of calcium carbonate has a positive effect on the hydration processes of Portland cement, its strength at an early age, microstructure and durability [2]. Thus, many studies have been conducted to clarify the mechanism of influence of calcium carbonate additives on the properties of cement paste, mortar and concrete [3], [4].

In 1938, Bessey et al. [2] with the addition of calcium carbonate in the process of hydration of cement for the first time established the formation of calcium hydrocarboaluminate, similar results were obtained in later studies [5].

It is now accepted that the density and density of the cement matrix can be increased by the introduction of calcium carbonate when it acts as a filler, ie its particle size is comparable to the particle size of cement, or even smaller, and the role of chemical reagent if involved in hydration process and this process can be accelerated due to the nucleation effect [2,6].

The number of scientific publications on the use of finely ground limestone and other carbonate additives in concrete has increased almost 6 times over the past 20 years and this topic attracts scientists from many countries. Based on studies of the effect of calcium carbonate on the properties of cement composites, many standards have been adopted in different countries, which are listed in Table 1.
Table 1. Standards of different countries governing the use of finely ground limestone additives in cement production.

| Year | Country (region) | Standard | Composition of cement with additives |
|------|------------------|----------|-------------------------------------|
| 1991 | Brazil           | NBR 11578/91 | Portland cement LS containing 6-10% limestone filler |
| 1999 | Mexico           | NMX C-414-099 | Portland cement LS containing 6-35% limestone filler |
| 2000 | Europe           | EN 197-1 | Determined 4 types of Portland Cement LS, containing 6-20% limestone (types II / A-L and II / A-LL) and 21-35% limestone (types II / B-L and II / B-LL) respectively |
| 2007 | China            | GB 175-2007 | LS can be used as an activated mix in the cement industry |
| 2007 | Argentina        | IRAM 50000/07 | Portland cement LS may contain 25% shell rock |
| 2008 | Canada           | CSA A3001-08 | Portland cement containing <15% limestone filler LS |
| 2010 | Canada           | CSA A3001-10 | Portland cement LS is defined as GUL |
| 2012 | USA              | ASTM C 595 | Portland cement containing <15% limestone filler LS |
| 2008 | Ukraine          | DSTU B EN 1971:2008 | Cement. Composition, technical specification and conformity criteria for conventional cements |
| 2010 | Ukraine          | DSTU B B.2.7-46-2010 | Cements for general construction purposes. Specifications |

Finely ground limestone (or calcium microcarbonate) has a particle size (1 μm … 1 mm), and can be in the form of powder or limestone dust, widely used in cement production as a mineral additive. Although calcium carbonate has no pozzolanic activity and cannot react with alkaline substances such as Ca(OH)₂, the introduction of calcium carbonate into the cement can have both physical and chemical effects on the hydration process, as well as a positive effect on rheology of fresh concrete mix and physical and mechanical properties of hardened cement stone.

K. Vance et al. [7] investigated the effect of particle size of finely ground limestone during cement hydration using three types of powders of different degrees of dispersion. The finer limestone powder (average particle size 0.7 and 3 μm) significantly accelerates the hydration process of calcium silicate and increases the hydration peak (see Figure 1 [7]), as the finer limestone powder has a larger specific area and surface energy, which provides additional nucleation zones for the formation and development of calcium hydrosilicates (CSH) [7], [8]. This effect is known as the nucleation effect. In addition, the second peak on the heat curve associated with the hydration of calcium aluminate shows a significant increase in the introduction of limestone powder with a grain size of 0.7 μm, which means the formation of new hydration products such as hemicarboaluminate (C₃A·0.5CaCO₃·12H₂O) and monocarboaluminate (C₃A·CaCO₃·11 H₂O).

Figure 1. Influence of fine particle size of finely ground limestone (0.7… 15 μm) on heat release during cement hydration [7].

The formation of carboaluminates has also been confirmed by many other researchers [9]. At the same time, hemicarboaluminate is not thermostable and is recrystallized to monocarboaluminate. The
formation of carboaluminate depends on many factors, including the kinetics of formation of hemi- and monocarboaluminate, and the dissolution of calcium carbonate is lower with increasing pH, due to the fact that the amount of reactive calcium carbonate involved in the formation of carboaluminate is much less than the content of limestone powder [9]. The authors of [7], [10] showed that at a constant content of limestone powder, the compressive strength at an early age (up to 7 days) increases with decreasing particle size of the carbonate additive. In the later stages of hardening, the introduction of finely ground limestone can sometimes adversely affect the strength of cement compositions [11], which may be due to the fact that the physical effect of filling the pores will outweigh the chemical effect.

It is also proven that with increasing content of finely ground limestone (meaning the amount exceeding the optimal), the compressive strength and flexural strength decrease [7], [12]. On the other hand, the introduction of more carbonate additives increases the water consumption of the concrete mixture, which causes a higher effective water-cement ratio and reduces the strength. Given the above data, it becomes clear the scientific interest in the use as carbonate additives of nanoparticles with a grain size of less than 100 nm [13]. Compared to microcarbonate, calcium nanocarbonate has a smaller particle size and a higher specific area, and thus should have a greater impact on hydration processes, as well as on the rheology of concrete mixes and on the physical and mechanical properties and durability of cement composites.

The effect of calcium nanocarbonate on the hydration process of cement depends on its content, particle size and crystal structure [14].

T. Sato et al. [15] studied the effect of calcium nanocarbonate content and particle size on cement hydration. Nanocarbonate (50… 120 nm) is very effective in accelerating the hydration of cement, especially during the induction of tricalcium silicate (C₃S) due to the manifestation of the nucleation effect. However, calcium nanocarbonate can also react with C₃S to form C-S-H gel and Ca (OH)₂, and this can cause more heat to be released during hydration and at an earlier time.

The crystal structure of nanocalcium carbonate can also affect the hydration process of cement. The influence of nanocarbonate additives of calcite and aragonite composition on the properties of concrete capable of self-compaction was studied [15] and the significantly higher efficiency of calcite additive addition than aragonite was shown. Comparing the effect of calcite and aragonite nanocarbonate on the change in flexural and compressive strength, it can be noted that calcite is more effective because it significantly accelerates the formation of C-S-H phases.

Physico-mechanical properties of cement composites containing nanocarbonate additives mainly depend on their content, namely when the additive content increases to a certain (optimal) amount, the strength indicators first increase, and then, when using excessive amounts of nanocarbonate decrease [16].

The reasons are that, on the one hand, nanocarbonate can accelerate the hydration process and react with C₃S and C₃A to form C-S-H and carboaluminates, and this effect is more significant with a certain amount of additive. With increasing amount of additive, the dilution effect may occur and the strength of the composite decreases.

Agglomeration of nanocarbonate particles is also possible, which can lead to loss of both physical and chemical activity [18]. In addition, a denser matrix formed by the addition of nanocarbonate cannot provide the synthesis of a sufficient number of hydration products of the hydrosilicate composition [16].

2. Materials and Methods
The aim of this research is to study the features of the structure formation process when adding nanocarbonate additives of different physical state to Portland cement and to establish the appropriate technology of their introduction to provide the best conditions for the synthesis of artificial stone.

The Portland cement CEM I 42.5 R (according to DSTU B B.2.7-46: 2010) of CRH company (PJSC “Podilsky Cement”) with a specific surface area of 390 m² / kg according to Blaine was used in the research.
In order to form the structure of artificial stone and improve its physical and mechanical characteristics, a superplasticizer based on polycarboxylates (MS PowerFlow 3100) with a molecular weight of PEG of about 3000 units was used.

As nanocarbonate additives used technical products of the Norwegian company "Nordcalk" in the form of dry powder "Enrich C" and dispersion "Enrich C 50", the main characteristics of which are presented in table 2. The additives were introduced into the cement in terms of dry matter.

| Table 2. General characteristics of nanocarbonate additives by "Nordkalk" company. |
|-------------------------------------------------|---------------------------------|------------------|------------------|
| Technical characteristics                      | Units of measure                | «Enrich C»       | «Enrich C50»     |
| Dry matter content                             | %                               | > 99             | 50               |
| Average density                                | g / cm$^3$                      | 0,75             | 1,45             |
| pH of the dispersion                           | 7...9                            | 7...9            |
| Appearance (at T = 250°C)                      | White powder                    | White dispersion |
| Size of the particles d50                      | µm                              | 25               |
| Particle size distribution d50%                 | nm                              | 130              |
| d90%                                           | nm                              | 300              |

As a microcarbonate additive, finely ground limestone of Humentsi quarry of Khmelnytsky region was used, the chemical and mineralogical composition of which is given in Table 3.

| Table 3. Chemical and mineralogical properties of finely ground limestone (microcarbonate additive). |
|-------------------------------------------------|---------------------------------|------------------|------------------|
| The content of oxides, mas. %                  | SiO$_2$                         | 1,59             | 0,49             |
|                                                | Al$_2$O$_3$                     | 0,44             | 0,51             |
|                                                | Fe$_2$O$_3$                     | 53,89            | 42,94            |
|                                                | MgO                             | 2,16             |                  |
|                                                | CaO                             |                  |                  |
|                                                | L.O.I.                          |                  |                  |
|                                                | SiO$_2$, R$_2$O$_3$             |                  |                  |
|                                                | CaCO$_3$ - 96,16; MgCO$_3$ - 1,26; clays (SiO$_2$, R$_2$O$_3$) | 2,27             |

Given the influence of polycarboxylate superplasticizers and nanocarbonate additives on the rheological properties of cement paste and on the processes of structure formation of cement compositions, it was rational to first study the physico-mechanical properties of cement paste samples to eliminate the effect of fine aggregate on strength and reduce error. Studies of the strength of cement paste were performed using cube samples 2×2×2 cm, which were tested after curing under standard conditions on a hydraulic press. The kinetics of compressive strength of the investigated compositions on the basis of cement pastes are presented in Table 4.

| Table 4. Evaluation of the effectiveness of the use of micro- and nanocarbonate additives for the modification of cement compositions. |
|-------------------------------------------------|-------|------------------|------------------|
| Binder composition                              | Strength gain of paste samples, MPa, after curing for, | 3 days | 7 days | 28 days | 365 days |
| Portland cement+water                           | 43    | 61              | 74              | 79          |
| Portland cement+water + 1% MCPF 3100           | 64    | 82              | 94              | 96          |
| Portland cement+water + 1% MCPF 3100 + microcarbonate additive | | | |
| 10%                                             | 79    | 85              | 90              | 92          |
| 12,5%                                           | 85    | 89              | 95              | 97          |
| 15%                                             | 75    | 76              | 78              | 79          |
| Portland cement+water + 1% MCPF 3100 + nanocarbonate additive | | | |
| 2,5% in a form of powder                        | 54    | 64              | 94              | 100         |
| 3,5% in a form of powder                        | 59    | 69              | 96              | 106         |
| 4,5% in a form of powder                        | 55    | 63              | 94              | 99          |
| 2,5% in a form of dispersion                    | 71    | 95              | 124             | 125         |
| 3,5% in a form of dispersion                    | 77    | 99              | 129             | 133         |
| 4,5% in a form of dispersion                    | 74    | 96              | 127             | 128         |
3. Results and Discussion
The analysis of the given data allows to note that in case of use of finely ground limestone as carbonate additive to Portland cement, efficiency of its action (in comparison with cement paste without limestone addition) is shown mostly at early terms of hardening and makes (17… 23)% on 3 days and (3.6… 8.5)% at 7 days. On the 28th day, the effect of the additive does not exceed 1%, or almost leveled off. The data obtained are confirmed by the results of research by other scientists [17], [18].

At the same time, using a nanocarbonate additive in the form of a dispersion, the strength gain of the artificial stone is (10… 20)%, (15… 20)% , (31… 37)% and (30… 38)% by 3,7,28 and 365 days respectively, so there is a relatively stable increase in strength over time, which indicates the direct crystallization of low-basic hydroxilicates, and it is likely that the introduction of nanocarbonate additive (relatively small amount compared with the addition of finely ground limestone) specifically contributes to the nucleation structure not only at the micro-, but also at the nanoscale.

The process of hydration of C₃S in the presence of nano-CaCO₃ is accelerated due to the reduction of the induction period [14]. This is due to the fact that the additional surface created by nano-CaCO₃ particles promotes the effect of nucleation and increasing of sites of hydration products of Portland cement, including calcium hydroxilicates.

![Figure 2. Scheme of the mechanism of C₃S hydration in the induction period in the presence of a nanocarbonate additive.](image)

Usually the induction period during C₃S hydration occurs due to the formation of a protective layer (Figure 2a), which significantly inhibits the hydration process [2]. The presence of nano-CaCO₃ particles near the C₃S surface weakens the protective layer (Figure 2b) and in places of weakening the permeability increases and access to the surface of the C₃S particle solution with a high concentration of Ca²⁺, which leads to accelerated growth of C-S-H (Figure 2c). Nano-CaCO₃ particles, due to their crystal chemical similarity to hydroxilicate compounds (Fig. 3), act as "substrates" for C-S-H crystallization, providing additional nucleation centres (Figure 2d).

Comparison of the results of physical and mechanical tests of samples modified with nanocarbonate additives in the form of powder and dispersion (Table 4), confirms the effectiveness of the introduction of nanoadditives specifically in the form of dispersion together with a plasticizing additive, which ensures uniform distribution throughout the volume of cement paste particles [19].

The effectiveness of the nanocarbonate additive compared to control mixtures is especially noticeable on the 28-th day and later curing, due to the formation of a stable composition of products of hydration, dominated by gillebrandite, low-basic calcium hydroxilicates similar to tobermorite 11.3 A and hydrocarboaluminates.

In order to confirm the phase composition of products of hydration, electron scanning microscopy of Portland cement stone samples was performed after 28 and 365 days of hardening. The results of the study are shown in Figures 4-7.
Figure 3. Parameters of crystal lattices C-S-H and CaCO₃.

Figure 4. - Microstructure of the spall surface of Portland cement stone modified with polycarboxylate superplasticizers after 28 days of curing: magnification: (a) × 1200 (b) × 3000.

Figure 5. - Microstructure of artificial stone based on Portland cement modified with nanocarbonate dispersion in the presence of polycarboxylate plasticizer after 28 days of curing: magnification x2500 (a); x250 (b).
Comparison of the results of electron scanning microscopy allows us to note the directional crystallization of hydrosilicate phases in the presence of nanocarbonate additives, associated with the effect of nucleation, which is clearly manifested on the 28-th day and then recorded at later curing age.

**Figure 6.** Photos of the spall surface of Portland cement stone modified with polycarboxylate superplasticizers after 365 days of curing: magnification (a) × 600; (b) × 5000

**Figure 7.** Microstructure of artificial stone based on Portland cement modified with nanocarbonate dispersion in the presence of polycarboxylate plasticizer after 365 days of hardening: magnification: x 1000 (a); x2500 (b) x5000 (c).

Calcium nanocarbonate acts as a substrate for the directed growth of calcium hydrosilicates, which is confirmed by theoretical calculations by comparing the parameters of the crystal lattices of minerals, and the results of electron microscopic analysis, which allows to record changes in the morphology of products of hydration. According to the Ruyet-Friedel rule, the criterion for the possibility of crystal fusion can be the value \( \Delta = (a_1-a_2)/a_1 \), where \( a_1, a_2 \) are the parameters of mineral lattices in the area of their fusion, and the difference between the parameters of fused crystals should not exceed 15% [20] - [22].
Calcite, which is the basis of the nanocarbonate additive, may act as a substrate for the crystallization of ettringite and low-basic calcium hydrosilicates. In the CaCO$_3$ crystal lattice (Fig. 8a) there is a layer consisting of CaO atoms, which is similar to the Ca-O layer in the structure of gillebrandite (Fig. 8b), tobermorite (Fig. 8c) and ettringite (Fig. 8d).

The length of Ca - O bonds is 2.35 Å for calcite, (2.28 - 2.41) Å for gillebrandite, (2.4 - 2.52) Å for tobermorite and (2.43 - 2.61) Å for ettringites, the value of $\Delta$ is close to zero.

![Diagram of the crystal structure of minerals](image)

**Figure 8.** Diagram of the crystal structure of minerals, where the selected crystallographic area indicating the layer Ca - O: calcite (a), gillebrandite (b), tobermorite (c), ettringite (d).

Directional crystallization is possible on crystallographic planes passing through the Ca-O layer. Below are diagrams of possible fusion of calcite and ettringite (Fig. 9a) on the crystallographic planes (001) and (001), calcite and gillebrandite (Fig. 9b) on the planes (036) and (010), calcite and tobermorite (Fig. 9c).) on the planes (036) and (001).
In particular, the crystallochemical similarity of the hydration products of cement compositions both after 28 and after 365 days can explain the stability of the increase in strength over time, and the manifestation of the nucleation effect in the presence of nanocarbonate additives increases crystal nuclei and directional crystallization of hydrosilicates (tobermorite and hillebrandite), especially in late stages of hardening of artificial stone.

4. Conclusions

The introduction of a nanocarbonate additive provides a directed synthesis of the strength of an artificial stone and the effectiveness of the nanoadditive in comparison with a microcarbonate additive is 3,7,28 and 365 days (10 ... 20)%, (15...20)%, (31 ... 37)% and (30 ... 38)%, respectively. The introduction of nanocarbonate additives in the form of dispersion provides better kinetics of the cement stone strength gain, and the effect of the introduction of dispersion exceeds the effect of the introduction of powder on 7th day by (43 ... 48)%, on 28th day - (27... 30)% and 365th day by (25 ... 29)%.

The introduction of the dispersion is more economically efficient, while preventing the aggregation of particles provides a directed synthesis of crystal-chemically similar compounds. The nanocarbonate additive acts as a substrate for the directional formation of hydrosilicate phases, providing microreinforcement and the formation of a more homogeneous and improved structure of artificial stone at both nano- and micro-levels.

References

[1] Schneider M, Romer M, Tschudin M and Bolio H 2011 Sustainable cement production - Present and future Cem. Concr. Res. 41 pp 642-650

[2] Wang D, Shi C, Farzadnia N, Shi Z, Jia H and Ou Z 2018 A review on use of limestone powder in cement-based materials: Mechanism, hydration and microstructures Constr. Build. Mater. 181 pp 659–672
Dweck J, Buchler P, Coelho A and Cartledge F 2000 Hydration of a Portland cement blended with calcium carbonate Thermochim Acta 346 pp 105-113

Ye G, Liu X, De Schutter G, Poppe A and Taerwe L 2007 Influence of limestone powder used as filler in SCC on hydration and microstructure of cement pastes Cem. Concr. Compos. 29 pp 94-102

Bonavetti V, Rahhal V and Irassar E 2011 Studies on the carboaluminate formation in limestone filler-blended cements Cem. Concr. Res. 31 pp 853-859

Soroka I and Stern N 1976 Calcareous fillers and the compressive strength of portland cement Cem. Concr. Res. 6 pp 367-376

Fernandes F, Manari S, Aguayo M, Santos K, Oey T, Wei Z and Falzone G 2014 On the feasibility of using phase change materials (PCMs) to mitigate thermal cracking in cementitious materials Cement and Concrete Composites 51 pp 14-26

Kirk V, Matthew A, Tandre O, Gaurav S and Narayanan N 2013 Hydration and strength development in ternary portland cement blends containing limestone and fly ash or metakaolin Cem. Concr. Compos. 39 pp 93-103

Thongsanitgarn P, Wongkeo W, Chaipanich A and Poon C 2014 Heat of hydration of Portland high-calcium fly ash cement incorporating limestone powder Effect of limestone particle size Constr. Build. Mater. 66 pp 410-417

Zajac M, Rossberg A, Le Saout G and Lothenbach B 2014 Influence of limestone and anhydrite on the hydration of Portland cements Cem. Concr. Compos. 46 pp 99-108

Lertwattanaruk P, Sua-iam G and Makul N 2018 Effects of calcium carbonate powder on the fresh and hardened properties of self-consolidating concrete incorporating untreated rice husk ash J. Clean. Prod. 172 pp 3265-3278

Kenai S, Soboyejo W and Soboyejo A 2004 Some engineering properties of limestone concrete Mater. Manuf. Process. 5 pp 949-961

Turk K and Nehdi M 2018 Coupled effects of limestone powder and high-volume fly ash on mechanical properties of ECC Constr. Build. Mater. 164 pp 185-192

Silvestre J, Silvestre N and de Brito J 2016 Review on concrete nanotechnology Eur. J. Environ. Civ. Eng. 20 pp 455-485

Sato T and Beaudoin J 2011 J Effect of nano-CaCO3 on hydration of cement containing supplementary cementitious materials Adv. Cem. Res. 23 pp 33-43

Yes-ilmen S, Al-Najjar Y, Balav M, Sahmaran M, Yildirim G and Lachemi M 2015 Nano-modification to improve the ductility of cementitious composites Cem. Concr. Res. 76 pp 170-179

Wu Z, Shi C, Khayat K and Wan S 2016 Effects of different nanomaterials on hardening and performance of ultra-high strength concrete (UHSC) Cem. Concr. Compos. 70 pp 24-34

Kozlova V, Manyukha A and other 2012 Vliyanie karbonatsoderzhashhikh dobavok na svojstva kompozicionnykh cemmentov/ Czement i ego primenenie 3 pp 53-57

Kropivnizcua T 2013 Vpliv karbonatnih dobavok na vlastivosti portlandcementu kompoziciijnogo Visnik Nacjonalnogo universitetu Lvijska politekhnika Teoriya i praktika budivnicstva 755 pp 214-220

Bondarenko O, Guziiz S, Zakharchenko K and Novoselenko Ye 2015 Razrabotka zashhitnykh materialov na osnove steklo- i shlaksoderzhashhikh portland cemmentykh kompozicij Eastern-European Journal of Enterprise Technologies 6/11 (78) pp 41-47

Pushkareva E, Sukhanievich M and Marcizik A 2013 Tehnologicheskie aspekti vvedeniya uglerodnykh pri modificirovanii portlandcementnykh kompozicij/Proizvodstvo e`nergo- i resursosberegayushshikh stroitel`nykh materialov i izdeliy Sb. trudov IT nauchno-prakt. sem. Tashkent, TASI 1 pp 102-108

Pushkareva K, Gonchar O and Kaverin K 2019 The role of the crystallo-chemical factor in the evaluation and improvement of the nanomodification efficiency of mortar and concrete IOP Conf. Series: Materials Science and Engineering TRANSBUD-2019 708 012102 11