The impact of nano SiO$_2$ and superplasticizers on hydration and physical mechanical properties of cement

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Abstract. The aim of work is to determine the lowest and effective amount of nano SiO$_2$ (NS) for cementitious paste and identify the complex impact of NS and chemical admixtures on cement hydration and physical-mechanical properties. In order to achieve the aim, cementitious specimens with different types and amounts of NS were formed. Further, after the selection of NS and its amount, specimens were formed with various superplasticizers. The work analysis the following properties of cementitious mixtures and hardened cement stone: flow diameter, exothermal temperature, density, ultrasound pulse velocity, compressive strength, microstructure and mineralogical composition. It was determined that the greatest strength of cementitious specimens was obtained when 0.02 wt.% of NS was used, and, compared to control specimens, it increased by ~15%. Additionally, the greatest increment in strength was observed for specimens with melamine-based superplasticizer. Compared to control specimens, the strength increased up to 23% and the obtained density and ultrasound pulse velocity were the greatest. XRD analysis showed that all specimens had analogue crystal hydrates formed but their amounts are different. SEM analysis showed that structure of the specimens with NS is denser.

1. Introduction
Currently, an analysis of the impact of various nano- additives (nano-TiO$_2$, nano-CaCO$_3$, nano-Al$_2$O$_3$, carbon nano-tubes, nano silica (NS), etc.) on the properties of cementitious materials gains the popularity. One of the most effective nano- additives is NS which fills the cavities between cement particles and has high reactivity with calcium hydroxide of the cement. Moreover, NS increases the density of cementitious materials, reduces drying shrinkage, capillary absorption and water demand [1-3]. The use of NS makes concrete financially more attractive and reduces the CO$_2$ footprint of the produced concrete products [4]. Authors [5] suggest using nano particles in small amounts of (0.01-0.005)% by cement weight. Different NS in scientific studies of cementitious materials is used in various amounts – from 0.01% to 0.5% and sometimes more than that [6-9].

Properties of cement mixtures with NS in literature [10-11] show that the strength of all specimens with NS was higher than that of specimens with micro SiO$_2$. Consistent use of NS in cement mixtures increases compressive strength in early stages by 10–20%, after 28 days – by 16–24%, and after an addition of plasticizers – up to 30% [12]. Other authors [13] state that adding of 0.25% of NS without a plasticizer to the cement paste enhanced the compression strength of the samples after 1-3 days up to 6%, at that, after 7 days cement specimens demonstrated no strength increase, while after 28 days and
after 90 days cements specimens even lost some of their strength. Addition of 0.1% of a superplasticizer ensured an increase the compression strength of concrete after 3-7 days by 28-30% and after 28 days – by 10%.

It is determined [14-15] that NS acts as an active pozzolanic additive which accelerates hydration reactions. Additionally, it is proved that NS has an effect on the cement paste structure, and fills the voids between the cement particles [16-17]. It was reported that NS generated more CSH gel in cement stone [18-19]. In addition, the results showed that the suitable content of nano-SiO$_2$ improve the durability of concrete significantly and such concrete has lower water permeability than the normal concrete [20-21]. In authors’ works [22-24], the impact of micro-silica and NS on a durability of cement materials is determined. The results show that NS has to be used together with micro-silica. Moreover, NS has a greater demand for plasticizer and cementing efficiency compared to micro-silica. Authors [25] tested the impact of NS on transporting and mechanical properties of superhydrophobic cement mixtures; therefore, they determined that the nature and amount of superplasticizer are extremely important.

Partial replacement with NS (up to 2.5%) in mortars and cement pastes determines portlandite minerals after 9 hours of hardening. Furthermore, the density reduction effect is observed, i.e. density reduces by 2.4% [26].

Scientists [27] tested NS impact on various properties of ultra light cement composites. Combined expanded glass granules and cenospheres were used as fine aggregates which facilitate the density of ultra light cement composites. The density of these specimens is 1075 kg/m$^3$ and compressive strength after 28 days of hardening – 20 MPa. Small amount of NS increases a compressive strength of ultra light cement composites up to 27 MPa. Water accessible porosity values of ultra light cement specimens are in the range of 15–19%. It is as well determined that increased viscosity appears due to ultra fine particles in suspension. They detain air in mixtures; therefore, water accessible porosity increases.

Work [28] presents the positive complex impact of nano-clay and NS on compound cement hydration. Chemically bonded water content is analysed and loss on ignition at 900°C after 2 h is determined. It is the main parameter which evaluates the kinetics of Portland cement hydration. In compound cement paste, the content of chemically bonded water increases with the addition of NS/nano-clay amount. It is explained by the hydration speed increment which is caused by the interaction between amorphous aluminosilicate NS/nano-clay with free calcium hydroxide to form CSH, CAH and CASH.

Article [29] analysis the impact of three different materials based on silicon dioxide (quartz, ultrafine quartz, and silica fume) on cement hydration, rheology, structure and compressive strength. Calorimetric tests showed that 2.5% of silica fume and NS accelerate the hydration of cement paste. In case of quartz, no effect, compared to control specimen, is observed when a median particle size of 0.6 µm is reached. Other authors [30] analysed the impact of NS size on compressive strength of cement materials. Cement specimens with 40 nm size NS were characterised by a higher compressive strength than those with 12 and 20 nm-sized NS. Such impact is explained by a particles’ agglomeration and ineffective dispersion. By changing 3%, 6%, 9% and 12% cement with NS, the optimum NS quantity is 9%.

The amounts of NS used by scientists vary widely, as are the size of particles and their effects. The aim of our work is to select the lowest effective NS amount and to determine its effect on the properties of cement mixtures and hardened specimens using different types of superplasticizers.

2. Materials and Methods

In the research, cement CEM I 42.5 R was used; its chemical composition is presented in Table 1 and physical mechanical properties – in Table 2. Mineral composition of the cement: C$_3$S – 56.6 %, C$_2$S – 16.7 %, C$_3$A – 9.0 %, C$_4$AF – 10.6 % and 7.1 % others (alkaline sulphates and CaO).

For the research, two types of nano SiO$_2$ (A and B) were used, their properties are presented in Table 3. The effect of three different superplasticizers (with potassium hydroxide (pH 9.0), based on melamine (pH 9.4) and based polycarboxylate (pH 6.5) on the properties of cementitious mixtures and hardened samples was investigated. Drinking water was used to prepare mixtures. The compositions of cement mixtures are given in Table 4.
Table 1. Chemical composition of cement, %.

| CaO  | SiO₂    | Al₂O₃ | Fe₂O₃ | MgO  | K₂O  | Na₂O | SO₃  | Cl   | L.O.I. |
|------|---------|-------|-------|------|------|------|------|------|--------|
| 63.2 | 20.4    | 4.0   | 3.6   | 2.4  | 0.9  | 0.2  | 3.1  | 0.05 | 2.15   |

Table 2. Physical-mechanical properties of cement.

| Particle density, g/cm³ | Soundness “Le chatelier”, mm | Passing 32 µm, % | Compressive strength after 2 days, MPa | Compressive strength after 28 days, MPa | Vicat initial, min | H₂O, % |
|-------------------------|-----------------------------|------------------|---------------------------------------|----------------------------------------|-------------------|-------|
| 3.1                     | 1.0                         | 78.5             | 30                                    | 55                                     | 180               | 27.5  |

Table 3. Properties of NS.

| Mark | Size, nm | Surface area, m²/g | Purity, % | Relative molecular weight, g/mol | pH (40 g/l) | Relative density, g/cm³ |
|------|----------|--------------------|-----------|---------------------------------|-------------|-------------------------|
| A    | 12       | 205                | 99.8      | 60.08                           | 4.2         | 2.6                     |
| B    | ~10-30 nm| 202                | 99.8      | 60.08                           | 4.0         | 2.2                     |

Table 4. The compositions of cement mixtures.

| Mark | Cement, g | Nano SiO₂, g | Nano SiO₂, % | Superplasticizer, g | Superplasticizer, % | Water, g |
|------|-----------|--------------|--------------|--------------------|---------------------|----------|
| C    | 3000.0    | 0.0          | 0.0          | 0.0                | 0                   | 1050     |
| A1   | 2997.0    | 3.0          | 0.1          | 0.0                | 0                   | 1050     |
| A2   | 2994.0    | 6.0          | 0.2          | 0.0                | 0                   | 1050     |
| A3   | 2991.0    | 9.0          | 0.3          | 0.0                | 0                   | 1050     |
| A01  | 2999.7    | 0.3          | 0.01         | 0.0                | 0                   | 1050     |
| A02  | 2999.4    | 0.6          | 0.02         | 0.0                | 0                   | 1050     |
| A03  | 2999.1    | 0.9          | 0.03         | 0.0                | 0                   | 1050     |
| B2   | 2999.4    | 0.6          | 0.02         | 0.0                | 0                   | 1050     |
| BH   | 2999.4    | 0.6          | 0.02         | 6                  | 0.2                 | 850      |
| BM   | 2999.4    | 0.6          | 0.02         | 6                  | 0.2                 | 850      |
| BP   | 2999.4    | 0.6          | 0.02         | 6                  | 0.2                 | 850      |

Primarily, only one type of nano SiO₂ (A, particle size 12 nm) was selected for determine optimum amount of this additive. Later, it was checked or the optimum amount (according to the A type SiO₂) of B type SiO₂ would change significantly properties of cement specimens, as the price of A type SiO₂ and B type SiO₂ differs several times (B is cheaper). Since, the results of cement specimens properties with B type SiO₂ were slightly better than with A type, only B type SiO₂ was used in further studies.

When preparing the mixtures, nano SiO₂ was first dispersed in 350 g of water with equipment UZDN-2T. Disperse duration was 15 min at 400 W 22 kHz. The resulting mixture is then mixed with the rest of the water to bring the water temperature to 20°C. If the mixture is prepared with a superplasticizer, the superplasticizer is also poured into the prepared suspension. Mixing was performed in the mixer for 3 min, and 16×4×4 cm samples were formed. The consistence of prepared mortars was established according to the flow diameter established according to EN 1015-3.

The X-ray diffraction (XRD) analysis of the phase composition of materials was carried out upon applying diffractometer DRON-7. The parameters of the tests were following: voltage - 30 kV; current - 12 mA; the range of the diffraction angle – from 4 to 60°, the detector movement step – 0.02°; the duration of the intensity measuring in a step – 0.5 s. Phase identification was carried out by decoding the XRD patterns according to ICDD diffraction databases. The quantitative changes in the XRD patterns were assessed according to the height of the peak of the main diffraction maximum of a mineral.
The microstructure of the materials was explored upon use of scanning electron microscopy (SEM) equipment JEOL JSM-7600F. The parameters of electron microscopy were following: voltage - 10 kV; the distance to the surface of the specimen – from 7 to 10 mm. The peculiarities of the microstructure were identified on examining the split surface of the specimens. The image was formed on registering the signal of secondary electrons. Prior to the test, the cleavage surface was covered with thin golden layer upon applying the method of gold electron vacuum evaporation.

For exothermal tests of mixtures, the specimens were prepared as follows: cement mortar mixtures (the total weight 1500 g) were poured into forms and a thermocouple in a glass pipe was immersed in the form. The prepared mixture with the form was immediately placed into a metal box with internal 50 mm thick foam polymer insulation. Temperature was measured and its values were uninterruptedly fixed until heat emission processes took place in the specimen. The exothermal tests were carried out at the room temperature (20±1) °C, the temperature of the used raw materials and water was the same, i.e. (20±1) °C. This test was provided in semi-adiabatic conditions.

The density of the specimens was established according to EN 196. Ultrasound propagation time is determined using the equipment “Pundit 7” (frequency of converters is 54 kHz) and ultrasound propagation speed is calculated based on the following equation (V, m/s):

\[
V = \frac{l}{\tau};
\]

where: \( l \) – length of the specimen, m; \( \tau \) – signal propagation time, s.

The compressive strength of specimens after their hardening in water for 7 and 28 days was established upon using hydraulic press ALPHA3-3000 S according EN 196.

3. Tests results and analysis
Consistence (determined by flow table) results in mixtures with superplasticizers were from 19.7 cm to 20.6 cm. The use of superplasticizers has reduced the amount of water, and it is aimed to ensure that all mixtures do not spread more than 10 mm. In this case, the flow diameter varied from 15.4 cm (BH) to 16.4 cm (BP). The BH superplasticizer also has air-absorbing properties, resulting in lower flow diameter of this mixture.

The results of density and ultrasound pulse velocity after 28 days of specimens hardening are shown in figure 1.

![Figure 1. The results of density and ultrasound pulse velocity.](image_url)

It can be observed that the density values at different amount of NS change only slightly, i.e. up to ~1%. However, a greater density change is seen in addition to the use of plasticizing admixtures. The minimum density is obtained for specimens BH, and compared to control specimen C0, it reduces up to ~3%, while the greatest density is obtained for specimens BM and it increases by ~5%. The difference in density when using different superplasticizers is ~ 8%. Ultrasound pulse velocity (UPV) change after addition of NS is 4%. When superplasticizing admixtures are used, UPV, compared to control specimen, increases by ~9%. The UPV results showed that the NS compacts the structure and especially the
positive effect of NS was observed using melamine- and polycarboxylate-based superplasticizers. In specimens with potassium hydroxide-based superplasticizer, more pores are formed. Producers describe this plasticizing admixture as a material which increases water resistance and has air-absorbing properties.

Figure 2 presents the results of the compressive strength of the specimens, which show that the A NS additive when used without superplasticizers increases the compressive strength by ~11% after 7 days of hardening and approx. 16% after 28 days of hardening.

![Figure 2. The results of compressive strength (fc).](image)

Interestingly, the changes in the compressive strength of the specimens with A NS depending on the content of admixture varied slightly, i.e. by ~5%. Perhaps this is due to the agglomeration of the particles and the low degree of dispersion. The best results were obtained for Type A NS at 0.02% by cement weight, but this material is more expensive than Type B NS due to its variable size. Therefore, it was tried to mix the best-performing batch with Type B NS at 0.02% by cement weight. The results of compressive strength are even better in this case than in Type A NS. In this case, the compressive strength after 7 days hardening increased by ~17% and after 28 days – by 19%. Similar results were obtained by other scientists who found that 40 nm-sized NS increases the strength more than 12 nm-sized NS [30] and based their results on stronger agglomeration of smaller NS particles. Further studies were conducted with the highest strength having B2 mixtures containing various types of superplasticizers. The results show that by selecting the appropriate superplasticizer, the compressive strength of the specimens increases even more. The best results are obtained when melamine-based superplasticizer is used. The compressive strength of these BM specimens after 7 days compared to the control sample C0 after 7 days hardening increased by 23% and after 28 days – by 27%. Similar tendencies have been found in other authors’ works [12]. However, after the addition of a different type superplasticizer (BH), the strength may be reduced by up to ~2%. It should be noted that this chemical admixture is used to improve the frost and water resistances of mixtures.

In the literature, the increase in compressive strength by using the NS additive is justified by its high pozzolanicity, bonding of free calcium hydroxide and water, as well as the formation of a denser structure. In order to determine the effect of our used NS on cement hydration processes, exothermic curves (figure 3) of the most characteristic batches are given and the highest reached temperature and time to reach it are presented in Table 5. Table 5 and figure 3 show that NS accelerates cement binding and raises exothermic temperature. Stronger effects are captured with superplasticizers.

| Mark  | C0 | A2  | A02 | B2  | BH  | BM  | BP  |
|-------|----|-----|-----|-----|-----|-----|-----|
| Duration, h | 10.97 | 9.8 | 10.58 | 10.72 | 8.75 | 9.35 | 8.20 |
| Max temperature, ºC | 77.8 | 84.1 | 80.1 | 79.7 | 84.8 | 87.5 | 88.3 |

The most obvious acceleration of cement binding (2.77 h) is observed when polycarboxylate-based superplasticizer is used, in these specimens obtained the highest exothermic temperature (88.3 ºC).
Similar exothermic temperatures have been determined using melamine-based superplasticizer. In this case, cement binding was accelerated by 1.62 h. When comparing the batches of A02 and B2, which used an analogous amount of 0.02% NS, only the characteristics of it were different but the obtained results were similar. The difference in time to reach the maximum temperature is 1.3%, and the maximum difference in temperature is only 0.5%. After adding 0.2% NS, the process began to run faster. Hence, the greater impact on hydration of cement had the content of NS and the composition of the superplasticizer. Literature [31] states that after cement hydration begins, hydrate products diffuse and envelop nanoparticles as kernels, which can promote the cement hydration and make the cement matrix more homogeneous and compact.

![Exothermic curves of characteristic batches.](image1)

**Figure 3.** Exothermic curves of characteristic batches.

Figure 4 shows microstructure images of C0 and A2 batch samples after 7 days hardening. It can be observed that the structure of the C0 samples without NS is more porous, with more voids in which the ettringite crystals grow. The structure of samples with NS is denser, less ettringite can be seen while CSH dominates. Therefore, the changes in structure have determined the density and compressive strength.

The results of XRD analysis of the most characteristic specimens are presented in Table 6 and figure 5. Analysis of XRD results by peak intensity shows that NS accelerates CSH formation. It has been found that the use of NS reduces the amount of unreacted minerals alite and belite, reduces the amount of ettringite and increases the amount of CSH and CASH. Likewise, a lower amount of portlandite was obtained from the samples with NS, which is explained by a quicker reaction of NS and calcium hydroxide and formation of CSH and CASH [1, 20]. Such tendencies are even more pronounced with the use of a superplasticizer.

![Images of microstructure, magnification 5000 times.](image2)

**Figure 4.** Images of microstructure, magnification 5000 times.
Table 6. The results of XRD (intensity) analysis of hydrates formed in compositions.

| Mark | Hardening | Ettringite | Calcite | Portlandite | Alite | Belite | C-S-H | CASH |
|------|-----------|------------|---------|-------------|-------|--------|-------|------|
| C0   | 7p        | 303        | 187     | 355         | 199   | 178    | 99    | 215  |
| A2   | 7p        | 286        | 228     | 320         | 195   | 177    | 106   | 214  |
| BM   | 7p        | 287        | 172     | 264         | 182   | 168    | 108   | 226  |

Figure 5. XRD curves of C0 and A2 batches (E – ettringite, S – CASH, P – portlandite, H – CSH, C – calcite, A – alite, B – belite).

Therefore, incorporation of NS in Portland cement materials affects strength development and hydration processes due to the following effects [32]: physical effect and pozzolanic activity. Physical effects are mainly attributed to the addition particles filling ability associated to their deposition in the intergranular voids between cement particles, which leads to a denser cement matrix and, therefore, to the mechanical properties improvement. Pozzolanic effect also promotes an increase in the mechanical properties related to the occurrence of the pozzolanic reaction that forms additional strength-providing reaction products i.e., C-S-H and C-A-H [33]. Cement hydration process and physical-mechanical properties highly depends on the type and amount of superplasticizer used. Superplasticizers bind with hydration products crystals and stop or delay the growth of new crystals over the old ones, especially in the initial hydration period. Melamine based plasticizers often retard cement binding, whereas synthetic polycarboxylate resin-based superplasticizers may accelerate hydration. Such different effect of superplasticizers is explained by their action mechanism: polycarboxylate resin-based superplasticizers act under the mechanism of electrostatic and dispersion forces. The dispersive effect of this additive is caused not only by electrostatic repulsion of particles, as it is in the case of melamine superplasticizer, but first of all by spatial repulsion related with long side chains of the ether [34-35].

4. Conclusions
The effect of NS amount on the cement properties was greater than that of NS characteristics. In order to select the minimum effective amount of NS, physical-mechanical properties and best results were obtained using 0.02% NS by cement weight. Then, the maximum density, UPV and compressive strength are obtained. An even greater effect is achieved through the use of superplasticizers. The maximum compressive strength was determined for specimens with 0.02% NS where melamine-based superplasticizer was used. Then, the compression strength was increased by 27% compared to the control samples after 28 days hardening.
It was found that using the NS, the structure of the specimens is denser (macro pores are not visible) and the hydration process is approximately 1 h faster. The most obvious accelerating of cement
hydration (2.77 h) is observed when polycarboxylate-based superplasticizer is used; these specimens produced the highest exothermic temperature (88.3 °C). Hydration acceleration was also confirmed by XRD studies, which showed that in specimens with NS due to the intense Ca(OH)₂ and SiO₂ reaction, more CSH, CASH, less ettringite and portlandite are produced, lower levels of alite and belite are detected.

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