The Synergistic Effect of Secondary Raw Materials and Nano Additive on the Properties of Cement Matrix

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Abstract. The purpose of the research presented in this paper was to analyse the synergistic effect of nano SiO2 (NS), fluidized catalytic cracking catalyst waste (FCCCw) and calcinated at 700°C temperature paper sludge waste (PSw) on the properties the cement matrix. Nano materials are known to reduce voids between cement particles, accelerate cement hydration, and increase the strength of cement matrix. A certain amount of FCCCw and PSw in the cement mix also accelerates cement hydration and increase the compressive strength of the system, but it is important to analyse the synergistic effect of these materials on the properties of cement matrix. The results showed that both waste materials are active pozzolanic additives. The optimal quantities in terms of positive effect on the cement matrix are 10% of FCCCw and 2.5% of PSw. The paper presents the results of XRD analysis, density, ultrasonic pulse velocity and compressive strength tests with hardened cement paste. A 22% increase in compressive strength compared to the control specimen was observed in specimens where 10% of cement was replaced by FCCCw and where NS was additionally added. The replacement of cement by 2.5% of PSw increases the compressive strength about 7%. Moreover, the compressive strength of specimens containing 10% of FCCCw, 2.5% of PSw and NS increases even though the content of cement is reduced. Hardened cement paste specimens containing FCCCw, PSw, and NS have better density and ultrasonic pulse velocity values. XRD analysis showed that a combination of FCCCw, PSw, and NS added to the cement mix increases the amount of calcium hydrosilicates formed, reduces the amount of free portlandite and unreacted cement minerals (allite and belite).

1. Introduction
Pozzolanic additions are commonly used to improve the particle size distribution in cement-based materials resulting in lower water demand of average consistency cement paste, and for the pozzolanic reaction. The pozzolanic reaction converts portlandite produced during cement hydration to low-basic calcium hydroxysilicates, which have a positive effect on the microstructure and mechanical properties of cement-based materials [1-3].

Nano SiO2 (NS) is one of the most widely used pozzolanic additions in cement-based materials. NS added to the cement mix at 1%–2% increases the strength and densifies the microstructure of cement matrix. More CSH is produced due to high pozzolanic activity of SiO2 and thus mechanical characteristics of concrete are improved [4]. Accelerated cement hydration and subsequently a faster development of the early strength of concrete is a big advantage of NS [5]. Among the positive effects of NS on the microstructure of the cement matrix researchers have identified [6] a lower volume of cavities and a lower water absorption rate. SEM analysis revealed that the pozzolanic effect of NS on
the cement matrix depends on the content of this addition in the cement mix [7]. A too high amount of NS may significantly reduce the pH of the cement system, thus preventing the formation of protective passive layers around metal fibres or rebar and creating favourable conditions for corrosion. A lot of clinker fails to react in the cement paste with lower pH of and therefore the cement content in the mix must be increased.

Pulp and paper industry generates big amounts of waste, which is either incinerated at high energy costs or disposed in landfills. Recovery methods are usually expensive due to the large volumes of waste generated, the high moisture content of the waste and the changing waste composition depending on process conditions, while the environmental impact of recovery is still uncertain [8]. Researchers make attempts to activate paper sludge waste (PSw) at different temperatures to enhance its pozzolanic properties and to use it as an active mineral addition to replace a portion of cement in the mix [9]. The tests results described in a research paper [10] show that PSw obtains the best pozzolanic properties when calcinated at 700°C and maintained at this temperature for 2 hours. Researchers have established [11–12] that dried PSw will delay cement hydration, whereas burnt at 700°C and maintained at controlled temperature for 2 hours PSw will accelerate cement hydration when added to the cement mix at 5% by weight of cement.

Oil processing industry in Lithuania generates about 200 tons of fluidised catalytic cracking waste (FCCCw) per annum [13–14]. Researchers [15-16] found that FCCCw could be utilised in the manufacture of mortars, concretes and other cement-based materials. FCCCw was found [17-18] to have pozzolanic properties, and its pozzolanic activity depends on particle size and activation technique [19]. FCCCw increases the compressive strength, density and freeze-thaw resistance of the cement matrix by changing the structure of the matrix. FCCCw added at the rate of 5%–10% by weight of cement accelerates cement hydration [20]. Researchers [21–22] identified a 10%–26% increase in the compressive strength of hardened cement paste where 10%–15% of cement was replaced by FCCCw.

The properties of cement-based materials can be improved by adding different pozzolanic additions, such as NS, FCCCw, and calcined at 700°C paper sludge waste (PSw) generated by pulp and paper industry. FCCCw and PSw is industrial waste that can be utilised to replace a portion of cement in the cement matrix. The effect of each separate addition on the properties of cement-based materials is analysed in research papers. The aim of this paper is to analyse the synergistic effect of different wastes (FCCCw and PSw) combined with NS on physical and mechanical properties and phase composition of the cement matrix.

2. Materials and methods
Cement CEM I 42.5 R, which conforms to the requirements of EN 197-1 for pozzolanic activity and mortar tests, was used. The chemical composition of cement (weight, %) is as follows: 63.2 of CaO; 20.4 of SiO$_2$, 4.0 of Al$_2$O$_3$, 3.6 of Fe$_2$O$_3$, 2.4 of MgO, 0.9 of K$_2$O, 0.2 of Na$_2$O, 3.1 of SO$_3$, 0.05 of Cl; L.O.I is 2.15. Mineral composition of the cement used: C$_3$S – 56.6%, C$_2$S – 16.7%, C$_3$A – 9.0%, C$_4$AF – 10.6 % and 7.1 % of other substances (alkaline sulphates and CaO). Particle density is 3.1 g/cm$^3$, compressive strength after 28 days is 55 MPa, and the initial setting time is 180 minutes.

The pozzolanic activity was determined according ASTM C311 (less amounts were used in compliance with the standard), standard sand (EN 196) was used.

FCCCw used for the tests is production residue from AB Orlen Lietuva oil refinery (Lithuania). The chemical composition of FCCCw (weight, %) is as follows: 50.1 of SiO$_2$; 39.4 of Al$_2$O$_3$; 2.30 of SO$_3$; 1.30 of Fe$_2$O$_3$; 0.50 of CaO; 0.49 of MgO; 0.20 of Na$_2$O; 0.07 of K$_2$O; and 0.06 of Mn$_2$O$_3$. FCCCw particles are spherical, the average diameter is ~40 μm, particle density is 2.75 g/cm$^3$. The pozzolanic activity of FCCCw measured according to NF P18-513 Chapelle test is 1017 mg/g.

Distilled water boiled for 30 minutes was used for NF P18-513 Chapelle test. Drinking water was used to prepare the specimens.

Properties of NS: purity 99.8%, specific surface area 202 m$^2$/g, relative molecular weight 60.08 g/mol, pH (40 g/l) 4.0, relative density 2.2 g/cm$^3$, size 10–30 nm.
Dried PSw was burnt at 700 °C and maintained at controlled temperature for 2 hours. Afterwards it was ground and sieved through a 0.125 mm sieve. PSw was added to cement mixes in the form of dry powder.

XRD analysis revealed that calcinated at 700 °C PSw consists of calcite and calcium oxide.

Superplasticizer Melment F10 (SP) is free-flowing spray dried powder of a sulphonated polycondensation product based on melamine. The pH value of 20% solution is 9.41 at 20 °C temperature.

160×40×40 mm specimens were moulded from the materials mentioned above by replacing a portion of cement by FCCCw, PSw and NS. Particle size distribution of industrial waste aggregates is presented in Table 1.

| Table 1. Compositions of cement mixtures |
|----------------------------------------|
|                                        |
| **For pozzolanic activity**             |
| **Cement, g**                           |
| **Sand, g**                             |
| **W/B**                                 |
| **FCCCw, g**                            |
| **PSw, g**                              |
| **NS, g**                               |
| **SP, g**                               |
| **K**                                   |
| 900                                     |
| 2700                                    |
| 0.5                                     |
|                                           |
| **FCCCw5**                              |
| 855                                     |
| 2700                                    |
| 0.5                                     |
| 45.0                                    |
|                                           |
| **FCCCw10**                             |
| 810                                     |
| 2700                                    |
| 0.5                                     |
| 90.0                                    |
|                                           |
| **FCCCw15**                             |
| 765                                     |
| 2700                                    |
| 0.5                                     |
| 135                                     |
|                                           |
| **PSw2.5**                              |
| 877.5                                   |
| 2700                                    |
| 0.5                                     |
| –                                       |
| 22.5                                    |
|                                           |
| **PSw5**                                |
| 855                                     |
| 2700                                    |
| 0.5                                     |
| –                                       |
| 45.0                                    |
|                                           |
| **PSw10**                               |
| 810                                     |
| 2700                                    |
| 0.5                                     |
| –                                       |
| 90.0                                    |
|                                           |
| **For synergistic effect**              |
| **Kc**                                  |
| 3000                                    |
|                                           |
| **NS**                                  |
| 2999.4                                  |
|                                           |
| **FCCCw10c**                            |
| 2700                                    |
|                                           |
| **PSw2.5c**                             |
| 2925                                    |
|                                           |
| **NSP**                                 |
| 2999.4                                  |
|                                           |
| **FCCCw10NSPc**                         |
| 2699.4                                  |
|                                           |
| **FCCCw10NSPPSw2.5**                    |
| 2624.4                                  |
|                                           |

To prepare the mixtures nano SiO₂ was first dispersed for 15 minutes in 350 g of water using an ultrasonic dispersion device UZDN-2T at the frequency of 22 kHz with a power of 400 W. If the mixture is prepared with a superplasticizer, the superplasticizer is also poured into the prepared suspension. The mixing time in the mixer was 3 minutes; dimensions of specimens moulded were 160×40×40 mm.

X-ray diffraction (XRD) analysis of the phase composition of materials was carried out by means of diffractometer DRON-7. The parameters of the tests were as follows: voltage – 30 kV; current – 12 mA; the range of 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 density of the specimens was established according to EN 196. Ultrasonic pulse velocity was determined using the Pundit 7 device (frequency of converters is 54 kHz). The ultrasonic pulse velocity was calculated from the following equation (V, m/s):

\[ V = \frac{l}{\tau}; \tag{1} \]

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

The compressive strength of the specimens after curing in water for 7 and 28 days was measured by hydraulic press ALPHA3-3000 S according to EN 196. Pozzolanic activity index AI was calculated from the equation:

\[ AI = \frac{f_{c}}{f_{c}}; \tag{2} \]
where: $f_c$ is compressive strength of the control specimen, MPa; $f_c$ is compressive strength of the batch analysed, MPa.

3. Results
The pozzolanic activity results are presented in Table 2.

| Replacement of cement, % | Activity index after 7 days, % | Activity index after 28 days, % |
|-------------------------|-------------------------------|-------------------------------|
| 0.                      | –                             | –                             |
| 5 of FCCCw              | 0.996.                        | 1.003.                        |
| 10 of FCCCw             | 0.987.                        | 1.066.                        |
| 15 of FCCCw             | 0.852.                        | 0.992.                        |
| 2.5 of PSw              | 1.13.                         | 1.07.                         |
| 5 of PSw                | 1.04.                         | 1.01.                         |
| 10 of PSw               | 1.01.                         | 0.96.                         |

According to results the activity index of catalyst waste added to replace 5%–15% of cement in the standard cement mix changes from 0.85 (when 15% of waste was used) to 1.07 (when 10% of waste was used). Activity index for PSw changed from 0.96, when added at the rate of 10%, to 1.13, when added at the rate of 2.5%. The additive is regarded to be an active pozzolan when the pozzolanic activity index (AI) is higher than the amount of cement replaced. For example, the strength of a specimen where 10% of cement is replaced by a pozzolan should drop less than 10%. In our tests in the specimen where 10% of cement was replaced by FCCCw the pozzolanic activity index AI was 0.987 after 7 days of curing, whereas after 28 days of curing the AI was 1.066 (106.6%). It means that the strength is very similar to the strength of control specimen even at the reduced amount of cement in the mix. Therefore, FCCCw and PSw are active pozzolanic additions. The best strength results were found in the specimens where cement was replaced by 10% of FCCCw and 2.5% of PSw. The effect of the determined optimum amount of waste on the physical and mechanical properties of the cement matrix was analysed further.

Figure 1 shows the relationship of the cement matrix density and the amount of NS. The lowest density was determined in control specimens and the specimens containing 10% of FCCCw. The highest density value was recorded in specimens modified only with NS and superplasticiser together with of FCCCw and PSw additions. This increase in density can be explained by NS filling the gaps between cement and other pozzolanic additions and the reduction of various cavities. Besides, the addition of pozzolans increases the amount of denser minerals, which subsequently increases the density of the entire system. When FCCCw addition is used alone, the density of the cement matrix may drop slightly below the density of the control specimen due to the lower density of FCCCw particles (2.75 g/cm$^3$) compared to the density of cement particles (3.1 g/cm$^3$). Ultrasonic pulse velocity values (Fig. 2.) confirm the trends of density variation in relation to the content of waste materials added.
Figure 1. The effect of addition on the density of the cement matrix

Figure 2. The effect of additions on the ultrasonic pulse velocity in the cement matrix

Ultrasonic pulse velocity values showed that cement-based specimens modified by an integrated addition of FCCCw, PSw and NS had the densest structure. NS densifies the structure by filling in the gaps between particles. Being a hollow addition FCCCw can absorb a certain amount of water and gradually release it later, thus accelerating the hydration processes. PSw is also a pozzolanic addition. It reduces the content and negative effect of portlandite, bigger-size crystals of which may cause cracking during cement hydration, and activates the formation of CSH, which increases the density and strength of hardened cement paste.

The compressive strength value of hardened cement paste after 7 and 28 days of curing are illustrated in Fig. 3. The highest compressive strength was found in specimens containing the integrated addition of FCCCw, PSw and NS. The 28th day strength of these specimens was ~24% higher than the strength of the control specimen. Similar strength values were obtained in specimens modified with FCCCw and NS and specimens modified with NS together with a superplasticizer.
Figure 3. The effect of additions on the compressive strength of cement matrix

To further the transition to circular economy and to mitigate the climate change it is important to reduce the amount of cement used by utilising industrial waste in the manufacture of cement-based materials. The replacement of cement by pozzolanic additions increases the compressive strength of hardened cement paste because pozzolans improve the particle size distribution, increase the relative density of the cement mix and thus reduce water demand of normal consistency cement paste. Active mineral additions, through the pozzolanic reaction, convert portlandite produced during cement hydration into low-basic calcium hydrosilicates, which have a positive effect on the microstructure and mechanical properties of concrete (Fig. 4.)

Figure 4. XRD analysis results (E – ettringite, P – portlandite, A – alite, B – belite, H – calcium silicate hydrate, Ch – calcium aluminium silicate hydrate)

X-ray analysis revealed the formation of analogous minerals in all batches after 28 days of curing: portlandite, ettringite, calcite, alite, belite, calcium silicate hydrate, calcium aluminium silicate hydrate. The peak intensity of the main minerals shows that the smallest amounts of portlandite, ettringite and calcite formed in specimens modified with integrated additions (NS+FCCCw and
NS+FCCCw+PSw). These specimens also demonstrated the lowest intensity of unreacted cement minerals alite and belite and the highest intensities of calcium hydroxides. The highest intensities of CSH and CASH were found in specimens modified with integrated addition. XRD analysis confirmed that NS, FCCCw and PSw are pozzolanic additions that accelerate cement hydration.

Conclusions
FCCCw and PSw are active pozzolanic additions. The optimum FCCCw content according to pozzolanic activity index is 10% by weight of cement and the optimum PSw content is 2.5 wt%.

The combination of FCCCw, PSw and NS additions produces the highest 28th day compressive strength of 98.5 MPa, the highest ultrasonic pulse velocity and the highest density. The compressive strength of modified specimens is ~24% higher than the strength of the control specimen.

The lowest portlandite and ettringite contents were observed in specimens modified by integrated additions (NS+FCCCw and NS+FCCCw+PSw). These specimens also had the lowest amount of unreacted alite and belite and the highest amount of calcium hydroxides.

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