THE INFLUENCE OF PRIMARY PAPER SLUDGE ON CONCRETE PROPERTIES

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The possibilities of primary paper sludge (PS) only dried at 75 °C from the paper production industry used in concrete composition are discussed. For pursuing the set object, the concrete mixes were chosen where part of the cement content was, in one case, replaced by the PS waste and, in the other case, part of the sand content was replaced by the PS waste. It was found that if 2.5 % of the sand is replaced by the PS waste, the compressive strength of the concrete increases by about 15 %, its density decreases by 4 % and the water absorption remains analogous to the reference samples. SEM analysis showed that when the content of the PS waste in the mix does not exceed 7.5 %, it adhered well to the cement stone and crystals grew on it. The X-ray images showed that analogous minerals were formed in the tested concrete samples and only their contents were different.

INTRODUCTION

Managing waste is a major challenge for modern society. Many scientists have concentrated on the recycling of waste in civil engineering materials [1]. Paper production waste is classified as non-hazardous waste according to the European List of Waste [2]. Because paper production is well-developed in the wide world, huge quantities of the said waste are formed. For example, 11 million tonnes of waste are produced yearly by the European pulp and paper industry, 70 % of which originates from the production of deinked recycled paper; in Japan 5.1 million tonnes PS waste are formed per year [3-5]. Because of this, it is very important to solve this problem and to strive to use paper production waste as a secondary raw material. Scientists are involved in examining the opportunities of using the said waste as an additive to various materials; there are abundant publications on the investigation of the impact of this waste on the properties of heat insulating materials and structural materials in the course of their production.

The PS waste composition consists of organic (cellulose fibres, organic binder) and inorganic materials (calcite, kaolinite, talc, chlorite, mica) and it is high alcalinity material [6-9]. In literature, cellulose and other materials of similar composition are indicated to be cement hardening retarders [10-11], whereas calcite may accelerate the hydration process and affect the formation of hydrates [12-13].

A majority of scientists are involved in the investigation of the impact that paper sludge ash has on the properties of cement mortar and concrete, but it requires a lot of energy. It was found that ash of superhydrophobic paper production waste (12 %) considerably reduces the water absorption of concrete and reduces its sorptivity by about 80 %. When the content of the waste in the mix is increased, the electric conductivity of the concrete decreases. If 8 % of the cement content is replaced by PS waste, the compressive strength of the samples increases considerably; on further increasing the waste content in the mix, the density and the compressive strength begin to decrease [14].

In the work [15], it was found that PS waste acquired its best pozzolanic properties after its heat-treatment at the temperature of 700 °C for 2 h. Then, if 10 % of the cement content is replaced by the said waste in the cement mixes, the strength of the sample increases by several percent. In their review of the scientific literature on this subject in 2015, Frias et al. [16] showed that other scientists proposed heat-treatment of the said waste at the temperature of 700 - 800 °C for ensuring its effective pozzolanic properties also [17]. In the review [16], the scientists show that after processing the paper production waste at the temperature of 650 - 850 °C, the following key oxides are presented in its chemical composition: SiO₂ – from 13.9 to 30.2 %; Al₂O₃ – from 8.3 to 18 %; CaO – from 31.4 to 47.1 %; MgO – from 0.5 to 4.0 % [18-23]. The key oxide remains CaO that while reacting with water at a temperature over 700 °C transforms into portlandite (Ca(OH)₂).

Other scientists [24] proposed to use up to 10 % of the paper production waste in low density cement mixes; however, it was established that the said waste reduced the strength of the samples. The impact of paper production waste on the properties of very light cement bricks was investigated in the work [25-26], it was proposed to use the obtained products for internal walls.
The investigation described by [27-28] shows that paper production waste reduces the compressive strength of normal concrete. However, in the work [29], it is pointed out that paper production waste reduced the strength and durability of the concrete, if the above-mentioned waste is used in the mix only; if fly ash is used in addition, the indicators of concrete durability are improved.

The opportunities of using paper production waste not processed at a high temperature were analysed in the paper [30]. In the said work, the scientists show that paper production waste (up to 20 %) may be used in wood cement boards, if CaCl₂ (5 %) is used in the mix. Because the waste under analysis includes cellulose that has a penchant for retarding the hydration processes, it is useful to neutralise it by adding a concrete hardening accelerator.

The authors [31] analysed the possibilities to use a paper sludge layer as a low permeability barrier on waste landfills. The results of the preliminary geotechnical studies of the PS waste indicate the low strength properties, high compressibility and a low coefficient of permeability. They improved the strength of the composite by using cement or others pozzolanic materials (fly ash, bentonite).

Our previous studies [32] with non-burnt PS waste have shown that by increasing the amount of PS waste in cement mortars, the hydration process is slowed down and the hydration temperature decreases. 20 % PS waste significantly reduces mortar flowability and cone penetration depth. PS waste can be used for mortar mixtures in small amounts – up to 5 %, thus, reducing the amount of cement or sand. In this case, the strength of the mortar changes slightly.

The aim of this work is to establish the opportunities of using paper production waste only dried at 75 °C in concrete mixes, when the 2/4 fraction is used as a fine aggregate (one case) or when the fine fraction 0/0.5 is used to replace a part of cement (the other case). A low temperature has been chosen upon in order to strive for the cost-effective utilisation of large quantities of the waste generated in cement mixtures, because the problems of PS waste utilisation are not resolved and thermal treatment of the waste at a high temperature aggravates its secondary use.

### EXPERIMENTAL

#### Methodology and Materials

For the formation of the samples, the following raw materials were used: Portland cement CEM I 42.5 R that conforms to the provisions of the EN 197-1 standard. The mineral composition of the cement: C₃S – 56.6 %, C₂S – 16.7 %, C₃A – 9.0 %, C₄AF – 10.6 % and 7.1 % of other components (alkaline sulphates and CaO). Its principal characteristics are provided in Table 1 below.

Natural sand that conforms to the provisions of the EN 12620 standard with the maximum particle size of 4 mm (particle density 2630 kg·m⁻³, water absorption 0.62 %, bulk density 1660 kg·m⁻³), a coarse aggregate that conforms to the provisions of the EN 12620 standard with a fraction of 4/16 (particle density 2670 kg·m⁻³, water absorption 1.3 %, bulk density 1600 kg·m⁻³), the super-plasticiser Dynamon Xtend, the accelerator Mapefast SA (the characteristics obtained from the manufacturer are provided in Table 2 below) and the paper production waste that will be marked as PS.

The PS waste under discussion is formed in paper production after deinking. The PS waste bulk density of the fraction 0/0.5 is 420 kg·m⁻³ and of the fraction 2/4 is 390 kg·m⁻³. The image of the microstructure of the PS waste is presented in Figure 1. In the course of the X-ray diffraction analysis, calcite and cellulose were found to be the key minerals in the PS waste. It can be seen from

![Figure 1. The image of the PS waste microstructure (C – calcite, Ce – cellulose).](image)

<table>
<thead>
<tr>
<th>Particle density (g·cm⁻³)</th>
<th>Bulk density (g·cm⁻³)</th>
<th>Fineness (cm²·g⁻¹)</th>
<th>Compressive strength after 2 days (MPa)</th>
<th>Compressive strength after 28 days (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>1.1</td>
<td>3700</td>
<td>22</td>
<td>55</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Title</th>
<th>Type</th>
<th>Viscosity (mPaS)</th>
<th>Density (kg·m⁻³)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dynamon Xtend</td>
<td>Liquid</td>
<td>&lt; 30</td>
<td>1060 ± 20</td>
<td>6.5 ± 1</td>
</tr>
<tr>
<td>Mapefast SA</td>
<td>Liquid</td>
<td>&lt; 15</td>
<td>1480 ± 30</td>
<td>6 ± 1</td>
</tr>
</tbody>
</table>

Table 1. Cement CEM I 42.5 R characteristics.

Table 2. Properties of the chemical admixes.
the presented image of the microstructure (Figure 1) that the dried PS waste consists of cellulose fibres (with an average width of 15 - 20 µm and length up to 150 µm) and calcite aggregates.

According to the methodology as per the literature [33], it was found that the PS of the fraction 0/0.5 was an active additive. After seven days of hardening together with lime in air and three days of soaking in water, the samples remained hardened.

Prior to adding to the mixes, the PS waste was dried for 48 h at the temperature of 75 °C upon using a laboratory dryer, then crushed by an alligator crusher and sifted through a sieve of relevant fineness. The waste was added to the mixes in the form of a dry powder.

On formation of the mix, the dry raw materials were, first of all, mixed for 1 minute in a mixer. Then the needed quantity of the hardening accelerator was poured into the weighed water and the obtained mix was poured into the mixer. Later the superplasticiser was poured and everything was mixed once more for 2 minutes. When the concrete mix is ready, its slump and density are established.

The concrete samples (with dimensions 100 × 100 × 100 mm) were made and the hardening (to determine strength) was performed according to standard 12390-2. The compressive strength of the concrete samples was determined following the standard EN 12390-3, while the density of the hardened concrete – according to EN 12390-7. The water absorption and the capillary mass flow rate of the concrete samples were established according to the methodology described in the literature [34].

To analyse the microstructure, a scanning electron microscope JEOL JSM-7600F was used: its resolution was 1.5 nm, amplification – from 25 to 1,000,000 times; during the tests, the voltage of 10.0 kV was applied; the surface of the tested samples was covered by gold.

The X-ray diffraction analysis was carried out by the diffractometer DRON-7. The X-ray patterns were encoded according to the reference tables provided in literature, where the values of distance d between the planes and the relative intensity I were assessed. The impact of the PS waste on the cement setting time was established according to standard EN 196-3.

The compositions of the concrete were chosen by replacing a part of the cement content by the waste of the fraction 0/0.5 (the first case is marked as CC) or by replacing a part of the sand content by the waste of the coarse fraction 2/4 (the second case is marked as CS). On choosing the compositions, the results of the earlier research work performed by other scientists, i.e., that the maximum content of the PS waste cannot exceed 20 % and the best effect is usually ensured when the content of the waste is up to 10 %, were taken into account. The compositions of the concrete mixes are provided in Table 3 below.

The water/binding materials ratio for all the mixes was 0.5. In the CS4 mix, the contents of the cement and water were increased gradually to ensure the easier formation of the mix because the paper production waste absorbs water rapidly and worsens the workability of the concrete mix.

The data grouping and preparation for the regression analysis was carried out with Microsoft Excel software. A statistical analysis of the researched indicators was carried out as per the literature [35]. This function was selected to determine the mathematical relationship, which describes the data distribution the most precisely, as well as assessing whether the multi-unit correlation and determination ratios are close to one.

**RESULTS AND DISCUSSION**

It was found that if the PS waste content in the cement mix is increased, the setting slows down (Figure 2). 15 - 20 % waste content elongates the initial setting time of cement about 3 times and the final setting time – from about 3 to 5 times. For this reason, in the investigation of the concrete the said values were
not assessed anymore because of the slow setting and poor workability; for mixes with a lower content, an accelerator of setting was used. In order to establish the dependence of the setting times on the content of the waste in the mix, empirical equations were formed; in the said equation, the correlation coefficients were close to 1 and the determination coefficients $R^2 > 0.85$. The signs before the variables in the linear equations show that a higher content of waste causes a longer setting time. It happens because of the weak pozzolanic properties of the waste that per the literature [15] may be optimised by heat-treatment at the temperature of 700 °C.

The density of the hardened concrete is shown in Table 4. When the content of the PS waste in the concrete mix is increased, the density of the concrete decreases. It could be explained that the bulk density of the PS waste is more less than sand or cement. In addition, it was observed that in the case of the higher content of the PS waste in the mixes, the sizes of the pores and their number in the concrete increase. If part of the sand content in the mix is replaced by the PS waste, the decrease in the density becomes more intensive because of the higher content of the waste (g). The calculations showed that when 10 % of sand content was replaced by PS waste, the density of the concrete samples decreased approximately by 10 %; when 5 % of the sand content was replaced by the PS waste – approximately by 5 %. When 10 % of the cement content was replaced by the PS waste, the density of the hardened concrete decreased approximately by 5 % and when 5 % of the cement content was replaced by PS waste, – by approximately 2 %.

The water absorption tests (Figures 3, 4) showed that the PS waste distinguishes itself for good water absorption and increasing its content in the mix causes higher values of water absorption of the concrete. When part of the cement content is replaced by the PS waste, the water absorption increases uniformly (Figure 3). When part of the sand content is replaced by the PS waste, the changes in the water absorption become step-like. For example, when 2.5 % of the sand content is replaced by the PS waste, the water absorption remains almost the same as that of the reference samples, although the density decreases by about 4 %; in such a case, the water absorption is 3 % after 72 h. In the samples where 5 and 7.5 % of the sand content was replaced by the PS waste, the water absorption varies in a very similar way and

Table 4. Results of the density.

<table>
<thead>
<tr>
<th>Batch</th>
<th>K</th>
<th>CC1</th>
<th>CC2</th>
<th>CC3</th>
<th>CS1</th>
<th>CS2</th>
<th>CS3</th>
<th>CS4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (kg·m⁻³)</td>
<td>2420</td>
<td>2400</td>
<td>2380</td>
<td>2350</td>
<td>2380</td>
<td>2330</td>
<td>2240</td>
<td>2180</td>
</tr>
</tbody>
</table>
becomes equal at approximately 4.1% after 72 h. The largest jump took place when 10% of the sand content in the mix was replaced – in such a case, the water absorption was about 6% after 72 h.

It may be seen from Figures 5 and 6 that an increase in the PS waste causes an increase in the capillary mass flow rate. When 5% of the cement content is replaced by the PS waste, the capillary mass flow rate remains analogous to the reference sample; if the waste content is increased to 15%, the capillary mass flow rate increases approximately 3 times after 60 and 120 minutes. When 2.5 and 5% of the sand content is replaced by the PS waste, the capillary mass flow rate increases approximately 2 times after 60 and 120 minutes; and when 10% of the sand content is replaced by the waste, the capillary mass flow rate increases about 7 times. So, the higher the PS waste content causes the formation of larger quantities of open capillaries. In order to establish the changes to the concrete structure on using the PS waste, a SEM analysis was performed (Figure 7).

It can be seen from Figure 7 that the structures of the concrete provided in the images a), b) and d) are similar. Pores of similar size predominate, the same minerals are identified. In the cavities, needle-shaped ettringite, calcium hydroxides, hexagonal plates of portlandite and calcite are visible. The PS waste is presented as sticks and splints. When the PS waste content does

![Image](image_url)

Figure 5. The impact of the PS waste used to replace part of the cement content on the capillary mass flow rate of the concrete.

![Image](image_url)

Figure 6. The impact of the PS waste used to replace part of the sand content on the capillary mass flow rate of the concrete.

![Image](image_url)

Figure 7. The images of the concrete microstructure: a) concrete without the waste, b) concrete where 5% of the cement content is replaced by the waste, c) concrete where 15% of the cement content is replaced by the waste (C – calcite, PS – PS waste, P – portlandite, E – ettringite, CSH – calcium hydroxides). (Continue on next page)
not exceed 5 %, it is covered with crystals and may be considered one of centres of the crystallisation, because of the good water absorption possibilities. However, when the waste content is increased (c, e), the PS waste is not completely covered by crystals and separate splints of the waste become visible. In such a case, the porosity of the samples and the sizes of the pores increase. When 15 % of the cement content is replaced by the PS waste, the samples are fragile and calcium hydrosilicates are hard to identify. The adhesion between the waste and the cement stone is good, if the waste content is up to 7.5 %; in such a case, crystals grow on the PS waste.

The key minerals formed in the structure were established upon applying the X-ray analysis as well. The results are provided in Figure 8 and Table 5 below.

The X-ray analysis confirm that the key minerals formed in the structure include portlandite (Ca(OH)$_2$), quartz (SiO$_2$), ettringite (3CaO·Al$_2$O$_3$·3CaSO$_4$·31H$_2$O), calcite (CaCO$_3$). In addition, alite (3CaO·SiO$_2$), belite (2CaO·SiO$_2$) and dolomite (CaMg(CO$_3$)$_2$) are identified. In the samples of all the compositions, the same minerals were formed; however, the intensity attests to the different contents of them. When the waste was used, particularly low contents of ettringite were obtained. In the concrete with the PS waste, higher calcite contents are visible, as compared to the reference sample. Some R & D works prove the improvement of the strength of the concrete, if CaCO$_3$ is added to the concrete mixes. For example, scientists [36] found that if 5 % CaCO$_3$ is added to the concrete mixes, the strength of the concrete upon certain conditions increases by about 20 %. Other authors found that because of the calcium instability in the wet air at R_h > 50 %, healing of the concrete cracks takes place [37] that may cause a positive impact on the concrete structures. It is supposed that the said effect would be more useful in dry air conditions [38]. In the samples with the PS waste, it decreases the contents of portlandite and CSH and increases the content of alite. In the samples that replaced the cement by the PS waste, these trends are much higher. By reducing the amount of the cement and adding the PS waste in the mixtures, less CSH is formed and the process of cement hydration slows down.

In Figures 9 and 10, the dependence of the compressive strength of the concrete on the waste content in it is shown.

When part of the cement content is replaced by the waste, the linear decrease in the strength of the concrete takes place. The dependences were described
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by the equations where the correlation coefficients and the determination coefficients were very close to one, so it is possible to forecast the compressive strength of the concrete on the basis of the said equations with a low error. After both 28 days and 130 days, the trend of the decrease in the compressive strength of the concrete remains analogous. The minus sign before the first multiplier shows that if the waste content is increased, the compressive strength of the concrete in this case will decrease. It is caused by the negative structural changes, higher water demand and poorer adhesion of the PS waste with the cement matrix. When 5 % of the cement content is replaced by the PS waste, the compressive strength decreases by 15 % after 28 days and by approximately 10 % after 130 days. When 15 % of the cement content is replaced by the PS waste, the compressive strength decreases by 37 % after 28 days and by approximately 34 % after 130 days. After a longer period, the decrease in the compressive strength is less. It may be partially explained by the retard of the hydration process caused by the PS waste.

Another situation is observed, when part of the sand content is replaced by the PS waste. If a small amount (2.5 %) of the waste is added, the compressive strength increases by about 15 %. On further increasing the amount of the PS waste, the compressive strength begins to decrease; when 10 % of sand content is replaced by the PS waste, the compressive strength decreased by about 40 %. The closest mathematical model where the correlation coefficients and the determination coefficients are closest to one and the minimum error is obtained is a polynomial of the third degree. In this case, the increase in the compressive strength was caused by the addition of the small amount of the substance having some pozzolanic properties instead of the usual fine aggregate. In addition, in this case (Figure 7d), a dense and defect-free structure of the cement stone where the waste is covered by crystals and is well adhered to the cement matrix was obtained. When the waste content is increased (Figure 7e), the pores increase and more cavities & cracks appear as well; in such a case, the poorer adhesion of the PS waste to the cement matrix is observed.

On assessment of the obtained results, it was established that the best version would be ensured when 2.5 % of the fine aggregate (sand) is replaced by the PS waste: in such a case, the strength of the concrete increases, the density is reduced and the water absorption remains similar to the absorption of the reference sample.

**CONCLUSIONS**

The dried PS waste at 75 °C is a porous substance where the key components are cellulose and calcite. PS waste retards the initial setting time and the final setting time of the cement stone, reduces the slump of the concrete and the density of the mix. Because the PS waste slows down the hydration process, a setting accelerator or a superplasticiser having such properties should be added to the mixes.

The SEM analysis showed that when the content of the PS waste in the mix does not exceed 7.5 %, it adhered well to the cement stone and crystals grew on it. If the content of the PS waste is increased, a scattering of splints is observed, i.e., some splints do not appear to be adhered firmly to the cement matrix. The X-ray analysis showed that analogous minerals were formed in the tested concrete samples and only their contents were different.
The analysis of the results of the investigation enabled one to establish that application of the dried PS waste at 75 °C in the concrete production is useful, when 2.5 % of the natural aggregate (sand) is replaced by the said waste. In such a case, the density of the concrete decreases by approximately 4 %, as compared to the reference sample, but the compressive strength increases by about 15 % and the water absorption remains analogous.

REFERENCES

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