Impact of Differently Prepared Paper Production Waste Sludge (PSw) on Cement Hydration and Physical-Mechanical Properties

Jurgita Malaiskiene¹, Vilma Baneviciene¹, Renata Boris¹, Olga Kizinievic¹
¹Laboratory of Composite Materials, Vilnius Gediminas technical university, Linkmenų str. 28, Vilnius, Lithuania

Abstract. After analysis of calorimetric tests results of the cement mixtures with PSw prepared at different temperatures and SEM, XRD, physical-mechanical properties results of cement stone hardened for 7 and 28 days, it is determined that PSw can be utilized/used for the preparation of cement mixtures by adding up to 5%. Depending on the environmental working conditions, the preparation of PSw can be selected. To slow down cement hydration processes, it is useful to use only dried PSw, which slows down the hydration of the cement due to the high content of cellulose contained in PSw. To accelerate cement hydration, it is expedient to use PSw which is burned at 700°C. Dried PSw performs an extended induction hydration period and significantly delays the second heat release time. After the addition of 5% dried PSw, the phase III effect time compared to the control sample is 1.8 h, and after 10% addition, it is extended to 4.4 h. After the addition of 5% burnt PSw, the phase III effect time compared to the control sample is hastened to 1.9 h, after inserting 10% – to 2.4 h. The use of PSw saves the environment, reduces the amount of cement in the mixture and improves the properties of cement materials. Using 5% PSw burned at 700°C instead of cement increases the compressive strength of the specimens, and the density as well as ultrasound pulse velocity values are slightly changed compared to the control sample. It is determined that burnt PSw significantly changes mineral composition and structure. It is found that the microstructure of samples without PSw and samples with dried 5% PSw is similar, crystals formed are visible. With a higher (10%) amount of dried PSw, the microstructure of the cement stone differs significantly from the control samples. Larger voids with plenty of ettringite are also visible, as well as higher levels of calcite. The microstructure of specimens with burnt PSw is significantly denser. XRD studies show that with a higher amount of PSw burned at 75°C, the main peak intensities of crystallohydrates ettringite and portlandite are lower, while the peak intensities of calcite are higher compared to samples without PSw. By increasing the amount of dried PSw in mixtures and reducing the amount of cement, the peak intensities corresponding to CSH and CASH are lower compared to those of the control samples. Using burnt PSw also reduces the peak intensities of ettringite, portlandite, CSH and belite, but significantly increases peak intensities of calcite and CASH.

1. Introduction

Paper production waste sludge (PSw) is a world-wide problem in most countries, for example, 11 million tonnes of such waste are already produced in Europe every year [1], while Korea reaches 26 million tonnes [2–3]. Paper production intensifies and the amount of waste generated increases. It is established
that waste from paper production is classified as non-hazardous waste [4-6]. Another important ecological problem is the reduction of CO₂ emission in cement production. Approximately 1 tonne of CO₂ is generated during production of 1 tonne of Portland cement [7–8]. The composition of PSw varies from one production plant to another depending on the raw materials and the production technology used, but all of the PSw contains a large amount of Ca, Si, Al, Mg, K and other elements [8]. It also contains ~30% organic matter that slows down cement hydration processes. As a result, scientists usually test PSw ash or in another way activated PSw. Authors [9-10] activated PSw by milling it with 4% stearic acid and obtained a hydrophobic powder. 12% of it to a minimum reduced the water permeability of concrete [10].

The literature describes the properties of PSw burned at different temperatures (500–900°C), as well as changes in its structure and mineralogical composition, and describes the effects on cement and ceramics properties. The work [11] found that PSw acquires the best pozzolanic properties when it is burned at 700°C for 2h. Then, after replacing 10% of cement in cementitious mixtures, the strength of the samples increases by a few percent. Research of Frias et al. [12] has shown that other scientists suggest burning paper waste at 700–800°C to provide efficient pozzolanic properties [13]. The investigation described in [14-15] shows that paper production waste reduces the compressive strength of normal concrete. However, in the work [16], it is pointed out that paper production waste reduces the strength and durability of concrete, if only the above-mentioned waste is used in the mixture; if fly ash is used in addition, the indicators of concrete durability are improved.

Our previous studies [6] with non-burnt PSw have shown that by increasing the amount of PSw in cement mortars, the hydration process is slowed down and the hydration temperature decreases. 20% PSw significantly reduces mortar flowability and cone penetration depth. PSw 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 purpose of this work is to investigate and compare the properties of PSw dried at 75°C and burnt at 700°C and to determine their effect on hydration and physical-mechanical properties of cement.

2. Materials and methods
In the research, cement CEM I 42.5 R was used; its chemical composition is presented in Table 1.

| 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 |

Particle density 3.1 g/cm³, bulk density 1.1 g/cm³, start of hardening process 160 min, end of hardening process, 215 min. Mineral composition of the cement: C₃S – 62.5 %, C₂S – 16.9 %, C₃A – 7.1 %, C₄AF – 11.5 % and 2 % others (alkaline sulphates and CaO).

The chemical composition of dried PSw is provided in Table 2.

| Table 2. Chemical composition of PSw |
| C_O(org) | CaO | SiO₂ | Al₂O₃ | Fe₂O₃ | MgO | TiO₂ | SO₃ | Cl | Na₂O | Others* |
|---------|-----|------|-------|-------|-----|------|-----|----|------|--------|
| 34.08   | 58.2 | 3.48 | 2.36  | 0.52  | 0.64 | 0.10 | 0.18 | 0.06 | 0.09 | 0.28   |

Others: slight amounts of P₂O₅, K₂O, MnO, NiO, CuO, ZnO, SrO, ZrO₂

PSw was dried for 48 h at 75°C in laboratory drier SNOL, then crumbled up by a jaw crusher and passed through a 0.5 mm-sized sieve. The dried PSw was burned at 700°C, maintaining this temperature for 2 h, crushed with a blender and sieved through a 0.125 mm-sized sieve. To the mixtures, the PSw was added in the form of dry powder.

The XRD analysis of differently prepared PSw is presented in Fig. 1 and the image of its microstructure – in Fig. 2. It can be seen from the XRD analysis of PSw that the main ingredients of it...
include calcite, chlorite and cellulose. The same is obtained by SEM analysis of dried PSw. It can be seen from Fig. 2 that PSw is a mix of agglutinated filaments and particles. Cellulose is a fibre with length up to 100 µm and the width of 20 µm. Calcite particles are of an irregular shape and are agglutinated to larger particle or cellulose fibre. CaO is additionally identified in PSw burned at 700ºC. The main difference between dried and burnt PSw is that CaO already exists and the organic part is no longer present.

![XRD analysis of the paper sludge: C – calcite, Ce – cellulose, L – CaO](image)

**Figure 1.** XRD analysis of the paper sludge: C – calcite, Ce – cellulose, L – CaO

The main difference between the microstructure in the dried and burnt PSw is that the cellulose fibers are no longer visible, the material is crumbly, and more pores are observed (Fig. 2). Thermal analysis (Fig. 3) of PSw shows two main endo-effects which arise from burning it at 1000ºC temperature. At ~352°C temperature, crystal hydrates disintegrate, connected water liberate and specimen loses 16% of its mass. At ~765 oC temperature, calcium carbonate decomposes to CaO and CO₂. It is determined that burnt PSw has significantly changed its mineral composition and structure. The specimen loses approx. 50% of its mass when it is burned up to 760ºC temperature. Unburnt PSw has ~34% of cellulose and the rest of it is calcite.

160×40×40 mm-sized specimens were formed from the described raw materials by replacing part of the cement with PSw. Cement was replaced with 5% and 10% of dried PSw (PSwD5 and PSwD10) while burnt PSw replaced 2.5%, 5%, 10% of cement (PSwB2.5, PSwB5, PSwB10).

The calorimetric tests of kinetics of cement paste hydration were performed upon applying differential conduction microcalorimeter “ToniCAL III”. The measurements were carried out at the temperature of 20 °C for 48 h. V/(C+PS)=0.35.

The X-ray diffraction (XRD) analysis of the phase composition of materials was carried out upon applying diffractometer DRON-7. In order to obtain X-ray radiation Cu Kα spectrum (λ = 0.1541837 nm), a graphite monochromator was used. The parameters of the tests were following: voltage – 30 kV; current –12 mA; the range of the diffraction angle – from 4 to 80°, 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.

Figure 2. Microstructure of PSw: a) dried PSw, magnification 1000 times, b) dried PSw, magnification 5000 times, c) burnt at 700 °C PSw, magnification 5000

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.
Ultrasound pulse velocity time is determined using the equipment “Pundit 7” (frequency of converters is 54 kHz) and ultrasound pulse velocity 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 40×40×40 mm specimens after their hardening in water for 7 and 28 days was established upon using hydraulic press ALPHA3-3000 S.

3. Results and discussions

The results of calorimetric tests of cement mixtures are presented in Fig. 4. The calorimetric tests enable establishing the effect of PSw on cement hydration processes. During the stage I of the hydration, PSw inconsiderably affects the rate of heat liberation. However, PSw extends the induction hydration period (the stage II) and dried PSw causes a considerable delay of the secondary heat release effect (the stage III), in particular, in case of the maximum content of waste (10%). When 5% dried PSw is added, the time of the stage III effect is retarded by 1.8 h, at 10% PSw – the effect is retarded by 4.4 h, as compared to the control specimen. But when 5% burnt PSw is added, the time of the stage III effect is accelerated by 1.9 h, at 10% burnt PSw – the effect is accelerated by 2.4 h, as compared to the control specimen.

The total amount of heat released (Fig. 5) shows that the samples with burnt PSw exhibit a very similar heat content as the control specimens, while the total amount of heat released in the samples with dried PSw is significantly lower (reduces approx. 14% at 5% dried PSw and 21% at 10% dried PSw). Unburnt PSw contains ~30% cellulose that slows down the hydration. Literature states that cellulose and other materials of similar composition are indicated to be cement hardening retarders [17–18], whereas materials with CaO or CaCO$_3$ may accelerate the hydration process [19–21].
Figure 4. The curves of heat flow released in cement pastes with PSw

Figure 5. The impact of PSw on the total heat released in course of time

Density and ultrasound pulse velocity results (Fig. 6–7) show that at 5% burnt PSw, sample density and ultrasound pulse velocity increase, with a higher amount, i.e., 10% burnt PSw, density and ultrasound pulse velocity begin to decrease. Compared to control samples, when dried PSw is used, density of samples hardened for 28 days’ decreases from 3.4% (5% PSw) to 6.2% (10% PSw), the reduction of up to ~9% in ultrasound pulse velocity is observed as well.

Figure 6. Results of density after 7 and 28 days
Figure 7. Results of ultrasound pulse velocity after 7 and 28 days

The results of compressive strength and microstructure are shown in Figures 8-9.

Figure 8. The impact of PSw amount and preparation method on compressive strength

The compressive strength of the samples after replacing up to 5% cement by burnt PSw increases (Figure 8). The highest compressive strength is determined in PSwB5 specimens and it is by 12.6% greater than that of control samples. With a higher amount of burnt PSw or dried PSw, the compressive strength decreases. Compared to control samples, after the addition of 10% dried PSw, the compressive strength of samples hardened for 28 days’ decreases by 38.5%. The reduction in strength is due to the structural changes in the material (Figure 9) which are formed by the high demand of water and the amount of cellulose in dried PSw.

The microstructure of control samples and samples with 5% waste is similar. There are visible ettringite, CSH formation, structure is dense, only the PSwD5 shows more micro cracks and pores (Figure 9a, 9b, 9d). The structure of the samples in which the cement is replaced with 10% dried PSw is more porous, larger crystals are formed, larger voids are visible. These specimens have the lowest density, ultrasound pulse velocity and compressive strength.
X-ray analysis was done to determine the effect of hydrates on the hydration and physical-mechanical properties of cement, and Table 3 presents the relative quantities of the main identified minerals based on the maximum peak height.

**Table 3.** The results of XRD analysis of hydrates formed in all compositions

| Marking of composition | Ettringite | Calcite | Portlandite | CSH+CASH |
|------------------------|------------|---------|-------------|----------|
| PSw0                   | 348        | 161     | 482         | 287      |
| PSwD5                  | 322        | 188     | 358         | 272      |
| PSwD10                 | 322        | 261     | 270         | 260      |
| PSwB5                  | 305        | 299     | 359         | 346      |
| PSwB10                 | 307        | 368     | 313         | 344      |

Table 3 shows that increasing the amount of PSw in samples increases the amount of calcite that is abundant in the PSw and decreases the amount of ettringite and portlandite. The amount of CSH+CASH in the samples is mostly dependent on the way PSw is prepared. Dried PSw reduces the amount of calcium hydrosilicates produced and slows down hydration processes. Burnt PSw significantly increases
the relative amounts of CSH+CASH and accelerates the hydration. It also shows that increasing the amount of burnt PSw from 5% to 10% begins to decrease the amount of portlandite.

4. Conclusions

In this work, it is determined that PSw can be utilized/used for the preparation of cement mixtures by adding up to 5%. Depending on the environmental working conditions, the preparation of PSw can be selected. To slow down cement hydration processes, it is useful to use only dried PSw. To accelerate cement hydration, it is expedient to use PSw which is burned at 700°C.

The use of PSw saves the environment, reduces the amount of cement in the mixture and improves the properties of cement materials. Using 5% at 700°C burnt PSw instead of cement, increases the compressive strength of the specimens, and the density as well as ultrasound pulse velocity values slightly change compared to the control sample.

It is determined that PSw changes mineral composition and structure. It is found that the microstructure of samples without PSw and samples with 5% PSw is similar, crystals formed are visible. With a higher (10%) amount of dried PSw, the microstructure of the cement stone differs significantly from the control samples. Larger voids with plenty of ettringite and calcite are also visible.

XRD studies show that the amount of burnt PSw produce the highest amounts of CSH+CASH, and the lowest amounts of ettringite, while in the samples with dried PSw, CSH+CASH were the lowest, which confirms that burnt PSw accelerates and dried PSw slows down the cement hydration.

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