RESEARCH ARTICLE | SEPTEMBER 27 2023

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AIP Conf. Proc. 2928, 080028 (2023)
https://doi.org/10.1063/5.0170356

The Impact of Paper Sludge Waste on Physical & Mechanical Properties of Cementitious Materials

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Abstract. The global production of paper is on the rise, thus leading to increasing amounts of waste in different stages of paper manufacture. Paper sludge waste is the most abundant and there is a big potential to reuse it after appropriate processing. This research paper analyses paper sludge waste fired at 900°C temperature for 2 h in terms of mineral composition, particle density and water demand in cement-based mixtures, as well as the effect of paper sludge waste on the density, ultrasonic pulse velocity, compressive strength and mineral composition of cement-based specimens. In the cement paste mixtures 0%, 2.5%, 5%, 7.5% and 10% of cement was replaced with paper sludge waste fired at 900°C temperature for 2 h. The ratio between water and solid substances was 0.35. Gehlenite and calcium oxide were found to prevail in the mineral composition of paper sludge waste, whereas water demand of cement-based mixture incorporating paper sludge waste increased 30%. The intensity of XRD curves revealed that a higher content (more than 7.5%) of paper sludge waste fired at 900°C temperature for 2 h in the mix increases the amount of portlandite and reduces the amounts of cement minerals: alite and belite. An empirical equation was drawn on the grounds of statistical analysis to calculate the compressive strength according paper sludge waste content fired at 900°C temperature for 2 h. The correlation and determination factors more than 0.9 demonstrate that the change of compressive strength in relation to paper sludge waste content can be described by the second degree polynomial equation and the optimum content of paper sludge waste fired at 900°C temperature for 2 h in the cement matrix is 5%. The highest density and ultrasonic pulse velocity values of cement stone specimens after 28 days of curing were obtained of specimens containing 5% paper sludge waste.

INTRODUCTION

The European Commission has adopted a new Circular Economy Action Plan that announces initiatives along the entire life cycle of products. Waste reduction is one of the measures specified in the Action Plan [1]. Sustainable manufacturing of the 21st century faces two main challenges: the lowering of carbon footprint and waste recycling.

The growing urban population and increasing demand for new buildings urge to look for alternative construction materials developed or obtained from other sources. In line with the growing demand of construction products the development of sustainable building materials is receiving greater attention.

The pulp and paper industry are among the most polluting industries worldwide. Paper manufacturing generates big amounts of waste [2]. Paper sludge is one of the by-products in paper manufacture.

European pulp and paper industry generates about 11 million tons of waste per annum. 70% of this waste comes from recovered paper recycling and de-inking processes [3]. One tone of paper produced leads to 300 kg of dry sludge generated. As different amounts of paper are recovered in the regions, the amount of waste generated also differs geographically [4]. High amounts of waste and possibilities of reusing it gives a significant role to the construction industry in recycling and reusing paper manufacturing waste.

World Multidisciplinary Civil Engineering-Architecture-Urban Planning Symposium WMCAUS 2022
AIP Conf. Proc. 2928, 080028-1–080028-7; https://doi.org/10.1063/5.0170356
Published by AIP Publishing. 978-0-7354-4663-2/$30.00

Intelligent utilisation of industrial waste is the major component in the definition of sustainable and integrated development in modern days. Reuse of industrial waste and by-products reduces the exploitation of natural resources and the need to produce certain raw materials. Reduced amounts of waste also alleviate the pressure on landfills as well as reduce the emission of greenhouse gasses.

It was found that 2-5 hours of paper sludge waste (PSw) activation at high temperatures from 500ºC to 900°C determines them with high pozzolanic properties, and kaolin presented in it transforms into metakaolin [5, 6]. The articles [7-9], show that the basic oxides of chemical composition of PSw after treatment at 650–850°C temperature are as follows: SiO_2 (13.9–30.2%), Al_2O_3 (8.3–18%), CaO (31.4–47.1%) and MgO (0.5–4.0%). The main oxide remains CaO which reacts with water to form portlandite $Ca(OH)_2$. It should also be noted that PSw contains cellulose fiber and organic binder, and the main minerals that make up PSw are calcite, kaolinite, talc, chlorite, mica [10-13]. It was established that if 10–20% cement is replaced by the said thermally processed waste, the compressive strength remains practically the same; however, frost resistance of hardened cement mortar increases considerably [14]. It was established that if PSw is burnt at 650°C temperature for 2 h, it may be used in construction industry [15]. However, there is little work in the literature on the effect PSw burnt at 900°C temperature on the properties of cement materials. Only work [16] analysis the properties and composition of PSw burnt at different temperatures, and it is determined that calcite decomposes at 900ºC to forms gehlenite. Furthermore, traces of anorthite is found. These minerals are characterized by the higher chemical and thermal stabilities than calcite or kaolinite; therefore, it may have a negative effect on pozzolanic activity.

In our previous studies [17] was determined, that 5% of cement replacement by PSw decreased approximately 0.5% the density of the specimens and the SAI (activity index) after 28 days of hardening increased by approximately 4%. Thermal analysis of PSw showed that at ~352°C, the cellulose disintegrated and the connected water was liberated and at ~765°C, calcium carbonate decomposed to CaO and CO_2.

The aim of this paper is to determine the properties (particle density, mineral composition, water demand) of PSw fired at 900°C temperature for 2 h and analyse the effect of the waste on the density, ultrasonic pulse velocity and compressive strength of cement-based materials.

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.

TABLE 1. Chemical composition of cement [18].

CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	Na_2O	SO_3	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 [18].

Particle density, g/cm^3	Soundness, mm	Passing 90 µm, %	Compressive strength after 2 days, MPa	Compressive strength after 28 days, MPa	Vicat Initial, min	Amount of water for normal consistency, %
3.1	1.0	78.5	30	55	180	27.5

Mineral composition of the cement: C_3S - 56.6%, C_2S - 16.7%, C_3A - 9.0%, C_4AF - 10.6% and 7.1% others (alkaline sulphates and CaO). [18]

First, the PSw was dried at 75ºC temperature for 48 hours in a SNOL dryer, then crushed with a jaw-type crusher and sieved through a 1 mm sieve. The prepared PSw was burned at 900˚C temperature. Further, it was kept at such temperature for 2 hours. Temperature increase speed 3.2 C/min. To the mixtures, the waste was added in the form of dry white powder. The chemical composition of dried PSw is provided in table 3.

The X-ray analysis showed, that the main compounds of PSw burnt at 900ºC are calcium oxide and a few gehlenite.

Gehlenite has higher chemical and thermal stability than calcite. Similar mineral composition of PSw burnt at higher than 800ºC temperature was determined by other scientists as well [16]. Gluth et al. [19] and Segui et al. [20] at temperature 850ºC also detected gehlenite ($Ca_2Al_2SiO_7$) as main crystalline mineral phase.

TABLE 3. Chemical composition of PSw [18].

C_O(org)	**CaO**	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**MgO**	**TiO_2**	**SO_3**	**Cl**	**Na_2O**	**Others***
34.08	58.21	3.48	2.36	0.52	0.64	0.10	0.18	0.06	0.09	0.28

*Others: slight amounts of P_2O_5, K_2O, MnO, NiO, CuO, ZnO, SrO, ZrO_2.

At 900ºC temperature burnt PSw particle density according to the EN 993-2 is ~2.5 g/cm^3. PSw water demand is determined based on EN 450-1, and it is quite high 130%, because of that the using higher amounts of such waste could be complicated.

In the cement paste mixtures formed of the above-described raw materials, 0%, 2.5%, 5%, 7.5% and 10% of cement was replaced with PSw. The ratio between water and solid substances was 0.35. [18]

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. [18]

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 1) (V, m/s):

$$V = \frac{l}{\tau} \tag{1}$$

where: l - length of the specimen, m; τ - 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. Strength results are the averages of 4 tested specimens.

A statistical analysis of the researched indicators was carried out according to literature [21, 22]. This function was selected to determine the mathematical relationship, which describes the distribution of data most precisely, also assessing if multi-unit correlation and determination ratios are close to one. Literature does not provide with strict regulations when the correlation is considered to be weak, and when it is strong, the suggestions of authors [23] are taken into consideration: when $R \leq 0.2$ - correlation is considerably weak, the relationship does not exist. When $0.2 < R \leq 0.4$ - the correlation is weak, there is slight relationship; when $0.4 < R \leq 0.7$ - correlation is average, the relationship is average; when $0.7 < R \leq 0.9$ - correlation is very strong.

RESULTS

Density results (Figure 1) of specimens with PSw show that the density of cement samples reduces uniformly with the addition of PSw.

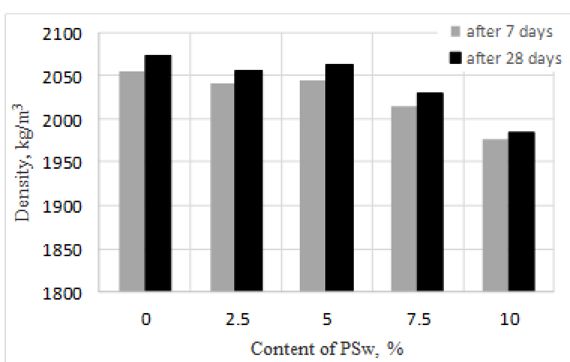

FIGURE 1. Density dependence on PSw content.

This is due to the slightly lower PSw particle density (2.5 g/cm^3) compared to cement (3.1 g/cm^3), as well as increased demand of water for PSw (30%). As the amount of water was not increased, due to lack of water, more pores could be formed in the mixture. After adding 5% PSw, the density of the specimens decreased only by ~0.5%, and after the addition of 10%, the water shortage was clearer and the density of PSw-based cement specimens reduced by ~4%.

The results of ultrasound pulse velocity (Figure 2) with the insertion of PSw change insignificantly. Replacing the minimum amount of 2.5% cement to PSw, ultrasound pulse velocity after 7 and 28 days decreases by ~2%, while the addition of maximum of 10% PSw reduces it up to 3.5%. Hence, using the PSw, cement stone structure is slightly porous.

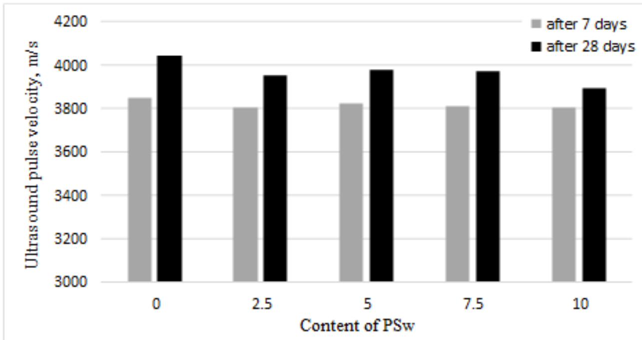

FIGURE 2. Ultrasound pulse velocity dependence of PSw content.

The results of compressive strength (Figure 3) showed that using up to 5% PSw instead of cement, analogue or higher compressive strength is obtained. After 28 days of hardening the maximum compressive strength was obtained in specimens where 5% cement was replaced by PSw. In this case, the strength increased by ~4%. With further additions in the amount of waste and reduction of cement content, the strength began to decline. The strongest decrease in strength was in specimens with 10% PSw, it was reduced by ~16%. This effect could be explained by the water demand in cement-based materials with PSw. While the amount of water is sufficient for hydration (PSw water demand is ~130%), PSw easily absorbs water and becomes a hydration center. Hydration process accelerates with increasing PSw content as shown by X-ray analysis (Figure 4–5) and other authors works [24, 25]. However, when using >7.5% PSw, the temperature of the mixture rises up to ~35-40°C due to reaction of CaO. The specimens are complicated to form without increasing the amount of water, the likelihood of internal defects develops increases and strength begins to decrease.

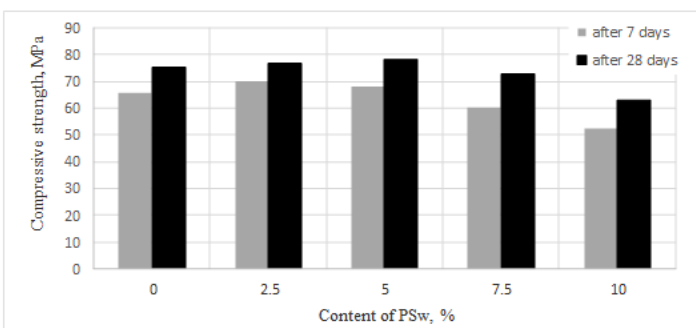

FIGURE 3. Compressive strength dependence on PSw content.

In order to determine the appropriate amount of PSw according to the compressive strength, a regression equation was concluded which, together with the statistical indicators, is presented in table 4.

The correlation coefficient of the equation is higher than 0.9; therefore, a correlation between compressive strength and content of PSw is very strong. Determination coefficient is more than 0.9, consequently, the selected mathematical model may be applied for the prediction of compressive strength. Content of PSw parameter expressed in the equation is significant because Stjudent's criterion of this parameter is higher than that presented in statistical table 4. The selected mathematical model is a parabola with a peak at ~5% PSw where the highest compressive strength is obtained.

TABLE 4. Predictable equation for compressive strength (fc) based on content of PSw (p), and its statistical parameters

Equation	Correlation coefficient	Determination coefficient	Stjudent's criterion of *p* parameter	Stjudent's criterion of p^2 parameter
$fc=74.3+2.39p-0.35p^2$	0.965	0.931	6.70	10.3

X-ray analysis of the most characteristic batches is shown in Figure 4 (with 2.5% PSw) and Figure 5 (with 7.5% PSw).

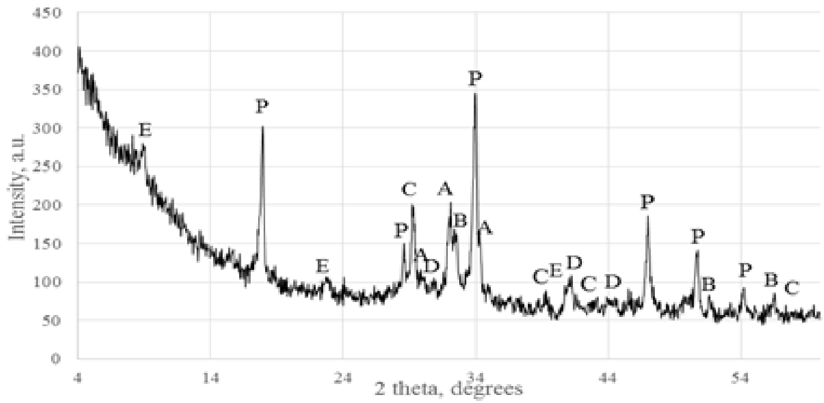

FIGURE 4. X-ray analysis of specimen with 2.5% PSw.

Figure 4–5 show that analogue minerals dominate in cement specimens: ettringite (E), portlandite (P), calcite (C), dolomite (D), alite (A), belite (B). The adding a higher amount of PSw increases the amount of portlandite, while ettringite, alite and belite **-** decreases. Calcite remains very similar, it only varies by ~1%. According to these data, PSw accelerates cement hydration by reducing the amount of unreacted cement minerals.

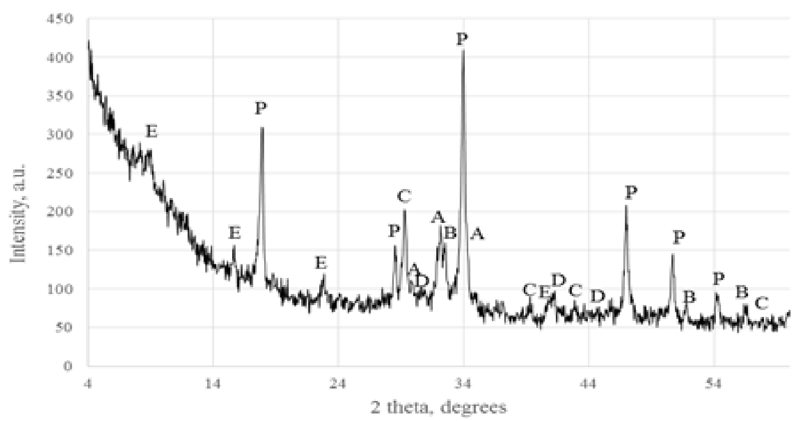

FIGURE 5. X-ray analysis of specimen with 7.5% PSw.

CONCLUSIONS

Calcium oxide and a few gehlenite prevail in the mineral composition of PSw fired at 900°C temperature for 2 h. Water demand increases 30% compared to the control mix. The highest density and ultrasonic pulse velocity values were obtained after 28 days of curing in specimens modified with 5% PSw added by weight of Portland cement, compared to other compositions with PSw. The values, however, are insignificantly lower compared to the control specimen.

The highest compressive strength values were obtained after 28 days of curing in specimens modified with 5% PSw added by weight of Portland cement. The empirical equation revealed that compressive strength values change in relation to PSw content according to the mathematical model of the second degree polynomial equation (determination factor > 0.9).

The intensity of XRD curves revealed that a higher content of PSw fired at 900°C temperature for 2 h in the mix increases the amount of portlandite and reduces the amounts of ettringite, alite and belite.

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