Construction and Building Materials 169 (2018) 689–696

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Analysis of the effect of paper sludge on the properties, microstructure and frost resistance of clay bricks

Olga Kizinievič *, Viktor Kizinievič, Jurgita Malaiškienė

Laboratory of Composite Materials, Institute of Building Materials, Vilnius Gediminas Technical University, Linkmenų g. 28, LT 08217 Vilnius, Lithuania

HIGHLIGHTS

- Paper sludge (PS) mainly consists of cellulose and calcite.
- Cellulose fibre (CF) reduce the shrinkage of clay bricks.
- CF and $CaCO_3$ decomposition products change the microstructure of the clay body.
- The optimal amount of PS additive in a clay brick is up to 15%.

ARTICLE INFO

Article history:
Received 7 November 2017
Received in revised form 26 February 2018
Accepted 1 March 2018
Available online 20 March 2018

Keywords:
Paper sludge
Recycling
Cellulose fibre
Properties
Frost resistance
Microstructure
Clay brick

ABSTRACT

The paper analyses the effect of waste sludge from paper industry (paper sludge) on physical and mechanical properties of clay bricks, their microstructure and resistance to freezing and thawing. Paper sludge is not hazardous industrial waste mainly consisting of cellulose and calcite. Clay bodies were made from the mix containing from 5% to 20% of paper sludge and fired at 900 °C and 1000 °C temperatures. Open pore structure in the clay body is developed as a result of burnt cellulose fibres and calcite decarbonization. Physical and mechanical properties of clay bodies change depending on the content of added PS: shrinkage, density and compressive strength reduce, water absorption and effective porosity increase. It is recommended to add 5% of paper sludge to the clay body and fire it at 900 °C temperature, or alternatively add 5–15% of paper sludge and fire the clay body at 1000 °C temperature. In terms of resistance to freezing and thawing, such products are regarded as frost resistant in moderately aggressive environment, i.e. in structures protected from direct environmental effects.

1. Introduction

Directive 2008/98/EC on waste provides to avoid waste generation and to use waste as a resource. Attempts should be made to recycle, re-use and utilize waste. Paper manufacturing is a complex industry involving multiple processes where different products are produced and large quantities of waste of primary, biological or de-inking origin are generated, waste water treatment sludge, primary sludge, and secondary sludge among them [1]. The primary sludge is generated in the largest quantities [2]. The production of 1 ton of paper generates about 30 kg of primary sludge, as it is mentioned elsewhere [3]. Nowadays this sludge is used for energy generation through incineration [4–7]. Sludge incineration process is regulated in the EU and typically uses fluidised bed combustion from 850 °C to 1100 °C. The incineration process, however, generates ash, which must be utilised as well. Researchers [8,9] found that paper sludge ash can be utilised in concrete manufacturing, where part of cement is replaced by hydrophobic paper sludge ash additive. It is stated that 12% of paper sludge ash added to the concrete mix significantly reduces water absorption of concrete without compromising on either density or compressive strength [8].

Authors [10–18] argue that paper sludge fired at 700–750 °C temperature acquires pozzolanic properties. Such substance can be utilised in cement manufacturing because under high temperature conditions kaolin present in paper sludge turns into metakaolin, which has the properties similar to those of commercial metakaolin [14]. Besides, the resulting ash retains more regular (chemical composition) properties compared to the bottom ash from the incineration of municipal waste.

It is also known that paper sludge can be used in concrete and cement brick manufacturing [19,20] as a substitute for certain natural additives such as lightweight aggregates [21].

* Corresponding author.
E-mail addresses: olga.kizinievic@vgtu.lt (O. Kizinievič), viktor.kizinievic@vgtu.lt (V. Kizinievič), jurgita.malaiskiene@vgtu.lt (J. Malaiškienė).

https://doi.org/10.1016/j.conbuildmat.2018.03.024
0950-0618/

Other authors suggest producing wood-paper sludge boards where a certain amount of wood chips is replaced with paper sludge waste. Unfortunately, such boards have a much lower compressive strength due to weak bonding between wood chip and paper sludge particles. The optimal content of paper sludge in such boards is up to 10% [22].

Paper sludge can be also used in clay brick manufacturing [21,23–28]. On the one hand, paper sludge additive reduces the density and thermal conductivity of construction products; on the other hand it impairs their mechanical properties. Authors [28,29] propose to modify clay and paper sludge mix with glass scraps. Such modification improves mechanical properties of construction products, reduces the number of pores, intensifies the sintering, and changes the mineral composition of the final products.

In spite of numerous papers analysing this issue, there is no consensus on the appropriate amounts of paper sludge additive and firing temperatures. Besides, no information on the effect of this additive on the durability of clay bricks in terms of frost resistance was found in research literature.

Lithuanian paper mills generate about 12–13 thousand tons of primary paper sludge per year. The average humidity of this sludge is approx. 60%. The sludge contains 40–50% of organic matter (paper fibre) and 50–60% of mineral matter. Paper sludge properties and composition remain constant. At present paper sludge is not utilised in Lithuania. Instead, it is accumulated in the territory of the paper mill and afterwards removed to the landfill. Researchers have to find new and cheap utilisation techniques in order to solve the problem of waste accumulation in large quantities and to meet environmental requirements. Paper sludge utilisation in ceramic manufacturing industry could be a prospective and economically viable solution. This technique would protect the environment and support the production of ecological ceramic products. The main objective of this study is to examine the effects of paper sludge (primary sludge) additive on physical and mechanical properties, porosity, microstructure, and frost resistance of fired clay bricks. This is the first study in Lithuania on the utilisation of paper sludge in fired clay bricks.

2. Materials and methods

Clay, sand and paper were used in this experimental research. The clay was dried at 105 ± 5 °C temperature, crushed and sieved through 0.63 mm sieve. The sand was dried and sieved through 2.5 mm sieve. The humidity of paper sludge was 50–60%. Paper sludge was dried at 75 ± 5 °C temperature, ground and sieved through 2.5 mm sieve (Fig. 1). Paper sludge contains 40–50% of organic paper fibre and 50–60% of inorganic matter. The pH of the paper sludge was 8 ± 0.2, bulk density was 410 kg/m^3.

Fig. 1. Dried paper sludge (left) sieved through 2.5 mm sieve (right).

Initially, the components were mixed under dry conditions; then, the mixture was watered until the humidity level suitable for brick forming (e.g., 22–29%). The tests revealed that higher content of paper sludge additive increased water demand required to obtain the moulding compound of adequate plasticity. The reason is high water absorption of organic cellulose fibres. The plasticity index of the moulding compound reduces with the addition of paper mill sludge (Table 1). The plasticity of the clay was determined by the standard Vasiliev cone testing method. 60 × 30 × 18 mm, 30 × 54 mm and 70 × 70 × 70 specimens were formed from the moulding compound. 70 × 70 × 70 mm size specimens are used in frost resistance tests, 50 × 50 × 50 mm size specimens are used to test the mechanical characteristics, and 60 × 30 × 18 mm size specimens are used to test the physical characteristics. The compositions of the moulding compounds are shown in Table 1. The samples were dried at 105 ± 5 °C until stable masses were reached. The dried samples were then fired at 900 °C and 1000 °C for 1 h.

Classical chemical analysis was used to determine the chemical composition of primary silicate raw materials used for the tests by means of Si(Li) detector INCA PentaFET × 3 from Oxford Instruments. Physical and mechanical properties of the fired specimens were determined by following the standard testing methodologies: density was determined in accordance with the standard LST EN 772-13:2003 [30]; water absorption was determined in accordance with the standard LST EN 772-21:2011 [31]; the compressive strength was determined in accordance with the standard LST EN 772-1:2011 [32]; loss on ignition was determined in accordance with the standard LST EN 15935:2012 [33], and bulk density was determined in accordance with the standard LST EN 13041:2012 [34]. The durability of the specimens was evaluated as freeze and thaw resistance in accordance with the standard LST 1985:2006 [35].

The drying shrinkage and firing shrinkage was calculated from equations 1 and 2 below.

$$L = \frac{L_0 - L_1}{L_0} * 100\% \tag{1}$$

$$L_B = \frac{L_0 - L_2}{L_0} * 100\% \tag{2}$$

where L_0 is the distance between two reference marks in the wet specimen, mm; L_1 is the distance between two reference marks in the dried specimen, mm; L_2 is the distance between two reference marks in the fired specimen, mm.

The granulometric composition was determined by means of liquid analyser Cilas 1090. A dilatometer Linseis L76 was used for dilatometric analysis at 4 °C/min. A dilatometer Linseis PT-1600 was used for dilatometric analysis at 10 °C/min. X-ray analysis was performed using a diffractometer DRON-7 X-ray (Co anode and Fe filter). The microstructure was analysed by means of SEM Quanta 250 with SE detector. Differential thermal analysis was done by means of derivatograph Q 1500D. The content of heavy metals was determined by Atomic Absorption Spectroscopy technique using the spectrophotometer Buck Scientific 2010 VGP with air-acetylene flame.

The two-sided confidence intervals, with the confidence level of 0.95, of means of the measured quantities (porosities, shrinkage, density, water absorption, strength) were calculated by assuming that the porosities, shrinkage, density, water absorption and strength are normally distributed random variables. The Student distribution was applied to calculate the confidence intervals $(m - td,(1-\alpha/2) \cdot s/\sqrt{n}) \leq \mu \leq (m + td,(1-\alpha/2) \cdot s/\sqrt{n})$ of the means, where m and s are estimations of the mean and standard deviation of the random variables, n = 6 is the sample size, $td,(1-\alpha/2) \approx 2.57$ is $(1-\alpha/2) = 0.975$ quantile of the Student distribution, where

Table 1
Composition of moulding compounds.

Raw materials	Composition of moulding compounds (% wt)				
	PS0	PS5	PS10	PS15	PS20
Clay	90	85	80	75	70
Sand	10	10	10	10	10
Paper sludge	0	5	10	15	20
Optimum moisture content	22	23	25	27	29
Liquid limit	37	38	40	42	44
Plastic limit	20	22	26	29	33
Plasticity index	17	16	14	13	11

$\alpha = 0.05$ is a level of significance and $d = n - 1 = 5$ is the degree of freedom.

3. Results and discussion

The experimental tests showed that SiO_2 content in the clay is 63.56%, $Al_2O_3 + TiO_2$ content is 19.53, the content of colouring Fe_2O_3 oxides is 6.55%. Clay is a dispersion by granulometric composition (Table 2). The natural humidity of clay is 18.6%, density is 2.42 kg/m^3, and plasticity is 19.3.

The analysis of clay microstructure is presented in Fig. 2. Clay particles have a shape of 2–11 μm size plates and are distributed evenly. Clay particles are connected to the particles of other substances via thin bridges made of clay particles. Some debris is visible among the clay plates. The prevailing minerals in the clay detected by X ray analysis (Fig. 3) are: micro clay, quartz, kaolinite, and feldspar.

The quartz sand with the following chemical composition was used for the tests: $SiO_2 > 98.5\%$, $Fe_2O_3 < 0.05\%$, $Al_2O_3 < 0.60\%$; the distribution particle size in sand: 0% of 2500 μm particles, 0.20% of 1250 μm particles, 0.30% of 1000 μm particles, 1.50% of 800 μm particles, 630 μm particles 2.70%; 7.50% of 400 μm particles, 9.40% of 315 μm particles, 34.40% of 200 μm particles 17.20% of 160 μm particles, 17.80% of 100 μm particles, 8.30% of 63 μm particles, 0.65% of 50 μm particles, and 0.05% of bottom particles.

It was found that humidity of paper sludge (PS) dried at 75 ± 5 °C temperature was 2.8%, the organic matter (cellulose fibre) content was 48.8%, inorganic matter (calcite) content was 51.2%. X-ray diffraction analysis of the paper sludge evidenced the presence of calcite (inorganic component) and cellulose (organic component) (Fig. 4). Tests done by other researchers revealed the presence of other inorganic materials – kaolinite, talc, quartz – in paper sludge [10,14,15]. Table 3 presents the results of eluate test and extractable metals detected in the solid residue, as well as other properties of the sludge. According to the analysis results, the detected residues do not pose a major threat for the environment in regard to heavy metal content; therefore, paper sludge can be classified as non-hazardous waste (see Table 5).

The analysis of PS microstructure is presented in Fig. 5. Cellulose fibres and fine calcite particles with coarse surface are observed in micrographs. Fibre thickness ranges from 5 μm to 20 μm. Larger calcite particles are located separately, while finer particles are seen on the surface of cellulose fibre.

Fig. 6 illustrates DTA and TGA curves of paper sludge. The DTA curve has two exothermic peaks at 340 °C and 430 °C and an endothermic peak at 750 °C. Corresponding to the two peaks, the TGA curve shows a two-step weight loss of 4.0% at 250 °C, a 50.0% loss between 250 and 560 °C and a 15.0% loss between 560 °C and 760 °C. The distinct exothermic peaks at 340 and 410 °C with big related weight losses correspond to the burning of organic fibres (cellulose). The endothermic peak and weight loss at about 760 °C is attributed to the decarbonisation of $CaCO_3$. During the firing, calcium carbonate undergoes a reaction where bound CO_2 with excessive kinetic energy is released. For this reason cracks may appear on the surface of the matrix and particle interaction may become weaker.

No defects, such as bloating or cracking, were observed after the firing of clay bodies containing PS additive at 900 °C and 1000 °C temperature. The following irregularities occurred: some specimens had a lighter colour, some specimens had white spots on the surface indicating higher calcium content in the clay body. The appearance of black coring should be also noted. It is known [36] that black coring is caused by the gas released by the burning organic compounds. Black coring may deteriorate the final properties of a clay body.

The drying shrinkage of moulding compounds without PS additive (moulding compound PS0) reaches 7.5%; the firing shrinkage at 900 °C temperature is 8.3%, and 10.5% at 1000 °C temperature. The drying and firing shrinkage of clay bodies with PS additive depends on the amount of PS added. Higher content of PS additive reduces the drying and firing shrinkage of the clay body. Depending on the moulding compound composition, the firing shrinkage at 900 °C temperature changes from 5.9% to 7.6% and from 7.5% to 9.2% at 1000 °C temperature (Fig. 7). The drying shrinkage diminishes because of the organic cellulose fibre framework formed inside the formed specimen. This framework prevents the moving of clay particles closer to each other during the drying. The cellulose fibre present in PS additive stabilises the drying process irrespective of higher water demand in the forming phase.

Cellulose fibres burn during the firing process and additional structure of pores is created. The liquid phase developed in clay during the firing process is not sufficient to fill in that pore

Table 2
Chemical and granulometric composition of the clay.

Raw materials	Chemical composition of the clay							
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3
Clay	63.56	19.53	6.55	1.38	2.68	0.18	5.56	0.56
	Granulometric composition of the clay							
	>0.5 mm amount, %		0.5–0.063 mm amount, %		0.063– 0.01 mm amount, %		>0.01 mm amount, %	
	0.2		1.8		22.4		75.8	

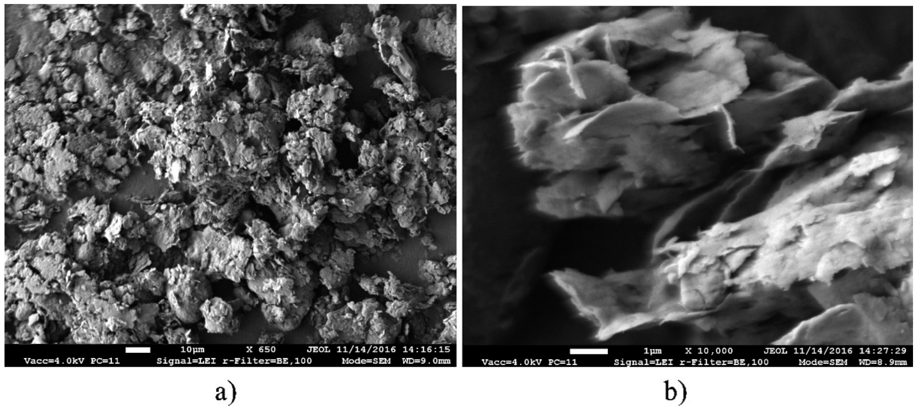

Fig. 2. Microstructure of the clay.

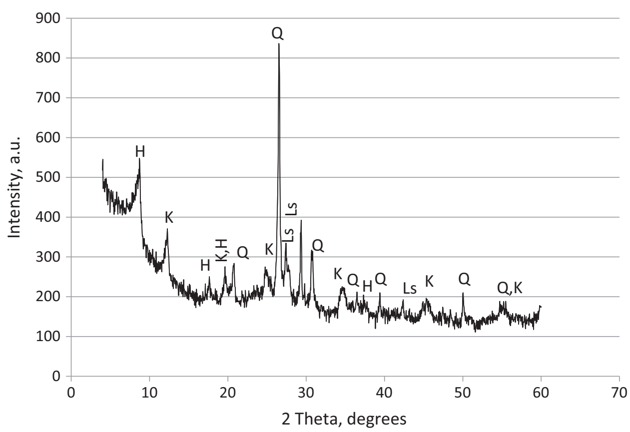

Fig. 3. Clay X-ray diffraction analysis: H – mico clay, Q – quartz, K – kaolinite, Ls – feldspar.

structure and to smooth the way for clay particles to get closer. For this reason specimens containing PS additive have lower firing shrinkage.

The density of clay bodies without PS additive was evaluated depending on the firing temperature. The obtained density values were 1.80 g/cm^3 and 2.10 g/cm^3 (fired at 900 °C and 1000 °C temperature respectively). The addition of 5% PS into the moulding compound results in lower densities of 1.72 g/cm^3 and 1.86 g/cm^3 at the same temperatures. The highest PS additive content of 20% (clay body PS20) reduces the density to 1.31 g/cm^3 and 1.42 g/cm^3. Specimens with denser structure have higher compressive strength. The compressive strength reduces with higher PS content and lower density. The clay body containing 15% of PS additive and fired at 1000 °C temperature has a sufficient compressive strength of 12 MPa and can be used in load bearing brick structures. Clay body PS20 had the lowest compressive strength. The average reduction of compressive strength of this clay body fired at 900 °C or 1000 °C was even 80% compared to clay body PS0 (Table 4). The compressive strength reduces not only due to the burning of organic fibres, which make up to 50% of PS additive, and the formation of the porous structure, but also due to decarbonisation of calcite. Upon heating calcium carbonate undergoes a reaction where bound CO_2 is released. The kinetic energy generated in this process may cause cracks to appear on the surface of the matrix and weaken particle bonding.

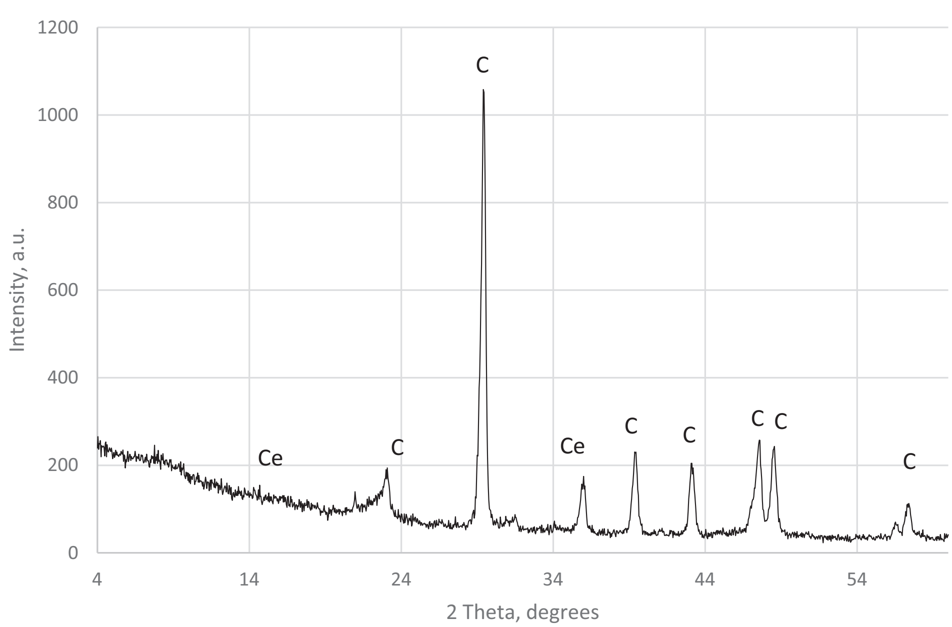

Fig. 4. Paper sludge X-ray diffraction analysis: C – calcite, Ce – cellulose.

Table 3
Analysis of extractable metals in the solid residue and other properties of the sludge.

Species	Test method		Unit of measurement
	Method reference number	Results	
Cadmium	LST EN ISO 15586:2004 (N)	0.250 ± 0.028	mg/kg s.m.
Chromium	LST EN ISO 15586:2004 (N)	4.91 ± 0.87	mg/kg s.m.
Copper	LST EN ISO 15586:2004 (N)	22.6 ± 3.5	mg/kg s.m.
Nickel	LST EN ISO 15586:2004 (N)	<0.5	mg/kg s.m.
Lead	LST EN ISO 15586:2004 (N)	3.71 ± 0.58	mg/kg s.m.
Zinc	LST EN ISO 15586:2004 (N)	288 ± 27	mg/kg s.m.
Mercury	LST CEN TS 16175–2-2013 (N)	0.11	mg/kg s.m.
Total nitrogen	LST EN ISO 16169:2012. EN 11261/1995	1.100 ± 94	mg/kg s.m.
Total phosphorus	LST EN 14672:2005	0.084 ± 0.009	mg/kg s.m.
Dry solids content	LST EN 15934:2012, method A	466 ± 20	g/kg
pH	LST EN 15933:2012, LST ISO 10390:2005	8.0 ± 0.2	pH value
Loss on ignition (ash content)	LST EN 15935:2012	65.1 ± 4.7	%

Authors [37,38] concluded that the compressive strength of laboratory-made clay bricks designed and tested for industrial application must not fall below 20 MPa. Different minimum strength requirements are set forth in national standards, e.g. the minimum average compressive strength required by the Turkish standard TS 705 and Indian standard IS 1077 for clay hollow bricks should be not less than 5 MPa. According to ASTM, the compressive strength of clay bricks ranges from 10.3 MPa to 20.7 MPa, depending on the brick specification (structural or facing brick). No minimum compressive strength values are set forth in the European Union Standard EN 771-1:2011 [32]. Manufacturers must declare the average compressive strength of supplied products and designers must consider these values in designing the structures. Usually, the compressive strength of clay hollow bricks declared in the European Union is at least 10 MPa.

Water absorption and open porosity are important properties, which depend on the amount, size and distribution of pores in the clay body. There is a strong correlation between water absorption and open porosity.

The lowest water absorption and open porosity values were found in the clay body PS0 fired at 1000 °C temperature. This clay body had water absorption value 8.2% and total open porosity value 21%. 5% of PS additive in the clay body increase water absorption up to 11.2% and total open porosity up to 23.4%. 20% of PS additive in the clay body increase water absorption up to 18.6% and total open porosity up to 39.0%. Clay bodies fired at 900 °C temperature have slightly higher water absorption and total open porosity values. European standard LST EN 771-1:2011 +A1:2015 (Specification for masonry units – Part 1: Clay masonry units) does not establish requirements for water absorption in clay masonry units. Manufacturers must declare the water absorption values for clay masonry units in accordance with the standard LST EN 772-21:2011 (Methods of test for masonry units – Part 21: Determination of water absorption of clay and calcium silicate masonry units by cold water absorption). According to ASTM the minimum water absorption value of such products ranges between 17% and 22%.

Higher firing temperature improves the crystallisation process resulting in intensive sintering of clay bodies, increased volume of liquid phase, closing of open pores, reduced porosity of specimens.

Structural changes in the specimens cause the density and compressive strength of clay bodies with PS additive to decrease, water absorption and total open porosity to increase. Clay bodies with higher PS additive content have more open pores and capillaries resulting from the burnt cellulose fibres and $CaCO_3$ decarbonisation. These pores have an effect on physical and mechanical properties of clay bodies. This is confirmed by further research into the microstructure of clay bodies.

There is little difference between the surface morphologies of clay bodies PS0 and PS5. The microstructure is sufficiently dense with low numbers of pores prevailing. The pores are small and evenly distributed along the entire clay body. The microstructure of clay body PS20 with the highest content of PS additive (20%) is different: big pores resulting from the burnt cellulose fibres prevail. Pores also develop due to intensive removal of CO_2 during the firing and decomposition of calcium carbonate (Fig. 8).

The results of the leaching of heavy metals from clay bricks are presented in Table 5. Heavy metal leaching data reveal that, irrespective of the firing temperature, no traces of heavy metals Cd, Cr, Cu, Ni, Pb, and Hg were detected in clay bricks. Small amounts of Zn were detected only in clay bricks PS15 and PS20. Therefore, there are no environmental limitations for using paper sludge in clay brick manufacture.

In the next stage of experimental research the frost resistance of specimens was tested. The resistance of specimens to freezing and thawing was tested by visual evaluation of damage types. Control specimens and specimens containing 5% of paper sludge additive fired at 900 °C temperature resisted at least 25 freeze-thaw cycles (The cycle consists on one freezing (−18 °C) and one thawing (+18 °C) phase). Specimens containing 5–15% of paper sludge additive fired at 1000 °C temperature also resisted at least 25 freeze-thaw cycles. According to LST EN 771-1:2011+A1:2015 [39] and LST EN 1985:2006 [34] requirements, such products can be used in moderately aggressive environments (frost resistance

Table 4
Properties of clay body.

Properties	Ceramic body Firing temperature 900 °C/1000 °C				
	PS0	PS5	PS10	PS15	PS20
Density, g/cm^3	1.8 ± 0.003/2.1 ± 0.002	1.72 ± 0.002/1.86 ± 0.002	1.65 ± 0.002/1.78 ± 0.004	1.58 ± 0.003/1.65 ± 0.002	1.31 ± 0.004/1.42 ± 0.003
Compressive strength, MPa	20.0 ± 0.9/25.0 ± 1.1	14.0 ± 0.9/22.0 ± 1.2	8.3 ± 1.2/16.0 ± 1.4	7.5 ± 1.1/12.0 ± 1.5	4.0 ± 1.5/5.0 ± 1.4
Water absorption, %	15.0 ± 1.1/8.2 ± 1.4	18.0 ± 1.5/11.2 ± 1.7	20.4 ± 1.3/14.5 ± 1.5	22.0 ± 1.8/15.3 ± 2.0	26.3 ± 2.0/18.6 ± 2.4
Total open porosity, %	25 ± 1.8/21 ± 2.1	28.0 ± 2.2/23.4 ± 1.6	34.3 ± 1.9/30.8 ± 2.0	42 ± 2.2/35 ± 1.9	46 ± 2.0/39 ± 1.5

Table 5
Leaching results.

Species	Ceramic body (firing temperature 900 °C/1000 °C) Results mg/kg					2003/33/EC	
	PS0	PS5	PS10	PS15	PS20	Inert limit, mg/kg	Non-hazardous limit, mg/kg
Cadmium	n.d/n.d	n.d/n.d	n.d/n.d	n.d/n.d	n.d/n.d	0.04	1.0
Chromium	n.d/n.d	n.d/n.d	n.d/n.d	n.d/n.d	n.d/n.d	0.5	10.0
Copper	n.d/n.d	n.d/n.d	n.d/n.d	n.d/n.d	n.d/n.d	2.0	50.0
Nickel	n.d/n.d	n.d/n.d	n.d/n.d	n.d/n.d	n.d/n.d	0.4	10.0
Lead	n.d/n.d	n.d/n.d	n.d/n.d	n.d/n.d	n.d/n.d	0.5	10.0
Zinc	n.d/n.d	n.d/n.d	n.d/n.d	0.08/0.10	0.11/0.1	4.0	50.0
Mercury	n.d/n.d	n.d/n.d	n.d/n.d	n.d/n.d	n.d/n.d	0.01	0.2

n.d – no detectable concentration with the measuring equipment.

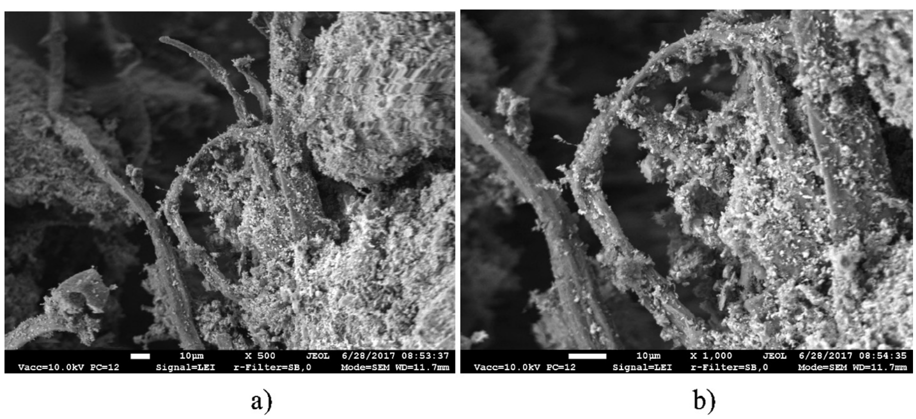

Fig. 5. Microstructure of paper sludge.

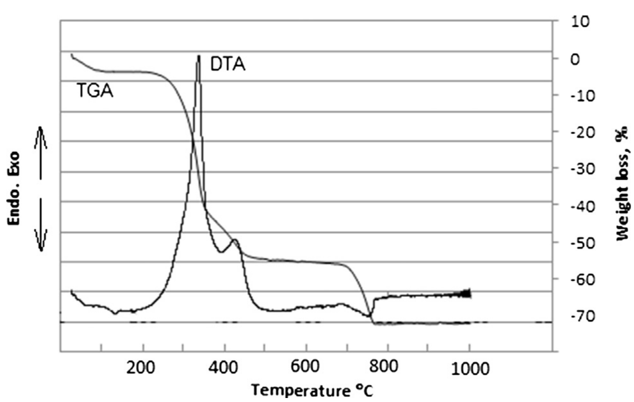

Fig. 6. DTA and TGA curves of paper sludge.

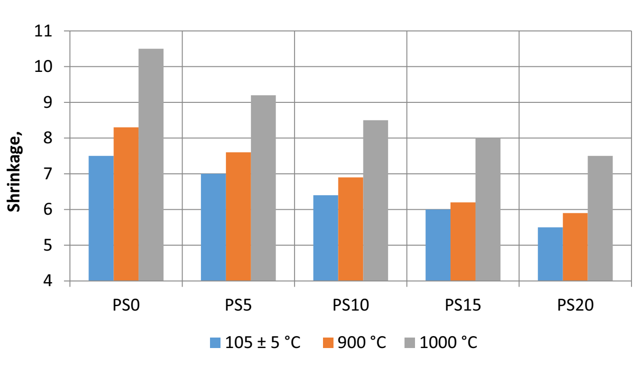

Fig. 7. Linear shrinkage of clay bodies.

class F.1), i.e. in structures protected from direct environmental effects. Specimens containing 10–20% of paper sludge additive fired at 900 °C temperature broke into pieces after 21 and 16 freeze-thaw cycles. Specimens containing 20% of paper sludge additive fired at 1000 °C temperature broke into pieces after 18 freeze-thaw cycles.

Some authors [40] state that up to 30% of paper sludge can be added to clay brick moulding compounds fired at 1100 °C temperature. This additive reduces the density, thermal conductivity and compressive strength of clay bricks. Other authors [41] argue that only 3% of paper sludge waste should be added to clay bricks fired at 750 °C temperature. A higher content (5%) of paper sludge has a negative effect on water absorption and mechanical characteristics of clay bricks. Other authors [24] argue that 10% of paper sludge be added to clay bricks fired at 900 °C temperature. There is no scientific consensus regarding the amount of paper sludge waste to be added to moulding compounds in clay brick manufacture. The amount of paper sludge may depend on the chemical composition of the clay used and the highest firing temperature applied. No information regarding the effect of paper sludge on the clay brick frost resistance was found in scientific papers. Frost resistance is a complex characteristic which has an effect on the durability of clay bricks. Our tests revealed that 5% to 15% of paper sludge can be added to clay brick moulding compounds, where the additive content depends on the highest firing temperature (900 °C–1000 °C). Such clay bricks incorporating paper sludge waste can be used in civil construction.

4. Conclusions

Waste sludge from paper industry (paper sludge) containing cellulose fibres and calcite belongs to the group of non-hazardous waste and can be used as an additive in clay brick man-

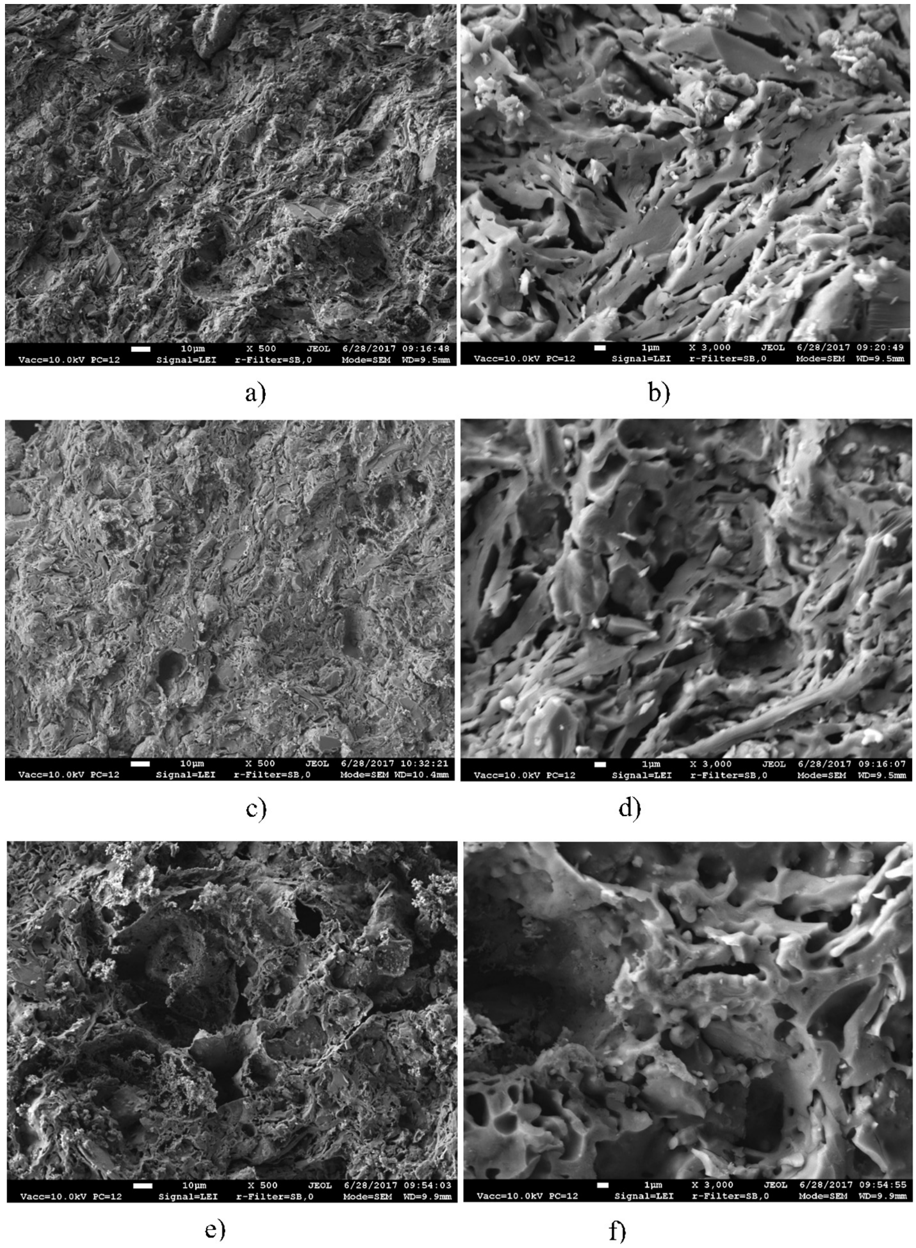

Fig. 8. SEM images of clay bodies: clay body PS0 (a, b), clay body PS5 (c, d), clay body PS15 (e, f).

ufacturing. It was found cellulose fibres stabilize drying and firing shrinkage and reduce shrinkage values. Burnt cellulose fibres and decomposition of calcium carbonate during the firing change the microstructure of the clay body by developing open porosity, which has an effect on physical and mechanical properties and frost resistance of clay bodies.

Tests proved that 5% of PS additive can be added to the moulding compound of clay bricks fired at 900 °C temperature. Such clay brick has the following values: density 1.72 g/m^3, shrinkage 7.6%, compressive strength 14.0 MPa, water absorption 18%, total open porosity 28%, and frost resistance (determined by repeated freezing and thawing) more than 25 cycles. A bigger amount of paper sludge from 5 to 15% can be added to clay bricks fired at 1000 °C temperature. According to test results, such clay bodies have the following characteristics: density 1.65–1.86 g/m^3; shrinkage 8.0–9.2%, compressive strength 12.0–22.0 MPa, water absorption 11.2–15.3%, total open porosity 23.4–35.0%, and frost resistance (determined by repeated freezing and thawing) more than 25 cycles. Higher PS additive content has a negative effect on clay body's mechanical properties and frost resistance.

References

[1] M.C. Monte, E. Fuente, A. Blanco, C. Negro, Waste management from pulp and paper production in the European Union, Review. Waste Manag. 29 (2009) 293–308.

[2] M.R. Boni, L. D'Aprile, G. De Casa, Environmental quality of primary paper sludge, J. Hazard. Mater. B108 (2004) 125–128.

[3] S. Maschio, E. Furlani, G. Tonello, N. Faraone, E. Aneggi, D. Minichelli, L. Fedrizzi, A. Bachiorrini, S. Bruckner, Fast firing of tiles containing paper mill sludge, glass cullet and clay, Waste Manage. 29 (2009) 2880–2885.

[4] S. Cordiner, G. De Simone, V. Mulone, Experimental–numerical design of a biomass bubbling fluidised bed gasifier for paper sludge energy recovery, Appl. Energy 97 (2012) 532–542.

[5] A. Demirbas, Progress and recent trends in biofuels, Prog. Energy Combust. Sci. 33 (1) (2007) 1–18.

[6] H.Y. Yu, S.D. Kim, J.M. Lee, H.K. Lee, Kinetic studies of dehydration, pyrolysis and combustion of paper sludge, Energy 27 (5) (2002) 457–469.
[7] L. Yanfen, M. Xiaoqian, Thermogravimetric analysis of the co-combustion of coal and paper mill sludge, Appl. Energy 87 (11) (2010) 3526–3532.
[8] H.S. Wong, R. Barakat, A. Alhilali, M. Saleh, C.R. Cheeseman, Hydrophobic concrete using waste paper sludge ash, Cem. Concr. Res. 70 (2015) 9–20.
[9] S. Sajad Ahmad, M.I. Malik, M.B. Wani, R. Ahmad, Study of concrete involving use of waste paper sludge ash as partial replacement of cement, J. Eng. 3 (11) (2013) 06–15.
[10] J. Pera, A. Amrouz, Development of highly reactive metakaolin from paper sludge, Adv. Cem. Based Mater. 7 (2) (1998) 49–56.
[11] I. Vegas, J. Urreta, M. Frías, R. García, Freeze–thaw resistance of blended cements containing calcined paper sludge, Constr. Build. Mater. 23 (8) (2009) 2862–2868.
[12] P. Banfill, M. Frias, Rheology and conduction calorimetry of cement modified with calcined paper sludge, Cem. Concr. Res. 37 (2) (2007) 184–190.
[13] R. García, R. Vigil de la Villa, I. Vegas, M. Frías, M.I. Sánchez de Rojas, The pozzolanic properties of paper sludge waste, Constr. Build. Mater. 22 (7) (2008) 1484–1490.
[14] R. Vigil de la Villa, M. Frías, M.I. Sánchez de Rojas, I. Vegas, R. García, Mineralogical and morphological changes of calcined paper sludge at different temperatures and retention in furnace, Appl. Clay Sci. 36 (4) (2007) 279–286.
[15] M. Frias, M.I. Sanchez de Rojas, O. Rodriguez, R. Garcia, R. Vigil de la Villa, Characterisation of calcined paper sludge as an environmentally friendly source of metakaolin for manufacture of cementitious materials, Adv. Cem. Res. 20 (1) (2008) 23–30.
[16] M. Frías, O. Rodríguez, M.I. Sánchez de Rojas, Paper sludge, an environmentally sound alternative source of MK-based cementitious materials. A review, Constr. Build. Mater. 74 (15) (2015) 37–48.
[17] M. Moisés Frías, O. Rodríguez, I. Vegas, R. Vigil, Properties of calcined clay waste and its influence on blended cement behavior, J. Am. Ceram. Soc. 91 (4) (2008) 1226–1230.
[18] J. Péra, J. Ambroise, M. Chabannet, Transformation of wastes into complementary cementing materials, in: V.M. Malhotra, (Ed.), Seventh CANMET/ACI/JCI intern. Conference on fly ash, silica fume, slag and natural pozzolans in concrete 2001; SP199: 459–75;
[19] Ahmadi W. Al-Khaja, Utilisation of paper waste sludge in the building construction industry, Resour. Conserv. Recycl. 32 (2001) 105–113.
[20] S.P. Raut, R. Sedmake, S. Dhunde, R.V. Ralegaonkar, S.A. Mandavgane, Reuse of recycle paper mill waste in energy absorbing light weight bricks, Constr. Build. Mater. 27 (1) (2012) 247–251.
[21] C.T. Liaw, H.L. Chang, W.C. Hsu, C.R. Huang, A novel method to reuse paper sludge and co-generation ashes form paper mill, J. Hazard. Mater. 58 (1998) 93–102.
[22] S. Kim, H.J. Kim, J.C. Park, Application of recycled paper sludge and biomass materials in manufacture of green composite pallet, Resour. Conserv. Recycl. 53 (12) (2009) 674–679.
[23] C.M.F. Vieira, R.M. Pinheiro, R.J.S. Rodriguez, V.S. Candido, S.N. Monteiro, Clay bricks added with effluent sludge from paper industry: technical, economical and environmental benefits, Appl. Clay Sci. 132–133 (2016) 753–759.
[24] G. Goel, A.S. Kalamdhad, An investigation on use of paper mill sludge in brick manufacturing, Constr. Build. Mater. 148 (1) (2017) 334–343.
[25] M. Sutcu, J.J.C. Dia, F.P.A. Rabanal, O. Gencel, S. Akkurt, Thermal performance optimisation of hollow clay bricks made up of paper waste, Energy Build. 75 (2014) 96–108.
[26] M. Sutcu, S. Akkurt, Utilisation of recycled paper processing residues and clay of different sources for the production of porous anorthite ceramics, J. Eur. Ceram. Soc. 30 (8) (2010) 1785–1793.
[27] J.A. Cusido, L.V. Cremades, C. Soriano, M. Devant, Inogracion of paper sludge in clay brick formulation: ten yers of industrial experience, Appl. Clay Sci. 108 (2015) 191–198.
[28] F. Furlani, G. Tonello, S. Maschio, E. Aneggi, D. Minichelli, S. Bruckner, E. Lucchini, Sintering and characterisation of ceramics containing paper sludge, glass cullet and different types of clayey materials, Ceram. Int. 37 (2011) 1293–1299.
[29] V. Mymrin, W. Klitzke, K. Alekseev, R.E. Catai, A. Nagalli, Luis dos Santos, R. Izzo, C.A. Romano, Red clay application in the utilisation of paper production sludge and scrap glass to fabricate ceramic materials, Appl. Clay Sci. 107 (2015) 28–35.
[30] LST EN 772-13:2003. Methods of test for masonry units – Part 13: Determination of net and gross dry density of masonry units (except for natural stone), p. 18.
[31] LST EN 772-21:2011. Methods of test for masonry units – Part 21: Determination of water absorption of clay and calcium silicate masonry units by cold water absorption, p.40.
[32] LST EN 772-1:2011. Methods of test for masonry units – Part 1: Determination of compressive strength, p. 17.
[33] LST EN 15935:2012. Sludge, treated biowaste, soil and waste – Determination of loss on ignition, p. 23.
[34] LST EN 13041:2012. Soil improvers and growing media – Determination of physical properties – Dry bulk density, air volume, water volume, shrinkage value and total pore space.
[35] LST 1985:2006. Determination of freeze and thaw resistance of clay masonry units, p. 22.
[36] I. Demir, M. Serhat Baspınar, O. Orhan, Utilisation of kraft pulp production residues in clay brick production, Build. Environ. 40 (11) (2005) 1533–1537.
[37] A. Mancuso, Degree thesis. University of Modena and Reggio Emilia. Tutor Lancellotti I, Andreola F. 2009.
[38] L. Barbieri, F. Andreola, I. Lancellotti, R. Taurino, Management of agricultural biomass wastes: preliminary study on characterisation and valorisation in clay matrix bricks, Waste Manage. 33 (2013) 2307–2315.
[39] EN 771-1:2011+A1:2015. Specification for masonry units – Part 1: Clay masonry units, p. 44.
[40] M. Sutcu, S. Akkurt, The use of recycled paper processing residues in making porous brick with reduced thermal conductivity, Ceram. Int. 35 (7) (2009) 2625–2631.
[41] R.M. Pinheiro, C.M.F. Vieira, R.S. Rodriguez, S.N. Monteiro, Recycling of waste. From the paper production into red ceramic, Materia 13 (1) (2008) 220–227.