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USE OF TANNERY SLUDGE IN CLAY BRICK MANUFACTURING

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Abstract

The paper analyses the possibilities of recycling tannery sludge (TS) in clay brick manufacture. The physico-mechanical properties and microstructure of clay brick and cement mortars vary depending on TS content in the mix. 2.5 %–15.0 % TS (by weight) was added to clay bricks fired at 1000 °C temperature and maintained at maximum heat for 1 hour. The tests revealed that 2.5 % TS addition had a positive effect on physical and mechanical properties of clay brick: reduce drying and firing shrinkage, reduce water absorption, and increase compressive strength. Chromium leaching values in clay brick (2.5 % TS) were found not to exceed the limit values set forth in 2003/33/EC.

Key words: chromium (III), clay brick, recycling, tannery sludge, waste

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1. Introduction

The tanning industry is a pollution-intensive industry worldwide because it uses a large number of chemical and organic substances (sodium carbonate, chromium sulphate, vegetable and synthetic extracts (e.g. phenols)), various solvents and acids, heavy metals etc. Although hides can be tanned using different tanning agents, about 90% of world tanneries use chromium salts (most commonly chromium sulphate) in their tanning processes (Houshyar et al., 2012; Kiliç et al., 2011; Shakir et al., 2012; Torras et al., 2012). During the tanning process, a part of chromium salts react with raw materials while the other part remains in tanning tubs from where they are transported to tannery sludge storage sites (Basegio et al., 2002; Cassano et al., 1996). Basegio et al. (2002) state that only about 60% of chromium salts react with raw skins in the tanning process. Sludge containing chromium is classified under code 04 01 06 (EC Directive, 2000).

Tannery sludge is not classified as hazardous waste in the List of Wastes. Nevertheless, the sludge generated by leather industry is hard to process/utilize and it pollutes the environment. Therefore, researchers keep looking for ways how to reduce, neutralize/utilize the chromium rich tannery sludge from leather industry (Alibardi and Cossu, 2016; Aravindhan et al., 2004; Bien et al., 2017; Kanagaraj et al., 2006; Meshram et al., 2009; Mathuriya, 2014; Namasivayam and Höll, 2004; Tahir and Naseem, 2007; Wistalska and Sobik-Szoltysek, 2019).

Chromium rich tannery sludge removal methods applied by leather industry depends on sludge composition, especially on chromium content in the sludge. The selection of recycling/utilization possibilities shall be evaluated in each specific case with respect to the normative documents applicable in the country. Table 1 illustrates the total allowable chromium (III) levels in industrial effluent to sewer and ground waters in different countries (limit values are given only for Cr^{3+}) (Alves at al., 1993).

In Lithuania the maximum levels of chrome (total) in the effluent discharged to sewer is 2.0 mg/L and 0.5 mg/L to the natural environment (OM, 2006). In Lithuania leather processing companies may not

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discharge sewage sludge to municipal waste water treatment plants because chromium (III) concentration in the tannery sludge exceeds the limit values set forth in the normative documents (OM, 2006, 2015). Sludge classification by the concentration of heavy metals is significant for the assessment of further sludge utilization possibilities and treatment methods.

Table 1. Total allowable chromium (III) level in industrial effluent to sewer and ground waters by countries (Alves et al., 1993)

Country	***Total allowable chromium discharge to environment (mg/L)***	
	Ground water	***Sewer***
Austria	4.0	15.0
Brazil	0.5	0.5
Denmark	2.0	2.0
Spain	2.0	4.0
France	1.0	-
Greece	0.5	0.5
The Netherlands	0.05	2.0
Italy	2.0	4.0
New Zealand	-	5.0-50.0
Poland	-	0.5
Portugal	2.0	2.0
United Kingdom	2.0	5.0-10.0
Switzerland	2.0	2.0

Literature sources (ABNT NBR 10004, 1987; USEPA, 1998) reveal that this sludge can be regarded as toxic and hazardous due to the levels of chromium compounds and other pollutants. Authors (Fernandez-Sampere et al., 1997) claim that in leather processing plants the humidity of tannery sludge may reach 56.4 % and dry sludge pH may range from 3.3-4.9. Major elements present in the sludge are Na, Si, S, Ca, Cl, Cr, Mg, P, Al, Ti, K.

It is widely known that thermal treatment of this type of waste containing Cr (III) may produce $Cr_2(SO_4)_3$, $CrOCl_2$, and Cr_2O_3 , which subsequently create possibilities to the formation of Cr (VI) (Chen et al., 2003; Mao et al., 2015; Skrypski-Mantele and Bridle, 1995). It is also known that Cr (VI) is a carcinogen and is mobile, whereas Cr (III) is less toxic and relatively immobile (Avudainayagam et al., 2003; Abreu and Taffoli, 2009; Alibardi and Cossu, 2016; Ohtake, 1992). Warrier et al. (1995) indicated that dried tannery sludge can be stabilized by starved-air combustion at 800°C in order to avoid Cr^{3+} and Cr^{6+} conversion. Afterwards, the fired sludge can be mixed with fly ash, Portland cement and gypsum. Authors produced masonry blocks with the strength of 83-156 kg/cm^2 and proved that in this way Cr^{3+} was stabilized in cement matrix. Abreu and Taffoli (2009) found the way to reduce the content of chromium (III) and iron (III) in treated tannery sludge through appropriate selection of formation temperature and pH, and by adding cement. This tannery sludge neutralization method is rather cheap and sufficiently effective.

Basegio et al. (2002) specified that tannery sludge can be safely used in ceramic product manufacturing. They found that up to 10 % of tannery sludge can be added to the molding compound that is fired at 1000°C-1080°C temperature. The obtained product has sufficient properties (water absorption, compressive strength) to be used in civil engineering. Thus, tannery sludge can be safely utilized in ceramic bodies. Warrier et al. (1995) stated that up to 15% of tannery sludge can be utilized in ceramic bodies when appropriate firing parameters are selected and controlled. There is also evidenced that tannery sludge added at a rate of 10% increases the porosity of ceramic bodies, reduces freeze-thaw resistance and flexural strength (Giugliano and Paggi, 1985). The addition of 10%-40% tannery sludge to molding compounds that are fired at 950°C -1050°C temperature reduces the density and compressive strength of ceramic bodies and increases porosity (Houshyar et al., 2012). Yang et al. (2014) proposed to add 8% of tannery sludge to the mix of coal (10%) and clay and fire the moulding compound at 950°C temperature, keeping the mould at the highest temperature for 4 h. A higher, up to 12%, content of tannery sludge has a negative effect on water absorption, density, shrinkage, and compressive strength. Tests have proved that clay bricks containing 10% of tannery sludge and 5% of clinoptiolite fired at 800°C temperature have similar characteristics to those of standard bricks fired at 920°C temperature (Köseoglu et al., 2017). Chromium-rich tannery sludge can be also used as a ceramic pigment in conventional glaze compositions (Abreu and Toffoli, 2009; Muñoz et al., 2004). Juel et al. (2017) specified that tannery sludge can be used in ceramic product manufacturing. They found that from 10 % up to 40 % of tannery sludge can be added to the molding compound that is fired at 900-1000°C temperature. Clay bricks containing sludge, met criteria of Bangladesh and ASTM, as a construction material, after demonstrated to have strength ranging from 10.98 MPa to 29.61 MPa and water absorption from 7.2% to 20.9%.

One medium size company in Lithuania can generate from 15 to 20 tons of tannery sludge per year. Our leather manufacturers face a serious problem related to the utilization of chromium (III) rich tannery sludge. Environment pollution undermines the companies' image. Landfills accept this type of sludge, however the costs of dumping the sludge are high and keep increasing. Besides, the dumping of such sludge in landfill is not a preventive measure that would have a positive effect on the country's ecological balance. Therefore new economically sound methods for recovery, recycling, and utilization of such waste must be sought and innovative environmentally friendly technologies should be used.

The main goal of this paper is to evaluate the possibilities of recycling tannery sludge from leather industries in clay brick manufacturing. It also aims to evaluate the effect of tannery sludge on physical and mechanical properties, porosity, microstructure and mineral composition of clay bricks. Another aim is to assess the ecological aspects of such recycling, i.e. to evaluate the possibilities of chrome leaching from clay bricks. It is the first study in Lithuania testing the incorporation of chromium-rich tannery sludge in fired clay bricks.

2. Material and methods

Tests with tannery sludge (TS) from a leather processing plant containing a large amount of chromium (III) are described in this paper. The sludge is light blue, the humidity is about 80%, non-dried sludge has a specific unpleasant pungent odor. The sludge was dried at 105°C±5°C temperature and crushed afterwards. The clay for brick moulding was dried at 100 °C±5 ºC temperature, crushed and sieved through 0.63 mm sieve. The sand was dried and sieved through 1.25 mm sieve.

Molding compounds presented in Table 2 were used to make 70×70×70 mm size clay specimens to determine mechanical properties (compressive strength) and freeze-thaw resistance, and 60×30×18 mm size clay specimens to determine physical properties (density, water absorption, drying shrinkage and firing shrinkage, initial rate of absorption and total open porosity). The results of clay-sand-tannery sludge mixtures indicate that the value of plasticity index decreases with the increase of tannery sludge content in the mixture (Table 2). Later the specimens were dried at 105°C±5°C temperatures and fired at 1000 °C temperature by keeping them at the highest firing temperature for 1 hour. The firing schedule was selected and used with respect to the standard firing schedule used in one local brickyard.

Table 2. Clay brick compound compositions and formation parameters

Raw materials and parameters	***Mixture composition (% by weight)***				
	TS0	***TS2.5***	***TS5***	***TS10***	***TS15***
Clay	90	85	80	75	70
Sand	10	10	10	10	10
Tannery sludge	0	2.5	5.0	10	15
Liquid limit, %	37	37	39	40	40
Plastic limit, %	20	20	23	26	27
Plasticity index	17	17	16	14	13

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. X-ray analysis was performed using a diffractometer DRON-7 X-ray (Co anode and Fe filter). Differential thermal analysis was done by means of derivatograph Q 1500D. Microstructure analysis was done by the scanning electron microscope SEM JOEL JSM-7600F with resolution of 1.5 nm and magnification from 25 to 10 000 times. 4.0 kV voltage was used for the tests and the surface of tested specimens was lined with gold. In accordance with LST EN 12457-2:2003, analysis of extractable materials was conducted and in accordance with LST EN 15934:2012, humidity of TS was determined. Amount of chromium in the eluate was reasoned using Buck Scientific 2010 VGP spectrometer with air-acetylene flame and atomic absorption spectral analysis was applied. In accordance with LST EN 12457-2:2003, the eluate was prepared for chromium leaching tests. Leaching values of Cr^{3+} were estimated opposed to the limit values specified in 2003/33/EC.

Physical and mechanical properties of fired molding compounds were determined by the following standard testing methodologies: density was determined in accordance with LST EN 772-13:2003; water absorption was determined in accordance with LST EN 772-21:2011, compressive strength was determined in accordance with LST EN 772-1:2011. The durability of specimens was evaluated as resistance to freezing and thawing cycles in accordance with LST 1985:2006. The drying shrinkage and firing shrinkage were calculated from Eqs. (1-2).

$$L = \left(\frac{L_0 - L_1}{L_0}\right) \cdot 100 \quad (\%) \tag{1}$$

$$L_B = \left(\frac{L_0 - L_2}{L_0}\right) \cdot 100 \quad (\%) \tag{2}$$

where: L_0 is distance between markings in the wet specimen, mm; L_1 is distance between markings in the dried specimen, mm; L_2 is distance between markings in the fired specimen, mm.

3. Results and discussion

3.1. Characterization of raw materials

The results of the elution tests and other properties of the sludge are presented in Table 3.The results show that tannery sludge contains chlorides, sulphates, fluorides, heavy metals. Tannery sludge humidity reaches 78.4%, pH is 7.9, total organic carbon is 0.66 %. Tannery sludge had the bulk density of 0.46 g/cm^3, particle density of 1.67 g/cm^3, and specific surface area of 16700 cm^2/g. X-Ray test results of tannery sludge showed that $CaCO_3$ and SiO_2 minerals are mainly present and contains a big amount of amorphous phase. Additionally, small amounts of chromium oxide and calcium sulphite hydrate were found (Fig. 1). Tannery sludge microstructure analysis revealed that the sludge the sludge, containing different shaped articles is amorphous. Found particles are shaped round; contain an uneven surface and a loose structure. The size of larger particles is ~ 0.10 μm (Figs. 2a, b). Energy Dispersive X-Ray Analysis (EDS) revealed that the particles mainly consist of the following elements: Cr - 58.47%, O - 23.49%, C – 7.62%, Ta - 3.19%, Ca - 2.99%, Mg - 2.32%, Zn - 1.92%.

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

Parameter	***Results***
pH	7.9
Dry matter	78.4 (%)
Chlorides	3688 (mg/kg)
Sulphates	6288 (mg/kg)
Fluorides	0.80 (mg/kg)
Cadmium	<0.001 (mg/kg)
Lead	<0.001 (mg/kg)
Chrome	0.416 (mg/kg)
Nickel	<0.052 (mg/kg)
Copper	0.208 (mg/kg)
Zinc	0.544 (mg/kg)
Barium	0.152 (mg/kg)
Selenium	<0.001 (mg/kg)
Stibium	<0.001 (mg/kg)
Arsenic	0.024 (mg/kg)
Mercury	0.001 (mg/kg)
Dry residue	15728 (mg/kg)
Molybdenum	0.024 (mg/kg)
Dissolved organic carbon	42.4 (mg/kg)
Total organic carbon	0.66 (%)

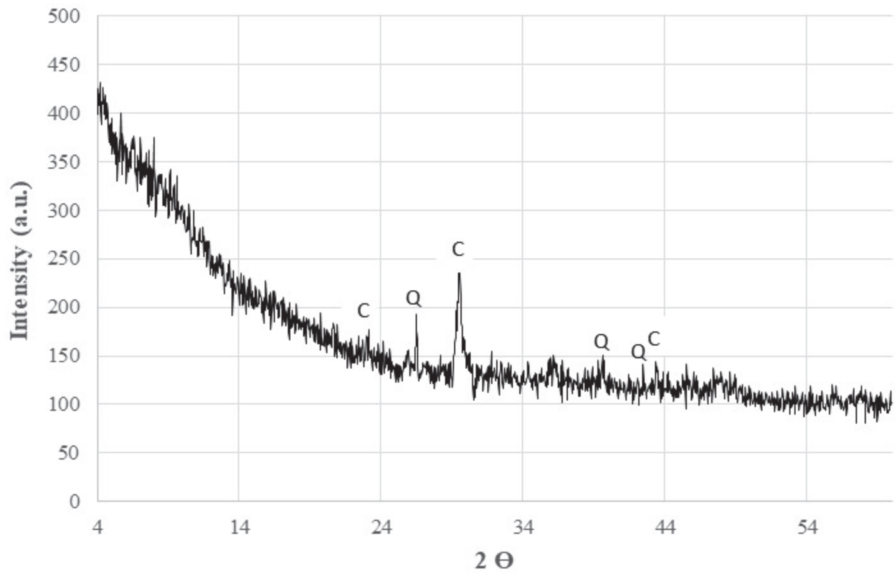
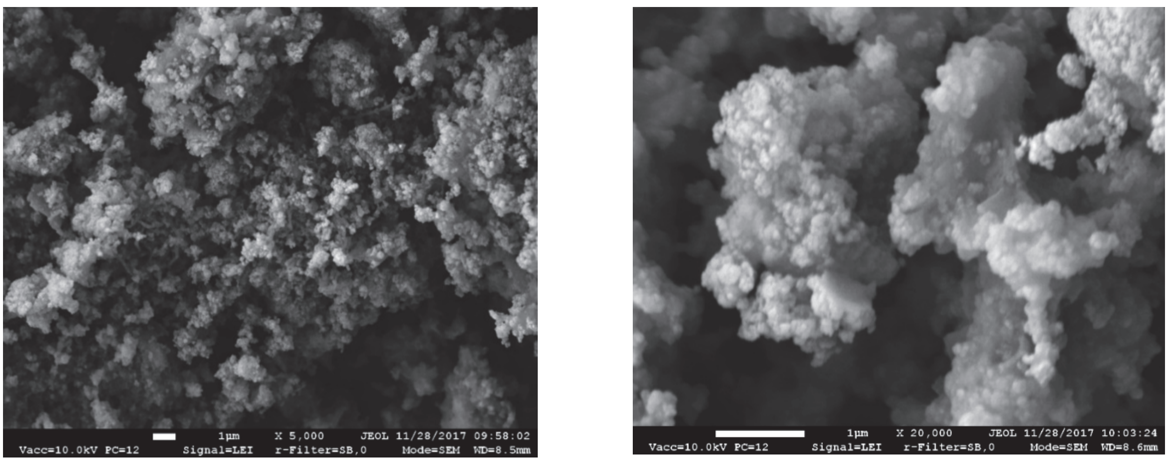


Fig. 1. X-ray diffraction patterns of tannery sludge: C - $CaCO_3$, Q - SiO_2



(a) (b)

Fig. 2. SEM images of tannery sludge: (a) represent × 5000; (b) represent ×20000

DTA analysis of tannery sludge revealed (Fig. 3) a slight endothermic effect in 70°C-220°C temperature range related with evaporation of humidity from the sludge. Loss on ignition in the temperature up to 220°C reaches 12%. The exothermic peak starts at ~250°C temperature and stops suddenly at 380°C temperature. The maximum exothermic effect is observed at 320°C temperature and is related to decomposition of organic matter in tannery sludge. The loss on ignition at 380°C temperature reaches 30%, and at 1000 °C temperature it increases to 39%.

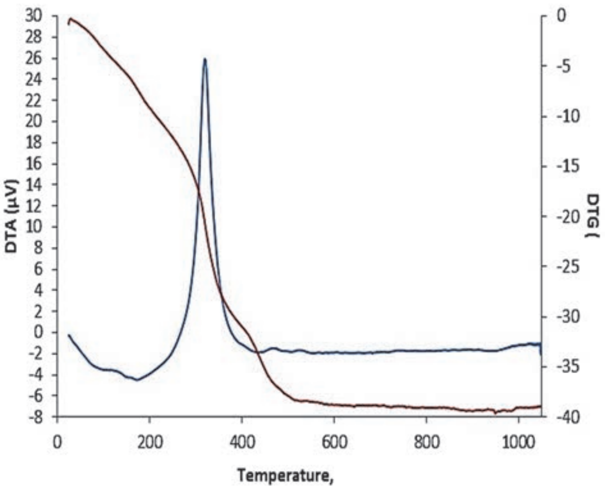


Fig. 3. DTA, DTG diagram of tannery sludge

Chemical composition tests of the clay showed that it contained 63.56% of SiO_2, 19.53% of Al_2O_3+TiO_2 , 6.55% of coloring Fe_2O_3 oxides, also 1.38% of CaO, 2.68% of MgO, 0.18% of Na_2O, 5.56% of K_2O, 0.56% of SO_3. Clay is a dispersion by particle size distribution. The amounts of particles by size are as follows: 0.2% of >0.5 mm particles, 1.8% of 0.5-0.063 mm particles, 22.4% of 0.063-0.01 mm particles, and 75.8% of < 0.01 mm particles. The natural humidity of clay is 18.6%, density is 2.42 kg/m^3, and plasticity is 19.

Chemical composition of quartz sand used to produce clay brick specimens was as follows: >98.5% SiO_2, < 0.05% Fe_2O_3, < 0.60% Al_2O_3.

3.2. Effect of tannery sludge addition on clay brick properties, mineral composition, and microstructure

Chromium-rich tannery sludge was found to reduce the drying shrinkage and firing shrinkage of the specimens. The drying shrinkage of clay brick TS0 was 7.8%, and shrinkage after firing at 1000°C temperature was 11.5%. Drying shrinkage and firing shrinkage of all clay bricks containing tannery sludge were lower compared to TS0 clay brick. The lowest shrinkage values were observed in specimens containing 2.5% of tannery sludge: the drying shrinkage was 4.9% and the firing shrinkage was 5.4%. Drying shrinkage and firing shrinkage increased with higher content of tannery sludge in molding compounds. In specimens with 15% of tannery sludge the drying shrinkage increased to 5.8% and shrinkage after firing at 1000 °C increased to 8.0% (Fig. 4).

Presumably, the drying shrinkage is caused by the uniform distribution of sludge particles, which form a framework in the molded specimen. This framework prevents the intensive attachment of clay particles. The sludge seems to stabilize the drying process.

Organic matter is removed from TS in the firing process (Fig. 3) and $CaCO_3$ decarbonization process during firing also reduces the shrinkage of the ceramic body. It is known (Tahiri et al., 2007) that at high temperature the amount of Cr^{3+} may increase even up to 35.8%. The increase of Cr^{3+} content in the ceramic body also lowers the firing shrinkage.

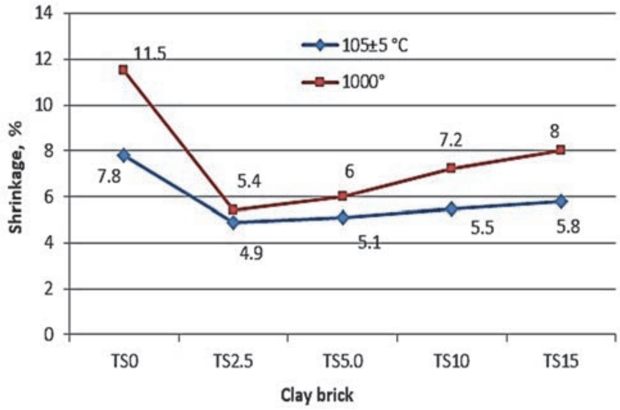


Fig. 4. Ceramic body shrinkage after drying at 105 ±5°C and firing at 1000 °C temperature

Physical and mechanical properties of clay brick are presented in Table 4. Clay bricks containing 2.5 % of tannery sludge have the density of 2.0 g/cm^3, which is close to that of the reference ceramic body, and the compressive strength increases up to 35 MPa. The highest content of TS of 15% reduced the clay brick density by 20% (compared to TS0 clay brick) down to 1.75 g/cm^3 and compressive strength down to 16 MPa. The decrease of density and compressive strength with higher than 2.5 % addition of tannery sludge may be related with the changes of micro and macro structures of specimens during firing. Additional structure of pores and capillaries is formed after the ignition of organic matter in the ceramic body (Fig. 3). It was confirmed by the tests of water absorption, sorptivity, and total open porosity. The content of water absorbed by ceramic bodies usually depends on the volume, dimensions and distribution of pores. Sorptivity indicates the presence of interconnected pores, capillaries and voids in the ceramic body. Water absorption, sorptivity, and total open porosity values increase with higher than 2.5% addition of tannery sludge.

A positive effect of 2.5% of tannery sludge on water absorption and compressive strength indicates that a clay brick has a sufficiently dense framework where a small amount of pores of different size, shape and diameter are distributed. A TS2.5 clay brick was found to have a water absorption value of 6.9%. Total open porosity is another property that correlates strongly with water absorption. A TS2.5 clay brick was found to have the total open porosity of 18.5%.

Water absorption is an important property that has an effect on freeze-thaw resistance of ceramic bodies. Freeze-thaw resistance of a clay brick increases with lower water absorption and, obviously, such products will also have better durability characteristics. Some authors argues that the highest water absorption value may not exceed 26%, while other authors say that 30% is the limit (Mačiulaiti, 1994; Phonphuak, 2013). No water absorption requirements are set forth in the European standard LST EN 771-1:2011+A1:2015 (Specification for masonry units - Part 1: Clay masonry units). Manufacturers must declare water absorption values of ceramic masonry units determined in accordance with 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 C373-14 the minimum water absorption values of these units range from 8% to 22%. Clay bricks containing 5%-15% tannery sludge have water absorption value of 8.1-11.6%, initial rate of absorption of 0.7- 0.98 ($kg/m^2 \cdot min$), and total open porosity of 20%-25%.

Freeze-thaw resistance of clay bricks was tested next. The resistance of specimens to freezing and thawing cycles was tested by visual evaluation of damage types. Tests of clay brick freeze-thaw resistance revealed that TS0, TS2.5 and TS5 resisted 100 freezing and thawing cycles without noticeable damage. According to LST EN 771-1:2011+A1:2015 and LST EN 1985:2006 requirements, such products can be used in averagely aggressive environments (freeze-thaw resistance class F.1), i.e. in structures protected from direct exposure to environmental impact. Signs of damage were observed on clay bricks containing 10% and 15% of tannery sludge after 89 and 76 of freezing and thawing cycles.

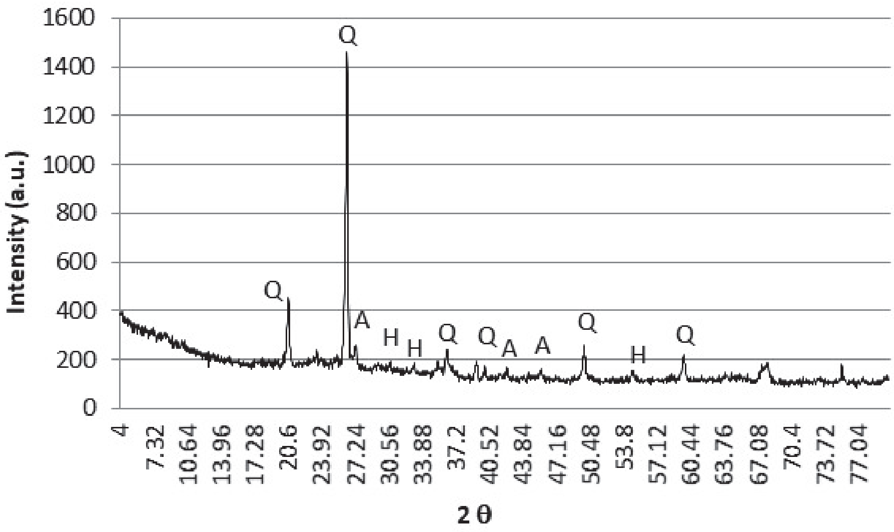
Tannery sludge was found to have an effect on the color of ceramic bodies during the tests. The change in color indicates that TS addition actively participates and influences physical and chemical processes during clay brick firing. As seen in Fig. 5, TS0 specimen is light brown. Products of this color are usually obtained from low-melting clays. With 2.5 % tannery sludge addition the specimen color becomes darker. The higher is the tannery sludge content in the ceramic body, the darker is its color. Literature sources (Chmielewska et al., 2010) state that chromium is one of the elements having an influence on the color of manufactured items and tannery sludge changes the color of the final product (Ariful et al., 2017). There is test evidence that tannery sludge containing Cr^{3+} is an addition with intensive coloring effect. Even a small amount up to 2.5% of tannery sludge makes the color of a ceramic body darker. Clay brick specimens (TS15) containing the highest 15% content of tannery sludge significantly differs by color from the ceramic body without tannery sludge addition. The intensity of the color comes from chromium present in the sludge.

Fig. 5. Colours of laboratory-made ceramic bodies made (ceramic bodies from right to left: TS2.5, TS5, TS10, TS15)

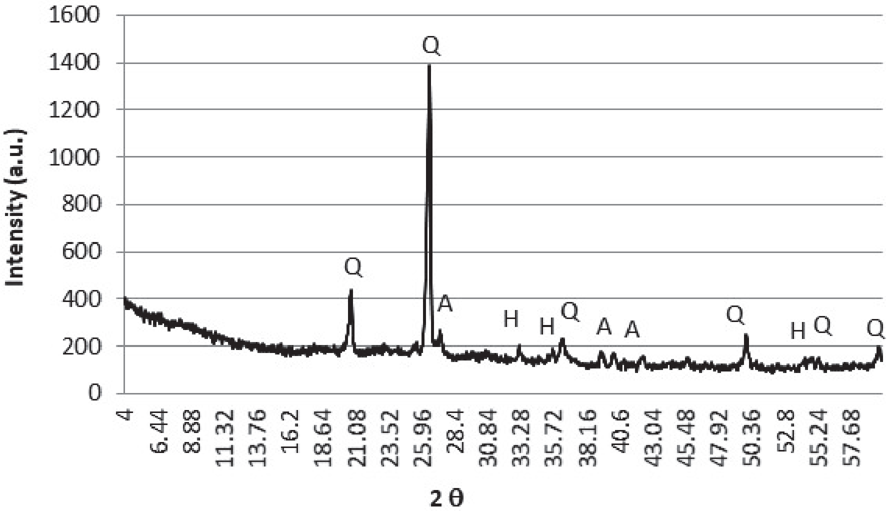
Mineral composition tests revealed that ceramic bodies containing 2.5% of tannery sludge have a mineral composition similar to that of a ceramic body without any addition (Fig. 6). X-ray diffraction patterns revealed mineral characteristic of ceramic bodies: quartz, hematite, anortite. X-ray diffraction patterns of clay bricks containing a higher amount of tannery sludge revealed peaks of Cr_2O_3 and $Ca(CrO_4)_3 \cdot O_{0,5}$. It means that with higher chromium-rich tannery sludge content and at higher firing temperature the amounts of chromium and its compounds in the ceramic body significantly increase. Literature sources (Tahiri et al., 2007) state that the amount of chromium may increase up to 35.8 % with the temperature increase from 500°C to 1100°C.

Microstructure tests showed that TS0 and TS2.5 have a very similar microstructure. The microstructure is sufficiently dense with low numbers of pores prevailing. The pores are small and evenly distributed along the entire ceramic body. The obtained results correlate with the obtained results of physical and mechanical properties tests (Fig. 7 a).

The microstructure changes with the addition of 10% and 15% of TS and the prevalence of coarse unevenly distributed pores is observed (Figs. 7c-d). The liquid phase amount is insufficient to fill up the majority of pores. Previous tests (Table 4) showed that these bricks have high water absorption and total open porosity values. EDS tests of clay bricks revealed (Table 5-6) that all ceramic bodies contain O, Mg, Al, Si, K, Fe, and Ca elements. Chromium is an additional element found in clay bricks with tannery sludge. Chromium and calcium content increases with higher tannery content in the brick, but the amounts of Si, O, Al, Fe decrease.



(a)



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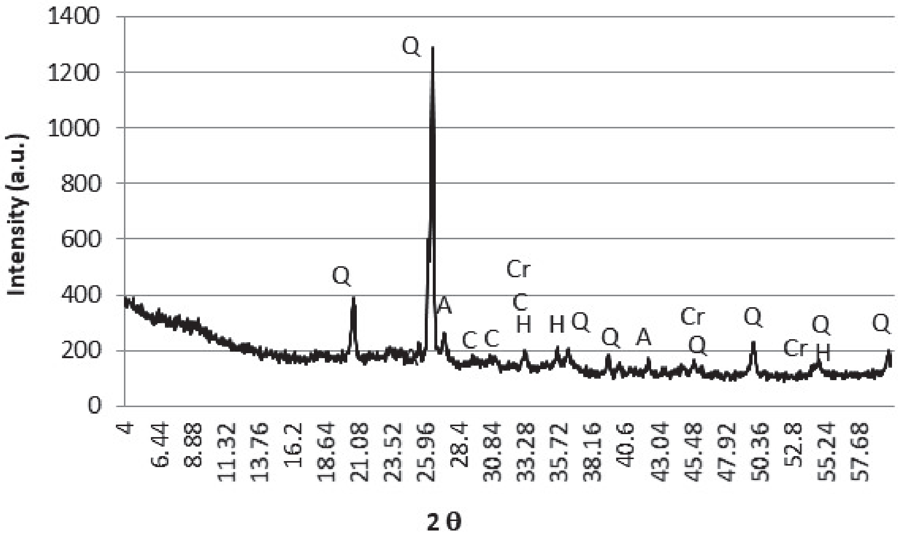

(c)

Fig. 6. X-ray diffraction analysis of clay brick: (a) TS0; (b) TS2.5; (c) TS5.0 (Q - quartz, H - hematite, A - anortite, C - $Ca(CrO_4)_3{\cdot}O_{0,5}$, Cr - Cr_2O_3)

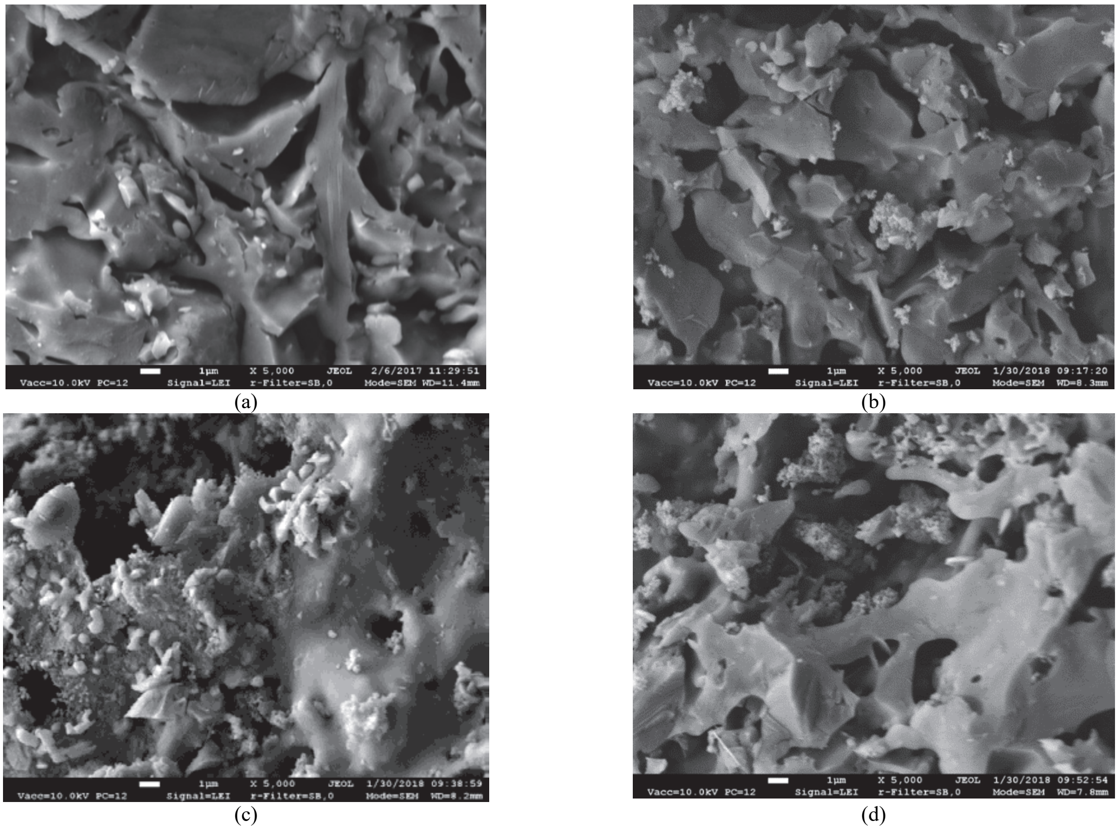

Fig. 7. Microstructure of clay brick: a) TS0; b) TS2.5; c) TS10; d) TS15

Table 4. Physical and mechanical properties of clay body

Properties	*Clay brick*				
	TS0	*TS2.5*	*TS5*	*TS10*	*TS15*
Density, g/cm^3	2.2±0.002	2.0±0.0015	1.88±0.0025	1.8±0.003	1.75±0.0034
Compressive strength, MPa	30.0±0.9	35.0±1.0	20.5±1.2	17.0±1.0	16.0±1.3
Water absorption, %	7.3±1.1	6.9±1.0	8.1±1.2	10.8±1.1	11.6±1.3
Initial rate of absorption, (kg/m^2·min)	0.6±0.04	0.48±0.027	0.7±0.048	0.86±0.045	0.98±0.051
Total open porosity, %	19.4±1.64	18.5±1.1	20.0±1.7	23.2±2.1	25.0±2.4

Table 5. EDS spectrum of fired clay brick

Clay brick	*Elemental analysis (mean)*							
	O	*Mg*	*Al*	*Si*	*K*	*Fe*	*Ca*	*Cr*
TS0	46.44	2.97	10.46	25.02	4.59	9.83	0.68	-
TS2.5	45.29	3.05	10.01	24.63	5.57	8.58	0.97	1.89
TS5	39.81	3.47	9.56	23.39	6.81	6.91	3.96	5.09
TS10	32.37	3.29	7.08	20.88	7.47	6.74	7.88	14.28
TS15	21.66	3.66	4.71	16.77	10.19	5.40	10.04	27.57

Table 6. Tests in chromium leaching from clay brick

Parameters	*Clay brick*				
	TS0	*TS2.5*	*TS5*	*TS10*	*TS15*
Cr, mg/L	< 0.2	1.9	4.7	9.4	13.5

3.3. Tests in chromium leaching from clay brick

To use tannery sludge in clay brick manufacture, the leaching of chromium must not exceed the limit values. According to Decision 2003/33/EC the chrome leaching from non-hazardous waste may not exceed 2.5 mg/L and according to (USEPA, 1996) the chrome content may not exceed 5.0 mg/L. The tests revealed that the leaching of chromium from clay bricks containing 2.5%-15.0% of tannery sludge is higher and does not meet the requirements of the normative document (EC Directive, 2003). However, according to the normative document (USEPA, 1996) the leaching of chromium from specimens TS2.5 does not exceed the limit values and tannery sludge can be used in clay brick manufacture. Authors (Ariful et al., 2017; Liew et al., 2014) found that chromium present in tannery sludge can be safely utilized in clay brick matrix as the chrome leaching does not exceed the normative document (USEPA, 1996) requirements. It was also found (Ariful et al., 2017; Verbinnen et al., 2013, 2014) that at higher firing temperatures (up to 900°C-1000°C) the leaching of chromium can be lower compared to the firing at lower temperatures. At higher temperature chromium compounds may form an amorphous phase with SiO_2 (Verbinnen et al., 2013, 2014) or a crystal phase with magnesium chromites (MgCr2O4) (Abreu and Toffoli, 2009; Kavouras et al., 2015; Wei et al., 2005) therefore, chromium compounds can be safely locked in clay brick matrix.

Tests of chromium leaching from clay brick revealed that with the tannery sludge addition of 2.5%. According to a normative document (2003/33/EC), rates of leached chromium does not surpass the limit values of non- hazardous waste (2.5mg/L). Therefore, it can be stated that tannery sludge can be safely recycled in clay brick manufacture.

4. Conclusions

The research was done with the aim to evaluate the possibilities of utilizing tannery sludge by developing and analyzing clay bricks. The test results revealed that 2.5 % of chromium-rich tannery sludge had a positive effect on physical and mechanical properties of clay brick: reduced shrinkage (5.4 %), water absorption (6.9 %), total open porosity (18.5 %), increased compressive strength (35 MPa). Chromium in the mix acted as a pigment of clay bricks. Chromium leaching values in clay brick (2.5 % TS) were found not to exceed the limit values set forth in 2003/33/EC.

Tests of chromium leaching from clay brick revealed that chromium leaching (5.0-15.0 % TS) exceeded the limit values of non-hazardous waste specified in the normative document 2003/33/EC. Therefore, the use of tannery sludge in clay brick manufacture has environmental limitations.

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