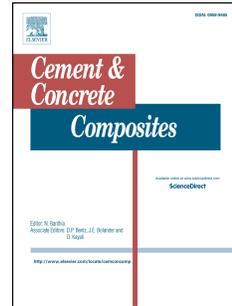


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Smectite clay waste as an additive for Portland cement

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1 SMECTITE CLAY WASTE AS AN ADDITIVE FOR PORTLAND CEMENT

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7 Abstract

8 This study aims at investigating the possibility of using smectite clay waste, generated during the
9 oil bleaching process as an additive for Portland cement. The smectite clay waste consists of
10 montmorillonite, quartz, anorthite, calcium sulfate, and amorphous phase. For the regeneration of
11 this waste, the extraction with hexane and thermal method were chosen. The results showed that the
12 extraction of smectite clay waste with hexane significantly increased the pozzolanic activity of this
13 waste; however, the extracted additive prolonged the induction period of Portland cement hydration,
14 slowing down initial cement hydration, and reduced the compressive strength of Portland cement
15 samples.

16 The thermal activation method achieves the best results by calcining smectite clay waste at 600
17 °C. The calcined additive indicated the strong pozzolanic activity. However, this phenomenon is
18 associated with the formation of the amorphous phase by activating the smectite clay with the
19 sulfuric acid rather than the degradation of the clay minerals during the combustion. The calcined
20 smectite clay waste (CSCW) accelerates the hydration of calcium silicates in the second period of
21 the exothermic reaction. The results of the investigation showed that in samples with the CSCW
22 additive proceed the intense pozzolanic reaction, which can be clearly identified after 28 days of
23 hydration. Up to 15 wt.% of the Portland cement can be replaced by the smectite clay waste
24 additive calcined at 600 °C without reducing the compressive strength of Portland cement samples.

25 **Keywords:** smectite clay waste, Portland cement, hydration, pozzolanic reaction

26 1. Introduction

27 Nowadays one of the most current issues is the environmental pollution caused by industrial
28 waste, which is being produced by large-scale production in various industries. Only a small part of
29 the industrial waste is recycled and its application in other industries is highly important. Various
30 studies have shown [1-5] that some industrial waste can be used by replacing a part of the clinker in
31 cements or a part of the cement in concrete. In this case, when the waste is used as an additive for
32 binding materials, not only the pollution issue is solved but also the cost of Portland cement or
33 concrete is decreased.

34 Oil bleaching is one of the processes applied in oil industry during which the impurities that add
35 colour to the oil are removed and oil is purified from carotenoids, peroxides, chlorophyll, etc. Oils
36 are bleached using a powdered, surfactant materials, which are called bleaching earths. Bleaching
37 earths can composed of up to different types of clay minerals, such as smectite, bentonite,
38 attapulgite and sepiolite. The bleaching process is carried out under vacuum, with temperature in
39 the range of 80-120 °C and contact time ranging from 20-40 min. The dosage of bleaching earth
40 usual is 0.5-2 % by weight. After bleaching, the mix of clay and oil are separated by the vacuum
41 filtration into two phases: oil and clay waste. As a consequence, the oily clay becomes hardly
42 recycled waste. Market demand for activated bleaching earth was predicted to rise to ~9M/year
43 tones until 2022, therefore, the amount of waste produced through the edible oil bleaching process,
44 is considerable [6].

45 The bleaching efficiency of oils is increased when the used clay is activated by using physical or
46 chemical methods. Clay can be activated by acids and regenerated by thermal or alkaline methods.
47 Sulfuric and hydrochloric acids are commonly used for the acid activation because they are cheap
48 and have better clay activation properties than other acids [7].

49 The activation by the acid is a chemical treatment of the clay to increase a specific surface area,
50 porosity and absorption capacity of the clay. During the treatment of smectite clay with inorganic

51 acids, calcium ions are replaced by hydrogen ions and iron / aluminum / magnesium cations are
52 liberated. In this way, the smectite layer structure is changed and the specific surface area and
53 porosity are increased. This leads to a higher absorption capacity of activated clay [8]. Smectite clay
54 waste (SCW) usually contains 20-40% of oils, pigments, free fatty acids, phospholipids and metals.
55 At the end of the bleaching process, the temperature of the clay is 80-120 °C, so absorbed materials
56 easily are oxidised. Peroxides which are formed during the process of oxidation decompose into
57 free radicals [9]. Although studies have shown that the clay waste can be recycled and re-used in the
58 course of the bleaching process, yet it is expensive and the efficiency is only 70%.

59 Thermally activated clay is widely used as a pozzolanic material. The use of calcined clay as
60 supplementary cementitious material is one of the ways for reducing CO₂ emissions from the
61 cement industry. This additive is also widespread in nature and has a relatively low cost [10]. The
62 optimum combustion temperature of the clay depends on the chemical and mineralogical
63 composition of the clay. Usually, it is in the range of 600-900 °C, although it can exceptionally
64 reach 1000 °C [11]. The pozzolanic activity of calcined clay is associated with the removal of
65 structural water from the clay layers. Kaolinitic clay is the most popular material and widely used
66 due to its relatively low activation temperature (600-800 °C) and high pozzolanic activity. The
67 calcination of kaolinitic clay results the formation of an amorphous phase – metakaolinite [12]. A
68 great number of published scientific studies [13-16] state that calcined kaolinite is a suitable
69 additive for Portland cement, as the samples exhibit a higher compressive strength, durability and it
70 improves other properties of the samples.

71 The removal of hydroxyl groups from clay layers by heating also activates other clay minerals,
72 for instance, illite and montmorillonite [17]. The major mineral that forms smectite clay is
73 montmorillonite. Activated montmorillonite has a positive effect on the hydration of Portland
74 cement and its properties. Replacing 10 wt.% of the Portland cement with montmorillonite increases
75 the compressive strength of the samples [18]. The destruction of the montmorillonite structure

76 begins at 800 °C. Montmorillonite exhibits the highest pozzolanic activity when it is calcined at 900
 77 °C. Studies have shown [19] that clay calcination at 1000 °C leaves no montmorillonite minerals,
 78 yet pozzolanic activity decreases. When dehydroxylation of montmorillonite occurs, it retains its
 79 structure. Since aluminum is located between silicon tetrahedra in the montmorillonite crystal, the
 80 pozzolanic activity is lower than that of metakaolinite [17]. Comparing the pozzolanic activity of
 81 thermally activated clay minerals, it decreases in the following sequence: kaolinite-
 82 montmorillonite-illite [17].

83 Although industrial waste used in the production of Portland cement is currently a widely studied
 84 subject, the use of acid-activated smectite clay waste (SCW), generated during oil bleaching, in the
 85 cement industry has not been investigated. Therefore, the purpose of this work is to investigate the
 86 possibility of using SCW as an additive to Portland cement

87 2. Materials and methods

88 2.1 Materials

89 In this research, Portland cement CEM I 42.5 R was used. The specific surface area was equal to
 90 380 m²/g. The composition of minerals: 52.97% 3CaO·SiO₂, 19.61% 2CaO·SiO₂, 9.16%
 91 3CaO·Al₂O₃, 9.74% 4CaO·Al₂O₃·Fe₂O₃, 5.37% CaSO₄·2H₂O. The chemical composition of
 92 Portland cement is given in Table 1. After the oil the bleaching process, smectite clay waste (SCW)
 93 was used. The moisture content in the SCW was 9 wt.%, bulk density – 1740 kg/m³, specific
 94 surface area 250 m²/kg. SCW chemical composition is given in Table 1.

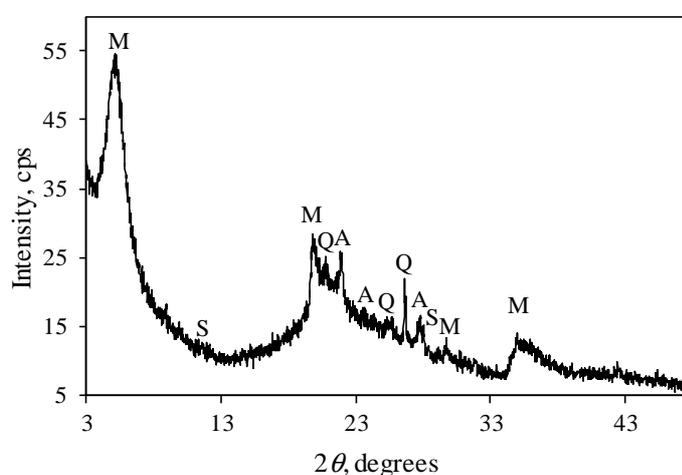
95 **Table 1.** Chemical composition of raw materials

Material	Chemical composition, wt.%									
	SiO ₂	Al ₂ O ₃	CaO	MgO	Fe ₂ O ₃	Na ₂ O	K ₂ O	SO ₃	Cl	Mass loss
CEM I	19.52	5.03	61.39	3.93	3.05	0.12	1.06	2.50	≤0.1	-
SCW	53.20	8.37	0.88	1.64	3.13	0.24	0.49	1.54	0.01	30.4

96

97 According to the XRD analysis data of SCW (Fig.1), this waste contains montmorillonite (*d*-
 98 spacing 1.760, 0.449, 0.150 nm), quartz (*d*-spacing 0.425, 0.334, 0.181 nm), anorthite (*d*-spacing

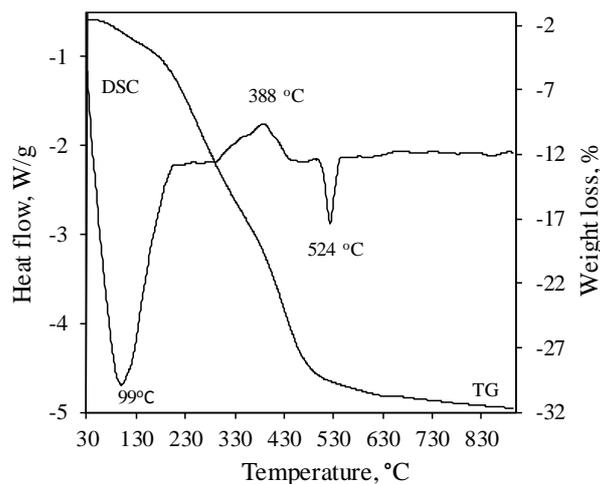
99 4.0600; 3.7863; 3.1909) and calcium sulfate (*d-spacing* 0.760, 0.428, 0.306 nm). CaSO₄ was
 100 identified in connection with the fact that, in oil bleaching process, the smectite clay treated with the
 101 sulfur acid is used [8]. Due to the effect of the sulfur acid, a part of clay minerals are amorphised,
 102 as, in the XRD curve, a blunt diffraction peak in the 18-29° diffraction angle range attributed to the
 103 amorphous structure compounds is seen. For this reason, the pozzolanic activity of the raw material
 104 was investigated. It was estimated that smectite clay pozzolanic activity was equal to 117 mg
 105 CaO/g.



106

107 **Fig. 1.** X-ray diffraction pattern of smectite clay waste. Indexes: M – montmorillonite
 108 ((Na,Ca)_{0.3}(Al,Mg)₂Si₄O₁₀(OH)₂·nH₂O); S – calcium sulfate (CaSO₄·2H₂O); Q - quartz (SiO₂); A –
 109 albite (NaAlSi₃O₈)

110 STA analysis data of the SCW has shown (Fig. 2) that endothermic peak at 99°C in the DSC
 111 curve is associated with the adsorbed water elimination from the investigated material, while the
 112 exothermic peak fixed in the temperature range from 300 to 470°C is related to the decomposition
 113 of organic compounds. The effect at 524°C is related to the elimination of chemically bound water
 114 from the smectite structure [20], and during this process, the weight loss reached 0.8 %. Based on
 115 the TGA curve, the total weight loss of the SCW in the 30–900°C temperature range is 30.4 wt.%,
 116 of which 13.5% of the weight loss attributed to the decomposition of organic compounds.



117

118 Fig.2 STA analysis results of SCW

119

120 **2.2 Methods**

121 Clay preparation by combustion. The investigated clay waste was mixed with water in the ratio
 122 2:1. The formed granules (\varnothing 1.5 cm) were dried at 60°C temperature for 24 h and then burnt at
 123 500–900°C for 1h (10°C/min). The burned granules were crushed and homogenised in a “Turbula”
 124 homogeniser with solid bodies for 5 minutes up to 400 m²/kg specific surface area.

125 Clay extraction with hexane. The SCW was mixed together with hexane in a ratio 1:5, 1:7 and
 126 1:10. Mixtures were heated and stirred on a magnetic stirrer at 40 °C for 20, 30 and 40 minutes,
 127 then filtered off with a vacuum filter. The wet clay was dried for 24h at 60°C and homogenised in a
 128 “Turbula” homogeniser with solid bodies up to 400 m²/kg specific surface area.

129 Compressive strength test. The samples (30×30×30 mm) were formed from the OPC paste with
 130 0, 5, 10, 15, 20 and 25 wt.% extracted/washed or calcined SWC additives. Within the first day, the
 131 samples were kept in molds at 20 ± 1 °C at 100% of humidity. After 24 hours of hydration, the
 132 samples were transferred into the distilled water and kept at 20 ± 1 °C for 7, for 28 and 90 days. The
 133 compressive strength was determined using Form+Test Mega 10-400-50 press. After the
 134 compressive strength measurements, the samples were crushed. The hydration of samples was
 135 stopped by isopropanol. The dried cement stone grains (60 ± 5 °C; 24 h) were ground 5 times (each

136 5 sec) by a disk mill at 600 rpm. The water consumption of the normal consistency of the cement
137 paste and the setting time were determined according to EN 196-3:2016 [21].

138 The calorimetric analysis was performed using the TAM Air III calorimeter. The duration of
139 measurement was 72 h, measurement error <0.03 W/g. The generated heat was normalised per gram
140 of the Portland cement.

141 The pozzolanic activity was estimated by the modified method of Chapelle. This method is
142 described in more detail in previous work [22]. The hydraulic activity of materials was estimated
143 according to EN 196-5:2005 [23].

144 The specific surface area of the used materials was measured by the automatic Blain equipment.

145 The X-ray powder diffraction (XRD) data was performed using the D8 Advance diffractometer
146 Bruker AXS (Karlsruhe, Germany) with Bragg–Brentano geometry. The movement of the detector
147 -0.02° , measuring angle $-2\theta = 3-70^\circ$.

148 The simultaneous thermal analysis (STA) was carried out on a Netzsch STA 409 PC Luxx
149 instrument in the temperature range from 30°C to 1000°C , accuracy of measurement $\pm 3^\circ\text{C}$.

150 FT-IR spectra were measured using a Perkin-Elmer Fourier transform infrared system Spectrum
151 X spectrometer. The spectral analysis was performed in the range of $4000 - 400\text{ cm}^{-1}$ with a
152 spectral resolution of 1 cm^{-1} .

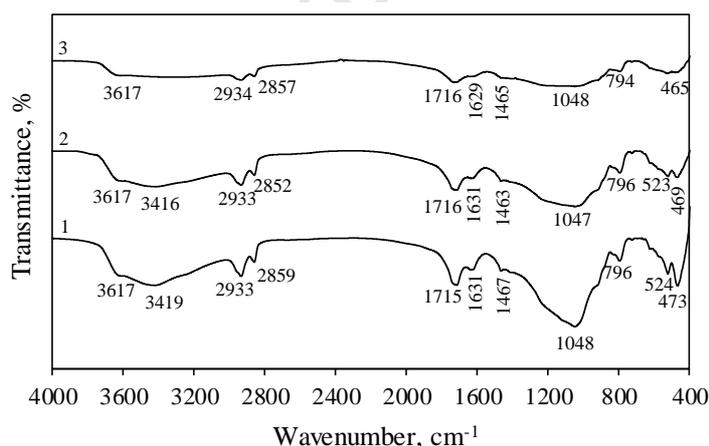
153 **3. RESULTS AND DISCUSSION**

154 **3.1. Extracted smectite clay waste**

155 Organic solvents are used to clean/regenerate oily clay in the oil industry [24, 25]. Therefore, in
156 the first part of this work, smectite clay extraction with hexane was chosen. To determine the
157 optimum extraction time and the clay-to-hexane ratio, extraction times of different lengths (20, 30

158 and 40 min) were performed using ratios of 1:5, 1:7 and 1:10. The efficiency of the oil impurity
 159 removal was evaluated by using FT-IR analysis.

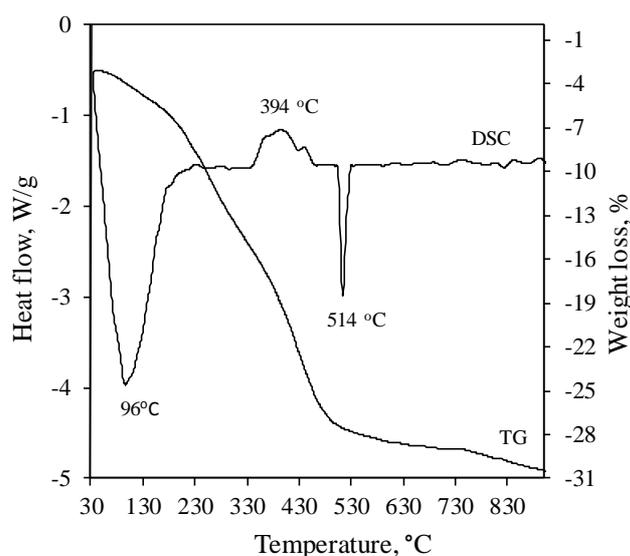
160 The FT-IR analysis of all extracted SCW samples showed that the absorption bands identified in
 161 the 1715-1716 cm^{-1} wavelength are assigned to RC-OOR vibrations (R - hydrocarbon radicals),
 162 while 794 - 796 cm^{-1} indicated C = O vibrations. These bonds are attributed to the rest of
 163 unremoved oil. As the clay-to-hexane ratio and the extraction time increased, the intensities of the
 164 bands indicating RC-OOR and C=O vibrations decreased. The highest decrease in peak intensity is
 165 seen at a 1:7 clay-to-hexane ratio and 40 min extraction time (Fig. 3), but peaks identifying the
 166 organic compounds remained in all samples. Thus, FT-IR analysis results demonstrated that not all
 167 oil impurities are removed from this waste during SCW extraction by hexane.



168

169 **Fig. 3.** FT-IR spectra of the extracted SCW (1:7) when the duration of extraction: 1 – 20 min; 2 –
 170 30 min; 3 – 40 min.

171 The results of the FT-IR analysis were confirmed by STA analysis. As can be seen in Figure 4,
 172 an exothermic peak in the DSC analysis curve at a temperature range of 340 to 460 °C, which is
 173 typical for the decomposition of organic compounds, remained in the SCW sample after 40 minutes
 174 of extraction by hexane when the molar ratio was 1:7. The reduction of mass loss during this
 175 decomposition was negligible (from 13.5 to 10.28 wt.%) compared to the untreated waste, and the
 176 total mass loss was reduced from 30.4 to 27.7 wt.%.



177

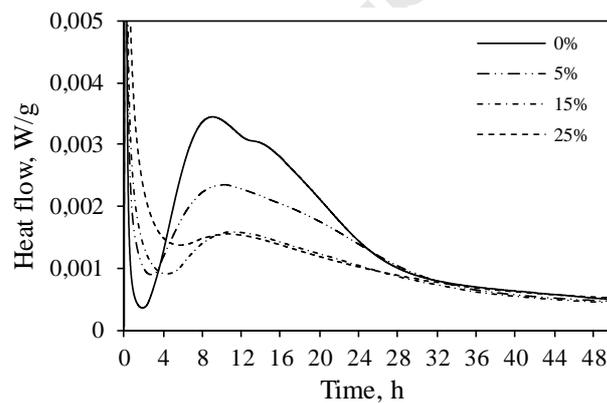
178 **Fig. 4.** STA analysis data (TG and DSC curves) of extracted SCW (1:7, 40 min)

179 A study of the pozzolanic activity of the hexane-extracted smectite clay waste showed that the
 180 pozzolanic activity of the treated waste increased from 117 to 216 mgCaO/g, i.e., almost twice.
 181 Considering this factor, it was decided to use hexane-extracted SCW as a pozzolanic additive to
 182 Portland cement.

183 To assess the effect of the additive on the initial hydration of Portland cement, the calorimetric
 184 analysis was carried out by replacing 5, 15 and 25% cement by weight with the analysed hexane-
 185 extracted SCW. The heat flow (Fig. 5) and the amount of heat (Fig. 6) released during the hydration
 186 were determined during the study.

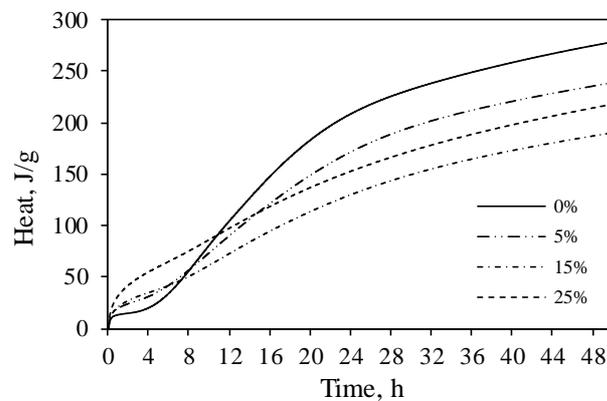
187 The obtained data showed that the induction period in samples with the hexane-extracted SCW
 188 additive is significantly longer than in the pure cement sample (1 h 50 min), and lasts from 2 h 48
 189 min to 6 h 16 min. Figure 5 demonstrates that the intensity of second active heat evolution peak
 190 decreased with increasing amount of additive in the Portland cement, whereas in samples with 25
 191 wt.% additive this peak was slightly visible. The shoulder of the second peak is related to the
 192 reaction of aluminates and gypsum and it was identified only in samples without the additive.

193 It was determined (Fig. 6) that until ~8 hours of hydration, samples with hexane-extracted SCW
 194 additive emits more heat than pure cement sample. This effect indicated that the hexane-extracted
 195 SCW samples increased nucleation sites and total quantity of calcium silicates dissolved and
 196 hydrated although the induction period is prolonged. Presumably that the oil impurities adsorbed on
 197 the SCW particles during the induction period do not block the formation of hydrates on the surface
 198 of these particles. At a later period of hydration, the alkali break down the structure of the oil
 199 impurities and form films that block the hydration of the cement, because the pure cement sample
 200 emits noticeably more heat (283 J/g) than the samples with hexane-extracted SCW additive (182 -
 201 230 J/g) after 50 hours of hydration.



202

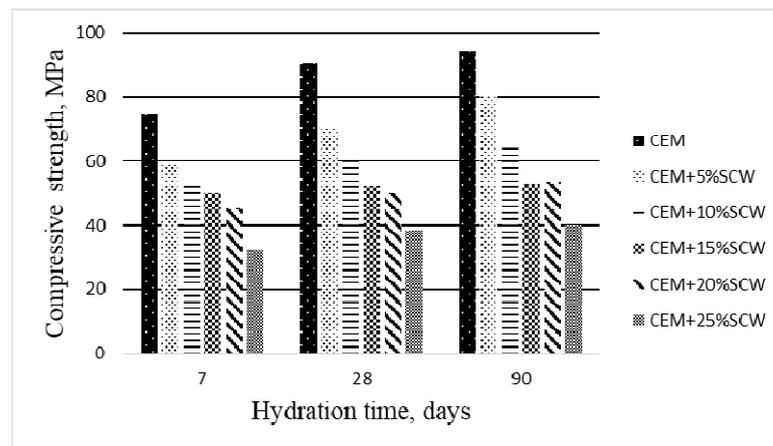
203 **Fig. 5.** Calorimetric curves of heat flow in samples with hexane-extracted SCW additive



204

205 **Fig. 6.** Calorimetric curves of total heat in samples with hexane-extracted SCW additive

206 The results of compressive strength tests (Fig. 7) showed that the hexane-extracted smectite clay
 207 additive adversely affects the compressive strength of the Portland cement samples: the more
 208 additive is added, the lower compressive strength of the tested samples was recorded. Within all
 209 hydration time, the sample with 25wt.% of the additive was more than twice as weak as the pure
 210 Portland cement sample.



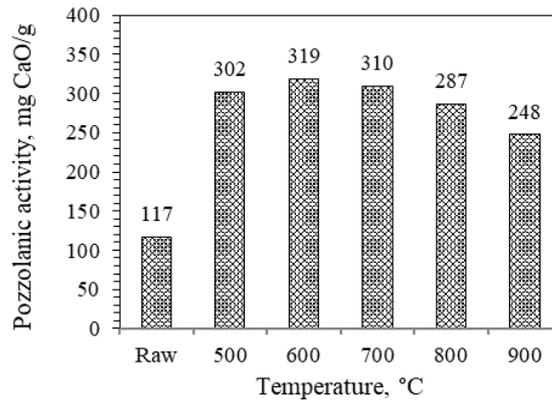
211

212 **Fig. 7.** Compressive strength of the cement samples after 7, 28 and 90 days hydration

213 Summarizing the obtained results, it can be stated that the extraction of SCW with hexane
 214 significantly increased the pozzolanic activity of this waste, but after this process a large amount of
 215 organic impurities (oil) remained in the SCW. For this reason, the extracted additive slowed down
 216 initial cement hydration and reduced the compressive strength of Portland cement samples. As the
 217 extraction by hexane did not remove all organic impurities from the smectite clay waste, a method
 218 of thermal activation of this waste was chosen for the next step of the research.

219 3.2. Calcined smectite clay waste (CSCW)

220 According to the data given in Fig. 2 and Fig. 4, the thermal activation of the SWC was
 221 performed in the 500-900 °C temperature range, because the residues of organic admixtures
 222 remained at a lower temperature. In the first stage of investigation, the influence of calcining
 223 temperature on the SWC pozzolanic activity was determined. The results are presented in Fig. 8.



224

225

Fig. 8. Pozzolanic activity of CSCW after 1h calcination at 500–900 °C temperature

226

227

228

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230

231

It was determined (Fig. 8) that the CSCW pozzolanic activity varied from 300 to 320 mg CaO/g when the temperature of the clay calcination increased from 500 °C to 700 °C. These results indicated the strong pozzolanic activity of tested samples [26]. Meanwhile, the pozzolanic activity of the CSCW begins to decrease after the combustion at the temperature above 700 °C and the pozzolanic activity values of 287 and 248 mg CaO/g, was determined after burning at 800 and 900 °C respectively.

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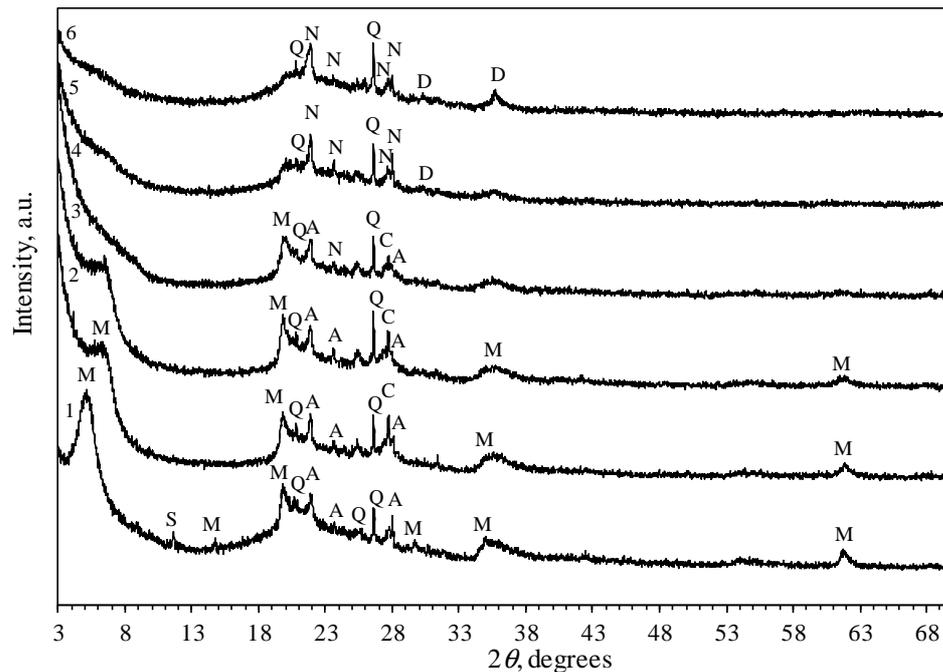
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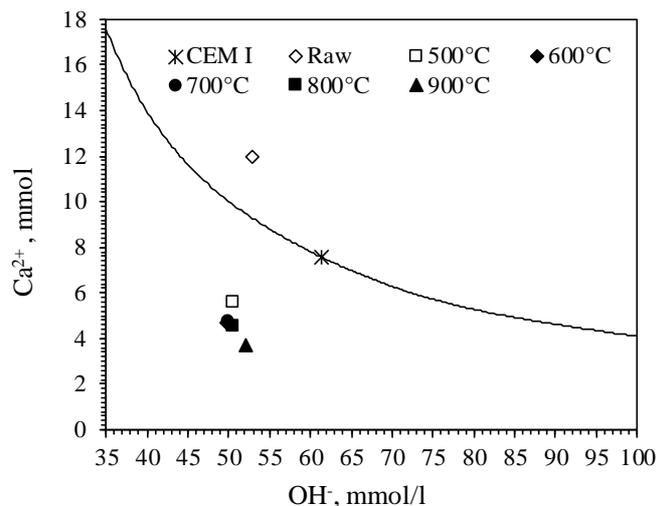
It is important to note, that the pozzolanic activity of CSCW only slightly depended on the thermal decomposition of clay minerals during the activation process. As can be seen in Fig. 9, even in the sample with the highest pozzolanic activity (Fig. 9, curve 3) remained a part of the undecomposed montmorillonite (*d-spacing* 1.760, 0.449, 0.150 nm). Furthermore, regardless of the combustion temperature, the wide diffraction peak in the 18-29 ° diffraction angle typical for amorphous compounds is clearly visible on all curves. This indicates that, in the composition of the acid-activated smectite clay remains an initial amorphous phase during the combustion. Only at a higher temperature (800-900 °C), a part of this amorphous phase begins to bind into the inactive compounds (such as anorthoclase (*d-spacing* 0.406, 0.375, 0.322, 0.318 nm) and diopside (*d-spacing* 0.638, 0.294, 0.249 nm) Fig. 9, curves 4–6).



242

243 **Fig. 9.** X-ray diffraction patterns of smectite clay waste after 1h thermal activation at different
 244 temperatures: 1 – SCW; 2 – 500 °C; 3 – 600 °C; 4 – 700 °C; 5 – 800 °C; 6 – 900 °C. Indexes: Q –
 245 quartz (SiO_2); M – montmorillonite $((\text{Na,Ca})_{0.3}(\text{Al,Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O})$; A – albite
 246 $(\text{NaAlSi}_3\text{O}_8)$; N – anorthoclase $((\text{Na,K})\text{AlSi}_3\text{O}_8)$; S – calcium sulfate $(\text{CaSO}_4 \cdot 2\text{H}_2\text{O})$; D – diopside
 247 $(\text{CaMgSi}_2\text{O}_6)$; C – calcium aluminum silicate $(\text{Al}_3\text{Ca}_{0.5}\text{Si}_3\text{O}_{11})$

248 The results of the hydraulic activity analysis (Fig. 10) confirmed the CSCW pozzolanic activity
 249 data. It was determined that, after replacing 15 wt.% of Portland cement with investigated material
 250 activated at 500-900 °C, all points representing OH^- and CaO concentrations were located below the
 251 curve representing CaO saturation. This means that all Portland cement samples with a thermally
 252 activated additive passed the hydraulic activity test. Meanwhile, the 15 wt.% non-activated SCW
 253 additive had a contrary effect, i.e. the point is above the curve and the Portland cement sample did
 254 not pass the hydraulic activity test.



255

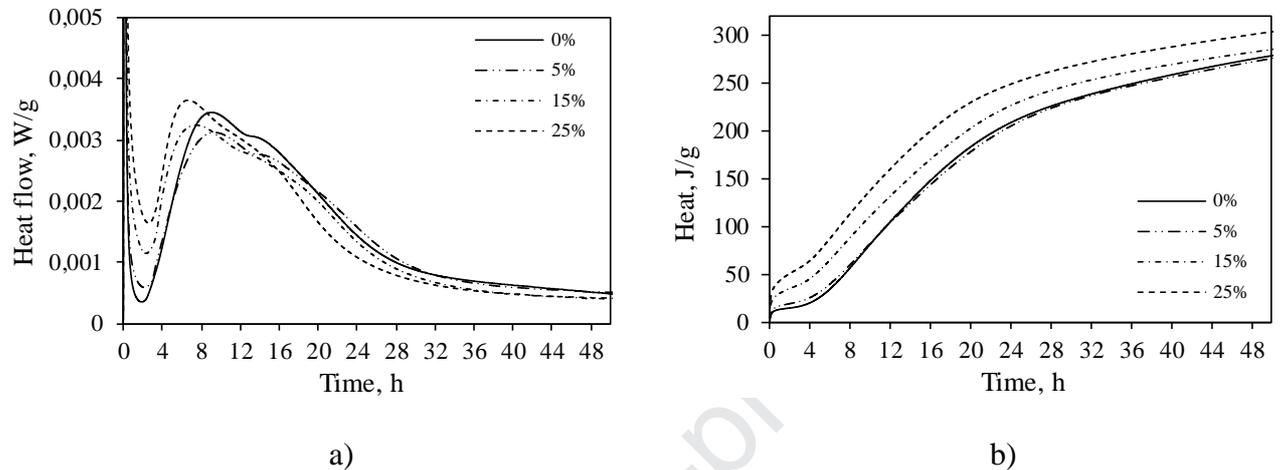
256 **Fig. 10.** Hydraulic activity of the Portland cement samples with 15 wt.% smectite clay waste
 257 additive calcined at different temperature

258 Thus, during the SCW thermal activation at 500-900 °C, the organic compounds were
 259 completely degraded and CSCW samples exhibited high pozzolanic activity over the entire range of
 260 thermal activation temperatures. Since the CSCW calcined at 600 °C had the highest pozzolanic
 261 activity, this sample was used in the following studies.

262 The calorimetric analysis was performed by replacing 5, 15, and 25% by weight of Portland
 263 cement with the additive calcined at 600 °C. The heat flow (Fig. 11, a) and the total heat (Fig. 11, b)
 264 were determined. It was identified that, in the samples with 5, 15 and 25 wt.% additive, the
 265 induction period expires later than in the pure cement sample (1 h 50 min), respectively, 2 h 05 min,
 266 2 h 20 min and 2 h 35 min, though lasts the same duration.

267 All samples have two exothermic peaks and the shoulder of the second peak is visible. It was
 268 determined that, in the second period of the exothermal reaction, the maximum heat flow value was
 269 reached after 8h 15 min in the pure Portland cement sample, while in samples with 15 and 25 wt.%
 270 of additive, the maximum heat flow values were recorded earlier, respectively, after 6 h 50 min and
 271 6 h 15 min. In the cement sample with 5 wt.% SCW additive, the mentioned maximum was finally
 272 reached after 8 h 25min.

273 In addition to this, the highest amount of heat was released in samples with 25 and 15 wt.% of
 274 additive - 315 J/g and 288 J/g, respectively, whereas in samples of pure cement and with 5 wt.% of
 275 additive, the amount of the released heat was almost similar ~ 283 J/g.



276 **Fig.11.** Calorimetric curves of the thermal flow (a) and heat (b) in cement samples with
 277 combusted SCW samples (0 wt.%, 5 wt.%, 15wt.% and 25 wt.%) at 600 °C for 1 h

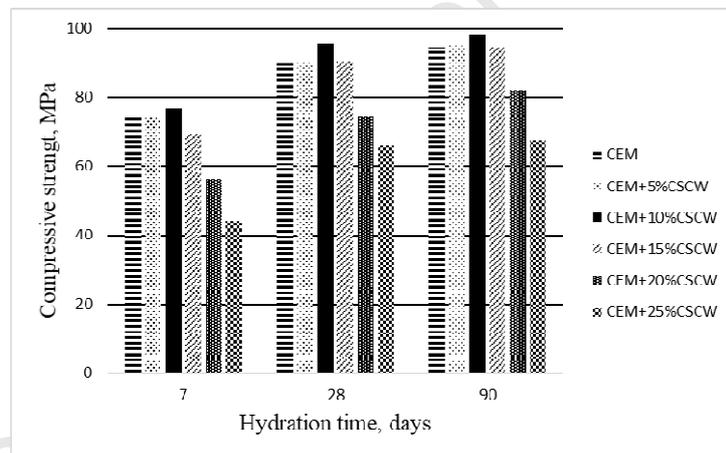
278 In the next stage of the research, the samples of Portland cement paste with different amount of
 279 the CSCW additive (5, 10, 15, 20, and 25 wt.%) were formed. The water-to-cement (w/c) ratio and
 280 the setting time were determined. The data given in Table 2 shows that w/c increased with the
 281 increasing amount of the additive. These effects are related to the partial substitution of cement with
 282 calcined clay, causing excessive consumption of water and absorption of part of the water for
 283 hydration [27]. After replacing 20 and 25 wt.% Portland cement by the CSCW, these mixtures
 284 begin to bind quickly and only meet the lower limit of EN 196-3 (45 min) [21]. This may occur due
 285 to the presence of sulfates ($SO_3 = 1.54\%$) in the SCW, which might influence the setting duration.

286 **Table 2.** Water-to-cement ratio and setting time of cement with CSCW samples

Sample	W/C	Initial setting time, min	Final setting time, min
CEM	0.275	70	120
CEM+5 wt.% CSCW	0.320	93	113
CEM+10 wt.% CSCW	0.330	60	82
CEM+15 wt.% CSCW	0.340	54	76
CEM+20 wt.% CSCW	0.390	48	65
CEM+25 wt.% CSCW	0.430	45	60

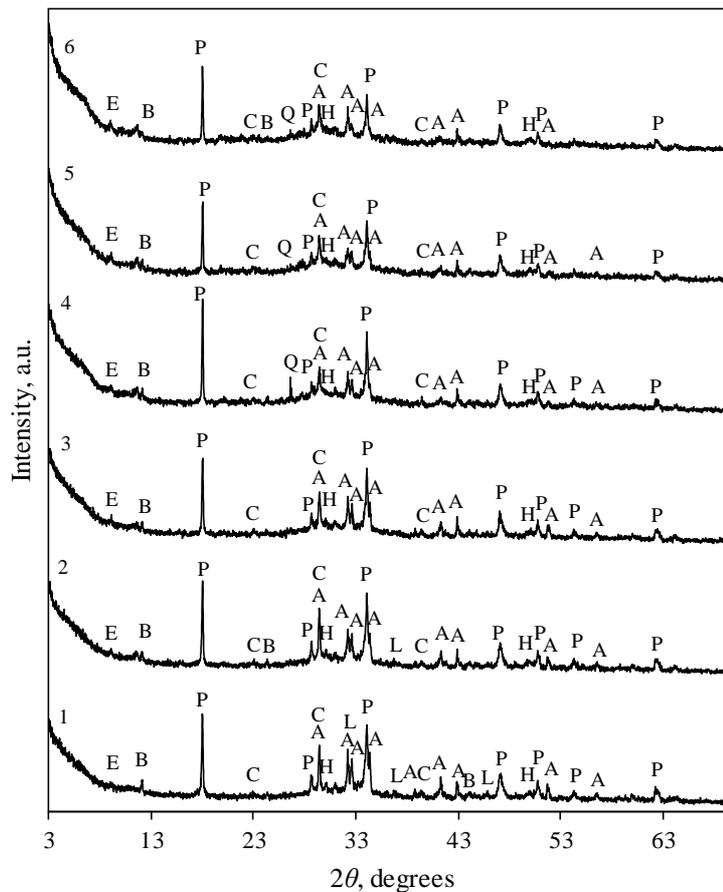
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288 The compressive strength test (Fig. 12) showed that after 7 days of hydration, a sample with 10
 289 wt.% CSCW additive had the highest (76.9 MPa) compressive strength. When the content of the
 290 CSCW additive was increased, the compressive strength decreased. It was determined that cement
 291 sample with 10 wt.% CSCW also exhibited the highest compressive strength (95.8 MPa) after 28
 292 days of hydration. The samples with 5 and 15 wt.% CSCW and without any additive had the same
 293 compressive strength (~90 MPa). This tendency remained after 90 days of hydration. The
 294 compressive strength of samples with 20 and 25 wt.% of additive was lower than in the pure cement
 295 sample during all investigated duration of hydration.



296

297 **Fig. 12.** Compressive strength of cement samples with CSCW additive after 7 – 90 days of
 298 hydration

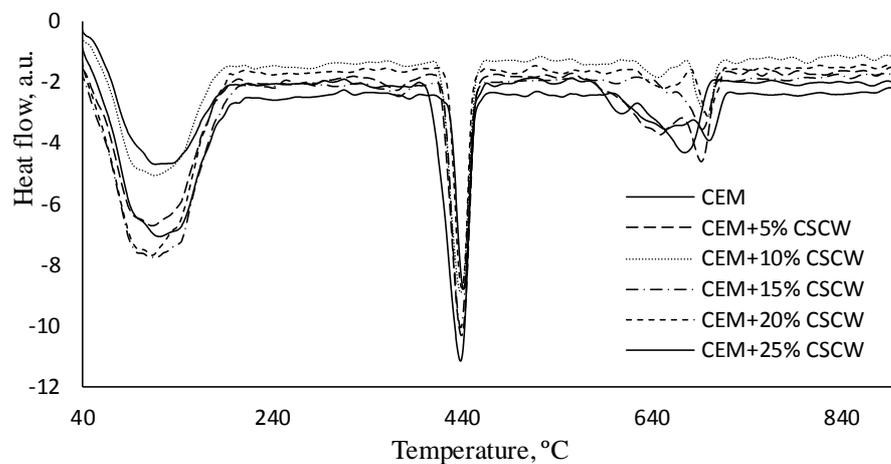


299

300 **Fig. 13.** X-ray diffraction patterns of cement samples with CSCW additive after 28 days
 301 hydration: 1 – CEM, 2 – 5 wt.% additive, 3 – 10 wt.% additive, 4 – 15 wt.% additive, 5 – 20 wt.%
 302 additive, 6 – 25 wt.% additive. Indexes: E – ettringite ($\text{Ca}_6(\text{Al}(\text{OH})_6)_2(\text{SO}_4)_3 \cdot 26\text{H}_2\text{O}$); B -
 303 brownmillerite (C_4AF); P – portlandite ($\text{Ca}(\text{OH})_2$); H – calcium silicate hydrates; C – calcite
 304 (CaCO_3); A – alite (C_3S); L – larnite (C_2S); Q - quartz (SiO_2).

305 The X-ray diffraction analysis of the 7, 28 and 90 days hydrated cement samples was performed.
 306 Since all patterns of XRD were very similar, only the data of 28 days hydrated samples are given
 307 (Fig. 13). As can be seen in the XRD curves, the ordinary hydrates of Portland cement, such as
 308 portlandite (*d-spacing* 3.1139, 4.9280, 1.9322, 1.7978, 1.4529 nm), calcium silicate hydrate (*d-*
 309 *spacing* 0.304, 0.279, 0.182 nm) and ettringite (*d-spacing* 9.7514, 5.6300, 3.8858, 2.7807, 2.5680
 310 nm) were formed during hydration. Unhydrated minerals like C_3S (*d-spacing* 3.0330, 2.7446,
 311 2.6066, 2.1837, 1.7642 nm); brownmillerite (*d-spacing* 2.7920, 2.6870, 2.6560, 2.0603, 1.9361

312 nm), C_2S (d-spacing 0.279, 0.278, 0.274 nm) were also identified. It was determined that the
 313 intensity of the unhydrated calcium silicates diffraction peaks decreased, and the intensity of the
 314 Portlandite peaks varied slightly when the content of the CSCW additive increased in the samples.
 315 Diffraction peaks attributed to quartz (d-spacing 4.255, 3.344, 2.457 nm) were also identified in the
 316 samples with the CSCW, as this is an integral part of the additive. In all curves of the samples,
 317 $CaCO_3$ (d-spacing 3.0303, 2.4950, 2.2835, 1.9071, 1.8726 nm) was also identified.



318

319 **Fig. 14.** DSC curves of cement samples with CSCW additive after 28 days of hydration

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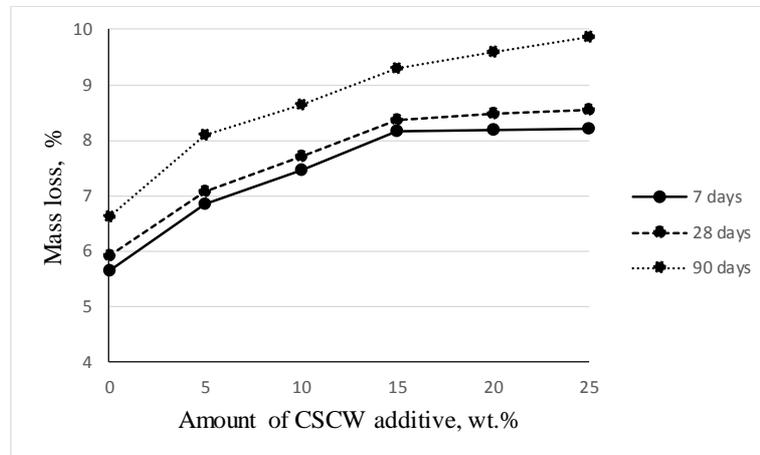
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As in case the X-ray diffraction analysis, all curves of DSC were very similar, therefore only the
 data of 28 days hydrated samples are given (Fig. 14). In the DSC analysis curves, the intensity of
 peaks ($\sim 450^\circ C$) identifying $Ca(OH)_2$ decomposition was the highest in the samples without any
 additives. Meanwhile, in all samples with the CSCW, the intensities of the peaks describing
 Portlandite decay decreased with the increasing amount of additive. In the temperature range of
 carbonate decomposition ($600-780^\circ C$), the most intense peaks were also presented in the samples
 without any additives, indicating that the CSCW additive inhibits the carbonation of the samples.
 This is due to two reasons – less portlandite is formed in samples with lower cement clinker content
 and a part of portlandite is consumed for pozzolanic reaction in the samples with CSCW additive. It
 is important to note that a contrary trend in the DSC curves in the dehydration zone of the major

330 cement hydrates at 80 - 200 °C is estimated. These peaks were more intense in samples with the
 331 CSCW additive throughout all period of samples hydration.

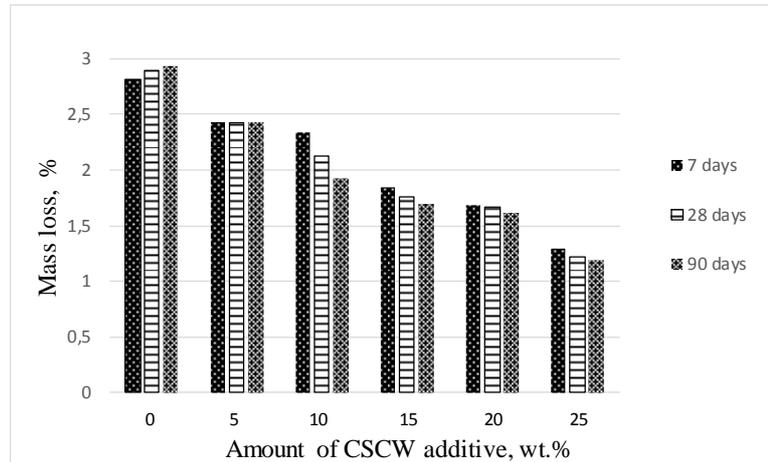


332

333 **Fig. 15.** Thermogravimetric analysis data in the temperature range 80-200 °C after 7, 28 and 90
 334 days of hydration

335 The results of the thermogravimetric analysis are shown in Fig. 15 and 16. It was determined
 336 that, in the temperature range 80-200 °C, the weight loss in the samples with the CSCW additive
 337 was higher than in the samples without the additive during the whole duration of hydration. These
 338 weight losses consistently increased with the increasing hydration time and the CSCW additive
 339 content in the samples (Fig. 15).

340 However, it would be inaccurate to attribute this large difference in weight loss between the pure
 341 cement samples and the samples with the additives only to the formation of new cement hydrates.
 342 As the studies on the consistency of normal cement paste (Table 2) and literature data [8]
 343 demonstrated, the CSCW had a peculiar absorption capacity and not all of the absorbed water can
 344 be removed by drying of samples at ordinary temperature (60 ± 5 °C). Therefore, these higher
 345 weight losses may also be partly related to the removal of the adsorbed water from the CSCW
 346 additive. If the weight loss was only related to the formation of new cement hydrates, the samples
 347 with 15-25 wt.% of the additive would have the highest compressive strength unlike it was found
 348 (Fig. 12).



349

350 **Fig. 16.** Thermogravimetric analysis data in the temperature range 420-460 °C after 7, 28 and 90
 351 days of hydration

352 On the other hand, the fact that the pozzolanic reaction observed in the samples with the additive
 353 is confirmed by the change in mass loss in the region of Portlandite decomposition (~ 450 ° C). In
 354 pure cement samples, these losses increased consistently with increasing hydration time and were
 355 the highest of all tested samples (Fig. 16). Meanwhile, in the samples with 10-25 wt.% of additive,
 356 the weight loss decreased with the increasing hydration time, while in the sample with 5 wt.%
 357 additive the weight loss remained the same. It should be noted that in the samples with the 10-
 358 25wt.% CSCW additive, the weight loss during Portlandite decomposition begins to decrease after
 359 28 days of hydration, compared with weight loss after 7 days of hydration. This confirms that the
 360 CSCW additive is a very active pozzolanic additive, since ordinarily the pozzolanic reaction is only
 361 noticeable in the later period of hydration [28, 29]. The greatest decrease in mass loss in the area of
 362 Portlandite decomposition is observed in the sample with 10% of the additive, having the highest
 363 compressive strength over the entire curing time.

364

4. Conclusions:

365

- 366 1. Smectite clay waste consists of montmorillonite, quartz, anorthite, calcium sulfate, and amorphous phase. Smectite clay loses 30.4% of its weight in the temperature range of 30 - 900

- 367 °C, and 13.5% of its weight loss is attributed to the decomposition of organic compounds. The
368 SCW exhibits a pozzolanic activity of 117 mg CaO/g.
- 369 2. The extraction with hexane for the SCW regeneration increases the pozzolanic activity almost
370 twice - from 117 mgCaO/g to 216 mgCaO/g. However, after this process, the SCW retains a
371 high content (10.28 wt.%) of organic impurities. The extracted SCW additive extends the
372 induction period of Portland cement hydration, slows the initial cement hydration and reduces
373 the compressive strength of Portland cement samples; therefore, the extracted SCW is not a
374 suitable additive for Portland cement.
- 375 3. The thermal activation method achieves best results by calcining SCW samples at 600 °C. The
376 calcined additive indicated the strong pozzolanic activity, because this index increases to 320
377 mg CaO/g. High pozzolanic activity of samples associated with the formation of the amorphous
378 phase by activating the smectite clay with the sulfuric acid rather than the degradation of the
379 clay minerals during the combustion.
- 380 4. The CSCW additive accelerates the hydration of calcium silicates and in samples with the
381 CSCW additive proceed intense pozzolanic reaction, which is clearly identified after 28 days of
382 hydration.
- 383 5. Up to 15 wt.% of the Portland cement can be replaced by the smectite clay waste additive
384 calcined at 600 °C without reducing the compressive strength of Portland cement samples.

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Highlights

- The smectite clay waste consists of montmorillonite, quartz, anorthite, calcium sulfate, and amorphous phase.
- The thermally activated at 600 °C smectite clay waste distinguished for high pozzolanic activity, however, this phenomenon is associated with the formation of the amorphous phase by activating the smectite clay with the sulfuric acid rather than the degradation of the clay minerals during the combustion.
- The calcined smectite clay waste accelerates the hydration of calcium silicates and increases the compressive strength of samples, because up to 15 wt.% of the Portland cement can be replaced by the smectite clay waste additive calcined at 600 °C without reducing the compressive strength of Portland cement samples.