# 1 2 **Compressed Earth Blocks Stabilised** 3 with Glass Waste and Fly Ash 4 **Activated with a Recycled Alkaline** 5 **Cleaning Solution** 6 7 <sup>a</sup> Jhonathan Rivera; <sup>b</sup> João Coelho; <sup>c</sup> Rui Silva; <sup>d</sup> Tiago Miranda; <sup>e</sup> Fernando 8 Castro; <sup>f,\*</sup> Nuno Cristelo 9 10 11 12 <sup>a</sup> CQ-VR, Department of Engineering, University of Trás-os-Montes e Alto Douro, Quinta de Prados, 5000-13 801 Vila Real, Portugal 14 E-mail address: jhonathan@utad.pt 15 16 17 <sup>b</sup> Department of Civil Engineering, University of Minho, 4800-058 Guimarães, Portugal 18 E-mail address: id7225@uminho.com 19 20 21 22 23 24 25 26 <sup>c</sup> ISISE, Department of Civil Engineering, University of Minho, 4800-058 Guimarães, Portugal E-mail address: ruisilva@civil.uminho.com <sup>d</sup> ISISE, Institute of Science and Innovation for Bio-Sustainability (IB-S), Department of Civil Engineering, University of Minho, 4800-058 Guimarães, Portugal 27 E-mail address: tmiranda@civil.uminho.com brought to you by CORE boutugal View metadata, citation and similar papers at core.ac.uk 30 E-mail address: fcastro@w2v.pt

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#### 37 Abstract

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39 The study reported in this paper focused on the physical-mechanical properties of compacted 40 earth blocks (CEB) stabilised with a sustainable alkali activated cement, completely 41 produced from wastes and residues, including coal fly ash and glass waste (from the 42 production of ophthalmic lenses) activated with an alkaline solution resulting from the 43 aluminium industry. A common Portuguese silty clay was used as the mineral skeleton of the 44 blocks, which were then evaluated based on the protocols of the UNE 41410 and DIN 18945-45 47 standards. The results evidenced the effectiveness of the alkaline cementing agent in forming a binding matrix for the soil particles, and the resulting material was used to 46 47 manufacture the earth-based masonry elements. After a careful optimisation of the 48 sustainable binder, an average compressive strength of 17.23 MPa, in unsaturated conditions, 49 was obtained for the blocks. The newly formed soil-binder structure was very capable to 50 withstand wetting and drying cycles, ice-thaw cycles and erosion. The microstructure of the 51 material was further analysed, using scanning electron microscopy and energy dispersive 52 spectroscopy. The results demonstrated the real possibility of using this type of cement as a 53 viable alternative to traditional soil stabilisation binders used in earth construction.

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56 Key words: Alkali activated cements; sustainability; earth construction; soil stabilisation;
57 glass waste

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### 59 1. Introduction

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61 For millennia compacted earth has been one of the most used materials around the world, 62 mostly for housing construction, using two techniques known as "rammed earth" and 63 "adobe". Rammed earth is a thick wall of soil rammed inside a wooden formwork, while 64 adobe is formed by blocks of compressed soil, usually slightly larger than a clay brick, they 65 may or may not include reinforcing fibres. Compacted earth blocks (CEB) are considered an 66 evolution from adobe (Pacheco-Torgal and Jalali, 2012), since the manufacturing follows the 67 same principle, only the compaction process has been improved and, additionally, chemical 68 stabilization is applied, thus improving mechanical properties and durability. The compaction 69 technique has also evolved, from the appearance of the first CINVA-RAM compactor 70 machine, to the current use of hydraulic presses, capable of significantly improving the 71 geometry and material properties of the CEB (Silva et al., 2015).

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73 The chemical stabilization of soils to manufacture CEB is traditionally done with Portland 74 cement (OPC) or lime. However, in some cases, these traditional cements are not a viable 75 solution due to the financial cost of the material, if high cement contents are required to 76 obtain adequate properties. Therefore, it is justifiable to research alternative binders, 77 preferably capable of producing a more environmentally friendly material. In that context, 78 alternative binders based on industrial wastes or by-products are gaining acceptance, thus 79 becoming ideal for this particular application. From a relatively large pool of possibilities, 80 fly ash (FA) is a clear target, due to its extensive research in the last 20 years, which includes applications as a soil stabilizer and as a precursor in alkaline activation reactions. This residue 81 82 from the combustion of coal, in thermoelectric powerplants, can act as a soil filler, reducing the settlement of the resulting material, or can also be used together with a source of calcium,
taking advantage of its pozzolanic properties (Horpibulsuk et al., 2009; Siddiqua and Barreto,
2018).

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87 Slags are also one of the most used wastes in this type of applications, and especially ground 88 granulated blast furnace slags (GGBS), because of its high content in calcium oxides and 89 hydraulic character, that makes them very similar to OPC. Oti et al. (2009a, 2009b) used 90 mixtures of GGBS and quick lime or hydraulic lime to stabilize a clayey soil, which was then 91 compacted with a hydraulic press to produce CEB. The GGBS/lime binder improved 92 compressive strength and especially the durability, in terms of ice/thaw cycles. Mixtures of 93 GGBS and OPC showed less effective results, which was attributed to the increased cationic 94 exchange capacity between the soil and the lime-based binder. In addition to FA and GGBS, 95 it is also worth mentioning the successful use, as chemical stabilizers for the manufacture of 96 BTC, of ashes from sugarcane bagasse and marble stone cutting muds. El-Mahllawy et al. 97 (2018) and Lima et al. (2012) mixed this type of waste with OPC and lime, in varied 98 percentages, effectively improving properties such as compressive strength and absorption 99 of the CEB.

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Glass wastes (GW) are used, since the 1970s, in the manufacture of baked bricks. Due to its very specific composition, they function as a melting material in the sintering process of clay minerals (Hwang et al., 2006; Zhang et al., 2018). However, the use of glass waste as a chemical stabilizer in the manufacture of BTC is not possible, because it is completely inert if not in contact with a strong alkaline substance or a high acidic medium. Therefore, in geotechnics, they are used mostly as a filler material, as a plasticity modifier or to increase 107 the internal friction angle of clay soil particles (Olufowobi et al., 2014). In order to improve 108 and use glass wastes as cementing materials, methods such as alkaline activation are showing 109 significant potential, mostly due to the capacity of the alkaline activators, mainly alkali metal 110 salts, to dissolve the previously pulverized glass. Several authors (Avila-López et al., 2015; 111 Espinoza and Escalante García, 1970; Lin et al., 2012; Novais et al., 2016; Pascual et al., 112 2014; Rivera et al., 2018) have successfully used alkaline activated glass waste as a 113 cementitious material in various applications, demonstrating that pulverized glass waste can 114 be an alternative to traditional Portland cements, either when used as the sole precursor or 115 mixed with other aluminosilicate-rich precursors.

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117 The alkaline activation technique is no stranger to the development of masonry elements 118 made of raw earth. This technique, combined with precursor residues or commercial 119 aluminosilicates, such as metakaolin, have been used to chemically stabilize soils for 120 subsequent compaction and manufacture of BTC. Very interesting results have been obtained 121 (Leitão et al., 2017; Omar Sore et al., 2018; Silva et al., 2015), showing the capacity of the 122 technique to greatly improve the mechanical properties, durability and stability in water of 123 the compacted elements; and even acquire properties comparable to the BTC stabilized with 124 OPC. Furthermore, a step forward was already given towards the implementation of 125 alternative, more environmentally friendly activators, with an optimised incorporated energy, 126 with the purpose of producing masonry with a very low carbon footprint. Recent research 127 (Cristelo et al., 2019; Fernández-Jiménez et al., 2017) has shown that the use of glass waste, 128 combined with precursors like fly ash and aluminium anodizing sludge, activated with a recycled alkaline cleaning solution, can originate a sustainable alkaline cement. 129

131	In the present work, the physical-mechanical characterization of chemically stabilized CEB
132	was carried out, integrating various types of industrial waste into the soil stabilization process
133	and manufacturing of the CEB, with the intention of replacing traditional precursors, such as
134	blast furnace slag or metakaolin, and alkaline activators such as hydroxides or silicates.
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137	2. Materials and methods
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139	2.1 Materiales
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141	The soil was collected in the area of Chaves, a city in the Northern Region of Portugal. The
142	fly ash was generated by the Portuguese thermo-electric powerplant of Pego. According to
143	ASTM C618 (2012), it was classified as a class F. The glass waste powder results from the
144	production of optical lenses at the Portuguese company POLO. The chemical composition of
145	the soil and precursors is presented in Table 1, obtained by x-ray fluorescence with a
146	PHILLIPS PW-1004 spectrometer.
147	
148	The recycled cleaning solution acting as the alkaline activator has a high pH, between 12 and
149	14, with an approximate density of 1.3 g/cm <sup>3</sup> . It previously underwent a homogenization
150	process. Table 2 shows the elementary composition of the cleaning solution, determined by
151	Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES), with plasma power
152	of 1.4 kW, plasma gas flow of 15.00 l / min and gas nebulizer flow of 0.85 l/min, with a
153	reading time of 5s.
154	

Element (oxides)	Fly ash	Soil	Waste glass
SiO <sub>2</sub>	56.11	61.74	58.37
$Al_2O_3$	21.44	23.27	3.94
Fe <sub>2</sub> O <sub>3</sub>	8.20	5.68	0.15
CaO	1.31	0.33	6.13
MgO	1.46	1.65	0.49
TiO <sub>2</sub>	1.15	0.08	-
MnO	0.07	0.89	2.73
Na <sub>2</sub> O	1.12	0.58	8.75
K <sub>2</sub> O	2.81	5.12	4.66
$P_2O_5$	0.29	0.09	5.07
LOI	5.05	0.33	1.85

155 Table 1. Chemical composition of the Fly ash, Soil and Waste glass (%w)

157 Table 2. Elemental composition of the cleaning solution

Al <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	$SO_3$	H <sub>2</sub> O	pН	<sup>a</sup> [OH] <sup>-</sup>	Density (g/cm <sup>3</sup> )
7.14	12.13	1.18	79.5	12-14	5.3	1.30
<sup>a</sup> Acid-base reaction with 5 N HCL (Panrea S.A.)						

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Figure 1 shows the particle size distribution of the soil and both precursors. The curves were obtained by laser diffraction, using a Sympatec Helos BF particle size analyser, with a measuring range between 0.9 mm and 175 mm. The particle size below 45µm was 75.6, 81.3 and 99.2% for fly ash, soil and glass waste, respectively.

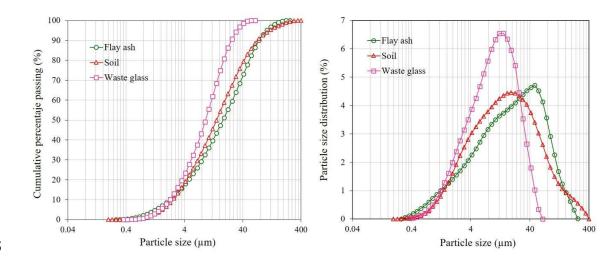
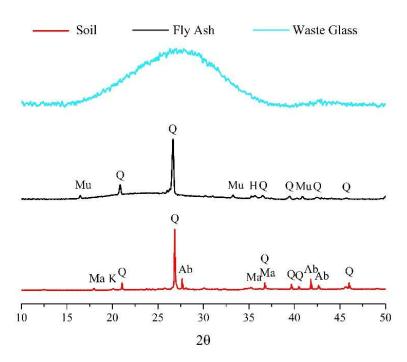




Figure 1. Cumulative particle size and particle size distribution of the Fly ash, Soil and Waste glass

The mineralogical composition of the soil and precursors and the soil was determined using 168 169 X-ray diffraction (XRD), with a PANAlytical X'Pert Pro MPD, with CuKa radiation at 170 40Kev and 30mA, equipped with a detector X'Celerator and a secondary monochromator. 171 The diffractograms are presented in Figure 2. The glass residue is a highly amorphous material, as evidenced by the large halo between the  $17^{\circ}(2\theta)$  to  $37^{\circ}(2\theta)$  angles. The fly ash 172 173 is a semi-crystalline material, also with some amorphous content, represented by a smaller 174 halo between angles  $18^{\circ}(2\theta)$  and  $32^{\circ}(2\theta)$ . It is mineralogy composed essentially by quartz, mullite and hematite. As expected, the soil is a totally crystalline material, composed of 175 176 several minerals such as quartz, kaolinite magnetite and albite.

177



178

179Figure 2. XRD Pattern of the original materials . Fly ash: Mu=Mullite, Q= quartz, H=Hematite; Soil:<br/>Q=quartz, K=Kaolinite, Ma=Magnetite, Ab= Albite

184 Prior to the stabilization of the soil, it was necessary to define the composition of the alkaline 185 activated cement (AAC) that would be used as a binder. This AAC was prepared with the 186 described cleaning solution (CS), which was used to activate the glass waste (GW) and the 187 fly ash (FA), acting as the precursor, in a 50/50 weight ratio. The CS was added according 188 with pre-defined activator/precursor weight ratios of 0.50, 0.57 and 0.75. The lowest of these 189 values was defined based on the minimum workability requirements. The pastes were then 190 moulded in 4 cm cubic specimens, which were cured at 50°C and 10% relative humidity in a 191 climatic chamber, for 7 days. Figure 3 presents the uniaxial compressive strength (UCS) 192 obtained by each of the AAC tested. The highest UCS (11.6 MPa) was obtained with the 193 lower activator/precursor ratio of 0.50.

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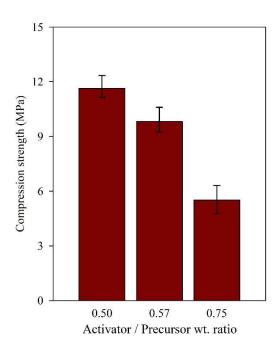


Figure 3. Compressive strength, after 7 days curing, of the 50% FA + 50% GW precursor paste

## 198 2.3 Definition of the AAC/soil composition

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To define the most adequate activator content, in terms of dry density, a Standard Proctor test was carried out based on the methodology proposed by the EN13286-42 (2004), using the AAC with an activator/precursor ratio of 0.50 as a starting point. The test was performed with 3 layers and 12 blows per layer, on pastes with a precursor/soil weight ratio of 30/70. A curve was obtained (Figure 4) by adding more or less activator to the solids (precursor + soil), from which the maximum dry density and optimum moisture content were identified as 1.77 g/cm<sup>3</sup> and 17%, respectively.

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However, when the CEB was compacted, significant expansion was registered, which was attributed to excessive moisture. To avoid this effect during the fabrication of the CEB, it was decided to further optimise the moisture content in the AAC/soil composition, aiming at a value lower than 17%, without reducing the density of 1.77 g/cm<sup>3</sup> obtained during the Proctor test. This was possible due to the higher energy applied by the earth block compaction machine, compared with the dynamic energy transmitted by the Proctor hammer.

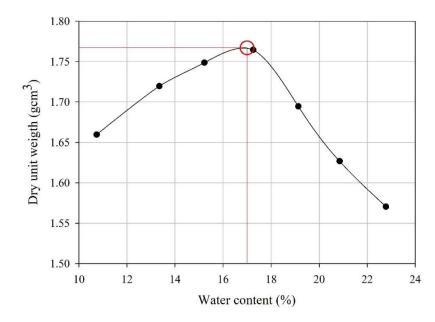


Figure 4. Proctor test results for the stabilised soil, using the activator as the liquid phase and a precursor/soil weight ratio of 30/70

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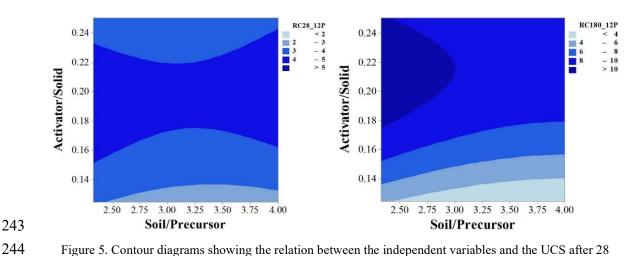
219 This optimisation was developed through an experiment design based on the response surface methodology (RSM). A Central Composite Design (CCD) was configured with the aim of 220 221 finding a relation between the independent variables and the response variable (compressive 222 strength) capable of maximize the latter (Montgomery and Runger, 2014), therefore defining 223 the most effective AAC/soil combination. Table 3 presents the independent variables 224 considered (i.e. soil/precursor and activator/solids), as well as their respective range. The 225 commercially available software Minitab 17 was used which, based on the number of 226 independent variables assumed, established a total of 13 random runs. The soil/precursor 227 range was defined based on previous experience by the research team (Corrêa-Silva et al., 228 2019; Cristelo et al., 2018; Miranda et al., 2017; Rios et al., 2016); while the activator/solid 229 range was defined after the maximum and minimum CS content in the paste that presented 230 the most adequate workability. This range was on the 'dry side' of the Proctor curve, thus below the 17% humidity threshold that produced the expansion of the paste. The response 231

- variable was assessed through compressive strength tests on compacted specimens with 70
- mm in diameter and 140 mm in height, cured at  $20 \pm 1$  °C for 28 and 180 days.
- The influence of each independent variable and the corresponding compressive strength is presented in Figure 5. For the 28-day curing period, higher UCS were attained when the pastes showed the highest CS content, regardless of the precursor content; while for 180-day period the higher UCS was recorded when the CS and precursor contents simultaneously
- assumed their higher values.

Table 3. Definition of the independent variables and corresponding value range

Variable	Level	Value
Activator/Solids	Lower (-)	0.12
	Upper (+)	0.25
	Central Point	0.18
Soil/Precursor	Lower (-)	2.3
	Upper (+)	4.0
	Central Point	3.1





- 245 days (left) and 180 days curing (right) on the AAC/soil

- 248 The final values of each independent variable, based on the compressive strength data of 11.4
- 249 MPa (desirability of 0.82), obtained after 180 days (Figure 6), were set at soil/precursor =
- 250 2.3 and activator/solids = 0.21.
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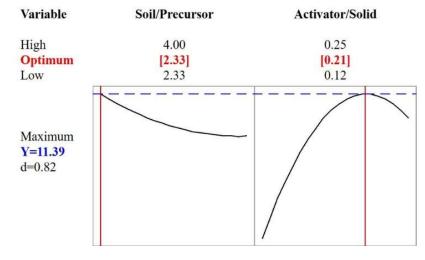


Figure 6. Optimised independent variables and resulting UCS and desirability values

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255 2.4 Fabrication of the Compressed Earth Blocks

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257 The CEB were fabricated with the optimised AAC-soil combination. The main steps towards 258 the production of each block are presented in Figure 7, and involve, after a thorough mixture 259 of the soil with the binder, the filling of two simultaneous moulds, in a fully manually 260 operated CEB machine, their subsequent compression and, finally, the curing and drying 261 stage. Considering that the 180-day curing result was chosen as the reference, and to avoid 262 such prolonged waiting, the CEBs were cured at 85°C for 20h, to accelerate the dissolution 263 stage and the production of binding gel (Bakharev, 2005; Criado et al., 2010; Fernández-Jiménez et al., 2008, 2006; Torres-Carrasco et al., 2014; Torres-Carrasco and Puertas, 2015). 264 265



Figure 7. Main steps in the fabrication process of the CEBs, including, after mixture of the soil with the alkaline cement, the filling of the moulds (a and b), the subsequent compression (c) and the curing and drying of the resulting blocks (d)

271	The physical-mechanical characterization of the CEBs was carried out with compressive
272	strength tests, water absorption tests, wetting-drying tests, ice-thawing tests and water
273	erosion tests. Furthermore, the microstructural characterization of the AAC-soil was
274	performed using Fourier Transform Infra-Red Spectroscopy (FTIR) and Scanning Electron
275	Microscopy (SEM).
276	
277	

- **3. Results and discussion**

## 280 3.1 Mechanical performance of the CEBs

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282 The compressive strength is mostly accepted as a universal property to determine the quality 283 of the CEBs. In general, the compressive strength is related to the type of soil; type and 284 amount of stabilizer; compaction pressure and process. Table 4 summarizes the compressive 285 strength results performed on the CEBs in both dry and saturated conditions, together with 286 the percentage of water absorption until saturation. The maximum compressive strength 287 reached by the CEB (17.23 MPa) was significantly higher than the uniaxial compressive 288 strength developed by the optimum AAC/soil formulation (11.4 MPa). Such increase, of 289 more than 50%, is not attributed to the geometry differences between the two types of 290 specimen, but mostly to the thermal curing process that was implemented for the CEB. 291 According to some authors (Bakharev, 2005; Singh and Subramaniam, 2019) fly ash-based 292 alkaline cements generate mechanical strength very slowly at room temperature. On the 293 contrary, the dissolution of the amorphous phase of the fly ash is improved if the curing 294 occurs under an increased temperature (Rivera et al., 2018; Torres-Carrasco and Puertas, 295 2015), generating aluminosilicate gel in shorter periods and, thus, increasing the strength 296 development rate of the material (Ryu et al., 2012; Šimonová et al., 2018; Singh and 297 Subramaniam, 2019).

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- 299

Table 4. Compressive strength and water absorption of the CEBs (UNE 41410, 2008)

Property		Type of specimen		
		Unsaturated CEB	Saturated CEB	
Compressive strength (MPa)	Average	17.23	7.45	
	Range	14.94 - 19.39	6.35 - 9.29	
	N° of specimens	4	4	
	Average		16.21	
Water absortion (%)	Range	-	15.92 - 16.49	
	N° of specimen		4	

301 The UNE 41410 (2008) standard classifies the CEBs in three categories, according to its 302 respective compressive strength: CEB1, CEB3 and CEB5. Each category corresponds to the 303 minimum compressive strength of the CEB, e.g. category CEB5 corresponds to the blocks 304 with a strength of at least 5 MPa. According to this standard, it is possible to classify the 305 present CEB in the CEB5 category. ASTM C62-17 (2017) specifies the minimum 306 requirements of solid masonry made of compacted clay or similar materials, sintered at high 307 temperatures. Based on this standard, the CEB designed in this research can be classified as 308 a 'MW' grade brick, with the advantage that in the manufacturing process of the block no 309 high temperatures were used for sintering its components. This means that good mechanical 310 properties were achieved with an amount of incorporated energy well below the energy 311 required to fabricate a cooked brick.

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#### 313 *3.2 Durability tests*

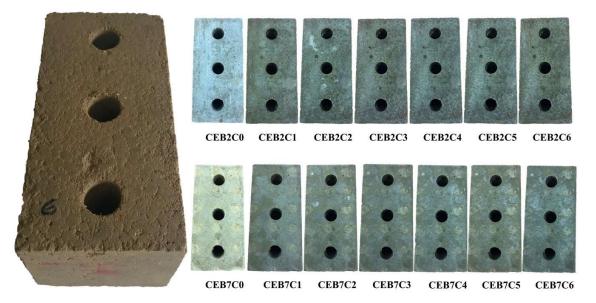
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Figure 8 shows images of the evolution of the wetting-drying test, using a total of 7 blocks, following the contents of the UNE 41410 standard. After detailed visual inspection, no significant deterioration was observed after the planned 6 cycles of wetting-drying. This corroborates that the stabilization of the soil and the cementation of its particles was very effective, to the point where the physical integrity of the blocks was not affected by the volume changes intentionally induced by the test.

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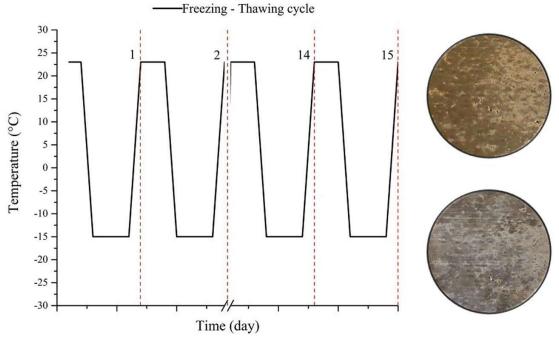
The ice-thaw test used for BTCs was done based on DIN 18945-47 (2013). The durability assessment of the blocks is very important since they mostly measure the longevity of the 324 CEB. Moreover, sequential submission to freezing and thawing is one of the most aggressive 325 environmental conditions for this class of compacted earth masonry elements. The humidity 326 lodged in the structure of the compacted piece, at the time of the freezing, generates internal 327 pressure in the pores due to the increase in volume of the frozen water, which can even cause a structural collapse (Jamshidi et al., 2016; Mak et al., 2016). Figure 9 presents the 328 329 temperature profile used during the test, comprising a total of 15 cycles. The exposed surface 330 of the block was moistened and submitted to the temperature variations. At the end of the 15 331 cycles, no significant damage was observed, including gaps, cracks, fractures or delamination 332 of the material, demonstrating that the structure of the stabilized CEB was strong enough to 333 withstand the stresses caused by the internal pressure of the frozen water during the test.

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Figure 9. Freeze-thaw temperature cycles

341 The durability of the CEBs was also evaluated through their resistance to water erosion, 342 tested according to the Swinburne test (SAET), as established in the Spanish standard UNE 41410 (2008). This test was specifically developed for earthen materials and simulates the 343 344 accelerated erosion action of hitting rain. The test setup consists of a deposit, elevated 1 m 345 above the exposed surface of the CEB, which continuously drops water on the surface of the 346 CEB from an outlet of 5 mm diameter, while keeping a constant water head of 0.5 m (Figure 347 10a). The surface of the CEB is inclined 27° relatively to the horizontal plane. The water 348 dropping lasts 10 minutes, after which the specimen is opened and the pitting depth caused 349 by the water stream is measured, using a 3 mm diameter probe. According to the contents of 350 the mentioned standard, the CEBs are suitable if the pitting depth is not higher than 10 mm. 351

352 The results of the three specimens tested are presented in Table 5. As can be seen in Figure 353 10b, the water stream did not cause any surface degradation, meaning that the stabilisation 354 solution used is highly effective in providing water erosion resistance to the CEBs. The 355 moisture penetration depth was additionally measured, by breaking the specimens into 2 356 halves along the longitudinal section hit by the stream (Figure 10b). An average value of 357 9 mm was observed, although all specimens showed some variation in the penetration depth (Figure 10c), which was caused by the presence of some clogs formed during the mix located 358 359 near the surface, facilitating the water intake.

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361

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Figure 10. Swinburn test setup (a); surface of the CEB after exposure (b); water penetration depth (c)

364 Table 5. Results of the Swinburn test (CoV in brackets)

Specimen	Pitting depth (mm)	Moisture penetration depth (mm)
S1	0	9
S2	0	10

365 <u>S3 0 8</u> Average 0 9 (16%)

366 *3.3 FTIR* 

367

368 Figure 11 shows the IR spectra of the raw material with which the CEBs were manufactured. 369 The FA and WG residues have several signals in common – bands centred around 455, 774 and 776 cm<sup>-1</sup>, associated with Si-O (quartz) functional groups. The main band of the FA is 370 located around 1023 cm<sup>-1</sup>, characteristic of Si-O-T (T = Al, Si) type links. This spectrum is 371 372 typical of a material rich in aluminosilicates (Criado et al., 2007; Gao et al., 2014; Panias et al., 2007; Rivera et al., 2019). The GW has a main band centred around 959 cm<sup>-1</sup>, and the 373 signals located between 950 - 1000 cm<sup>-1</sup> are associated with vibration modes of Si-O-Na 374 375 functional groups in condensed units of type Q2 and Q3 silicates, typical of a calcium sodium glass (Khalil et al., 2010; Rivera et al., 2018; Varma et al., 2009; Véron et al., 2013). The 376 characteristic spectrum of the soil reveals signals at 455 cm<sup>-1</sup>, 748 cm<sup>-1</sup> and 998 cm<sup>-1</sup> wave 377 378 lengths, associated with vibration modes of Si-O-Si and Si-O functional groups (i.e. quartz). The band signal around 529 cm<sup>-1</sup> can be attributed to stretching vibrations of Fe-O. Fe2O3 379 and Si-O-Al type bonds, while bands in the region 850-950 cm<sup>-1</sup> are characteristic of O-H-380 Al type links, and the band identified at 1633 cm<sup>-1</sup> is attributed to bending vibration modes 381 of O-H-O type bonds of water molecules (Kaufhold et al., 2012; Nayak and Singh, 2007; 382 383 Saikia and Parthasarathy, 2010).

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The cleaning solution, being a highly alkaline aqueous solution contaminated by the aluminium foundry industry, is basically composed by products from the reaction between caustic soda and aluminium waste. In its IR spectrum, a signal centred at 527 cm<sup>-1</sup> can be 388 observed, attributed to non-condensed octahedral species of AlO6 (these octahedral species can present signals between 400 - 530 cm<sup>-1</sup>). The region between 700 - 900 cm<sup>-1</sup> is 389 390 characteristic of AlO4 tetrahedral species (Tarte, 1967). Therefore, it is not surprising that ionic species of Al(OH)<sup>-4</sup> aluminates in solution were identified in this same region. These 391 392 aluminate species are predominant in pH values between 8-12, with vibrations of Al-OH type 393 bonds (Li et al., 2014; MA et al., 2007). According to Ram (2001), the bands in the IR spectrum of the cleaning solution around 1019 and 1420 cm<sup>-1</sup> could be considered as 394 395 vibration signals of double bond stretching of Al=O of amorphous compounds. In short, and 396 as expected, signals of aluminate compounds and aluminium hydroxides were found in the 397 spectrum of the cleaning solution.

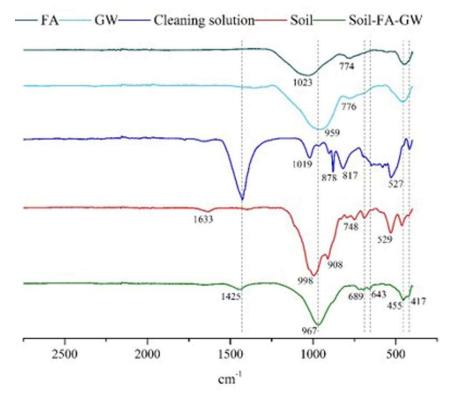
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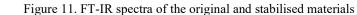
When stabilizing the soil-FA-GW mixture with the cleaning solution, some changes in the IR spectrum of the stabilized material were noted. The cleaning solution, being highly alkaline (pH between 12-14), attacks the amorphous acid oxides included in the precursor materials (FA and GW), and even oxides such as FeO and Fe<sub>2</sub>O<sub>3</sub> can be affected by the alkaline attack (Lemougna et al., 2013; Lloyd et al., 2009; van Deventer et al., 2007). Some signals are preserved, such as those from the crystalline quartz 455 cm<sup>-1</sup>.

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406 On the other hand, bands around 643 and 689 cm-1 can be attributed to new reaction products. 407 According to Criado et al. (2007), in the region between 500 - 800 cm<sup>-1</sup> the typical signals of 408 various cyclic structures of aluminosilicates formed by the union of SiO4 and AlO4 409 tetrahedra, linked by oxygen atoms resulting from the alkaline attack, are identified. The 410 compounds identified in the cleaning solution apparently now form part of the new structure 411 of the cementing gel, since the signals of the Al(OH)<sup>-4</sup> aluminates and AlO4 tetrahedra are 412 not noticeable in the new stabilized material, and even the signal identified as representing the Al=O link (1425 cm<sup>-1</sup>) has decreased almost until disappearing. The main band of the 413 stabilized material located around 967 cm<sup>-1</sup>, can represent different types of overlapping links 414 and structures. Generally the region between 950-1250 cm<sup>-1</sup> of the FTIR spectrum 415 416 corresponds to Si-O-T type bonds (T = Si, Al) which indicates that the main reaction product generated by the dissolution of the precursors is an aluminosilicate gel. This region is also 417 related to signals from reactive terminals of the type Si-O-Na plus whichever ions are 418 419 responsible for generating the aluminosilicate chains (Lee and Van Deventer, 2003). The 420 precise location of the band in this region will depend on the type of generated structure, of 421 alkaline activator used and of the composition of the binding gel (Criado et al., 2007).

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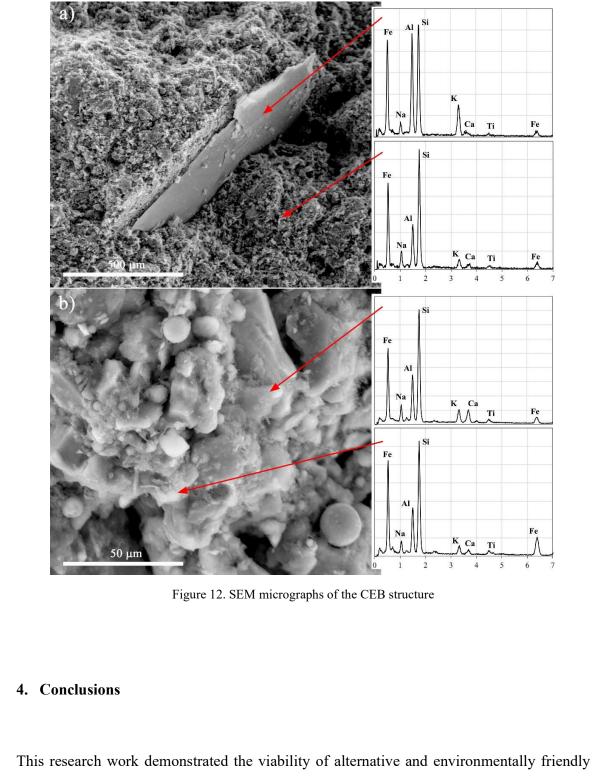


425

426 *3.4 SEM* 

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428 The microstructure of the stabilized soil was examined with scanning electron microscopy, 429 complemented with energy dispersive spectroscopy, for chemical assessment of the binding 430 gel developed. Some of the images obtained (the analysis was performed on a sample 431 collected from one of the previously tested CEBs) are presented in Figure 12, showing the overall morphology of the stabilised soil (Figure 12a), where the binding effect of the 432 433 material synthesized from alkaline activated residues is clear, resulting in a homogeneous 434 and fairly compacted structure with apparently well cemented soil particles. Figure 12b 435 presented the cemented soil particles in higher detail, where it is possible to detect both 436 precursor and soil particles embedded in what appears to be the cementitious matrix. The 437 nature of the reaction products was identified as a sodium aluminosilicate gel (N-A-S-H), 438 which corroborates the characterization done with FTIR. Indeed, it was previously proposed 439 that the nature of the reaction products was a sodium aluminosilicate gel, due to the nature 440 of the precursors and the alkaline activator.



soil stabilisation, with the specific purpose of manufacturing masonry elements commonlyknown as "compressed earth blocks", or CEBs. The alternative synthesized cements are

451 100% based on industrial waste, and its applicability to soil stabilisation was thoroughly 452 assessed through strength and durability tests. The results showed that such material can be 453 an effective alternative to traditional chemical stabilisation of soils, namely to calcium-based 454 cements, such as lime or Portland cement. The manufacture of compacted earth masonry 455 elements using this type of cementitious material suggests both a technical and environmental 456 advantage since, in theory, the amount of incorporated energy in waste-based binding agents 457 is significantly lower than the energy associated with traditional binders. However, and in 458 order to fully corroborate this, it will be necessary to perform a comparison between both 459 types of binders, in order to characterised and make evident and all the advantages and 460 disadvantages. 461 462 463 Acknowledgments 464 465 The authors would also like to acknowledge the contribution of the Electronic Microscopy 466 Unit of the University of Trás-os-Montes e Alto Douro (Dr. Lisete Fernandes), for the 467 microstructural analysis. 468 469 470 Funding 471 472 This work was funded by the R&D Project JUSTREST- Development of Alkali Binders for 473 Geotechnical Applications Made Exclusively from Industrial Waste, with reference

474	PTDC/ECM-GEO/0637/2014, financed by the Foundation for Science and Technology -
475	FCT/MCTES (PIDDAC).
476	
477	The research was supported by the GEO-DESIGN project, nº17501, co-financed by the
478	European Regional Development Fund (ERDF) through NORTE 2020 (North Regional
479	Operational Program 2014/2020).
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