

1 TOWARDS PREPARATION CONDITIONS FOR THE SYNTHESIS OF  
2 ALKALI-ACTIVATED BINDERS USING TUNGSTEN MINING WASTE

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10  
11 **ABSTRACT**

12 This study evaluated the results of preparation conditions for the production of an alkali-  
13 activated binder (AAB) based on a binary mixture of tailings from tungsten mine waste  
14 (TMW), and waste glass (WG) activated with a mixture of sodium silicate (SS) and sodium  
15 hydroxide (SH). 40 wt.% WG increased the amorphous nature of the binary blend by 21%  
16 without initiating the alkali-silica reaction. SS/SH activator solution was subjected to a  
17 variation of mixing times, and its sensitivity was measured using temperature monitoring, and  
18 Fourier Transforms Infrared Spectroscopy (FTIR). After 20 minutes of mixing, the SS/SH  
19 activator solution showed a 3.13°C reduction in temperature, a 21.4% increase in unbound  
20 water content and as a result imparted a 26% drop in the mechanical resistance of TMW-WG  
21 AAB at 28-days. The TMW-WG AAB was also determined to develop the highest  
22 compressive strength when cured at 80°C for 24h in sealed conditions. The following  
23 conditions, supported by X-ray diffraction (XRD) and Fourier transforms infrared analysis  
24 (FTIR), are responsible for the most significant dissolution of the alumino-silicate oxides.

25 *Author keywords:* alkali-activated binder; binary blend; curing temperature; geopolymer;  
26 material preparation; mixing time; precursor reactivity; synthesis conditions; tungsten mining  
27 waste; waste glass

## 28 **INTRODUCTION**

29

30 Although the development of Portland cement (PC) research and its application has  
31 considerably matured in last few decades, it is still facing challenges due to its impact on the  
32 environment. The production of cement is one of the industry's most energy intensive  
33 processes next only to steel and aluminium (Napp et al. 2014). In 2011, the European states  
34 accounted for 7.6% of total global cement production (European Cement Association 2014).  
35 The manufacture of PC can consume approximately 3.2-6.3 GJ of energy (thermal and  
36 electrical) per tonne of clinker product (Rahman et al. 2016) with almost half of this being  
37 used for the fine grinding of clinker to make the cement. The main raw material used in  
38 cement production has traditionally been the abundantly available limestone which, by its  
39 inevitable transformation into lime, is responsible for over 60% of the cement industry's CO<sub>2</sub>  
40 emissions (Mikulčić et al. 2012). For every kg of PC clinker produced, about 0.87 kg of CO<sub>2</sub>  
41 is released (Telesca et al. 2017). Therefore, the main challenge of the cement industry is  
42 focused on the CO<sub>2</sub> emission reduction to 1.55 Gt per year (about 45% of the current value)  
43 by 2050 (Telesca et al. 2017).

44 To reduce the carbon footprint and conveniently dispose of the variety of waste material  
45 available from multiple industries, alkali-activated binders (AABs for short hereafter) have  
46 attracted increasingly more attention from the scientific community as environmentally  
47 favourable alternatives to PC (Barbosa et al. 2000; Bădănoiu et al. 2015). Aluminosilicate  
48 rich materials can be chemically activated to produce a three-dimensional polymer like  
49 network containing both crystalline and amorphous phases (Davidovits 1981). These

50 particular binders yield high strength with rapid setting, good durability and high resistance to  
51 chemical attack (Hardjito et al. 2009; Ariffin et al. 2013; Thomas and Peethamparan 2015).  
52 Despite the existence of strong economic and environmental drivers, alkali-activated binders  
53 are still not widely implemented throughout the world. They represent an attractive  
54 alternative for the partial or complete substitution of PC, offering comparable performance  
55 (Neupane 2016) and cost (Duxson et al. 2007a) while reducing greenhouse gas emissions  
56 (Duxson et al. 2007b).

57 The raw materials used for synthesising AABs are typically calcined clays or low-calcium fly  
58 ashes (Duxson et al. 2007a). However, the supply of fly ash in Europe is in decline due to the  
59 industry becoming increasingly less reliant on coal-fired power stations (Carroll 2015) while  
60 the disposal of the 85% of host rock generated from kaolin clay mining is an increasingly  
61 critical issue (Murray 2002). On the other hand, mining and quarrying waste still represent  
62 15% of the total waste in Western Europe and 31% in Eastern Europe (Pacheco-Torgal et al.  
63 2009b), while the USA alone is estimated to produce between 1000-2000 Mt of mining waste  
64 annually (Szczepańska and Twardowska 2004). The favourable mineralogical composition of  
65 mining waste for alkali activation (Jiao et al. 2013; Ye et al. 2014; Zhang 2014) combined  
66 with its continuously large production make it an attractive and environmentally friendly  
67 feedstock for AABs.

68 Some mining and quarrying wastes can be reused in earthworks and construction, in  
69 particular, the coarser fractions. Typical applications include use in asphalt pavements  
70 (Albuquerque et al. 2006; Akbulut and Güreş 2007) and concrete (Yellishetty et al. 2008;  
71 Hebhouh et al. 2011). However, recent studies on the reuse of fine tailings as raw material for  
72 AABs are considered to be most promising; from an environmental, technical and economic  
73 point of views. For this study, the wastes of particular interest are fine tailings derived from  
74 tungsten mining. Preliminary research has been conducted on the transformation of this type

75 of waste into AABs and has shown promising results. Pacheco-Torgal et al. (2007) first  
76 highlighted the potential of using calcined tungsten mining waste mud blended with calcium  
77 hydroxide for the development of a high early strength geopolymeric binder. Tungsten  
78 mining waste also identified to be very effective for stabilizing/solidifying heavy metals  
79 particularly when used in conjunction with blast-furnace slag (Choi et al. 2009) and overall,  
80 suggested that mortar with acceptable properties can be developed using up to 10% by mass  
81 tungsten mining waste. Later, alkali-activated artificial aggregates were produced from such  
82 mining waste mud, and their properties were studied as a potential substrate for fixed-film  
83 wastewater treatment processes (biofilm reactors). The results showed that the aggregates  
84 obtained have suitable resistance to acid attack and may be used as a substrate for fixed-film  
85 biological reactors for the treatment of acid wastewaters (Silva et al. 2012a). Also, mine  
86 tailings blended with other industrial by-products such as fly ash have resulted in the  
87 production of an AAB with high compressive strength, mainly due to the Si/Al ratio of the  
88 raw material blend falling within the optimum Si/Al ratio for alkali-activation (Zhang et al.  
89 2011; Ahmari and Zhang 2012).

90 Despite the research conducted so far, it remains that tungsten mining waste possesses a low  
91 degree of reactivity due to its crystalline phases. Thermal treatments have previously been  
92 studied to improve the amorphicity of tungsten mining waste, and satisfactory strengths have  
93 been achieved (Pacheco-Torgal et al. 2009b), nonetheless at the expense of the high amount  
94 of energy. A more sustainable method would be to blend the tungsten mining waste with a  
95 material that would increase not only its level of amorphicity but also maintain its  
96 environmental appeal. In this case, waste glass would be the ideal candidate since it is a very  
97 common construction and household waste material with a highly amorphous structure. It is  
98 estimated that out of 18 million tonnes of glass wastes accumulated in 2012 in the EU, only  
99 35% of this was recycled (Glass for Europe 2013). The feasibility of using ground waste

100 glass to improve mechanical performance has already been achieved with PC concrete (Shao  
101 et al. 2000a) and initiated with metakaolin based AABs (Christiansen and Sutter 2013).

102 Also when assessing novel binder materials, it is of as much importance to study the  
103 preparation/manufacturing techniques as it is the final material properties. This is a domain  
104 which currently remains understudied for AABs in general, let alone those based on tungsten  
105 mining waste.

106 Thus, the primary objective of this study is to determine the fundamental aspects of AAB  
107 synthesis using tungsten mining waste as the principle raw material with the added feasibility  
108 of its partial replacement by waste glass. Particular focus will be on (1) the influence of waste  
109 glass on tungsten mining waste reactivity; (2) alkali activator solution preparation and  
110 kinetics; (3) AAB curing temperature and curing duration.

111

## 112 **MATERIALS AND METHODS**

113

### 114 **Materials**

115 The raw materials used in this investigation consisted of tungsten mining waste (TMW),  
116 waste glass (WG), sodium hydroxide (NaOH) (SH), and sodium silicate ( $\text{Na}_2\text{SiO}_3$ ) (SS). The  
117 TMW was derived in powder form from the Panasqueira mine in Castelo Branco, Portugal,  
118 and the WG was received from the local municipality of Covilhã, Portugal. The chemical  
119 composition of the TMW and WG as obtained by SEM-EDX (SUPRA 35VP/EDAX). Due to  
120 the waste nature and microscopic inhomogeneity of the TMW, chemical analyses were made  
121 from different batches collected from the mine. Therefore, the results of TMW reported in  
122 Table 1 are the average values accompanied with the standard deviation (S.D). According to  
123 Table 1, for TMW, the oxides  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{SO}_3$  are the most abundant, while the  
124 oxides  $\text{SiO}_2$ ,  $\text{MgO}$ ,  $\text{SO}_3$  and  $\text{Fe}_2\text{O}_3$  showed the greatest variability. Grain size distribution  
125 analysis was performed for the precursor materials after mechanical sieving by laser

126 diffraction analysis according to BS ISO 13320:2009. The TMW has a mean particle size of  
127 26 $\mu$ m while the waste glass has a mean particle size of 39.6 $\mu$ m. The WG was intentionally  
128 used with a slightly larger mean particle size to reduce the energy consumption during the  
129 milling process. The bulk powder densities of TMW and WG were determined using a gas  
130 displacement pycnometer (AccuPyc II 1340) and were determined as 3.08 and 2.53 g/cm<sup>3</sup>,  
131 respectively. Sodium hydroxide solution was prepared by dissolving sodium hydroxide  
132 pellets (98% purity obtained from Fisher Scientific) in de-ionized water and allowed to cool  
133 before use. Sodium silicate (obtained from Solvay SA, Portugal) had a SiO<sub>2</sub>/Na<sub>2</sub>O = 3.23  
134 (8.60 wt.% Na<sub>2</sub>O, 27.79 wt.% SiO<sub>2</sub>, 63.19wt.% H<sub>2</sub>O, 0.4wt.% Al<sub>2</sub>O<sub>3</sub>).

### 135 **Synthesis of samples**

136 All experiments were carried out at 20°C. TMW alkali-activated binders with up to 40 mass-  
137 % replacement with WG were blended with an IKA Ultra-Turrax T50 mixer at 360 rpm for  
138 60 s. Based on the research on alkali-activation available in the literature concerning  
139 mechanical strength and efflorescence formation potential in AABs combined with the  
140 experience gained from previous studies (Pacheco-Torgal et al. 2008; Silva et al. 2012b;  
141 Kastiukas et al. 2016), the following ranges were selected for the constituents of the AABs:

- 142 • Molarity of SH = 10M
- 143 • Weight ratio of SS/SH = 4
- 144 • Weight ratio of precursor/activator = 3.6

145 The following ratios produced an AAB with a flowability of 130  $\pm$  5mm determined using  
146 the method proposed by EN 1015-3:1999 (2006) and initial and final setting times of 90 and  
147 110 minutes determined EN 196-3 (European Committee for Standardization 2005). In the  
148 precursor/activator ratio, the precursor is the TMW and WG, and the activator is the solution  
149 containing the alkali, the silicate and the water.

150 To produce the TMW-WG AAB, the TMW, and WG were mixed in the dry state for five  
151 minutes, forming the precursor materials. The sodium hydroxide and sodium silicate  
152 solutions were mixed for a period ranging from 2.5 to 60 mins at 700 rpm, depending on the  
153 type of condition being tested, forming the alkali activator. The alkali-activator solution was  
154 slowly added to the precursor materials, and the resulting paste was stirred for 2.5 minutes at  
155 200 rpm, followed by 2.5 minutes at 400 rpm. The resulting AAB was then placed in  
156 40x40x160 mm<sup>3</sup> prismatic Styrofoam moulds. The mould was filled with the AAB in three  
157 stages and manually vibrated after each successive filling stage to release trapped air bubbles,  
158 and sealed with a film to avoid the loss of water and ingress of CO<sub>2</sub>. Samples which were  
159 made to test curing exposed to the atmosphere were cured unsealed. The specimens were  
160 placed in a temperature and humidity controlled environmental chamber at 50% RH for  
161 curing between 20 and 80°C for 4-36h, depending on the type of condition being tested.  
162 After curing, prisms were de-moulded and left in a laboratory condition of 20°C for curing  
163 until the test age. The specimens cured at 20°C were de-moulded after 48 h due to a slow  
164 setting. Table 2 summarises synthesis conditions tested in this study i.e. activator solution  
165 mixing time, curing temperature and curing time.

166 To observe for chemical changes in the activator solution during mixing, the first it was  
167 decided to isolate the activating solution and monitor its temperature during the mixing  
168 process. The temperature evolution of the activator solution was measured using the setup  
169 shown in Fig. 1. The activator solution was prepared at the same SS/SH solution ratio as that  
170 used to make the TMW-WG ABB i.e. 4.0. A polystyrene enclosure was used to contain the  
171 activator solution and provided a thermodynamically stable environment. Two K-type  
172 thermocouples with the tips wrapped in temperature sensitive copper tape were connected to  
173 a multi-channel data logger and used to measure the temperature of the activator solution and

174 enclosure's interior, respectively. Once the activator temperature was deemed constant,  
175 mixing was started and continued for 20 minutes at 700 rpm.

176

### 177 **Compressive Strength**

178 The demoulded samples were left to rest at 20°C and a relative humidity of 75 % until the  
179 specific age of testing. The compressive strength of the prismatic sample fractured  
180 counterparts was tested after 1, 3, 7, 28 days in accordance with EN 196-1 using a universal  
181 testing machine (Instron 5960) at a constant loading rate of 144 kN/min. The compressive  
182 strength value was the average of values obtained from three specimens.

### 183 **X-ray Diffraction (XRD) Analyses**

184 The mineralogical compositions of the TMW and WG were obtained by powder X-ray  
185 diffraction (BRUKER D8 Advance) with an automatic slit, monochromated CuK $\alpha$  radiation  
186 ( $\lambda=1.5405 \text{ \AA}$ ), 5-80° 2 $\theta$  range, 0.600 s count time, Cu radiation, 40kV and 40mA. Peak  
187 shapes were studied using the program DIFFRACT.SUITE.

### 188 **Fourier Transform Infra-Red (FTIR) Analyses**

189 FTIR spectra were recorded from 400 to 4000 cm<sup>-1</sup> with a 2cm<sup>-1</sup> resolution, 5 kHz scanning  
190 speed and 25 scan count using a Shimadzu IRAffinity-1 fitted with a Specac Quest attenuated  
191 total reflectance (ATR) accessory.

### 192 **Scanning Electron Microscopy (SEM)**

193 Microstructural studies utilised SEM (Zeiss Supra 35VP) equipped with EDS analyser  
194 (EDAX). Backscattered and Secondary electron images were collected from polished  
195 specimens to overcome the main limitation of fracture surfaces. To prepare the polished  
196 specimens, 5-mm-thick slices were cut using a low-speed saw. The samples were first  
197 impregnated with ultra-low viscosity resin and then polished.

198



## 199 **Stopping the activation process**

200 Both the XRD and FTIR samples were tested in a state where the alkali activation process  
201 was stopped using the combined water and solvent extraction protocol developed by Chen et  
202 al. ( 2014). In summary, it involved stirring the AAB specimen in deionized water and then  
203 removing the liquid by centrifuging. Upon addition of methanol, soluble silicate species  
204 could be observed in the liquid layer. Thus water extraction by centrifuging was used to  
205 remove the precipitates. Specimens were then ground to micron-sized particles using a mortar  
206 and pestle, and a solvent of methanol/acetone mixture was added, followed by further  
207 grinding. The solvent was removed using vacuum filtration; this latter procedure was  
208 repeated for five times.

209

## 210 **RESULTS AND DISCUSSION**

### 211 **Influence of Waste Glass on Tungsten Mining Waste Reactivity**

212 The recorded FTIR spectra of raw TMW and WG and blended as TMW/WG are shown in  
213 Fig.2. For the spectra of WG, the highest absorption coefficient is associated with the Si-O  
214 bending vibration near  $453\text{ cm}^{-1}$ . A weaker band due to the bending mode near  $1000\text{ cm}^{-1}$  is  
215 accompanied by the still weaker feature near  $775\text{ cm}^{-1}$ . For the TMW, the highest absorption  
216 coefficient is associated with the bending vibration of the Si-O between  $465$  and  $424\text{ cm}^{-1}$ .  
217 Weaker features are associated with the bending vibration of Si-O at  $984\text{ cm}^{-1}$  and its  
218 symmetric stretching vibration between  $797$  and  $694\text{ cm}^{-1}$ . The weakest bands at  $827\text{ cm}^{-1}$  and  
219  $1163\text{ cm}^{-1}$  can be associated with the bending of the Si-O bond of the original TMW. The  
220 absorbance spectrum of the TMW/WG blend displays the same spectral bands as the raw  
221 TMW, only at lower intensities, obviously due to the combination of different intensities.

222 Results of the XRD analyses shown in Fig.3 reveal that the TMW precursor material  
223 predominantly consists of muscovite and silica with traces of sodium aluminosilicate,

224 rudashevskyite and pyrite and is similar to the TMW chemical composition identified by  
225 Pacheco-Torgal et al. (2009). The WG is revealed to consist of silica, lime and sodium oxide  
226 with traces of potassium and iron oxide. Using a general non-linear least squares system  
227 software (TOPAS V5), the TMW and WG were determined to be 97% and 15% crystalline,  
228 respectively. Compared to other materials commonly used as AAB precursors such as fly ash  
229 (Van Jaarsveld and Van Deventer 1999) and metakaolin (Provis et al. 2005), the TMW is of a  
230 far less amorphous nature. In this study, a sustainable approach was chosen to increase the  
231 amorphicity of the TMW through the addition of WG. The addition of 40 wt.% WG led to an  
232 increase in the amorphicity, qualitatively indicated by the more intense amorphous  
233 background from 15° to 45° in the TMW/WG blend XRD spectrum and also by a 21%  
234 calculated reduction in crystallinity. The compressive strength of TMW-WG AAB was used  
235 to evaluate the strength contribution potential as a function of the degree of amorphicity.  
236 Thus Fig.4 shows the evolution of compressive strength in TMW-WG AAB with 20, 30 and  
237 40 wt.% WG replacement over 28 days. The results obtained for pure TMW AAB are also  
238 included. Each reported result corresponds to the average measurement in three specimens  
239 per each WG replacement value and age; the deviation of results fluctuated between 0.22 and  
240 1.4%. In Fig.4 it can be observed the compressive strength increased with an increase in the  
241 WG content at all ages. The highest 28-day strength was obtained by the 60TMW40WG  
242 sample at 41MPa, which is 127% higher than the control sample 100TMW. The compressive  
243 strength would be influenced primarily by the additional release of reactive silica. However,  
244 it also expected that the CaO content in the WG would contribute to the strengthening of the  
245 reaction products, most likely in the form of a (C, N)-A-S-H gel.

246 The compressive strength results with the highest replacement level of WG i.e. 40wt.% is  
247 consistent with the compressive strength results previously obtained by Pacheco-Torgal et al.  
248 (2009b), specifically 39.6 MPa at 28 days, for mortar prepared with TMW. However, this

249 was achieved only after an energy intensive calcination treatment of the TMW at 950°C for 2  
250 hours.

251 Finally, the reactive silica-containing WG combined with the highly alkaline activator  
252 solution may create the potential for the deleterious process of alkali-silica reaction (ASR)  
253 and required validation. TMW-WG AAB with the highest replacement of WG i.e. 40 wt.%  
254 was stored at a RH of 80% at 38°C to accelerate the ASR reaction; a thin-section of this  
255 sample shown in Fig.5. Observation of the section, which is representative of the WG as a  
256 whole, revealed that there were no signs of ASR gel formation around the WG particles or in  
257 the open voids. Data reported in the literature established that if the waste glass is ground  
258 under 75 µm, the ASR effect does not occur, and binder durability is guaranteed (Shao et al.  
259 2000b). Water is also a necessary condition for ASR; considering the TMW-WG AAB only  
260 required a water/precursor demand of 0.179, this may also be the reason for the absence of  
261 ASR.

#### 262 **Alkali Activator Preparation Conditions**

263 To prepare the TMW-WG AAB, it is necessary that the alkali activator is in a homogeneous  
264 state upon mixing with the powder precursors. Fig.6 shows the effect of activator mixing time  
265 on the 80TMW20WG AAB compressive strength. It can be seen that the 28-day strength  
266 increases when using the activator which has been mixed between 2 and 5 minutes only (i.e.  
267 M2.5 and M5), reaching the maximum 28-day strength of 17 MPa at an activator mixing time  
268 of 5 minutes (i.e. M5). As the activator mixing time is extended, an immediate drop in  
269 compressive strength is observed. The activator solution mixing time has a strong impact on  
270 the 28-day strength, as a 26% drop in compressive strength is recorded for the TMW-WG  
271 AAB when prepared using an activator solution stirred for 20 minutes i.e. M20. Fig.7  
272 presents the results of the activator solution temperature during mixing. The black and red  
273 curves represent the activator and enclosure air temperature, respectively. Over the course of  
274

275 20 minutes of mixing, an average reduction of 3.13°C in activator temperature was recorded  
276 from three identical tests, while the enclosure temperature was recorded to remain stable at  
277 23°C±0.1°C. This drop activator solution temperature is an endothermic process resulting  
278 from the reorientation of the water molecules, leading to a disruption of the hydration shells  
279 surrounding the ions. The positive metal ions, in this case, Na<sup>+</sup>, are particularly at risk since  
280 they inherently possess weaker attractions to the negative oxygen end of the water molecule.  
281 The prolonged mixing can be thought to cause a net stripping effect of the water molecules  
282 from the ions. The latter would impact the dissolution and subsequent mobility of the  
283 siliceous material present in TMW and WG, leading to a less intense attack on the silicon-  
284 oxygen bonds and thus a reduction in mechanical performance, as verified by the results in  
285 Fig.6.

286 Further interpretation of this is shown by the ATR-FTIR spectra of the activator mixed for 5  
287 and 20 minutes in Fig.8. The 3270cm<sup>-1</sup> band (which is a sensitive and well-defined band  
288 corresponding to the O-H vibrations in water) is revealed to increase in intensity by 21.4%,  
289 which based on literature concerning FTIR spectra of water at different temperature  
290 (Praprotnik et al. 2004), may be considered as a significant amount. It is an indication that the  
291 activator solution mixed for 20 minutes possesses a higher unbound water content with fewer  
292 solvated ions and more available as free molecules. Also, visually observed after 20 minutes  
293 of mixing was the partial gelation of the soluble silicate anions detected by the loss of  
294 uniform fluid flow and the adherence of solid gel to the glass wall. Polymerization of silicates  
295 commonly occurs at pH close to neutral, but can also be triggered by an increased water  
296 content (Hu et al. 1993). Gelation would also contribute to reducing the effectiveness of the  
297 activator to balance the charge of the aluminate groups in the phyllosilicate, resulting in a  
298 negative effect on the kinetics of the reaction and therefore the development of mechanical  
299 strength. From a practical outlook, it must be emphasised that the preparation of the alkali

300 activator is independent of the mixing of the final binder. Therefore, the alkali-activators  
301 dependence on mixing time should not be considered to interfere with the upscaling potential  
302 of AABs.

### 303 **TMW-WG AAB Curing Temperature and Curing Time**

304 Samples T20 through to T80 in Table 2 were made so that the effect of different curing  
305 temperatures on compressive strength of TMW-WG AAB could be studied. The prisms cast  
306 were cured under sealed conditions at 20, 40, 60 and 80°C for 24h, then tested for  
307 compressive strength after 1, 3, 7 and 28 days. The compression strength results in Fig.9  
308 present details on the role of temperature on the properties of TMW-WG AAB. The  
309 compressive strength of all the samples at all ages increased with increasing curing  
310 temperature. Samples cured at 20°C (i.e. T20) did not develop appreciable compressive  
311 strength for the first 7 days of curing and were only able to attain 2.6 MPa after 28 days. The  
312 highest compressive strengths were obtained by curing at 80°C (i.e. T80), allowing the  
313 TMW-WG ABB to attain 22MPa at 28 days. From this, it can be concluded that the reaction  
314 that took place was a temperature-driven process. Van Jaarsveld et al. (2002) and Bakharev  
315 (2005) reported comparable compressive strength results for fly ash based AABs. Curing the  
316 samples above 80°C was not attempted due to the sufficient strength gained from curing at  
317 80°C. Higher temperatures would also require a greater energy input; a factor this study  
318 wanted to avoid by keeping the production of the binder as less energy intensive as  
319 practically possible.

320 Fig.10 shows the FTIR spectra of the TMW/WG blend of raw materials and the TMW-WG  
321 AAB cured at different temperatures (i.e. T20-T80). The TMW-WG AAB cured at 20°C (i.e.  
322 T20), as expected, displays the highest absorbance, which can be inferred as reduced  
323 hardening activity and thus slow strength development. The spectra of samples cured at 40

324 and 60°C (i.e. T40 and T60) match each other closely indicating similar molecular structures  
325 are present in both samples when curing at the respective temperatures. However, the change  
326 in absorbance for the sample cured at 80°C (i.e. T80) is more evident. The latter spectrum  
327 shows a great reduction in absorbance and broadening between 850 and 1100  $\text{cm}^{-1}$  associated  
328 with the Si–O–Si symmetric stretching vibrations for the gel product and is an indication of  
329 increased activation. A similar feature can be observed at 775 and 694  $\text{cm}^{-1}$ , the region of the  
330 spectrum also representing symmetric stretching vibration of the raw material Si–O bonds.  
331 The development of a more amorphous gel phase with the increase in curing temperature can  
332 be inferred from the spectrum of the TMW-WG AAB sample at 80°C matching that of the  
333 raw WG, which is confirmed to be inherently amorphous from the XRD results (refer to  
334 Fig.3). Nonetheless, the presence of asymmetric stretching vibration (Si–O–Si) related to  
335 non-solubilised particles at  $\sim 1000 \text{ cm}^{-1}$  and  $\sim 450 \text{ cm}^{-1}$  in the TMW-WG AAB indicates that  
336 unreacted precursor materials are still present, supporting the same result found in the XRD  
337 analysis. Milling the precursor materials to a fine particle size has been shown to improve  
338 reactivity and dissolution in an alkali activator solution. In the case of fly ash, Temuujin et al.  
339 (2009) showed that vibration milling could reduce the median particle size by more than 50%  
340 and improve the compressive strength by 80%. This method of mechanical activation could  
341 potentially be used to improve the dissolution properties of TMW further, as long as the  
342 additional energy input did not compromise the low energy potential of the TMW-WG AAB.  
343 Just as important as curing temperature is the AAB heat curing duration. Samples D4 through  
344 to D36 in Table 2 were prepared to study the effect of curing time on the compressive  
345 strength of TMW-WG AAB. Samples were cured in sealed conditions for 4, 12, 24 and 36h  
346 at 80°C and tested for compressive strength after 1, 1.5 (36h), 3, 7 and 28 days. Fig.11 shows  
347 that the compressive strength improves with an increase in curing time from 4 to 24h. The  
348 improvement in compressive strength continues at an even higher rate when the curing time

349 increases from 12 to 24h. However, after 36h of curing a depreciation of the compressive  
350 strength at 36h (identified by the yellow marker in Fig.11), 3 days and 7 days is observed,  
351 leaving the 28-day strength unchanged. Thus, it can be concluded that the activation reaction  
352 that took place was time-dependent. Fig.12 shows the SEM images of TMW-WG AAB  
353 samples cured at 80°C for 24 and 36h. The microstructure of the sample cured for 24h  
354 consists of close-packed quasi-unreacted WG particles embedded in a continuous matrix of  
355 gel products while the sample cured for 36h exhibits visible contraction, particularly around  
356 the WG particles. Although samples were kept in sealed conditions during curing, it was  
357 observed during de-moulding that some water was still able to evaporate into the surrounding  
358 air within the curing bag. Previous work by Mo et al. (2014) suggested that the contraction of  
359 AAB samples cured under sealed conditions at 80°C occurs after 7days. However, the results  
360 of this study suggest that contraction can initiate as early as 36h. It is possible that prolonged  
361 exposure to the elevated temperature may have led to the water evaporation rate being greater  
362 than that of re-saturation, thus triggering the accumulation of internal stresses and subsequent  
363 contraction of the AAB matrix.

364 The absorbance spectra for the raw TMW/WG blend and TMW-WG AAB, cured for varying  
365 periods of time (i.e. D4-D36) are shown in Fig.13. A reduction in the absorption intensity of  
366 the main bands at  $\sim 1000$ ,  $\sim 775$  and  $\sim 446 \text{ cm}^{-1}$  indicates that longer curing times led to the  
367 further dissolution of Si-O from the raw materials. Also, the position of Si-O bending  
368 vibration peaks shifted from 999 and  $463 \text{ cm}^{-1}$  in the raw TMW/WG to 989 and  $446 \text{ cm}^{-1}$   
369 respectively for the TMW-WG AAB specimen cured for 24h, a type of shift associated with a  
370 greater extent of polymerization in aluminosilicates (Sarkar et al. 2015). Also, it is important  
371 to observe that the absorbance spectrum for the TMW-WG AAB sample cured for 24h (i.e.  
372 D24) displays lower absorbance intensities than the TMW-WG AAB sample cured for 36h. It  
373 can be inferred from this latter result that curing times above 24h can lead a reduction in Si-O

374 dissolution and complements the mechanical strength results in Fig.11 which clearly show  
375 reductions in compressive strength for samples cured for 36h. Previous research regarding the  
376 curing time of AAB's made from fly ash (Li et al. 2013) and metakaolin (Heah et al. 2011)  
377 have uncovered similar results. Also, the broadening of the characteristic bands between  
378  $1100-850\text{ cm}^{-1}$  and  $800-750\text{ cm}^{-1}$  implies the overlap of more bands with a higher intensity  
379 which in this case is attributed to the asymmetric stretching vibrations of T-O-Si (where T=  
380 Si or Al) (Khater 2013).

381

## 382 **CONCLUSIONS**

383

384 The effect of waste glass addition to tungsten mining waste alkali-activated binders was  
385 assessed by strength testing, XRD, SEM and FTIR. Additionally, preparation conditions such  
386 as activator mixing time, curing temperature and curing time on hardening kinetics was  
387 assessed, leading to the following discoveries:

- 388 • The addition of WG is a very sustainable and practical method of improving TMW  
389 degree of amorphicity, compared to traditional calcination treatments. Up to 40 wt.%  
390 of WG with a mean particle size of  $39.6\mu\text{m}$  can be successfully blended with TMW to  
391 increase the amorphous nature of the binary blend by 21%, without the initiation of  
392 the alkali-silica reaction.
- 393 • Prolonged activator mixing can reduce the dissolution of the aluminosilicate precursor  
394 due to fewer available alkali metal ions in solution. The initiation of silicate gelation  
395 due to prolonged stirring would also contribute to reducing the activator effectiveness.  
396 The correct preparation of the activator solution is imperative and would be expected  
397 to extend to other classes of alkali activated cementitious systems.
- 398 • The optimum conditions for obtaining the most significant dissolution of the aluminosilicate  
399 oxides were curing for  $80^{\circ}\text{C}$  for 24h. When curing time is greater than 24h i.e.



400 36h as investigated in this study, it can lead to a reduction in compressive strength and  
401 contraction of the AAB matrix, even under sealed conditions.

402

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409

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564 **Table 1.** Chemical Composition (wt.%) of raw TMW, WG determined by SEM-EDX

<b>Chemical compound</b>	<b>TMW (%)</b>	<b>TMW S.D</b>	<b>WG (%)</b>
Na <sub>2</sub> O	1.31	1.45	9.72
MgO	1.01	2.98	0.00
Al <sub>2</sub> O <sub>3</sub>	21.06	2.53	0.00
SiO <sub>2</sub>	47.88	3.86	73.93
SO <sub>3</sub>	8.72	2.83	0.00
K <sub>2</sub> O	4.12	0.78	0.69
Fe <sub>2</sub> O <sub>3</sub>	9.97	2.73	0.40
P <sub>2</sub> O <sub>5</sub>	0.00	0.27	0.00
CaO	0.88	0.99	12.83
TiO <sub>2</sub>	0.66	0.35	0.00

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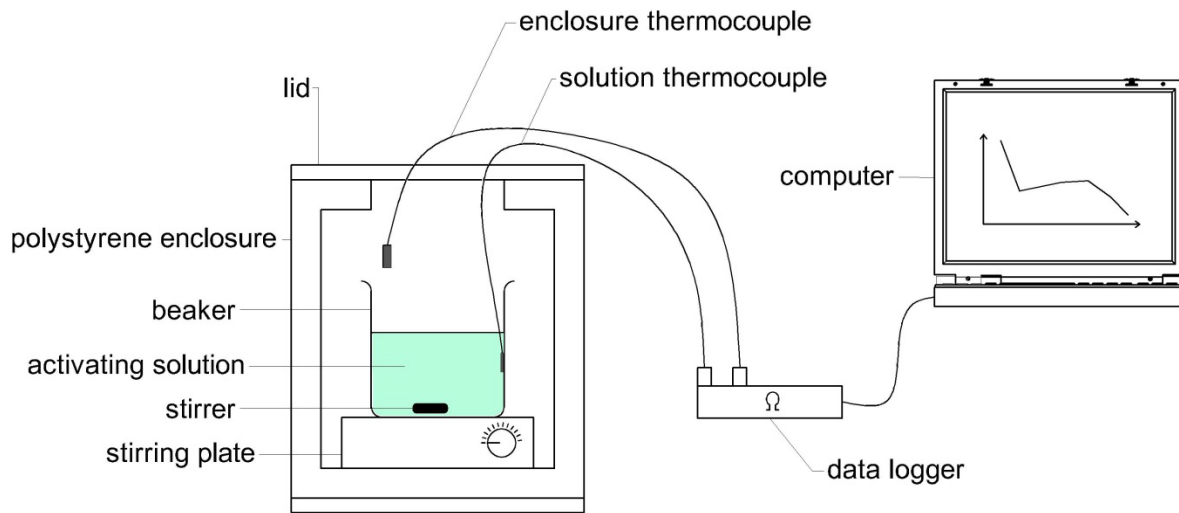
567 **Table 2.** Summary of preparation and curing regimes for the variables studied

Sample	Activator mixing time (mins)	Curing temperature (°C)	Oven curing duration(hours)
M2.5	2.5		
M5	5		
M10	10	60	24
M15	15		
M20	20		
T20		20	
T40		40	
T60	5	60	24
T80		80	
D4			4
D12			12
D24	5	80	24
D36			36

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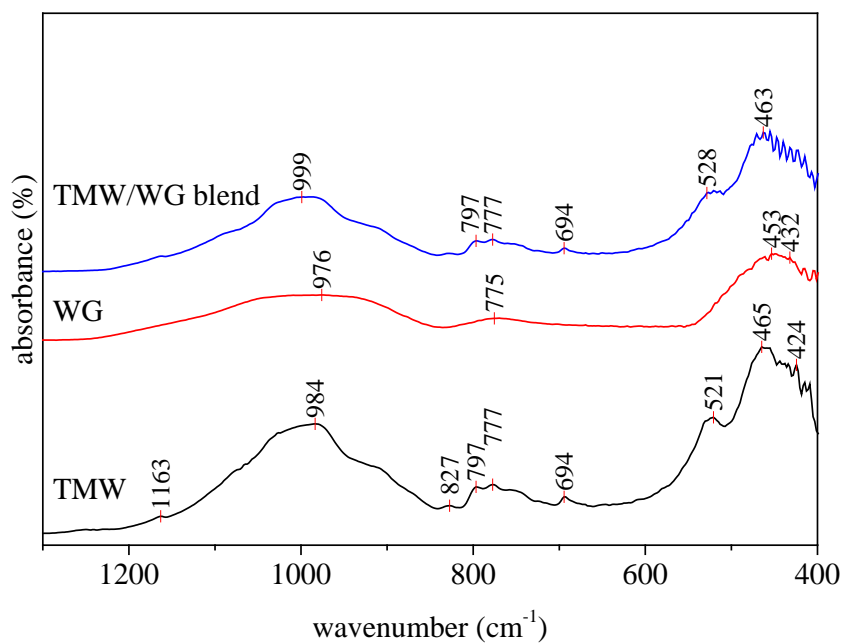


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572 **Fig.1** SS/SH activator solution temperature measurement set up

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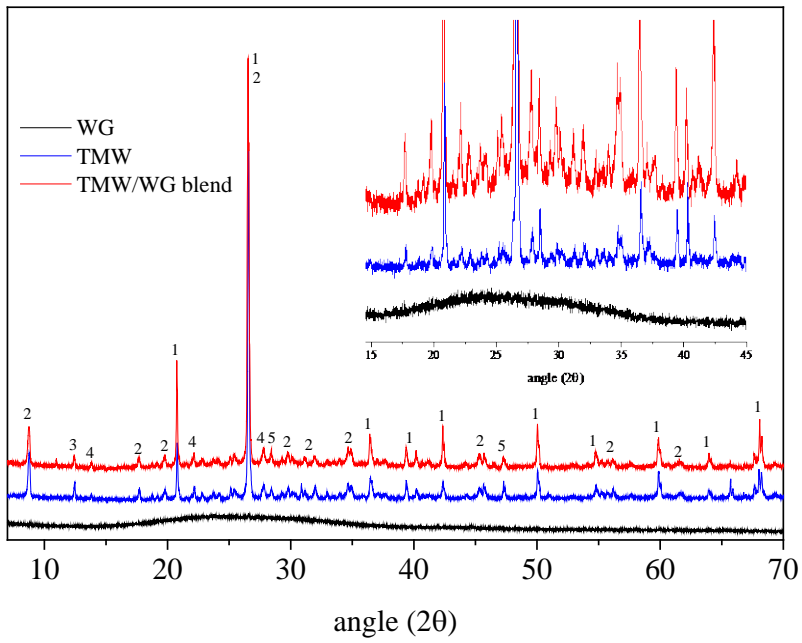
575

576 **Fig.2** ATR-FTIR absorbance spectra of the as received raw TMW, WG, and TMW-WG

577 blend (80 and 20% mass fractions, respectively)

578

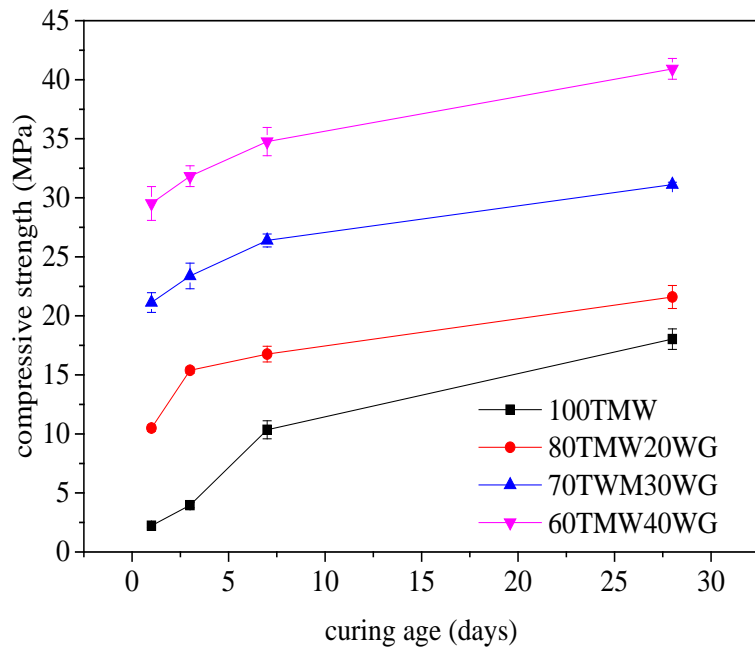




579

580 **Fig.3** XRD patterns of TMW, WG and blended TMW/WG WG (1- silica, 2- muscovite, 3-  
 581 sodium aluminosilicate, 4- rudashevskyite, 5- pyrite)

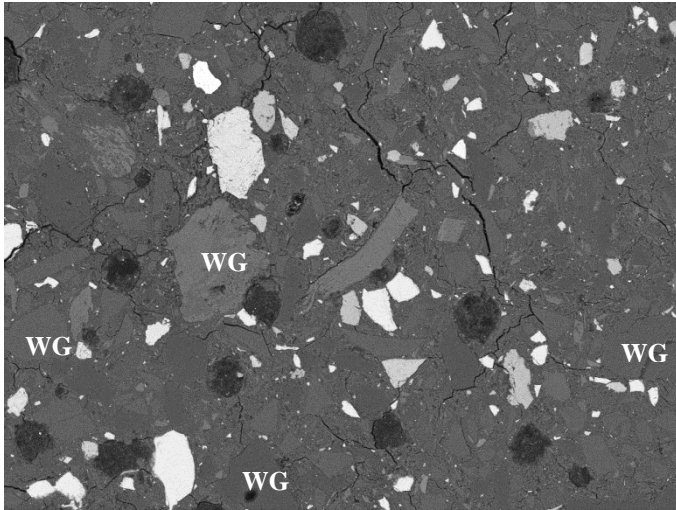
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584 **Fig.4** Effects of WG substitution on TMW AAB compressive strength

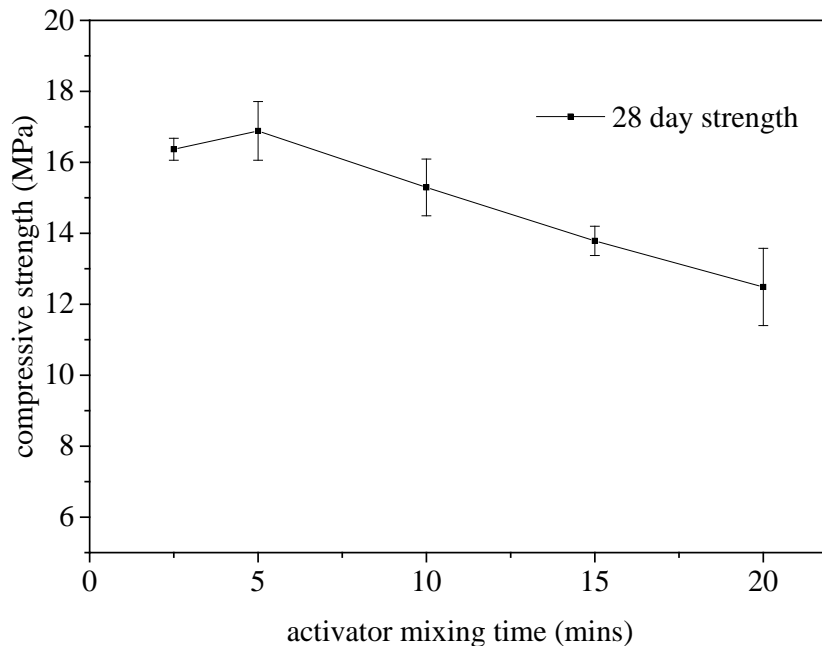
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587 **Fig.5** Polished thin-section of TMW-WG AAB with 40 wt.% WG at 28-days

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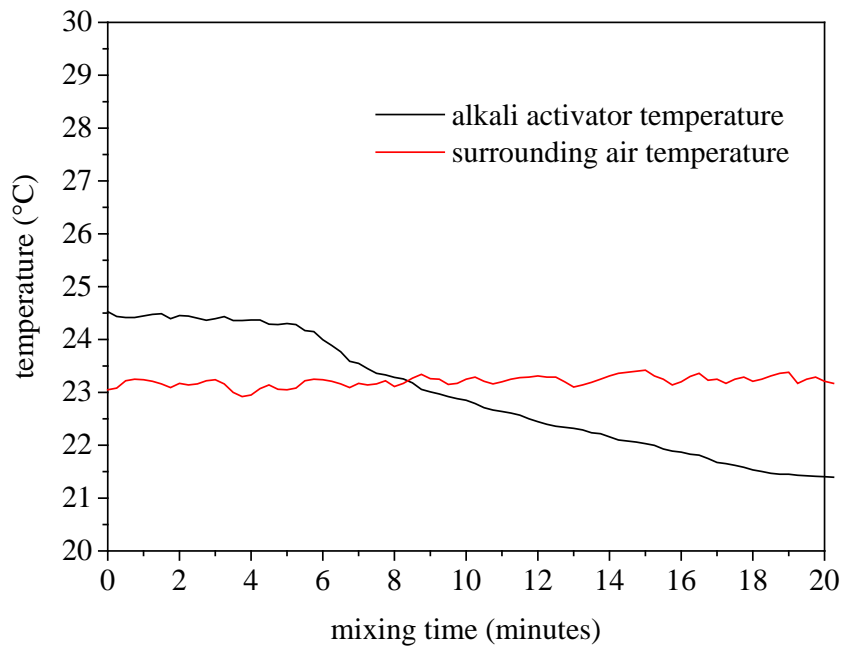


589

590 **Fig.6** Effect of SS/SH activator solution mixing time on 28-day compressive strength of

591 TMW-WG ABB cured at 60°C for 24 hours

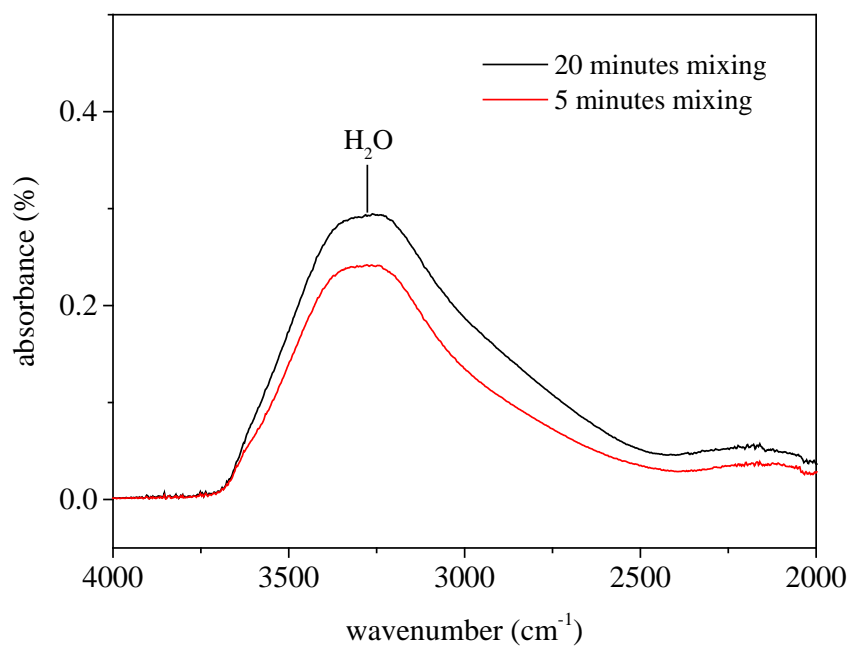
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594 **Fig.7** SS/SH activator solution temperature due to prolonged mixing

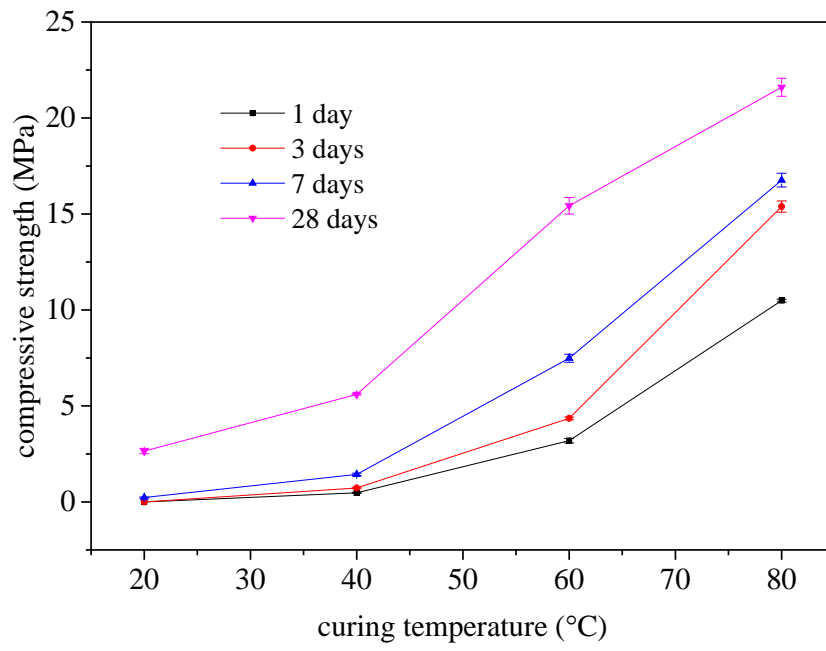
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597 **Fig.8** ATR-FTIR spectrum of SS/S activator solution with varying mixing time

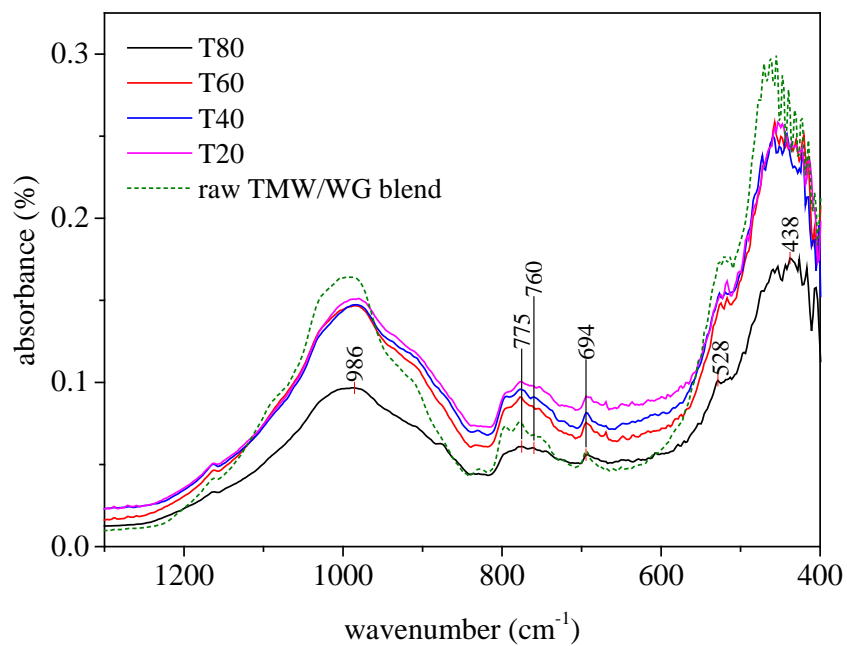
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600 **Fig.9** TMW-WG AAB compressive strength (1-28d), for samples cured for 24 h at 20, 40, 60  
 601 and 80°C.

602



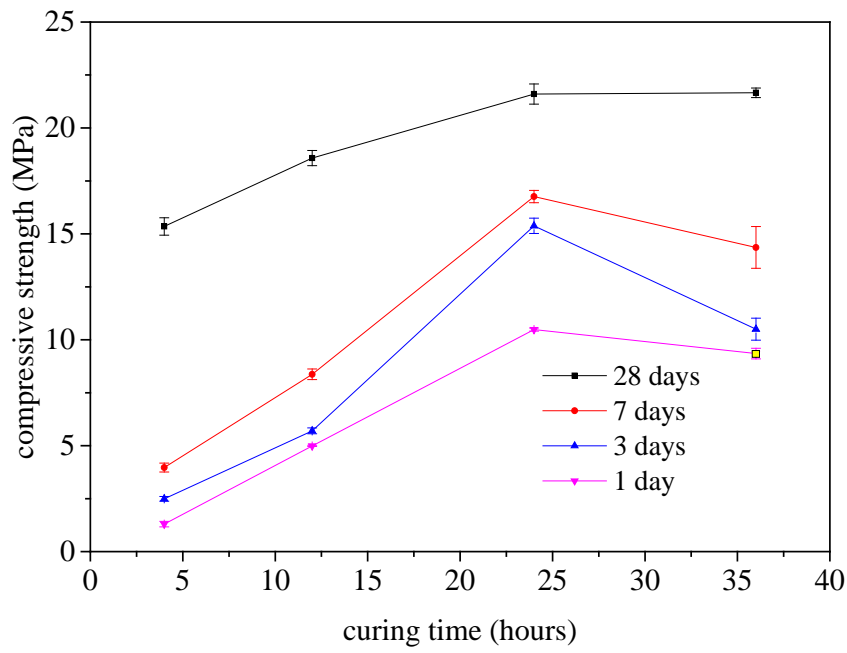
603

604 **Fig.10** ATR-FTIR absorbance spectra of as received raw TMW/WG and TMW-WG AAB at

605 28 days cured at 40, 60 and 80°C

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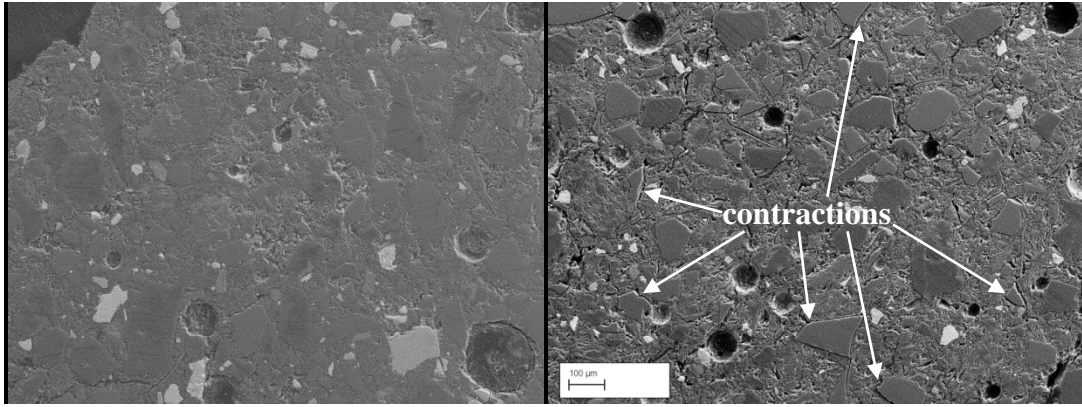




607

608 **Fig.11** TMW-WG AAB compressive strength (1-28d), for samples cured at 80°C for 4, 12,  
 609 24 and 36 h.

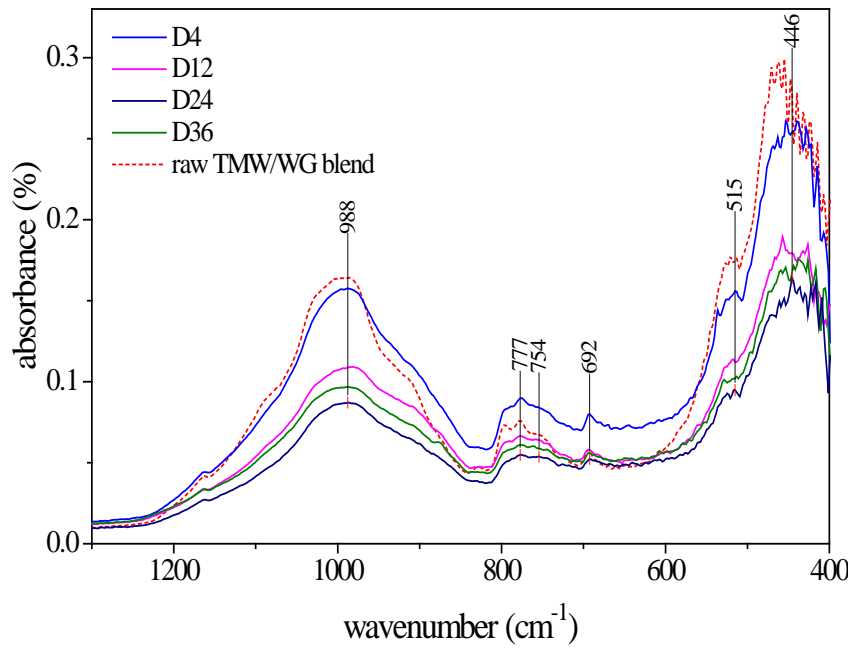
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612 **Fig.12** TMW-WG ABB sample cured at 80°C for (a) 24 h and (b) 36 h

613



614

615 **Fig.13** ATR-FTIR absorbance spectra of as received raw TMW/WG and TMW-WG AAB at  
 616 28 days cured at 80°C for 4, 12, 24 and 36 h.

617