

Alkali-activated slag concrete: fresh and hardened behaviour

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Abstract

The behaviour of fresh and hardened alkali-activated slag (AAS) and OPC concretes was compared and the effect of mixing time assessed. OPC and AAS concrete slump and rheological results proved to differ, particularly when the slag was activated with waterglass (WG). The nature of the alkaline activator was the key determinant in AAS concrete rheology. Bingham models afforded a good fit to all the OPC and AAS concretes. In OPC and NaOH-activated AAS concretes, longer mixing had an adverse effect on rheology while improving hardened performance only slightly. In WG-AAS concrete, longer mixing times, improved mechanical properties and also rheological behaviour was enhanced, in which those conditions were required to break down the microstructure. Longer mixing raised thixotropy in OPC and NaOH-activated AAS concretes, but lowered the value of this parameter in waterglass-activated slag concrete.

Keywords: rheology, concrete, alkaline activation, blast furnace slag, Bingham model, hardened behaviour

1. Introduction

For over 20 years, the study and development of alkaline activated materials (AAMs), mainly cements and concretes has been the subject of great interest by the scientific community [1-6]. That is largely due to the enormous promise of these products as sustainable alternatives to portland cement-based binders. AAMs are natural or artificial aluminosilicates activated by hydroxide-, silicate- or alkaline carbonate-solutions. Their manufacture not only generates lower GHG (especially CO₂) emissions, but is more economically and environmentally sustainable, for the raw materials or precursors used are often valorised industrial by-products [7-10]. The manufacture of some alkaline activators, sodium silicate or waterglass (WG) especially, also carries adverse environmental impacts, however [11]. The production of possible alternative activators by processing different types of waste (such as glass or rice husk ash) would consequently constitute a further step toward sustainability [12-15] in new binder development.

Alkali-activated slag (AAS) cements and concretes are among the most prominent AAMs, for their manufacture emits 73% less GHGs than portland cement and consumes less energy and water [16]. These AAS systems are also characterised by high mechanical strength and durability [17-22]. They Nonetheless AAS cement, mortar and concretes exhibit two shortcomings that hamper their standardisation and more general use, namely high drying shrinkage [2,23-25] and quick setting when activated with waterglass solutions [26-28].

The reason for such quick setting lies in the initial and speedy formation of a primary C-S-H gel, which hardens sodium silica-activated AAS pastes. Shi and Day [29] used isothermal conduction calorimetry to study slag activation with different activators. They observed two contiguous signals in the pre-induction period in sodium silicate-activated pastes. The first was attributed to slag dissolution and the second to the formation of a primary C-S-H gel as a result of the presence of [SiO₄]⁴⁻ ions in the solution. This latter signal intensified as the WG silica modulus rose. Primary C-S-H formation was also observed in constant shear rate rheology tests [28,30] on waterglass-activated AAS pastes. After an initial rise, shear declined and flattened, attendant upon paste deflocculation possibly attributable to primary C-S-H flocks gel breakdown. Lengthening mixing time from 3 min to 10 min was also shown to retard initial setting by 40 min and final setting by over 4 h. At a mixing time of 30 min, initial and final settings were also delayed [26].

More recently, the intensity and timing of this rheological signal at constant shear rate in WG-activated AAS pastes have been shown to depend on the Na₂O concentration and the

58 $\text{SiO}_2/\text{Na}_2\text{O}$ modulus in the activating solution used. The higher the latter and consequently the
59 greater the silicon content in the solution, the earlier and more intense the signal [31].

60 Such rapid setting obviously affects rheology and therefore on-site paste and concrete casting.
61 As the literature shows [28,30,31], rheological studies contribute to an understanding of the
62 reasons for such behaviour and the pursuit of possible solutions. Few studies have focused on
63 researching sodium silicate-activated AAS system rheology, however.

64 Palacios et al. [28, 30] found that NaOH-activated AAS pastes fit a Bingham model, whereas
65 WG-activated materials conform to the Herschel-Bulkley model. Studies comparing OPC and
66 AAS rheology based on minislump test-determined workability [31, 32] showed that WG-
67 activated pastes were less workable than NaOH-activated and OPC pastes. Kashani et al. [33],
68 studying hydroxide- and alkaline silicate-activated AAS paste rheology, found that the latter
69 had lower initial shear stress than the former due to the adsorption of silicate ions on the
70 particles, which had a fluidising effect as a result of the increase in the double electrical layer.
71 When these results were studied in conjunction with isothermal conduction calorimetry
72 findings on degree of reaction, the times at which yield stress rose were found to be correlated
73 to the heat release pattern. Those data were consistent with the results reported by Varga et
74 al. [31], where initial yield stress was observed to be lower in WG- than in NaOH-activated AAS
75 pastes. Unlike Varga et al., however, Kashani et al. [33] observed that yield stress was lower in
76 the first 20 min in WG- than in alkaline hydroxide-activated AAS pastes. Different authors may
77 on occasion report contradictory findings due to variations in the activators used and paste
78 mixing history, as well as in the specific rheological study conducted.

79 Fluidity loss has been shown to be greater in sodium silicate-activated AAS mortars than in
80 OPC and NaOH-activated AAS mortars [2,32]. Waterglass-activated AAS mortars have also
81 been found to exhibit lower workability and greater fluidity loss than alkali-activated fly ash
82 mortars [34, 35].

83 Sight should not be lost of the fact that the end product is concrete, however. An
84 understanding of its workability and rheology is consequently of cardinal importance [36,37].
85 Empirical findings such as yielded by the slump test, V-funnel or J-ring [38] not only furnish
86 very valuable information on concrete workability, but can be readily and economically
87 conducted. As operator-sensitive, single-point tests [39,40], they may nonetheless find two
88 very different concretes to be in the same workability class. AAS concrete systems should
89 therefore be studied with multi-point tests that furnish information on rheological parameters
90 such as yield stress, plastic viscosity and information about thixotropy [39–42].

91 Portland cement concrete rheology has been exhaustively studied and found to fit a Bingham
92 model (Equation 1):

$$93 \quad \tau = \tau_0 + \mu \cdot \dot{\gamma} \quad (1)$$

94 where $\dot{\gamma}$ is shear rate (s^{-1}), τ_0 is yield stress (an indication of the force needed to initiate flow)
95 and μ is plastic viscosity (Pa·s) or the material's resistance to flow [40,43]. OPC thixotropy has
96 also been explored by many authors [44–46]. Thixotropy is the property of these systems
97 whereby viscosity gradually declines with rising shear rate and the initial structure is recovered
98 when shear is removed [40,47]. It should not be confounded with the irreversible 'structural
99 breakdown' in cement pastes defined by Tattersall and Banfill [40].

100 Any number of studies have shown that portland cement concrete rheology, thixotropy and
101 workability vary with the presence of additions [48–50], the presence and composition of
102 superplasticisers [51–53] and the composition and particle size distribution of the aggregates
103 [54–57].

104 In contrast, rheological studies on alkali-activated concretes are scant to non-existent. The
105 addition of ultrafine fly ash [58] or lime slurry [59] has been observed to improve AAS paste,
106 mortar and concrete workability (lower lost of slump). No information has yet been
107 forthcoming on AAS concrete rheological parameters, however. More specifically, no studies
108 comparing NaOH- or sodium silicate-activated AAS to OPC concrete rheology have been
109 published to date. As noted, moreover, as longer mixing times may induce initial breakdown of
110 the primary C-S-H gel in WG-AAS systems, improving the workability as has been proven in
111 previous studies on AAS paste and mortars [31, 60]. The motivation of this study was to know
112 the effect of longer mixing time of AAS concrete rheology with different alkaline activators
113 (NaOH and Wg) and to compare the results with OPC concretes. Mixing time must be factored
114 into experimental designs to determine NaOH- and WG-activated AAS concrete workability
115 and rheology.

116 **2. Experimental procedure**

117 **2.1 Materials**

118 CEM I 52.5 R portland cement (OPC) and ground-granulated blast furnace slag (S) were used as
119 binder to prepare the concretes studied. The chemical composition of these materials was
120 listed in **Table 1** and determined by a PHILIPS PW-1004 X-Ray Fluorescence (XRF)
121 spectrometer, together with the loss on ignition (found further to European standard EN-

122 196-2:2014). The ground-granulated blast-furnace slag used in this study had a Blaine specific
 123 surface of 346 m²/kg and a specific gravity of 2,880 kg/m³. The cement used, the chemical
 124 composition for which is given in **Table 1**, had a Blaine specific surface of 420 m²/kg and a
 125 density of 3,100 kg/m³. The rolled sand fines had a specific gravity of 2,600 kg/m³ and an
 126 absorption of 0.23 %, both coarse siliceous aggregates had a specific gravity of 2,640 kg/m³,
 127 with 0.36 % absorption in the 4-8 mm material and 0.40 % absorption in the 8-12 mm gravel
 128 (**Table 2**). The particle size distribution of the coarse aggregates is shown in **Figure 1**.

129

130 **Table 1.** Chemical composition of blast furnace slag and 52.5R OPC (XRF analysis)

Material	Component (oxide; wt%)										
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	*Lol
Slag	38.71	10.46	0.33	0.21	7.58	40.62	0.54	0.35	0.37	0.05	-0.30
OPC	19.32	7.90	2.69	0.06	0.81	61.81	0.11	1.02	0.23	0.06	2.90

131 *Lol = Loss on ignition at 1000 °C

132

Table 2. Physical properties of natural aggregates

Aggregate	Maximum grain size (mm)	Specific gravity (kg/m ³)	Water absorption (%)
Sand 0-4 mm	4	2,600	0.23
Coarse (4-8 mm)	8	2,640	0.40
Coarse (8-12 mm)	12	2,640	0.36

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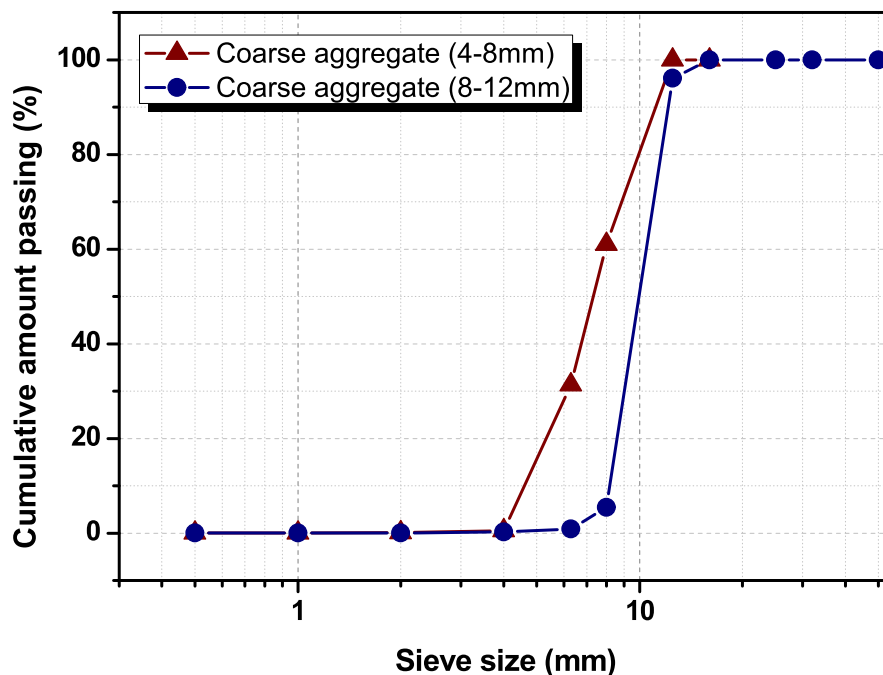
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146 **Figure 1.** Particle size distribution of coarse aggregates in OPCC and AASC concretes

147 **2.2 Mixture proportions and mixing protocols**

148 The blast furnace slag and cement concretes were designed to a total content of 357 kg/m³.

149 The OPC concrete was mixed with water and 0.1 % (cement weight) chemical admixture,
 150 whereas the alkali-activated slag concretes were mixed with one of two solutions (**Table 3**):

- 151 - Panreac 98 % pure, 10 M NaOH (5 % Na₂O by slag mass)
- 152 - Sodium silicate hydrate or waterglass (5 % Na₂O by slag mass, SiO₂/Na₂O modulus of
 153 1.2), prepared with Merck sodium silicate (SiO₂: 27 wt%; Na₂O: 8 wt%; H₂O: 65 wt%).

154 A slump of 120 mm or larger was sought in all cases.

155 **Table 3.** Concrete batching (per 1 m³)

Material (kg)	OPCC	AASC N	AASC WG
Cement	357.0	-	-
Blast furnace slag	-	357.0	357.0
Water	197.5	177.75	145.0
Water in solution	-	19.75	52.5
Fine aggregate	720.5	711.3	563.0
Coarse aggregate 4-8	540.3	533.5	548.0
Coarse aggregate 8-12	540.3	533.5	728.3
L/S	0.55	0.55	0.55
Admixture (wt%)	0.1	-	-
NaOH and sodium silicate	-	23.0	42.5
SiO ₂ /Na ₂ O modulus	-	-	1.2
pH solution	7.0	13.6	13.8

156
 157 Two mixing protocols were deployed to prepare both the OPCC and AASC systems (see **Figure**
 158 **2**). Protocol 1 corresponds to AAS concrete dosage previously determine in RILEM TC 247-DTA
 159 (the stability and good mechanical strenght behaviuor were the main factors considered). In
 160 protocol 2 a longer mixing time of all concrete components were considered according to
 161 previous rheological studies [26, 31, and 60].

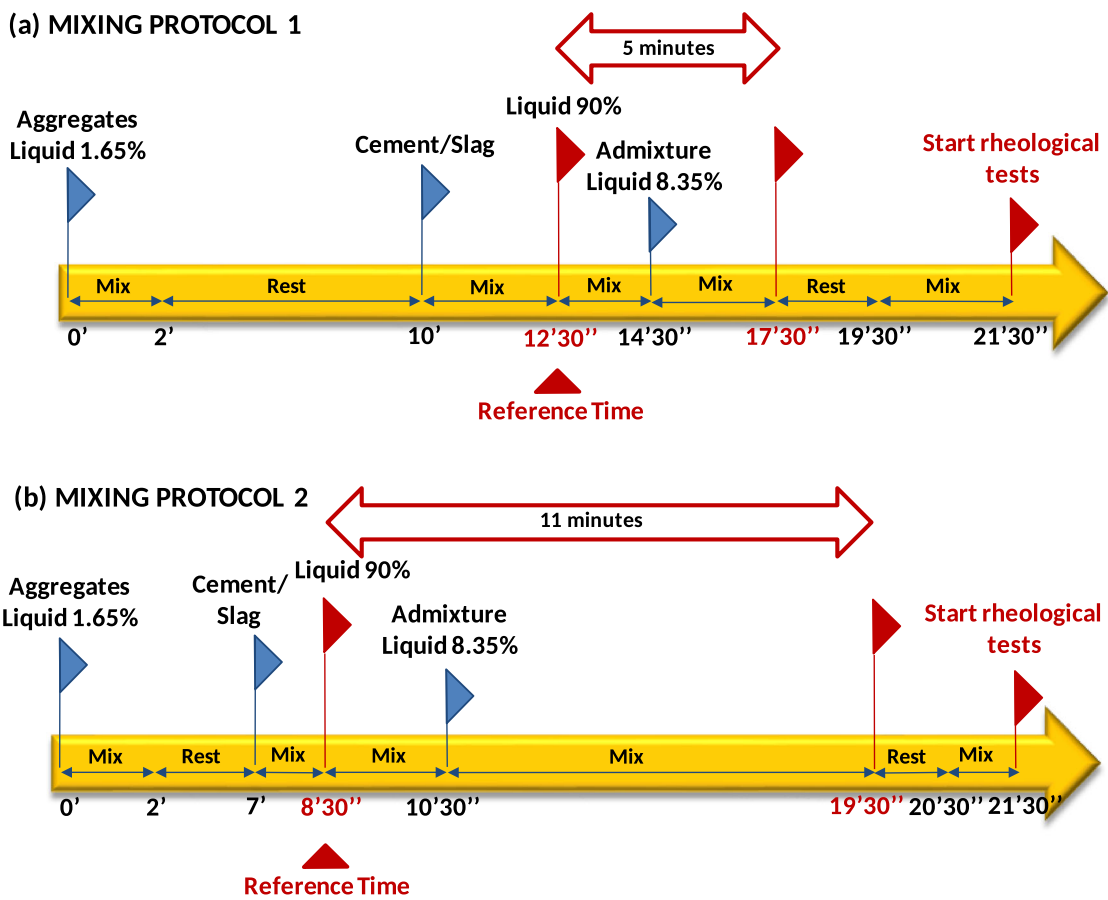
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 163 In the first (protocol 1), the aggregates were blended for 2 min in the mixer with 1.65 % of the
 164 water. The aggregates were then allowed to stand for 8 min to absorb the mixing water. The
 165 binder (portland cement or ground-granulated blast furnace slag) were added and mixed with
 166 aggregates during 2 minutes 30 seconds. At this moment, 90% solution (water or alkaline
 167 solution) was added and the reference time started when the solution was in contact with the
 168 binder. Two minutes later, the rest of the liquid was added, along with the admixtures in the
 169 OPCC systems. In this mixing protocol, the mixing time between the aggregates, binder and
 170 solution (water or alkaline activator) was 5 minutes. Finally, the mixture is allowed to stand for

171 2 minutes and again mixed for 2 additional minutes before to start the rheological tests. Entire
 172 test lasts 21 minutes 30 seconds (see Figure 2a).

173

174 The same stages were followed in protocol 2, although the times varied. The aggregate, binder
 175 and liquid were mixed for 11 min rather than 5 min. To maintain the same 21.5 min total time
 176 as in protocol 1, that 6 min difference was adjusted as follows: the rest time after blending
 177 liquid and aggregate was shortened by 3 min (ending at 7 min), the aggregate-binder blending
 178 time by 1 min, the standing time after mixing aggregate, binder and liquid by 1 min and the
 179 final mixing time by 1 min (Figure 2(b)).

180



181

182

183 **Figure 2.** Mixing protocols for OPCC and AASC: (a) protocol 1; (b) protocol 2; (note differences
 184 in mixing and standing times)

185

186 Hereinafter, the concretes will be named with a suffix denoting the mixing protocol used.

187 **2.3 Testing program**

188 The slump test described in European standard EN-12350-2 was conducted on all the fresh
189 concretes at each test age. The fresh concrete was also analyzed in an ICAR portable rotational
190 rheometer fitted with a four-bladed vane able to ensure axial symmetry at variable speeds
191 (Figure 3). Static (or at-rest) yield stress was determined by stress growth test, while Bingham
192 parameters for dynamic yield stress and plastic viscosity were found by flow curve test
193 method. In this study, rheology tests were performed at 15 min, 30 min, 45 min and 60 min
194 after the liquid was added to the solid.

195
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198
199 **Figure 3.** ICAR rheometer
200

201 After the mixing process, part of the concrete was poured from the mixer into the
202 rheometer container. At each testing age, the slump test was carried out. Before beginning
203 this test, the concrete was remixed 30 s. At the same time, the rheological tests were
204 started from the concrete being at rest:

- 205 I. The stress growth test started when the vane immersed in the concrete. A constant
206 speed of 0.025 rps was applied as torque was monitored on the computer screen.
207 II. When peak torque was reached, the vane was removed and the concrete was remixed
208 with a shovel.
209 III. The vane was reinserted and the flow curve test started. The material rotated at a
210 constant 0.5 rps for 20 s, after which torque was measured at decreasing speeds.

211 IV. The vane was removed at the end of the test and the concrete was re-shovelled and
212 allowed to stand until the following test time.

213 The concrete was moulded into 100 mm cubic specimens, demoulded after 24 h and cured in a
214 chamber for 7 d or 28 d, when it was tested for compressive strength as per European
215 standard EN 12390-3. The testing frame was programmed to gradually increase the load at a
216 rate of 0.6 ± 0.2 MPa·s⁻¹ to failure.

217 Cylindrical 150 mm x 200 mm specimens were also prepared for the water permeability test,
218 conducted on the 28 d samples to European standard EN 12390-8. These specimens were
219 placed in a water tank connected to an air compressor fitted with a valve to adjust the
220 pressure, which was applied at 500 kPa (5 bar) for 72 h. They were then tested for splitting
221 tensile strength as per European standard EN 12390-6 and the water penetration depth was
222 measured on the split specimens. Density was found in the fresh concrete as described in
223 European standard EN 12350-6 and density of hardened concrete in the 1 d cured 100 mm
224 concrete cubes as per EN 12390-7.

225 Total porosity and pore size distribution were found for the 7 d and 28 d specimens on a
226 Micromeritics Autopore IV 9500 mercury intrusion porosimeter.

227 Hydration was monitored in all systems with a Thermometric TAM Air isothermal conduction
228 calorimeter. The pastes were mixed in a special device fitted with a mechanical stirrer and a
229 syringe to add the liquid to the solids and record the reaction data from the very earliest
230 stages. The liquid/solid ratios used were the same as to prepare the concretes (**Table 3**).

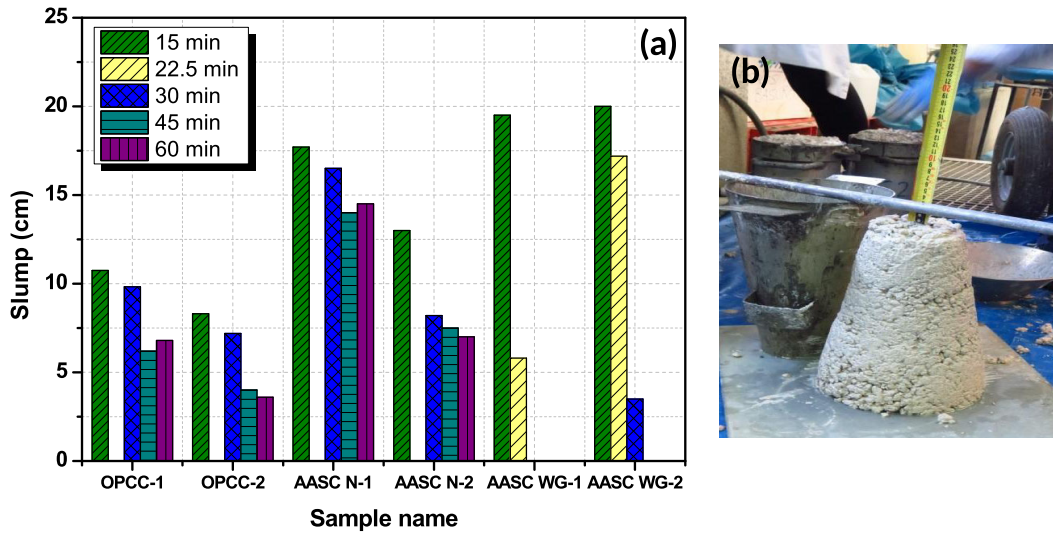
231 **3. Results and discussion**

232 The results obtained for the fresh and hardened concretes are described below.

233 **3.1. Fresh behaviour**

234 The slump values for the OPCC and AAS concretes (AASC N and AASC WG) in **Figure 4(a)**
235 showed that the AASC (and particularly the waterglass-activated) concretes had a larger slump
236 than the OPC concretes.

237 Similar findings have been reported for mortars [60]. Mixing time was also observed to affect
238 slump, for longer times lowered fluidity in all the mortars. As expected, the slump for OPCC
239 and AASC N declined at longer test times. In the AASC WG concretes, the decline was so steep
240 that it could not be measured at 30 min or 45 min (see **Figure 4(b)**). Mixing protocol 2 had a
241 beneficial effect on these concretes, which remained fluid for longer periods.



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244 **Figure 4. (a)** Slump test findings for the concretes studied, where suffix denote the mixing
 245 protocol used; **(b)** 22.5 min slump for AASC WG prepared with mixing protocol 1

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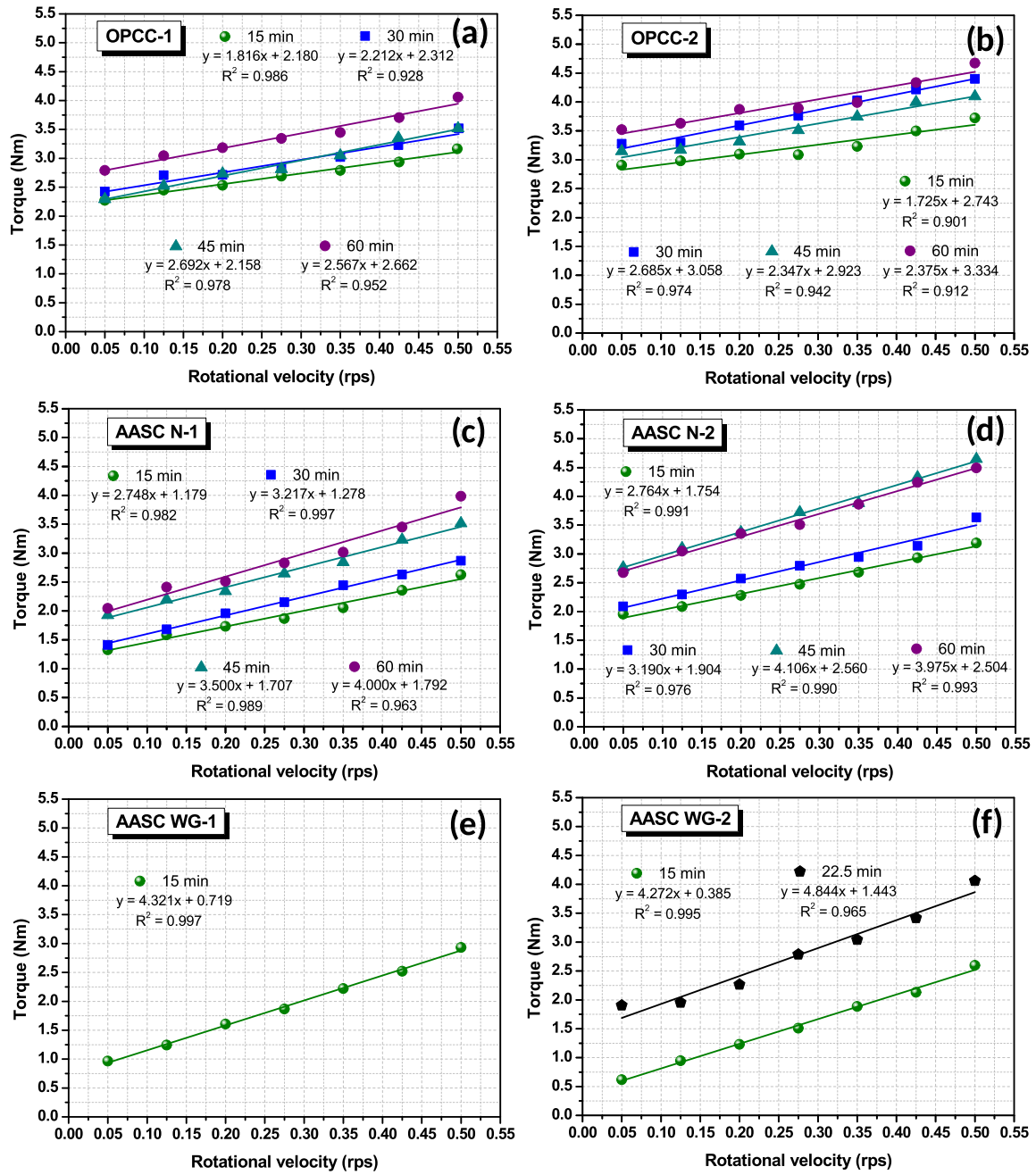
247 Different models such as the Herschel-Bulkley model or the modified Bingham model can be
 248 considered to describe the behaviour of certain vibrated or self-consolidating concretes.
 249 However, as the applied rheological model should be as simple as possible, the Bingham model
 250 (Equation 1) for yield stress and plastic viscosity is recommended.

$$251 \quad \tau = \tau_0 + \mu \cdot \dot{\gamma} \quad (1)$$

252 Before applying this model, the effect of thixotropy should be verified by checking for torque
 253 equilibrium at each rotational velocity on the flow curve, whilst the mix should be examined
 254 visually for segregation both during and after the test. These measurements may describe
 255 apparently non-linear behaviour due to thixotropy and segregation and should be eliminated
 256 [61].

257 In this study, this possible non-linear behaviour was checked and as it did not occur, in light of
 258 the foregoing, the Bingham model was applied, the results of which are shown in **Figure 5** for
 259 all the concretes studied.

260 It can be seen that the standard Bingham model accurately represents all the systems studied,
 261 for as the coefficients of determination found for all the curves denoted good correlations.
 262 Therefore the flow curves for the concretes studied could be assumed to fit a linear model.



264

265 **Figure 5.** ICAR rheometer-determined flow curves for: (a) OPCC-1; (b) OPCC-2;

266 (c) AASC N-1; (d) AASC N-2; (e) AASC WG-1 and (f) AASC WG-2

267

268 The standard Bingham model accurately represented all the systems studied, for as the

269 coefficients of determination found for all the curves denoted good correlations, the flow

270 curves for the concretes studied could be assumed to fit a linear model.

271 The Reiner-Riwlin equations [62] for the Bingham model were applied to the experimental
 272 data to convert the torque-rotational velocity relationship into a shear stress-shear rate
 273 relationship, expressed in fundamental units (Pa and Pa·s) (Equations 2 and 3). This procedure
 274 transforms a relationship between torque and rotational velocity into a relationship between
 275 shear stress and shear rate, expressed in fundamental units (Pa and Pa·s).

$$276 \quad \tau_0 = \frac{\left(\frac{1}{R_1^2} - \frac{1}{R_2^2}\right)}{4\pi h \ln\left(\frac{R_1}{R_2}\right)} G \quad (2)$$

$$277 \quad \mu_p = \frac{\left(\frac{1}{R_1^2} - \frac{1}{R_2^2}\right)}{4\pi^2 h} H \quad (3)$$

278 where:

279 R_1 is the vane radius (m)

280 R_2 is the outer container radius (m)

281 h is the vane height (m)

282 G is the y-intercept on the flow curve (Nm)

283 H is the slope of the flow curve (Nm·s)

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285 The findings on plastic viscosity and dynamic and static yield stress are shown in **Figure 6**.

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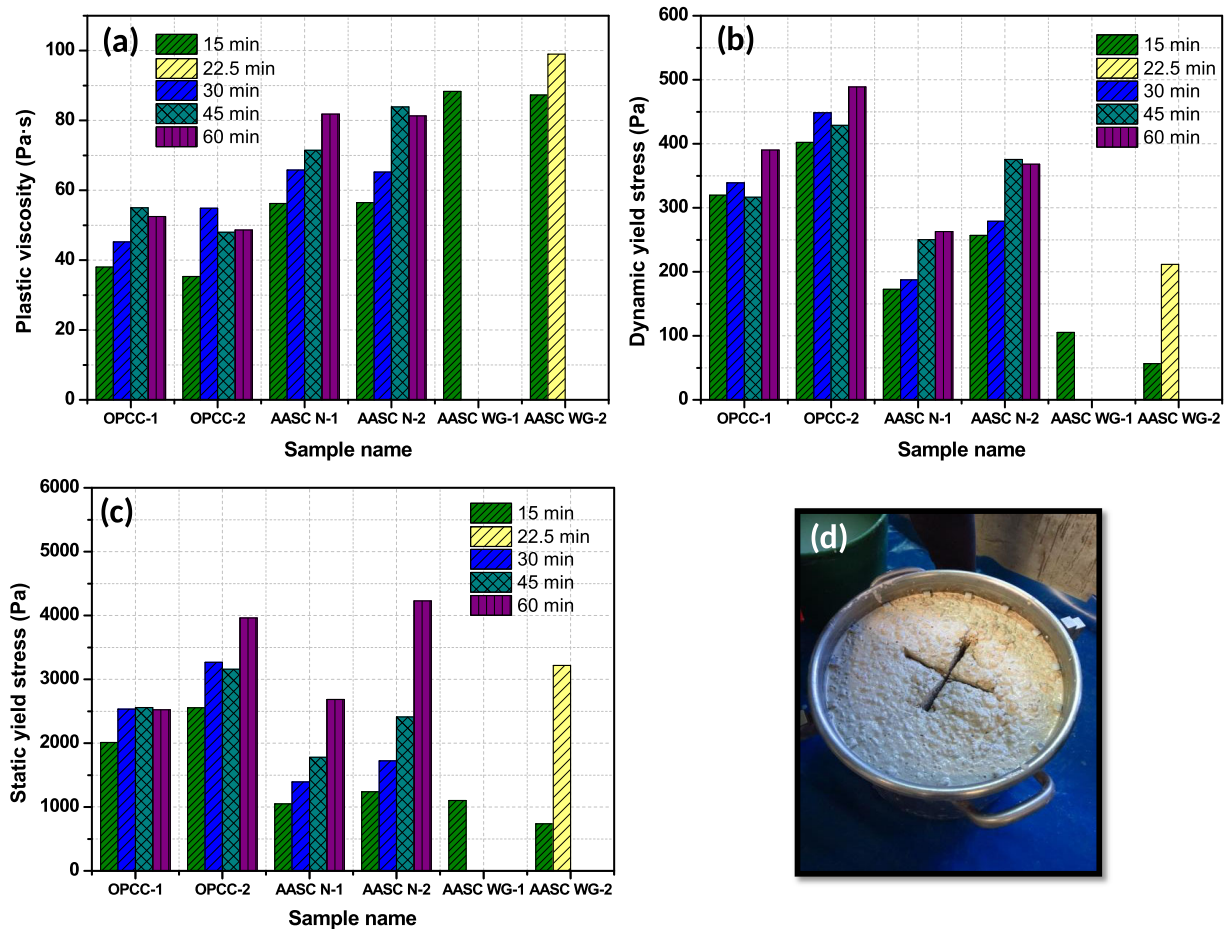
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294 **Figure 6. (a) Plastic viscosity; (b) dynamic yield stress; and (c) static yield stress for the**
 295 **concretes studied; (d) 30 min AASC WG-1**

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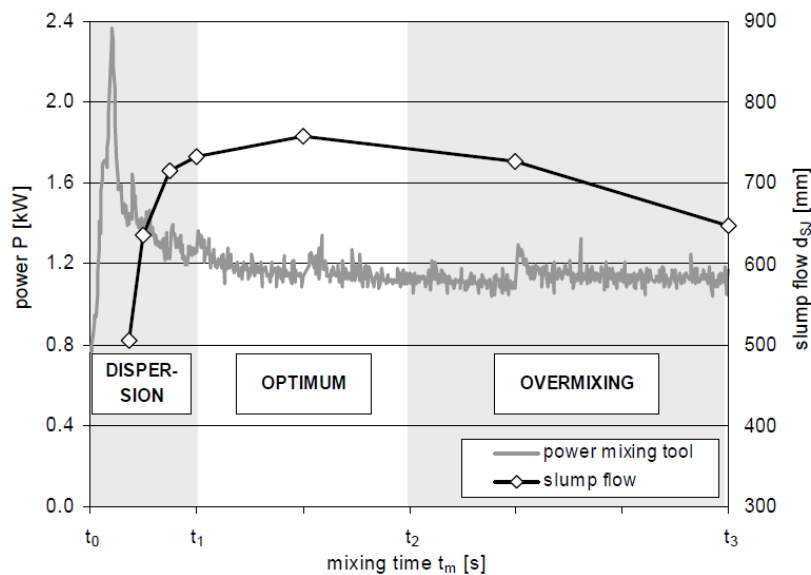
297 In the 15 min trials, the OPC concretes exhibited higher static and dynamic yield stress and
 298 lower plastic viscosity than the alkali-activate materials. More specifically, the highest yield
 299 stress was observed in OPCC -2, although it shared very similar plastic viscosity with OPCC -1.
 300 Dynamic yield stress barely rose in the first 45 min in the OPC concretes, and by only 20 %
 301 after 60 min, whilst plastic viscosity rose by 40 % after 60 min.

302 The 15 min static and dynamic yield stress values were higher and viscosity was lower in the
 303 AASC N than in the AASC WG concretes. The values of these parameters were lowest in
 304 protocol 1, sodium hydroxide (N) mixes and somewhat higher in the sodium silicate hydrate
 305 (WG) materials mixed to the same protocol. When mixed to protocol 1, the AASC N concretes
 306 exhibited 60 min dynamic yield stress 52 % higher than at the outset and 43 % higher when
 307 mixed to protocol 2, whilst plastic viscosity grew by 46 % in protocol 1 and 44 % in protocol 2.

308 These parameters rose so dramatically in protocol 1 AASC WG concretes that the rheological
309 tests could not be conducted after 15 min, or after 22.5 min with protocol 2, at which time the
310 rheological parameters were observed to rise significantly.

311 Further to the aforementioned findings, longer mixing times raised dynamic yield stress in
312 both OPCC and AASC N. Whilst the mixing protocol did not appear to affect plastic viscosity in
313 OPCC concretes, viscosity rose at later ages when the AASC N mixes were prepared to protocol
314 2. Longer mixing times improved AASC WG rheology (dynamic yield stress and plastic
315 viscosity).

316 Some authors describe three mixing stages [63] (**Figure 7**). The first, in which the solid is
317 dispersed in the liquid, is characterised by the transition from initially high inter-particle forces
318 (calling for high mixer power) to a suspension with a significant decline in such forces. The
319 second or optimum stage exhibits asymptotic power demand. It delivers the maximum slump
320 and encompasses the optimal mixing time. Upon finalisation of this stage, inter-particle and
321 particle-mixer collisions may induce wear on the aggregate and cement particles and abrasion
322 in the early hydration products. The result is the third or 'over-mixing' stage, i.e., the
323 appearance of new reaction nuclei that raise rheological parameters and accelerate the
324 decline in workability.



325

326

Figure 7. Effect of mixing time [63]

327 The rise in plastic viscosity and yield stress attendant upon longer mixing times in OPCC and
328 AASC N was indicative of a more compact fresh microstructure. While occasioning over-mixing
329 in these materials, protocol 2 appeared to generate optimum stage conditions in the AASC WG
330 concretes.

331 As gels seem to be generated at very early ages in AASC WG, longer mixing times would be
332 required to break down the microstructure and improve rheological behaviour in these
333 materials.

334 When a 15 min at-rest period was used, static yield stress rose by 26 % between 15 min and
335 30 min in both OPC concretes (**Figure 6(c)**) and remained steady after 45 min (also with 15 min
336 at-rest). After 60 min (15 min at-rest), however, yield stress remained constant under mixing
337 protocol 1 only, rising significantly under protocol 2. In the latter, the over-mixing effect
338 induced by the longer mixing time might have accelerated hydration. These findings infer that
339 the longer mixing protocol prompted significant and irreversible coagulation among cement
340 particles (decline in workability).

341 Static yield stress rose over time (with a constant 15 min at-rest period) in the concretes
342 activated with either solution. The waterglass-activated samples mixed to protocol 1 could not
343 be tested in the rheometer (for times of over 15 min) due to the high torque generated at the
344 test speed. See **Figure 6(d)** for a photograph of this concrete 30 min after mixing. Static yield
345 stress rose in NaOH-activated concretes mixed to protocol 2 procedures, whereas those same
346 procedures reduced the stress in materials activated with waterglass so effectively that
347 rheological parameters could even be measured after 22.5 min.

348 The calorimetric findings afforded an explanation for the behaviour induced by protocol 2.
349 Further to those findings (**Figure 8**), heat of hydration declined in the OPC and AAS N pastes at
350 around 20 min-60 min (induction period), i.e., approximately the duration of the rheology
351 tests, an indication that no significant hydration-induced gel formation took place in this stage.
352 In contrast, under the same conditions the AAS WG pastes exhibited a first heat flow peak,
353 attributed to the formation of a C-S-H gel. Gel formation would explain the rheological
354 behaviour of the WG-activated alkaline concretes, which would improve under protocol 2 due
355 to the partial destruction of such primary gels.

356 Slump values are plotted against dynamic yield stress per density in these concretes in **Figure 9**
357 [64, 65]. The density values are listed in **Table 4**.

358 An analysis of the data in **Figure 9** showed that both the OPC and AAS concretes, irrespective
359 of the mixing protocol, exhibited similar trends that were, moreover, consistent with the
360 patterns reported in the literature [65]. In other words, the relationship between empirical
361 (slump) and rheological (dynamic yield stress) findings were similar in NaOH- and WG-
362 activated AAS concretes and both were similar to the data for OPC concretes [64, 65].

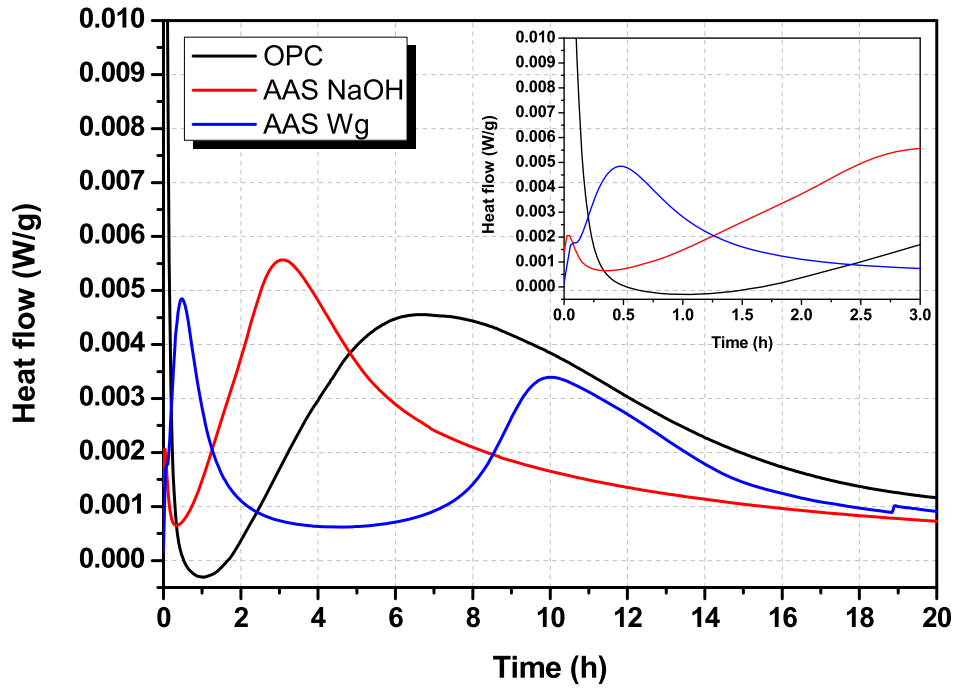


Figure 8. Calorimetric curves for OPC, AAS N and AAS WG pastes

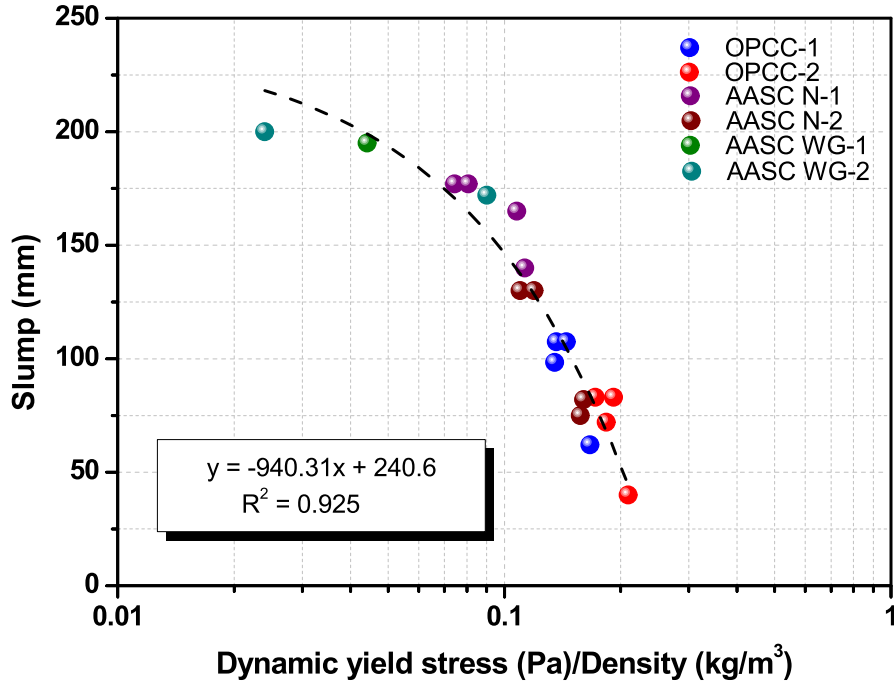


Figure 9. Slump vs dynamic yield stress/density

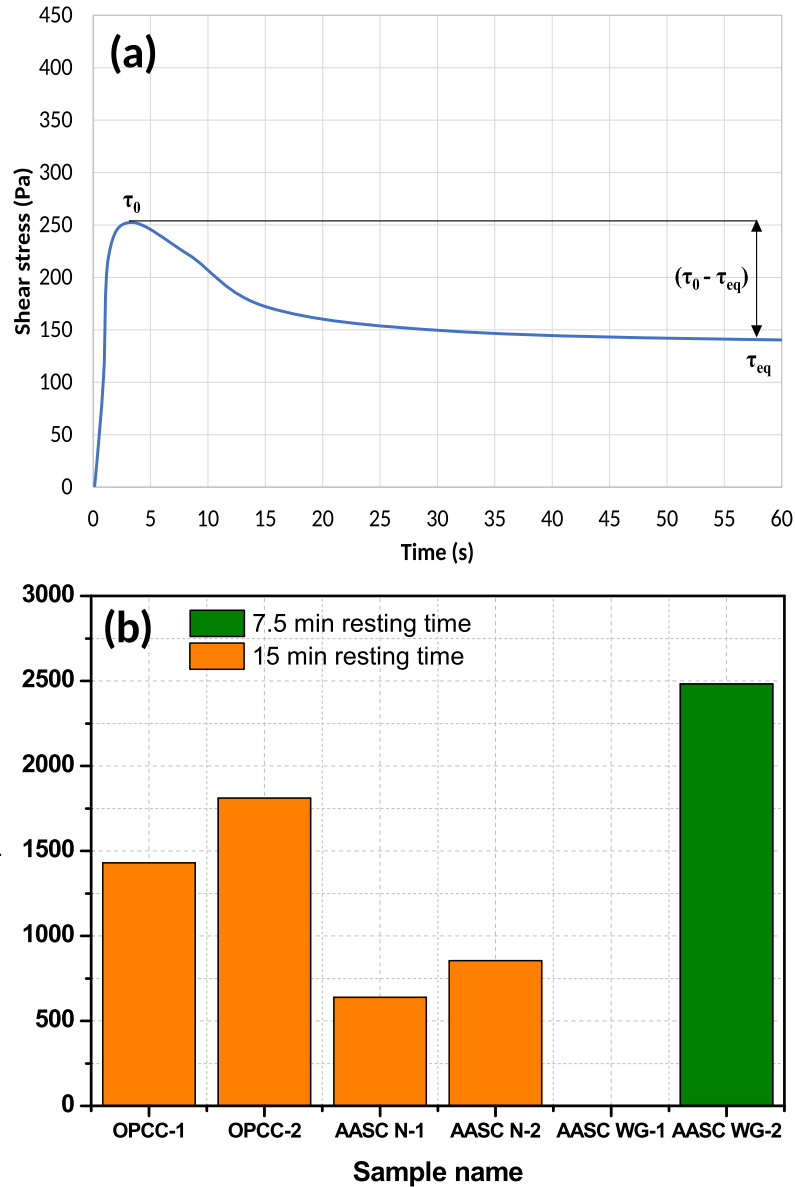
Concrete thixotropy was assessed as the difference between the peak shear stress and the shear stress at equilibrium in the Stress Growth Test at 30 min (15 min of resting time), except for the AASC WG 2 at 22.5 min (7.5 min of resting time) (see Figure 10 (a)). The greater the

390 difference between peak and equilibrium shear stress, the higher the thixotropy [66-67]. As
391 noted earlier, the test could not be run on AAS WG1 irrespective of the rest time.

392 The data in **Figure 10(b)** show that longer mixing times generated greater thixotropy in OPCC
393 and AASC N. Those results, which are consistent with the rheological results, can be attributed
394 to the formation of fine particles induced by over-mixing [63, 68]. In contrast, lengthening the
395 mixing time in AASC WG favoured system deflocculation [31], thanks to which the test could
396 be conducted; thixotropy was found to be much higher in this than in the OPC and AASC N
397 systems. At shorter mixing times (protocol 1), which hampered deflocculation, these
398 measurements could not be taken under the protocol conditions established for this study.
399 The findings suggest that longer and perhaps more energetic mixing may have yielded less
400 thixotropic AASC WG concretes.

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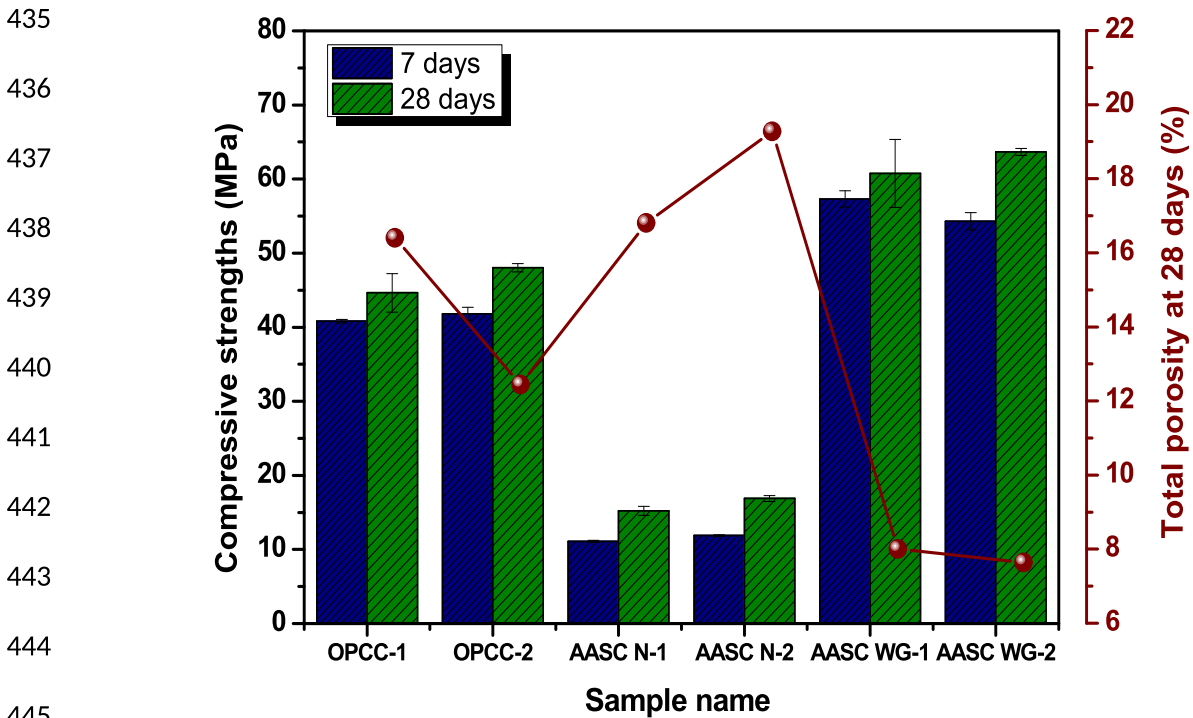


421 **Figure 10. (a) Test protocol; (b) peak stress at equilibrium in the concretes**

422 **3.2. Hardened behaviour**

423 **Figure 11** shows the 7 d and 28 d compressive strength findings for all the concretes, as well as
 424 the 28 d total porosity data. The highest strength was observed for the slag concrete alkali-
 425 activated with the commercial sodium silicate solution (waterglass), with a 28 d value upward
 426 of 60 ± 4.5 MPa. Such performance was comparable to earlier results [20] in which the use of a
 427 commercial sodium silicate hydrate (waterglass) induced high strength due to the silicon
 428 present in the solution. Lower 28 d strengths, on the order of 16 ± 0.4 MPa, were found when
 429 slag was activated with a 5 % Na_2O solution of NaOH. Portland cement exhibited strength 25 %

430 lower than AASC WG at both ages studied. Mechanical strength appeared to be scantily
 431 affected by the mixing protocol used, although when mixed to protocol 2 the materials
 432 exhibited slightly higher strength. An increase in mixing time may have favoured
 433 reorganisation of the system particles, yielding a somewhat more orderly and compact
 434 microstructure that would explain these findings.



445 **Figure 11.** 7 and 28 d compressive strength and 28 d total porosity

447 The strength findings were related to the total porosity (shown as per cent of total sample
 448 volume), density and water permeability data shown in **Table 4**.
 449

450 **Table 4.** 28 d water permeability front, total porosity (%) and density in the concretes studied

Concrete	Water Permeability front (mm)	Total porosity (%)	Fresh density (kg/m ³)	Hardened density (kg/m ³)
OPCC -1	11.0	16.4	2,342.7	2,359.4
OPCC -2	6.8	12.4	2,337.9	2,362.2
AASC N-1	11.0	16.8	2,325.3	2,371.1
AASC N-2	9.5	19.3	2,339.7	2,366.5
AASC WG-1	0	8.0	2,385.8	2,406.6
AASC WG-2	0	7.6	2,348.8	2,390.1

451

452 The NaOH-activated slag concretes had 16 %-20 % total porosity, whereas the lower total
453 porosity (7 %-8 %) in the sodium silicate-activated materials was attributed to the presence of
454 silicon in the medium. These total porosity data were directly related to the compressive
455 strength values observed. Total porosity was not as low in portland cement as expected on the
456 grounds of its mechanical strength, however. The explanation lies in the microstructural
457 differences (due to the formation of different hydration products) in alkali-activated and
458 portland cement concretes that determine the way the cementitious matrices bond to the
459 aggregates. In alkali-activated systems, aggregate and cementitious matrix bond well,
460 affording these systems high mechanical stability [20].

461 Another explanation for the difference in mechanical performance between alkali-activated
462 and portland cement concretes lies in the difference in their respective hydration products:
463 C-A-S-H and C-S-H gels. The main product of blast furnace slag activation is a calcium
464 aluminosilicate hydrate (C-A-S-H) gel, similar to the gel generated in ordinary portland cement
465 hydration, but with a lower Ca/Si ratio, which generally ranges from 0.9 to 1.2 [69-73]. When
466 the activator used is a sodium silicate hydrate (waterglass), the silicon present in the activating
467 solution, and consequently in the system, induces a decline in the Ca/Si ratio to around 0.8.
468 That in turn prompts the formation of longer mean chain lengths and structures comparable to
469 tobermorites [72], yielding an end product that exhibits high mechanical strength and the low
470 porosity required to ensure durability.

471 Further to the water penetration data (**Table 4**), permeability front depths were similar in the
472 OPCC and AASC N systems, and slightly shallower with protocol 2 than with protocol 1, a
473 finding consistent with the strength data. Longer mixing times yielded higher strength and
474 durability. Water failed to penetrate the AASC WG systems, an observation likewise consistent
475 with the mechanical behaviour observed. In these systems, the silicon sourced from the
476 activating solution induced the formation of longer gels, which would account for the low
477 porosity of the final products.

478 Fresh and hardened concrete density data are shown in **Table 4**. The AASC WG concretes were
479 the densest and most compact in both states. These concretes are known to exhibit a very
480 compact microstructure [72]. The longer mixing time (protocol 2) appeared to have a
481 beneficial effect on these concretes. In OPCC and AASC N, which exhibited similar and lower
482 densities, the mixing procedure appeared to have less of an impact than in (especially the
483 fresh) AASC WG concretes.

484 The mixing protocol appeared to affect concrete rheology more than its strength. In AASC WG,
485 both rheological and mechanical behaviour improved at longer mixing times. Mixing protocol 2
486 had an adverse effect on OPCC and AASC N rheology, while improving the performance of the
487 hardened materials only slightly.

488 **4. Conclusions**

489 The main conclusions obtained from this study are:

- 490 • The slump and rheological behaviour of OPCC and AASC differed, particularly where
491 AASC was activated with waterglass. It has been demonstrated that the nature of the
492 alkaline activator is the key determinant in AAS concrete rheology. For first time has
493 been proved that the relationship between the empirical and rheological parameters
494 in OPCC and AASCC followed a similar pattern, which was likewise similar to the trend
495 identified in the literature for OPC systems.
- 496 • Bingham models afforded a good fit to all the OPCC and AASC studied.
- 497 • Longer mixing times had an adverse effect on dynamic and static yield stress and
498 prompted significant and irreversible coagulation among cement particles (decline in
499 workability) in OPC and AAS N concretes. In contrast, longer mixing times were
500 favourable in AAS WG concrete, in which they would be required to break down the
501 microstructure to enhance rheological behaviour. These results proved that for AAS
502 Wg concrete preparation is recommended to longer mixing time. That would have
503 effect on future standardization of these eco-efficient building materials.
- 504 • Thixotropy rose in OPC and AAS N concretes with mixing time, whereas in AASC WG
505 the opposite was observed. The findings reported hereunder showed that in
506 waterglass-activated AAS concretes, longer or more energetic mixing would yield less
507 thixotropic materials.
- 508 • The mixing protocol also appeared to affect concrete rheology (fresh behaviour) more
509 than its strength (hardened behaviour). In AASC WG, both rheological and mechanical
510 behaviour improved at longer mixing times. Mixing protocol 2 had an adverse effect on
511 OPCC and AASC N rheology, while improving the performance of the hardened
512 materials only slightly.

513

514 **5. Acknowledgments**

515 This study was funded by the Spanish Ministry of the Economy under Projects BIA2013-
516 47876-C2-1-P and BIA2014-58063-R.

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