Capillary flow characteristics of an autogenic and autonomic healing agent for self-healing concrete

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ABSTRACT

Capillary flow through discrete cracks is the main mechanism by which healing agents embedded within cementitious matrices travel to zones of damage to afford the host matrix a healing ability. However, the nature of the interaction between the healing agents in their fluid state and the host matrix is unknown and may limit the ability to predict the behaviour and efficacy of self-healing systems. This study considers the capillary flow characteristics of a low viscosity cyanoacrylate and Ground Granulated Blast Furnace slag in a water suspension using glass capillaries and channels formed from a range of concrete mixes. Both healing agents conformed closely to Poiseuille's law and experienced increases in viscosity over the 40 minute period that they were exposed to a cementitious environment. Numerical simulations of the capillary rise response of the healing agents in a discrete

crack confirmed that the rate of damage and degree of saturation of the concrete element will have a significant influence on the choice of healing agent in the design of self-healing systems.

INTRODUCTION

Self-healing cementitious materials are receiving significant interest from not only the research community but also the general public and industry, due to their ability to address the social, financial and environmental concerns with infrastructure degradation (King 2013; Ortolani 2014). Numerous techniques have been proposed for achieving self-healing cementitious materials which either rely on enhancing the material's intrinsic ability to heal (Engineered Cementitious Composites, use of supplementary cementitious materials) or engineering the material via the use of inclusions within the cementitious matrix that carry autogenic (natural) or autonomic (man-made) healing agents. Both techniques primarily rely on the transport of fluid (water or healing agent) in a discrete crack to microcracked zones of damage.

The selection of a healing agent is driven mainly by cost and availability, although it is important that its physical properties such as viscosity, surface tension, bonding characteristics and its compatibility with the cementitious matrix over time, are considered during the selection process. In general, healing agents with low viscosity and significant capillary potential are usually preferred.

Compared to autonomic healing agents, autogenic healing agents such as those based on supplementary cementitious materials (Sahmaran et al. 2013), mineral admixtures (Ahn and Kishi 2010) and geomaterials (Kishi 2013) afford improved compatibility with the host matrix due to the nature of the chemical composition of the healing products. Moreover, through the use of a pozzolanic material, bond strengths comparable with those of undamaged cementitious materials may be achieved. Varying methods have been proposed to embed autogenic healing agents into cementitious materials. These range from combining them in their natural form with other mix

50 components or encapsulating them within microcapsules of varying shell material (Kanellopoulos et
51 al. 2015; Van Tittelboom and De Belie 2013). In the former their long term reactivity is questionable
52 particularly since their supply will be exhausted as part of the continual cement hydration process.
53 Conversely, in the latter, their longevity is improved but their reactivity is dependent on the host
54 matrix environment and the presence of water to carry the dry-powder-based healing agent from its
55 point of encapsulation to the site of damage via a range of transport mechanisms, including capillary
56 action.
57
58 Chemical agents such as epoxies, cyanoacrylates, and polyurethane are frequently used as concrete
59 repair products and as such have been employed in a range of autonomic self-healing concrete
60 studies (Cao et al. 2014; Wang et al. 2013; Joseph et al. 2010; Maes et al. 2014). These healing agents
61 have been encapsulated in either microcapsule or vascular based systems. Nevertheless, in all cases
62 the predominant transport mechanism is capillary action.
63
64 Self-healing studies on cementitious materials are generally conducted at small scale to demonstrate
65 the feasibility and effectiveness of the particular healing system. This necessitates the use of mortar
66 rather than concrete to avoid excessive heterogeneity, which occurs when the maximum aggregate
67 particle size becomes large relative to the principal structural dimension (Van Tittelboom and De
68 Belie 2013; Joseph et al. 2010). Similarly, previous studies conducted on the capillary rise response of
69 healing agents have also been predominantly limited to mortar based cementitious materials
70 (Gardner et al. 2012; Gardner et al. 2014). The need to upscale self-healing materials is now apparent
71 and dictates a move to concrete specimens that replicate structural elements, environmental
72 conditions and typical damage events found in civil engineering infrastructure. As a result, the
73 capillary flow may be influenced by (i) the crack morphology, as cracks deviate around coarse
74 aggregate particles; (ii) the absorptivity of the cementitious matrix as a result of coarse aggregate
75 particle inclusion, (iii) the density of the matrix for differing strength concretes and (iv) the degree of

76 saturation of the concrete. All of these factors have the potential to influence the parameters used in
77 modelling the capillary rise response, namely the surface tension, contact angle and viscosity of the
78 healing agent.
79
80 To date, there have been a limited number of reported studies on the mechanisms of capillary flow
81 and the flow properties of healing agents in concrete. Whilst acknowledging the contributions of
82 previous investigations (Gardner et al. 2012; Gardner et al. 2014; Dong et al. 2015), it remains true that
83 the mechanisms governing these processes are neither fully understood nor properly characterised.
84 The aim of this study is to address this by establishing the capillary flow characteristics of both an
85 autonomic healing agent and autogenic healing agent through a series of experimental investigations,
86 with particular attention given to their Hagen-Poiseuille and capillary flow characteristics.
87
88 This paper firstly presents experimental data concerning the characterisation of the flow properties of
89 the two healing agents, in particular the Hagen-Poiseuille flow properties, time-surface tension, time-
90 contact angle and time-viscosity relationships. A brief summary of previously developed flow theory
91 (Gardner et al. 2014) is then provided and a numerical model is used to simulate the capillary rise
92 behaviour of the two healing agents in a discrete crack, using the flow properties reported earlier in
93 the paper.
94
95 **CHARACTERISATION OF FLOW PROPERTIES**
96 The flow properties of two healing agents, alongside water, were characterised in this experimental
97 study. The autonomic healing agent was a low viscosity cyanoacrylate (PC20) (Cyanotech, 2016) with
98 a specific gravity of 1.06. The autogenic healing agent was a suspension of Ground Granulated Blast
99 Furnace Slag in water (GGBS(S)) (Hanson, 2015). The GGBS had a specific gravity of 2.9 and was
100 combined with water in the ratio of 40:60 by mass to give a suspension with a density of 1358kg/m^3. A
101 series of characterisation tests were performed on the healing agents in both a non-cementitious and

cementitious environment. These tests and the associated results are reported in detail in the next 4 sections.

Hagen-Poiseuille flow of healing agents

Firstly, to characterise the flow properties of the healing agents and establish the applicability of Poiseuille's Law to the present situation, the experimental arrangement presented in Fig. 1 and the Hagen-Poiseuille (H-P) flow equation, given in Equation (1), were used. For Poiseuille's law to be applicable to a particular fluid, its dynamic viscosity should be insensitive to both pressure and flow rate.

$$\Delta P = \frac{8\mu L Q}{\pi r^4} \quad (1)$$

where L = channel length (m); Q = flow rate (m^3/s); r = capillary radius (m); μ = dynamic viscosity (Ns/m^2) and ΔP= Pressure drop (N/m^2) over the channel length L.

In this study, the flow channel comprised glass capillary tubes with internal diameters of 0.8mm and 1.2mm and lengths of 100mm, 200mm and 300mm. These tube dimensions were chosen to limit the influence of end effects and to allow the development of laminar flow, with the aim of obtaining reliable flow properties. The authors were not trying to replicate the tubes in any particular vascular or encapsulated self-healing system in these particular tests.

The tests were conducted using initial heights (h_0) ranging from to 450 to 1900mm, dependent on the capillary tube radii, length and healing agent, as summarised in Table 1. The change in surface height (h(t)) was measured using an AOS X-Motion high speed video camera.

The results, presented in Figure 2, demonstrated that the response of both healing agents conformed closely to Poiseuille's law, with a minimum correlation coefficient of 0.9968 for the 200L 0.8D PC20

127 test. The viscosity of the healing agent calculated from each test is given in Table 2. The average
128 viscosity of PC20 was subsequently calculated as 3.15 x 10^{-3} Ns/m^2, which falls within the viscosity
129 range published by the manufacturer (Cyanotech 2016). Similarly the GGBS(S) had a viscosity of 3.20
130 x 10^{-3} Ns/m^2.
131
132 **Time-surface tension relationship**
133 A Lauda TVT1 drop volume tensiometer (see Fig. 3), calibrated with distilled water and ethanol
134 samples, was used to examine the influence of healing agent curing (PC20) and settling (GGBS(S)) on
135 the variation of surface tension (γ) with time. A syringe volume of 1ml was chosen with a 1.35mm
136 inner diameter needle employing a drop rate of 0.2-40s/µl. PC20 is known to cure in the presence of
137 moisture and therefore surface tension measurements were repeated with 2.5ml of water in the base
138 of the drop receiving cell. GGBS(S) suspensions were made with tap water (TW) and the sample for
139 measurement was taken from the middle layer of the sample following 30 seconds vigorous shaking
140 and 30 seconds settling time. However, further settling of the suspension was observed during the
141 course of the measurement and could be clearly seen on removal of the syringe from the tensiometer.
142 In order to address this, a series of readings over three drop rates (and hence drop times) were taken
143 to observe the change in GGBS(S) surface tension with time.
144
145 Table 3 presents the surface tension results measured to an accuracy of 0.1mN/m. Similar surface
146 tension results have been published in the literature for water at 20°C (Richards and Coombs 1915)
147 and Ethyl Cyanoacrylate (O'Neil 2006). The addition of GGBS to water results in a 30% reduction in
148 the surface tension compared to tap water alone. Of significant interest is the consistency in the
149 surface tension measurements for each healing agent, regardless of (a) the presence of moisture in the
150 cell to encourage curing (PC20) or (b) a change in drop time which would affect the degree of
151 sediment settling (GGBS(S)). In the case of the former this supports the theory that PC20 will only
152 start to cure/bond when in contact with a surface, and therefore a suspended drop of PC20 is unlikely

153 to demonstrate any significant change in surface tension over the timescales considered in these
154 experiments. For the GGBS(S) surface tension results it can be seen that there is negligible change in
155 surface tension for the 3 different drop rates.
156
157 **Substrate-contact angle relationship**
158 The influence of a range of substrates on the contact angle (θ) of the healing agents was examined *via*
159 the sessile drop technique. Three different substrates were used, the first being Thermo Scientific
160 Gerhard Menzel Superfrost glass slides in the "as supplied" condition (described by the manufacturer
161 as washed and polished). The second substrate was the open cast face of a high strength concrete
162 (HSC) cube, manufactured using the mix proportions in Table 4 and dried for 12 hours at 25°C prior
163 to testing to provide an unsaturated surface (HSC UNSAT). The third substrate was a HSC cube
164 which was soaked in water for 1 hour to provide a saturated surface (HSC SAT). The two latter
165 substrates were used to observe changes to the contact angle when in contact with a cementitious
166 surface. The HSC cubes were cast 7 days prior to testing.
167 The sessile drop technique, a schematic view of which is given in Figure 4a, was performed using a
168 drop volume of 10μl. The technique was performed 3 times on each substrate. Images of the drops
169 were captured with a Veho Discovery VMS-001 microscope, an example of which is given in Figure
170 4b. Imaging techniques developed by Stalder et al. (2006) were used to obtain the drop profile and
171 contact angles on either side of the drop, as indicated in Figure 4c, which were then used to provide
172 an average contact angle for the drop. The contact angle reported for each substrate was taken as the
173 average contact angle of the 3 drops on that substrate and is reported in Table 5 along with the
174 coefficients of variation (COV%).
175
176 For all fluids analysed, the contact angle is greater for the HSC surfaces than the glass surface. This
177 may be expected since it is well known that, in general, contact angles increase with surface
178 roughness (Wenzel 1936; Cassie and Baxter 1944; Fox and Zissman 1950; Momber 2000) and the HSC

179 samples certainly had a higher surface roughness than the glass. The two main issues that cause this
180 increase are the greater relative contact area present when a surface is rough (Wenzel 1936) and the
181 fact that the surface will absorb some of the fluid and the resulting capillary actions provide an
182 increased pinning force (Momber 2002). It is also clear that the contact angles are slightly greater for
183 the saturated HSC specimens than for the unsaturated cases. It may be that, in effect, the presence of a
184 more continuous fluid phase around the droplet increases the pinning perimeter, although the latter
185 would have to be verified with further investigation.
186
187 Although higher contact angles are reported on HSC substrates than on glass for all the healing
188 agents considered, the magnitude of the difference between the contact angles varies, indicating the
189 presence of an additional interaction between the healing agent and the substrate. The curing time of
190 a thin cyanoacrylate film on a borosilicate glass plate was reported by the Cambridge Polymer Group
191 (2004) to be 5 minutes with 80% curing observed in the first 2 minutes. It is therefore suggested in the
192 current study that the increased alkalinity and presence of moisture on the surface of the HSC, even
193 in the unsaturated state, will increase this curing rate such that immediate curing of the drop at the
194 adhesive/surface interface effectively pins the drop in place preventing further wetting of the surface.
195 Conversely, the latent hydraulic and pozzolanic properties of GGBS(S) have reaction times in the
196 order of weeks/months, which are greatly in excess of the duration of the tests reported herein.
197
198 The sessile drops were observed for one hour following the initial measurement. Negligible change in
199 the contact angle was observed for PC20 after this one hour period, whilst the water and GGBS(S)
200 sessile drops evaporated after 15 minutes of exposure to the laboratory environment.
201
202 **Time-Viscosity relationship**
203 The development of a bespoke viscometer, as shown in Figure 5, designed to examine the change in
204 viscosity of the healing agent when in contact with a cementitious matrix has previously been

205 reported by the authors (Gardner et al. 2014). A modified version of this viscometer, which comprises
206 two flexible tubes and a narrow rectangular channel in a concrete specimen, is reported herein.
207
208 A series of flow tests over time were conducted in which a rectangular channel 25mm wide by 1mm
209 deep formed through concrete blocks of varying strengths (mix proportions given in Table 6) was
210 connected to two L-shaped flexible tubing channels, 4mm in inner diameter. The rectangular channel
211 was selected to represent the flow conditions in a planar crack. The connection between the flexible
212 tubing channels and the rectangular channel was made by countersinking the flexible tubing 10mm
213 into the side of the concrete specimen and affixing it with cyanoacrylate glue. The channels were
214 cleaned with pressurised air and the block arrangement was tilted to the left hand side about the
215 pivot point, at which point the healing agent was introduced into channel 1 (see Figure 5) such that
216 the channel was almost full. A stopper was placed in the end of channel 1 and the block arrangement
217 was then returned to the horizontal position and the stopper removed. This allowed the movement of
218 the healing agent through a clean, non-coated channel in the concrete to be observed. Subsequent
219 tests involved the movement of the healing agent through the previously coated concrete channel.
220 The movement of the healing agent free surface (i.e. dh_1/dt) was recorded using a high speed video
221 camera. The test was repeated at 20 second intervals for 1 minute, and then at 3 to 4 minute intervals
222 for a further 15 minutes followed by 3 further readings at 20 minute intervals. Tests were conducted
223 using saturated (SAT) concrete specimens, which had been soaked in water for one hour prior to
224 testing and unsaturated (UNSAT) concrete specimens, which were dried for 12 hours at 25°C prior to
225 testing. The GGBS(S) tests are denoted UNSAT because the specimens were initially dry; however,
226 the near surface zones of the channels quickly became saturated. Preliminary tests for GGBS(S) with
227 both initially saturated and unsaturated specimens showed no appreciable difference and thus only
228 the initially unsaturated specimen results are reported.
229

The theory related to the displacement of the free surface, previously presented by Gardner et al. (Gardner et al. 2012; Gardner et al. 2014), is summarised below. Here, an amendment is made to the K_{HP} term to account for the rectangular central channel, and to the solution to the governing differential equation to allow for instances when the discriminant of the associated characteristic equation has positive roots.

The moment balance inside the viscometer is given by equation (2), in which u_i is the flow velocity of the fluid in channel i (i designating the flexible tube or channel in the mortar), and the superior dot denotes the time derivative. L_i is the length of channel i (m); h_i is the height of the healing agent above the centre line of the horizontal portion of channel i (m); A_i is the area of channel i (m^2); r_i is the radius of channel i (m); d_c is the depth of the rectangular concrete channel (m); ρ is the healing agent density (kg/m^3) and μ is the dynamic viscosity (Ns/m^2).

Mass continuity of the fluid implies that $u_i = -\dot{h}_i$, $\bar{h} = \frac{h_1 + h_2}{2}$ and $A_i u_i = const.$

Applying these conditions in equation (2) and rearranging gives the governing differential equation in (3).

$$\rho g(h_1 - h_2)A_1 - 8\mu\sum_{i=1}^{2} A_i \frac{L_i u_i}{r_i^2} - 12\mu\frac{A_3 L_3 u_3}{d_c^2} - \rho\sum_{i=1}^{3} A_i L_i \dot{u}_i = 0 \qquad (2)$$

$$\ddot{h}_1 + \frac{K_{HP}}{\rho L_T}\dot{h}_1 + \frac{2g}{L_T}h_1 = \frac{2g}{L_T}\bar{h} \qquad (3)$$

in which $K_{HP} = 8\mu\sum_{i=1}^{3}\frac{L_i}{r_i^2} + 12\mu\frac{L_3}{d_c^2}$ (4a)

and $L_T = \sum_{i=1}^{3} L_i$ (4b)

A solution to equation (3) is given in equation (5) for the case when the discriminant of the associated characteristic equation has positive roots;

$$h_1 = \frac{e^{\lambda t}\left(h_{10} - \bar{h}\right)}{\left(1 - \frac{\lambda}{\chi}\right)}\left[1 - \frac{\lambda}{\chi}\right] + \bar{h} \qquad (5)$$

where $\lambda = \frac{-\alpha + \sqrt{\alpha^2 - 4\beta}}{2}$ and $\chi = \frac{-\alpha - \sqrt{\alpha^2 - 4\beta}}{2}$ and $\alpha = \frac{K_{HP}}{\rho L_T}$ and $\beta = \frac{2g}{L_T}$

Similarly, a solution to equation (3) is given in equation (6) for the case when the discriminant of the associated characteristic equation has complex roots;

and $h_1 = e^{\lambda t}\left(h_{10} - \bar{h}\right)\left[cos\ \chi t + \left(\frac{\dot{h}_{10} - \lambda}{\chi}\right) sin\ \chi t\right] + \bar{h}$ (6)

where $\lambda = -\left(\frac{\alpha}{2}\right)$ and $\chi = \sqrt{\beta - \left(\frac{\alpha}{2}\right)^2}$ and α, β as above

The initial conditions used in the solution to derive (5) and (6) are as follows:

$h_1 = h_{10}$ and $\dot{h}_1 = \dot{h}_{10}$ @ t=0

The viscosities for the two healing agents over time were computed by using a least squares fit of equation (5 or 6) to the associated experimental data and are shown in Figure 6. It can be observed that there is no significant change in the viscosity of the PC20 in both a saturated (SAT) and unsaturated (UNSAT) environment over the first 5 minutes of the test. However, on constant exposure to air and the cementitious matrix, there is evidence of PC20 curing after 5 minutes characterised by a continual increase in viscosity beyond this point. It is difficult to determine whether the viscosity change of the PC20 results from gradual hardening of the bulk fluid or hardening of the PC20 on the flow channel edges, the latter resulting in a reduction in the central channel cross section. Initial investigations would suggest that since the total length of fluid in the test at t= 30 mins remains within 3% of the length of fluid at t=0 secs, then gradual hardening of the bulk fluid as a result of repeated agitation and contact with an alkaline environment would seem the most

likely reason. There is a marked difference in the time-viscosity relationship between SAT and UNSAT specimens and specimens of differing strength. For saturated specimens the higher strength specimens have a slower rate of viscosity change, which may be attributed to lower permeability of the concrete matrix which helps maintain, rather than absorb, a layer of water on the surface, thereby offering a temporary barrier between the concrete matrix and the healing agent. This temporary barrier would diminish with time due to water loss from the specimen through evaporation. For unsaturated specimens the effect of concrete strength is not as well defined and after 35 minutes no movement of the PC20 was recorded in any of the specimens. It is hypothesised that, in the absence of a water rich layer on the flow channel surface, the curing of the PC20 was not impeded and that the moisture naturally present within the specimens was sufficient to allow curing to occur.

The minor increase in viscosity of PC20 over the first 5 minutes of exposure to the cementitious environment has negligible impact on the extent of capillary rise. This makes PC20 a potentially suitable healing agent for structures in which damage occurs quickly and a rapid healing response is required. However, if damage occurs at a slow rate, such that crack propagation happens gradually then the self-healing efficiency of the system will be limited by the PC20 curing process. Moreover, with smaller apertures than those employed in the current viscometer study, particularly those apertures approaching the bonding width of PC20, this viscosity increase may be accelerated. Below 5 minutes, viscosities in the range of 1.82 – 2.94 x 10^{-3} Ns/m^2 were recorded and are similar to those calculated according to the Poiseuille law, suggesting little influence of the alkaline environment on the viscosity of PC20 at the point when they first come into contact with each other

The viscosity of GGBS(S) increases significantly over the first 40 seconds (Figure 7a), although the magnitude of this viscosity increase is dependent on the concrete mix under consideration, which in turn is an indirect indicator of the channel surface. There was evidence of water absorption into the matrix for the C20 specimens over the first 40 seconds resulting in a change in the concentration of the

297 suspension. Nevertheless, this change was negligible (58.5:41.5 as opposed to 60:40) and therefore the
298 increase in viscosity may be primarily attributable to the settling of the suspension and subsequent
299 blocking of the flow channel. Further investigation is required here to fully quantify this effect.
300
301 **NUMERICAL SIMULATION OF CAPILLARY RISE RESPONSE**
302 In this section a previously reported capillary rise model is used to demonstrate the influence of the
303 flow characteristics presented in this paper, summarised in Table 7, on the capillary rise response of
304 GGBS(S) and PC20 in a discrete planar crack. The theory supporting the capillary model is provided
305 in full by Gardner et al. (2014). The correction parameters associated with frictional dissipation at the
306 moving front (β_m), stick-slip behaviour of the meniscus (β_s) and wall friction (β_w) are 0.35Ns/m^2, 0.12
307 and 0m^3/Ns respectively, as suggested by Gardner et al. (2014) for 7 day old concrete. Simulations of
308 capillary rise are conducted for a crack width of 0.2mm using the flow characteristic parameters
309 associated with C50 concrete. Although the viscosity of both healing agents demonstrated time-
310 dependence, when in contact with the cementitious matrix, this effect was more apparent and
311 prolonged in the PC20 viscosity measurements. Therefore, simulations are presented using the
312 healing agents' viscosity at 20 seconds (GGBS(S) and PC20) and 30 minutes (PC20 alone), as shown in
313 Figure 8.
314
315 It is the higher contact angle associated with saturated specimens that reduces the equilibrium rise
316 height in comparison to unsaturated concrete specimens. Although further viscosity tests for
317 increasing exposure times were conducted for GGBS(S), significant settling of the suspension was
318 observed after 2 minutes. The numerical simulation suggests that the GGBS(S) reaches its equilibrium
319 capillary rise height in approximately 10s. Experimental capillary rise simulations of similar GGBS(S)
320 suspensions in planar concrete cracks (Gardner et al. 2013) have shown that, once the equilibrium
321 capillary rise height of GGBS(S) is reached, the meniscus starts to rise again after approximately 5
322 seconds. This is caused by the settlement of GGBS particles and the subsequent capillary rise response

being driven by the flow characteristics of pure water rather than GGBS(S), provided that the crack plane is not blocked by GGBS particles. If the viscosity of water is assumed to be constant then the difference in capillary rise response between saturated and unsaturated concrete specimens will be negligible since the contact angle of water in contact with the cementitious matrix is similar in both saturated and unsaturated states.

From Figure 8 it can be seen that the capillary rise response of the PC20 healing agent at 20 seconds exposure time is the same in both saturated and unsaturated concrete specimens due to the limited effect the concrete surface condition has on viscosity and contact angle at this exposure time. In practice, this suggests that when PC20 is introduced into the crack at the time of crack formation (with <20 seconds exposure to the cementitious matrix) the moisture state of the concrete at the time of damage has negligible impact on the capillary rise response of the healing agent. At short exposure times for PC20, the capillary rise time is short (approx. 15 seconds) compared to the timescale involved in viscosity changes (approx. 660 seconds). Therefore, the introduction of a time dependent viscosity function into the numerical model at short exposure times would have limited influence on the capillary rise response.

As discussed previously, slow propagation of cracks and hence continued exposure of PC20 to the cementitious environment has the potential to significantly retard the capillary rise response. Indeed, the simulations of capillary rise confirm that PC20 exposed to the cementitious matrix for 1800 seconds takes 17 times longer (326.7 seconds as opposed to 18.5 seconds) to reach the equilibrium capillary rise height compared to PC20 exposed for only 20 seconds. Moreover, during the capillary rise, further increases in PC20 viscosity will occur upon additional exposure to the cementitious environment, which, according to the results may impede capillary flow to the point that the full equilibrium rise height is never realised. What is shown in this paper is therefore an upper limit of capillary rise for longer exposure times.

Whilst the simulations performed here have yet to be refined further in terms of imbibition of fluid into the cementitious matrix around the crack plane, they do provide an indication of the influence of healing agent type on the capillary rise response and hence the potential success or limitations of self-healing systems employing the types of healing agent investigated herein.

CONCLUSIONS

In order to correctly model the rate of capillary rise, the time dependent properties of two healing agents were investigated. Firstly, the H-P flow characteristics of water, PC20 and GGBS(S) were investigated. Both fluids were shown to have Newtonian flow characteristics. Contact angles were also time independent, nevertheless, contact with unsaturated and saturated mortar surfaces yielded higher contact angles compared to a glass surface. Viscosity measurements of PC20 showed little influence of time dependency over the first 5 minutes of exposure to a cementitious environment. However, between 5 minutes and 40 minutes the viscosity of the PC20 increased to such a value that it was no longer possible to induce movement of the column of PC20 in the experimental arrangement. This effect was more pronounced in unsaturated specimens of lower concrete strengths. For the GGBS(S), the rate of viscosity increase was greater than that observed for PC20 (over the first 40 seconds), although this may be attributed to blockage of the flow channels via the settling of the GGBS(S) rather than a true increase in viscosity of the suspension through any form of chemical interaction with the cementitious environment.

The numerical simulation of the capillary rise response of both healing agents in a discrete planar crack using the experimentally determined flow parameters has proven that the time taken to a achieve the equilibrium capillary rise height is dependent on the viscosity of the healing agent which in turn is influenced by the saturation of the concrete specimen and the exposure time of the healing agent to the cementitious matrix. The rate of damage or rather crack propagation together with the

375 saturation state of the concrete structure will therefore have a significant influence on the choice of
376 healing agent for any embedded self-healing system.
377
378 In summary, it has been demonstrated that it is possible to measure the flow characteristics of self-
379 healing agents in order to better simulate their capillary rise response in discrete cracks in concrete.
380 These simulations will in time inform the efficient design of self-healing systems, through the correct
381 selection of healing agent for the intended healing time and volume.
382
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466 **Fig. 1.** Hagen-Poiseuille experimental arrangement

467 **Fig. 2.** Hagen-Poiseuille flow characteristics

468 **Fig. 3.** Drop volume tensiometer arrangement

469 **Fig. 4.** (a) Sessile drop measurement arrangement; (b) typical microscope image of sessile drop and (c)

470 Image-J drop snake analysis on sessile drop

471 **Fig. 5.** Bespoke viscometer for time-viscosity measurements

472 **Fig. 6.** Full Time-Viscosity relationship for GGBS(S) and PC20.

473 **Fig. 7.** Time Viscosity relationship for GGBS(s) and PC20 over a) the first 40 seconds of exposure and

474 b) the first 1200 seconds of exposure

475 **Fig. 8.** Capillary rise simulations for GGBS(S) and PC20 using experimentally measured flow

476 characteristic parameters.

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Table 1. Hagen Poiseuille experimental variables

Healing agent	Capillary tube diameter (mm)	Capillary tube length (mm)	Initial h_0 range (mm)	Test reference
Water	0.8	100	750 - 450	100L 0.8D Water
		200	1000 - 700	200L 0.8D Water
		300	1600 - 1100	300L 0.8D Water
	1.2	100	750 - 350	100L 1.2D Water
		200	1000 - 450	200L 1.2D Water
		300	1000 - 650	300L 1.2D Water
GGBS(S)	0.8	100	1500 - 1300	100L 0.8D GGBS(S)
		200	1900 - 1500	200L 0.8D GGBS(S)
	1.2	100	1500 - 1300	100L 1.2D GGBS(S)
		200	1500 - 1000	200L 1.2D GGBS(S)
		300	1900 - 1200	300L 1.2D GGBS(S)
PC20	0.8	100	1500 - 1200	100L 0.8D PC20
		200	1600 - 1300	200L 0.8D PC20
	1.2	100	1300 - 1000	100L 1.2D PC20
		200	1500 - 1000	200L 1.2D PC20
		300	1600 - 1300	300L 1.2D PC20

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500 **Table 2.** Viscosity results for healing agents and water for all Hagen-Poiseuille test arrangements

Test reference	Viscosity ($x10^{-3}$ Ns/m^2)	Average Viscosity ($x10^{-3}$ Ns/m^2)
100L 0.8D Water	1.26	1.42
200L 0.8D Water	1.14	
300L 0.8D Water	1.13	
100L 1.2D Water	2.06	
200L 1.2D Water	1.53	
300L 1.2D Water	1.38	
100L 0.8D GGBS(S)	2.95	3.20
200L 0.8D GGBS(S)	2.77	
100L 1.2D GGBS(S)	4.66[a]	
200L 1.2D GGBS(S)	3.48	
300L 1.2D GGBS(S)	3.37	
100L 0.8D PC20	2.65	3.15
200L 0.8D PC20	2.63	
100L 1.2D PC20	4.05	
200L 1.2D PC20	3.22	
300L 1.2D PC20	2.96	

501 [a] omitted from average calculation due to settling of suspension observed in the test causing tube blockage

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512 **Table 3.** Surface tension for tap water (TW) and healing agents PC20 and GGBS(S) over a range of

513 drop times

Healing agent	Relative Humidity in cell (%)	Drop rate (s/μl)	Drop time (s)	Surface Tension, γ (mN/m)
TW	53	0.20	7.4	72.2
PC20	53	0.25	5.5	34.8
PC20	53	1.00	22.0	34.4
PC20	70	1.00	22.0	34.5
PC20	70	40.00	714.0	34.2
GGBS(S)	53	0.20	5.0	49.9
GGBS(S)	53	0.70	17.4	49.7
GGBS(S)	53	1.20	28.3	49.9

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527 **Table 4.** High strength concrete (HSC) mix proportions

Cement	Fine Aggregate[a]	Coarse Aggregate[b]	Water	Silica Fume	Superplasticiser
437kg/m^3	664kg/m^3	1113kg/m^3	140kg/m^3	48kg/m^3	28.5ml/kg

528 [a] max aggregate size 4mm [b] max aggregate size 10mm

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544 **Table 5.** Contact angle results for varying substrate and healing agent

Healing agent	Glass (°) (COV[a]%)	HSC UNSAT (°) (COV%)	HSC SAT (°) (COV%)
TW	10.9 (21.6)	22.8 (10.9)	24.8 (11.4)
GGBS(S)	14.7 (13.5)	20.9 (17.8)	28.1 (12.5)
PC20	9.5 (19.8)	14.1 (18.0)	15.6 (18.3)

545 [a] coefficient of variation (%)

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560 **Table 6.** Mix proportions for concrete specimens

Designation	Cement (kg/m^3)	Fine aggregate[a] (kg/m^3)	Coarse aggregate[b] (kg/m^3)	Water (kg/m^3)
C20	402.8	781.2	974.5	241.6
C30	409.6	794.5	991.1	204.8
C50	416.7	808.3	1008.3	166.7

561 [a]max aggregate size 4mm [b]max aggregate size 10mm

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575 **Table 7.** Flow characteristics for simulation of the capillary rise response of PC20 and GGBS(S) in a

576 planar crack in C50 concrete.

Flow characteristic	GGBS(S) (@20s)	PC20 (@20s)	PC20 (@1800s)
Healing agent viscosity on unsaturated surface, μ_{UNSAT} (x10^{-3} Ns/m^2)	4.60	1.95	42.00
Healing agent viscosity on saturated surface, μ_{SAT} (x10^{-3} Ns/m^2)	4.60[a]	1.57	8.54
Surface tension, γ (mN/m)	49.85	34.56	34.56
Contact angle on unsaturated substrate, θ_{UNSAT} (°)	20.9	14.1	14.1
Contact angle on saturated substrate, θ_{SAT} (°)	28.1	15.6	15.6
Healing agent density, ρ (kg/m^3)	1358	1060	1060
Correction factor frictional dissipation at moving front, β_m (Ns/m^2)	0.35	0.35	0.35
Correction factor stick slip behaviour of meniscus, β_s (unitless)	0.12	0.12	0.12
Correction factor wall friction, β_w (m^3/Ns)	0	0	0

577 [a]viscosity of GGBS(S) not recorded in saturated concrete therefore viscosity in unsaturated concrete
578 assumed for simulation purposes.

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