

Comparison of the effect of mix proportion parameters on behaviour of geopolymer and Portland cement mortars

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| 1 | Comparison of the effect of mix proportion parameters on behaviour of |
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| 2 | geopolymer and Portland cement mortars |
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| 18 | |
| 19 | ABSTRACT |
| 20 | This work focuses on low-purity kaolin, widely accessible throughout the globe. Room |
| 21 | temperature cured geopolymer mortars (GPMs) were formulated using an aluminosilicate |
| 22 | precursor based on calcined lithomarge and potassium silicate activator. The effect of mix |
| 23 | proportion parameters on the engineering properties of GPMs was investigated. The |
| 24 | behaviour of GPMs was compared with that of Portland cement-based mortars (PCMs). |
| 25 | Statistically designed experiments revealed that an increase in water-to-solid (w/s) ratio had |

a dominant effect on increasing the workability and setting time while decreasing the
compressive strength of GPMs. In contrast to PCMs, GPMs proportioned with a constant
water content showed a non-linear relationship between the w/s ratio and workability, which
could be associated with changes to paste/sand proportions and/or water/alkali proportions.
Like-for-like comparison of GPMs and PCMs showed that GPMs require lower free water
content, and can offer shorter setting times and a rapid strength development.

32

Keywords: Kaolin; Lithomarge; Geopolymer mortars; Portland cement mortars; Centre composite design; Workability; Setting time; Compressive strength;

35

36 1 INTRODUCTION

37 Geopolymer-based concretes are a new class of construction materials, where the cementitious 38 binder is replaced with geopolymer alternatives, typically of low carbon footprint. Geopolymer 39 binders are produced by reacting an alumino-silicate precursor, often a waste or a by-product 40 material, with an alkali-silicate solution, also called chemical activator [1]. An inorganic 41 polymerisation reaction results in the formation of hardened material with a three-dimensional 42 and amorphous microstructure. Thanks to the unique, ceramic-like microstructure, 43 geopolymer-based materials have been reported to have potentially equivalent, or even superior, 44 physical and durability properties when compared to conventional materials made with 45 Portland cement [2]. Geopolymers are most frequently renowned for a fast rate of strength 46 development, fast setting time, resistance to chemical attack and improved fire resistance [3]. 47 However, where the concrete/construction industry is concerned, geopolymer concrete still has 48 to be proven to be more user-friendly and cost-effective, and to comply with specific engineering properties in order to gain more popularity. 49

51 Various alumino-silicate source types can be used as precursors for geopolymerisation. Among 52 the most common are metakaolin (*i.e.* high purity kaolin) [4, 5] and different types of calcined 53 clays [6-9], slags [2, 10, 11] and ashes [2, 12-14]. However, due to geographical or industrial 54 diversity across the globe, precursors containing metakaolin or some industrial by-products 55 (such as fly ash or ground granulated blast furnace slag) may not be locally available. Economy 56 and sustainability of geopolymer technology are hindered by the need to source the precursor elsewhere and transport it to the place of further processing or intended use. Therefore, it is 57 58 important to investigate the possibility of using locally available, naturally occurring, low 59 purity materials, such as clays. These clays, being abandoned by industry, have the advantage 60 of being cheaper than the high purity alternatives (e.g. metakaolin) or materials which are 61 difficult/expensive to get access to. It has been recently shown that low purity kaolinitic clays 62 can be calcined and used to produce geopolymer binders with compressive strengths exceeding 63 50 MPa [15-21].

64

65 Large deposits of kaolin-containing soft rock, called lithomarge, exist in Northern Ireland as part of the Interbasaltic Formation (IBF) [22]. Cooper [23] reported that lithomarge primarily 66 67 contains kaolinite (Al₂Si₂O₅(OH)₄), gibbsite (Al(OH)₃), goethite (FeO(OH)), hematite (Fe₂O₃) 68 and various smectite minerals. IBF material is typically seen as a nuisance by quarry owners. 69 However, because of its kaolinite content, IBF could be used as an aluminosilicate source for 70 the commercially viable formation of geopolymer binders, hence providing a large resource 71 for future commercial production. Since the mineralogy of lithomarge varies, it is important 72 to have an appropriate methodology in place to be able to identify the most appropriate 73 precursor material for the production of geopolymer binder. McIntosh et al. [19] developed a 74 protocol, not geographically limited to Northern Ireland, for refining the selection process of lithomarge suitable for calcination. It was shown that to produce binders with minimum 75

76 compressive strength of 50 MPa, the kaolinite content should exceed 60% by weight of the77 original rock [19].

78

79 After decades of research evidence, it has been well established that the water-to-cement (w/c)80 ratio (or water-to-binder ratio for concrete made with additions, also called supplementary 81 cementitious materials) is the dominant factor influencing most properties of conventional Portland cement-based concrete [24]. For a given set of concrete ingredients, selection of the 82 83 w/c ratio and binder content are required at the mix design stage to produce concretes that meet 84 specific strength and durability requirements. On the other hand, to achieve a desired 85 workability at a given w/c ratio, a suitable content of free water in the mix or, more specifically, 86 a suitable content of paste filling spaces between the aggregate particles, is needed. In the 87 upcoming years, geopolymer binder concretes formulated using low purity kaolinitic clays will likely gain wider construction market access. Therefore, it is of importance to understand their 88 89 behavior and compare it to that of conventional concretes. Recognising these needs, the 90 overall aim of this work was to characterise the behaviour of lithomarge-based geopolymer 91 mortars (GPMs), paving the way for the future development of a mix design of geopolymer 92 concrete. GPM mixes were compared to Portland cement mortars (PCMs) to demonstrate 93 whether the GPMs can be used by the industry in a similar way to a Portland cement system. 94 Therefore, the primary objective of this research was to assess the effect of mix proportion 95 parameters, *i.e.* water-to-solid (w/s) ratio, paste volume and free water content, on workability, 96 setting times and compressive strengths of room temperature cured geopolymer mortars 97 formulated using an aluminosilicate precursor based on calcined lithomarge and a potassium 98 silicate activator. Design of experiments approach (DoE) was used to simultaneously 99 investigate the effect of w/s ratio and paste volume on the properties of GPMs. In addition, the effect of a wide range of w/s ratios was studied on GPM mixes made with either fixed paste 100

101 volume (varied free water content) or with a fixed free water content (varied paste volume).
102 The behaviour of these two groups of GPM mixes was compared with that of Portland cement
103 counterparts made with varied w/c ratios. The secondary objective was to directly compare
104 the performance of selected GPMs with that of Portland cement alternatives in the same
105 strength class (normal and high strength) and formulated with the same paste volume.

106

107

2 RESEARCH SIGNIFICANCE

108 In recent years there has been tremendous research effort into development and characterisation 109 of cement free binders and concretes, to overcome shortcomings and lower the overall 110 environmental impact of Portland cement concrete. However, most of the effort has been 111 dedicated towards usage of slags, ashes or pure metakaolin. This paper provides data regarding 112 the effect of variation in selected mix proportion parameters (w/s ratio, paste volume and free water content) on workability, setting time and compressive strength of geopolymer mortars 113 114 formulated with a lithomarge based precursor, *i.e.* a low purity kaolin. An essential part of this 115 work was devoted to benchmarking the behaviour of mortars made with the new binder against 116 that of conventional Portland cement mortars, to find similarities and differences between these 117 two binder systems. This data should lay strong foundations towards the development of 118 methodologies for the mix design of concrete made with low purity kaolin geopolymer binders, 119 encouraging their popularisation and industrial acceptance. Such data can be of interest to the 120 wider scientific community, designers and producers of concrete, as well as contractors, to 121 better understand key mix proportion parameters affecting fundamental properties of geopolymer concrete formulated using a lithomarge based binder. 122

124 **3 EXPERIMENTAL PROGRAMME**

125 The research methodology is first outlined, followed by a short overview of the design of 126 experiments technique (*i.e.* central composite design) which was adopted in the opening part 127 of this work. Afterwards, the description of materials and mix proportions used is shown. 128 Mortar mixing and sample preparation are then described, followed by the presentation of 129 testing procedures.

130

131 **3.1 Methodology**

132 To satisfy the first objective, seven families of mortars, five GPMs and two PCMs, were tested.

133 Their mix proportion parameters are reported in Table 1.

134

135 Table 1: Investigated mix proportion parameters and tested properties.

| Mix family | Μ | Mix proportion parameter | | | | | | | |
|------------|----------------------------|---|-------------------------------------|---|--|--|--|--|--|
| name | w/s* or w/c** ratio [-] | Free water content [L/m ³] | Paste volume [L/m ³] | Properties tested | | | | | |
| GPM-0 | Varied: 0.279–0.421* | Varied [#] | Varied: 439.5–510.4 | Workability Setting time Compressive strength | | | | | |
| GPM-1 | Varied: 0.275–0.6* | Varied [#] | Kept constant at 500 | Workability Compressive strength | | | | | |
| GPM-2 | Varied: 0.275–0.6* | Kept constant at 235 | Varied [#] | Workability Compressive strength | | | | | |
| GPM-3 | Varied: 0.275-0.6* | Kept constant at 259 | Varied [#] | Workability | | | | | |
| GPM-4 | Varied: 0.275-0.6* | Kept constant at 282 | Varied [#] | Workability | | | | | |
| PCM-1 | Varied: 0.375-0.6** | Varied [#] | Kept constant at 500 | Workability Compressive strength | | | | | |
| PCM-2 | Varied: 0.375–0.75** | Kept constant at 264 | Varied [#] | Workability Compressive strength | | | | | |

136 # - this mix parameter was varied to keep mix proportions yielding 1 m³, but it was not a factor in the investigation.

137

Design of experiments (DoE) [25] approach was used to simultaneously investigate the influence of w/s ratio (factor A) and paste volume (factor B) on workability, setting times and compressive strengths of geopolymer mortars (GPMs) – mixes called GPM-0. The DoE approach has been chosen because it allows identification of the most influential factor(s) or factor interaction(s) affecting the investigated properties. Taking into account that the investigated properties were not expected to change linearly, the GPM-0 group of mortars was proportioned with a wide range of w/s ratios and paste volumes according to 2^2 full central composite design (CCD) plan, to obtain quadratic mathematical response models. A summary of the investigated levels of factors, in terms of actual and coded values (*i.e.* transformed actual values), is given in Table 2, while an overview of the CCD is presented in the subsequent section.

149

150 Table 2: Overview of investigated levels of experimental factors in actual and coded values for GPM-0

151 mortars.

| Factor | Level of factors in actual values | | | | | | | | |
|-------------------------------------|-----------------------------------|-------|-------|-------|-----------|--|--|--|--|
| A: w/s ratio [-] | 0.279 | 0.300 | 0.350 | 0.400 | 0.421 | | | | |
| B: Paste volume [L/m ³] | 439.6 | 450 | 475 | 500 | 510.4 | | | | |
| Level of factors in coded values | -α | -1 | 0 | +1 | $+\alpha$ | | | | |

152

In addition to the DoE work, workability and compressive strengths of GPMs were studied using a wider range of w/s ratios, *i.e.* from 0.275 to 0.6, either by keeping a constant paste volume or a free water content. For this range of w/s ratios, ten mortars were made with a constant paste volume of 500 L/m³ (GPM-1) and another ten were made with a constant water content of 235 L/m³ (GPM-2). To verify workability findings for GPM-2 mixes, two additional mortar families, *i.e.* GPM-3 and GPM-4, having a constant water content of 259 L/m³ and 282 L/m³, were investigated.

Behaviour of GPM-1 and GPM-2 mixes in fresh and hardened states was compared with that of two families of Portland cement-based mortars (PCMs): mixes proportioned with a constant paste volume of 500 L/m³ (PCM-1) and with a constant water content of 264 L/m³ (PCM-2). In the first case the w/c ratio was varied from 0.375 to 0.6 while in the second from 0.375 to 0.75. Significantly, from the preliminary tests it transpired that workable GPMs could be

166 proportioned with lower water contents (resulting in relatively low w/s ratio) than the 167 corresponding PCMs. In order to avoid mixes with a very low workability or dry mixes (slump 168 of 0 mm), which would have to be rejected from the analysis of results as inconclusive, a 169 minimum slump value of 5 mm was set. Therefore, after preliminary testing of both PCM and GPM mixes, the minimum w/c ratio for PCMs was intentionally set at 0.375 compared to a w/s 170 171 ratio of 0.275 for GPMs. For the same reason, the free water content of PCM-2 proportioned with a constant water content was set at 264 L/m³ compared to 235 L/m³ for GPM-2. Water 172 173 demands of the aluminosilicate precursor and Portland cement were also determined.

174

175 It is worth noting that for each family of mixes reported in Table 1, one of the mix proportion 176 parameters was assigned with # symbol. These parameters had to be varied in order to keep 177 the mortar mix proportions yielding 1 m³. As such, they were not the subject of the 178 investigation, but were reported in Table 1 for transparency.

179

To allow a like-for-like comparison, two GPM mixes and two PCM mixes were selected based on results obtained for all seven previously described families of mortars. The mortars had equivalent paste volumes (500 L/m³) and characteristic compressive strengths to satisfy normal (37.5 MPa) and high strength (60 MPa) applications. They were tested for workability, setting time and compressive strength.

185

186 **3.2** Central composite design (CCD)

187 DoE is a systematic and versatile tool for determining relationships among independent 188 variables (factors) affecting a dependent variable (response) [25]. It allows for simultaneous 189 investigation of a number of factors and for building of a mathematical model providing 190 information on the effect of individual factors and factors' interactions on the studied response within previously defined boundaries of the experimental domain. Such statistically designed
experiments based on factorial design are far more time- and labour-efficient than the "onefactor-at-a-time" approach.

194

The experimental plan was generated according to CCD, based on a two-level factorial design (2^k) to fit the second-order response surface model (RSM) to each studied property (Eq. 1) [25]. Because only two factors were investigated (k = 2), *i.e.* w/s ratio (factor A) and paste volume (factor B), a full CCD of 2^2 (2 factors each at 2 levels) was considered. The concept of CCD is presented below and is graphically depicted in Figure 1.

200

201
$$y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i^2 + \sum_{i < j} \beta_{ij} x_i x_j + \epsilon$$
 Eq. 1

202

where *y* is the response, β_0 , β_i , β_{ii} , β_{ij} are regression coefficients, x_i , x_j are variables in coded values that represent levels of *i*-th and *j*-th factors (in given case they represent levels of factors A and B, respectively), $\sum_{i=1}^{k} \beta_i x_i$ is linear effect of *i*-th factor, $\sum_{i=1}^{k} \beta_{ii} x_i^2$ is quadratic effect of *i*th factor, $\sum_{i < j} \beta_{ij} x_i x_j$ is interaction effect of *i*-th and *j*-th factors, and \in is a random error component representing the effects of uncontrolled variables in response *y*.





211

Figure 1: A graphical layout of the 2² CCD in coded values of factors for GPM-0 mixes.

213 The two-level factorial design with two factors (2^2) led to a total of four factorial runs (mixes 214 1 to 4 in Table 3). The low and the high levels of each factor were assigned coded values of -1 and +1 respectively. The centre point (mid-level) was assigned coded value of θ for each 215 216 factor (mixes 9 to 13 in Table 3). These five replicated mixes at the centre were used for evaluating the random error. The 2^2 factorial experimental design would result in a first-order 217 218 (linear) model for the factors and their effects. In CCD, in order to obtain a second-order model 219 (quadratic), additional experimental units are required. These are introduced by considering axial points, coded values of $\pm \alpha$, where $\alpha = (n_F)^{0.25} (n_F - a \text{ number of points used in the factorial})$ 220 221 portion of the design, in this case 4). Therefore, for each factor, two additional experimental 222 units are considered (mixes 5 to 8 in Table 3), with their levels at $\pm \alpha$ from the centre point (in this case it was $\alpha = \pm 1.414$), and levels of all other factors fixed in the θ level. This choice of 223 224 the value of α ensured that the CCD was rotatable, *i.e.* the variance of predicted response is 225 constant at all points that are the same distance from the centre point of the design [25].

227 Table 3 presents the low and high levels (coded -1 and +1), the centre points (coded 0 for each 228 factor), and the axial points (coded $-\alpha$ and $+\alpha$) for each factor, resulting in a total of five levels 229 for each factor. A model described by Eq. 1 may be used to represent the effects obtained for 230 mixes 1 to 8. It is noteworthy that this equation contains a random error term (\in). As 231 mentioned above, in order to estimate this error term five additional points were introduced, all 232 replicating the centre point of all factors (mixes coded 0 for each factor – Table 3). Four 233 randomly selected verification points (mixes 14 to 17 in Table 3) were used for checking the 234 accuracy of developed models.

235

Table 3: Levels of experimental factors, given in actual and coded values, for GPM-0 mortars designed
 according to 2² CCD.

| | | Actua | l values | Code | Coded values | | |
|-------------------|-----------------|-------------------------------|--|-------------------------------|----------------------------------|--|--|
| Type of points | GPM-0 mix nr | Factor A: w/s ratio [-] | Factor B: paste volume [L/m ³] | Factor A: w/s ratio [-] | Factor B: paste volume [-] | | |
| | 1 | 0.3 | 450 | -1 | -1 | | |
| Factorial | 2 | 0.4 | 450 | 1 | -1 | | |
| points | 3 | 0.3 | 500 | -1 | 1 | | |
| | 4 | 0.4 | 500 | 1 | 1 | | |
| | 5 | 0.2793 | 475 | -1.414 | 0 | | |
| Axial | 6 | 0.4207 | 475 | 1.414 | 0 | | |
| points | 7 | 0.35 | 439.6 | 0 | -1.414 | | |
| | 8 | 0.35 | 510.4 | 0 | 1.414 | | |
| | 9 | 0.35 | 475 | 0 | 0 | | |
| C (| 10 | 0.35 | 475 | 0 | 0 | | |
| Centre | 11 | 0.35 | 475 | 0 | 0 | | |
| points | 12 | 0.35 | 475 | 0 | 0 | | |
| | 13 | 0.35 | 475 | 0 | 0 | | |
| | 14 | 0.3136 | 466.1 | -0.728 | -0.356 | | |
| Validation | 15 | 0.3829 | 481.6 | 0.658 | 0.264 | | |
| points | 16 | 0.3693 | 455.8 | 0.386 | -0.768 | | |
| | 17 | 0.3341 | 495.4 | -0.318 | 0.816 | | |

The levels of factors in Table 2 and Table 3 are shown in actual and coded values. Coding is a linear transformation of the original range of the dependent variable. It aids in the interpretation of the regression coefficients' fit to statistical model by introducing a relative

size of a factor level. For a given factor, its level in coded value can be calculated as the difference between the level of factor in actual value and the value corresponding to the central point divided by half of the difference between the low and high levels of this factor. The equations for coding factors investigated in this work are shown in Eq. 2 and Eq. 3.

246

247 w/s ratio in coded value =
$$\frac{\text{w/s ratio in actual value - 0.35}}{0.5 \cdot 0.1}$$
 Eq. 2

248 Paste volume in coded value = $\frac{\text{paste volume in actual value - 475}}{0.5 \cdot 50}$ Eq. 3

249

250 3.3 Materials

The geopolymer binder used was a two component system produced by banah UK Ltd [26], 251 252 *i.e.* an aluminosilicate precursor being the powder component and a chemical activator the 253 liquid component. The aluminosilicate precursor was comprised of a calcined lithomarge and 254 ground granulated blastfurnace slag (GGBS) at a fixed weight ratio of GGBS to calcined 255 lithomarge of 0.142 [26]. The calcined lithomarge was manufactured by calcination of the 256 altered basalt (lithomarge) at 750 °C in a rotary calciner and subsequent grinding in a ball mill 257 [18-20]. The altered basalt was sourced from the IBF of the Antrim Lava Group (Northern 258 Ireland). GGBS was produced by Civil & Marine Slag Cement Ltd. and conformed to BS EN 259 15167-1:2006 [27]. Portland cement CEM I 42.5N produced by Quinn Cement in Northern 260 Ireland and conformed to the requirements of BS EN 197-1:2011 [28], was used. The chemical 261 composition of the aluminosilicate precursor based on calcined lithomarge and Portland cement, 262 determined using X-ray fluorescence spectrometry, are given in Table 4. X-ray powder 263 diffraction patterns of the aluminosilicate precursor and Portland cement are given Figure 2. The main peaks in the XRD pattern of the aluminosilicate precursor are due to hematite, which 264 is present as a result of calcination of goethite and magnetite in the original kaolinitic clay [18]. 265

- 266 The Portland cement was found to be comprised of the following crystalline phases: alite, belite,
- aluminate, brownmillerite and gypsum. Particle size distributions (PSDs) of thealuminosilicate precursor and Portland cement are shown in Figure 3.
- 269 270
- Table 4: Oxide composition and physical properties of the calcined lithomarge based aluminosilicate

| Oxide composition [%] | Aluminosilicate precursor | Portland cement |
|--------------------------------|---------------------------|-----------------|
| SiO ₂ | 32.04 | 20.21 |
| Al ₂ O ₃ | 24.99 | 4.79 |
| Fe ₂ O ₃ | 25.21 | 2.78 |
| CaO | 7.78 | 63.01 |
| MgO | 1.71 | 1.93 |
| MnO | 0.37 | 0.08 |
| TiO_2 | 3.17 | 0.27 |
| Na ₂ O | 0.36 | 0.19 |
| K ₂ O | 0.15 | 0.59 |
| SO_3 | 0.22 | 2.60 |
| P_2O_5 | 0.14 | 0.12 |
| LOI [%] | 3.08 | 3.16 |
| Specific gravity | 2.89 | 3.13 |

271 precursor and Portland cement.

272

An aqueous solution of potassium silicate with a water content of 41.2%, a SiO₂/K₂O molar ratio of 1.65 and specific gravity of 1.57, was used as a proprietary chemical activator for the lithomarge based precursor. Potable water from the mains supply $(17 \pm 1 \text{ °C})$ was used as the mixing water.

277

Sand, rich in quartz and also containing albite, muscovite and clinochlore (as per XRD pattern
shown in Figure 2), was sourced from Creagh's quarry (Creagh Concrete Products Ltd.,
Draperstown, Northern Ireland). The sand had oven-dry particle density of 2695 kg/m³. Its
water absorption at 1-h and 24-h was 0.92% and 1.1%, respectively. Both density and water
absorption were determined according to BS 812-2:1995 [29]. The PSD of the sand was
determined according to BS 812-103.1:1985 [30] and is shown in Figure 3.





Figure 2: XRD patterns of the calcined lithomarge based aluminosilicate precursor, Portland cement and

sand.



287





Figure 3: Particle size distribution of the calcined lithomarge based aluminosilicate precursor, Portland

290

cement and sand.

292 **3.4 Mortar proportions**

The proportions of all GPM mixes are shown in Table 5 and those of PCM mixes in Table 6. Mix proportions of GPM-0 mixes are shown in the same order as in Table 3, while GPM-1, GPM-2, GPM-3, GPM-4, PCM-1 and PCM-2 mixes are organised with increasing w/s or w/c ratio. All GPMs had the same aluminosilicate precursor to chemical activator weight ratio of 1.41. All mortars were designed using the absolute volume method [31].

298

The paste volume was the sum of the volume of all materials in the mix with the exception of sand and 1-h absorption water. The w/s ratio for GPM was calculated according to Eq. 4, by dividing the total mass of free water in the paste portion of the mix by the total mass of solids in the paste. The w/c ratio for PCM was calculated using similar principle (Eq. 5).

303

304
$$w/s = \frac{m_{Fw}}{m_{s,paste}} = \frac{m_{Adw} - m_{Abw} + m_{w,act}}{m_{Prec} + m_{s,act}}$$
 Eq. 4

305
$$w/c = \frac{m_{Fw}}{m_{PC}} = \frac{m_{Adw} - m_{Abw}}{m_{PC}}$$
 Eq. 5

306

307 where m_{Fw} is the mass of free water, [kg], $m_{s,paste}$ is the total mass of solids in the paste, [kg], 308 m_{Adw} is the total mass of added water during mortar mixing, [kg], m_{Abw} is the mass of water 309 absorbed during aggregates pre-saturation, [kg], $m_{w,act}$ is the mass of water in the chemical 310 activator, [kg], m_{Prec} is the mass of aluminosilicate precursor, [kg], $m_{s,act}$ is the mass of solids 311 in the chemical activator (comprised mainly of alkali and silicate species), [kg], m_{PC} is the mass 312 of Portland cement, [kg].

Table 5: Mix proportions of GPM-0, GPM-1, GPM-2, GPM-3, GPM-4 mixes.

| | | Paste | aste Material quantity per cubic metre [kg/m³] | | | | | |
|-----------|-----------|----------|--|-----------|---------|------------|-------------|-------|
| Mix ID | w/s ratio | volume | Aluminosilicate | Chemical | Sand | Absorption | Total added | Free |
| | 0.000 | [L/III'] | precursor | activator | 1.400.0 | water | water | water |
| GPM-0-1 | 0.300 | 450.0 | 483.8 | 343.2 | 1482.3 | 13.6 | 17.6 | 205.7 |
| GPM-0-2 | 0.400 | 450.0 | 419.9 | 297.8 | 1482.3 | 13.6 | 128.6 | 238.0 |
| GPM-0-3 | 0.300 | 500.0 | 537.6 | 381.3 | 1347.5 | 12.4 | 83.6 | 228.5 |
| GPM-0-4 | 0.400 | 500.0 | 466.5 | 330.9 | 1347.5 | 12.4 | 140.2 | 264.4 |
| GPM-0-5 | 0.279 | 475.0 | 527.6 | 374.2 | 1414.9 | 13.0 | 67.8 | 208.6 |
| GPM-0-6 | 0.421 | 475.0 | 431.2 | 305.8 | 1414.9 | 13.0 | 143.5 | 257.2 |
| GPM-0-7 | 0.350 | 439.6 | 439.2 | 311.5 | 1510.3 | 13.9 | 103.1 | 217.8 |
| GPM-0-8 | 0.350 | 510.4 | 509.9 | 361.7 | 1319.5 | 12.1 | 115.8 | 252.9 |
| GPM-0-9 | 0.350 | 475.0 | 474.6 | 336.6 | 1414.9 | 13.0 | 109.4 | 235.4 |
| GPM-0-10 | 0.350 | 475.0 | 474.6 | 336.6 | 1414.9 | 13.0 | 109.4 | 235.4 |
| GPM-0-11 | 0.350 | 475.0 | 474.6 | 336.6 | 1414.9 | 13.0 | 109.4 | 235.4 |
| GPM-0-12 | 0.350 | 475.0 | 474.6 | 336.6 | 1414.9 | 13.0 | 109.4 | 235.4 |
| GPM-0-13 | 0.350 | 475.0 | 474.6 | 336.6 | 1414.9 | 13.0 | 109.4 | 235.4 |
| GPM-0-14 | 0.314 | 466.1 | 491.0 | 348.2 | 1438.9 | 13.2 | 87.9 | 218.2 |
| GPM-0-15 | 0.383 | 481.6 | 459.7 | 326.1 | 1397.1 | 12.9 | 128.0 | 249.4 |
| GPM-0-16 | 0.369 | 455.8 | 443.3 | 314.4 | 1466.6 | 13.5 | 115.9 | 232.0 |
| GPM-0-17 | 0.334 | 495.4 | 506.3 | 359.1 | 1359.9 | 12.5 | 104.3 | 239.7 |
| GPM-1-1 | 0.275 | 500 | 558.9 | 396.4 | 1347.5 | 12.4 | 66.9 | 217.8 |
| GPM-1-2# | 0.300 | 500 | 537.6 | 381.3 | 1347.5 | 12.4 | 83.8 | 228.5 |
| GPM-1-3# | 0.325 | 500 | 517.9 | 367.3 | 1347.5 | 12.4 | 99.6 | 238.5 |
| GPM-1-4# | 0.350 | 500 | 499.5 | 354.3 | 1347.5 | 12.4 | 114.2 | 247.7 |
| GPM-1-5# | 0.375 | 500 | 482.5 | 342.2 | 1347.5 | 12.4 | 127.8 | 256.4 |
| GPM-1-6# | 0.400 | 500 | 466.5 | 330.9 | 1347.5 | 12.4 | 140.5 | 264.4 |
| GPM-1-7 | 0.450 | 500 | 437.6 | 310.4 | 1347.5 | 12.4 | 163.6 | 279.0 |
| GPM-1-8 | 0.500 | 500 | 412.0 | 292.2 | 1347.5 | 12.4 | 183.9 | 291.9 |
| GPM-1-9 | 0.550 | 500 | 389.3 | 276.1 | 1347.5 | 12.4 | 202.0 | 303.4 |
| GPM-1-10 | 0.600 | 500 | 368.9 | 261.7 | 1347.5 | 12.4 | 218.3 | 313.7 |
| GPM-2-1 | 0.275 | 540.3 | 603.9 | 428.3 | 1238.9 | 11.4 | 70.3 | 235.3 |
| GPM-2-2 | 0.300 | 514.9 | 553.6 | 392.6 | 1307.3 | 12.0 | 85.6 | 235.3 |
| GPM-2-3# | 0.325 | 493.4 | 511.0 | 362.4 | 1365.3 | 12.6 | 98.6 | 235.3 |
| GPM-2-4# | 0.350 | 475.0 | 474.6 | 336.6 | 1414.9 | 13.0 | 109.7 | 235.3 |
| GPM-2-5# | 0.375 | 459.0 | 442.8 | 314.1 | 1458.0 | 13.4 | 119.3 | 235.3 |
| GPM-2-6 | 0.400 | 445.0 | 415.2 | 294.5 | 1495.7 | 13.8 | 127.8 | 235.3 |
| GPM-2-7 | 0.450 | 421.7 | 369.1 | 261.8 | 1558.5 | 14.3 | 141.8 | 235.3 |
| GPM-2-8 | 0.500 | 403.1 | 332.2 | 236.6 | 1608.6 | 14.8 | 153.1 | 235.3 |
| GPM-2-9 | 0.550 | 387.9 | 302.0 | 214.2 | 1649.6 | 15.2 | 162.3 | 235.3 |
| GPM-2-10 | 0.600 | 375.1 | 276.7 | 196.3 | 1684.1 | 15.5 | 169.9 | 235.3 |
| GPM-3-1* | 0.275 | 594.1 | 664.1 | 471.0 | 1093.8 | 10.1 | 74.8 | 258.8 |
| GPM-3-2* | 0.325 | 542.6 | 561.9 | 398.6 | 1232.8 | 11.3 | 105.9 | 258.8 |
| GPM-3-3*# | 0.400 | 489.3 | 456.5 | 323.8 | 1376.2 | 12.7 | 138.1 | 258.8 |
| GPM-3-4* | 0.500 | 443.3 | 365.2 | 259.1 | 1500.5 | 13.8 | 165.9 | 258.8 |
| GPM-3-5* | 0.600 | 412.5 | 304.4 | 215.9 | 1583.3 | 14.6 | 184.4 | 258.8 |
| GPM-4-1* | 0.275 | 648.1 | 724.5 | 513.8 | 948.2 | 8.7 | 79.3 | 282.3 |
| GPM-4-2* | 0.325 | 591.9 | 613.1 | 434.8 | 1099.9 | 10.1 | 113.3 | 282.3 |
| GPM-4-3* | 0.400 | 533.9 | 498.1 | 353.3 | 1256.3 | 11.6 | 148.4 | 282.3 |
| GPM-4-4* | 0.500 | 483.5 | 398.4 | 282.6 | 1391.9 | 12.8 | 178.7 | 282.3 |
| GPM-4-5* | 0.600 | 450.0 | 332.1 | 235.5 | 1482.2 | 13.6 | 198.9 | 282.3 |

316 * - only workability was tested for these mixes, # - extra validation points for checking accuracy of models

317 developed using CCD method.

| 31 | 9 |) | Table | 6: | Mix | pro | portions | of P | CM-1 | and | PCM-2 | mixes. |
|----|---|---|-------|----|-----|-----|----------|------|------|-----|-------|--------|
|----|---|---|-------|----|-----|-----|----------|------|------|-----|-------|--------|

| | | Paste | | Material quantity per cubic metre [kg/m³] | | | | | | | |
|----------|-----------|-------------------------------|-----------------|---|---------------------|----------------------|---------------|--|--|--|--|
| Mix ID | w/c ratio | volume [L/m ³] | Portland cement | Sand | Absorption water | Total added water | Free water | | | | |
| PCM-1-1 | 0.375 | 500.0 | 720.0 | 1347.5 | 12.4 | 282.4 | 270.0 | | | | |
| PCM-1-2 | 0.400 | 500.0 | 694.9 | 1347.5 | 12.4 | 290.4 | 278.0 | | | | |
| PCM-1-3 | 0.420 | 500.0 | 676.1 | 1347.5 | 12.4 | 296.4 | 284.0 | | | | |
| PCM-1-4 | 0.450 | 500.0 | 649.8 | 1347.5 | 12.4 | 304.8 | 292.4 | | | | |
| PCM-1-5 | 0.500 | 500.0 | 610.1 | 1347.5 | 12.4 | 317.5 | 305.1 | | | | |
| PCM-1-6 | 0.550 | 500.0 | 575.1 | 1347.5 | 12.4 | 328.7 | 316.3 | | | | |
| PCM-1-7 | 0.600 | 500.0 | 543.8 | 1347.5 | 12.4 | 338.7 | 326.3 | | | | |
| PCM-2-1 | 0.375 | 489.1 | 704.3 | 1376.9 | 12.7 | 276.8 | 264.1 | | | | |
| PCM-2-2 | 0.400 | 475.0 | 660.2 | 1414.9 | 13.0 | 277.1 | 264.1 | | | | |
| PCM-2-3 | 0.450 | 451.6 | 586.9 | 1477.9 | 13.6 | 277.7 | 264.1 | | | | |
| PCM-2-4 | 0.500 | 432.8 | 528.1 | 1528.6 | 14.1 | 278.2 | 264.1 | | | | |
| PCM-2-5 | 0.550 | 417.5 | 480.2 | 1569.8 | 14.4 | 278.5 | 264.1 | | | | |
| PCM-2-6 | 0.600 | 404.7 | 440.1 | 1604.3 | 14.8 | 278.9 | 264.1 | | | | |
| PCM-2-7* | 0.650 | 393.9 | 406.3 | 1633.4 | 15.0 | 279.1 | 264.1 | | | | |
| PCM-2-8* | 0.700 | 384.6 | 377.2 | 1658.5 | 15.3 | 279.4 | 264.1 | | | | |
| PCM-2-9* | 0.750 | 376.6 | 352.1 | 1680.0 | 15.5 | 279.6 | 264.1 | | | | |

320 * – only workability was tested for these mixes.

321

322 **3.5** Mix preparation

All constituent materials, except mixing water $(17 \pm 1 \,^{\circ}\text{C})$, were stored in dry locations at room temperature $(20 \pm 2 \,^{\circ}\text{C})$ prior to batching to ensure that no other parameters influenced the results. Sand was oven-dried $(105 \pm 5 \,^{\circ}\text{C})$ for over 48 hours until a constant mass was reached, subsequently cooled and stored in sealed plastic bags until mixing. All mixes were batched following exactly their pre-determined mix proportions, *i.e.* no additional water (other than what is given in the mix design) was added during mixing. Mixes listed in Table 5 and Table 6 were prepared in a randomised order to minimise the experimental error.

330

All mortar mixes were prepared in a 10 L capacity planar-action high-shear mixer in batchesof 3.7 L. The mixing procedure consisted of the following steps:

Step 1 – Pre-saturation of sand started 15 minutes before the actual mortar
 mixing (Step 2). The dry portion of sand was placed in the mixer's pan with ½ of the
 total added water (free + absorption water) and mixed for approximately 1 minute.

- Step 2 The dry portion of binding material, *i.e.* aluminosilicate precursor or
 Portland cement, was introduced into the mixing bowl followed by 1 minute of mixing.
 Step 3 Addition of the remaining water (free + pre-saturation water) and, in
 the case of GPMs, addition of the chemical activator followed by 2 minutes of mixing
 at a low speed. The beginning of this step is referred to as time zero.
- Step 4 Stopping of the mixer for 1 minute to crush any lumps of remaining
 solids.
- Step 5 Mixing for 2 minutes at a high speed.
- Step 6 Mixing for 1 minute at a low speed.
- 345

346 3.6 Sample casting, demoulding and conditioning

All mortar specimens were cast in two layers. Each layer was compacted on a vibrating table. 347 348 After casting, the moulds with samples were wrapped with cling film to prevent water 349 evaporation and placed in the conditioning room (RH >95% and 20 \pm 1 °C). Samples were 350 demoulded at 24 ± 0.5 hours, counting from time zero, and placed in plastic boxes on 15 mm height spacers. Boxes were filled with water to the height of 5 mm, then covered with tightly 351 352 fitting lids and stored in the conditioning room (20 \pm 1 °C). This procedure allowed the conditioning of the samples at RH of >95%, prevented unintentional carbonation of the samples 353 354 and leaching of alkalis.

355

356 **3.7** Test techniques

Workability – the slump test and the flow table test commenced immediately after the end of mixing (approximately 7 min after time zero). A metal cone-shaped mould described in BS 6463-103:1999 [32] (90 mm in height, wider bottom end with 66 mm internal diameter and narrower top end with 38 mm internal diameter), was placed in the centre of a flow table disk. 361 The mould was filled with mortar in three layers. Each layer was compacted by 10 short strokes 362 of a metal bar (10 mm in diameter). Then the conical mould was gently lifted (approximately 363 30 s after the finishing of mortar placing), and the slump of the mortar was measured (following 364 the same procedure as for the concrete slump test [33]) and reported in mm. Immediately after 365 the slump measurement, the mortar sample was subjected to 15 table jolts. The mortar spread 366 was measured in two perpendicular directions and the average was reported as the mortar flow in mm. The above test procedure was very similar to that used for the determination of 367 368 consistence of mortar mixes (i.e. mortar flow using a flow table), described in BS EN 13395-369 1:2002 [34]. The two dissimilarities were: (i) a conical mould with different dimensions (as 370 reported above) was used in present study, which allowed for measurement slump of fresh 371 mortar sample, and (ii) the jolting of the sample was not applied immediately after the cone-372 shape mould was lifted, but it started after the slump reading was taken (*i.e.* it was delayed by 373 approximately 30 s).

374

375 Water demand – the water demand of the aluminosilicate precursor and Portland cement was determined by testing slurries/pastes with varying water-to-powder (w/p) ratio or w/c ratio, 376 377 similar to the method described in [Error! Reference source not found.]. The conical mould, 378 used for testing workability of mortars (see previous paragraph), was placed in the middle of a 379 Plexiglas table (400 mm in diameter). Slurry was placed (poured) in the mould. Then the conical mould was gently lifted (approximately 10 s after completing the slurry/paste 380 381 placement). Once the flow stopped, the slurry/paste spread was measured in two perpendicular 382 directions and the average was reported as the flow in mm. Average spread results (y-axis) 383 were plotted against the w/c ratios and w/p ratios (x-axis). The minimum w/p or w/c ratio 384 required to initiate the flow (indicating the water demand of the aluminosilicate precursor or Portland cement, respectively) was determined as the intersection of a line fitted to the 385

experimental data with a horizontal line corresponding to the internal diameter of the wider(bottom) end of the conical mould (66 mm in diameter).

388

389 Setting time – initial and final setting times of mortars were determined by the penetration 390 resistance method described in ASTM C403 [36]. Samples for setting time were cast and 391 compacted in the same way as the cubes for compressive strength determination. Samples 392 were left in the conditioning room at 20 \pm 1 °C and between testing were covered to prevent 393 water evaporation. At least eight penetrations were performed on the sample using a range of 394 standarised needles (with surface area of 651, 326, 160, 65, 32 and 16 mm²) to obtain a 395 resistance of the mortar to penetration. In order to obtain the minimum required number of 396 penetration values, the intervals between subsequent penetrations were adjusted as necessary, 397 which depended upon the rate of setting. The bearing surface of the needle was brought into 398 contact with the sample surface. Then, within 10 ± 2 s, a uniform vertical force was applied on 399 the penetrometer to drive the needle into the sample to a depth of 25 ± 2 mm. The force required 400 to penetrate the sample and the elapsed time after time zero were recorded. The recorded force 401 was divided by the surface area of the testing needle to obtain the penetration resistance [MPa] 402 of the mortar at given time. Penetration resistance results were plotted against elapsed time. 403 For each mix, the times of initial and final setting (counting from time zero) were determined 404 as the times when the penetration resistance equalled 3.5 and 27.6 MPa, respectively. Setting 405 time results are reported in minutes, as the elapsed time after time zero.

406

407 **Compressive strength** – the compressive strength of mortar specimens at a given age were 408 determined by crushing three $50 \times 50 \times 50$ mm cubes each time using a similar procedure to that 409 given in BS EN 12390-3:2009 [37] (to reflect sample size, a proportionally lower loading rate 410 of 50 kN/min was used). The applied load [kN] was divided by the test sample surface area 411 [mm²] to calculate the compressive strength [MPa]. An average of the three measurements
412 was reported.

- 413
- 414

4 **RESULTS AND DISCUSSION**

The development of statistical models for workability, setting times and strengths of GPM 415 416 mixes proportioned using CCD methodology (GPM-0) will be outlined first followed by the 417 evaluation of to the repeatability and accuracy of the developed models. Models developed for 418 GPM-0 mixes will then be discussed, followed by the presentation and discussion of results 419 obtained for GPM and PCM mixes formulated with either constant paste volume (GPM-1 and 420 PCM-1) or constant water content (GPM-2, GPM-3, GPM-4 and PCM-2). Finally, a direct 421 comparison of workability, setting times and compressive strengths of selected GPM and PCM 422 mixes, having the same paste volume and strength grade, will be presented.

423

424 4.1 Response surface models development and validation

425 Response surface models (RSMs), *i.e.* statistical models, were developed by multi-regression 426 analyses, based on results presented in Table 7, using a statistical software package Design 427 Expert [38]. Analysis of variance (ANOVA) was carried out to test the significance of 428 regression models and their regression coefficients. *F*-test and *t*-test were performed to identify 429 the nonsignificant (NS) variables, which were subsequently eliminated from derived models 430 (step-by-step process with the most nonsignificant effects first). Probability values below 0.05 431 were considered as significant evidence that the factor's effects or the effect of factors' 432 interactions have a highly significant influence on the modelled response, while values above 433 0.10 suggest no significant effect. All these statistical tools rely on the assumption that data is 434 normally distributed. Therefore, before undertaking ANOVA, responses were checked for normality using the Shapiro-Wilk test [39]. For results that were not normally distributed, the 435

436 Cox-Box method [40] was used to identify an appropriate power-based transformation, which

437 was then applied to the data.

438

| M: ID | w/s | Paste | Slump | Flow | Setting ti | me [min] | Compre | essive streng | th [MPa] |
|----------|--------|---------------------|-------|-------|------------|----------|--------|---------------|----------|
| MIX ID | ratio | [L/m ³] | [mm] | [mm] | Initial | Final | 1-day | 7-day | 28-day |
| GPM-0-1 | 0.300 | 450.0 | 15 | 110.0 | 69 | 89 | 36.1 | 65.3 | 70.5 |
| GPM-0-2 | 0.400 | 450.0 | 67 | 189.5 | 117 | 145 | 19.6 | 41.2 | 49.6 |
| GPM-0-3 | 0.300 | 500.0 | 55 | 139.0 | 72 | 85 | 37.1 | 60.2 | 69.2 |
| GPM-0-4 | 0.400 | 500.0 | 78 | 211.5 | 90 | 112 | 20.7 | 42.8 | 49.7 |
| GPM-0-5 | 0.279 | 475.0 | 6 | 95.5 | 46 | 59 | 40.7 | 60.1 | 68.4 |
| GPM-0-6 | 0.421 | 475.0 | 78 | 206.0 | 100 | 123 | 17.3 | 35.2 | 41.9 |
| GPM-0-7 | 0.350 | 439.6 | 38 | 137.0 | 75 | 91 | 24.8 | 53.3 | 59.4 |
| GPM-0-8 | 0.350 | 510.4 | 73 | 181.5 | 92 | 112 | 26.8 | 52.7 | 53.3 |
| GPM-0-9 | 0.350 | 475.0 | 69 | 173.5 | 89 | 115 | 25.4 | 51.9 | 55.6 |
| GPM-0-10 | 0.350 | 475.0 | 69 | 166.0 | 87 | 104 | 26.9 | 53.0 | 52.4 |
| GPM-0-11 | 0.350 | 475.0 | 64 | 161.0 | 83 | 104 | 26.9 | 48.7 | 60.6 |
| GPM-0-12 | 0.350 | 475.0 | 67 | 175.5 | 80 | 102 | 29.2 | 53.3 | 56.0 |
| GPM-0-13 | 0.350 | 475.0 | 68 | 172.0 | 91 | 116 | 29.9 | 51.5 | 61.8 |
| GPM-0-14 | 0.3136 | 466.1 | 57 | 141.5 | 74 | 92 | 33.9 | 67.0 | 71.9 |
| GPM-0-15 | 0.3829 | 481.6 | 76 | 201.0 | 83 | 107 | 21.7 | 48.2 | 53.6 |
| GPM-0-16 | 0.3693 | 455.8 | 70 | 181.0 | 83 | 107 | 24.3 | 47.6 | 56.2 |
| GPM-0-17 | 0.3341 | 495.4 | 72 | 192.0 | 72 | 90 | 30.7 | 58.9 | 67.2 |

439 Table 7: Results for GPM-0 mixes.

440

441 Derived RSMs for each measured response are given by Eq. 6–12 (where, x_A and x_B represent 442 levels of coded values of factors A and B, respectively). Applied transformation, correlation 443 coefficients, parameter estimates, and probability values (*P* value) of the RSMs are shown in 444 Table 8. Models are valid only within the main investigated experimental domain, *i.e.* in the 445 range between -1 and +1 of coded values of each factor. Most of the models had high 446 correlation coefficients ($\mathbb{R}^2 > 0.85$), thus indicating a good correlation between predicted values 447 (calculated with developed RSMs) and experimental results.

| 448 449 | $(Slump)^{1.5} = 553.5 + 215.6 \cdot x_A + 130.1 \cdot x_B - 52.3 \cdot x_A \cdot x_B - 92.0 \cdot x_A^2 - 53.4 \cdot x_B^2$ | E q. 6 |
|------------|--|---------------|
| 450 | $Flow = 167.3 + 38.5 \cdot x_A + 14.2 \cdot x_B - 7.1 \cdot x_A^2$ | E q. 7 |
| 451 | | |
| 452 | Initial setting time = $84.0 + 17.7 \cdot x_A$ | Eq. 8 |
| 453 | | |
| 454 | Final setting time = $104.3 + 22.0 \cdot x_A$ | Eq. 9 |
| 455 | | |
| 456 | $Ln(1-day \text{ compressive strength}) = 3.296 - 0.300 \cdot x_A$ | Eq. 10 |
| 457 | | |
| 458 | Ln(7-day compressive strength) = $3.960 - 0.195 \cdot x_{A} - 0.051 \cdot x_{A}^{2}$ | Eq. 11 |
| 459 | | |
| 460 | 28-day compressive strength = $57.6 - 9.7 \cdot x_A$ | Eq. 12 |
| 461 | | |

63 Table 8: Parameter estimates of derived models for mixes GPM-0.

| Property Slump | | Flow | | Initial set | Initial setting time Fina | | Final setting time 1-day c | | y compressive 7 strength | | 7-day compressive strength | | 28-day compressive strength | |
|---|-----------------------|--------------------|-----------------------|-------------|---------------------------|---------|----------------------------|---------|-----------------------------|----------------------|-------------------------------|----------|--------------------------------|----------|
| Transformation | (Slun | np) ^{1.5} | No | ne | No | ne | No | ne | Ln(1-0 | day f _c) | $Ln(7-day f_s)$ | | None | |
| \mathbb{R}^2 | 0.9 | 98 | 0.9 | 97 | 0.7 | 74 | 0.7 | 2 | 0.9 | 96 | 0.9 | 95 | 0.8 | 87 |
| Effect | Estimated coefficient | P value | Estimated coefficient | P value | Estimated coefficient | P value | Estimated coefficient | P value | Estimated coefficient | P value | Estimated coefficient | P value | Estimated coefficient | P value |
| Intercept (β_0) | 553.5 | - | 167.3 | - | 84.0 | - | 104.3 | - | 3.296 | - | 3.960 | - | 57.6 | - |
| Main effect of factor A (β_A) | 215.6 | < 0.0001 | 38.5 | < 0.0001 | 17.7 | 0.0002 | 22.0 | 0.0002 | -0.300 | < 0.0001 | -0.195 | < 0.0001 | -9.7 | < 0.0001 |
| Main effect of factor B (β_B) | 130.1 | < 0.0001 | 14.2 | < 0.0001 | NS | NS | NS | NS | NS | NS | NS | NS | NS | NS |
| Interaction $A \times B (\beta_{AB})$ | -52.3 | 0.0260 | NS | NS | NS | NS | NS | NS | NS | NS | NS | NS | NS | NS |
| Quadratic effect of factor A (β_{AA}) | -92.0 | 0.0003 | -7.1 | 0.0154 | NS | NS | NS | NS | NS | NS | -0.051 | 0.0065 | NS | NS |
| Quadratic effect of factor B (β_{BB}) | -53.4 | 0.0068 | NS | NS | NS | NS | NS | NS | NS | NS | NS | NS | NS | NS |

464 NS – nonsignificant effect.

In order to quantify the repeatability of data, results obtained for the five centre points were statistically analysed. Table 9 reports the mean value, \bar{x} , the sample standard deviation, s_d , the coefficient of variation (COV), the estimated error with 95% confidence limit, $E_{E95\%}$, and the relative error, E_R . For all responses COV was below 10%, indicating good repeatability.

| 47 | 0 | Table 9: Repeatabilit | y of test resu | ults for the | five centre | points of (| GPM-0 mixes |
|----|---|-----------------------|----------------|--------------|-------------|--------------------|--------------------|
| | | | •/ | | | | |

| Statistical parametersSlum(see description below)[mm | Slump | Flow [mm] | Setting time [min] | | Compressive strength [MPa] | | |
|--|-------|--------------|--------------------|-------|----------------------------|-------|--------|
| | [mm] | | Initial | Final | 1-day | 7-day | 28-day |
| $\overline{x} = \frac{\sum_{i=1}^{n} x_i}{n} , [*]$ | 67.4 | 169.6 | 86.1 | 108.1 | 27.6 | 51.7 | 57.3 |
| $s_{d} = \sqrt{\frac{\sum_{i=1}^{n} (x_{i} - \overline{x})^{2}}{n-1}}$, [*] | 2.1 | 6.0 | 4.5 | 6.7 | 1.8 | 1.8 | 3.9 |
| $COV = 100\% \cdot \frac{s_d}{\bar{x}} \ , [\%]$ | 3.1 | 3.5 | 5.3 | 6.2 | 6.7 | 3.5 | 6.8 |
| $E_{E95\%} = \frac{t_{\alpha/2,\nu-1} \cdot s_d}{\sqrt{n}}$, [*] | 2.6 | 7.4 | 5.6 | 8.3 | 2.3 | 2.3 | 4.8 |
| $E_{R} = 100\% \frac{E_{E95\%}}{\bar{x}}$, [%] | 3.8 | 4.4 | 6.5 | 7.7 | 8.3 | 4.4 | 8.4 |

Where \bar{x} is the arithmetic mean value of five centre observations x_9 , x_{10} , ... x_{13} , n is the size of the sample (n = 5), s_d is the sample standard deviation, $E_{E95\%}$ is the estimated error with 95% confidence limit, $t_{\alpha/2, \nu-1}$ is the percentage point of the *t* distribution, α is the confidence level $(\alpha = 0.05)$, ν are the degrees of freedom $(\nu = 5)$, E_R is the relative error.

471 * – value in given unit.

472

Accuracy of developed models was checked by comparing predicted-to-measured values obtained with four randomly selected verification mortar mixes (GPM-0-14 – GPM-0-17). In addition, nine mixes (five from GPM-1 family: GPM-1-2 – GPM-1-6, three from GPM-2 family, GPM-2-3 – GPM-2-5, and one mix from GPM-3 family: GPM-3-3) made with w/s ratios and paste volumes which fitted the main experimental domain of the CCD plan were used as extra validation points. The predicted-to-measured values for five centre points, four validation points and nine extra validation points are shown in Figure 4. All figures show the 480 identity line (1:1 line for predicted values) and the estimated error at a 95% confidence limits 481 calculated for the five centre points (using values given in Table 9). It was assumed that the 482 error was random and normally distributed, so the residual terms representing the difference 483 between the predicted and actual values should exhibit similar properties [25]. Data points 484 below the identity line indicate that the derived statistical model overestimates the measured 485 values, while those above the line indicate an underestimation of the measured values. The average ratios between predicted and measured value, calculated for four validation points, for 486 487 slump, flow, initial setting time, final setting time, 1-day strength, 7-day strength and 28-day 488 strength were 0.90, 0.92, 1.07, 1.05, 0.99, 0.94 and 0.93, respectively. The average ratios 489 calculated for all thirteen validation points for slump and flow, and twelve validation points for 490 1-, 7- and 28-day strengths, were 0.97, 0.95, 0.89, 0.97, and 1.01, respectively. Both sets of 491 ratios indicate good accuracy of the derived statistical models.

492

It is important to emphasise that the developed RSM models are valid for a given set of materials. Substantial changes in the materials used (*e.g.* discrepancies in chemical composition and/or physical properties) will require validation of these models. Preliminary validation can be performed by examining the accuracy of the proposed models, *i.e.* comparing the difference between predicted values (obtained using the developed models) and the measured values obtained for the validated variable, *e.g.* new source of lithomarge.

499





Figure 4: Predicted vs. measured values of investigated properties of GPM-0 mixes.

502 4.2 Influence of mix proportion parameters on the behaviour of geopolymer and
503 Portland cement mortars.

504

505 4.2.1 Workability

506 Information on the workability of GPM-0 mixes, designed according to CCD methodology, 507 can be gained from the developed RSMs given by Eq. 6 and Eq. 7. Contour plots of the slump 508 and flow models, in the coordinates of the two investigated factors, viz. w/s ratio and paste 509 volume, are shown in Figure 5a and Figure 5b, respectively. RSMs indicate that workability depended on both w/s ratio and paste volume. As expected, an increase in either of these factors 510 511 caused an increase in slump and flow values. When the main effects of both factors are 512 concerned, an increase in w/s ratio had ca. 1.7 times and 2.7 times higher impact on the value 513 of slump and flow, respectively, than an increase in the paste volume. Higher order effects (i.e. β_{AB} , β_{AA} and β_{BB} – see Table 8, Eq. 6 and Eq. 7), if significant, caused a decrease in the slump 514 515 and flow of GPM-0 mixes.



518 Figure 5: Contour plots developed for a) slump and b) flow of GPM-0 mixes.

519

520 The slump and flow results of all five families of geopolymer mortars (GPM-0, GPM-1, GPM-

521 2, GPM-3 and GPM-4) and two of the cement-based mortars (PCM-1 and PCM-2) are shown

- 522 in Figure 6 and Figure 7, respectively.
- 523



Figure 6: Influence of w/s ratio and w/c ratio on the slump of GPM and PCM mixes respectively, made
with a) a constant and varied paste volume, and b) a constant free water content.



Figure 7: Influence of w/s ratio and w/c ratio on the flow of GPM and PCM mixes respectively, made with
a) a constant and varied paste volume, and b) a constant free water content.

530

As expected, an increase in the w/c ratio for PCM-1 mixes, *i.e.* mortars made with constant paste volume of 500 L/m³, resulted in a large increase in slump (Figure 6a) and flow (Figure 7a) values. Since the paste volume was fixed, an increase in the w/c ratio resulted in the increase in the free water content of these mortars (Table 6) and a simultaneous decrease in the content of cement causing coarsening of the overall PSD of the mixes (Figure 8c). In the case of the PCM-2 mortars, proportioned with a constant water content of 264 L/m³, an increase in the w/c ratio resulted in a slight increase in slump (Figure 6b) and flow (Figure 7b) values. As

shown in Table 6, for PCM-2 mixes an increase in the w/c ratio resulted in a decrease of the cement content and simultaneous increase in the sand content. For that reason, with an increase in w/c ratio, the surface area of solids (cement and sand) to be lubricated with water was reduced (see coarsening of the overall PSD of the mixes in Figure 8d), hence the mortar showed a slight improvement in workability. Both trends were as expected, and in good agreement with the literature [24], [41], [42].

547

For GPM-1 mixes, proportioned with a constant paste volume of 500 L/m³, an increase in w/s 548 549 ratio up to a value of ca. 0.375 resulted in a sharp increase in slump (Figure 6a). Further 550 increases in w/s ratio resulted in minor changes in slump (for w/s ratios between 0.375 and 0.6 551 the slump varied in the range of 78-87 mm). Results obtained for flow of GPM-1 mixes show 552 similar trend to that of slump, however, the transition between sharp increase in flow and 553 plateau appears to be around w/s ratio of 0.5 (Figure 7a). The plateaus observed for the slump 554 and flow results indicate that the upper range limits of these tests were approached. 555 Nevertheless, the explanation given in previous paragraph for trends observed for PCM-1 mixes is also valid for the increase in both slump and flow values of GPM-1 mixes. Specifically, 556 557 for GPM-1 mixes an increase in the w/s ratio led to an increase in free water content and a 558 decrease in binder content (expressed as $m_{s,paste}$ in Eq. 4), causing the overall PSD of the mixes 559 to coarsen (see Table 5 for mix proportions and Figure 8a for the overall PSDs of GPM-1 560 mixes).



Figure 8: Overall particle size distributions of a) GPM-1 mixes, b) GPM-2 mixes, c) PCM-1 mixes and d) PCM-2 mixes.

In the case of GPM-2 mixes, made with a constant free water content, the slump and flow initially increased with an increase in the w/s ratio, reaching a maximum value at a w/s ratio of ca. 0.4-0.45 (see Figure 6b and Figure 7b, respectively). Further increases in the w/s ratio led to a decrease in the value of both properties. These trends were most likely the result of:

567

•

- 568
- The quantity of paste available for lubrication of sand.
- The content of free water available for the geopolymerisation process.
- 569

570 Where the first cause is concerned, a general concept of filling the space between aggregate particles with paste is applicable [43]. As shown in Table 5, as a result of the constant water 571 572 content of GPM-2 mixes, an increase in w/s ratio resulted in a decrease in paste volume from approximately 540 to 375 L/m³ (*i.e.* a decrease in aluminosilicate precursor content and 573 574 simultaneous increase in sand content caused coarsening of the overall PSD of the mixes – see 575 Figure 8b). Therefore, with the increase in the w/s ratio there was gradual increase in volume 576 of sand, hence an increase in surface area of sand to be lubricated with paste. Using the void content measurement method described in BS 812-2:1995 [29], it was found that for the sand 577 578 used, the voids in a loose oven-dried state equated to ca. 38% (380 L/m³). GPM-2 mixes with 579 w/s ratios of 0.5, 0.55 and 0.6 had a paste volume of 403, 388 and 375 L/m³, which is relatively 580 close to what would be required to fill the voids between sand particles in the loose oven-dried 581 state. Portland cement based-mixes (PCM-2) proportioned with w/c ratio of 0.6-0.75 had a comparable paste volume (in the range of $405-377 \text{ L/m}^3$) to the three GPM-2 mixes, but this 582 583 relatively low paste volume did not translate to any negative influence on slump (Figure 6b) or 584 flow (Figure 7b). It is also important to note that workability trends similar to that observed 585 for the GPM-2 mixes were also seen for GPM-3 and GPM-4 families of mixes (Figure 6b and 586 Figure 7b). As for GPM-2 mixes, these two families of GPMs were tested in order to evaluate the effect of w/s ratio on workability at a constant free water content, but they were 587

588 proportioned with reduced sand contents. GPM-3 and GPM-4 families of mixes were made 589 with the same w/s ratio range as GPM-2 mixes (0.275 and 0.6), but the free water contents were intentionally set at higher dosages (fixed at 259 and 282 L/m³, respectively). Obviously, 590 591 the increase in free water contents led to lowered sand contents, and in turn resulted in higher paste volumes for GPM-3 and GPM-4 than those calculated for GPM-2 mixes (see Table 5). 592 593 As a consequence, GPM-3 and GPM-4 mixes showed higher workability values than their 594 GPM-2 counterparts. Based on the above evidence, the trends observed for GPM-2, GPM-3 595 and GPM-4 cannot be solely explained with the concept of filling the space between the 596 aggregate particles with paste.

597

598 The second proposed cause can be explained using the conceptual geopolymerisation process 599 proposed by Duxon el al. [44] and the work of Zuhua et al. [45]. During the addition of 600 activator to the powder portion of the binder, silicates present in the activator, as well as 601 alumina and silica from the powder portion of the binder (rapidly dissolved due to the high pH 602 of the activator), form a supersaturated aqueous mixture of silicate, aluminate and 603 aluminosilicate species. In the first phase of geopolymerisation, a part of the added free water 604 is used to facilitate the dissolution and hydrolysis process of these aluminosilicate compounds 605 [45]. In the second phase, hydrolysis and polycondensation of different aluminate- and silicate-606 hydroxyl species in the supersaturated aqueous mixture leads to the formation of a gel (*i.e.* 607 setting and microstructure formation), and water consumed during dissolution is released [44, 608 45]. These two phases can co-exist [45]. In this work, the slump and flow were measured between 7th and 10th minute after time zero, hence are mostly concerned with the first stage of 609 610 the geopolymerisation process (dissolution and hydrolysis). Therefore, it was assumed that 611 water release due to polycondensation had not yet taken place at the time of the workability 612 measurement.

614 Zuhua et al. [45] postulated that both water content and alkali concentration (alkalinity) in the 615 activator play an important role during the polymerisation process (geopolymer mixes 616 composed of calcined kaolin and sodium-based activator Na₂O·1.2SiO₂ of 35 wt.% were tested). Specifically, when alkalinity is high, the high water content increases the initial 617 618 reaction rate (associated with water consumption for dissolution and hydrolysis of 619 aluminosilicates). When studying metakaolin systems with different water contents, Yao et al. 620 [46] observed that excess content of water diluted the activator (lowered concentration of OH⁻). 621 hindering the ability of the activator to dissolve the precursor. Further evidence was provided 622 by Rahier et al. [47], confirming that at low and high water contents the geopolymer reaction 623 rate was decreased, with a maximum recorded for an optimum water content.

624

In our experiments, it was observed that when the activator was added to the mixing bowl (step 625 3 of the mixing procedure – see section on mix preparation) and until the 2^{nd} minute of mixing, 626 the GPM mixes seemed very stiff. This was caused by the very high water demand (more than 627 twice the value determined for Portland cement - see Figure 9) of the finely ground 628 629 aluminosilicate precursor, which at this early stage of mixing came into contact with the lubricating liquid. However, with further mixing (sometimes between 3rd and 5th minute 630 631 counting from time zero), the mixes became much more workable. By partially dissolving the 632 solid part of the precursor, the amount of liquid to solid was increased, hence the mixes became 633 more workable.

634







Figure 9: Water demand of the aluminosilicate precursor and Portland cement.

638 In our work the water content of GPM-2 mixes was kept constant, but their alkalinity (related 639 to the content of the chemical activator), increased with the increase in paste volume – see mix 640 proportions shown in Table 5. Therefore, based on above assumptions it can be postulated that 641 at low w/s ratios (*i.e.* between 0.275 and 0.375), there was high alkalinity from the activator in 642 the system, but insufficient amount of water slowed the dissolution process. At high w/s ratios 643 (i.e. > 0.45), there was too much water, and the alkalinity of the system was compromised, 644 which slowed the dissolution. The optimum ratio of water-to-alkalinity, for which the 645 dissolution rate of aluminosilicates was high, seems to be between w/s ratio of 0.375 and 0.45. 646 As the aluminosilicate precursor had a very high water demand, the lower dissolution degree 647 (at low and high water contents) would cause an increase in an overall surface area of solids 648 which has to be lubricated. This in turn would negatively impact the workability of fresh 649 geopolymer mortars. Further effort is required to understand the role of water and its content 650 on the initial kinetics of the geopolymer reaction and the resulting implications for the 651 workability/rheology of fresh geopolymer mix.

653 All of the GPM mixes presented in this paper were made with an activator of constant 654 composition (i.e. water content and SiO₂/K₂O molar ratio) and a constant mass ratio of 655 activator to aluminosilicate precursor (*i.e.* alkali dosage). It is assumed that changing these 656 composition parameters could result in the shift of the optimal range of the w/s ratios necessary 657 to obtain maximum workability. Since the activator is the most expensive component of the 658 geopolymer binder, the above findings have significant practical implications on the mix design 659 of this type of concrete. In order to provide an economic geopolymer mix proportion and 660 obtain maximum workability, mix composition optimisation, targeting a minimum content of 661 activator, is necessary.

662

663 The general trends for the slump and flow of both GPM-0 and GPM-1 mixes were very similar 664 even though the workability of the GPM-0 mixes was slightly lower than that of the GPM-1 mixes (Figure 6 and Figure 7). GPM-0 mixes were made with varied paste volumes (439.5-665 510.4 L/m³) while GPM-1 were with a fixed paste volume of 500 L/m³, and thus the lower 666 667 slump and flow values of GPM-0. For a given w/s ratio GPM-1 mixes showed significantly higher workability than their PCM-1 counterparts made with the same w/c ratio (all made with 668 500 L/m³ of paste). Similarly, for GPM-2 mixes both the slump and flow had higher values 669 670 than for the corresponding PCM-2 mixes proportioned with a constant water content. It is 671 worth emphasising that GPM-1 and GPM-2 mixes had lower design free water contents than 672 the corresponding PCMs (see Table 5 and Table 6). Therefore, it was possible to make highly 673 workable GPM mixes with w/s ratios below 0.35, which is rather unachievable for Portland 674 cement systems without the use of plasticisers or superplasticisers.

675

676

678 **4.2.2** Setting time

Determination of the initial and final setting times is very important, because they give practitioners an indication of the time available for handling the fresh concrete (transport, placing, compaction and finishing). The effect of the w/s ratio and the paste volume variation on initial and final setting times of GPM-0 mixes, modelled using the CCD, is shown in Figure 10a and Figure 10b, respectively. Models for these two properties are shown in Table 8 and are given by Eq. 8 and Eq. 9.

685



686

687 Figure 10: Contour plots developed for a) initial setting time and b) final setting time of GPM-0 mixes.

The setting times were relatively short; ranging from 46 to 117 minutes for initial set and from 59 to 145 minutes for final setting. It was found that an increase in the w/s ratio caused an increase in both properties. Neither paste volume, nor any of the higher degree effects, had a significant influence on the setting times.

693

694 As mentioned earlier, for all GPM mixes the geopolymer binder was made with an activator of constant composition and a constant mass ratio of activator to aluminosilicate precursor. 695 696 Therefore, for mixes with the same paste volume, an increase in w/s ratio resulted in an increase 697 in the free water content and a decrease in both the activator content and precursor content. 698 Consequently, an increase was observed in the initial and finial setting times with an increase 699 in w/s ratios resulting in a lower rate of geopolymerisation reaction (i.e. mainly 700 polycondensation reaction responsible for microstructure forming [48]), caused by dilution of 701 the chemical activator [45].

702

703 The relatively short setting times of GPM mixes were a consequence of blending the calcined 704 lithomarge with small addition of GGBS in the aluminosilicate precursor [26]. It was reported 705 that the addition of GGBS provides a source of calcium which facilitates reduction in setting 706 time [48, 49]. Removal of GGBS from the blend with calcined lithomarge would still result in 707 the geopolymer mixes setting, but the setting process would take several hours [26, 49]. Therefore, changing the content of GGBS in the aluminosilicate precursor based on the 708 709 calcined lithomarge gives the advantage of controlling the setting time, hence allowing the 710 setting characteristics to be tailored for the specific application.

The time interval between initial and final setting times decreased with a decrease in the w/s ratio (see Table 7). This may have adverse practical implications, as it gives relatively short time for finishing the surface of cast concrete.

715

716 **4.2.3** Compressive strength

The effect of the w/s ratio and the paste volume on compressive strengths (at 1-, 7- and 28day) of GPM-0 mixes, established using the CCD, is shown in Figure 11. Models for these strengths are also reported in Table 8 and are given by equations 10, 11 and 12.

720

721 It was found that the w/s ratio had the largest influence on the compressive strength at each 722 investigated age; an increase in the w/s ratio led to a decrease in compressive strength. Effects 723 of the paste volume and all high order effects, except for the β_{AA} effect for 7-day strength, were found to be insignificant. Similar results on the effect of w/s ratios were reported in literature 724 725 [50, 51]; however, the strength of the kaolin based geopolymer concrete was mainly controlled 726 by the intrinsic strength of the geopolymer binder (related to its chemical composition); the 727 effect of paste volume was insignificant [50]. The negative effect of increasing w/s ratio on 728 the compressive strength can be attributed to the increase in space occupied by water within 729 the geopolymer matrix, resulting in increased porosity, which in turn leads to a decrease in 730 compressive strength [51].





Figure 11: Contour plots developed for a) 1-day compressive strength, b) 7-day compressive strength, and
c) 28-day compressive strength of GPM-0 mixes.

The 1-, 7- and 28-day compressive strengths of PCM and GPM mixes are shown in Figure 12.
At each testing age, the strength of mortars made with both types of binder decreased with the
increase in w/s ratio or w/c ratio, respectively.

737

Linear trends between w/c ratio and compressive strength were established for PCM, 738 739 irrespective of testing age. The relationship between the w/s ratio and compressive strength 740 were found to be approximately linear for GPM-0 mixes, while they were nonlinear for 741 geopolymer mix families GPM-1 and GPM-2. The deviation from linearity in GPM-1 and 742 GPM-2 mixes was observed at w/s ratios of above 0.4. The linear relationship established for 743 GPM-0 was most probably the consequence of varying both w/s ratio and paste volume 744 according to the CCD experimental plan. Nevertheless, the nature of the nonlinear behaviour 745 of GPM mixes is unclear and requires further investigation.

746

Considering each investigated age (Figure 12), for given w/c ratios, the strengths of Portland cement mixes proportioned with a fixed paste volume (PCM-1) and with a fixed water content (PCM-2) were comparable. Therefore, it can be concluded that the paste volume had no effect on 1-day strength and only a minor influence at later ages. Similar assumptions can be made for geopolymer mixes, as the paste volume had only a minor effect on the compressive strength of GPM-1 and GPM-2 mixes made with the same w/s ratio.





respectively at a) 1-day, b) 7-day and c) 28-day.

760 It is worth noting that, irrespective of the w/s ratios used, GPMs had very high 1-day strengths 761 when compared to the room temperature cured metakaolin mixes reported in literature [49]. 762 Relatively high strengths resulted from blending the calcined lithomarge with a small quantity 763 of GGBS to form the aluminosilicate precursor [26, 49].

764

At equivalent w/s and w/c ratios (between 0.375 and 0.6), GPMs had slightly lower or comparable 1-day compressive strengths to PCMs. At 7-days and 28-days the strength of GPMs was much lower than matching PCM mixes. GPMs gained strength up to the age of 7 days, and afterwards there was no significant increase in strength (strength at 7-day and 28-day were very similar). This indicates that the geopolymer reaction was nearly completed at this age. In contrast, due to cement hydration, PCMs gained strength up to the age of 28 days.

771

772 4.3 Direct comparison of properties for selected geopolymer and cement based 773 mortars

774 To directly compare the performance of geopolymer and Portland cement mortar mixes, two formulations with the same paste volume of 500 L/m^3 were investigated for each of these two 775 776 binder types (see Table 10). Considering normal and high strength applications, two 777 characteristic strength grades were chosen: 37.5 MPa and 60 MPa. To calculate the desired 778 target mean strength, a margin was added to the characteristic strength (see equations 13 and 779 14) [52]. Based on the BRE mix design guidelines [52], the following parameters for equations 780 13 and 14 were chosen: s = 8 MPa and k = 1.64 (for 5% defective samples), which give the 781 margin value of 13.1 MPa.

782

783
$$f_m = f_c + M$$
 Eq. 13

785
$$M = k \cdot s$$

Eq. 14

786

where f_m is the target mean strength, [MPa], f_c is the specific characteristic strength, [MPa], Mis the margin, [MPa], s is the standard deviation, [MPa], k is a constant representing a percentage of defectives, [-].

790

Preliminary w/s or w/c ratios were estimated based on the 28-day strength results presented in Figure 12c. The final w/s and w/c ratios were evaluated after trial mixes and along with mix proportion parameters are shown in Table 10 (reference to mix compositions already presented in Table 5 and Table 6 are also reported). Mixes were tested for workability, setting time and compressive strength. It is worth noting that, behaviour assessment and direct comparison of the resistance of these four mortar mixes to chemical attacks by sulfate and mineral acid solutions has been reported elsewhere [21].

798

The results for four selected mixes were reported and are summarised in Table 10:

Workability, determined with slump and flow, was higher for mixes having high w/s or
 w/c ratios. Even though geopolymer mixes had very low free water contents (at least 65
 L/m³ less water than comparable PCMs) resulting in very low w/s ratios, their slump was
 comparable to that of PCM mixes.

Initial and final setting times increased with the increase in w/s ratio or w/c ratio.
 However, geopolymer mixes showed much shorter initial and final setting times compared
 to those obtained for cement-based mixes. Also, time intervals between initial and final
 setting times were much shorter for geopolymer mixes, giving only a limited time to finish
 the surface.

Geopolymer mixes showed very rapid strength gain, achieving 55–66% of their 28-day
strength in the first 24 hours after mixing whilst equivalent PCMs gained only 18–28%.
Therefore, at the age of 1 day, GPM-37.5 had a strength 3 times higher than PCM-37.5,
while GPM-60 strength was more than double that of PCM-60. The average 28-day
compressive strengths were within a maximum of 4.3 MPa (6%) of the target strength
values, *i.e.* 50.6 and 73.1 MPa.

815

816 From the findings in both phases it transpires that lithomarge-based geopolymer binder can be 817 used to proportion workable, fast setting GPM mixes cured at room temperature. A range of 818 w/s ratios can be used to achieve a wide range of compressive strengths. Importantly, high 1-819 day compressive strength can be achieved using low w/s ratios.

820

821 Table 10: Properties of selected GPM and PCM mixes

| Mortar binder type | Geopolyr | ner-based | PC-based | | |
|--|-----------------------|---------------------|-----------------------|---------------------|--|
| Characteristic strength class | 37.5 MPa | 60 MPa | 37.5 MPa | 60 MPa | |
| Mix reference (ID of mix composition in Table 5 and Table 6) | GPM-37.5 (GPM-1-5) | GPM-60 (GPM-1-1) | PCM-37.5 (PCM-1-7) | PCM-60 (PCM-1-3) | |
| w/s ratio | 0.375 | 0.275 | - | - | |
| w/c ratio | - | - | 0.600 | 0.420 | |
| Paste volume [L/m ³] | 500 | 500 | 500 | 500 | |
| Free water content [kg/m ³] | 256 | 218 | 326 | 284 | |
| Slump [mm] | 82 | 12 | 65 | 17 | |
| Flow [mm] | 212 | 106 | 223 | 162 | |
| Initial setting time [min] | 78 | 49 | 323 | 213 | |
| Final setting time [min] | 98 | 63 | 440 | 307 | |
| 1-day compressive strength [MPa] | 27.9 | 51.2 | 9.3 | 22.0 | |
| 7-day compressive strength [MPa] | 42.5 | 69.7 | 30.3 | 57.9 | |
| 28-day compressive strength [MPa] | 49.9 | 77.0 | 50.6 | 77.4 | |

822

823 5 CONCLUSIONS

824 On the basis of the presented results, the following conclusions have been drawn:

• Statistically designed experiments (mixes GPM-0) revealed that the workability of the

826 GPM formulated using the aluminosilicate precursor based on calcined lithomarge and verified

using slump and flow tests, was governed by both w/s ratio and paste volume, but the w/s ratio
had a dominant effect on this property. GPM mortars had very short initial and final setting
times. Both setting times were influenced by w/s ratio only. It was found that at each
investigated age, *i.e.* 1, 7 and 28 days, the w/s ratio had the only influence on decreasing the
compressive strength.

The slump and flow of GPM and PCM mortar mixes made with a constant paste volume
 (GPM-1 and PCM-1, respectively) increased with an increase in w/s or w/c ratio.

• GPM mixes proportioned using a constant water content (GPM-2, GPM-3 and GPM-4) showed a non-linear relationship between w/s ratio and workability. It was established that this behaviour could be associated with changes to paste/sand proportions and/or water to alkali proportions. In contrast, the workability of conventional Portland cement mixes made with a constant free water content (PCM-2) increased linearly with an increase in w/c ratio.

• Direct comparison of GPM and PCM mixes, proportioned with the same paste volume and two compressive strength classes (normal of 37.5 MPa and high of 60 MPa), showed that workable geopolymer mixes could be proportioned with at least 65 L /m³ less free water than comparable Portland cement mixes. Geopolymer mixes had much shorter initial and final setting times than those obtained for cement-based mixes. GPMs showed very rapid compressive strength development, achieving 55–66% of their 28-day strengths within the first 24 hours after mixing. Corresponding PCMs gained only 18–28% within this time.

846

The results presented are very promising for designers and producers of concrete. Despite differences in established relationships, the investigated geopolymer mix proportion parameters influenced the tested properties of GPMs in a similar way as the mix proportion parameters of Portland cement systems affected the properties of PCMs. Therefore, this lithomarge-based geopolymer binder can be used to make mortars, and potentially concretes, in the same way and using the same techniques as those used for cement-based mixes. Work
is continuing aiming at the development of a concrete mix design methodology for this
geopolymer binder.

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