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1 **Long Term Durability Properties of Concrete Modified with Metakaolin and**
2 **Polymer Admixture**

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7
8 **ABSTRACT**

9 Previous studies show that both metakaolin (MK) and polymer can respectively improve certain
10 mechanical and durability properties of concrete. Also, recent studies show that a combination of
11 MK and polymer further enhances the mechanical properties by complement of each other.
12 However, the knowledge of the effect on durability, a critical governing factor of concrete for the
13 applications in extreme environments such as sewage, off-shore and bridge structures, has not
14 been well established yet. This paper reports on a comprehensive study of the effect of
15 metakaolin as a supplementary cementitious material together with polymer as admixture on the
16 durability of concrete at relatively old ages. The results confirm that replacing Portland cement
17 with 15% metakaolin and an additional 5% polymer (by weight) provide the optimum
18 improvement for Portland cement concrete on both mechanical properties and durability.

19
20 **Keywords:** Metakaolin; Polymer; High Performance Concrete; Durability

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22
23 **1. INTRODUCTION**

24 Using mineral supplementary cementitious materials (SCM), such as fly ash (FA), silica fume
25 (SF) and thermally activated kaolin (also known as metakaolin (MK)), as additives has already
26 been proved effective to improve properties of concrete (Kamseu et al., 2014). MK requires less
27 energy to produce compared to cement (Rashad, 2013; Souri et al., 2015), which, in recent years,
28 has attracted more and more interest in the use for the SCM (Aiswarya et al., 2013; Srinivasu et
29 al., 2014) because of the environmental concern and the decreasing supply capacity of fly ash
30 and silica fume(Souri et al., 2015). The MK product has predominant alumina (Al_2O_3) and silica
31 (SiO_2) composition, which have an active pozzolanic nature (Ambroise et al., 1994). The
32 pozzolanic reaction of MK with portlandite ($\text{Ca}(\text{OH})_2$) will result in significant compositional
33 changes of calcium silicate hydrate (CSH) gel to give high Al uptake and low Ca content in a
34 new gel formation known as CASH, which has a low $\text{Ca}/(\text{Al} + \text{Si})$ ratio but a high Al/Ca ratio
35 (Souri et al., 2015).

36

37 Previous research showed that a 20% replacement of cement using MK resulted in a substantial
38 50% increase of the compressive strength of mortar (Khatib et al., 2012), and the concrete using
39 MK additive displayed a lower water sorptivity compared to that using silica fume (Guneyisi et
40 al., 2012). Recently, Pouhet and Cyr (2016) studied the pore solution carbonation of MK-based
41 geopolymer and found that the pH decreased rapidly in the first few days when the normal
42 concrete was exposed to natural CO_2 conditions. Moreover, a high CO_2 content or a relatively
43 high environmental temperature led to durability issues when the pH was lower than 10.
44 However, the pozzolanic nature of MK increased the pH and kept it above 12 even after one
45 year, indicating a minimum carbonation inside the concrete. Another study (Kannan and
46 Ganesan, 2014) showed that self-compacting concrete (SCC) with a high MK content (up to
47 30%) exhibited a significant resistance to chloride ion penetration. For acid attack resistance, the

48 same SCC with 5 and 10% of MK showed the lowest weight loss after 12 weeks immersed in 5%
49 HCl and 5% H₂SO₄ solutions, respectively. Contrary to these advantages, it was also found,
50 however, that the MK significantly reduces the workability of concrete and thus more water is
51 required to improve the workability (Ambroise et al., 1994). However, the additional water to
52 improve the workability would lead to durability issues, causing aggregate segregation, excess
53 voids and increased porosity of the concrete.

54

55 Polymers, such as styrene-butadiene rubber (SBR) latex and polyvinyl acetate (PVA) emulsion
56 have been commonly used as admixtures in concrete practice (Atkins et al., 1991; Konar et al.,
57 2011). Polymer admixtures are known to not only increase the workability but also modify the
58 physical properties of cement pastes by reducing macro voids and improving the bond strength of
59 the polymer cement mortars to aggregates. For example, the mortar of SBR showed
60 improvement in chloride penetration resistance along with general ionic permeability. SBR also
61 slightly reduced portlandite content and mitigated the carbonation process (Yang et al., 2009).

62

63 The nature of the interactions between the polymers and the Portland and aluminous cements is
64 significantly different. For Portland cement both SBR and PVA were found to retard the
65 hydration rate to some extent, but SBR appeared to have very little chemical interaction with
66 ordinary Portland cement (OPC) while PVA is fully hydrolysed (Atkins et al., 1991). A recent
67 study on polymer-modified pervious concrete also found that both SBR and PVA polymers
68 retarded the hydration reactions of cement particles and thus improved mechanical resistance and
69 durability at prolonged curing time, for which PVA showed a better performance, but SBR
70 showed no increase of the concrete stiffness (Giustozzi, 2016). For aluminous cement, SBR
71 showed very little effect on the rate of hydration, but PVA was partially hydrolysed. PVA, when

72 added to aluminous cements, produces a so-called macro-defect-free (MDF) matrix of superior
73 strength and fracture toughness (Atkins et al., 1991).

74

75 A literature study shows that the MK and polymer complement each other in order to improve
76 the mechanical and durability properties. A study on Portland cement concrete using polymer,
77 MK and FA showed a significant effect on the compressive strength, the flexural strength and the
78 modulus of elasticity (Kou and Poon, 2013). However, it is noted that the knowledge of the
79 durability properties of concrete modified with polymer and MK have not been well established
80 yet (Ahmed, 2011). To meet the high-performance requirement for sewage and off-shore
81 applications, where the durability of concrete governs the use of concrete, a series of
82 investigations have been conducted on the combined effect of the use of MK and a polymer
83 mixture together on the mechanical properties and durability of the modified concrete. A
84 previous publication has reported a study of the conventional mechanical properties (Al Menhosh
85 et al., 2016). This paper at first gives a brief review on the major findings in the previous work.
86 After then, it reports a followed on experimental investigation on the long term durability
87 properties of the optimum mixture identified in the previous study on mechanical properties. The
88 durability of the optimum mix has been compared with other three benchmarks to understand the
89 effects of the MK, polymer and their combination.

90

91

2. MIXTURES

92

2.1 Raw Materials

93 Portland limestone cement, CEM II/A-LL (BS EN 197-1:2011), supplied by Lafarge cement UK
94 LTD under the trade name of Mastercrete, and a premium metakaolin, produced by IMERYYS

95 group under the trade name of MetaStar 501, were used in the study. The material compositions
 96 are referenced in Table 1.

97 Table 1: Typical composition of cement and metakaolin

| Component | CEM II/A-LL Cement (BS EN 197-1:2011) | | Metakaolin (Ambroise et al., 1994) |
|--------------------------------|--|-----------------|---------------------------------------|
| | Values % | Standard | Values % |
| Al ₂ O ₃ | 4.19 | 3 – 5% | 40.18 |
| Fe ₂ O ₃ | 2.75 | 2.0 – 3.5% | 1.23 |
| CaO | 65.00 | 60 – 70% | 2.0 |
| SO ₃ | 3.19 | Less than 3.5% | 0.0 |
| MgO | 0.86 | 0.5 – 1.5% | 0.12 |
| Na ₂ O | 0.14 | Less than 0.75% | 0.08 |
| K ₂ O | 0.51 | - | 0.53 |
| SiO ₂ | 16.19 | 15 – 25% | 51.52 |
| TiO ₂ | - | - | 2.27 |
| Loss on ignition (L.O.I) | - | - | 2.01 |

98

99 The polymer additive was styrene butadiene rubber (SBR) latex, poly vinyl acetate (PVA)
 100 emulsion and their mixtures. Normal sands were used for the fine aggregates while crushed
 101 limestone gravels were used for the coarse aggregates with a maximum size of 10 mm. The
 102 particle size distributions of the aggregates (Menhosh et al. 2016) follow the requirements in BS
 103 882:1992.

104

105 2.2 Mixture Design

106 Various combinations of the MK and polymers as listed in Table 2 were tested in a previous
 107 study on conventional mechanical properties (Menhosh et al. 2016). An optimum proportion was
 108 derived based on the mechanical properties of the modified concrete. To establish a baseline, a
 109 mass ratio of 1:1.5:3 for cement:sand:gravel was considered as a control mix.

110

Table 2: The mixtures designed (Al Menhosh et al., 2016)

| |
|-------------------|
| Concrete Mixtures |
|-------------------|

| MK/Cementitious Binder (MK/C) %* | Polymer/Cementitious Binder (P/C) % | | | | Water/Cementitious Binder ratio W/C | | |
|--|---|----|----|----|--|----|-----|
| 0 | 0/2.5/5/7.5 | | | | 0.35/0.38/0.40/0.45/0.50 | | |
| 10 | | | | | | | |
| 15 | | | | | | | |
| 20 | | | | | | | |
| 30 | | | | | | | |
| 40 | | | | | | | |
| Composition of Polymer Admixture | | | | | | | |
| Component | Percentage % | | | | | | |
| SBR | 0 | 20 | 40 | 50 | 60 | 80 | 100 |
| PVA | 100 | 80 | 60 | 50 | 40 | 20 | 0 |

111 * % by weight, cementitious binder = cement +MK

112

113 3. CONVENTIONAL MECHANICAL PROPERTIES AND THE OPTIMUM MIX

114 All the mixes in the Table 2 were tested for their workability and the mechanical properties at the
115 ages of 7 and 28 days. Figure 1 shows that MK significantly reduces the workability of the
116 modified mixes. The mix of 10% MK/C ratio has a slump value much lower than the targeted
117 range of 75 mm to 100 mm even at a high W/C ratio of 0.5. Figure 2 shows the cubic
118 compressive strengths of the MK modified concretes at the age of 7 and 28 days for the W/C of
119 0.45. It shows that the MK/C ratio in the range of 15~20% presents the maximum compressive
120 strength at the two ages.

121

122 Figures 3~5 show the effect of two polymers and their mixtures on their modified concretes. It
123 can be seen that when the polymer to cementitious binder ratio (P/C) is more than 5%, the
124 strength of the modified concrete starts to deteriorate considerably. Meanwhile, when W/C ratio
125 is more than 0.45, the deterioration on concrete strength accelerates using polymer. Figure 5
126 shows that the polymer mixture of 80% SBR and 20% PVA at the 5% P/C and 0.45 W/C
127 presents the highest improvement on concrete strength. Figure 6 shows that the polymer mixture

128 of 80% SBR and 20% PVA gives the modified mixture a slump value of about 82 mm at 0.45
129 W/C.

130

131 Figure 7 compares the 28 days compressive strength of mixtures using the optimum polymer
132 mixture at 5% P/C and MK at 15% MK/C separately and both together. Figure 8 shows the effect
133 of three different curing methods on the compressive strength of the mixtures using 15% MK/C
134 and varied P/C ratios. All the results have suggested that using 15% MK/C, 5% P/C of a polymer
135 mixture of 80% SBR and 20% PVA, 0.45 W/C and moist curing gives the modified concrete an
136 optimum mechanical properties.

137

138 **4. LONG-TERM PROPERTIES OF THE OPTIMUM CONCRETE**

139 This paper focuses on the long-term durability properties of the optimum mixture identified in
140 section 3, and compares it with three other representative benchmark mixtures. All the four
141 mixtures are listed in Table 3. For each data point, three samples were tested and their average
142 value is presented as the result.

143

Table 3: Mixtures studied in this paper

| Mixtures | MK/C %* | P/C %* | Water to cement ratio W/C |
|-------------|---------|--------|------------------------------|
| 1 (Control) | 0 | 0 | 0.45 |
| 2 | 15 | 0 | 0.45 |
| 3 | 15 | 5 | 0.45 |
| 4 | 0 | 5 | 0.45 |

144

* % by the weight of cementitious binder (cement + MK)

145 **4.1 Mechanical Properties**

146

- **Compressive Strength**

147 Long-term compressive strengths of concrete cubes (BS EN 12390-3: 2009) of these four
148 mixtures up to 545 days are shown in Figure 9. It can be seen that mixtures 2 and 3 present a

149 significant improvement on the control mix 1 in the long term with about 16% increase of the
150 compressive strength at the age of 545 days. The results indicate that MK has a considerable
151 effect on strength increase, but the polymer at 5% P/C has little influence on this property.

152

153 • **Splitting and Flexural Tensile Strength**

154 Figure 10 shows the splitting and flexural strengths at four ages up to 180 days. The tests were
155 conducted according to BS EN 12390- 6:(2009) and BS EN 12390- 5:(2009), respectively. The
156 results show that both the splitting and flexural strengths developed with age. Either using
157 polymer (5% P/C) or MK (15% M/C) increases the tensile strength. The combination of 15%
158 MK/C and 5% P/C resulted in the highest splitting and flexural strengths at almost all ages.

159

160 • **Young's Modulus**

161 Figure 11 shows the modulus of elasticity at the age of 28 days. The cast concrete cylinders (150
162 mm in diameter and 300 mm in height) were at first moist cured for 28 days according to BS
163 1881 Part -121: (1983). It can be seen that using MK has increased the Young's modulus of
164 elasticity while polymer shows the opposite effect. The mix of 5% P/C and 15% MK/C shows a
165 similar result as that of 5% P/C only. This suggests that the influence of MK on modulus in the
166 presence of polymer has been minimised.

167

168 **4.2. Durability**

169 • **Drying Shrinkage**

170 Drying shrinkage is an important characteristic of concrete (Guneyisi et al., 2008), which affects
171 the long-term mechanical properties and durability properties of structures (BS ISO 1920-
172 8:2009; Hossain et al., 2016). Concrete prisms (100×100 ×400 mm) were cast and moist cured

173 for 7 days. Thereafter they were stored in open atmosphere and their dimensional changes along
174 the length of the prisms were monitored and recorded up to 365 days. Figure 12 shows that both
175 MK and polymer respectively reduce the drying shrinkage. However, the optimum mix using
176 both of them shows the lowest drying shrinkage at all ages.

177

178 • **Rate of Water Absorption**

179 Measurement of the rate of absorption of water was made according to ASTM C1585-04. This
180 test method determines the rate of absorption of water by measuring the increase in the mass of a
181 specimen due to water absorption when only one surface of the specimen is exposed to water, as
182 shown in Figure 13. Concrete cylinders (100 mm diameter and 50 mm height) of all the mixes
183 were cast and moist cured for 28 days. ASTM C1585-04 recommends conducting the
184 investigation at the age of 28 days. However, reaction of MK with hydrated cement product
185 continues over time and changes the internal microstructure (Aiswarya et al., 2013; Justice et al.,
186 2005). In order to understand the long-term reaction of MK and changes in the microstructure,
187 which influences the rate of water absorption, half of the specimens were dry cured for a further
188 28 days. After the curing, the specimens were treated for 3 days at a temperature of 50 degrees
189 Celsius and relative humidity of 80%. One circular surface was immersed in water to a depth of 1
190 to 3 mm only, such that water ingress of unsaturated concrete was dominated by capillary suction
191 during initial contact with water. The rate of water absorption I in the unit of mm is defined by
192 Eq. (1) (ASTM C1585-04):

193

$$194 \quad I = \frac{m_t}{A \times D} \quad (1)$$

195

196 where m_t is the change of weight with time (t), A is the cross-sectional area of the cylinder and
197 D is the density of water. For the purpose of this test, the temperature dependence of the density
198 of water is neglected and a value of 0.001 g/mm^3 is used. Figure 14 (a) and (b) show the water
199 absorption test results for the concrete specimens cured for 28 days and the comparison of
200 control and combined MK and polymer samples between 28 and 56 days, respectively. It can be
201 seen that the combination of MK and polymer significantly reduces the water absorption in along
202 run, which can be attributed to a significant reduction in the capillary pores because of the
203 pozzolanic reaction of MK with the cement hydrated products and the hydrophobic effect of
204 polymer.

205

206 • **Carbonation Test**

207 Concrete cylinders (100 mm in diameter and 200 mm in height) were made and moist cured for 7
208 days. After then having the two end surfaces coated using epoxy resin, they were stored openly
209 exposed to atmosphere. At the ages of 21, 28, 56, 90, 120 and 180 days, the cylinders were split
210 in half along the diameter to examine the depth of carbonation in the radial direction using 1%
211 phenolphthalein (BS 1881-210, 2013; Papadakis, 2000; Chang and Chen, 2006). The carbonation
212 depths were measured at six different locations in the direction of the height of the specimens
213 (Otieno et al., 2014). Figure 15 shows the average values of carbonation depth. It can be seen
214 that both MK and polymer helped to decrease the carbonation rate. The optimum mixture of 5%
215 P/C and 15% MK/C shows the lowest carbonation rate, at approximately half of that of the
216 control mixture at 180 days.

217

218 • **Chloride Penetration**

219 Similar cylindrical specimens as those used for the carbonation test were prepared and moist
220 cured for 28 days. Thereafter, they were immersed in a 3% NaCl solution in order to simulate a
221 chloride environment. The chloride penetration depth was monitored up to 180 days following a
222 similar method as that used in the carbonation test. Chloride penetration depth was identified
223 using a solution containing 0.1% sodium fluorescein and 0.1 N silver nitrate solution sprayed on
224 the two surfaces exposed by splitting through the specimens along the diameter (Andrade et al.,
225 1999; Meck and Sirivivatnanon, 2003). The penetration depth was measured in the same way as
226 that for carbonation. Figure 16 shows a similar trend as that of the carbonation test. Both polymer
227 and MK decreased the chloride penetration rate considerably. The optimum mixture of 5% P/C
228 and 15% MK/C demonstrated the best resistance to chloride penetration.

229

230 • **Corrosion Weight Loss**

231 Reinforced concrete cubes (100×100×100 mm) were cast with a 60 mm long carbon steel rebar
232 of diameter 16 mm positioned in each cube and parallel to a surface at a depth of 25 mm from
233 that surface. Before casting, the carbon steel rebar was thoroughly cleaned and weighed to
234 confirm its initial weight as that described by Parande et al. (2008). These cast reinforced
235 specimens were moist cured for 28 days (Parande et al., 2008). To simulate the real world
236 situation where concrete is subjected to various service conditions from normal atmosphere to
237 submerged under saline environments over time, the samples were divided into three groups and
238 each group was exposed to different conditions. One group was exposed to an open atmospheric
239 environment, another group was immersed in a 20% NaCl solution, and the last group was
240 alternately put in these two environmental conditions for 7 days each and up to 38 cycles in 365
241 days. On the time after 180, 270 and 365 days, the concrete specimens were split open using
242 compressive machine and subjected to visual observation at first. Thereafter the steel

243 reinforcements were pulled out from the concrete and their surfaces were carefully cleaned
244 thoroughly using steel wire brush to get rid of all the concrete remains and the rusts of corrosion.
245 Later the cleaned steel rebars were weighed again to work out their weight loss due to corrosion
246 (Chung, 2000; Parande et al., 2008). Figure 17 shows that the weight losses of all samples under
247 all three conditions are obvious, particularly, for the samples of the control mix of 0% P/C and
248 MK/C. However, the samples of the optimum mix of 5% P/C and 15% MK/C has the lowest
249 weight loss. It can be also noticed that the weight loss became significant after 270 days.
250 Particularly, the alternated exposure to atmospheric condition and immersion in 20 % NaCl
251 demonstrates a critical influence. It can be concluded that an alternating environmental condition
252 accelerate the corrosion rate in concrete.

253

254 • **Chemical Resistance**

255 The chemical resistance was inspected by immersing cubic specimens (100×100×100 mm), after
256 28 days moist curing, in four different chemical solutions for 180 days. These solutions were
257 20% sodium hydroxide (NaOH), 5% sodium chloride (NaCl), 5% sulphuric acid (H₂SO₄) and 5%
258 hydrochloric acid (HCl). They were selected to simulate various environmental conditions
259 (Beulah and Prahallada, 2012). In practice, special cements (for example sulphur resistance
260 cement), which are very expensive, have been used for the application in severe environments.
261 This experimental investigation aims to help understand how effective using ordinary MK and
262 polymer modified Portland cement to replace the special cements to meet these special
263 requirements.

264

265 Figure 18 shows the appearance of the samples modified with 5% P/C and 15% MK/C after 90
266 days exposed to HCl and H₂SO₄, and all the samples after 180 days immersed in the acidic

267 solutions. The weight changes of the specimens were recorded at 7, 14, 28, 56, 90 and 180 days.
268 Figure 19 show that the mixtures using either MK or polymer had less weight increase when
269 exposed to the alkaline and salty solutions, and less weight loss when exposed to acidic
270 solutions, compared to the control mix with no modification using MK and polymer. It can be
271 noticed, however, that when exposed to alkaline and salty solutions all mixtures had a steep
272 weight increase in the first 56 days, which indicates that the cured concrete underwent further
273 chemical reactions with infiltrated salt and alkali ions in an early stage. The MK modified
274 mixtures have a significantly reduced weight change in all the tests. It effectively confirms the
275 pozzolanic reactions between MK and cement hydration products, which result more hydration
276 gel products with a formation of CASH and NASH (Kannan and Ganesan, 2014) to help the
277 resistance to chemical attack. The optimum mixture of 5% P/C and 15% MK/C presents the least
278 weight change in all the cases. It also can be seen that all these curves present a flattening trend
279 after 90 days, indicating a long-term durability, in which the optimum mixture shows the best.

280

281 • **Water Flow Rate of Concrete**

282 In this study, both mortar and concrete specimens, of the dimension of 2.54 cm in diameter and
283 2.54 cm in length, were tested. The specimens were moist cured for 28 days and tested at ages
284 28, 56 and 90 days. The PERL-200 permeameter, provided by Core Lab Instruments, was used
285 for the test. Similar to the test apparatus used by Kameche et al. (2014) and Li et al. (2016),
286 incorporating a digital pressure transducer and a calibrated visual flow (measurement) cell, it
287 uses the valves to control a flow system to enable the determination of flow rate of water through
288 a one-inch diameter core sample plug. The water flow rate through the sample is determined by
289 measuring the time required for the water (10 cm^3) to pass between the calibrations marks.
290 Figure 20 shows the schematic diagram of the experimental setup. The permeability of the

291 sample can be determined in terms of the Darcy's Law:

292

$$293 \quad Q = \frac{k \times A (P_1 - P_2)}{\mu \times L} \quad (2)$$

294

295 where, Q is flow rate (cc/sec), k is the permeability, L is the length of flow (cm), μ is the
296 viscosity, A is the cross-sectional area of flow (cm²), P_1 is the upstream pressure, and P_2 is the
297 downstream pressure. All the concrete and mortar samples were tested using this apparatus.
298 Figures 21 (a) and (b) illustrate the results obtained from concrete and mortar, respectively. Clear
299 evidence can be seen that the water flow rate significantly reduced for concrete modified by MK
300 and polymer. The mortar sample of the optimum mix of 5% P/C and 15% MK/C shows the
301 lowest the permeability.

302

303 • **Depth of Penetration of Water under Pressure**

304 The water penetration test (BS EN-12390-8, 2009), the most commonly used test to evaluate the
305 permeability of concrete, was conducted as well. In this test, water was applied on one face of the
306 150×150×150 mm concrete cube specimens under a pressure of 0.5 MPa (5 bars), as shown in
307 Figure 22. This pressure was maintained constant for a period of 72 hrs. After the completion of
308 the test, the specimens were taken out and split open into two halves. The water penetration front
309 profile in concrete was then marked (Figure 23(a)) and the maximum depth of water penetration
310 front in specimens was recorded and considered as an indicator of the water penetration (Dinakar
311 et al., 2013). This test was conducted at 28, 56 and 90 days after moist curing for 28 days. As can
312 be seen in Figures 23(b), the depth of penetration of water significantly reduced in the specimen
313 of the optimum mix of 4% P/C and 15% MK/C compared with the rest of the samples.
314 Furthermore, there is a development in water permeability of the modified concrete with

315 increased age of the specimens compared with the control sample. This can be attributed to the
316 continuous reaction of MK with the hydrated cement product, producing a less permeable matrix
317 with time.

318

319 • **Gas Penetration of Concrete under Pressure**

320 In this test, the similar experimental setup and samples were used as in the test for depth of
321 penetration of water under pressure. However, the CO₂ was applied from the top instead from the
322 bottom with a pressure of 0.4 MPa (4 bars) for 8 hours. These arrangements were implemented to
323 maintain the constant pressure in order to simulate the concrete under sewerage conditions. After
324 the test, the specimens were taken out and split open into two halves. The penetration of
325 carbonation was determined by treating a freshly broken surface with 1% phenolphthalein. The
326 region of Ca(OH)₂ is coloured pink while the carbonated areas is uncoloured. The gas penetration
327 profile on the concrete surface was then marked and the maximum depth of gas penetration in
328 specimens was recorded and considered as an indicator of the gas penetration. Figure 24
329 compares the gas penetration depths of the four mixtures. It can be seen that using MK and
330 polymer respectively have exhibited reductions in the gas penetration. The optimum mix of 5%
331 P/C and 15% MK/C shows the best result for the gas penetration resistance.

332

333 **5. CONCLUSIONS**

334 This paper has reported an experimental study on long-term durability properties of concrete
335 modified with MK and polymer. Various long-term durability tests were carried out to
336 understand the behaviour of modified concrete subjected to an extremely harsh environment. The
337 following conclusions can be drawn based on the experimental results:

- 338 • Metakaolin will accelerate the setting time of cement pastes but reduce the workability of
339 concrete. However, polymer has an inverse influence on the two properties.
- 340 • The bi-polymer of composition 80% SBR and 20% PVA shows an optimised result when it
341 works together with MK.
- 342 • The addition of 5% optimised bi-polymer and 15% cement replacement by metakaolin
343 generates an optimised concrete mixture for long-term mechanical properties.
- 344 • All the long-term durability experimental investigations suggest that both MK and polymer
345 improve the properties. Their combination presents a complement to each other. The optimum
346 mix base on mechanical properties also demonstrates a great enhance on durability properties
347 compared to using MK or polymer only.

348

349

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352

353

References

- 354 Ahmed, S. F. U. (2011). Mechanical and durability properties of mortars modified with
355 combined polymer and supplementary cementitious materials. *Journal of Materials in*
356 *Civil Engineering*, 23(9), 1311-1319.
- 357
- 358 Aiswarya, S., Prince Arulraj, G., and Dilip, C. (2013). A review on use of metakaolin in
359 concrete. *IRACST – Engineering Science and Technology*.
- 360
- 361 Al Menhosh, A., Wang, Y., and Wang, Y. (2016). The mechanical properties of the concrete
362 using metakaolin additive and polymer admixture. *Journal of Engineering*, 2016, 1-6.
- 363
- 364 Ambroise, J., Maximilien, S., and Pera, J. (1994). Properties of metakaolin blended cements.
365 *Advanced Cement Based Materials*, 1(4), 161-168.
- 366
- 367 Andrade, C., Castellote, M., Alonso, C., and González, C. (1999). Relation between
368 colourimetric chloride penetration depth and charge passed in migration tests of the type
369 of standard ASTM C1202-91. *Cement and Concrete Research*, 29(3), 417-421.

370
371 Atkins, K. M., Edmonds, R. N., and Majumdar, A. J. (1991). The hydration of portland and
372 aluminous cements with added polymer dispersions. *JOURNAL OF MATERIALS*
373 *SCIENCE*, 26, 2372-2378.
374
375 ASTM Standards C1585 – 04(2004). *Measurement of Rate of Absorption of Water by*
376 *Hydraulic Cement Concrete*, U. S.
377
378 Beulah, M. A., and Prahallada, M. C. (2012). Effect of replacement of cement by metakalium on
379 the properties of high performance concrete subjected to hydrochloric acid attack.
380 *International Journal of Engineering Research and Applications*, 2.
381
382 BS EN 12390-3: (2009) : *Testing hardened concrete: Compressive strength of test specimens.*
383 BSI: London
384
385 BS EN 12390-5: (2009): *Testing hardened concrete: Flexural strength of test specimens*, BSI:
386 London
387
388 BS EN 12390- 6:(2009):*Testing hardened concrete: Tensile splitting strength of test specimens*,
389 BSI: London
390
391 BS EN 12390 – 8: (2009) : *Depth of penetration of water under pressure*. BSI: London
392
393 BS EN 197-1: (2011): *Cement: composition, specifications and conformity criteria for common*
394 *cements*. British Standards Institution, London.
395
396 BS ISO 1920-8:2009: *Testing of concrete. Determination of the drying shrinkage of concrete for*
397 *samples prepared in the field or in the laboratory*, BSI: London
398
399 BS 1881 Part -121: (1983): *Method for determination of static modulus of elasticity in*
400 *compression*, BSI: London
401
402 BS 1881 -210 : (2013) : *Determination of the potential carbonation resistance of concrete –*
403 *Accelerated carbonation method*. . BSI: London
404
405 BS 882: (1992): *Specification for aggregates from natural sources for concrete*, BSI: London
406
407 Chang, C. F., and Chen, J. W. (2006). The experimental investigation of concrete carbonation
408 depth. *Cement and Concrete Research*, 36(9), 1760-1767. doi:
409 10.1016/j.cemconres.2004.07.025
410
411 Chung, D. (2000). Corrosion control of steel-reinforced concrete. *Journal of Materials*
412 *Engineering and Performance*, 9(5), 585-588.
413
414 Dinakar, P., Sahoo, P. K., and Sriram, G. (2013). Effect of Metakaolin Content on the Properties
415 of High Strength Concrete. *International Journal of Concrete Structures and Materials*,
416 7(3), 215-223. doi: 10.1007/s40069-013-0045-0
417

- 418 Giustozzi, F. (2016). Polymer-modified pervious concrete for durable and sustainable
419 transportation infrastructures. *Construction and Building Materials*, 111, 502-512. doi:
420 10.1016/j.conbuildmat.2016.02.136
421
- 422 Guneyisi, E., Gesoglu, M., Karaoglu, S., and Mermerdas, K. (2012). Strength, permeability and
423 shrinkage cracking of silica fume and metakaolin concretes. *Construction and Building*
424 *Materials*, 34, 120-130.
425
- 426 Guneyisi, E., Gesoğlu, M., and Mermerdaş, K. (2008). Improving strength, drying shrinkage,
427 and pore structure of concrete using metakaolin. *Materials and Structures*, 41(5), 937-
428 949.
429
- 430 Hossain, M. M., Karim, M. R., Hasan, M., Hossain, M. K., and Zain, M. F. M. (2016).
431 Durability of mortar and concrete made up of pozzolans as a partial replacement of
432 cement: A review. *Construction and Building Materials*, 116, 128-140. doi:
433 10.1016/j.conbuildmat.2016.04.147
434
- 435 Justice, J. M., Kennison, L. H., Mohr, B. J., Beckwith, S. L., McCormick, L. E., Wiggins, B.,
436 Zhang, Z. Z., and Kurtis, K. E. (2005). Comparison of Two Metakaolins and a Silica
437 Fume Used as Supplementary Cementitious Materials. Paper presented at the Proc.
438 Seventh international symposium on utilization of high-strength/high performance
439 concrete, Washington D.C.
440
- 441 Kamseu, E., Cannio, M., Obonyo, E. A., Tobias, F., Bignozzi, M. C., Sglavo, V. M., and
442 Leonelli, C. (2014). Metakaolin-based inorganic polymer composite: Effects of fine
443 aggregate composition and structure on porosity evolution, microstructure and
444 mechanical properties. *Cement and Concrete Composites*, 53, 258-269.
445
- 446 Kameche, Z. A., Ghomari, F., Choinska, M., and Khelidj, A. (2014). Assessment of liquid water
447 and gas permeabilities of partially saturated ordinary concrete. *Construction and Building*
448 *Materials*, 65, 551-565. doi: 10.1016/j.conbuildmat.2014.04.137
449
- 450 Kannan, V., and Ganesan, K. (2014). Chloride and chemical resistance of self compacting
451 concrete containing rice husk ash and metakaolin. *Construction and Building Materials*,
452 51, 225-234. doi: 10.1016/j.conbuildmat.2013.10.050
453
- 454 Khatib, J. M., Negim, E. M., and Gjonbalaj, E. (2012). High Volume Metakaolin as Cement
455 Replacement in Mortar. *World journal of chemistry*, 7(1), 7-10. doi:
456 10.5829/idosi.wjc.2012.7.1.251
457
- 458 Konar, B. B., Das, A., Gupta, P. K., and Saha, M. (2011). Physicochemical Characteristics of
459 Styrene-Butadiene Latex- modified Mortar Composite vis-à-vis Preferential Interactions.
460 *Journal of Macromolecular Science, Part A*, 48(9), 757-765. doi:
461 10.1080/10601325.2011.596072
462
- 463 Kou, S. C., and Poon, C. S. (2013). A novel polymer concrete made with recycled glass
464 aggregates, fly ash and metakaolin. *Construction and Building Materials*(41), 146-151.
465

- 466 Li, X., Xu, Q., and Chen, S. (2016). An experimental and numerical study on water permeability
467 of concrete. *Construction and Building Materials*, 105, 503-510. doi:
468 10.1016/j.conbuildmat.2015.12.184
469
- 470 Meck, E., and Sirivivatnanon, V. (2003). Field indicator of chloride penetration depth. *Cement
471 and Concrete Research*, 33(8), 1113-1117.
472
- 473 Nguyen, D. D., Devlin, L. P., Koshy, P., and Sorrell, C. C. (2016). Effects of chemical nature of
474 polyvinyl alcohol on early hydration of Portland cement. *Journal of Thermal Analysis
475 and Calorimetry*, 123(2), 1439-1450. doi: 10.1007/s10973-015-5076-0
476
- 477 Otieno, M., Beushausen, H., and Alexander, M. (2014). Effect of chemical composition of slag
478 on chloride penetration resistance of concrete. *Cement and Concrete Composites*, 46, 56-
479 64. doi: 10.1016/j.cemconcomp.2013.11.003
480
- 481 Papadakis, V. G. (2000). Effect of supplementary cementing materials on concrete resistance
482 against carbonation and chloride ingress. *cement and concrete research*, 30, 291–299.
483
- 484 Parande, A., Babu, B., Karthik, M., Kumar, K., and Palaniswamy, N. (2008). Study on strength
485 and corrosion performance for steel embedded in metakaolin blended concrete/mortar.
486 *Construction and Building Materials*, 22(3), 127-134. doi:
487 10.1016/j.conbuildmat.2006.10.003
488
- 489 Pouhet, R., and Cyr, M. (2016). Carbonation in the pore solution of metakaolin-based
490 geopolymer. *Cement and Concrete Research*(88), 227-235.
491
- 492 Rashad, A. M. (2013). Metakaolin as cementitious material: History, scours, production and
493 composition—A comprehensive overview. . *Construction and building materials*, 41, 303-
494 318.
495
- 496 Souri, A., Kazemi-Kamyab, H., Snellings, R., Naghizadeh, R., Golestani-Fard, F., and
497 Scrivener, K. (2015). Pozzolanic activity of mechanochemically and thermally activated
498 kaolins in cement. *Cement and Concrete Research*(77), 47-59.
499
- 500 Srinivasu, K., Krishna Sai, M. L. N., and Venkata Sairam Kumar, N. (2014). *A review on use of
501 metakaolin in cement mortar and concrete*. Paper presented at the International journal of
502 innovative research in science, engineering and technology.
503
- 504 Wang, R., Li, X.-G., and Wang, P.-M. (2006). Influence of polymer on cement hydration in
505 SBR-modified cement pastes. *Cement and Concrete Research*, 36(9), 1744-1751. doi:
506 10.1016/j.cemconres.2006.05.020
507
- 508 Yang, Z., Shi, X., Creighton, A. T., and Peterson, M. M. (2009). Effect of styrene–butadiene
509 rubber latex on the chloride permeability and microstructure of Portland cement mortar.
510 *Construction and Building Materials*, 23(6), 2283-2290. doi:
511 10.1016/j.conbuildmat.2008.11.011
512