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Effects of Lactic and Citric Acid on Early-age Engineering Properties

of Portland / Calcium Aluminate Blended Cements

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Abstract: In this study, Portland / Calcium Aluminate blended cement (PC/CAC) was combined with citric acid or lactic acid as additives to investigate the effects of the aforementioned carboxylic acids on the hydration reactions of PC/CAC as a potential fast hardening and low cost repair material for concrete. Mortar specimens with the carboxylic acid additives of either 0.5, 1 or 3% by weight, prepared with a binder:sand:water ratio (by weight) of 1:3:0.5, were subjected to flexural and compressive strength tests at early ages up to 28 days. In order to understand the phase composition of the hydrates in the PC/CAC systems, XRD analyses were conducted on ground PC/CAC mortars with and without carboxylic acid at 7, 14 and 28 days. In combination with this, SEM images of selected mortar specimens were also taken at the same times for visual analyses of hydrates. Citric acid did not have

27 any beneficial effect on enhancing the calcium silicate phase as initially assumed

28 and instead reduced the strength of PC/CAC cement at all levels of concentration.

29 The experiment analyses revealed that Portlandite crystals were the major hydrate

30 phase in PC/CAC with lactic and citric acids. Lactic acid below 2% wt. improved both

31 compressive and flexural strength gained at early ages due to improved crystallinity

32 of the calcium hydroxide crystals. Combined with its inherent rapid setting time,

33 PC/CAC blended cements have a potential to be developed into a suitable repair

34 material for concrete.

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1 Introduction

1.1 PC/CAC based mortar

Repair technology has become increasingly important in modern construction practice. Demands for repair and protection of existing concrete infrastructure have dramatically increased in the last few decades which are consistent with greater appreciation of sustainability. A quality repair material often requires rapid setting and hardening, good adhesion, compatibility with existing concrete, dimensional stability, and corrosion resistance. Calcium aluminate cement (CAC) has the potential to meet these repair requirements[1].

CAC has proven high strength development which is usually attributed to the formation of $2CAH_8$, $3CAH_6$ and CAH_{10} [2], [3]. CAC was developed during the last decade of the nineteenth century as an alternative to Portland cement (PC) to prevent structural concrete elements from serious sulphate attack. Other major fields of CAC application are in refractory concrete for industrial use in processes involving high temperatures [4] and in so-called 'building chemistry' where it constitutes one part of a complex mixture of mineral and organic ingredients for applications such as self-levelling screeds and tile cement [5]. CAC distinguishes itself from PC by containing a much higher concentration of alumina, normally 30-90% by weight [6]. Besides, CAC is also considered as a type of sustainable cement since CAC clinker contains less calcium compounds than PC clinker. In this case, less limestone is used in the manufacturing of CAC clinker, thus reducing the CO_2 emissions derived from the raw materials compared with PC clinker production [7]. CAC clinker is comprised of the same basic oxides as PC clinker such as lime, silica, alumina, and iron oxide, however the proportions of oxides are fairly different in CAC and PC

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71 clinkers. All CACs contain mono-calcium aluminate (CA or $CaAl_2O_4$) as the main

72 hydraulic phase. Other phases may be present based on the type of CAC however it

73 is important to note that C_3A is not a normal component of CACs [2].

74 Advanced material research has recently focused on ettringite rich cement

75 compounds [8] which are known to be a dominant formation in CAC. Some

76 properties including the hydration inhibition phenomena in these ettringite rich

77 materials from PC/CAC/C$ (where C$ represents Calcium Sulphate (CS) systems),

78 have been recently evaluated [9][10][11] and are of key importance to the

79 engineering community as a more advanced appreciation on the mechanisms needs

80 to be developed. CAC's have several unique properties which could make them the

81 materials of choice in concrete repair applications. When CAC is used alone as a

82 conventional mortar, these properties include: 1. rapid hardening, even at low

83 temperatures; 2. high temperature resistance/refractory performance; 3. resistance

84 to a wide range of chemically aggressive conditions; and 4. resistance to impact and

85 abrasion [6][12][13][14]. Cementitious products based on ettringite have a broad

86 range of uses: formulations with water contents near the minimum requirement to

87 ensure plasticity are widely used in proprietary floor screeds, high performance tile

88 grouts, refractory kiln and sewage lining.

89 However the use of PC/CAC based systems as a repair material is not considered

90 as often as polymer-modified cementitious mortars which are traditionally strong

91 candidates for repair materials. One reason for this is that the annual production of

92 CAC is very small, around 1 per cent of PC in the UK market. Fondu, the brand of

93 CAC used in this study and produced by Kerneos Ltd, is 3 to 4 times more expensive

94 than PC, while white CAC is 10 times more expensive. This is governed by the cost

95   of alumina derived from the natural mineral bauxite which is also primarily used in

96   aluminium production, making it much more valuable than limestone used for PC

97   production. Due to the high market price of CAC, it has not been economical and

98   hence unpopular to use it alone for larger scale repairs. For this reason, research

99   has led us to investigate its use as a replacement in minor quantities in PC for some

100 desirable applications. If CAC is able to impart its attractive rapid hardening

101 properties to PC, it would make for a very useful repair material with relatively low

102 cost compared with pure CAC-based repair material. Due to its rapid setting, a

103 PC/CAC system could be utilized in rapid repair of PC structures, such as highways,

104 airport runways, and bridge decks. It could reduce the waiting time and cost

105 associated with ordinary PC repair materials. Periods of sustained interruption for

106 example in a busy highway, airport runway, bridge, etc., will cause significant

107 economic loss. By using PC/CAC materials, the potential to reduce interruption to

108 services could be greatly reduced, therefore allowing valuable time and resources to

109 be saved.

110 The efficient repair and replacement of concrete often requires a rapid setting

111 material that can be placed and cured in a relatively short period of time. Frequently,

112 temporary repairs are made using materials that are later found to be incompatible

113 with the existing pavement, structure, and environment. This practice causes these

114 materials to fail prematurely, frequently requiring re-repair [15]. However research

115 shows that PC/CAC based mortars may attain lower compressive strength

116 resistance than PC mortar [16][17]. Mortar based on this binary system drops in

117 compressive and flexural strength with increased concentrations of CAC[11] [16].

118 Previously, the main areas of research involving CAC in binary and tertiary systems

119 have been related to optimizing setting time, mechanical strength, and fracture

120   toughness [4][18][19], [20]. To the best of the authors' knowledge, research on the

121   combination of PC/CAC blends with chemical admixtures of organic and inorganic

122   nature has not been investigated, allowing this study to create the opening in this

123   field of research.

124   *1.2 Lactic and citric acid addition*

125   Lactic and citric acid are organic admixtures which belong to the carboxylic group of

126   acids. Citric acid has been found to be one of the more effective acids at retarding

127   PC hydration through the adsorption of citrate ions onto the surface of the Portland

128   cement grain surface [21]. Ions of calcium, alumina, silica and iron are all potentially

129   capable of chelating with organic compounds. In practice, the most widely used

130   retarders are chiefly hydroxyl carboxylic acids or their salts [22][23]. Other studies on

131   the interaction of citric acid with calcium sulphate hemihydrate, i.e. $CaSO_4 \cdot 1/2H_2O$,

132   confirm that the kinetics of hydration and setting time were governed by adsorption

133   of the acids on the surface of the gypsum crystals and reduced interlocking of the

134   microstructure [24]. The addition of citric acid to calcium sulphoaluminate cement

135   increased the setting time, modified the morphology of the ettringite, changed the

136   microstructural configuration and prevented a decrease in compressive strength by

137   delayed ettringite formation[25].

138   Further investigations have been aimed to understand the mechanisms of the

139   retardation using citric acid. Pore solutions, collected after different times of

140   hydration, have been analysed for ion concentrations and organic carbon. The zeta

141   potential as well as the composition of the hydrated solid phases has been studied

142   [25][26]. Singh et al. [21] found that the zeta potential of cement decreases with

143   increasing additions of citric acid, which was explained by the adsorption of citrate

144 ions onto the positively charged surfaces of the Portland cement grains. Schwarz

145 [26] concluded that citrate ions increase the dissolution rate of the ferrite phase. In

146 the presence of PC/CAC cement, it was found to have a beneficial effect on strength

147 development and appeared to reduce the retardation of the silicate phase hydration

148 [11]. On the contrary, lactic acid has been shown to accelerate the hydration of

149 Portland cement as proved by electrical conductivity measurements indicating that

150 lactic acid formed a salt of calcium lactate during the interaction with Portlandite [30].

151 This product would also be beneficial in PC/CAC systems.

152 The main objective of this study was to investigate and evaluate the effects of the

153 addition of lactic acid and citric acid on the compressive and flexural strength

154 development of ternary PC/CAC/CS blends focusing particularly on the

155 microstructure development and hydration products. The intention is also to develop

156 a mortar with high early ettringite precipitation through the addition of lactic acid and

157 reduce the disruption to the hydration of the silicate phases which contribute to the

158 long term strength through the addition of citric acid. For this purpose mortar

159 specimens were prepared using six PC/ CAC/CS blends of varying citric and lactic

160 acid additions to determine the compressive and flexural strengths up to 28 days.

161 Experimental techniques such as SEM/BEI/EDX and XRD were employed to

162 understand the mechanism of hydration of the ternary mortar at different ages.

163

2 Experimental Program

2.1 Materials and specimen preparation

The weight percentages of the cementitious materials in the mortar formulations are summarized in Table 3. The additional dose of 5% calcium sulphate anhydrite and 1% hydrated lime (HL) were used as part of the base mix due to these two parameters having the greatest influence on the increased precipitation of ettringite. Samples with 0.5,1 and 3% by weight lactic acid are named L05, L1 and L3, respectively. Samples with 0.5,1 and 3% citric acid are named C05, C1 and C3, respectively.

The raw materials used for the preparation of the 9 different mortar mixes in this study were CEM I 42.5 R Portland cement (PC) obtained from *Castle Cement Limited* and CAC cement (CAC) from *Kerneos Ltd*; the chemical composition determined by SEM-EDS and physical properties can be seen in Table 1 and in Table 2, respectively. In both cases, relevant EN Standards were met. CEN standard sand and distilled water were employed for preparing mortar mixes. ACS reagent grade CS ($CaSO_4$), HL ($Ca(OH)_2$), lactic acid ($CH_3CH(OH)COOH$) and citric acid ($HOC(COOH)(CH_2COOH)_2$, all purchased from *Sigma-Aldrich*, were used as the additives. All samples with HL and lactic acid or citric acid additives had a total cementitious materials ratio of 74:20:5:1 (i.e. PC:CAC:CS:HL) by weight to assess the influence of lactic acid and citric acid on these mixtures. Trial mixes were carried out prior to commencement of work to ensure that the mix design and material combinations met the requirements of the specification and method of use. The total cementitious materials: sand: water ratio of 1:3:0.5 by weight set by EN 196-1 for determining strength of cement was adopted. The $40x40x160mm^3$ mortar prism

188   specimens were prepared using a bench-top mortar mixer conforming to EN 196-1

189   and mechanically compacted in two layers.

190

191   **Table 1**

192   **Chemical composition of PC and CAC determined by SEM-EDS (% by weight)**

	CaO	Fe_2O_3	Al_2O_3	SiO_2	MgO	TiO_2	K_2O
PC	71.45	3.10	4.98	18.31	1.15	0	1.01
CAC	42.06	17.04	35.54	3.43	0	1.93	0

193

194   **Table 2**

195   **Physical properties of the cements (PC & CAC) used in this study**

	Blaine fineness (cm2/g)	Bulk density (kg/m3)
PC	4200	587
CAC	6030	1100

196

197   Immediately after casting and surface preparation, the specimens were covered with

198   0.2mm-thick polyethylene sheets to stop moisture loss and cured in a laboratory

199   environment at approximately 20°C.. The specimens were demoulded after 24h and

200   then moved into a humidity chamber to continue curing at the environment of 20±1°C

201   and relative humidity 95±5% until the designated testing age.

202   **Table 3**

203   **Weight percentages of cementitious materials in mortar formulations (% by weight)**

204

Mix ID	PC	CAC	CS Calcium Sulphate anhydrite	HL Hydrated lime	LA Lactic acid	CA Citric acid
R1	80	20	-	-	-	-
R2	75	20	5	-	-	-
R3	74	20	5	1	-	-
C05	74	20	5	1	-	0.5
C1	74	20	5	1	-	1
C3	74	20	5	1	-	3
L05	74	20	5	1	0.5	-
L1	74	20	5	1	1	-
L3	74	20	5	1	3	-

205

206

207   *2.2 Flexural Strength*

208   All specimens were taken directly from the curing chamber and tested under

209   controlled laboratory conditions. Three specimens at each specified age and each

210   lactic or citric acid content were broken in bending using a three-point bending test

211   conforming to EN 196-1 using an Instron universal testing machine. By doing so,

212   flexural strength of various mixtures was obtained.

213   *2.3 Compressive Strength*

214   Six specimens, each a broken half from a flexural test, were tested under uniaxial

215   compression conforming to EN 196-1 for compressive strength under the same

216 laboratory conditions applied in the flexural strength test. The crushing load was also

217 determined using the same Instron universal testing machine.

218 *2.4 Scanning Electron Microscope (SEM)*

219 SEM sample preparation was done through the removal of free water from hydrated

220 cement by solvent exchange. After drying, the samples were stored in air-tight plastic

221 cups in a desiccator containing silica gel to create a dry and CO_2-free environment.

222 For the microscopical investigations, pieces of the samples were collected after

223 testing for strength and immediately immersed in ethanol for 24 h to stop hydration

224 and then subsequently dried at 40 °C for 24 h. Following this, they were impregnated

225 using a low viscosity epoxy and polished down to 0.3 μm using an EcoMet 250

226 grinder-polisher. A SC7640 high resolution sputter coater was then used to coat the

227 samples with approximately 12nm of gold film to give the specimen surface better

228 conductivity. The coated samples were then examined using a Zeiss Supra 35VP

229 scanning electron microscope (SEM) coupled with an energy dispersive X-ray

230 spectroscopy (EDX) analyser from EDAX. The EDX point analyses were used to

231 determine the elemental compositions of the hydrate products. The analyses were

232 carried out using an accelerate voltage of 20 kV to ensure a good compromise

233 between spatial resolution and adequate excitation. Over 10 points (EDX spots) per

234 sample were analysed.

235 *2.5 X-ray Diffraction (XRD)*

236 Selected samples were analysed by XRD to investigate the effect of lactic and citric

237 acid dose on the cured PC/CAC mortar. The specimens were gently ground using a

238 mortar pestle and the mineral phases identified by Cu-K(α) radiation using a Bruker

239 D8 Advance diffractometer for powder analysis at 40 kV, 30mA. The powder sample

240 was mounted in a back loading sample holder and diffraction patterns were

241 evaluated with DIFFRAC SUITE software and powder diffraction database (PDF2

242 ICCD 2000).

243

244 3   Results and Discussion

245 The compressive and flexural strength results of the mortars are given in Figures 1-

246 4. SEM images and diffraction patterns of selected mixes are shown in Figures 5-7

247 and 8-10, respectively.

248 *3.1 Compressive and flexural strength*

249

250 The results of the compression test of investigated mortars are summarized in

251 Figures 1-4. It can be seen, for sample C3 containing 3% by wt. citric acid, at 7 days

252 the compressive and flexural strength reduced to 6.22% and 26.85% of the initial

253 value (the values of R3 samples without citric acid), respectively (see Figures 1 and

254 2). The reductions in strength at this particular age and all other ages clearly indicate

255 that addition of citric acid impedes the hydration process. Although this effect on

256 strength is apparent and is observed at all curing ages, the difference in compressive

257 and flexural strength is less severe at 14 days. The compressive and flexural

258 strength of mixture C05 containing 0.5% by wt. citric acid reached 26.6MPa and

259 5.56MPa, respectively. The dissolution of alite (C_3S) and aluminate slows down

260 considerably in the presence of citric acid therefore affecting the formation of the

261 different hydration products. However this effect has a short duration since all of the

262 citric acid gets removed from the pore solution in the early stages of hydration [27].

263 This may explain why the inhibiting effect of citric acid is less severe on the

264 mechanical strength at 14 and 28 days. Also from Fig. 1 it is interesting to observe

265 that there was no change in compressive strength from 7 to 14 days in the sample

266 C1 but a subsequent steep increase in 28 day strength. The strength enhancement

267 may be attributed to a modification of the microstructures in the presence of the citric

268 acid, which resulted in denser matrices of reaction products and has been reported

269 in similar work done on the behaviour of calcium sulphoaluminate cement with citric

270 acid [25]. The opposite relationship is observed in the sample C05 which

271 demonstrated an increase in compressive and flexural strength from 7 to 14 days but

272 a reduction from 14 to 28 days. Sample C3 exhibits the same but more subtle

273 change in compressive and flexural strength. It is observed that the mechanical

274 strength of PC/CAC binders with additions of citric acid other than at 1% wt.

275 contributed to a reduction in strength from 14 to 28 days. In addition, all samples

276 made with citric acid attained flexural strengths well below the reference mortar R3
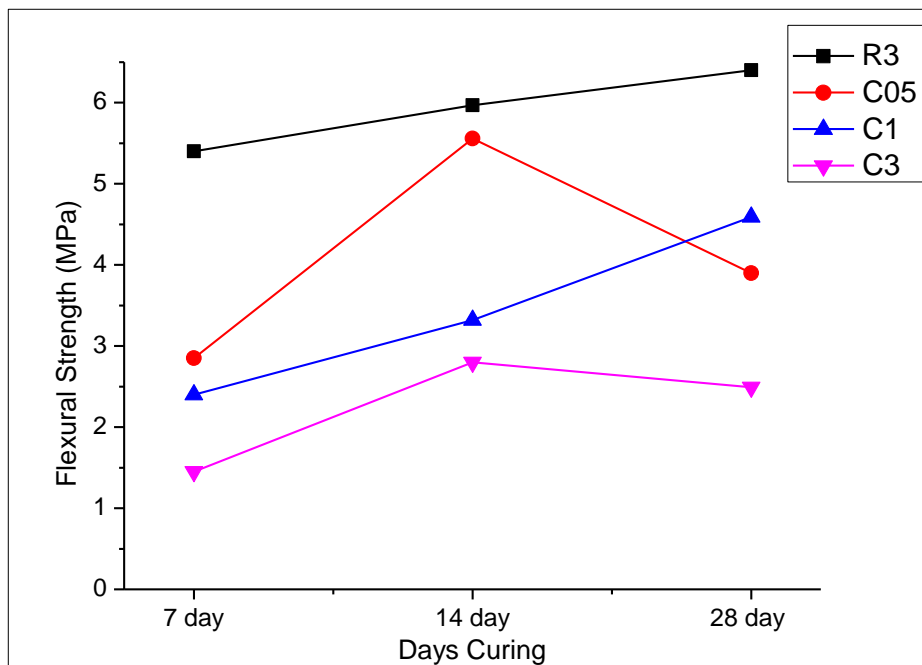
277 as shown in Figure. 2.

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279
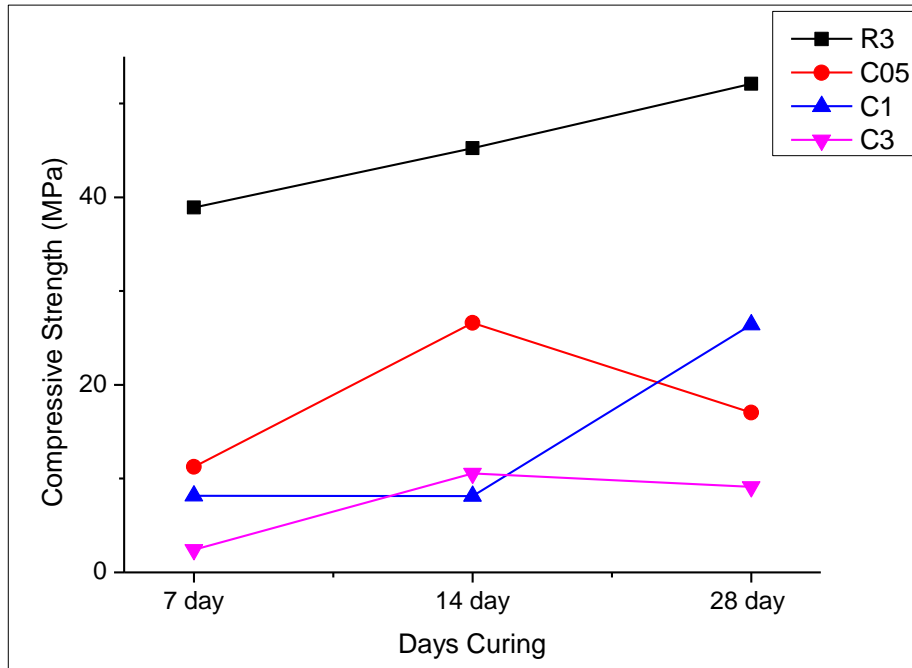
Figure 1 Influence of citric acid on compressive strength of mortar samples

281

Figure 2 Influence of citric acid on flexural strength of mortar samples

284

285 At concentration of 0.5 and 1% wt., lactic acid was able to improve the compressive

286 strength at ages 7 and 14 days, although eventually reaching the same 28 day

287 strength as the reference mix R3 without lactic acid (see Figure 3). This behaviour

288 may be attributed to the higher crystallinity of the calcium hydroxide crystals. The

289 improved crystallinity of the calcium hydroxide crystals can be seen in the SEM

290 image taken of mix L1 with 1% wt. lactic acid shown in Figure.5 (a). However an

291 increase to a 3% wt. dose of lactic acid reduces the compressive strength to below

292 that of the reference mortar R3. Although previous studies have shown that an

293 increase in lactic acid of up to 20% wt. at a water/solids ratio of 0.5 increased the

294 initial and final setting time of PC, they have not reported any improvement to

295 strength [31]. Perhaps a saturation limit exists after which the lactic acid produces a

296 hydrate which does not beneficially contribute to the strength. Another possibility is

297 that the lactic acid no longer enhances the precipitation of hydrates but instead

298 blocks it, a phenomenon exhibited by other carboxylic acids such as malic acid [22].

299 The flexural strength of mortars with additions of lactic acid remain relatively

300 unchanged throughout the 28 day curing and did not surpass the flexural strength of

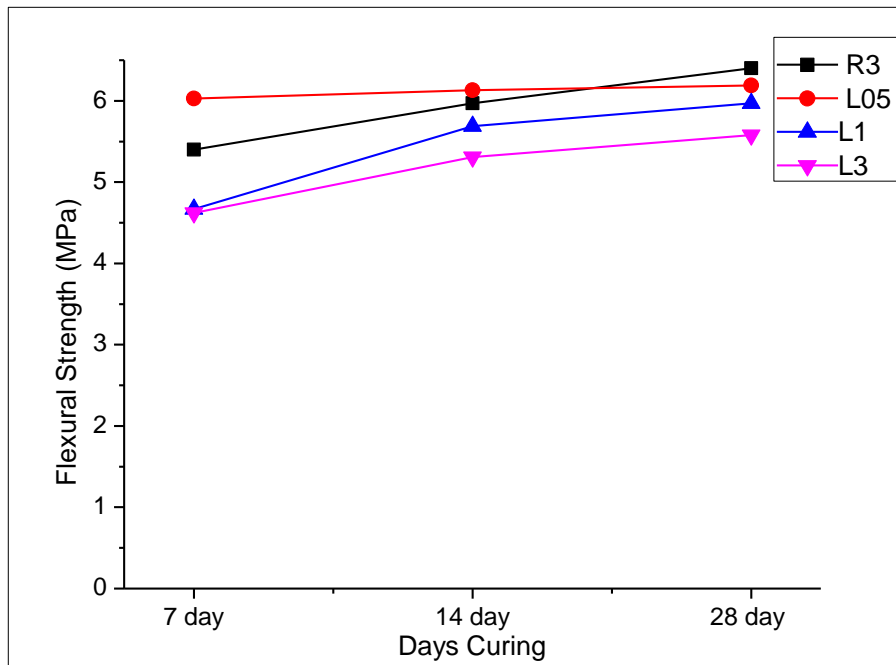301 the reference mix R3 except for the samples L05 at 7 and 14 days (see Figure 4).
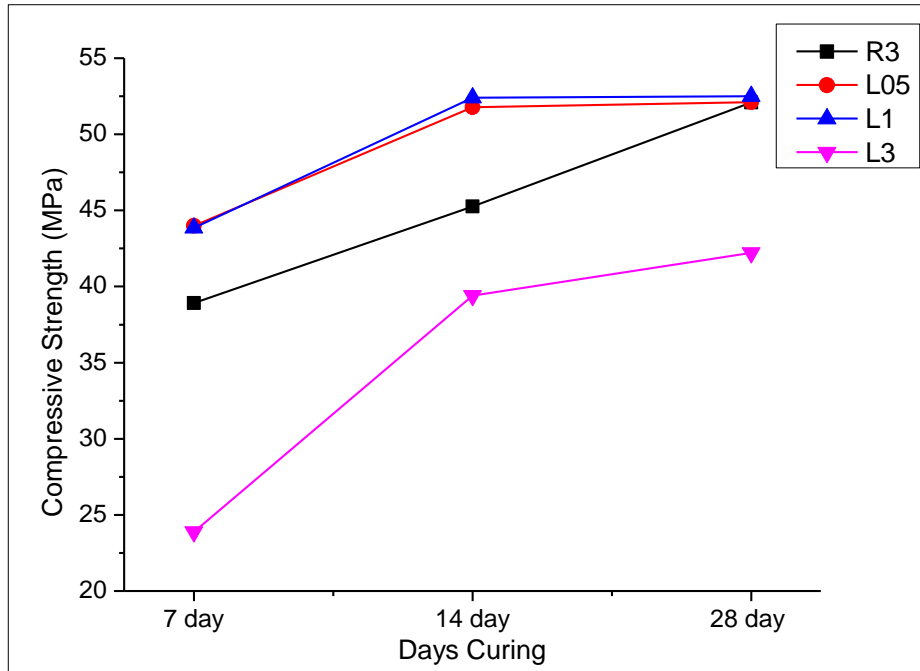
Figure 4 Influence of lactic acid on compressive strength of mortar samples

Figure 3 Influence of lactic acid on flexural strength of mortar samples

16

309   *3.2 Morphology*

310   It can be clearly seen the portlandite crystals which have formed in the R3 mix at 28

311   days shown in Fig. 5(a). The CH crystals have grown in large concentrated masses

312   in the form of clusters rather than finely dispersed particles of complex and irregular

313   shapes. Fig. 5(a) shows sample L1 containing 1% wt. lactic acid with larger

314   portlandite crystal formations which have grown on existing clusters rather than

315   precipitating new crystals in the microstructure. When increasing the addition of LA

316   to 3% by weight in sample L3, the Portlandite crystals fail to form as shown by Fig.

317   5(c). Calcium lactate salts were not observed in any of the samples with lactic acid

318   addition, contrary to what previous studies have shown [27]. These results are

319   consistent with the mechanical results presented in Figures. 3 and 4 which show the

320   sample L3 reaching lower compressive and flexural strengths respectively. In a

321   previous study using malic acid [23], a carboxylic acid from the same group as citric

322   acid and lactic acid, it was shown that very little Portlandite is also formed, indicating

323   a strong retardation of hydration in PC. This trend increased with higher

324   concentrations of malic acid. The probable cause for this, as pointed out by Rai et al.

325   [22], may be that during hydration, Portlandite can react with lactic acid evolving heat

326   of neutralisation causing the Portlandite to disappear. Furthermore the SEM image of

327   L3 in Figure 5(c) shows the mortar matrix without Portlandite crystals supporting the

328   idea that too high a dose of (>1.0%) of lactic acid obstructs the hydration of

329   Portlandite. An addition of lactic acid above 1% can be assumed to be detrimental to

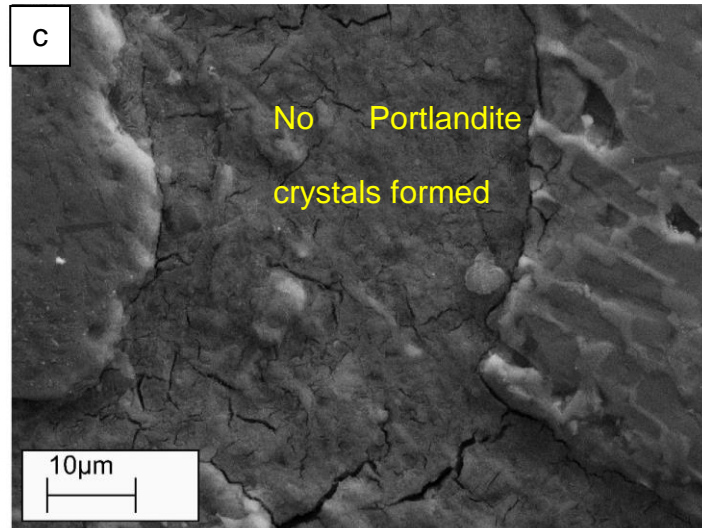330   the formation of portlandite crystals in PC/CAC cement binders.

Portlandite

crystals

10µm

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10µm

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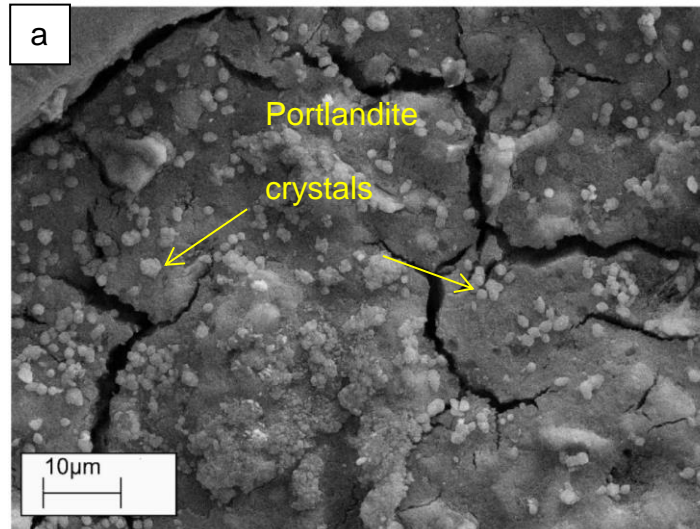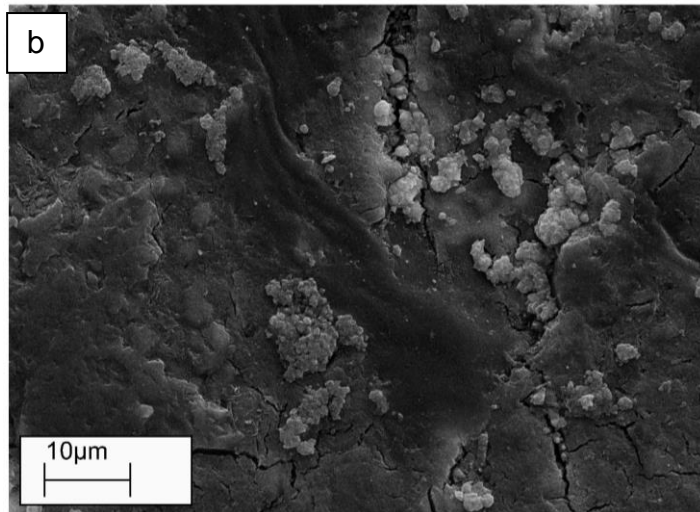
Figure 5: SEM images of (a) mix R3 (without LA) at 28 days x5k (b) mix L1 (with 1% LA) at 28 days 5k (c) mix L3 (with 3% LA) at 28 days x5k

Figure. 6 shows SEM image of the mix L1 at 28 days at a magnification of 16k in which the only hydrates visible are the Portlandite crystals with no appearance of calcium silicate hydrate. The crystal formations in sample L1 appear larger in size and more defined than for the reference sample R3 without the addition of lactic acid.
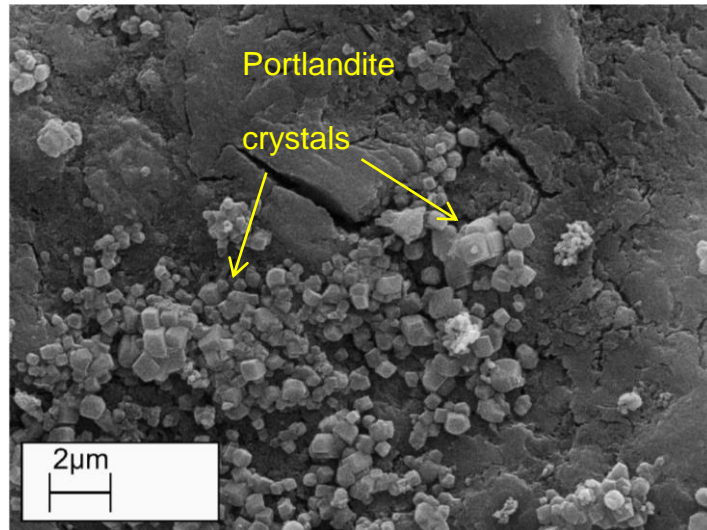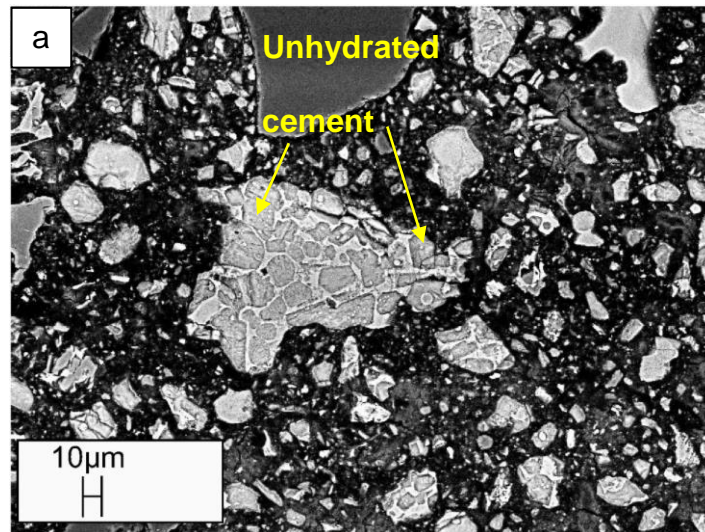
Figure 6: SEM images of mix L1 at 28 days x16k

Figure 7(a) and (b) shows backscattered images of sample C3 and L1 at 28 days respectively. It can be observed that a large quantity of unhydrated cement grains still remains present in the mortar matrix for sample C3; far more than in sample L1. Not only did the citric acid in larger quantities reduce the amount of strength inducing hydrates, but it also blocked the dissolution of existing cement grains. These observations support the strength results reported in Figures. 5-7 which indicate the L1 sample achieved in general higher flexural and compressive strength than the C3 sample and support the findings that the C3 sample reached compressive and flexural strengths far lower than the reference mix R3 and samples containing lactic acid.
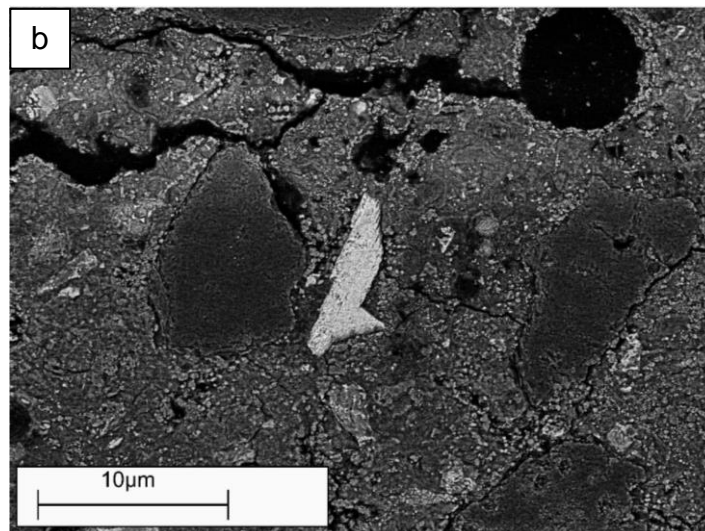
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Figure 7: (a) BS image of mix C3 at 28 days x1k (b) BS image of mix L1 at 28 days x1k

364

365 *3.3 X-ray diffraction*

366 Figure. 8 shows the diffraction patterns of R3, L1 and L3 samples with doses of 0, 1

367 and 3% lactic acid respectively. The main crystalline product found in all samples

368 was portlandite. Ettringite hydrate phase was also detected but in less pronounced

369 intensity. However after 28 days the intensity of the ettringite peaks decreased,

370 indicating that its formation reversed after the cement had hardened.
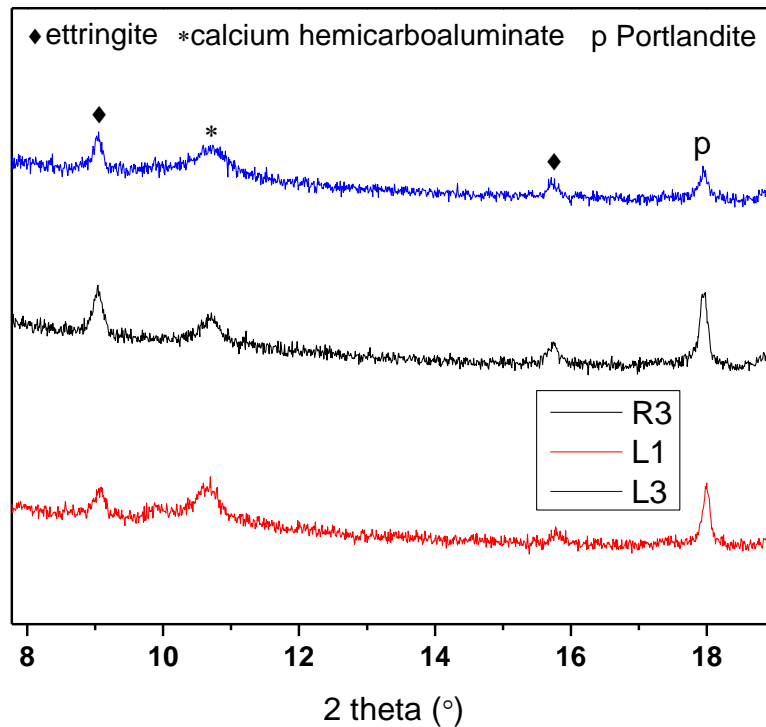
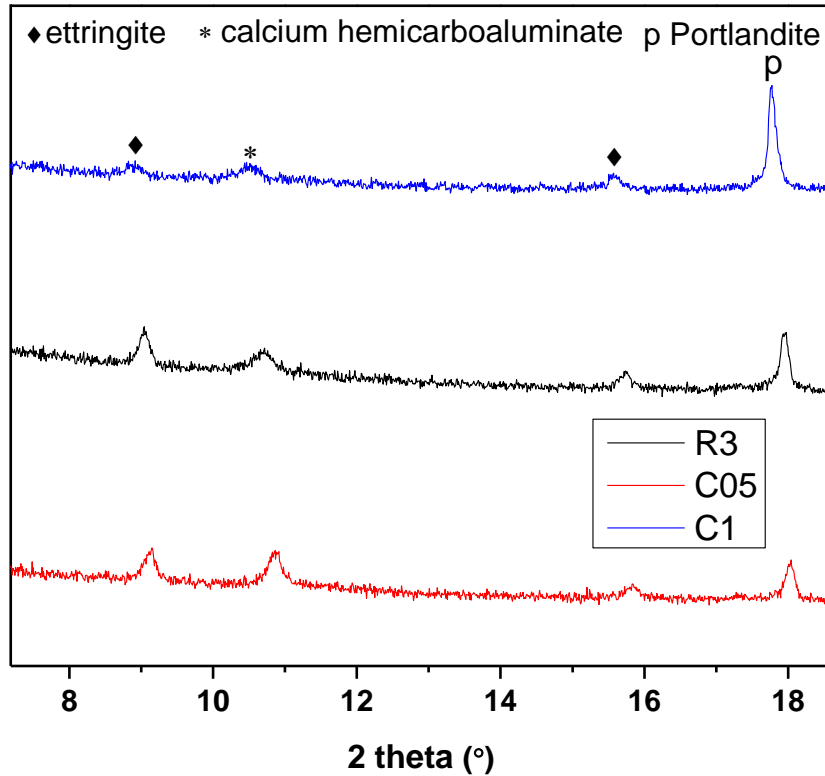**Figure 8: X ray diffraction spectrum comparing mixes R3, L1 and L3 at 28 days.**

374 The quantity of calcium sulphate added to the mortar mix influences the quantity of

375 the main hydrate phases ettringite and monosulphate that are produced so by

376 increasing amounts of calcium sulphate, more ettringite is formed [29]. No significant

377 trace of C-S-H was found in the reference sample and the addition of lactic acid did

378 not prove successful in improving this. This is the main reason why no significant

379 strength increase was measured relative to the reference mix R3 as shown in

380 strength results section. Möschner et al. [30] also observed that the formation of C-

381   S-H was retarded in the presence of citric acid and attributed this with the retardation

382   in the dissolution of C_3S in the presence of citric acid.

383   The amount of portlandite also reduced in mix L3 which can explain the reduction in

384   mechanical strength. Portlandite seemed to be the major hydrate providing strength

385   in PC/CAC cement mortar. To explain why C-S-H did not form, interactions between

386   the different phases would have to be further examined.   The diffraction patterns

387   were dominated by the peaks at 10.75° 2Θ degrees, attributed to calcium

388   hemicarboaluminate. These phases had formed when the samples were exposed to

389   CO_2 during sample preparation for the XRD analysis and most likely formed via

390   carbonation of the C_4AH_{19} [31] despite active efforts to exclude the exposure of

391   samples to CO_2. Figure. 9 shows the diffraction pattern for R3, C05 and C1

392   corresponding to samples with doses of 0, 0.5 and 1% citric acid. Mixes with

393   increased citric acid reduced in the quantity of ettringite but showed an increase in

394   portlandite crystal formation.

395

Figure 9: X ray diffraction spectrum comparing mixes R3, C05 and C1 at 28 days.

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397

398

399   Changes in the hydration phases formed did not only happen with increased

400   amounts of citric or lactic acid but also with age. Mix C05 displayed the highest

401   peaks of ettringite formation as seen from Figure.10. This increased hydrate

402   formation did reflect in the mechanical strength results and it can be observed that at

403   day 14, the compressive strength reached nearly that of the reference mix without

404   citric acid, R3. Furthermore, it can be seen from Figure.10 that mix C05 experiences

405   significant reductions in ettringite and portlandite going from 14 days to 28 days.

406   These results support the mechanical strength results from Figures. 3 and 4 which

407   also show a reduction in compressive strength from 14 to 28 days.
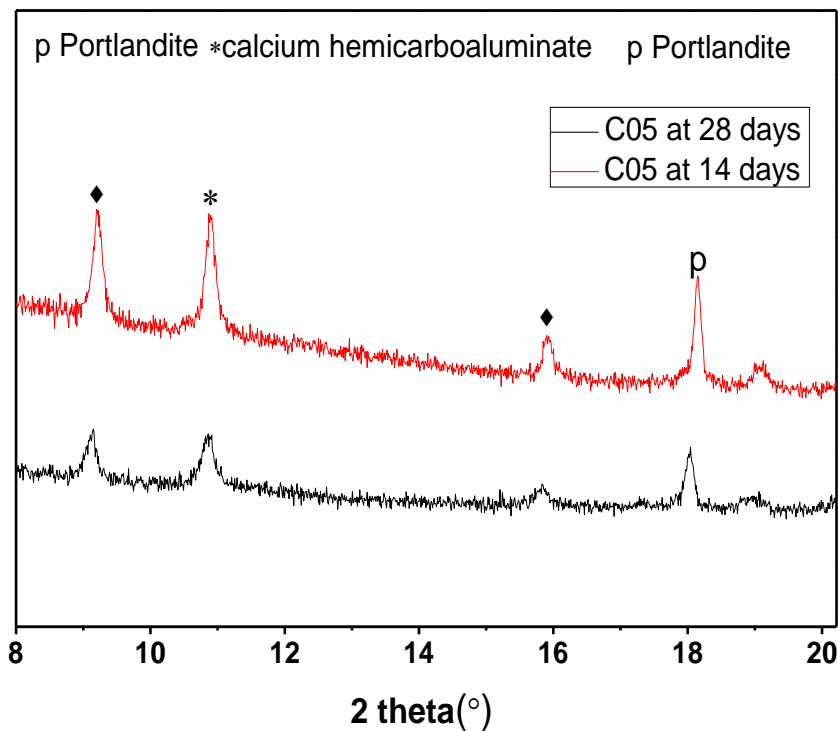
409   **Figure 10: X ray diffraction spectrum comparing mix C05 at 14 and 28 days.**

4   Conclusion

412   This research intended to uncover how citric and lactic acids, both carboxylic acids,

413   affect the strength development of PC/CAC blended cementitious binders at early

414   ages. These preliminary results show that organic admixtures, in this case of citric

415   acid, has not been effective at significantly increasing the ettringite formation but in

416   fact in higher concentrations, adversely affected strength development and

417   precipitation of C-S-H. These results however should not rule out the investigation of

418 other carboxylic acids which may, in varying quantities, assist in the hydration of

419 PC/CAC systems.

420 • The compressive and flexural strength of PC/CAC blended cement was

421 greatly reduced by the addition of citric acid. Addition of citric acid at 1% wt.

422 lead to an increase in Portlandite but at higher concentrations blocked the

423 dissolution of cement hydrates. From the three concentrations of citric acid

424 tested, 1% wt. addition was the only concentration that did not cause a

425 reduction in strength going from 14 to 28 days. Based on these findings, water

426 reducers containing citric acid would not be recommended for use with

427 PC/CAC blended cementitious materials.

428 • The addition of lactic acid in smaller amounts (0.5 and 1%) increases the

429 compressive strength by almost 20% for 7 and 14 days but left the 28-day

430 compressive strength unaffected and the 28-day flexural strength of PC/CAC

431 blended cement was not exceeded by the addition of lactic acid. However with

432 lactic acid, a reduction in Portlandite formation was observed at 3% addition.

433 Also observed was that an increase in portlandite is coupled with a decrease

434 in ettringite formation for mixes with increasing additions of lactic acid. Lactic

435 acid shows positive signs of strength enhancement at early stages and in low

436 concentrations i.e. 0.5 and 1% wt., but in higher concentrations i.e. 3% wt. is

437 responsible for initiating the consumption of Portlandite in PC/CAC binders.

438 • Contrary to the results of another study, citric acid is responsible for

439 reducing the amount of strength inducing hydrates in PC/CAC binders, but

440 also blocks the dissolution of existing cement grains up to 28 days. Also

441 the main long term strength contributing hydrate, C-S-H, remained undetected

442   for mixes with either lactic acid or citric acid at early ages up to 28 days

443   through SEM/XRD analysis.

444

445   **Acknowledgement**

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