1   Deformation and mechanical properties of the expansive cements produced by inter-grinding

2   cement clinker and MgOs with various reactivities

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12

13   Abstract

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16   Magnesia (MgO) either intrinsically contained in cement clinker or prepared separately as

17   expansive additive has been used to compensate for the shrinkage of cementitious materials.

18   In this study, for improving the homogenous distribution of MgOs, the cement clinker was

19   inter-ground with MgO expansive additives with various reactivities ranging from 50s to 400s

20   to prepare series of expansive Portland cements and blended cements with incorporation of

21   slag and fly ash. The deformations and mechanical properties of the expansive cements were

22 investigated. Results showed that the expansive cements containing more reactive MgOs

23 produced more rapid expansion under sealed condition or water curing, leading to effective

24 autogenous shrinkage compensations at early age. The reactivities of MgOs caused

25 insignificant influences on the mechanical strengths of expansive cements. The blended

26 cements had lower strengths at early age but higher strengths than that of the corresponding

27 Portland cements at late age due to the pozzolanic reaction.

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30 Keywords: MgO; mechanical strength; autogenous shrinkage; expansion

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33 1 Introduction

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36 Normally cementitious materials undergo various types of shrinkage, such as autogenous

37 shrinkage, drying shrinkage, thermal shrinkage, etc. When restrained, the shrinkage may cause

38 large enough tensile stress to crack the cementitious materials, and thus negatively affect the

39 mechanical performance and durability of the materials. Therefore, to mitigate the shrinkage

40 is of great importance for maintaining the long-term durability and safety of the cementitious

41 materials and relevant structures. Accordingly much work has been focused on this issue and

42 many strategies have been developed, e.g. development of novel curing technology, fiber

43 application, utilisation of supplementary cementing materials (SCMs), shrinkage

44 compensation, etc. [1-5].

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47 Expansion produced due to the hydration of expansive components contained in cement clinker,

48 such as calcium sulfo-aluminate, free calcium and periclase, has been widely used to

49 compensate for the shrinkage of the cementitious materials, based on which some types of

50 expansive cement were developed [6-8]. Furthermore, to well control the quantity and quality

51 of the expansive components, they were prepared separately from the manufacturing of cement

52 clinker and used as expansive additives [6-8]. Due to the fast hydration of CaO and the

53 relatively high solubility of its hydration product $Ca(OH)_2$, the application of CaO-based

54 expansive additive in normal concrete, particularly in the concrete for hydraulic structures

55 under deep water, was limited. The ettringite-based expansive additive can produce rapid

56 expansion at early age, mainly within 14 days, which has been widely used [7]. However there

57 are some challenges existing. The formation of ettringite consumes a large amount of water,

58 which may intensify the competition on the consumption of water with the hydration of cement

59 clinker [7]. Therefore in concrete with low w/c ratio or in the absence of sufficient exterior

60 water supply, the formation of ettringite may be insufficient to produce enough expansion

61 expected for the complete compensation of shrinkage. In addition, the ettringite is chemically

62 unstable when it undergoes a process with a temperature higher than 70 ºC, and thus might not

63 be used in mass concrete with high temperature rise [9].

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66 Free magnesia (MgO), known as periclase intrinsically contained in cement clinker, was used

67 to compensate for the thermal shrinkage at late age in mass dam concrete during the cooling

68 stage in China as the expansion produced by the periclase was very slow owing to its slow

69 hydration rate [6]. Owing to the advantages of MgO used as the expansive additive, e.g. the

70 relatively low water consumption for its transformation into brucite, and the chemical stability

71 and low solubility of the brucite, it has attracted increasing attention [6]. The hydration and the

72 corresponding expansion property of MgO depend on its hydration reactivity associated with

73 its microstructure, which is influenced by the high temperature history during its calcination

74 process [10]. MgO with higher reactivity may produce more rapid expansion at early age [10].

75 Accordingly, this could be used for the compensation of autogenous shrinkage at early age. Mo

76 et al. [11] demonstrated the effective compensating effects of MgO-based expansive additive

77 on the autogenous shrinkage of cement paste starting at 24h after casting, but the autogenous

78 shrinkage within 24h was not collected due to the limit of strain gauge used. Nevertheless the

79 autogenous shrinkage of cementitious materials starting from the initial setting time is very

80 dramatic at the early age, particularly within the first several hours after the setting time, due

81 to the low shrinkage resistance of the cement matrix, and thus it could not be ignored [12-13].

82 In fact, some amounts of reactive MgO may hydrate within 24h after being mixed with water

83 owing to its high hydration reactivity, and thus may have some potential to be used for

84 compensating the autogenous shrinkage at very early age. However limited work has been

85   performed on this.

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88   Two ways are usually taken to apply the MgO in reducing the shrinkage of cementitious

89   materials. One is to increase the periclase contents in cement clinker during the clinker

90   manufacturing process, which is called high magnesia cement and has been used for

91   approximately 40 years in China but mainly in dam concrete [6]. In this case, the MgO was

92   dead-burnt at the clinker temperature of $1450\,℃$, and moreover the content of MgO was limited

93   to be less than 5% by mass in order to avoid the potentially triggered unsoundness problem

94   [6,14]. Therefore the expansion property of the magnesia cement could not be adjusted flexibly

95   according to the practical engineering demands. Another way is to prepare MgO separately

96   through calcining magnesite at given temperature and then mix the MgO into concrete directly

97   as an expansive additive [6]. In terms of expansive additive, the expansion property as well as

98   the addition dosage of MgO can be well controlled. However, it is important to ensure the

99   homogenous distributions of MgO in concrete materials, which always needs special mixing

100 process, i.e. prolonging the mixing time. Otherwise, the heterogeneous expansion might be

101 caused and even lead to destruction of concrete materials.

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104 With the increasing demands on sustainability of cement materials, SCMs have been widely

105 used to prepare blended cement or directly mixed into concrete as partial substitutions of

106   Portland cement [15]. Due to the relatively slow development of strength at early age for the

107   blended cement, it may be more susceptible to shrinkage cracking. For this case, the prevention

108   of shrinkage at early age is of great importance. The influences of SCMs on the autogenous

109   shrinkage of cementitious materials depend on their pozzolanic reactivity as well as particle

110   size [16-18]. SCMs with high pozzolanic reactivity, e. g. ground slag and silica fume, were

111   reported to increase the autogenous shrinkage [17, 19], while the relatively inert materials, for

112   example the fly ash, was proved to reduce the autogenous shrinkage [18]. Combination of the

113   reactive and inert SCMs may produce the synergetic effects on the performance of blended

114   cement, obtaining high strength and meanwhile stable volume. Incorporation of MgO may also

115   contribute to the volume stability of the blended cement, but this needs to be investigated

116   further, particularly in the ternary blended cement system.

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119   This paper presents part work of our current research project that aims to develop expansive

120   cements containing MgOs with various reactivities and SCMs. In this study, four types of

121   MgO-bearing expansive cement were prepared by inter-grinding the cement clinker and MgO

122   expansive additive with different hydration reactivities. The blended cements were also

123   prepared by mixing the expansive cements with the ground granular blast furnace slag (GGBFS)

124   and fly ash. The effects of MgOs with various reactivities on the autogenous shrinkage at early

125   age under sealed condition, the long term expansion properties with sufficient water supply,

126   and the mechanical strengths of the expansive Portland cement (PC) as well as blended cement

127   were investigated. This study provides a guide for preparing series of expansive cement with

128   various expansion properties by using proper type of MgO.

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131   2 Experimental

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134   2.1 Raw materials and preparation of expansive cements

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137   Cement clinker provided by the Conch Cement Company, Jiangsu, China was used. Four types

138   of MgO expansive additive with four different reactivity values of 50s, 100s, 200s, and 400s

139   tested according to the citric acid neutralization method [10] were used, which were designated

140   as M_{50}, M_{100}, M_{200} and M_{400} respectively. The M_{50}, M_{100}, M_{200} and M_{400} contained MgO

141   contents ranging from 88.52% to 90.27% (Table 1), and had specific surface areas of 22.2, 15.1,

142   18.7 and 7.1 m^2/kg respectively tested by N_2 adsorption (BET). The cement clinker was inter-

143   ground with 8% MgO expansive additive by mass as the substitutions of the cement clinker and

144   5% gypsum by mass in a ball mill for 90 minutes to prepare expansive PCs. The four types of

145   expansive cements prepared with the M_{50}, M_{100}, M_{200}, and M_{400} were designated as PCM_{50},

146   PCM_{100}, PCM_{200} and PCM_{400} respectively. The particle size distributions of all the cements are

147   shown in Fig. 1. In order to investigate the expansion behaviour of MgOs and its implication

148   on the performance of the blended cement system, the blended cements were prepared by

149   mixing the expansive PCs with 40% GGBFS and 20% fly ash as the cement replacements.

150   According to the research results in our current project, it was showed that the blended cement

151   with that mix proportion exhibited excellent mechanical strengths at long term. These blended

152   cements made with the expansive PCs of PCM_{50}, PCM_{100}, PCM_{200} and PCM_{400} were

153   represented by BCM_{50}, BCM_{100}, BCM_{200} and BCM_{400} respectively. The GGBFS was supplied

154   by the Bao Steel Company in Shanghai, and fly ash was from Huaneng Power Plant in Nanjing,

155   China. The particle size distributions of the GGBFS and fly ash are shown in Fig. 1. Table 1

156   presents the chemical compositions of the PC clinker, slag, fly ash and MgO expansive

157   additives.

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160   2.2 Mechanical strength test

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163   To investigate the mechanical properties of cements, one part of cement was mixed with three

164   parts of sands by weight at a water to binder ratio of 0.5 to obtain homogenous mixtures, and

165   then the mixtures were cast into mould to prepare mortar specimens with size of 40mm×

166   40mm×160mm. All the mortar specimens were cured under moist condition with a relative

167   humidity of 98% and a temperature of 20±2℃. After 24±2h curing, all the specimens were

168   demoulded and continuously stored under the moist condition until the strength test at the age

169   of 3d, 28d and 90d respectively. According to the ASTM C349 [20], the flexural strength of

170   the mortar specimen was test first, and then the two portions of the fractured specimen after

171   the flexural test were used for examining the compressive strength. For each test, a mean

172   flexural strength value of three mortar specimens was used, and the compressive strength was

173   averaged on six mortar portions.

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176   2.3 Deformation examination

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179   The autogenous deformations of cement pastes were investigated according to the ASTM

180   specification C1698-09 "Standard test method for autogenous strain of cement paste and mortar"

181   [21] but with minor changes. For each type of cement, it was mixed with water at the same w/c

182   ratio of 0.38 to obtain a homogenous fresh mixture. Thereafter the cement mixture was cast

183   into corrugated low-density polyethene cylinderical mould with an outer diameter of 28.5mm

184   and a length of 440 mm. Two ends of the corrugated mould were sealed with two end plugs

185   and thus the moist exchange between the cement paste and exterior environment was avoided.

186   Immediately after the sealing, the corrugated cement pastes were then placed into the plastic

187   tube with a larger diameter of 38mm and very smooth inner wall, which produced minimal

188   friction on the free linear movement of the corrugated specimen undergoing volume

189   deformation. To precisely measure the linear deformation of cement paste, one end of the

190 corrugated mould was fixed on the table, and thus only another end of the specimen was able

191 to move freely. The intelligent laser optical displacement measurement (MICRO-EPSILON)

192 with a resolution of 0.1 μm was used to collect the displacement of the free end of specimen

193 for up to 120h. The whole preparing process of cement specimen was finished within 20

194 minutes, and then the autogenous deformation of the cement specimen can be recorded

195 immediately. The autogenous deformation of the cement paste was initialized at the initial

196 setting time. Fig. 2 shows the setup used for the autogenous shrinkage measurement. For each

197 mix, three duplicate corrugated cement specimens were prepared and measured, and the

198 average deformation of the three duplicate specimens was calculated.

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200

201 In order to investigate the deformation behaviour of MgOs in cement pastes with sufficient

202 water curing for a long term, the expansive cement pastes were prepared and cured in water for

203 up to 240d. For each mix, ten cement paste specimens with size of $20mm \times 20mm \times 80mm$

204 were prepared at a water-to-binder ratio of 0.38. The cement pastes were demoulded after being

205 cured under the moist condition for $24 \pm 2h$, and then the initial lengths of the cement pastes

206 were measured. Thereafter, half of the cement pastes were stored in water with a temperature

207 of $20 \pm 2℃$ and another half of the cement pastes were cured in $38 \pm 2℃$ water. After different

208 time intervals, the length changes of the cement pastes were measured. For each test, a mean

209 value of the five duplicate cement pastes was used.

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212 2.4 Microstructure analysis

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215 The morphology of the hydrated MgO contained in the cement paste was investigated by using

216 a FEI Nova NanoSEM 450 coupled with Bruker Energy Dispersive X-ray (EDX). In addition,

217 the cement pastes were sliced, dried, epoxy impregnated, polished and then investigated with

218 backscattered electronic microscopy.

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221 3 Results and Discussion

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224 3.1 Mechanical strength

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227 Fig. 3 shows the mechanical strengths of the cement mortars. As shown in Fig. 3(a), the

228 incorporation of MgO expansive additive had very slight influences on the flexural strength

229 regardless of its reactivity and the curing age. At 3d the flexural strengths of PC, PCM_{50},

230 PCM_{100}, PCM_{200} and PCM_{400} were 6.8, 6.6, 6.6, 7.2 and 6.6 MPa respectively. With the curing

231 age increasing to 28d, the flexural strengths of PC, PCM_{50}, PCM_{100}, PCM_{200} and PCM_{400} were

232 increased to be 8.6, 8.0, 8.4, 8.2 and 8.4 MPa respectively, and at 90d the strengths were very

233 close to that at 28d. In terms of the compressive strengths, similar increase trend was observed.

234 The incorporation of 8% MgO expansive additive caused slight reductions in the compressive

235 strengths of the cement mortars, particularly at late age. For example, the compressive strengths

236 of PCM_{50} were 34.4, 45.7 and 49.9 MPa at 3d, 28d and 90d respectively, which were lower

237 than that of the conventional PC mortars at the same ages. However the less the reactive MgO

238 expansive additive had, the slightly less the reduction in compressive strengths was caused.

239 The decreases in the mechanical strengths may attribute to the content reduction of PC due to

240 the substitution of MgO expansive additive, which thus resulted in the decrease of cement

241 hydration products.

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244 In comparison to the expansive PCs, the flexural strengths as well as the compressive strengths

245 of the blended cements containing 40% GGBFS and 20% fly ash were significantly reduced at

246 3d. For example the flexural strengths at 3d were 3.8, 3.4, 3.5, 3.2 MPa for BCM_{50}, BCM_{100},

247 BCM_{200}, and BCM_{400} respectively, being less than that of the corresponding expansive PC

248 mortars. This is related to the reduction of PC content in the blended cements due to the

249 replacements of cement with GGBFS and fly ash. However, after 28d of curing the flexural

250 and compressive strengths of the blended cement mortars were dramatically increased, being

251 very close to that of the corresponding expansive PC mortars. At 90d, the compressive

252 strengths of the blended cement mortars increased further, being slightly higher than that of the

253   corresponding expansive PC mortars and the conventional PC mortars. According to the above

254   results, it is obvious that the reactivity of MgO expansive additive caused insignificant

255   influences on the mechanical strengths in the cements during the test age in this study.

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258   3.2 Deformation behaviour

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261   Fig. 4 shows the autogenous deformations of the cement pastes. For all the cement pastes,

262   regardless of the incorporation of MgO, GGBFS and fly ash, the cement pastes underwent rapid

263   and dramatic shrinkage at early age particularly within the first 3-10h, and then the deformation

264   curves of the cement pastes reached inflexion points, starting from where the deformation

265   changed at much lower rate. For example, for the reference cement paste PC, an inflexion point

266   on the shrinkage curve occurred at approximately 8h, and thereafter the shrinkage curve

267   continued to decline but at a lower and relatively constant rate to reach -1000 microstrains at

268   the end of test. With the incorporation of MgO, the autogenous shrinkages of the cement pastes

269   were largely reduced, and moreover the time for inflexion points appearing as well as the

270   ultimate deformations of the cement pastes were changed accordingly. Cement pastes

271   containing more reactive MgO showed inflexion points on their deformation curves at earlier

272   ages and exhibited less ultimate shrinkages by the end of test. The ultimate autogenous

273   shrinkages of PCM_{50}, PCM_{100}, PCM_{200} and PCM_{400} were -180, -600, -620, and -780

microstrains respectively during this test age. Although the incorporation of MgO had not completely compensated for the whole shrinkage, it reduced the shrinking rate after the inflexion point as well as the ultimate shrinkage by the end of the test. This is attributed to the hydration of MgO and the consequently caused shrinkage compensation. This indicates that the MgO with higher reactivity compensated for more autogenous shrinkage of cement paste at early age. For instance, PCM_{50} reached the first inflexion point at around 2h with shrinkage of -107 microstrains, and thereafter the curves climbed up until 20h and then declined again to reach the shrinkage of -180 microstrains at the end of test.

For the blended cement pastes, with the incorporation of GGBFS and fly ash, the shrinkages were much less than that of the corresponding expansive PC pastes. This is related to that less cement contents were used in these blended cements. Moreover, as the water-to-binder ratio was the same, the replacement of PC with the GGBFS and fly ash contributed a dilute effect, which therefore provided more water in the sealed cement pastes and thus facilitated the hydration of MgO as well as the accordingly shrinkage compensating. As shown in Fig. 4, the cement paste BCM_{50} shrank quickly in the first several hours and reached the maximum shrinkage of -76 microstrains but thereafter the deformation curve climbed up, implying some expansion was caused due to the hydration of MgO. By the end of test, the cement paste BCM_{50} showed gentle expansion, being 220 microstrains. Similarly the deformation curves of BCM_{100}, BCM_{200} and BCM_{400} went up after their corresponding inflexion points, indicating the

295　expansion produced due to the hydration of MgO was larger than the shrinkage caused by the

296　cement hydration in the mean time. However the time for the inflexion points occurring on the

297　curves were different. The lower the reactivity of MgO expansive additive had, the longer the

298　time was needed for the inflexion points to occur. For example, the deformation curves of

299　BCM_{50}, BCM_{100}, BCM_{200}, and BCM_{400} started to climb up around 9h, 22h, 34h, and 34h

300　respectively.

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302

303　Fig. 5 shows the deformations of cement pastes cured in water at 20℃ and 38℃. As shown in

304　Fig. 5(a), all the cement pastes expanded. The cement paste PCM_{50} expanded more rapidly and

305　reached an expansion of 0.19% at the age of 70d and then expanded at lower rate, and

306　eventually ceased around 0.22% at 120d. For the cement pastes containing less reactive MgO,

307　after 70d, their expansion curves kept going up but at lower rate until the end of test at 240d.

308　PCM_{400} exhibited smaller expansion at early age compared to other cement pastes, but after

309　150d the expansion of $PCM4_{00}$ was slightly higher than that of PCM_{100} and PCM_{200}. At the age

310　of 240d the expansions of PCM_{100}, PCM_{200} and PCM_{400} were 0.195%, 0.195% and 0.21%

311　respectively, and all these cement pastes still showed slight increase trend and therefore were

312　supposed to expand further. In the blended cement, the expansions produced were smaller than

313　that generated in the corresponding PC pastes. This is understandable as in the blended cement

314　system, only 40% expansive PC was used and as a result the corresponding MgO contents were

315　reduced accordingly. Dissimilar to the expansive PC pastes, the blended cement paste prepared

316   with the most reactive MgO (BCM$_{50}$) showed the smallest expansion, being 0.075% at 70d.

317   This may due to the more amount of MgO in the M$_{50}$ had been hydrated within 24h but the

318   accordingly caused expansion was not recorded during this test. The blended cement pastes

319   BCM$_{100}$, BCM$_{200}$, and BCM$_{400}$ showed similar expansions, and slight expansion trend was also

320   observed at the late age.

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323   When cured in 38℃ water, due to the increased curing temperature, more rapid expansions

324   were caused in the expansive PC pastes as well as the blended cement pastes. This relates to

325   that the hydration of MgO was accelerated at the elevated temperature. As shown in Fig. 5(b),

326   all the expansive cement pastes expanded fast within 70d, and then the expansion curves

327   gradually leveled off. It is interesting that the PCM$_{50}$ with the highest reactivity exhibited the

328   smallest ultimate expansion, which was 0.20% at 70d. It was less than that of the PCM$_{100}$,

329   PCM$_{200}$, and PCM$_{400}$, which were 0.24%, 0.26%, and 0.26% respectively. The expansions of

330   the blended cement pastes were much less than that of the corresponding expansive PC pastes.

331   Particularly for the blended cement pastes, the BCM$_{50}$ produced the smallest expansion, being

332   around 0.04%. Comparison between the expansion properties of the cement pastes cured in 20℃

333   and 38℃ water, it indicates that the curing temperature had more significant influences on the

334   expansion of cement pastes containing MgO with lower reactivity. For instance, the expansions

335   of PCM$_{50}$ cured in 20℃ and 38℃ at 240d were 0.22% and 0.20% respectively, while that of

336   the PCM$_{400}$ were 0.17% and 0.25% respectively. This is consistent with the results in previous

337   studies, which showed that higher curing temperatures resulted in more rapid and larger

338   expansion of MgO [14] and particularly influenced more strongly on the expansion of less

339   reactive MgO [22].

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342   3.3 Morphology of the hydrated MgO in cement paste

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345   Fig. 6 shows the typical SEM morphology of the hdyrated M_{50} in the cement paste. As shown

346   in Fig. 6(a), a small particle of MgO circled by white dash elliptic line was sorrounded by the

347   cement hdyration products. Closer investigation shows that the dense inner hydration products

348   agglomerated together and however it is quite difficult to indentify very clearly the individual

349   brucite crystals (Fig. 6(b)). Fig. 6(c) shows the SEM image of M_{400} contained in the cement

350   paste, the M_{400} was also sourrounded by the cement hydration products. At high magnification

351   of ×10000, many sheet like brucites were observed, and all the brucite agglomorated tightly

352   and some of the inner pores were not filled up. As reported in the previous studies, the reactive

353   MgO has smaller inner pores while the less reactive MgO has larger inner pores which was

354   more difficult to be filled up due to the localized formation of brucite [10]. Fig. 7 shows the

355   typical BSE image of the blended cement paste. Accordingly there are obivous pozzolanic

356   reaction rims formed around the coarse GGBFS particles and some tiny particles of GGBFS

357   were hydrated completely.

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360   3.4 Discussion

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363   For the expansive cements containing MgO, the total deformation of cement paste depended

364   on the competitive effects between the volume shrinkage produced due to the hydration of

365   cement as well as SCMs and the expansion generated by the hydration of MgO. At given curing

366   age, when the expansion produced in cement matrix due to the hydration of MgO was larger

367   than the shrinkage induced by cement hydration in the meantime, the overall deformation

368   would be expansion and thus the deformation curves went up, and vise versa. MgO with low

369   reactivity reacted relatively slowly and correspondingly produced insufficient expansion to

370   completely compensate the shrinkage caused in the mean time. At early age, owing to the low

371   resistance of cement matrix, the autogenous shrinkage of cement paste is dramatic [12].

372   Therefore in order to compensate for the autogenous shrinkage at early age, reactive MgO

373   should be used as it hydrates relatively fast to produce enough expansion. Accordingly the

374   reactivity of MgO had strong influence on compensating for the autogenous shrinkage

375   particularly at early age.

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377

378   Althought the water consumption for MgO hydration is relative low, being 0.45, there is still

379   an competition on water consumption between the hydration of cement and MgO, particularly

380   under the sealed condition during the autogenous shrinkage test. For the blended cements, as

381   the pozzolanic reaction at early age was ignorable due to its extremely slow hydration process,

382   more water was provided for the hydration of cement clinker and MgO. This facilitated the

383   hydration of MgO and the corresponding compensation effects. In addition, only 40% PC was

384   used in the blended cement, which reduced the hydration products of cement, and accordingly

385   reduced the autogenous shrinkage. Thus the blended cement pastes showed less autogenous

386   shrinkages than the PC pastes. For example, PCM_{50} showed autogenous shrinkage whereas the

387   BCM_{50} produced gentle expansion in stead of shrinkage. Cured in water, with the sufficient

388   water supply for the hdyration of MgO, expansions were produced for all the cement pastes

389   regardless of the hydration reactivity of MgO. The expansions caused by MgO expansive

390   additives with various reactivities between 100s and 400s were very similar. This may relate

391   to the fine particles and homogenous distributions of MgOs. During the intergrinding process,

392   the MgO particles were ground into small particles (as shown in Fig. 6) and homogenously

393   distributed in the cement. This leaded to less expansion pariculary for the less reactive MgO

394   [14, 23].

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397   Curing temperature had influences on the expansion properties of the expansive cement pastes.

398   This is related to the hydration process of MgO, the elevated temperature accelerated the

399   hydration of MgO and therefore speeded up the expansion process. Besides the expansion rate,

400   the temperature affected the ultimate expansion of the cement paste. The less reactive MgO

401   may produce more ultimate expansion. This may because, as reported by Chatterji [24], the

402   MgO hydrated faster and produced more Mg^{2+} near the surface of MgO in a short time at higher

403   temperatures, which results in larger supersaturations and thus increased crystal growth

404   pressure.

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407   The incorporation of 8% MgO expansive additive reduced slightly the flexural strengths and

408   compressive strengths, which is mainly due to the reduction of cement content in the mortars.

409   In the blended cement pastes, the pozzonlanic reaction of GGBFS as well as fly ash contributed

410   to the strength increase. This is related to not only the densification as a result of pozzolanic

411   reaction but also the enhanced interface between the SCMs and the cement hydration products

412   [25]. According to this study, the expansive PC could be mixed with SCMs to prepare blended

413   cements with non-shrinakge and meanwhile maintained high mechanical strengths. In addition,

414   not only the hydration reactivity of MgO but also the mixed contents of MgO as well as SCMs

415   will influence the expansion behavior and mechanical strengths of cements, which are also

416   being investigated in our study.

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419   4 Conclusions

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Expansive cements were prepared by inter-grinding the cement clinker and MgOs with different reactivities. The influence of the reactivity of MgO on the deformation behaviour including the autogenous shrinkage at very early age as well as the long-term expansion property with sufficient water supply, mechanical performance, and the microstructure of the expansive cement were investigated. Main conclusions can be drawn as follows:

(i) In comparison to the conventional PC, by incorporating with MgO, the autogenous shrinkage of expansive PC paste at early age could be effectively compensated for. The higher reactivity the MgO had, the more the autogenous shrinkage of cement paste was reduced. This is due to that the reactive MgO hydrated more rapidly and thus produced more expansion at early age to offset the shrinkage of cement paste.

(ii) With the addition of GGBFS and fly ash, the autogenous shrinkages of the blended cement pastes were much less than the corresponding expansive PCs. This may not only attribute to the replacement of PC with the SCMs but also relate to the compensation effect of MgO. In the blended cement system under the sealed condition, more water was supplied owing to the dilution effects of SCMs, and thus facilitated the hydration of MgO and produced more expansion to compensate for the autogenous shrinkage accordingly. For example, PCM_{50} exhibited an autogenous shrinkage of -180 microstrains while BCM_{50} showed an expansion of 220 microstrains at the end of test (115h).

(iii) Under moist curing condition, with sufficient supply of water, all the expansive cements regardless of the incorporation of SCMs produced obvious expansions. By curing in 20℃

442 water, MgO with a high reactivity value of 50s reached an ultimate expansion at age of around

443 90d, whereas the cement pastes containing less reactive MgOs still showed gentle expansion

444 trend by the end of test in this study. However, at higher temperature of 38℃, all the cement

445 pastes expanded more rapidly and the expansion curves ceased at around 90d. Accordingly the

446 elevated temperature accelerated the hydration of MgO effectively and thus the expansion

447 ceased at earlier time.

448 (iv) Incorporation of 8% MgO expansive additive reduced slightly the mechanical strengths of

449 cement mortars. The blended cement pastes had lower strengths than that of the corresponding

450 expansive PCs at early age of 3d, but at late ages of 28d and 90d the mechanical strengths of

451 the blended cement mortars were higher than that of the corresponding expansive PC mortars

452 as well as that of the conventional PC mortars. The reactivity of MgO showed insignificant

453 influences on the strengths of cement mortars.

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456 According to the results in this study, series of expansive cement could be prepared with MgOs

457 of various reactivities. The expansion behaviour could be adjusted by changing not only the

458 reactivities of MgOs but also the incorporation contents. This is now being further studied in

459 our research.

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462 Acknowledgement

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475   References

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540   TABLES

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543   Table 1 Chemical compositions of PC clinker, GGBFS, fly ash and MgO expansive

544   additive

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547 Table 1 - Chemical compositions of PC clinker, GGBFS, fly ash and MgO expansive

548 additive

Type	Chemical compositions /%								
	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	Loss
Cement clinker	21.18	3.76	5.36	63.47	1.13	1.05	0.13	2.16	1.61
GGBFS	34.65	0.25	14.54	39.84	7.10	0.35	0.38	-	0.00
Fly ash	49.77	15.09	20.50	5.39	1.42	1.16	0.69	2.03	2.01
M_{50}	2.76	0.26	0.42	3.18	88.52	0.03	0.06	0.61	3.62
M_{100}	2.46	0.29	0.43	3.15	90.02	0.02	0.05	0.68	2.54
M_{200}	3.98	0.30	0.40	3.01	89.32	0.01	0.04	0.63	2.04
M_{400}	2.75	0.33	0.38	2.92	90.27	0.02	0.04	0.65	2.64

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552 FIGURES

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555 Fig. 1 Particle size distributions of PCs, GGBFS and fly ash

556 Fig. 2 Setup for the autogenous shrinkage measurement

557 Fig. 3 Mechanical strengths of the cement mortars: (a) flexural strength and (b) compressive

558   strength

559   Fig. 4 Autogenous deformations of the cement pastes

560   Fig. 5 Expansions of the cement pastes cured in water: (a) 20℃ and (b) 38℃

561   Fig. 6 Typical SEM morphology of the hydrated MgOs with different reactivities: (a) M_{50} in

562   PCM_{50} (38℃, 90d), (b) closer observation at Zone A in (a) at higher magnification of ×10000,

563   (c) M_{400} in PCM_{400} (38℃, 90d), and (d) closer observation at Zone A in (c) at higher

564   magnification of ×10000

565   Fig. 7 Typical BSEM of the hydrated blended cement pastes (BCM_{400}, cured in 38℃ water,

566   90d)

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