

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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5 Liwu Mo^{1,2*}, Meng Liu¹, Abir Al-Tabbaa², Min Deng^{1,3}

6 1. College of Materials Science and Engineering, Nanjing Tech University, Nanjing, China.

7 210009

8 2. Department of Engineering, University of Cambridge, Cambridge, UK. CB2 1PZ.

9 3. State Key Laboratory of Materials-Oriented Chemical Engineering, Nanjing, China. 210009

10 * Corresponding author: Email: andymoliwu@njtech.edu.cn, Tel. (86) 025 83587218

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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 °C, and thus might not
63 be used in mass concrete with high temperature rise [9].

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Free magnesia (MgO), known as periclase intrinsically contained in cement clinker, was used to compensate for the thermal shrinkage at late age in mass dam concrete during the cooling stage in China as the expansion produced by the periclase was very slow owing to its slow hydration rate [6]. Owing to the advantages of MgO used as the expansive additive, e.g. the relatively low water consumption for its transformation into brucite, and the chemical stability and low solubility of the brucite, it has attracted increasing attention [6]. The hydration and the corresponding expansion property of MgO depend on its hydration reactivity associated with its microstructure, which is influenced by the high temperature history during its calcination process [10]. MgO with higher reactivity may produce more rapid expansion at early age [10]. Accordingly, this could be used for the compensation of autogenous shrinkage at early age. Mo et al. [11] demonstrated the effective compensating effects of MgO-based expansive additive on the autogenous shrinkage of cement paste starting at 24h after casting, but the autogenous shrinkage within 24h was not collected due to the limit of strain gauge used. Nevertheless the autogenous shrinkage of cementitious materials starting from the initial setting time is very dramatic at the early age, particularly within the first several hours after the setting time, due to the low shrinkage resistance of the cement matrix, and thus it could not be ignored [12-13]. In fact, some amounts of reactive MgO may hydrate within 24h after being mixed with water owing to its high hydration reactivity, and thus may have some potential to be used for 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°C, 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 M₅₀, M₁₀₀, M₂₀₀ and M₄₀₀ respectively. The M₅₀, M₁₀₀, M₂₀₀ and M₄₀₀ 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 m²/kg respectively tested by N₂ 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 M₅₀, M₁₀₀, M₂₀₀, and M₄₀₀ were designated as PCM₅₀,
146 PCM₁₀₀, PCM₂₀₀ and PCM₄₀₀ 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 PCM₅₀, PCM₁₀₀, PCM₂₀₀ and PCM₄₀₀ were
153 represented by BCM₅₀, BCM₁₀₀, BCM₂₀₀ and BCM₄₀₀ 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°C. 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 cylindrical 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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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 $20\text{mm} \times 20\text{mm} \times 80\text{mm}$
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 $24 \pm 2\text{h}$, 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 $20 \pm 2^\circ\text{C}$ and another half of the cement pastes were cured in $38 \pm 2^\circ\text{C}$ 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, PCM₅₀,
230 PCM₁₀₀, PCM₂₀₀ and PCM₄₀₀ 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, PCM₅₀, PCM₁₀₀, PCM₂₀₀ and PCM₄₀₀ 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 PCM₅₀ 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 BCM₅₀, BCM₁₀₀,
247 BCM₂₀₀, and BCM₄₀₀ 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 PCM₅₀, PCM₁₀₀, PCM₂₀₀ and PCM₄₀₀ were -180, -600, -620, and -780

274 microstrains respectively during this test age. Although the incorporation of MgO had not
275 completely compensated for the whole shrinkage, it reduced the shrinking rate after the
276 inflexion point as well as the ultimate shrinkage by the end of the test. This is attributed to the
277 hydration of MgO and the consequently caused shrinkage compensation. This indicates that
278 the MgO with higher reactivity compensated for more autogenous shrinkage of cement paste
279 at early age. For instance, PCM₅₀ reached the first inflexion point at around 2h with shrinkage
280 of -107 microstrains, and thereafter the curves climbed up until 20h and then declined again to
281 reach the shrinkage of -180 microstrains at the end of test.

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284 For the blended cement pastes, with the incorporation of GGBFS and fly ash, the shrinkages
285 were much less than that of the corresponding expansive PC pastes. This is related to that less
286 cement contents were used in these blended cements. Moreover, as the water-to-binder ratio
287 was the same, the replacement of PC with the GGBFS and fly ash contributed a dilute effect,
288 which therefore provided more water in the sealed cement pastes and thus facilitated the
289 hydration of MgO as well as the accordingly shrinkage compensating. As shown in Fig. 4, the
290 cement paste BCM₅₀ shrank quickly in the first several hours and reached the maximum
291 shrinkage of -76 microstrains but thereafter the deformation curve climbed up, implying some
292 expansion was caused due to the hydration of MgO. By the end of test, the cement paste BCM₅₀
293 showed gentle expansion, being 220 microstrains. Similarly the deformation curves of BCM₁₀₀,
294 BCM₂₀₀ and BCM₄₀₀ 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 BCM₅₀, BCM₁₀₀, BCM₂₀₀, and BCM₄₀₀ started to climb up around 9h, 22h, 34h, and 34h
300 respectively.

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303 Fig. 5 shows the deformations of cement pastes cured in water at 20°C and 38°C. As shown in
304 Fig. 5(a), all the cement pastes expanded. The cement paste PCM₅₀ 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 PCM₄₀₀ exhibited smaller expansion at early age compared to other cement pastes, but after
309 150d the expansion of PCM₄₀₀ was slightly higher than that of PCM₁₀₀ and PCM₂₀₀. At the age
310 of 240d the expansions of PCM₁₀₀, PCM₂₀₀ and PCM₄₀₀ 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 (BCM₅₀) showed the smallest expansion, being 0.075% at 70d.
317 This may due to the more amount of MgO in the M₅₀ had been hydrated within 24h but the
318 accordingly caused expansion was not recorded during this test. The blended cement pastes
319 BCM₁₀₀, BCM₂₀₀, and BCM₄₀₀ showed similar expansions, and slight expansion trend was also
320 observed at the late age.

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323 When cured in 38°C 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 PCM₅₀ with the highest reactivity exhibited the
328 smallest ultimate expansion, which was 0.20% at 70d. It was less than that of the PCM₁₀₀,
329 PCM₂₀₀, and PCM₄₀₀, 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 BCM₅₀ produced the smallest expansion, being
332 around 0.04%. Comparison between the expansion properties of the cement pastes cured in 20°C
333 and 38°C 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 PCM₅₀ cured in 20°C and 38°C at 240d were 0.22% and 0.20% respectively, while that of
336 the PCM₄₀₀ 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 hydrated 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 surrounded by the
347 cement hydration products. Closer investigation shows that the dense inner hydration products
348 agglomerated together and however it is quite difficult to identify 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 surrounded by the cement hydration products. At high magnification
351 of $\times 10000$, many sheet like brucites were observed, and all the brucite agglomerated 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 obvious pozzolanic
356 reaction rims formed around the coarse GGBFS particles and some tiny particles of GGBFS
357 were hydrated completely.

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3.4 Discussion

For the expansive cements containing MgO, the total deformation of cement paste depended on the competitive effects between the volume shrinkage produced due to the hydration of cement as well as SCMs and the expansion generated by the hydration of MgO. At given curing age, when the expansion produced in cement matrix due to the hydration of MgO was larger than the shrinkage induced by cement hydration in the meantime, the overall deformation would be expansion and thus the deformation curves went up, and vice versa. MgO with low reactivity reacted relatively slowly and correspondingly produced insufficient expansion to completely compensate the shrinkage caused in the mean time. At early age, owing to the low resistance of cement matrix, the autogenous shrinkage of cement paste is dramatic [12]. Therefore in order to compensate for the autogenous shrinkage at early age, reactive MgO should be used as it hydrates relatively fast to produce enough expansion. Accordingly the reactivity of MgO had strong influence on compensating for the autogenous shrinkage particularly at early age.

Although 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, PCM₅₀ showed autogenous shrinkage whereas the
387 BCM₅₀ 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 leded to less expansion paricularly 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 be 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 pozzolanic 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-shrinkage 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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422 Expansive cements were prepared by inter-grinding the cement clinker and MgOs with
423 different reactivities. The influence of the reactivity of MgO on the deformation behaviour
424 including the autogenous shrinkage at very early age as well as the long-term expansion
425 property with sufficient water supply, mechanical performance, and the microstructure of the
426 expansive cement were investigated. Main conclusions can be drawn as follows:

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

432 (ii) With the addition of GGBFS and fly ash, the autogenous shrinkages of the blended cement
433 pastes were much less than the corresponding expansive PCs. This may not only attribute to
434 the replacement of PC with the SCMs but also relate to the compensation effect of MgO. In the
435 blended cement system under the sealed condition, more water was supplied owing to the
436 dilution effects of SCMs, and thus facilitated the hydration of MgO and produced more
437 expansion to compensate for the autogenous shrinkage accordingly. For example, PCM₅₀
438 exhibited an autogenous shrinkage of -180 microstrains while BCM₅₀ showed an expansion of
439 220 microstrains at the end of test (115h).

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

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°C, 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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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 ₂ O ₃	Al ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	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°C and (b) 38°C

561 Fig. 6 Typical SEM morphology of the hydrated MgOs with different reactivities: (a) M₅₀ in

562 PCM₅₀ (38°C, 90d), (b) closer observation at Zone A in (a) at higher magnification of ×10000,

563 (c) M₄₀₀ in PCM₄₀₀ (38°C, 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 (BCM₄₀₀, cured in 38°C water,

566 90d)

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