- 1 Deformation and mechanical properties of quaternary blended cements containing ground
- 2 granulated blast furnace slag, fly ash and magnesia

3

- 4 Liwu Mo^{1,2}*, Meng Liu¹, Abir Al-Tabbaa², Min Deng^{1,3}, Wai Yuk Lau²
- 5 1. College of Materials Science and Engineering, Nanjing Tech University, Nanjing, China.
- 6 210009
- 7 2. Department of Engineering, University of Cambridge, Cambridge, UK. CB2 1PZ.
- 8 3.State Key Laboratory of Materials-Oriented Chemical Engineering, Nanjing, China. 210009
- *: Corresponding author. Email: andymoliwu@njtech.edu.cn, Tel.: (86) 025 83587218

12

11

9

13 Abstract

15

14

Shrinkages of cementitious materials may lead to cracking under restrained conditions. This study
was motivated to develop non-shrinkage quaternary blended cements through blending slag and
fly ash with Portland cement containing reactive MgO. The hydration process, autogenous
shrinkage at early age, long-term volume deformation, mechanical properties, and microstructure
of cement specimens were investigated. Results showed that the autogenous shrinkage of the
cement pastes was effectively mitigated due to the compensation of the MgO present and the

reduction of cement content owing to the partial replacements with slag and fly ash. The
mechanical strengths of the blended cement mortars were lower than that of the corresponding
plain Portland cement mortars at early age of 3d, but increased significantly to be similar or
higher at late ages of 28d and 90d. This is attributed to the microstructure densification and the
interface microstructure enhancement due to the reaction of SCMs with clinker phases.

29 Keywords: A Calorimetry; B Microstructure; C Mechanical Properties; C Shrinkage; D Blended

30 Cement

33 1. Introduction

Cement-based materials normally undergo various types of volumetric shrinkage, such as autogenous shrinkage, drying shrinkage, thermal shrinkage, to name a few. Under restrained conditions, the volumetric shrinkage could induce tensile stress and may in turn lead to cracking. Autogenous shrinkage, which is caused by the self-desiccation of cement materials [1], normally contributes significantly to the total shrinkage occurring at early age when the cement materials are still of low strength and therefore have a high risk of shrinkage cracking. Many strategies have been developed to mitigate this autogenous shrinkage, e.g. inner curing, substitutions of

Portland cement (PC) with supplementary cementitious materials (SCMs) [2-5].

44

43

45

46

47

48

49

50

51

52

53

54

55

56

57

58

Expansion provided by the hydration of expansive components, e.g. calcium aluminate (C₃A), calcium sulfate aluminate (CSA), calcium oxide (CaO), and magnesia (MgO), was also widely used to compensate for the shrinkage of cement-based materials [6-8]. For decades, delayed expansive cement containing MgO was used in China for compensating the thermal shrinkage of mass dam concrete, in which the MgO was normally formed as dead burnt periclase at high calcining temperature of up to 1450°C [6]. However, hydration of the dead burnt periclase is very slow, and hence has no effect on compensating the shrinkage of concrete at early age. Moreover, the content of MgO in PC was limited to avoid unsoundness [6, 8]. To control the MgO content and reactivity, the MgO was separately prepared and used as expansive additive in the cement. In recent years, increasing attentions were attracted on the hydration and expansion properties of MgO with relatively high reactivity as it has important potential application in normal concrete [6]. However, much of this research focused on the expansion properties of MgO in cement-based materials cured in water, while limited work was carried out on their effects on compensating the

60

59

autogenous shrinkage at very early age.

61

62

63

With increasing emphasis on sustainability, SCMs have been widely used as replacements of PC to prepare blended cements [9-14]. The influence of SCMs on the shrinkage and mechanical

strengths of cement materials depends on the replacement levels and the pozzolanic reactivity of the SCMs used [15-21]. It is conceivable that the combined incorporation of SCMs with low and high reactivity at the same time, e.g. slag and fly ash, in a blended cement system may give rise to synergetic effects on the properties of blended cement materials, such as improving the mechanical strength [22-23], resisting sulfate attack and suppressing ASR [24-26].

For the blended cements with high substitution levels of SCMs, the strength at early age may be low and develop slowly, thus it may have low resistance to the tensile stress generated by autogenous shrinkage. Therefore it is of great importance to mitigate the autogenous shrinkage of such blended cements at early age. The present study was motivated to develop quaternary blended cements with stable volume as well as high mechanical strength via mixing the expansive PC, containing relatively reactive MgO-base expansive agent (MEA), with slag and fly ash. The hydration behaviour, deformations under sealed condition (autogenous deformation) starting at early age and under moist curing conditions for long-term, mechanical strength, and microstructures of the blended cement mortars were investigated. Moreover, the implications of SCMs as well as MgO on the mechanical strengths and deformation behaviour of the blended cements were analysed. The research will provide a new approach to preparing non-shrinkage blended cement that may have important application potential.

85 2 Experimental

86

87

2.1 Raw materials and preparation of blended cements

88

89

90

91

92

93

94

95

96

97

98

99

100

101

102

103

104

105

Cement clinker, provided by the Conch Cement Company, Jiangsu, China, was used. Two types of SCMs, namely slag and fly ash, were used for preparing the blended cements. The slag was supplied by the Bao Steel Company in Shanghai and class I fly ash according to the fly ash code in China [27] was from Huaneng Power Plant in Nanjing, China. The MEA had a specific surface area of 22.2 m²/kg and a reactivity value of 50s according to the citric acid test [28]. Table 1 presents the chemical compositions of the cement clinker, slag, fly ash and MEA. The conventional PC was prepared by inter-grinding the cement with 5% of gypsum by mass in a ball mill. In addition, two types of expansive PC were prepared, in which 5% and 8% of the MEA by mass were added as replacements of the cement clinker during the inter-grinding process, which are designated as EPCI and EPCII respectively. The particle size distributions (PSD) of the processed three types of PC, slag, and fly ash were measured with a Marlven Mastersizer 2000 particle size analyzer by dispersing the particles in alcohol, which are shown in Fig. 1. The PSD of cement plays an important role in the performance of cement-based materials, particularly at early age [29]. As reported by Zhang et al. [30], finer cement with a coarser fly ash improved the early-age strength and also maintained a good performance at later age in blended cement mixtures.

106	
107	
108	For the preparation of quaternary blended cements, three types of PC were replaced partially with
109	slag and fly ash and then inter-mixed together in a powder mixer. Two levels of slag, 20% and
110	40%, as well as two levels of fly ash, 20% and 35%, by mass were used as the substitutions of
111	EPCII to prepare the blended cements. For comparison, another two blended cements containing
112	40% of slag and 20% of fly ash as replacements of the PC and EPCI were also prepared. The mix
113	proportions of these blended cements are shown in Table 2. The mixes in this study were
114	designated as follows: the letters S and F stand for slag and fly ash respectively, e.g. mix
115	PC-S40F20 represents the blended cement containing 40% slag and 20% fly ash as replacements
116	of PC.
117	
118	
119	2.2 Test procedure
120	
121	
122	2.2.1 Isothermal calorimetry
123	
124	
125	The hydration heat release of PC and the blended cements within the first 72h was measured, on
126	4g samples, immediately after mixing with water at a water-to-binder (w/b) ratio of 0.38 by using

a Tam Air Calorimeter following the external mixing procedure (Method B) described in ASTM C1702-09 [31]. The cement was placed in a calorimeter specimen tube, and then the water was injected into the tube by using a syringe with an attached needle penetrating the dry cement powder. Consequently the tube was agitated by hand to distribute the water evenly throughout the cement powder.

2.2.2 Deformation measurement

For each cement formulation, it was mixed with water at the same w/b ratio of 0.38 in a cement paste mixer (Type NJ-160A, Shanghai Luheng Co. Ltd, China.). The cement and water were mixed firstly for 120s with a mixing blade rotation speed of 140 rpm and then for another 120s at a high blade rotation speed of 285 rpm to obtain a homogenous fresh cement mixture. Thereafter the cement mixture was cast into corrugated low-density polythene molds with an outer diameter of 28.5mm and a length of 440 mm according to the experimental procedure described in reference [32]. Two ends of the corrugated polythene molds were sealed with two plugs to avoid any moist exchange between the cement paste and the exterior environment. Immediately after the sealing, the corrugated cement specimens were placed into plastic tubes with larger diameter of 38mm and very smooth inner wall, which resulted in minimal friction on the free linear movement of corrugated specimens as a result of volume deformation. To precisely measure the

linear deformation of the cement pastes, one end of the corrugated mold was fixed on the table, and thus only the other end of the specimen was able to move freely. The laser optical displacement measurer supplied by MICRO-EPSILON with a resolution of 0.1 µm was used to measure the displacement of the end of the corrugated cement specimen after being placed into the plastic tube. The whole preparation process of the corrugated cement specimens including mixing with water, casting, sealing, and placing in the plastic tubes was finished within 20 minutes, and thereafter the deformation of the cement specimens could be recorded immediately. The autogenous deformation was initialized at the initial setting time. For each mix, three corrugated cement specimens were prepared and measured. The mean deformation value of the three specimens was used, and the corresponding coefficients of variation for the deformation ranged from 2.5% to 9.3%.

To investigate the deformation behaviour of the PC and blended cements cured in moist condition for long term, the aforementioned fresh cement mixtures were cast into molds to prepare prism cement pastes with size of 20mm×20mm×80mm. After 24h curing in moist room at a temperature of 20±2°C and a relative humidity of 98%, all the cement paste specimens were demoulded, and then their initial lengths were tested. Subsequently the cement pastes were cured in water at 20°C, and the length changes of all the cement pastes were measured at different intervals. Each length change value used was the mean value of five replicate specimens.

169

2.2.3 Mechanical strength

171

170

172

175

176

177

178

179

180

The flexural and compressive strengths of the cement mortars were measured according to the standard of ASTM C349 [33] but with some minor revisions. For each type of cement, mortar

prisms with size of 40mm×40mm×160mm were prepared. The mortar consisted of 1 part cement

and 3 parts standard sands by weight, and a w/b ratio of 0.5 was used. After three different ages of

curing, namely 3d, 28d and 90d, the flexural strengths as well as compressive strengths were

examined respectively. The flexural strengths of the mortars were first measured and then both of

the two portions of prisms broken in the flexural strength test were used for the compressive

strength test. For each test, three of the flexural strengths and six of the compressive strengths

were averaged.

182

183

184

185

2.2.4 Microstructure analysis

186

187

188

189

The pore structure of the mortar specimens was examined by using Mercury Intrusion

Porosimetry (MIP). The morphology of the blended cement pastes was investigated with a FEI

Nova NanoSEM 450 coupled with Bruker Energy Dispersive X-ray (EDX). In addition, the paste

and mortar samples were sliced, dried, epoxy impregnated, and polished for investigating the microstructures with backscattered electronic microscopy.

3 Results and Discussion

3.1 Hydration heat

Fig. 2(a) shows the isothermal calorimetry curves of the different types of cement blends. In comparison to PC, the addition of 8% MEA in EPCII caused no obvious retardation on the hydration heat flow during the acceleration period of cement hydration (within 7h) which was associated with the accelerated formation of calcium silicate hydrate (C-S-H). However it decreased the maximum value of heat flow and increased the heat flow slightly at the later age ranging from 12h to 48h. The blended cements with the addition of slag and fly ash exhibited longer induction and acceleration periods compared to PC and EPCII. Particularly for the EPCII-S40F20 and EPCII-S20F35, the maxima of the heat flow were reached approximately 2h later than that of PC. This implies a slight retardation of cement hydration was caused by fly ash and slag. As reported previously, the retardation of fly ash was dependent on the its replacement ratio and curing temperature, and prolonged by increasing level of fly ash replacement [34]. The

more fly ash was incorporated, the more retardation on the hydration heat was caused. Increasing content of fly ash reduced the heat flow as well as the total heat release. On the one hand, the fly ash may contribute little to the hydration heat release directly at early age due to its slow hydration process. As reported by Sakai et al [35], regardless of the glass content and composition, fly ash in cement pastes cured at 20°C did not react until 7 days. On the other hand, it influenced the hydration of cement due to the dilution effects [36], as the replacements of fly ash increased the real water-to-cement ratio, which may facilitate the cement hydration. The hydration of slag could also contribute to the heat release. The hydration of slag is more rapid than that of FA [37]. Nevertheless, compared to the PC hydration, the hydration of slag was still slower and had a much longer induction period. It is interesting that a second heat release peak occurring around 24h was observed for the blends of EPCII-S40F20, which may correspond to the formation of C-S-A-H [38].

Fig. 2(b) shows the cumulative hydration heat of the five types of mixes. Accordingly within the first 24h after mixing with water, large magnitudes of hydration heat was released. PC released the largest amount of hydration heat among all the mixes. For EPCII, addition of 8% MEA as replacement of cement decreased slightly the hydration heat release within 24h but after then caused a very slight increase in the hydration heat, which may be attributed to the hydration of MgO. This indicates that the addition of MEA insignificantly influenced the hydration of cement at early age. For the blended cement, the incorporation of slag as well as fly ash reduced the

232 hydration heat liberation.

233

234

235

3.2 Deformation

236237

238

239

240

241

242

243

244

245

246

247

248

249

250

251

252

Fig. 3 shows the autogenous deformations of all the cement pastes. The PC paste exhibited significant shrinkage in the first 6 hours, and after then the curves continued to go down but at relatively lower rate. At 115h, the autogenous shrinkage of cement paste PC reached around -1000 microstrains. With addition of 5% and 8% of MEA, the autogenous shrinkages of cement pastes EPCI and EPCII have been greatly reduced, being -720 and -195 microstrains respectively at the end of test. This indicates the autogenous shrinkage of cement pastes have been effectively compensated for due to the hydration of MgO. For the blended cements, regardless of the addition of MEA, the shrinkages were less than that of the corresponding PCs. The more Portland cement was replaced with slag and fly ash, the shrinkage was reduced more considerably. More importantly, the blended cements prepared with EPCII exhibited no shrinkage at the end of test age. Moreover, cement specimens EPCII-S20F20 and EPCII-40F20 showed gentle expansions, being around 200 microstrains. The general deformation of cement pastes depended on the competitive effects of MgO hydration and cement hydration on the volume change. For example, the cement paste shrinks when the expansion produced by MgO hydration is not sufficient to compensate the autogenous shrinkage. As the fixed w/b ratio of 0.38 was used, in the blended cements more water was supplied for the hydration of MgO and thus may have an acceleration effects on MgO hydration. More MgO hydrated at the early age in blended cements produced more expansion, which not only completely compensated for the autogenous shrinkage caused by the hydration of cement but even produced gentle expansions.

Fig. 4 shows the deformation of cement pastes cured in 20°C water at long term. None of the cement pastes showed shrinkage. For the cement pastes EPCI and EPCII, obvious expansions of cement pastes were caused due to the hydration of the incorporated MEA in comparison to PC. The cement pastes expanded rapidly within 42d, and then gradually slowed down. After 120d, the deformation curves of EPCII leveled off, while for PC and other blended cement pastes the expansion curves leveled off at 90d. The ultimate expansions of EPCI and EPCII are 0.12% and 0.21% respectively. With the increasing addition of slag and fly ash, the expansion of the blended cement pastes decreased. This is due to the reduction of MgO content contained in the blended cement with the decreasing content of expansive Portland cement. The ultimate expansions of the blended cement pastes prepared with the expansive PC were on the order of 0.06% to 0.08%.

3.3 Mechanical strength

Fig. 5 shows the flexural and compressive strengths of the mortar specimens. PC mortars developed strengths very quickly, the flexural and compressive strengths at 3d reached 6.8 MPa and 37.8 MPa, and at 90d they were 8.7 MPa and 62.1 MPa respectively. For EPCI and EPCII mortars, addition of MEA induced slight reductions in the flexural strengths but more decreases in compressive strengths. At late age of 90d, the compressive strengths of EPCI and EPCII mortars were decreased by 8.5 MPa and 12.2 MPa respectively in comparison to that of PC mortars. The reduction of late compressive strength when using MEA could be due to the less formation of C-S-H due to the reduction of PC in the blends which is replaced by MEA. The incorporation of slag and fly ash decreased the strengths at the early age. At 3d, the strengths of the mortar specimens made with the blended cements were lower than that made with PC. The more volume of slag and fly ash added, the lower the flexural and compressive strengths were gained. However, at 28d, the strengths of blended cement mortars increased significantly, being close to or even higher than that of the PC mortars. At 90d, all the blended cement mortars made with EPCII had higher strengths than the EPCII mortars. With the increasing curing age from 3d to 90d, the blended cement mortars exhibited more increase in both the flexural and compressive strengths than that of the corresponding PC mortars. For example, when the curing age increased from 3d to 90d, approximately 57%, 271%, 313%, and 257% increases in compressive strength were produced by mortars EPCII-S20F20, EPCII-S20F35, EPCII-S40F20 and EPCII-S40F35 respectively, which were much higher than the increase of 47% produced in the EPCII mortars. This may attribute to the hydraulic or pozzolanic reaction of slag and fly ash. Increase of slag from 20% to 40% caused ascent in strengths of the mortars whereas increase of fly ash from 20%

274

275

276

277

278

279

280

281

282

283

284

285

286

287

288

289

290

291

292

293

to 35% decreased the strength. This may be due to that slag has higher hydraulic and pozzolanic reactivity than fly ash.

3.4 Microstructure

Fig. 6 shows the pore structures of the cement mortars. At 28d, most of the pores in the mortars made with PC and EPCII were with pore diameter range of 0.02-0.2 μm. Blended cement mortars (EPCII-S20F20, EPCII-S40F20, EPCII-S40F35) had more pores with size less than 0.02μm. At 90d, the pore volume decreased and there were less pores at the size range of 0.02-0.2μm. As shown in Fig. 6b, compared to the PC mortars, the blended cement mortars exhibited smaller total porosities at 28d. EPCII-S40F20 has the smallest porosity of 8.7% at 28d and it decreased further to 6.0% at age of 90d. This is due to that the hydraulic or pozzolanic reaction of slag and fly ash caused a densification of the cement paste at later ages.

Fig. 7 shows typical SEM and BSE images of the hydrated blended cement paste EPCII-S40F20. As shown in Fig. 7(a), some hydration products were formed on the surface of fly ash particle and in the region nearby, which tightly bound together the fly ash particle with the surrounding hydration products matrix. The dense interface structure is beneficial for the increase of strength.

In Fig. 7(b), hydration rims were formed around the slag particle, and the hydraulic or pozzolanic reaction products grown gradually from the outer area of slag into the inner part of unhydrated slag. As seen the BSE image of Fig. 7(c), it shows some hydration rims of slag in the blended cement pastes. The interface structures of slag and fly ash particles were dense and therefore contributed to the strength augment. The contributions of the hydraulic or pozzolanic reaction of slag and fly ash may not only due to the densification on the pore structure but also closely related to the interface structure enhancement.

Fig. 8 presents the typical BSE images of the mortars prepared with blended cement mortars EPII-S40F20 after 90d curing in water. Fig. 8(a) shows the BSE image of blended cement mortar at magnification of x300. Lots of slag with coarse particles remained unhydrated. As shown in Fig. 8(b), close investigation of zone A indicates that the slag with small particle size had been hydrated completely while the larger slags were not completely hydrated but with obvious

3.5 Discussion

hydration rims.

In the blended cement systems, due to the reduction of cement clinker content associated with the

substitutions of slag and fly ash, the hydration heat release was reduced significantly. Accordingly this is beneficial for minimising the thermal shrinkage in concrete, particularly in the mass concrete. Replacements of PC with slag and fly ash in this study reduced the autogenous shrinkage of cement pastes. This is attributed to the dilution effects of SCMs on the blended cement system [34, 39]. Less water was consumed by the cement hydration and less C-S-H was formed at early age, reducing the shrinkage. However, the reaction of slag and fly ash consumes water, and hence may contribute to self-desiccation. Fly ash had a slow pozzolanic reaction rate and therefore contributed little to the autogenous shrinkage at early age. Slag had higher reactivity than that of fly ash but its reaction (hydraulic and pozzolanic) was also much slower compared to cement hydration. Accordingly it may also contribute insignificantly to the autogenous shrinkage at the early age. However, for a long term the pozzolanic reaction would contribute to the autogenous shrinkage. In addition to the pozzolanic reaction effects, the filler effects of fly ash may also influence the properties of cement materials. The unhydrated fly ash may behave like micro-aggregate in the cement paste, which is helpful to reduce the autogenous shrinkage [40].

351

352

353

354

355

356

357

337

338

339

340

341

342

343

344

345

346

347

348

349

350

Hydration of MgO produced expansion and thus partly or fully compensated for the autogenous shrinkage of cement paste. To some extent, there is some competition on the water consumption between the hydration of MgO and cement. When cured in water, with sufficient supply of water, the expansive cement pastes EPCI and EPCII produced obvious expansions. Under sealed condition without exterior water supply, the autogenous shrinkage of EPCI and EPCII were partly

but not completely compensated at early age (Fig. 3). Nevertheless, as the same w/b ratio was used in the blended cement in this study, the real w/b ratio was higher, and therefore more water was supplied for the hydration of MgO. Thus the blended cement pastes prepared with EPCII exhibited no shrinkage but even produced gentle expansion. Accordingly incorporation of appropriate addition of MEA as well as SCMs could produce non-shrinkage blended cements. Dissimilar to the delayed expansive cement containing relatively high content of periclase used in China, MEA with high reactivity was incorporated into cement during the inter-ground process in this study, and thus the MgO content can be easily adjusted according to the requirements. This provides a new approach to produce MgO-based expansive Portland cement. The incorporation of MgO into cement by inter-grinding is more homogenous compared to being mixed in concrete as an expansive additive during the concrete mixing process.

The mechanical strengths of blended cement mortars at early age were lower and developed more slowly compared to that of the normal PC mortars. This is due to that less cement hydration products were formed in the blended cement mortars at the early age. However, at the late age, with increasing curing time, the pozzolanic reaction of slag as well as fly ash increased the strengths significantly although the corresponding hydration products in the blended cement system were much less than that of the PC. As shown in Fig. 8, there are still significant quantities of slag that remained unhydrated and most of the fly ash could not hydrate completely. The strength increase of blended cement mortars at late age may not only attribute to the pore

structure densification but also be related to enhancement of the interface structure between the cement hydration products and SCM particles (fly ash, slag) due to their hydraulic or pozzolanic reaction [41, 42]. Incorporation of MEA caused gentle reductions in the strengths of cement mortars as it reduced the cement content. Moreover, the expansion produced by MgO hydration may also influence the strength depending on the magnitude of expansion and its corresponding influence on the microstructure of cement materials [6].

4 Conclusions

age and high mechanical strength at later ages were prepared by mixing slag and fly ash with expansive PC containing MgO. Main conclusions drawn are as follows:

(i) The autogenous shrinkage of blended cement pastes at the early age up to 5 days was less than that of the corresponding control PC pastes. Moreover, the blended cement pastes (EPCII-S40F20, EPCII-S40F35) prepared with the expansive PC containing 8% MEA, 40% slag and 20% or 40% fly ash exhibited gentle expansions of 200 microstrains rather than shrinkages under the sealed condition. This is attributed to the dilution effects of slag and fly ash on the PC component and the expansion caused by the MEA. Under moist curing condition, with the sufficient supply of water, both the expansive PC containing MEA and the relevant blended cements produced

Quaternary blended cements with low hydration heat release, low autogneous shrinkage at early

400 obvious expansions.

(ii) Replacement of PC clinker with up to 8% of MEA resulted in strength decrease. The blended cement mortars had lower strengths at early age of 3d, but gained equivalent or higher strengths at late ages of 28d and 90d compared to the corresponding control PC mortars. This is attributed to the microstructure densification as well as the interface microstructure enhancement due to the formation of pozzolanic reaction products of slag and fly ash.

(iii) Addition of slag and fly ash in the blended cements caused a delay of up to 2h on the

hydration kinetics compared to the control cements. The hydration heat flow as well as the total hydration heat was reduced significantly. This is beneficial for reducing the temperature rise and thus mitigating thermal cracking at early age.

412 Acknowledgements

The financial support from the Royal Academy of Engineering UK/China Exchange, The National Key Technology R&D Program (2011BAE27B01-1), the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD), and National Natural Science Foundation of China (51461135003) is acknowledged. The authors are grateful to the assistance from Mr. Jian Xu, Mr. Hailong Qian and Mr. Anqun Lu at the materials preparation stage. The assistance from Simon Griggs in the Department of Materials and Metallurgy, and Anne Bahnweg

- and Len Howlett in the Department of Engineering, University of Cambridge are gratefully
- 422 acknowledged.

423

424

425 Reference

- 428 [1] P. Lura, O. M. Jensen, K. van Breugel. Autogenous shrinkage in high-performance cement
- paste: an evaluation of basic mechanisms, Cem. Concr. Res. 33(2003) 223-232.
- 430 [2] M. Şahmaran, M. Lachemi, K. M. A. Hossain, V. C. Li. Internal curing of engineered
- cementitious composites for prevention of early age autogenous shrinkage cracking, Cem. Concr.
- 432 Res. 39 (2009) 893-901.
- 433 [3] O. M. Jensen, P. F. Hansen. Water-entrained cement-based materials: II. Experimental
- 434 observations, Cem. Concr. Res. 32(2002) 973–978.
- 435 [4] D. P. Bentz, O. M. Jensen. Mitigation strategies for autogenous shrinkage cracking, Cem.
- 436 Concr. Compos. 26(2004) 677-685.
- 437 [5] D. Cusson, T. Hoogeveen. Internal curing of high-performance concrete with pre-soaked fine
- 438 lightweight aggregate for prevention of autogenous shrinkage cracking, Cem. Concr. Res. 38
- 439 (2008) 757-765.
- 440 [6] L. Mo, M. Deng, M. Tang, A. Al-Tabbaa. MgO expansive cement and concrete in China: Past,
- 441 present and future, Cem. Concr. Res. 57(2014) 1-12.

- 442 [7] S. Nagataki, H Gomi. Expansive admixtures (mainly ettringite), Cem. Concr. Compos.
- 443 20(1998) 163–170.
- [8] H. F. W. Taylor. Cement Chemistry, Academic press, London, 1990.
- 445 [9] B. Lothenbach, K. Scrivener, R. D. Hooton. Supplementary cementitious materials, Cem.
- 446 Concr. Res. 41(2011) 217-229.
- 447 [10] M. D. A. Thomas, M. H. Shehata, S. G. Shashiprakash, D. S. Hopkins, K. Cail. Use of
- 448 ternary cementitious systems containing silica fume and fly ash in concrete, Cem. Concr. Res.
- 449 29(1999) 1207–1214.
- 450 [11] Lane DS, Ozyildirim C. Preventive measures for alkali-silica reactions (binary and ternary
- 451 systems), Cem. Concr. Res. 29(1999)1281–1288.
- 452 [12] M. R. Jones, R. K. Dhir, B.J. Magee. Concrete containing ternary blended binders: resistance
- 453 to chloride ingress and carbonation, Cem. Concr. Res. 27(1997) 825–831.
- 454 [13] M. S. Ahmed, O. Kayali, W. Anderson. Chloride penetration in binary and ternary blended
- cement concretes as measured by two different rapid methods, Cem. Concr. Compos. 30(2008)
- 456 576-582.
- 457 [14] T.K. Erdem, Ö. Kırca. Use of binary and ternary blends in high strength concrete, Construct.
- 458 Build. Mater. 22(2008) 1477-1483.
- 459 [15] S. Tangtermsirikul. Effect of chemical composition and particle size of fly ash on autogenous
- 460 shrinkage of paste, in: E. Tazawa (Ed.), Proceedings of the International Workshop on
- 461 Autogenous Shrinkage of Concrete, JCI, Hiroshima, Japan, 1998, pp. 175–186.
- 462 [16] K. M. Lee, H. K. Lee, S. H. Lee, G. Y. Kim. Autogenous shrinkage of concrete containing

- granulated blast-furnace slag, Cem. Concr. Res. 36(2006) 1279-1285.
- 464 [17] P. Termkhajornkit, T. Nawa, M. Nakai, T. Saito. Effect of fly ash on autogenous shrinkage,
- 465 Cem. Concr. Res. 35(2005) 473–482.
- 466 [18]S. M. Lim, T. H. Wee. Autogenous Shrinkage of Ground-Granulated Blast-Furnace Slag
- 467 Concrete, ACI Mater. J. 97(2000) 587-593.
- 468 [19] Y. Li, J. Bao, Y. Guo. The relationship between autogenous shrinkage and pore structure of
- cement paste with mineral admixtures, Construct. Build. Mater. 24(2010) 1855–1860.
- 470 [20] K. Wang, S. P. Shah, P. Phuaksuk. Plastic shrinkage cracking in concrete
- materials—influence of fly ash and fibers, ACI Mater. J. 98-M49(2001) 458–464.
- 472 [21] M. H. Zhang, C. T. Tam, M. P. Leow. Effect of water-to-cementitious materials ratio and
- silica fume on the autogenous shrinkage of concrete, Cem. Concr. Res. 33(2003) 1687–1694.
- [22] D. Li, J. Shen, Y. Chen, X. Wu. Study of properties on fly ash-slag complex cement, Cem.
- 475 Concr. Res. 30(2000) 1381-1387.
- 476 [23] K. Tan, X. Pu. Strengthening effects of finely ground fly ash, granulated blast furnace slag,
- 477 and their combination, Cem. Concr. Res. 28(1998) 1819–1825.
- 478 [24] G. Li, X. Zhao. Properties of concrete incorporating fly ash and ground granulated
- blast-furnace slag, Cem. Concr. Compos. 25(2003) 293–299.
- 480 [25] S. Kandasamy, M. H. Shehata. Durability of ternary blends containing high calcium fly ash
- and slag against sodium sulphate attack, Construct. Build. Mater. 53(2014) 267-272.
- 482 [26] S. Kandasamy, M. H. Shehata. The capacity of ternary blends containing slag and
- high-calcium fly ash to mitigate alkali silica reaction, Cem. Concr. Compos. 49 (2014) 92-99.

- 484 [27] GB/T 1596-2005, Fly ash used for cement and concrete, 2005.
- 485 [28] L. Mo, M. Deng, M. Tang. Effects of calcination condition on expansion property of
- 486 MgO-type expansive agent used in cement-based materials, Cem. Concr. Res. 40(2010) 437 446
- 487 [29] D. P. Bentz, A. S. Hansen, J. M. Guynn. Optimization of cement and fly ash particle sizes to
- produce sustainable concretes, Cem. Concr. Compos. 33(2011) 824-831.
- 489 [30] T. Zhang, X. Liu, J. Wei, Q. Yu. Influence of preparation method on the performance of
- 490 ternary blended cements, Cem Concr. Compos. 52(2014) 18-26.
- 491 [31] ASTM C1702-09, Standard test method for measurement of heat of hydration of hydraulic
- 492 cementitious materials using isothermal conduction calorimetry, 2009.
- 493 [32] ASTM C1698-09, Standard test method for autogenous strain of cement paste and mortar,
- 494 2009.
- 495 [33] ASTM C349-08, Standard test method for compressive strength of hydraulic-cement mortars
- 496 (Using portions of prisms broken in flexure), 2008.
- 497 [34] M. Narmluk, T. Nawa. Effect of fly ash on the kinetics of Portland cement hydration at
- 498 different curing temperatures, Cem. Concr. Res. 41(2011) 579–589.
- 499 [35] E. Etsuo Sakai, S. Miyahara, S. Ohsawa, S. H. Lee, M. Daimon. Hydration of fly ash cement,
- 500 Cem. Concr. Res. 35(2005) 1135-1140.
- 501 [36] D. G. Snelson, S. Wild, M. O'Farrell. Heat of hydration of Portland cement-metakaolin-fly
- ash (PC-MK-PFA) blends, Cem. Concr. Res. 38(2008) 832-840.
- 503 [37] I. Pane, W. Hansen. Investigation of blended cement hydration by isothermal calorimetry and
- thermal analysis, Cem. Concr. Res. 35(2005) 1155-1164.

[38] K. Meinhard, R. Lackner. Multi-phase hydration model for prediction of hydration-heat of blended cements, Cem. Concr. Res. 38(2008) 794-802. [39] P. Lawrence, M. Cyr, E. Ringot. Mineral admixtures in mortars: effect of inert materials on short-term hydration, Cem. Concr. Res. 33(2003) 1939–1947. [40] E. Yang, Y. Yang, V. C. Li. Use of high volumes of fly ash to improve ECC mechanical properties and material greenness, ACI Mater. J. 104(2007) 303-311. [41] C. M. Aldea, F. Young, K. Wang. Effects of curing conditions on properties of concrete using slag replacement, Cem. Concr. Res. 30(2000) 465-472. [42] C. Hao, M. Deng, L. Mo, K. Liu. Surface modification of fly ashes with carbide slag and its effect on compressive strength and autogenous shrinkage of blended cement pastes, J. Wuhan Univer. Technol.- Mater. Sci. Ed. 27(2012) 1149-1153.

526	
527	TABLES
528	
529	
530	Table 1 Chemical compositions of Portland cement clinker, slag, fly ash and MgO-based
531	expansive additive
532	Table 2 Mix proportions of Portland cement and blended cement
533	
534	
535	FIGURES
536	
537	
538	Fig. 1 Particle size distributions of PC, EPCI, EPCII, fly ash and slag
539	Fig. 2 Isothermal calorimetry hydration heat liberation of cement: (a) heat flow and (b)
540	cumulative hydration heat
541	Fig. 3 Autogenous deformation of cement pastes
542	Fig. 4 Deformation of cement pastes cured in water at 20°C
543	Fig. 5 Mechanical strength of mortar specimens: (a) Flexural strength and (b) Compressive
544	strength
545	Fig. 6 Typical pore structure of cement mortars: (a) derivative porosity curve (pore size
546	distribution) and (b) cumulative porosity curve

Fig. 7 SEM and BSE images of the hydrated blended cement EPCII-S40F20: (a) SEM image of hydrated fly ash, (b) SEM image of hydrated slag, and (c) BSE image of hydrated blended cement paste. S: slag, F: fly ash.

Fig. 8 BSE images of blended cement mortars EPCII-S40F20

Table 1 Chemical compositions of Portland cement clinker, slag, fly ash and MgO-based expansive 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	21.18	3.76	5.36	63.47	1.13	1.05	0.13	2.16	1.61
clinker									
Slag	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
MEA-50	2.76	0.26	0.42	3.18	88.52	0.03	0.06	0.61	3.62

Table 2 Mix proportions of Portland cement and blended cement

ID	Type of cement	Mix proportions / % by mass			
	used	Cement	Slag	Fly ash	
PC	PC	100	0	0	
EPCI	EPCI	100	0	0	
EPCII	EPCII	100	0	0	
EPCII-S20F20	EPCII	60	20	20	
EPCII-S40F20	EPCII	40	40	20	
EPCII-S20F35	EPCII	45	20	35	
EPCII-S40F35	EPCII	25	40	35	
PC-S40F20	PC	40	40	20	
PCI-S40F20	EPCI	40	40	20	

Note: PC, EPCI, and EPCII represent the Portland cements incorporated with 0%, 5% and 8% of

569 MgO-based expansive additives respectively.