1	Evaluation of sulfate resistance of calcined dolomite
2	activated ground granulated blastfurnace slag
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15	ABSTRACT: Aggressive environments significantly influence the durability and
16	serviceability of hardened cement and concrete. This paper presents an evaluation of
17	the resistance of ground granulated blastfurnace slag (GGBS) activated with calcined
18	dolomite, as a novel alkali activator, to 5% sodium sulfate attack and 5% magnesium
19	sulfate attack. Two calcined dolomites, D800 and D1000, were prepared in the
20	laboratory at 800 °C and 1000 °C respectively. The results demonstrated the good
21	potential of using calcined dolomite activated slag in resisting sulfate attack.
22	Immersion in $Na_2SO_4(aq)$ led to an increase in strength in both the D800 (D800S) and
23	the Portland cement CEM I 52.5N (PCS) activated slag, with a more pronounced
24	effect in the former, while a decrease in the D1000 (D1000S) activated slag. On the $\frac{1}{1}$

25 other hand, calcined dolomite activated slag had less strength loss than PCS after 26 MgSO₄ attack. The products of sulfate attack and the deterioration processes are also 27 analyzed by a range of tests including pH, weight change, corroded depth, XRD, TGA 28 and SEM/EDS. After Na₂SO₄ attack, the main product on D800S and D1000S was 29 gypsum with a larger amount in the later. Gypsum, thaumasite and M-S-H were the main products of D800S and D1000S after MgSO4 attack. The better resistance of 30 31 D800S to sulfate attack was attributed to the absence of portlandite in the hydrated paste. On the other hand, the presence of portlandite in D1000S led to the 32 33 inhomogeneous sulfate ions inward progression hence the severe deterioration of 34 sample was observed.

Key words: Alkali-activated slag, Calcined dolomite, Sulfate attack, Sodium sulfate,
Magnesium sulfate

37 Introduction

38 The resistance of cement-based materials to aggressive environments 39 significantly influences the durability and serviceability of hardened cement and 40 concrete of buildings and infrastructures. External sulfate attack (ESA) is the 41 consequence of impact of the sulfate ions that exist in soils, groundwater, seawater, 42 industrial waste water and mine tailings (Ercikdi et al. 2013; Neville 2004; Tariq and 43 Yanful 2013). It is an important degradation process of cement-based materials. ESA 44 involves the inward progression of sulfate ions through the cement matrix by means 45 of different mechanisms of transportation and the reaction of hydrated cement phases with aggressive solutions to form expansive products. This leads to expansion, cracking and deterioration of cement; hence a loss of stiffness, strength and adhesion (Cavdar and Yetgin 2010; Santhanam et al. 2001). Extensive studies have concluded that portlandite and aluminum containing phases are the most vulnerable hydrated cement phases to sulfate attack in the formation of expansive gypsum and ettringite (Hekal et al. 2002; Hill et al. 2003; Torres et al. 2003). The reactions form these two phases are as follows:

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$$Ca(OH)_2 + SO_4^{2-} + H_2O \rightarrow CaSO_4 \bullet 2H_2O (gypsum) + OH^{-}$$

54 $CaO \bullet Al_2O_3 \bullet 6H_2O + CaSO_4 \bullet 2H_2O + H_2O \rightarrow CaO \bullet Al_2O_3 \bullet 3CaSO_4 \bullet 32H_2O$ (ettringite) The enhanced resistance of cement-based materials to ESA can be achieved by 55 56 reducing the permeability of hardened matrix and/or the amount of portlandite and 57 aluminum containing phases. Thaumasite is another readily formed product by ESA 58 as a result of the reaction between C-S-H and sulfate ions, carbonate ions (either from salts or dissolution of atmospheric CO₂ in water) and water (Irassar 2009). 59 Thaumasite sulfate attack (TSA) may occur in mortar or concrete containing 60 limestone, as filler or aggregate, exposed to sulfate environment and cause severe 61 62 disintegration of mortar and concrete (Irassar 2009).

Most often, ESA has been analyzed in Portland cement, which has been the most widely used cementitious material. However, the cement industry currently contributes approximately 5-8% of global man-made CO₂ emissions (Provis and van Deventer 2014) due to the calcination of limestone and the consumption of fossil fuels. The search for more sustainable and environmental binders has led to the development 68 of alkali-activated cements (AACs), which utilize a large portion of supplementary 69 cementitious materials (SCMs), such as blastfurnace slag, fly ash and metakaolin with 70 the use of alkali activators (Demirboğa and Gül 2006; Memon et al. 2007; Provis 2013; 71 Shi et al. 2006, 2011; Singhal et al. 2008). The benefits of using AACs are not only in 72 terms of low energy costs and positive environmental impact, but also in terms of 73 enhanced durability (Al-Otaibi 2008; Elahi et al. 2010; Fernandez-Jimenez et al. 2006; 74 Provis and van Deventer 2014; Yüksel et al. 2007), mainly due to the lower content of portlandite in the hydrated cements and their lower permeability to aggressive 75 76 solutions in moist conditions (Shi et al. 2011). In addition, AACs have been 77 recognized as more promising option than Portland cement in a stabilization/solidification processes, due to lower leachability of contaminants from 78 79 AACs stabilized hazardous and radioactive wastes (Luna Galiano et al. 2011; Shi and 80 Fernández-Jiménez 2006).

81 An obstacle in the alkali activation processes is related to the alkali activators. 82 Most conventional activators (caustic hydroxides, silicates) do not exist naturally and 83 are obtained from energy intensive manufacturing processes, which significantly 84 reduces the energy saving credentials associated with AACs (Turner and Collins 2013). 85 Other technical and environmental challenges include their fast setting, high drying shrinkage and their highly corrosive nature of their alkali solutions (Van Deventer et al. 86 87 2012; Provis and van Deventer 2014; Yang et al. 2008, 2012). In this context, alternative activators such as reactive magnesia, quicklime, mixture of reactive 88 89 magnesia and quicklime, calcined dolomite have recently been explored in related

90 research initiatives at the University of Cambridge and reported to be effective 91 activators with one or more aforementioned challenges tackled including the reduced 92 drying shrinkage and the enhanced mechanical properties of MgO cements, the 93 relatively lower energy consumption in the manufacturing processes of these novel 94 activators, etc. (Gu et al. 2014a; b; Jin et al. 2014; Yi et al. 2013; Li 2012), but with 95 limited investigation on durability (Li 2012).

96 The study reported here evaluated the sulfate resistance of calcined dolomite 97 activated GGBS paste in accelerated exposure conditions up to 120 days. Two 98 calcined dolomites were prepared in laboratory conditions and used as alkali 99 activators for slag. Mechanical properties and microstructural changes of samples 100 after attack were analyzed using a range of different tests.

101 Materials and methods

102 Materials

103 GGBS from Hanson, UK, and raw dolomite DRB20 from IMERYS, UK, were 104 used in this study. Considering the fact that immediate global replacement of PC by 105 any of the possible alkaline cements is virtually impossible and the dilution of PC with 106 high volumes of SCMs is considered to be one of the possibilities to reduce the impact 107 of PC on environmental issues (Shi et al. 2011). Portland cement CEM I 52.5N from 108 Tarmac, UK, was also used to set a reference for calcined dolomites. The performance 109 of PC activated slag after a short term of sulfate attack will be presented. The 110 chemical compositions and physical properties of these materials are shown in Table

111 1.

112	Dolomite DRB20 was used to produce two different calcined dolomites. In the
113	calcination process, ~50 g of raw dolomite was placed in individual ceramic crucibles
114	and heated under atmospheric conditions to 800 °C or 1000 °C in an electric furnace.
115	Those two final temperatures were maintained for 1 h and then the samples were left to
116	cool down to room temperature. Two calcined dolomites, namely D800 and D1000,
117	were obtained referring to the products calcined at 800 °C and 1000 °C respectively.
118	D800 and D1000 were characterized by X-ray diffraction (XRD) and
119	thermogravimetric analysis (TGA). The XRD patterns were collected using a Siemens
120	D5000 X-ray diffractometer with CuK α radiation. The scanning range was between 5°
121	and 55° 20. The scanning speed of 1 s/step and resolution of 0.05 °/step were applied.
122	The TG measurements were carried out using a Perkin Elmer STA 6000 machine by
123	heating the samples from 40 °C to 1000 °C at the rate of 10 °C/min.

124 Preparation of paste and sulfate solutions

The D800, D1000 and CEM I were used as activators for the slag, with their 125 dosage controlled at 10% by weight. The nomenclatures of samples are given in Table 126 127 2. The slag paste with a water to binder (w/b) ratio of 0.35 was casted in $40 \times 40 \times 40$ mm cubic molds at 20±1 °C. The samples were then covered with cling film. After 24 128 h, the samples were demolded and stored in deionized water at 20±1°C for 28 days. 129 Then the samples were divided into two groups: one group immersed in sulfate 130 131 solutions for different times and the other group still immersed in deionized water for reference (Table 2). The 5% sulfate solutions were prepared by dissolving 50 g sodium sulfate (Na₂SO₄) or magnesium sulfate (MgSO₄) in 950 g deionized water at $20\pm1^{\circ}$ C.

135 *Test Procedure*

The compressive strengths of reference samples and the immersed samples were determined at a constant load rate of 2400 N/sec in triplicate at each curing age on the CONTROLS Uniframe test machine. For the immersed samples, their weight was measured before both the immersion and the compressive strength test. The solutions were refreshed at each age and the pH was recorded before renewal using a pH meter Eutech 520 with an accuracy of 0.01. The corroded depths of samples were measured using a digital vernier caliper after 90 and 120 days of exposure.

143 The degradation products were characterized by XRD and TGA using the same 144 equipment and parameters as stated in 'Materials' when characterizing the calcined 145 dolomites.

The deteriorated microstructure of exposed pastes after 60 days and 90 days was studied by scanning electron microscopy (SEM) combined with energy-dispersive X-ray spectroscopy (EDS). A JEOL 820 machine was used to analyze the microstructure of sample surfaces and a Hitachi S-3400N II machine equipped with a Horiba EX-250 EDS analyzer was used to analyze the deteriorative zone of samples.

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151 **Results and discussions**

152 Characterization of calcined dolomites

Figs.1 and Fig.2 give the XRD and TGA results of D800 and D1000, respectively. Fig.1 indicates that D800 consisted of MgO, CaO, CaCO₃ and a small proportion of undecomposed dolomite. The unknown fraction of undecomposed dolomite makes it difficult to determine the specific proportion of each composition. On the other hand, no dolomite was found in D1000 and hence it was estimated to consist of MgO, CaO [Ca(OH)₂ was also converted into CaO] and CaCO₃ with their specific proportion

159 35.8%, 54.6% and 9.6%, respectively, according to the TG curve (Fig.2).

160 Calcined dolomite activated slag paste

161 The hydration properties of calcined dolomite activated slag were investigated by 162 Gu et al. (2014) in a related paper. The results indicated that relatively higher 163 quantities of CaO and MgO in D1000 led to a higher hydration degree of slag with 164 higher contents of C-S-H and hydrotalcite-like phases than D800 did. The pore filling 165 effect of voluminous hydrotalcite-like phases resulted in a more compacted 166 microstructure of D1000S. In addition, CaO in D1000 caused the formation of 167 portlandite in D1000S while no portlandite was detected in D800S.

168 Development of compressive strength

169 Table 3 presents the compressive strength of the reference and the relative 170 strength of the immersed samples, which are expressed as percentages of the

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171 reference sample at each curing age. The exposure to $Na_2SO_4(aq)$ led to an increase in 172 the compressive strength of D800S and a decrease for D1000S, although there were some fluctuations of the results. After 28 days of exposure, the strength of D800S was 173 174 slightly increased by ~6.1% while there was a decrease of ~3.1% in strength of D1000S. Up to 120 days, there was ~12.7% strength increase of D800S whilst ~10.1% 175 176 strength decrease of D1000S. The PC activated slag (PCS) also had a slightly 177 enhanced strength after 28 days immersion, but less than D800S. Strength enhancement of alkali-activated slag in Na2SO4(aq) was also reported by others 178 179 (Catinaud et al. 2000; Komljenovic et al. 2013) and was explained by the reduction in 180 the porosity of the pastes, caused by the reaction products between the sample and 181 sulfate solution (Komljenovic et al. 2013; Puertas et al. 2002). Nevertheless, D800S 182 was more resistant to Na₂SO₄ attack than PCS, the D1000S showed the lowest 183 resistance to Na₂SO₄ attack.

184 Continuous strength decreases of all samples were observed when immersed in MgSO₄(aq). After 28 days of exposure, D800S lost ~7.7% of strength whilst D1000S 185 186 lost ~12.5%, and both of them exhibited better performance than PCS, which lost 187 ~16.5% of strength. The strength of D800S and D1000S after 120 days decreased to 188 ~51.0% and ~41.3% of the reference samples, respectively. It appeared that D800S 189 presented a higher resistance to MgSO₄ attack than D1000S since the strength loss of 190 D800S was much lower at each age. It can also be concluded that both calcined 191 dolomite activated slags showed higher resistance than PC activated slag to MgSO₄

attack.

193 *pH of sulfate solutions*

194 The pH of the environment has a significant impact, not only on the chemical 195 reactions but also on the products. Portlandite starts to decompose when the pH is below 12 (Shi and Stegemann 2000). As the pH drops, C-S-H could continuously 196 release Ca^{2+} ion until most of the Ca^{2+} is released when the pH is below 9 197 (Komljenović et al. 2012; Shi and Stegemann 2000). In terms of reaction products, 198 199 Brown (Brown 1981) noticed that ettringite was stable at a pH of 11.5, unstable at a 200 pH of 10 and highly unstable at a pH of 6. Indeed, ettringite starts to decompose when 201 the pH drops below 10.7 (Beddoe and Dorner 2005).

202 The initial pH of Na₂SO₄(aq) and MgSO₄(aq) was 6.4 and 5.7, respectively. After 203 immersion, the pH of solutions increased rapidly as a result of the release of OH⁻ ions 204 from the samples. After 30 days, the pH of Na₂SO₄(aq) containing D800S was 205 maintained above 12.1 while that containing D1000S was above 12.6 (Fig.3). As for 206 the MgSO₄(aq), D800S induced pH values staying around 9.0 at each age; whilst 207 D1000S induced a decrease from 9.9 to 9.0 then was stable around 9.0 after 90 days. It should be noted that, since the solutions were refreshed monthly, samples may 208 209 sometime experience lower pH environment than the result given in Fig.3 considering 210 the initial pH of solutions. As a result, the decomposition of portlandite, C-S-H and/or 211 ettringite should have occurred when the pH was below the lines marked in Fig.3. 212 According to the results, D1000S induced higher pH in both two sulfate

solutions and this could be attributed to its higher content of portlandite, which is

214	easier to release OH ⁻ than C-S-H (Taylor and Gollop 1997). In addition, lower pH of
215	$MgSO_4(aq)$ than $Na_2SO_4(aq)$ can be explained by the formation of insoluble $Mg(OH)_2$,
216	which significantly reduced the concentration of OH ⁻ in the solutions.

217 Weight changes

218 Changes of weight after exposure were used as an indicator for the resistance of 219 samples to sulfate attack in most relevant studies (Al-Amoudi 2002; Makhloufi et al. 220 2012). Fig.4 summarizes the weight changes of the samples after different exposure 221 times and reveals that there were weight increases with time for all sample. In the 222 $Na_2SO_4(aq)$, weight changes gradually increased with time and achieved an increase 223 of 0.22% for D800S and 0.66% for D1000S after 120 days of exposure. The relatively 224 larger weight increase of D1000S can be attributed to the higher content of portlandite 225 in D1000S, which led to the more intensive reaction between the sample and the 226 solution. Up to 28 days, PCS showed a larger weight increase than D800S while 227 slightly smaller than D1000S.

Notably higher weight increases of samples immersed in MgSO₄(aq) were observed. D800S showed +2.59% weight gain after 28 days and rapidly increased to +10.68% after 120 days. By contrast, D1000S showed much smaller weight gain, i.e. +0.95% after 28 days and +4.85% after 120 days. Regarding to PCS, it had a +2.26% weight gain after 28 days exposure, slightly smaller than D800S.

As can be seen, D800S showed smaller weight changes than D1000S in Na₂SO₄(aq) while larger in MgSO₄(aq) (Fig.4). The explanation should involve the 235 different formats of inward deterioration progression in D800S and D1000S236 (discussed in Section 3.7).

237 *Corroded depth*

Fig.5 gives the measured corroded depths of samples after 90 and 120 days of exposure. It is apparent that the corroded depth increased with exposure time. The relatively moderate reaction between the samples and $Na_2SO_4(aq)$ led to small corroded depths and no obvious visual degradation of the samples was observed. Up to 120 days, the depth was ~0.20 mm for D800S and ~0.38 mm for D1000S.

243 Much larger corroded depths were observed on samples immersed in MgSO₄(aq). 244 D800S, which had smaller strength loss (Table 3), however, had thicker deteriorative 245 surface than D1000S. The different formats of inward deterioration progress on 246 samples are likely to be attributable to this behaviour. The images took after 90 and 247 120 days of exposure (Fig.6) indicated that the MgSO₄(aq) gradually penetrated into D800S and only caused significant spalling along the edges rather than on the surface 248 249 (Fig.6a and c). In this case, the thickness of deteriorative surface was homogeneous. 250 By contrast, the attack products on D1000S caused significant expansion in some areas due to the high content of portlandite. Therefore, not only spalling along the 251 252 sample edges, but also bulging on the surface was observed. The deterioration was 253 accelerated within the bulging hence the corroded depth was not homogeneous and 254 may be much thicker than those 'normal' areas. However, only 'normal' areas were 255 measured when performed the corroded depth measurement. As a consequence, the

256 measured corroded depths of D1000S were smaller than those of D800S.

257 XRD and TG analysis

258 After exposure, the XRD and TGA of the paste from the deteriorative surface of samples showed different reaction products in D800S and D1000S (Fig.7-10). Fig.7 259 260 indicates that, after 60 days of exposure in Na₂SO₄(aq), the major products were gypsum accompanied by minor amount of ettringite in D800S deteriorative surface. 261 262 The small quantity of ettringite was attributable to the high sulfate concentration of the solutions (~33800 ppm in Na₂SO₄(aq) and ~40000 ppm in MgSO₄(aq)) since gypsum 263 264 was the primary reaction product of sulfate attack when the sulfate ion concentration 265 was higher than 8000 ppm (Santhanam et al. 2001). C-S-H and calcite were still 266 observed due to the moderate reaction between $Na_2SO_4(aq)$ and the samples. As for 267 D1000S, all phases which observed in D800S were also observed but with different 268 intensities. Clearly, there was still a considerable amount of porlandite left, because fresh paste may be intermixed with the corroded part during the preparation of 269 samples for analysis when the samples' corrode depth in Na₂SO₄(aq) was shallow 270 271 (Fig.5). TGA results which were given in Fig.8 consisted well with the XRD observation. The weight losses of ettringite, gypsum and C-S-H overlap in the 272 273 temperature range of 80 °C to 170 °C (Cassagnabère et al. 2009; Ciobanu et al. 2012) 274 and hence it is difficult to quantitatively estimate the individual amounts of each 275 phase in the deteriorative zone. Ettringite was also observed to decompose at a lower 276 temperature (50 °C to 80 °C) (Ciobanu et al. 2012; Gruskovnjak et al. 2008) therefore

a very small shoulder in this range was shown. In comparison to D800S, the presence
of portlandite in D1000S, which decomposes at 430 - 460 °C, was confirmed in the
DTG curve.

280 After 60 days of exposure in MgSO₄(aq), the presence of brucite was confirmed 281 in attacked calcined dolomite activated slag pastes (Fig.9). Its low intensity could be 282 attributed to the old age of the analyzed sample, in which case the dissolution of 283 brucite layer occurred and other reaction products had already formed. Nevertheless, brucite was more ready to form in D1000S because it notably consumes portlandite, 284 285 which was only found in D1000S. The pronounced aggression of $MgSO_4(aq)$ 286 considerably increased the amount of the reaction products, mainly gypsum, whose 287 peaks of high intensity were observed in both samples. On the other hand, ettringite 288 was more ready to decompose because of the low pH environment (Fig.3) and high SO_4^{2-} concentration, so only weak peaks were detected. In this context, the strong 289 290 characteristic peaks at $2\theta=26.1^{\circ}$ and 32.2° can be mainly attributed to the formation of 291 thaumasite, which is difficult to distinguish from ettringite (Irassar 2009; Torres et al. 292 2003). Extensive literature reported the formation of thaumasite in the presence of limestone under sulfate attack (Bellmann and Stark 2007; Irassar et al. 2003, 2005; 293 294 Kakali et al. 2003; Lee et al. 2008; Tsivilis et al. 2007). Although cold environments 295 (<15 °C) are preferable to thaumasite formation (Bellmann and Stark 2007; Köhler et 296 al. 2006; Tsivilis et al. 2007), it was also observed at ambient temperature (Irassar et al. 2003, 2005; Lee et al. 2008). As a result of magnesium attack, C-S-H gradually 297 298 converted into non-cementitious M-S-H (Gollop and Taylor 1996; Santhanam et al.

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2003) and/or simply silica gel (SiO₂·xH₂O) (Collepardi 2003) until most of Ca²⁺ was 299 300 released when pH dropped below 9. Therefore, C-S-H was not detected in 301 deteriorative D800S and D1000S (Fig.9). The characteristic peaks of non-cementitious M-S-H are recognized as board humps but difficult to detect by 302 XRD (Jin and Al-Tabbaa 2013). Surprisingly, small amount of portlandite, which was 303 304 supposed to have been depleted, was still detected in D1000S. It seems that this part 305 of portlandite was inaccessible to the solution, owing to the harbouring effect of other phases. Calcium sulfate hydrate, other than gypsum, was also detected in the attack 306 307 products.

308 According to the TGA results of samples immersed in MgSO₄(aq) (Fig.10), the 309 broad trough of C-S-H was replaced by a much narrower but deeper trough at ~ 310 130 °C, which represented the decomposition of gypsum. The decomposition of thaumasite mainly happened between 140-200 °C (Kresten and Berggren 1976) and 311 312 slightly overlapped with gypsum. M-S-H, which decomposes at ~400 °C and overlaps 313 with hydrotalcite-like phases, was confirmed although it was not clearly detected by 314 XRD analysis. The minor amount of portlandite left in D1000S induced the weight loss at ~440 °C. In comparison to the samples in Na₂SO₄(aq) (Fig.8), the amounts of 315 316 calcite in D800S and D1000S were significantly smaller, due to the participation of 317 calcite in forming thaumasite.

318 Microstructural analysis

Fig.11 shows the SEM images of D800S surface after exposure to $Na_2SO_4(aq)$.

320 The microstructure appears to be looser than the fresh D800S paste, whose SEM 321 image is not shown here. The inconspicuously corroded surface was covered with 322 gypsum, with some large crystals and small cracks observed.

Fig.12 presented the degraded surfaces of the samples after exposed to 323 MgSO₄(aq) for 60 days. In D800S (Fig.12a and b), the brucite layer had almost been 324 325 destroyed by that time, hence the severe decalcification of C-S-H was clearly 326 observed, leaving porous M-S-H. Gypsum crystals were found randomly distributed on the surface while ettringite and thaumasite were difficult to identify. As for 327 328 D1000S (Fig.12c and d), the brucite layer was observed to have decomposed. The 329 gypsum layer, which was originally beneath the brucite layer (Santhanam et al. 2003), was found to cover the surface due to the large amount of available Ca^{2+} released 330 331 from D1000S. Small quantity of ettringite was also found. In this case, decalcified 332 C-S-H cannot be observed in the images taken on the sample surface.

333 Fig.13 shows the deteriorative zone profiles of samples after 90 days attack. As can be seen, both D800S and D1000S had a narrow deteriorative zone (<300 µm) 334 335 after 90 days immersion in Na₂SO₄(aq), indicating a moderate reaction between the samples and the solution and agreed well with the corroded depth result (Fig.5). In 336 337 addition, the relatively denser structure of D800S deteriorative zone than the fresh 338 paste (Fig.13a) implied the pore filling effect of reaction products, by which the 339 compressive strength of sample was enhanced (Table 3). The micro cracks were only observed beneath the deteriorative zone, suggesting a potential weak structure after 340 341 the attack. Regarding to D1000S, although no clear difference in porosity from the

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outer area to the inner area was observed, the absence of slag particles in the deteriorative zone indicated the precipitation the reaction products on the surface, sometimes in a pore (Fig.13b). The consumption of Ca^{2+} by the $Na_2SO_4(aq)$ in forming these products caused the strength loss over time.

D800S had a thicker deteriorative zone than D1000S when immersed in 346 347 MgSO₄(aq) (Fig.13c and d). It can be attributed to (1) the loose structure of D800S, 348 which made the inward progression of the aggressive solution easier thus more attack 349 products (Fig.4); and (2) the formation of thaumasite. Due to the larger amount of available CO_3^{2-} in D800S, more thaumasite formed after attack (Fig.9) led to a higher 350 351 degradation degree. As suggested by the literature (Santhanam et al. 2002), the 352 deteriorative zone can be divided into two parts: Zone I (the disintegrated surface 353 zone) and Zone II (the zone of deposition of attack products), as marked in Fig.13c 354 and d. The degradation of paste and the precipitation of reaction products induced 355 inhomogenous and anfractuous layers in Zone II of D800S, with micro cracks and 356 voids developed (although there were original voids before attack). Deposit layers of 357 products were relatively more homogenous in Zone II of D1000S, suggesting a 358 gradual penetration process of aggressive solution due to its lower porosity. However, 359 such relatively stratified structure of D1000S deteriorative zone was ready to destroy 360 when external pressure was applied and therefore D1000S had higher strength loss 361 after attack.

Fig.14 presented the deteriorative zones of samples with EDS analysis results.
Fig.14a, which shows the surface of D800S immersed in Na₂SO₄(aq), illustrates the

dense matrix filled with a small amount of attack products. The penetration of aggressive solution could be retarded since no micro cracks were observed. A thin layer of calcite was observed on the surface of D1000S immersed in $Na_2SO_4(aq)$ (Fig.14b). Its formation can be attributed to the carbonation of D1000 during curing.

368 Fig.14c is the magnification of the red square marked in Fig.13c from D800S 369 immersed in MgSO₄(aq). A clear gypsum layer was observed with micro cracks 370 developed. Meanwhile, between the deteriorative zone and the fresh paste, a wide 371 crack formed and thereafter the new attack products would deposit in the crack. The 372 area with a smooth surface had a low Ca/Si atomic ratio (~1.3) due to the 373 decalcification of C-S-H, resulting in the coexistence of silica gel or M-S-H with 374 C-S-H gel. The decreased Ca/Si atomic ratio explained the decrease in strength 375 (Komljenović et al. 2012), which led to a more smooth surface than the fresh paste. 376 Indeed, the formation of brucite and gypsum caused the decalcification of C-S-H and 377 hence the convert of C-S-H to non-cementious M-S-H was confirmed in Fig.14d, with small amount of residual Ca²⁺ detected. Cracks and voids were ready to form due to 378 379 the poor performance of M-S-H in binding. D1000S immersed in MgSO₄(aq) also 380 showed the deposit of attack products (mainly gypsum) within the slag matrix 381 (Fig.14e). The darker grey conjunction area of the gypsum layer and slag matrix was 382 probably due to the lower Ca content after decalcification. The unreacted slag 383 particles incorporated matrix appeared to retard the development of micro cracks to 384 some extent.

386 Na₂SO₄ attack

No clear visual sign of deterioration on samples immersed in Na₂SO₄(aq) suggested a high resistance of calcined dolomite activated slag to attack. For D800S, OH⁻ ions released from cementitious C-S-H, which only occurs if portlandite is locally absent (Chen et al. 2006), rapidly increased the pH of the solution after immersion. On the other hand, the Ca²⁺ ions released from C-S-H reacted with the solution to form gypsum according to:

393 $\operatorname{Ca}^{2+} + \operatorname{SO}_4^{2-} + \operatorname{H}_2\operatorname{O} \to \operatorname{CaSO}_4 \bullet 2\operatorname{H}_2\operatorname{O} \text{ (gypsum)}$

394 This process may cause the loss of strength since C-S-H provides the binding capacity, 395 but the pore filling effect of gypsum may reduce the porosity of sample and somewhat compact the structure, resulting in an increase rather than a decrease in strength. 396 397 Moreover, the compacted structure also retarded the inward movement of the 398 aggressive solution. As for D1000S, that OH⁻ ions readily released from portlandite to 399 some extent prevents the dissolution of C-S-H, but also created high porosity with 400 increased permeability of the deteriorative zone. The precipitation of expansive attack 401 products in the pores (as observed in Fig.13b) may destroy the local structure and 402 became a stress raiser during strength test. Consequently, a decreased strength was 403 obtained although D1000S had a denser matrix than D800S. The very thin layer of calcite formed on the D1000S sample surface was due to the carbonation during 404 405 curing. Since calcite can result in a reduction of the material porosity and favor the

406 formation of a protective layer on the surface (Glasser et al. 2008), the presence of407 calcite could to some extent increase the sulfate resistance of D1000S.

408 3.7.2 MgSO₄ attack

409 After immersion in MgSO₄(aq), a layer of brucite rapidly formed on the surface 410 with a gypsum layer beneath (Bonen and Cohen 1992; Santhanam et al. 2002), 411 according to the reaction:

412
$$\operatorname{Ca}^{2+} + \operatorname{OH}^{-} + \operatorname{Mg}^{2+} + \operatorname{SO}_{4}^{2-} + \operatorname{H}_{2}\operatorname{O} \rightarrow \operatorname{CaSO}_{4} \circ 2\operatorname{H}_{2}\operatorname{O} \text{ (gypsum)} + \operatorname{Mg}(\operatorname{OH})_{2}$$

414 On the one hand, the formation of brucite consumed a considerable amount of OH 415 and accelerated the decalcification of C-S-H (Bonen 1993). On the other hand, the precipitation of brucite in turn results in a low and non-uniform rate of diffusion of 416 SO_4^{2-} parallel to the surface (Bonen and Cohen 1992). Due to the absence of 417 portlandite in D800S, C-S-H was directly attacked by MgSO4(aq) therefore the 418 419 formations of M-S-H and gypsum were clearly observed after 60 days of exposure 420 (Fig.12b). Consequently, the deteriorative zone with porous structure became more 421 accessible to sulfate ions and provided a favorable scenario for thaumasite formation 422 in the presence of C-S-H, sulfate ions, carbonate ions (mainly provided by D800), and 423 water, according to the following reaction:

424
$$C-S-H + SO_4^{2-} + CO_3^{2-} + H_2O \rightarrow CaSiO_3 \bullet CaSO_3 \bullet CaSO_4 \bullet 15H_2O$$
 (thaumasite)

As a result, a large amount of thaumasite (Fig.9) led to a thick deteriorative zone with
inhomogenous and anfractuous layers of precipitated attack products, which is
manifested by strength losses over time.

428 Unlike D800S, the dissolution of portlandite primarily occurred due to the attack 429 on D1000S, which led to a high porosity of the surface. Expansive products filled the 430 pores and caused expansive damages in some areas, where the penetration of the aggressive solution was accelerated. In this case, the reaction within these areas was 431 432 also accelerated and the expansion caused the formation of bulging on the surface. 433 The bulging may cause stress concentration, which explained the larger strength loss of D1000S after attack than D800S, although D1000S had denser matrix, lower 434 435 permeability, and less vulnerable C-S-H to attack and hence thinner deteriorative zone 436 (Fig.13d).

437 Hydrotalcite-like phases were not significantly affected by sulfate attack, with 438 only a slight change in Mg/Al atomic ratio observed according to the literature 439 (Gollop and Taylor 1996; Komljenovic et al. 2013). The dominant reactions in 440 forming brucite, M-S-H, gypsum and thaumasite in MgSO₄(aq) caused the 441 inconspicuous presence of hydrotalcite-like phases hence it was difficult to determine 442 the changes on hydrotalcite-like phases.

443 **Conclusions**

The results in this study demonstrated that D800 activated slag (D800S) was more resistant to Na_2SO_4 attack than PC activated slag (PCS) while D1000 activated slag (D1000S) showed the lowest resistance. In addition, calcined dolomites activated slag was more resistant to MgSO₄ attack than PCS. The absence of portlandite in D800S induced C-S-H susceptible to solution and calcite in D800 induced the formation of 449 thaumasite, but D800S had less strength loss than D1000S in terms of MgSO₄ attack, 450 which can be illustrated by the inhomogeneous sulfate ions inwards progression on D1000S. After Na₂SO₄ attack, the main product on D800S and D1000S was gypsum 451 with a larger content found in the later. Gypsum, thaumasite and M-S-H were the 452 453 main products of D800S and D1000S after MgSO₄ attack. Calcination temperature of 454 dolomite is the controlling factor on the sulfate resistance of calcined dolomite 455 activated slag, by changing the hydration products and the porosity of hydrated paste. By properly changing the calcination temperature, the amount of generated 456 457 portlandite and the porosity of hydrated paste can be reduced; therefore the resistance 458 to sulfate attack can be enhanced.

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	GGBS	DRB20*	CEM I 52.5N	
Chemical composition				
SiO ₂	37.0	0.037	19.47	
Al_2O_3	13.0	0.001	4.75	
CaO	40.0	33.7	63.16	
MgO	8.0	18.9	1.43	
K ₂ O	0.6	0.011	0.62	
Na ₂ O	0.3	0.016	0.28	
SO ₃	1.0	NM	2.68	
Fe ₂ O ₃	NM	0.006	3.43	
CO ₂	NM	47.3	NM	
Cl	NM	NM	0.0094	
LOI	NM	NM	3.26	
Physical properties				
Specific surface area (m ² /kg)	493	1700	400	
Bulk density (kg/m ³)	1050	900	NM	
Average particle size D50 (µm)	NM	4.9	NM	

Table 1. Chemical compositions and physical properties of materials

*The chemical composition of DRB20 were determined by ICP-OES

NM - Not Measured

Table 2. Why design and curring conditions of the samples							
Nomenclature	Composition (by weight)	w/b	Curing conditions				
D800S	10% D800 + 90% GGBS		24 h in mould, 28 d in water, and 28,				
D1000S	10% D1000 + 90% GGBS	0.35	60, 90, 120 d in solutions or water				
DCS	10% CEM I + 90% GGBS	0.55	24 h in mould, 28 d in water, and 28 d				
rC5			in solutions or water				

Table 2. Mix design and curing conditions of the samples

Tuble of Compressive strengths in where and remarke compressive strengths in surface solutions										
A	Compressi	ve strength of r	eference	Eve	In 5% Na ₂ SO ₄			In 5% MgSO ₄		
Age	samples cured in water (MPa)		Exposure	Relative strength (%)		Relative strength (%)				
(d)	D800S	D1000S	PCS	- time (d)	D800S	D1000S	PCS	D800S	D1000S	PCS
initial	19.3	27.8	33.4							
28	23.0	31.9	38.3	28	106.1	96.9	104.8	92.3	87.5	82.1
60	23.8	36.1	-	60	106.7	93.0	-	89.8	56.1	-
90	28.9	36.2	-	90	103.9	93.9	-	59.1	43.1	-
120	28.6	36.4	-	120	112.7	89.9	-	51.0	41.3	-

Table 3. Compressive strengths in water and relative compressive strengths in sulfate solutions









Figure 5 Click here to download Figure: Fig.5.tif



D800S

D1000S



90d

120d













Figure 13 Click here to download Figure: Fig.13.tif





List of figure captions:

- Fig.1 XRD patterns of D800 and D1000
- Fig.2 TG/DTG curves of D800 and D1000
- Fig.3 pH of solutions after different exposure times
- Fig.4 Weight changes of samples with exposure time
- Fig.5 Corroded depths of samples exposed to sulfate solutions
- Fig.6 Appearances of samples exposed to MgSO₄ solution for 90 and 120 days
- Fig.7 XRD diffractograms of degradation products of samples exposed to Na₂SO₄ solution for 60 days
- Fig.8 TG/DTG curves of degradation products of samples exposed to Na2SO4 solution for 60 days
- Fig.9 XRD diffractograms of degradation products of samples exposed to MgSO₄ solution for 60 days
- Fig.10 TG/DTG curves of degradation products of samples exposed to $MgSO_4$ solution for 60 days
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- Fig.12 Surfaces of samples exposed to MgSO4 solution for 60 days. a, b: D800S; c, d: D1000S
- Fig.13 Microstructures of samples exposed to sulfate solutions for 90 days. a, D800S in Na₂SO₄ solution; b,

D1000S in Na2SO4 solution; c, D800S in MgSO4 solution; d, D1000S in MgSO4 solution

Fig.14 SEM/EDS results of samples immersed in sulfate solutions for 90 days. a, D800S in Na₂SO₄ solution; b,

D1000S in Na₂SO₄ solution; c and d D800S in MgSO₄ solution; e, D1000S in MgSO₄ solution