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Author(s)	Zhai, Qi; Kurumisawa, Kiyofumi
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Effects of cation in sulfate, chloride and nitrite on Ca(OH)₂ activated ground granulated blast-furnace slag

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4 Qi Zhai^a, Kiyofumi Kurumisawa^{b, *}

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^a Division of Sustainable Resources Engineering, Graduate School of Engineering,

7 Hokkaido University, Japan

8 ^b Division of Sustainable Resources Engineering, Faculty of Engineering, Hokkaido

- 9 University, Japan
- 10

11 Abstract

This study explored the effects of cation in sulfate, chloride and nitrite on calcium hydroxide 12 activated blast furnace slag. Through the use of X-ray diffraction, thermal gravity analysis 13 14 and isothermal calorimetry, it was demonstrated that all the activators investigated can improve the early strength development. Compared with chloride and nitrite, it seems the 15 type of sulfate has evident influence during the process of slag hydration. Compared with 16 K₂SO₄ and Na₂SO₄, MgSO₄ has limited promotion effects on slag hydration at early age. In 17 MgSO₄, the precipitation of gypsum and brucite retard the formation of hydrates for 3 hours 18 and limit the hydration kinetics at initial stage, however, the high concentration of sulfate 19 ions in pore solution makes a certain amount of ettringite remain, which promote the strength 20 development. It was also found that the mechanism of pH rise in K₂SO₄ and Na₂SO₄ is due 21 to synergistic reactions between sulfate and Ca(OH)₂, while low pH in MgSO4 due to low 22 solubility of brucite inhibit the slag dissolution, the critical pH for promoting slag hydration 23 in this study is 13.1. 24

25 Keywords: Sulfates, GGBFS, Hydration products, Ca(OH)2-activation

26

27 1. Introduction

28 It is known that ordinary Portland cement (OPC) blended cement containing ground granulated blast-furnace slag (GGBFS) exhibits many advantageous properties such as 29 increased late strength, good chemical resistance and long term durability, etc.[1–5], which 30 has become the reason why blast furnace slag cement (BFSC) is used more and more. The 31 use of BFSC can not only exhibit the performance similar to that of OPC, but also reduce the 32 emission of carbon dioxide by replacing some cement with slag[6-8], which is good for the 33 34 environment. However, the system containing slag has the problems of lower hydration degree at early stage and insufficient early strength although the workability can be improved, 35

36 which seriously restricts the use scene of slag[9,10].

37 In order to improve the early strength of BFSC, chemical additives have become a common method, although this method has some problems like the amount of additives should be 38 39 restricted[11]. Alkali activated BFSC system has been widely studied. Many studies show that alkali activated system can obtain the strength equivalent to that of OPC in the early 40 41 stage and exceed that of OPC in the later stage of hydration[11–15]. Thomas et al. [12] reported the improvement of micro and macro properties of BFSC by sodium silicate in alkali 42 activated BFSC system. Nguyen et al.[13] investigated the effects of sodium sulfate (Na₂SO₄), 43 gypsum (CaSO $_4$ ·2H₂O) and sodium silicate on the early characteristics of BFSC and 44 concluded that Na₂SO₄ can shorten the setting time and enhance the early strength of BFSC. 45 However, the phase of these systems is too complex to distinguish the respective effects of 46 these additivities on the part of cement and slag. Therefore, many researchers have studied 47 48 alkali activated slag system alone[6,15–18]. In the alkali activated slag system, the type and dose of alkali activator are important factors affecting the strength development[15,18]. 49 Jimenez et al.[19] investigated the effects of sodium hydroxide (NaOH) and sodium 50 51 carbonate (Na₂CO₃) on slag hydration, reporting that the initial pH and anion of activator 52 plays a decisive role in the strength development of slag. Song et al.[20] showed the effects 53 of pore solution on alkali activated slag system. When pH was higher than 11.5, the hydration reaction of slag accelerated. At present, most studies analyze the influence of anions in 54 activators on alkali activated slag. On the one hand, in these systems, the mobility of anions 55 is much higher than that of cations in the early stage of hydration[5,21]. On the other hand, 56 57 it is difficult for cations in pore solution to have specific chemical interactions and the cations 58 are adsorbed on the surface of hydration products by physical adsorption in order to achieve charge neutrality[22–24]. Depending on the system, there are some studies that have looked 59 at cations in activator[21,25,26]. Edwards et al.[21] found that the effects of cations in soluble 60 inorganic salts on the early hydration of OPC is ranked as: $Ca^{2+} > Mg^{2+} > Li^+ > Na^+ > H_2O \gg$ 61 Zn^{2+} . The research by Myrdal et al.[27]came up with a similar result. Sun et al.[25] studied 62 the effects of various common cations in alite pastes mixed with simulated seawater on the 63 micro mechanical properties, in which the deleterious effect of Mg^{2+} on the micro mechanical 64 properties is dominant. De Weerdt et al. [28] reported the effect of various cations in chloride 65 salts on the chlorine binding capacity of Portland cement paste. The chlorine binding capacity 66 of Mg²⁺ and Ca²⁺ is lower than that of Na⁺ due to the effect of pH. 67

68 Sajid et al.[29] studied that the electricity charge and size of cation plays an important role 69 in the modification of slag structure. Calcium hydroxide (Ca(OH)₂) activated slag is an 70 important system to simulate the partial reaction of slag in BFSC. At present, few researchers 71 have investigated the effect of cations of various additives on the early hydration of Ca(OH)₂ 72 activated slag.

In this study, we first investigated the effects of chlorides (KCl, NaCl and MgCl₂), nitrites (KNO₂, NaNO₂ and Ca(NO)₂) and sulfates (K₂SO₄, Na₂SO₄ and MgSO₄) on the strength development, phase assemblage, hydration kinetics and degree of reaction of slag. The effects of chlorides and nitrites with different cation are similar from early to late age and there are no special hydrates formed due to the influence of different cation in the same kind of salt. However, the effects of sulfates seem quietly depend on the cation type and deserve further investigation.

At present, sulfate, especially Na₂SO₄, has been widely studied as an effective activator of slag hydration[13,16,30-33]. Na₂SO₄ mainly increase the pH value of the pore solution and promote the slag dissolution, as shown in the following formula[11,32,33]: 82

84
$$Na_2SO_4 + Ca(OH)_2 + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O \downarrow + 2Na^+ + 2OH^-$$

85

 $(1)^{-}$

83

86

Our previous studies have concluded that Na₂SO₄ has a very evident effect on the early 87 hydration of Ca(OH)₂ activated slag system[32]. On the one hand, Na₂SO₄ improves the pH 88 and promotes the formation of ettringite (AFt), on the other hand, it is related to limiting 89 90 equivalent ionic conductance ((LEIC) indicating the ionic mobility in solution) of sulfate ion (SO_4^{2-}) , the mobility of SO_4^{2-} in the early hydration of slag is faster than other anions like 91 NO₂⁻, NO₃⁻ and Cl⁻, which may penetrate into the hydrates and exchange with OH⁻ 92 effectively[5]. However, few researchers have studied the effect of other sulfate on Ca(OH)2 93 activated slag system. The effect of pH and sulfate on the system remains to be confirmed: 94

(2)

96 97

where X represents the corresponding cation. 98

 $XSO_4 + Ca(OH)_2 + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O \downarrow + XOH$

Kurumisawa [34] reported that in the Ca(OH)2 activated slag system, calcium sulfate (CaSO4) 99 is difficult to affect the system because the Ca^{2+} concentration is too high and the solubility 100 of CaSO₄ is very low. Therefore, this study mainly investigated the effect of different cations 101 in three kinds of sulfate (K₂SO₄, Na₂SO₄ and MgSO₄) on the hydration of slag to fill the 102 above-mentioned knowledge gap. 103

104

105 2. Materials and methods

106 2.1. Materials and sample preparation

The Ca(OH)₂ activated slag pastes were prepared by mixing a commercial GGBFS (ST60) 107 provided by NIPPON STEEL (Specific surface area is 4000 cm²/g compliant with JIS A 6206) 108 with Ca(OH)₂ powder (KANTO CHEMICAL CO., INC), which were the same as those used 109 in our previous research[32]. The chemical composition of GGBFS and Ca(OH)₂ detected by 110 111 X-ray fluorescence (XRF) is presented in Table. 1. The GGBFS is mainly made of amorphous with a broad hump between 25 and 35° 20, which was the analyzed by X-ray diffraction 112 (XRD) in Fig. 1. Fig. 2 shows the particle size distribution of slag and Ca(OH)₂. The chosen 113 dosage of activators was based on the previous study and except to enhance the early strength 114 properly considering the limitation of sulfate content in slag paste[11]. Moreover, for the sake 115 of working environment, strong alkalis present a hazard to handle[35]. Therefore, the 116 activators were prepared by dissolving analytical-grade chlorides, nitrites and sulfates 117 provided by KANTO CHEMICAL CO., INC (purity > 99%) in deionized water with the 118 dosage of 0.1mol /kg and placed at ambient temperature for 1 day to ensure full dissolution. 119 Table 2 shows the mix proportions and undertaken tests of pastes. The pastes with 80% 120 slag and 20% Ca(OH)₂ and a water/binder ratio 0.55 were prepared. For mixing, slag and 121

122 Ca(OH)₂ were firstly placed in the bowl of a 5-L HOBART mixer for low-speed mixing of 30s to achieve homogeneity. Then the pre-prepared activator was poured for low-speed 123 mixing for 90s and resting for 30s, the binders on the edge and blade were scraped down by 124 trowel. Finally, the binders were mixed at high speed for 120s. For mortar, the water/binder 125 ratio was also 0.55. The binder/sand ratio was 1:3 and the same mixing regime was used for 126 the mortar. The mortar was molded with cylinder (50mm diameter and length 100mm) and 127 paste was cast into a plastic cylinder (50mm diameter and length 50mm) and vibrating for 128 30s to remove air. After casting, the molds were immediately covered parafilm to minimize 129 carbonation and moisture exchange with air and placed in the special specimen curing 130 chamber until the specific testing age of 3, 7 and 28d, which are typically used. The curing 131 temperature was maintained at 20°C and the relative humidity was above 98%. 132

The mortars were used for the mechanical test, and the pastes were used for microstructural 133 134 analysis. At specific testing age, the pastes were crushed into smaller particles by hammer and passed through a sieve with a size of 2-5mm. Around 1g of the particles was used for the 135 loss of ignition (LOI). To terminate the hydration of the left particles, the solvent exchange 136 method was used. The particles were treated with acetone and after stopping hydration, some 137 of them were grounded into fine powder by hall mill. The powder samples were reserved in 138 vacuum condition until the testing day for XRD, scanning electron microscope (SEM), 139 thermogravimetric analysis (TGA) and selective dissolution. 140

141 Table 1

142 Chemical composition of GGBFS and Ca(OH)₂

	Chemical composition (wt%)											
D	EC	CaO	SiO ₂	Al_2O_3	MgO	SO_3	Fe ₂ O ₃	TiO ₂	Na ₂ O	K ₂ O	MnO	Others
BF2	41.7	33.8	13.9	7.5	0.6	0.8	0.5	0.4	0.3	0.2	0.1	
Ca(OH) ₂	$Ca(OH)_2$	CaCO ₃	Others									
	97.5	1.0	1.5									



Mix proportions and tests of pastes											
Mix	Slag	CH	w/b	Activator	Test						
ID	(wt%)	(wt%)	ration	(wt%)	CS	XRD	IC	SD	TGA	SEM	PSA
Con				-	×	×	×	×	×	-	×
NS				1.42%	×	×	×	×	×	-	×
KS				1.74%	×	×	×	×	×	-	×
MS				2.46%	×	×	×	×	×	×	×
KC				0.75%	×	×	×	×	-	-	-
NC	80	20	0.55	0.59%	×	×	×	×	-	-	-
CC				1.11%	×	×	×	×	-	-	-
MC				2.03%	×	×	×	×	-	-	-
KN				0.85%	×	×	×	×	-	-	-
NN				0.69%	×	×	×	×	-	-	-
CN2				1.51%	×	×	×	×	-	-	-

Note: CS-Compressive strength; IC-Isothermal calorimetry; SD-Selective dissolution;
PSA-Pore solution analysis.

153 2.2. Compressive strength

148

149

150

Table 2

On 3, 7 and 28d, the mortars were demolded. The compressive strength was measured on triplicate tests using an automatic testing machine (Hi-ACTIS-2000) with a constant load rate of 0.4N/mm²·Sec. An average value with standard derivation was reported as the compressive strength.

158 2.3. X-ray diffraction

Powder X-ray diffraction analysis for the powder samples was performed by an X-ray diffractometry (XRD, Multiflex, Rigaku Co., Ltd., Tokyo, Japan) with Cu-K α radiation under 40 kV voltage and 40mA current. The powder was scanned at the range of 5-70° (2 θ) at a step size of 0.02°/min and scanning speed of 2°/min to investigate the crystalline phases. 20% α -Al₂O₃ was added as internal standard to quantify the amorphous phase. The quantification of hydrates was investigated using Profex[36].

165 2.4. Isothermal calorimetry

The hydration heat of Ca(OH)₂ activated slag mixed with activator was evaluated using a 166 isothermal calorimeter (MMC-5116; Tokyo Riko). Before testing, the internal temperature of 167 the chamber was set at 20°C and kept for 1d to maintain stability. Internal automatic mixing 168 method cannot guarantee homogeneity and sufficiency, therefore external manual mixing 169 method is adopted[37]. Before mixing, the pre-prepared activators were placed at 20°C for 1 170 night to ensure full dissolve and reduce the error caused by internal and external temperature 171 difference. The binder above 20g was mixed externally for 5min in 100 ml ampoule, and the 172 binder was placed in the calorimeter quickly. Because the temperature difference inside and 173 outside the chamber is unavoidable, the initial 1 hours' measurement was omitted. 174

175 2.5. Selective dissolution

The reaction degree of slag was determined by selective dissolution based on EDTA. 176 250 mL triethanolamine 177 **EDTA** solution was prepared with (TEA), 93g Ethylenediaminetetraacetic acid (EDTA) dissolved in 500 mL distilled water and 173 mL 178 diethylamine (DEA) and dilute the solution to 1L[38]. The dissolution test was performed 179 with $0.5g\pm0.02g$ powder. Before test, the powder and cellulose acetate filter papers with 4.5 180 µm pore size (Toyo Roshi Kaisha, Ltd) were dried in a 105°C oven for 1h to avoid moisture 181 exchange. Before the test, the dissolution of raw slag was measured to determine the 182 undissolved proportion of the material, around 5 ± 1 wt% slag dissolved, which was below 183 10 wt% [38]. The powder was mixed with 50 mL EDTA solution in a beaker, then dilute to 184 800 mL with distilled water, which was stirred at 300 ppm for 2h with a magnetic stirrer 185 continuously. The residue was dried in a 105°C oven for 1h until the weight was stable. Then, 186 the weight of the residue was calculated. After weighing, the residue was gathered for XRD 187 test. The hydrotalcite-like phase, as a kind of main phase generated during the hydration of 188 slag, cannot be dissolved by EDTA solution, therefore in this study, the assumption was made 189 as follows: all the MgO was converted into hydrotalcite like phase, so that the mass of 190 hydrotalcite-like phase can be calculated at a mass ratio of 1:2.35[39]. The reaction degree 191 (α) of slag was calculated based on the formula as follows: 192

193
$$\alpha = \frac{100fR_s - R_r}{100fR_s - 2.35fM_{MgO}}$$
(3)

where f is the mass fraction of GGBFS in dry binder, R_s is the mass fraction of GGBFS undissolved in EDTA solution, R_r is the mass fraction of the residue in g/100g anhydrous binder, M_{MgO} is the mass of MgO in GGBFS.

197 Since the powder used in the dissolution test is from dried composite particles, 100g dried 198 composite pastes are converted to anhydrous binder using the following formula[38]:

199
$$m_{anhydrous} = \frac{m_{dried\ composite\ paste}}{1 - LOI}$$
 (4)

where $m_{anhydrous}$ is the mass of anhydrous binder, $m_{dried\ composite\ paste}$ is the mass of dried composite paste and LOI is the nonevaporable water content of the dried composite paste.

To determine the LOI of the binder, around 1g of the particles was dried in a 105°C oven for 1d to obtain a relative constant mass. Then the dried particles were heated from ambient temperature to 700°C for 2h in a furnace to obtain the LOI as above 700°C, S²⁻ will be oxidized to sulfate to increase the mass[40]. The calculation formula is as follows:

207
$$LOI = \frac{m_{105^{\circ}C} - m_{700^{\circ}C}}{m_{700^{\circ}C}}$$
 (5)

where $m_{105^{\circ}C}$ is the mass of particles after 105°C, $m_{700^{\circ}C}$ is the mass of particles after 700°C.

For TGA, the analysis was carried out by HITACHI TG7000. About 10 mg of the powdered sample was loaded into a Platinum crucible. The powder was heated from 20 to $100 \,^{\circ}C$ at a rate of 10 $^{\circ}C/min$, under a N₂ flux of 30 mL/min. The portlandite content was measured using the tangent method.

214 2.7. *pH of pore solution*

The pH value of pore solution was measured using a pH electrode calibrated using buffer solution before the hardening of the paste. The pastes were mixed manually at 30 minutes intervals to avoid the influence of bleeding phenomenon. The pore solution was extracted by KUBOTA 3700 centrifugation (set as 4000rpm and 60s) and the gathered solutions were used for pH measurement. Once the measurement finishing, the solution was filtered with a 4.5µm filter and 5ml injection as soon as possible. After filtering, the solution was stored in a refrigerator to avoid precipitation.

222 2.8. Pore solution composition

To investigate the influence of sulfate salts on the early stage of hydration, the filtered pore solutions at 1, 3, 6, 9, 12, 15, 18 and 24hours were diluted by a factor of 50 for Con and 500 for other samples with distilled water. The measurement was carried out using an ion chromatography (ICS-90, DIONEX, Sunnyvale, CA, USA) to determine the concentration of SO_4^{2-} and Ca^{2+} with the cica-reagent cation mixed standard solution.

228 2.9. Thermodynamic modelling

Thermodynamic modelling was carried out with Gibbs free energy minimization software GEMS with CEMDATA 18 and PSI/Nagra database and CNASH model[41]. The effects of sulfate salts on the phase transformation of slag were simulated in this program based on the hydration degree calculated by selective dissolution.

233 *2.10. SEM-EDS*

SEM was used for observing the morphology of the hydration products in MS. For the
specimen preparation, the powder was immersed in ethanol and treated with ultrasonic
dispersion for 5 min, one milliliter of the suspension was transferred on carbon disks.

The investigation was performed with a JEOL JSM-IT200 scanning electron microscope
 combined with an energy dispersive spectrometer (EDS) operated at an accelerating voltage
 of 15 kV.

240

241 **3. Results and discussion**

242 3.1. Compressive strength

As an essential part of additives evolution, the influence of different inorganic salts on the compressive strength of the mortars were investigated, the result is shown in Fig. 3. As shown in Fig. 3(a), all of the chloride used in this study could improve the early strength of the mortar. However, from 7d, the improvement is not so evident and even lower than that of the control group and one phenomenon can be observed that although the cation in chloride is different, the efficiency is almost same, which seems the influence of action in chloride is
small. The strength development of samples added with nitrites shows the similar tendency
as shown in Fig. 3(b)

It can be seen in Fig. 3(c) that in comparison with control group, KS, NS and MS increase the 1d and 3d compressive strength. At 28d, Con has the highest compressive strength. Moreover, it's noteworthy that at early strength development, KS always has the most evident promotion on the compressive strength and NS has the similar impacts, while the compressive strength of MS does not change much at 1d, at 28d, MS has higher strength than that of KS and NS and close to that of the control group.

It has been reported that sulfates could promote the development of early strength of slag 257 [42–50] and some of the research reported that this high early promotion effect also result in 258 the rate of late strength development reduced because of late porosity increased result from 259 260 crossover effect[49], thick layer of hydrates surrounded the undissolved slag[48] and relative relationship between capillary pores and limit radius[45,46,50]. etc. The results of this study 261 indicate that although sulfate salt promoted early strength development of mortars and 262 reduced the development rate of late strength which is similar to the results of the researchers 263 mentioned above, the effect of sulfate with different cation is a little different, which will be 264 further discussed in next sections. 265





269 3.2. X-ray diffraction

Fig. 4 show the XRD spectra from 5 to 35° (2 θ) of samples cured at 3 and 28d. The result of samples cured at 7d are shown in supplementary data (Fig. S1).

Fig. 4(a) and Fig. 4(b) shows the XRD pattern of samples added with chloride. Instead of SO₄-AFm and AFt, Friedel's salts around $11.16^{\circ}(2\theta)[22,23,28]$ was observed. Fig. 4(c) and (d) shows the XRD spectra of samples added with nitrite. NO₂-AFm was detected at $11.08^{\circ}(2\theta)$ in each spectrum[57,58].

Fig. 4(e) illustrate the development of the hydration phase assemblage at early stage in sulfate. At 3d, ettringite (AFt), hemicarboaluminate, monocarboaluminate and hydrotalcite were identified as the main crystalline hydrates[4,51–54]. In KS, NS and MS, higher sulfate content led to the initial AFt formation increased. Compared with KS and NS, MS has much more AFt around 9°(2 θ)[53] and almost no SO4-AFm was detected, for KS and NS, not only AFt but also a certain amount of SO4-AFm around 9.9°(2 θ)[55] also formed, which is clear 282 shown in Fig. 7, this indicates that based on the concentration of sulfate of the same equivalent, KS and NS promoted the dissolution of slag greatly, while in MS, the relative 283 $A1^{3+}$ concentration was lower than that of SO4²⁻, although the concentration of SO4²⁻ is little 284 low, no SO₄-AFm can form. This may be the reason why the strength of MS is a little bit 285 higher than that of control group but relative lower than that of KS and NS at 3d. In control 286 group, ettringite content was quite small because of the absence of additional sulfate and 287 almost no AFm-like phase was detected, instead, hemicarboaluminate formed, which may 288 relate to the quite slow dissolution rate of slag and result in the low strength at early stage. 289

At 28d (Fig. 4. (f)), the same products are formed, hemicarboaluminate, AFt and
monocarboaluminate as main calcium aluminate hydration products, hydrotalcite as Mg-Al
layered double hydroxide. Small differences were observed. For KS and NS, the intensity of
the peak of AFt is quite low compared with that of MS. For control group, the solid solution
SO4-AFm, OH-SO4 (mainly C4AH13) around 11.30°(20)[56] was observed.

Although the type of hydrate changed with the change of the anion of activators, the cation of the activators seems did not change the phase transformation. Combined with the results of compressive strength, it seems cation in nitrite and chloride has little influence on the hydration development of slag. However, the sulfate is unique enough and it is necessary to understand the effects of cation in sulfate on the slag paste.





Fig. 4. XRD patterns of pastes (a) chloride curing at 3d, (b) chloride curing at 28d, (c) nitrite
curing at 3d and (d) nitrite curing at 28d, (e) sulfate curing at 3d, and (f)sulfate curing at 28d.
The reflection peaks are marked as follows: E stands for Ettringite, SO4-AFm stands for
calcium monosulfaluminate, Hc for Hemicarboaluminate, Mc for Monocarboaluminate, OHAFm for hydroxy-AFm, P for portlandite and Cc for calcite.

309 *3.3. Isothermal calorimetry*

The heat flow curves and cumulative heat results of the pastes, which provide important information regarding the additives influence on hydration kinetics of pastes are displayed in Fig. 5. Fig. 5(a) and (c) shows the hydration heat flow of chloride and nitrite, evidently all the main peak of pastes occurs later than that of control group, although all of them are higher and broader. Compared with sulfate, it seems the shape of the peak did not change in nitrite and chloride. Although CC and MC seem retard the kinetic compare with other chloride, and CN2 seem retard the hydration kinetic compared with KN and NN, the difference in cumulative heat is limit as shown in Fig. 5(b) and (d). This result is consistent with the strength development at early stage.

Fig. 5(e) represents the hydration heat flow of pastes combined with different sulfates. 320 The main peak of Con around 9.8h, NS around 9.3h, KS around 9.85h and MS around 12.9h 321 was attributed to the precipitation of C-(A)-S-H and ettringite, which was confirmed by XRD 322 323 (Fig. S2) NS showed an almost 4 times higher and 0.5h earlier exothermic peak than that of control group around 9.3h, while KS had the similar effects. This may attribute to the 324 activators accelerated the dissolution of slag and the additional sulfate promoted the 325 formation of ettringite. However, for MS, it is clearly shown that the main peak of MS 326 occurred 3h later than that of control group and the rate of the heat generation before and 327 after 11.5h is quite different. Usually, this kind of peak presents undersulfated situation[30]. 328 329 From the result of XRD (Fig.S2), a certain amount of gypsum and a small amount of brucite 330 precipitated. This indicates that in MS, the initial kinetic was limited, which may relate to the initial lower pH value than that of other samples (Fig. 9a). Although the initial hydration of 331 MS is slower than that of other samples, a large amount of ettringite around 5% still can be 332 observed after 15h, which may promote the compressive strength at early age. Fig. 5(f) 333 presents the cumulative heat of pastes, evidently the additional of KS and NS increase the 334 overall hydration, for MS, before 12h, the cumulative heat of MS was almost same as control 335 group, after that, the cumulative heat of MS was a little bit higher than that of control group. 336 However, compared with KS and NS, the accumulated heat of MS was about 39% less at 3d. 337 338 which is consistent with the strength development.





Fig. 5. Effects of chemical activators on hydration kinetics of pastes (a) heat flow of chloride,
(b) cumulative heat of chloride, (c) heat flow of nitrite, (d) cumulative heat of nitrite, (e) heat
flow of sulfate and (f) cumulative heat of sulfate.

346 *3.4.* Selective dissolution

Fig. S3 presents the XRD pattern of samples after selective dissolution. Evidently, after selective dissolution, only hydrotalcite and amorphous phase remained, which illustrate that the selective dissolution method is responsible in this study to some extent. The reaction degree of slag is shown in Fig. 6(a), (b) and (c). It can be seen that the overall reaction degree of samples added with activators is higher than that of control group at early age due to the high activity, which is consistent with the results of compressive strength. With further hydration, the reaction rate of the samples added with activators increase slowly except MS, at 28d, the reaction degree of control even overpasses some samples added with activators. One interesting phenomenon is that in nitrite, although the reaction degree is different, the development rate of reaction degree is quite similar. The reaction degree difference in nitrite and chloride is slight, while in sulfate the tendency of reaction degree is quite different at early although at the late age it seems to be unified.

The relationship between reaction degree and compressive strength is shown in Fig. 6(d). The compressive strength of the samples developed quickly when the reaction degree of slag reaches more than 25%. At early age, the reaction degree quite affects the development of strength. At late stage, nonlinear correction between reaction degree and strength was observed, which indicates that some other factors influence the strength at late age, this has been discussed in the previous work[32].



365

366 Fig. 6. (a) Reaction degree of chloride (b)Reaction degree of nitrite (c) Reaction degree of 367 sulfate and (d) Relationship between reaction degree and compressive strength.

368

369 3.5. The effects of cation in sulfate on Ca(OH)₂ activated GGBFS

As discussed from section 3.1 to 3.4, although some slight difference exists in the development of hydration kinetics and degree of reaction in nitrite and chloride, the influence of this difference is limit in the strength development and phase transformation. The phase transformation and the shape of the exothermic peak in calorimetry seems mainly influenced by the type of anion in activators. However, the kinetic rate may mainly be affected by the anion in activators, and the difference in sulfate is larger than that of nitrite and chloride even influence the shape of the exothermic peak to some extent. Therefore, combined with the result of compressive strength, the effects of sulfates seem quietly depend on the cation type, from this section, the effects of sulfate are mainly discussed.

379 3.5.1.QXRD

Quantification of the hydration products in sulfate by XRD is presented in Fig. 7. The 380 content of C-(A)-S-H was determined by subtracting the amorphous phase from unreacted 381 slag calculated by selective dissolution in section 3.4. From Fig. 7(d), it is shown that quality 382 383 small amount of brucite formed not only in 3d but also at 28d. For MS, it is special because the solubility of brucite is quite low. Bernard et al.[59] investigated that at early age, the 384 brucite precipitated and intermixed with C-S-H, with the hydration progressed, the brucite 385 dissolved and M-S-H formed. Sun et al.[25] found that the at early age, the strength will 386 increase because brucite decrease the porosity. However, dissolution of brucite increased the 387 porosity and this phenomenon will decrease the hardness and modulus of pastes for long term. 388 In this study, the phenomenon is in adverse, the initial strength development was inhibited, 389 at 28d, the strength is a little bit higher than that of KS and NS and through this process a 390 little brucite not above 2% was observed from XRD, which may relate to the low 391 concentration of Mg²⁺ added in this study. Therefore, it is important to investigate the 392 hydrates transformation of MS before 1d, which is discussed in section 3.5.3. The QXRD also 393 394 show the consumption of Ca(OH)₂, with the hydration, the amount of Ca(OH)₂ decreased, 395 however, because the different additives were added, the solubility of portlandite also changed. Therefore, the consumption ratio of portlandite cannot be compared directly. The 396 portlandite content following the same trend as TGA results. 397





402 3.5.2.TGA

403 Fig. 8 displays the TGA/DTG data of pastes cured at 3d (7 and 28d in Fig. S4), which shows the effects of additive activators on the hydration products. From the DTG curves, 404 three peaks were clearly observed. The first peak from 80 to 200°C are considered as the 405 weight loss of several hydrates like C-(A)-S-H, ettringite, AFm phase and hydrotalcite is in 406 agreement with XRD analysis[60,61]. The peak between 380 to 460°C corresponding to the 407 dihydroxylation of portlandite [60,62] was always observed from 3 to 28d in all samples. The 408 third peak appears around 680°C, which occurs a little lower than the peak where calcite is 409 usually located, may be related to the formation of monocarbonates and hemicarbonate or 410 poorly crystalline carbonates due to carbonation of samples, which is consistent with the 411 report by Durdzinski at el.[63] Compared to the control group, all of other samples show the 412 great mass loss between 80 and 200°C, which indicates that sulfate salts greatly promote the 413 hydration of slag. Due to the presence of C-(A)-S-H in the portlandite region, the tangential 414 method was used to quantify the weight of portlandite[37,64]. The weight measured by TGA 415 presents the portlandite left in the hydrate binders, the mass fraction of portlandite in 416 anhydrous can be calculated by the formula as follows: 417

418
$$m_c = \frac{m_R}{0.243(1 - LOI)}$$
(6)

419

420 where m_c presents the residual mass fraction of Ca(OH)₂ in g/100g anhydrous, m_R presents 421 the residual mass fraction of portlandite in g/100 binders.

The results are shown in Table.3. It should be noted that the solubility of has been changed due to the addition of activators. Therefore, the results cannot be compared directly. However, from Table. 3, it is clearly shown that the residual mass of portlandite in most of samples show volatility and large quantity of portlandite precipitate during the whole hydration process as observed. This demonstrates that although Ca(OH)₂ was consumed with the hydration, the solubility of portlandite changed with the activity of slag. This maybe an important factor influences the reaction degree of slag.



429

430 Fig. 8. TGA and DTG curves of pastes cured at 3d.

431 Table 3

432 Resi	idual portland	ite in anhydrous.
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Sample ID	3d	7d	28d
Con	8.72%	12.96%	11.81%
KS	11%	9.63%	8.97%
NS	12.51%	12.09%	11%
MS	10.70%	9.96%	11.36%

433 *3.5.3.pore solution*

As discussed in section 3.3, it was found that differs from KS and NS, although MS 434 promote the strength development at 3d, the initial kinetic was inhibited in MS. To further 435 identify the influence of cations in sulfate at early stage, it is necessary to investigate the 436 phase transformation and early hydration progression. The pH value of the pore solution 437 before 1d is shown in Fig. 9(a). Evidently, KS and NS has higher pH value than that of Con 438 and MS in the whole hydration process before 1d. For MS, it is always similar to the control 439 440 group, even a little bit lower, although it is above the pH value that can promote the dissolution of slag[20]. Fig 9 (b) and (c) shows the concentration of Ca^{2+} and SO_4^{2-} in pore 441 solution changes with time. The tendency of ion concentration in all samples is similar, a 442 large drop was found around 12h corresponding to the large quantities of hydrations 443

444 formation, which is consistent with the result of isothermal calorimetry. Compared to KS and 445 NS, MS and Con always has a higher ion concentration because of the low reaction rate of slag. Fig. 9(d) indicates the relationship between pH and the ion concentration. Suraneni et 446 al.[65] reported that when the concentration of Ca^{2+} in solution is at 20 mM, it has a strong 447 inhibiting effect on the slag dissolution, while in this study the similar phenomenon was also 448 observed that most of the Ca²⁺ concentration in NS and KS is lower than 20 mM after 3h and 449 this may related to high pH value (above 13.1) promoted the dissolution of slag and the 450 hydrates consumed large amount of Ca^{2+} in the solution. 451

- The following mechanisms explaining the changes in the pH for the pore solution in different sulfates:
- For Na₂SO₄ an increase in the pH is observed, which may relate to synergistic reaction described in Eq. (1). The reaction between Ca(OH)₂ and Na₂SO₄ increases the concentration of SO₄²⁻ and results in the formation of more ettringite, while enough Na⁺ remain in the pore solution, which need OH⁻ to ensure charge neutrality. The increased pH of the solution accelerates the dissolution of slag.
- For K₂SO₄ the reason for increasing the pH value of pore solution is almost same as Na₂SO₄, which benefits from the fact that cations can hardly react chemically. The Eq. (7) summarized the mechanisms of pH changes in KS and NS[35]:

462
$$(Na, K)_2 SO_4 + Ca(OH)_2 + 2H_2 O \rightarrow CaSO_4. 2H_2 O \downarrow + 2(Na, K)^+ + 2OH^-$$
 (7)

463

In the case of MgSO₄, the MgSO₄ will react with Ca(OH)₂ and precipitate as brucite 464 465 shown in Eq.(8) because of the low solubility (Fig.S2), which hence reduce the pH value 466 and the precipitation of brucite will be attached on the surface of slag to extend the induction period (Fig. 6a) and decrease the dissolution rate of slag[66]. Moreover, high concentration 467 of Ca^{2+} in the pore solution also inhibits the dissolution of gypsum due to the common ion 468 effect. Such lower pH value and higher concentration of Ca²⁺ than KS and NS inhibit the 469 470 reaction of slag before the paste lose its plasticity. However, as the pH value still >12.5, the slag will be dissolved slowly and $A1^{3+}$ increase in solution consumes the gypsum (Eq.9, 10) 471 and 11)[35.67] and increase the pH value. The formation of brucite in addition of MgO in 472 pure water shows a pH value of 10.5, therefore, the high pH value will cause the metastable 473 brucite dissolve slowly[59]. 474

475

476
$$MgSO_4 + Ca(OH)_2 + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O \downarrow + 2Mg(OH)_2 \downarrow$$
 (8)

$$477 \equiv Si - O - Al \equiv +70H^{-} \rightarrow [SiO(OH)_{3}]^{-} + [Al(OH)_{4}]^{-}$$
(9)

478
$$[Al(OH)_4]^- + 4Ca^{2+} + 6H_2O + 6OH^- \rightarrow C_4AH_{13}$$
 (10)

479
$$C_4AH_{13} + 3CaSO_4 \cdot 2H_2O + 14H_2O \rightarrow C_3A \cdot 3CaSO_4 \cdot 32H_2O$$
 (11)

480



481

482 Fig. 9 pore solution of concentration and pH (a) pH, (b) Ca²⁺, (c) SO4²⁻ and (d) relationship
483 between concentration of Ca² and SO4²⁻ and pH.

Thermodynamic modelling was used to simulate the phase transformation of MS at low reaction degree. The reaction degree of slag before 1d was calculated based on the result of cumulative heat release:

488

$$489 \qquad \alpha(t) = \frac{Q(t)}{Q_{max}} \tag{12}$$

490 Where $\alpha(t)$ represents the reaction degree of slag, Q(t) is the heat release at time t and Q_{max} 491 is the total heat release.

The total heat release was obtained based on the result of reaction degree calculated by selective dissolution at 3d, which is stable. The results of reaction degree and phase transformation is shown in Fig. 10. In order to clearly show the hydrates, the unreacted slag was not shown because of the relatively large amount. At initial hydration process, gypsum and brucite precipitated as observed in XRD (Fig. S2), which also consistent with the results of pore solution. This kind phenomenon inhibits the dissolution of slag. However, the 498 concentration of Mg^{2+} is not so high and brucite gradually dissolved, this maybe the reason 499 that brucite cannot be detected at 3d. Although the initial hydration was inhibited, large 500 amount of AFt remain for quite a long time because of high concentration of $SO4^{2-}$ in the 501 pore solution, the formation of AFt increases the solid volume by 164.2%[67]. Therefore, the 502 strength of MS still higher than that of control group.



Fig. 10 (a) reaction degree of slag at early age and (b)phase transformation of MS at initialstage

507

508 *3.5.4.SEM-EDS*

Fig. 11 presents the SEM images of the MS paste at 1h and 9h. A large amount of plateshaped and little needle-like shaped hydrates is observed, which demonstrates the added MS accelerate the dissolution and hydration of slag. In Fig. 11(b), an extent amount of brucite, which has a plate-like shaped similar as Ca(OH)₂[68] has been observed. This indicates in MS, the initial hydration kinetics were limited and resulted in the precipitation of brucite, which is consistent with the result of XRD and thermodynamic modelling.

515



517

Fig. 11. SEM image of (a) the MS paste at 1h and (b) the MS paste at 9h.

518

519 4. Conclusions

In this study, the effects of cations in sulfate on Ca(OH)₂ activated GGBFS were mainly investigated by XRD, Isothermal calorimetry, TGA and thermodynamic modeling. The main conclusions are:

- Although all of the nitrite, chloride and sulfate activators could improve the strength
 of slag at early age, it seems the type of nitrite and chloride has little impact on the
 development of slag hydration.
- Sulfate activators with different cations can promote the compressive strength and hydration degree of Ca(OH)₂ activated blast furnace slag at early age as the order:
 K₂SO₄> Na₂SO₄ > MgSO₄, but their strength were comparable to strength of the mortar without activators at 28d.
- 3. As one of the main hydration products, the type of AFm like phase is quietly dependenton the anion of activators.
- 532 4. K₂SO₄ and Na₂SO₄ accelerate the hydration kinetics of pastes evidently because of hydrates like AFm and AFt produced. The hydration kinetics of MgSO₄ was limited due to the precipitation of gypsum and brucite at initial stage, which may relate to the change of pH value.
- 5. The development of compressive strength at early age may relate to the pH change at 537 initial stage. The mechanism of pH change in K₂SO₄ and Na₂SO₄ is almost same, a rise 538 on pH can be achieved due to synergistic reactions between sulfate and Ca(OH)₂, while 539 the low pH of MgSO₄ is mainly due to the low solubility of brucite and precipitation 540 of gypsum. The critical concentration of calcium ions is 20mM and critical pH value 541 is around 13.1 for promoting the slag hydration in this study.
- 5426. Compared with K_2SO_4 and Na_2SO_4 , although the hydration process in MgSO₄ is lower,543a large amount of AFt remain due to the high concentration of $SO_4^{2^-}$, which can still544promote the strength development at early age.

545

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549

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