Effect of different MgO on the hydration of MgO-activated granulated ground blastfurnace slag paste

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ABSTRACT

Reactive MgO recently emerged as a potential activator for granulated ground blast-furnace slag (GGBS), which is one of the most widely used by-products in the cement industry. However, it is known that the characteristics of reactive MgO vary significantly, which may affect the activation process. In this study, seven commercial reactive MgOs, whose reactivities vary widely, were chosen to activate GGBS. The unconfined compressive strength of the MgO-GGBS paste at up to 90 days was measured. It was found that both the reactivity and composition of the MgO samples have effects on the strength development. The major hydration products were identified as hydrotalcite-like phases (Ht) and calcium silicate hydrate (CSH) using X-ray diffraction (XRD). The microstructural characteristic was examined by scanning electron microscopy (SEM). It is concluded that the characteristics of MgO (e.g., reactivity, composition) significantly influence the performance of MgO-GGBS blends.

Key words: MgO, granulated ground blast-furnace slag, reactivity, hydration, microstructure

INTRODUCTION

Portland cement (PC) production generates a substantial amount of CO_2 from the decomposition of limestone at ~1450°C, the combustion of fuels in the kiln, as well as from power generation (Hbert et al., 2010). It is estimated that the cement production accounts for 5–8% of man-made CO_2 emissions (Scrivener and Kirkpatrick 2008). As a result, various attempts to reduce cement clinker production have been made, one of which is the extensive usage of industrial by-products. Alkali-activated binders based on ground granulated blast-furnace slag (GGBS) are sustainable alternatives to PC due to their low initial capital cost of the raw material and the saving of energy and resources resulting in lower CO_2 emission (Yang et al., 2012). It is estimated that more than 80% of CO_2 can be reduced by substituting alkali-activated binders for PC (Juenger et al., 2011). However, several issues concerning the use of strong alkali exist, which prevents the widespread use of alkali-activated binders

including over-rapid setting, the difficulty of handling the caustic alkali and uneconomical efficiency (Yang et al. 2012). In this sense, alkaline-earth hydroxides such as Ca(OH)$_2$, Sr(OH)$_2$ and Ba(OH)$_2$ were studied and found to be able to facilitate the hydration of GGBS (Roy et al. 1992; Yang et al. 2010). Recently, reactive MgO emerged as an effective activator for GGBS. Li (2012) and Yi et al. (2012) reported that reactive MgO increased the hydration of GGBS significantly and slag activated by 10-20% MgO outperformed corresponding lime-activated slag with strength values of up to 4 times higher. The effect of MgO in the alkali-activated slag system has been investigated by many researchers, either in the form of internal MgO from slag composition (Ben Haha et al. 2011), or external MgO addition (Shen et al. 2011). It should be noted that since the GGBS is usually produced between 1400-1600°C (Shi et al., 2006), the internal MgO is categorised as dead burned MgO (Shand 2006); whereas reactive grade (calcined under 1000°C) is often selected as the MgO added externally. Ben Haha et al. (2011) investigated the effect of MgO content (internal) on the performance of alkali activated cement and revealed that the main hydration products are calcium silicate hydrate (CSH) gel and hydrotalcite (Mg$_6$Al$_2$CO$_3$(OH)$_{16}$·4H$_2$O)-like phases (Ht). Higher content of MgO produced more Ht, which is more voluminous, resulting in higher strength. Reactive MgO was used to replace 40% of slag, activated with K$_2$CO$_3$ and sodium silicate, and it was found that the strength was only slightly lower than the control (Gu 1991). In the work by Shen et al. (2011), light-burnt dolomite (mainly contains reactive MgO and CaO) was added in sodium silicate-activated slag and fly ash blends, and the results indicated that hydration of reactive MgO decreased the shrinkage of the paste, and no interaction between MgO and other components was observed by the microstructural analysis. Although it is known that the characteristics of reactive MgO vary significantly (Shand 2006), which may affect the activation process, none of these studies investigated or presented the effect of the characteristics of MgO on the performance of MgO-GGBS blends.

Hence this paper presents an investigation of the hydration performance of MgO-activated GGBS using seven different commercially available reactive MgO samples. The unconfined compressive strength (UCS) of the pastes was measured at different curing times. X-ray diffraction (XRD) was used to identify the hydrated products and scanning electron microscopy (SEM) was employed to study the microstructure of the blends. The effect of the characteristics of the MgO samples on the slag activation process was discussed based on the experimental results obtained.

MATERIALS AND EXPERIMENTAL METHODS

The sources and chemical compositions of the seven commercial reactive MgOs studied are shown in Table 1: five MgO samples were obtained from calcined magnesite, one synthesised from seawater and one synthesised from chemicals. GGBS was obtained from Hanson, UK, whose composition is also presented in Table 1. The reactivity test was used to measure the time duration required for the neutralisation of an acidic solution (in this case 0.25M acetic acid) by a certain MgO sample mass (in this case 5.0g) and Phenolphthalein was adopted as the pH indicator (Shand 2006). The time from adding the MgO to the change of the solution colour is recorded as the reactivity and the shorter the time, the more reactive the MgO is. The test was performed in duplicate for each sample and the average value was reported here.

To prepare the MgO-GGBS pastes, raw materials were hand mixed for 5 minutes in a bench-scale food mixer and cast into ɸ3.4×6.8cm mini cylindrical moulds. The fresh cement paste were demoulded after 24 hours and then transferred into a water tank and cured for 7, 28 and

90 days. In this study, the MgO:GGBS ratio was fixed at 1:9 according to a preliminary study, and the water to cement ratio was fixed as 0.4 in order to focus on the influence of the MgO on the performance of the MgO-GGBS blend.

The unconfined compressive strength (UCS) of the samples, in triplicate, was determined according to British Standard (BS EN 196-1:2005) at each curing age. Some sliced specimens were collected after crushing and part of the samples were ground to powder. The powder and sliced specimens were stored in acetone to arrest the hydration and vacuum dried for at least 7 days before XRD and microstructure analysis. Once dried, the samples were further ground to pass through a 75µm sieve. XRD measurement was carried out on the Siemens D5000 X-ray diffractometer with a CuKα source operating at 40kV and 40mA using a scanning range from 5 to 55 (2Θ), with scanning speed of 1s/step and resolution of 0.05°/step. The sliced specimen was gold coated and the morphology was examined on the JEOL 820 scanning electron microscopy (SEM).

Table 1. Source, label and chemical compositions of the raw materials used in this study

Source	Supplier	Label	MgO	CaO	Fe_2O_3	Al_2O_3	SO_3	Cl	SiO_2	LOI
Magnesite	RBH*, Greece	CS	87.9	2.9	0.3	0.13	-	-	8.7	1.6
	Styromag, Austria	K10	80.0	6.9	2.8	-	-	-	6.0	7
	RBH*, Greece	CG	88.3	2.6	0.2	0.18	-	-	8.8	1.9
	RBH*, Greece	NOR	91.6	1.7	0.1	0.14	-	-	6.5	2.3
	RBH*, Greece	CR	88.9	2.6	0.2	0.15	-	-	8.2	2.2
Seawater	ICL Industrial Products, Israel[#]	DSP	99.2	0.2	0.01	0.004	0.125	0.1	0.02	0.8
Chemical reaction	Intermag Ltd, UK	IM	94.5	0.3	0.02	0.01	0.2	0.2	0.02	6
-	Hanson, UK	GGBS	8.5	39.5	0.5	12.5	1	-	36.5	-

[*] Richard Baker Harrison Ltd, UK; [#] Also contains traces of B_2O_3 and Na

RESULTS AND DISCUSSION

Characterisation of MgO

Table 1 shows the effect of the different origins on the chemical compositions of the different MgO samples. The MgO content ranged from 80% to 99.2%; where the synthetic MgO samples generally have higher purity, with MgO content of over 94% for both samples. The major impurities of calcined MgO are CaO and SiO_2, which originate from common minerals in rocks, while the major impurities of the synthetic MgO are CaO, Cl, and SO_3

derived from seawater and chemical reagents. It is noteworthy that K10 has a much higher CaO content than other MgO samples.

The reactivity values (as the time increases, the reactivity decreases) of all the seven MgO powders tested are plotted in Figure 1. It is found that the synthetic ones (i.e., IM and DSP), had the highest reactivities, which were quite similar, while the MgO samples calcined from magnesite showed much lower reactivities and a much wider range. This confirms that the reactivity of the calcined MgOs is strongly affected by the thermal conditions of the calcination process (Birchal et al. 2000; Mo et al. 2010; Sun et al. 1991). Higher reactivity suggests more brucite formed at the same curing age, which will participate in the reaction with GGBS.
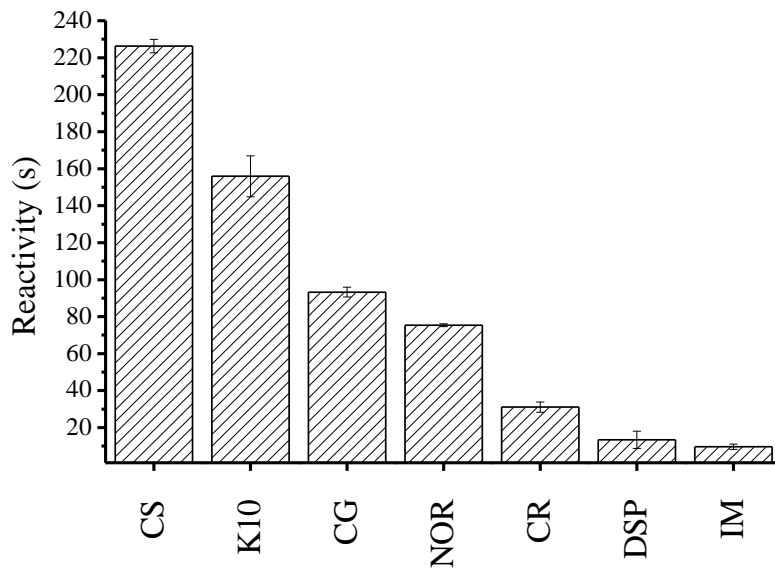

Figure 1. The reactivity of the different commercial MgOs tested

UCS Results

Figure 2 shows the UCS values of all MgO-GGBS pastes at curing ages of 7, 28 and 90 days, which clearly indicates that the MgO successfully activates the GGBS and the strength continues to increase with time. It is found that using different MgO samples, the UCS of MgO-GGBS pastes can achieve between 23~30MPa after 90 days' curing. The effect of reactivity on the UCS of MgO-GGBS pastes is shown in Figure 3. At the early age (7 days), the strength increased with reactivity (i.e., decrease of reactivity value). However, in the long term, the UCS of the less reactive MgOs increased more remarkably than those of the most reactive ones (IM and DSP), which will be explained later in this paper. In addition, K10 exhibited higher strengths than expected at all ages, which is attributed to its higher CaO content. This phenomenon is consistent with Lu et al. (1957) that the combined use of CaO and MgO is more beneficial for strength development. There are two roles that CaO plays in the system. Firstly, CaO increased the pH of the system since the equilibrium pH of $Ca(OH)_2$ is 12.5, which is much higher than $Mg(OH)_2$ (10.5) (Zhang et al. 2011). The increase of pH facilitates the dissolution of GGBS, resulting in higher hydration degree (Song et al. 2000). In addition, CaO, when it hydrates, participates in the reaction with GGBS to form more CSH, which contributes to strength.
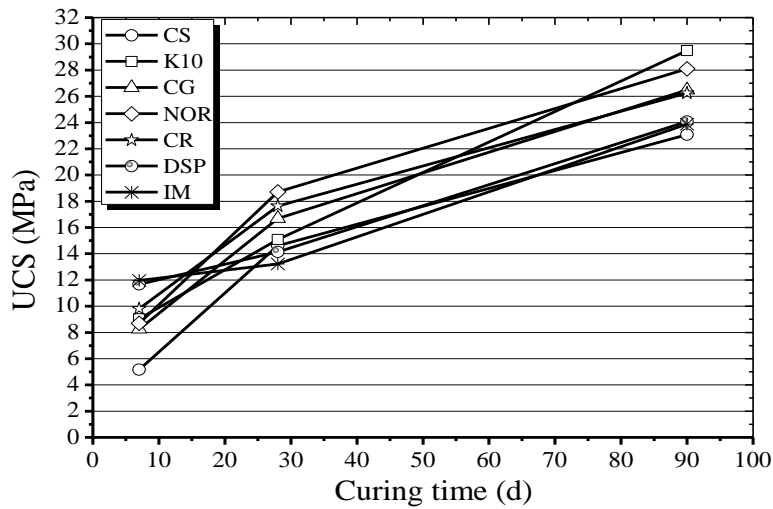
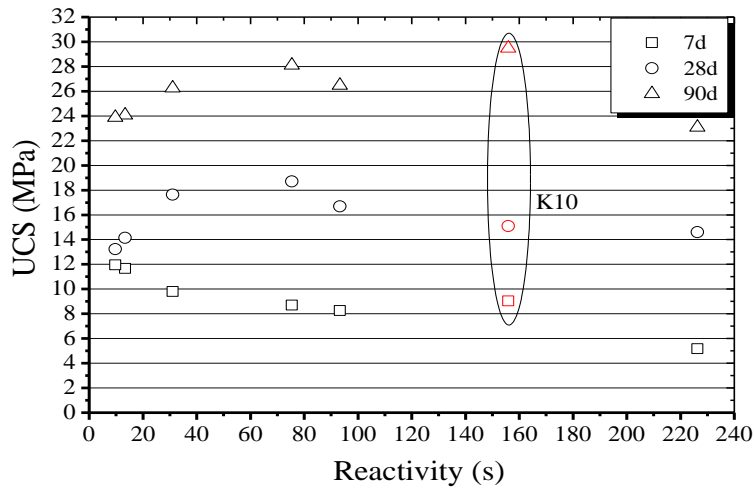**Figure 2. Strength development of MgO-GGBS pastes**

Figure 3. Effect of MgO reactivity on the UCS of MgO-GGBS pastes

XRD Results

To study the hydration products of the MgO-GGBS blends and the effect of MgO, the highly reactive and less reactive MgO samples (i.e., DSP and CS, respectively) activated GGBS were selected for XRD and SEM analysis. Figure 4 shows the XRD curves of the pastes at different curing ages. The broad and diffuse peak at 25-35° 2Θ reflects the short range order of the $CaO-Al_2O_3-MgO-SiO_2$ glass structure. The curves showed the presence of Ht and CSH as the major hydration products, which is consistent with (Ben Haha et al. 2011). The most obvious difference between the two reactive MgO-activated GGBS was the intensity of the MgO and Ht. As expected, higher reactivity resulted in less MgO remained in the blends at every curing time. When DSP (higher reactivity) was used, Ht was observed at 7 days and its intensity increased with curing time, while CS activated GGBS showed no sign of Ht in the short term (7 days). It should be noted that in both systems, there was no brucite detected indicating that the hydrated MgO was all consumed in the hydration. The fate of Mg ion was

probably attributed to the formation of magnesium silicate hydrates (MSH) first and Ht at later age. The existence of MSH by the reaction of MgO and silica fume at ambient temperature was confirmed in numerous papers (Ono and Wada 2007; Wei et al. 2006, 2011; Zhang et al. 2011). However in this study, due to the low crystallinity of MSH and its miscibility with CSH (Brew and Glasser 2005), it is hard to be distinguished by XRD. As suggested by (Ben Haha et al. 2011), Ht is more voluminous than CSH gels, resulting in a matrix with lower porosity in an adequate quantity; however, it is found that when too much Ht is present in the blend, the over-expansion causes volume instability and may be detrimental to the strength as presented in Figure 3. Although not detected here, ettringite is believed to be formed due to sulfate (S) in MgO-GGBS blends, which is confirmed in an early study using thermogravimetric analysis. Since both the highly reactive MgO contains S as well as slag itself, their low strength at later ages was also attributed to the expansion caused by formation of ettringite.
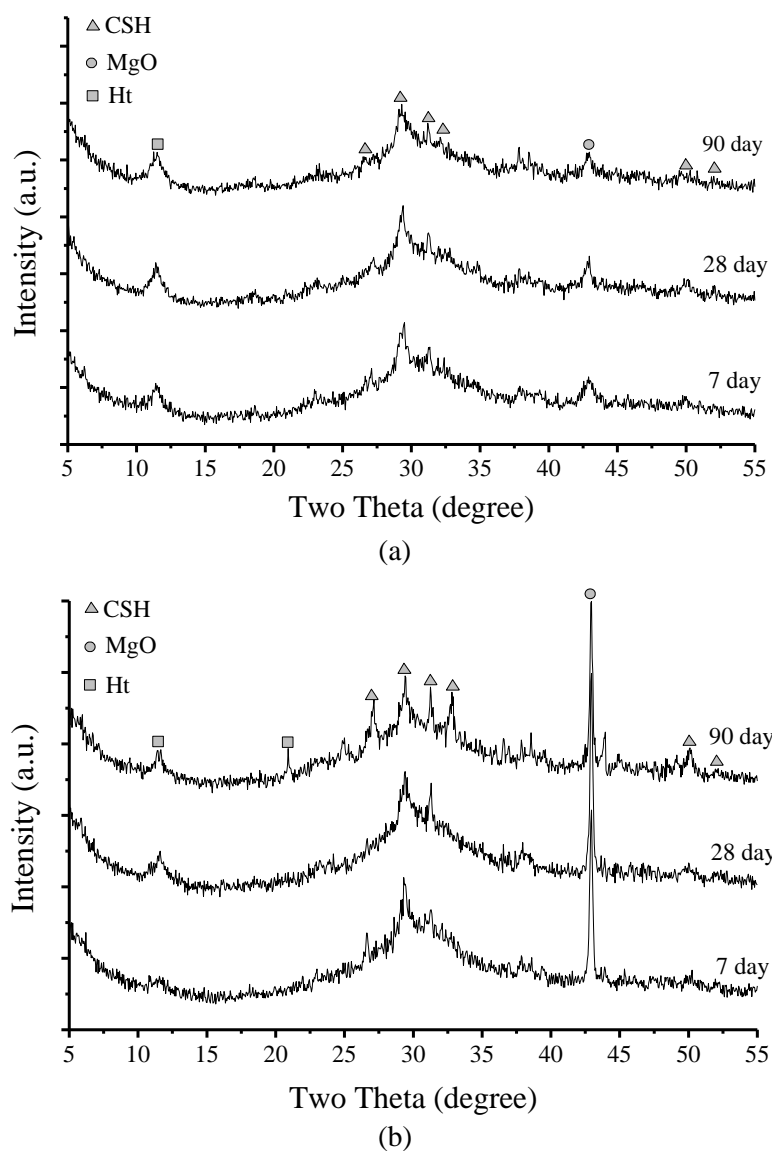

(a)

(b)

Figure 4. XRD curves of (a) DSP-GGBS blends; (b) CS-GGBS blends

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SEM Results

Figures 5 and 6 show the microstructure of CS-GGBS and DSP-GGBS blends at 28 and 90 days. At 28 days, micro-cracks were observed in DSP-GGBS blend with brucite aggregates dispersed on the surface of CSH gel. While for CS-GGBS blend, the irregular unhydrated slag particles were identified and no cracks were formed at this stage. This explains the UCS results that although DSP is more reactive than CS and produced more hydration products accordingly in the short term, the higher expansion destroyed the integrity of the matrix resulting in lower UCS. As mentioned before, the cracks could be attributed to the formation of ettringite and Ht. At 90 days, both blends were found to contain many cracks in the matrix with brucite particles on the surface, but the crack propagation is more significant in 83CS-GGBS than in DSP-GGBS blend. It is concluded that MgO with lower reactivity is more detrimental to the cement soundness in the long term due to the latent hydration of less reactive MgO.
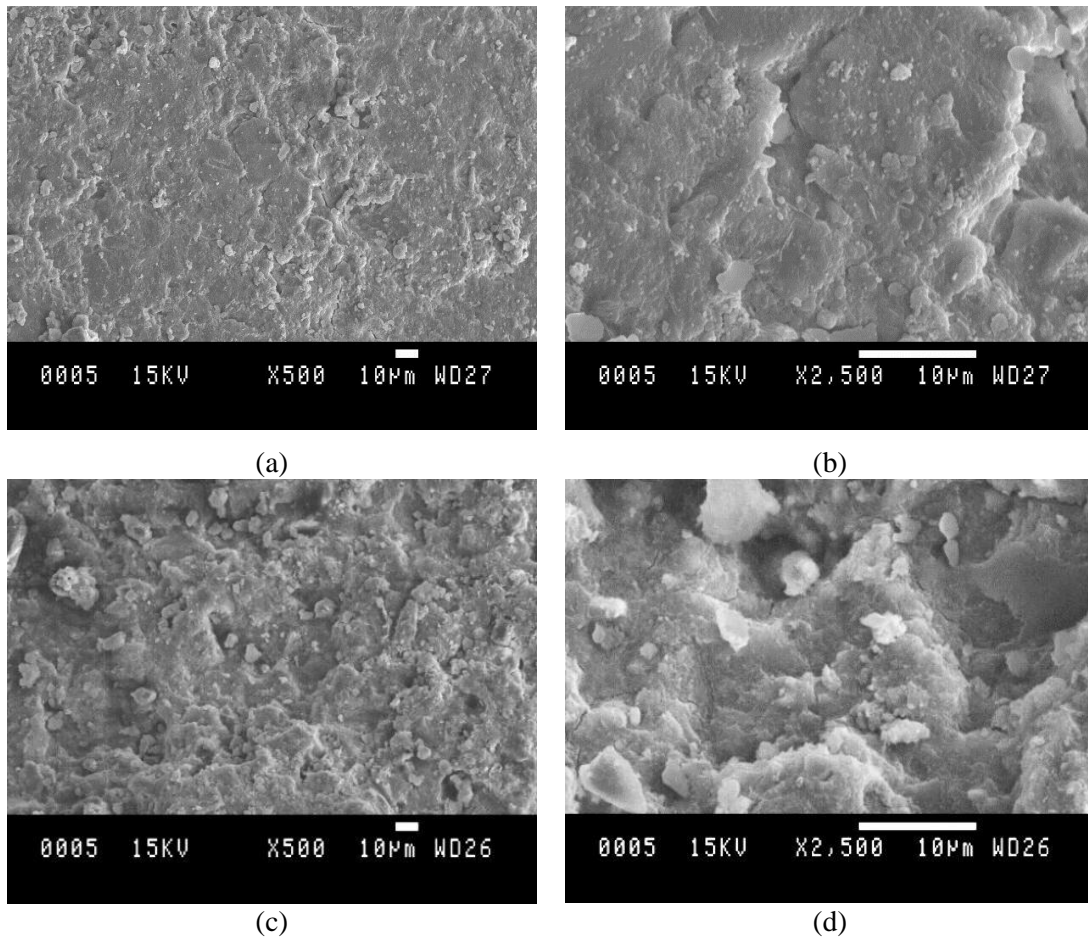

(a)

(b)

(c)

(d)

Figure 5. SEM images of DSP-GGBS blends (a) (b) at 28d; (c) (d) at 90d
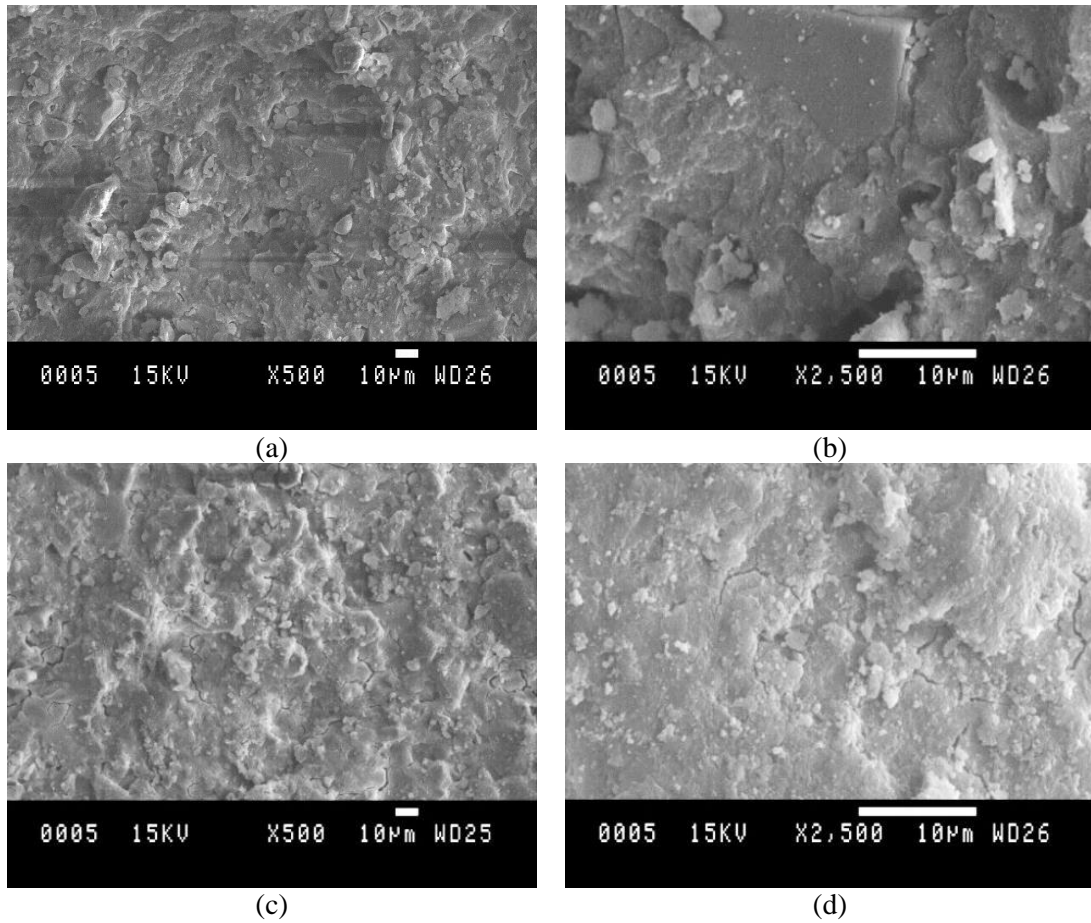
(a)

(b)

(c)

(d)

Figure 6. SEM images of CS-GGBS blends (a) (b) at 28d; (c) (d) at 90d

CONCLUSIONS

By investigating the hydration of different MgO activated GGBS pastes, the following conclusions can be drawn:

1. The characteristics of reactive MgO vary significantly in terms of their reactivity and chemical composition;
2. The strength of MgO-GGBS blend is affected by the reactivity of the MgO. More reactive MgO resulted in higher early strength.
3. The CaO content in the reactive MgO samples is beneficial to strength development;
4. The major hydration products are hydrotalcite-like phases (Ht) and CSH. More reactive MgO reacts faster than less reactive ones, leading to formation of Ht in a shorter time. However, it also causes cracks resulting in strength decrease earlier than less reactive MgO samples. In longer term, due to the latent hydration of less reactive MgO, the cement soundness is also destroyed.

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