

Strength Development and Microstructure of Alkali-activated Slag-MgO in Air Curing Condition

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Abstract. The aim of this study is to analysis the effect of MgO on strength development and microstructure of alkali-activated slag (AAS) in air curing condition. Four mixtures of AAS are prepared using different MgO content (0%, 5%, 10%, and 15 % by weight of slag) at water to binder ratio of 0.4. The flow, compressive strength, scanning electron microscopy, and X-ray diffraction are tested under relevant standards. The addition of MgO significantly accelerated the hydration rate of AAS. AAS with adding MgO tended to increase the compressive strength and to reduce the flow. The higher adding MgO content was associated with higher hydrotalcite-like phase (Ht) formation which improved the microstrure of AAS in the air curing condition.

1 Introduction

Ordinary Portland cement (OPC) has been widely used for the construction due to the many benefits from good properties to the cost of it. Based on the popular raw materials, the cement production can be easily conducted at many countries in the world. However, there is an estimation of about 1510 kWh consumed to produce one ton of cement as well as this process released about 900 kg of CO₂ into the atmosphere and approximately contributed about 5% of the global anthropogenic CO₂ production [1], [2].

In order to reduce the impacts into the environment as well as ensure sustainable development, using the alternative materials like as fly ash, ground granulated blast furnace slag (GGBFS), rice husk ash, lime stone powder and more to blend with OPC for reducing the consumption of OPC has focused in many researches [3]-[5]. On the other hand, alkali-activated slag (AAS) which is produced with 100 % GGBFS with activators such as sodium hydroxide, sodium silicate or sodium carbonate were considered as an alternative binder in the construction. This has certainly many advantages such as reuse the by-product, reduce the CO₂ emissions from cement productions, have similar or better properties to Portland cement. However, these materials have quick setting time and high drying shrinkage or micro-cracks. Different researchers had tried to mitigate the drying shrinkage of AAS. Bakharev et al. [6] used gypsum with 6 % by weight to reduce both of autogenous and drying shrinkage effects of AAS due to the ettringite (Aft) which is formed by the expansion of high voluminous of it. On the other hand, dolomite was also used as an expansion agent due to its content MgO, C₂S and a little

amount of CaO. Xu Lingling et al. [7] showed that, the burning condition of dolomite and the dosage of MgO-based expansive increased the paste expansion. Expansion of cement increases with the lower burning temperature and the coarser particles size of MgO. Additionally, the expansion increased with increasing the burning condition but the expansion time delayed.

Using magnesia (MgO) to improve the properties of AAS has been studied for long times ago. In their study, Ben Haha et al. [8] showed the performance of AAS with various of MgO content in different slag. The results illustrated that the main hydration products are still C-S-H gel and hydrotalcite-like phase (Ht) which are formed from the reaction between MgO and slag. The formation of Ht increases with an increasing content of MgO. On the other hand, the higher compressive strength in the mixture with high MgO content. In another research, Fejin et al. [9] used two kind of reactive MgO to modify the alkali-activated slag and the results showed that the high reactive MgO produced Ht quickly and filled in to the macro-pores to form the meso-pores, hence it improves the compressive strength of AAS. Moreover, the high reactive MgO released more the Ht lead to the decreasing drying shrinkage. Comparing with the high reactive MgO, the medium reactive MgO also form the Ht and C-S-H in the hydration products. However, the rate of reaction of medium reactive MgO is slower than the high reactive MgO. Moreover, the reactive MgO were used as an activator for AAS to replace for conventional activators. Another research of Fei Jin et al. [10] used two kinds of reactive MgO various from 2.5% to 20% by weight to activate the GGBFS. The results gave hydrotalcite-like phase and C-S-H gel were also the main hydration

products and the more reactive MgO released more hydration products which contribute to higher strength of AAS paste. The hydration products content increased with increasing the MgO content and curing time.

Even though, numerous researches have been done so far, still the problems are not fully resolved. This study investigated the effect of MgO on the fresh properties, strength development and microstructure of alkali-activated slag-MgO (AASM) in air curing condition. MgO was used with 5 %, 10 % and 15 % by weight of GGBFS, sodium hydroxide and sodium silicate with modulus SiO_2/Na_2O equal to 0.4 were used as an activator for AAS. The flow and compressive strength up to 28 days were used to estimate the mechanical properties of AASM as well as the XRD and SEM results were used to analysis the microstructure of AASM.

2 Materials and test method

2.1 Materials

Table 1. Characteristics of binder materials.

Items		S4000	MgO
Physical properties	Specific gravity	2.98	2.91
	Mean particle size	14.563	10.57
	Specific surface area (m^2/g)	1.44	1.62
Chemical composition (wt.%)	SiO_2	33.39	9.64
	Al_2O_3	14.39	-
	Fe_2O_3	0.19	0.15
	CaO	41.08	0.41
	MgO	7.22	89.2
	SO_3	0.11	0.75
	TiO_2	0.50	-
K_2O	0.60	-	

In this study, the GGBFS and MgO were collected from the companies located in Taiwan used to produce the AASM. Physical and chemical properties of these materials were examined and shown in Table 1. The mainly component of GGBFS was composed CaO (59.75%) and SiO_2 (26.74%), while MgO was pure material with 89.2% by weight. About the physical properties of these materials, MgO is presented a finer material than GGBFS based the lower mean particle size (10.57 μm compared with 14.563 μm , respectively) and higher specific surface area (1.62 (m^2/g) compared with 1.44 (m^2/g), respectively).

According to XRD patterns results in Figure 1, GGBFS is mainly found at amorphous phases, while MgO is pure and well crystallized material. On the other hand, MgO particle size was significantly smaller than GGBFS. In order to activate the AASM, a combination of sodium hydroxide (NaOH) with a purity higher than

98 % by weight and sodium silicate (Na_2SiO_3 with Na_2O : 8.26 %; SiO_2 : 25.7 % and water: 66.04 %) was used as an activator solution. Sodium hydroxide solution was mixed in water with molarity of 10M to dissolve the pellets before casting the samples. Local tap water was used in this study.

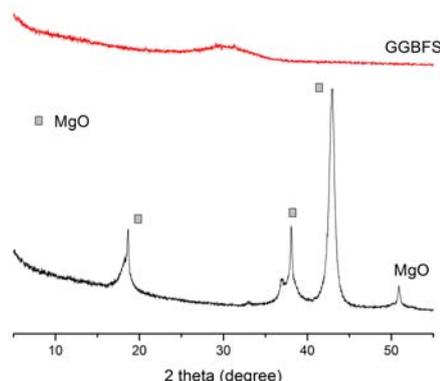


Fig. 1. XRD pattern of raw materials.

2.2 Mix proportions and test methods

The alkali-activated slag paste was prepared with proportions of adding MgO content of 0, 5, 10 and 15 % by weight of slag. All the parameters were kept constant, including the modulus SiO_2/Na_2O ratio of 0.4; the proportion of Na_2O of 4 % by the weight of binder, the water to solid equal to 0.4 and all of them were clearly shown in Table 2. First, sodium hydroxide and sodium silicate were mixed for two minutes to get homogenous activator solution before casting. Then, MgO was mixed with a part of water to homogenous for two 2 minutes and later slag and all the water were added. After 3 minutes, the activator solution was added and the AAS pastes resulted. For the fresh AAS paste, the flow test was conducted and 50x50x50 mm cubic paste samples were prepared with two layers as well as the mold was shaken by hand to limit the moisture content. To prevent the evaporation of water from the paste, all the samples were immediately covered by thin film and after 1 day, the samples were demolded and put into the chamber of $60\% \pm 1\%$ humidity at $27 \pm 2^\circ C$.

The compressive strength of AAS paste was measured on 1, 7, 28 days according to ASTM C 109 Microstructure analysis test was done for 1 & 28 age days specimens by using SEM. Finally, XRD test was conducted with a scanning range from 10 to 50 degree (2 theta) for 28 days of curing times.

Table 2. Mixtures design for the alkali-activated slag-MgO.

Samples	Ingredient (%)					Flow (cm)
	w/b	GGBFS	MgO	SiO_2/Na_2O	Na_2O	
M0	0.4	100	0	0.4	4	34
M5	0.4	95	5	0.4	4	31.5

M10	0.4	90	10	0.4	4	29.5
M15	0.4	85	15	0.4	4	28

3 Results and discussion

3.1 Flow and compressive strength development

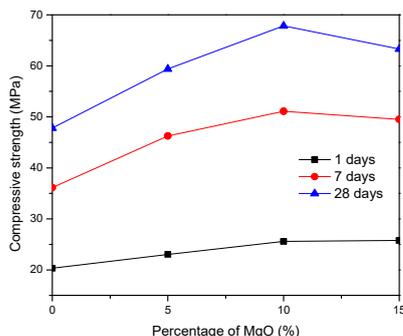


Fig. 2. Strength development of AASM.

The flow of AAS with various MgO contents is illustrated in Table 2. The flow reduced with increasing contents of the MgO. The flow of samples with 0%, 5%, 10%, and 15% MgO content were 34 cm, 31.5 cm, 29.5 cm, and 28 cm, respectively. The compressive strength of AASM pastes is shown in Figure 2. There is a slight increase in compressive strength of AASM for all proportions containing MgO on 1 day after demoulding. As expected, the paste with 15% MgO exhibits the highest compressive strength in 1 day. This result showed that high MgO content accelerated the hydration rate of AAS in the early age days [10]. At 28 days of air curing condition, the AASM showed the highest compressive strength with 10% MgO content. The compressive strength values of M5, M10, M15 were increased about 24.5 %, 42.5 %, 32.4 %, respectively, compared with mixture without adding MgO.

MgO accelerated the hydration reaction of AAS leading to more the hydration products formed [9], based on that, the compressive strength of AASM is higher than AAS without MgO content. Furthermore, the hydrotalcite-like phase is one of hydration products which is high voluminous to fill into the voids of aggregate to increase the compressive strength. However, the compressive strength of AASM increased with increasing MgO content up to 10 % and slightly reduced with 15% MgO content due to the large proportion of slag replaced by MgO lead to reduce the aluminosilicate content.

3.2 X-Ray diffraction analysis

The X-ray diffraction of AASM at 28 days of curing are portrayed by Figure 3. The results expressed that C-S-H gel and hydrotalcite-like phase are the two main hydration products which are shown on the amorphous

phase so the peak are too low [11]. It is found that the Ht peak was disclosed at $2\theta \sim 11.7^\circ$, the intensity of Ht peak raise with an increasing in MgO content and the more unhydrated MgO were observed at $2\theta \sim 42.9^\circ$ comparing with the mixture without adding MgO. The formation of hydrotalcite-like phase was exhibited by quick reaction between MgO with the broken Al-O and Si-O in the slag so the higher Ht was formed with increasing the MgO contents. Finally, the shaper peak of C-S-H gel was found at $2\theta \sim 29.5^\circ$ [12].

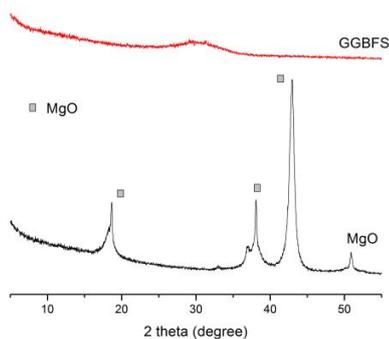


Fig. 3. XRD pattern of AASM at 28 age days.

3.3 SEM images

SEM images of AASM paste samples are presented by Figure 4 and 5. The results showed that after demoulding at 1 day, the AASM pastes exhibited high porous structures by un-hydrated slag and MgO particles. This result illustrated the low compressive strength in 1 day. Two main hydration products of AASM are C-S-H gel and hydrotalcite which covered around the slag particles. The extent of formation of hydration products depends on the content of MgO and it increases with a higher proportion of MgO. Based on that the porosities of AASM paste samples lightly decreased. Especially, hydrotalcite-like phase was found with the mixtures contained adding MgO after demoulding and the amount of Ht increased with more the adding MgO contents lead to the higher compressive strength of mixtures contained more adding MgO.

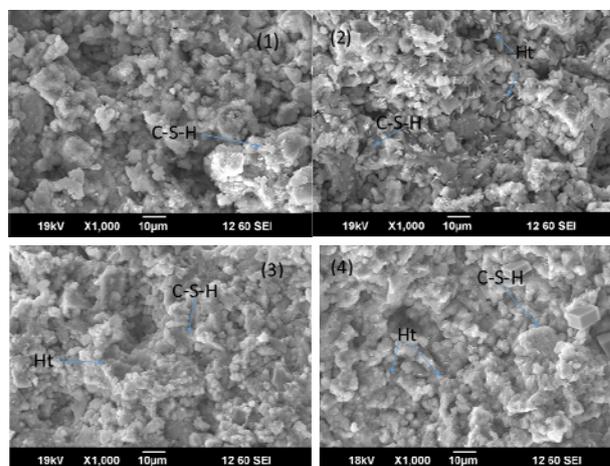


Fig. 4. SEM image of AASM paste samples at 1 day (1) M0; (2) M5; (3) M10; (4) M15.

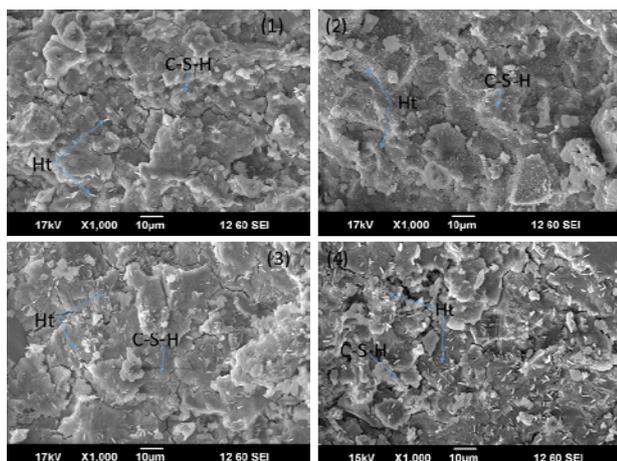


Fig. 5. SEM images of AASM paste samples at 28 days (1) M0; (2) M5; (3) M10; (4) M15.

After 28 days of curing, the denser structures were reported from all AASM samples due to consisting primarily of C-S-H gels. Fibrous Ht were detected in all AAS paste samples with and without adding MgO content which agreed with the XRD results. On the other hand, all the samples showed the small cracks in the structure because of high shrinkage of AAS.

4 Conclusions

Effect of various MgO contents into the alkali-activated slag on the fresh property, strength development and microstructure were studied. In this research, the AAS were added by 5%, 10% and 15% MgO by weight of slag to do the paste samples. The samples were tested the flow, compressive strength and microstructure based on XRD and SEM analysis test. Based on the results of investigation, the following conclusions are drawn:

- (1) The MgO has little effect to accelerate hydration reaction of AAS in the early age and reduce in the flow of AAS paste.
- (2) The optimum dosage of MgO which significantly increased the compressive strength of AAS in the air curing condition is 10% by weight of slag which contributed by hydrotalcite-like phase with high voluminous to fill into the macropores to form the mesopores hence the micro-structure becomes more denser.
- (3) The XRD and SEM analyses illustrated the hydration products are mainly C-S-H gel and Ht-like phase to contributes the strength development of AASM. In addition, the microstructure of AASM becomes denser with increasing the curing times by growing up the crystallization of hydration products. On the other hand, increasing the adding MgO presents the dense structure by more hydration products. However, it is found to decrease the strength with increasing of MgO content (15% by weight) since reduce the aluminosilicate content as well as the more late Ht formation lead to form cracks matrix.

Using MgO to modify the mechanical properties and microstructure of alkali-activated slag potentially offer

for reducing the impacts into environment as well as ensure the sustainable development. However, later Ht formation should be studied to limit the cracks by high voluminous of Ht. It is hoped that the more researches in this major will support for new greener materials.

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