Desulfurization Slag/Granulated Blast Furnace Slag Binder and Mortar without Portland Cement

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ABSTRACT: Molten iron desulphurization slag (DS) is a common industrial waste in Taiwan, with chemical constituents similar to Portland cement, high pH value, high calcium oxide and low heavy metal contents. DS has been considered serving as an alkaline catalyst to pozzolanic reactions with the mixture of granulated blast furnace slag (GBFS) powders. In this paper, we focus on using DS and GBFS powders as binders to produce mortar without Portland cement. Material properties and the microstructure of the constituents were examined. The fresh behaviors, hardening properties and microstructure of the mortar are also investigated. The test results show that DS can provide sufficient alkali condition for GBFS to activate pozzolanic reactions. The compressive strength of the mortar can reach 17MPa at 28 days of age. A linear proportion between the amounts of DS and water is also found in the flow test. Increasing the amount of GBFS can shorten the setting time; while increasing the DS amount can shorten the time interval between the initial and final setting.

1. INTRODUCTION

Molten iron desulphurization slag (DS) is a common waste of the steelwork industries that use iron ore as raw materials. It is produced from the desulphurization process of the molten irons in high temperature furnaces. Employing DS as recycling materials includes: ground improvement, soil modification, earth backfill, and the substituent of $CaCO_3$ for cementclinker manufacturing.

Granulated blast furnace slag (GBFS) is a by-product through the shock chilling process of high temperature furnaces. With sufficient and adequate alkali catalysts such as alkaline salts, the pozzolanic reactions of GBFS can be activated. With chemical constituents similar to Portland cement, high pH value, high calcium oxide (CaO) and low heavy metal contents, DS has been suggested as an economic option for producing binder and mortar without Portland cement. In this paper, we utilize the high alkali features of DS to activate the pozzolanic reactions of GBFS mixtures to investigate the feasibility of producing non-Portland cement mortar.

2. EXPERIMENTS

2.1 Materials

For the granulated blast furnace slag, Blaine fineness of $4500cm^2/g$ is selected and used. For the molten iron desulphurization slag powders (DS-P), the iron metal content is filtered by magnetic separation, crushing, and desiccation processes. The DS-P passing sieve #100 are then selected and used.

2.2 Variables

In this study, the water-to-binder ratio (W/B) is fixed to be 0.6 and 0.8. GBFS/DS-P are mixed as the binder with the proportion of 9:1, 8:2, 7:3, 6:4, and 5:5 by weight. The binder mixtures are poured into 2.5cm cubes for microstructure analysis. River sands are used as the aggregates and mixed with binders in the ratio of 2.75:1. The fresh behaviors and hardening properties of the mortar are then studied.

3. RESULTS AND DISCUSSION

3.1 Material Properties

The microstructure of the granulated blast furnace slag and molten iron desulphurization slag powders are observed using scanning electron microscope (SEM). Their corresponding chemical contents are also detected with X-ray diffraction (XRD).

3.1.1 SEM Images of GBFS and DS-P

Figure 1 shows the SEM images of GBFS and DS-P. As can be observed, the appearances of GBFS are irregular and similar to polygons, while with smooth surfaces. This phenomenon is mainly caused by the shock chilling process, which would strictly turn GBFS into glass [1] rather than crystals. As for DS-P, it is shown that a vast amount of particles are formed on the surfaces. These granular crystals ($Ca(OH)_2$ and $CaCO_3$) are the reaction products of CaO in DS-P with H_2O and CO_2 in the air.
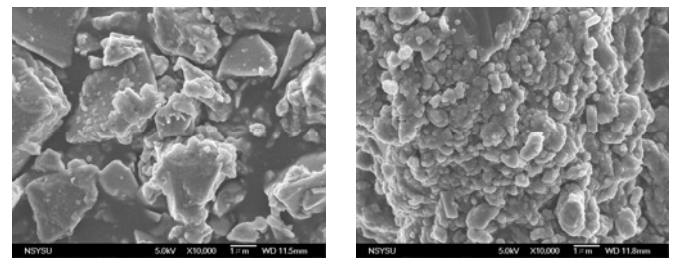
(a) GBFS   (b) DS-P
Figure 1 SEM images of GBFS and DS-P (×10000)

3.1.2 Chemical Composition and Physical Properties of GBFS & DS-P

Table 1 shows the physicochemical properties of GBFS and DS-P. As illustrated, the primary components of both materials are calcium oxide (CaO), silicon dioxide (SiO_2), and aluminium oxide (Al_2O_3). GBFS has rather higher contents of SiO_2 and Al_2O_3 than DS-P; while DS-P contains more iron oxide (Fe_2O_3) than GBFS. This indicates that even the DS-P has undergone the filtering processes such as magnetic separation, certain amount of iron remains. However, test results of standard toxicity characteristic leaching procedure (TCLP) suggest that both of GBFS and DS-P can be harmlessly recycled and used.

Table 1 Chemical composition and physical properties of GBFS & DS-P

	GBFS	**DS-P**
CaO(%)	43.11	66.16
MgO(%)	7.51	2.29
SiO_2(%)	30.48	15.71
Al_2O_3(%)	14.67	3.48
SO_3(%)	1.31	3.42
Fe_2O_3(%)	0.53	7.35
P_2O_5(%)	0.56	0.57
MnO(%)	0.53	0.45
K_2O(%)	0.27	–
Blaine Fineness (cm^2/g)	4734	3829
Specific gravity	2.91	2.38

Figure 2 shows the XRD results of GBFS and DS-P. The primary component of DS-P is shown to be CaO and the corresponding hydration product $Ca(OH)_2$ [2]. It is also found that there is a small amount of $CaCO_3$ which is produced by $Ca(OH)_2$ and dissolved CO_2 [3, 4].
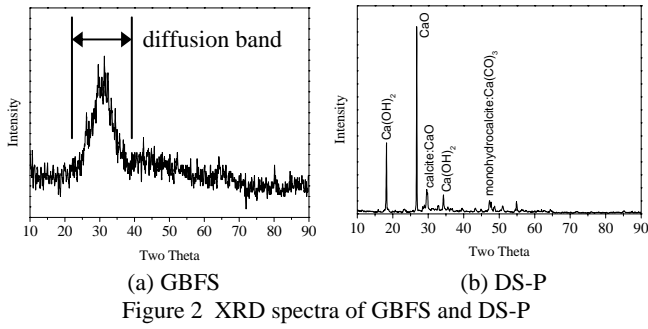
(a) GBFS (b) DS-P

Figure 2 XRD spectra of GBFS and DS-P

3.2 Fresh Behaviors and Hardening Properties

The fresh behaviors and hardening properties including setting time, fluidity, and compressive strength of the GBFS/DS-P mortar are also investigated.

3.2.1 Setting Time

As shown in Figure 3, both the initial setting time (165~246min) and final setting time (185~265min) of the mortar vary with the mixing ratios of GBFS/DS-P. The results suggest that mortar with higher DS-P contents tend to extend both the initial and final setting time. This phenomenon is primarily caused by the decreasing contents of Al_2O_3 as GBFS/DS-P ratio raise up (14.67% in GBFS and 3.48% in DS-P). Al_2O_3 is known as highly active a component with self-hydration capability at room temperature and thus, plays an important role in expediting the hydration process of mortar [5, 6]. It is also observed that the time interval between the initial and final setting of GBFS/DS-P binder is shorter than cement. The interval also varies with the GBFS/DS-P ratio as higher DS-P contents tend to expedite the setting process. Rapid setting is caused by the OH^- ions in alkali mixtures which would crush the vitreous structures of GBFS particles, activate the hydration process, and quickly generate a vast amount of C-S-H colloids. This phenomenon would be more prominent with higher alkali concentrations of the mortar mixtures.
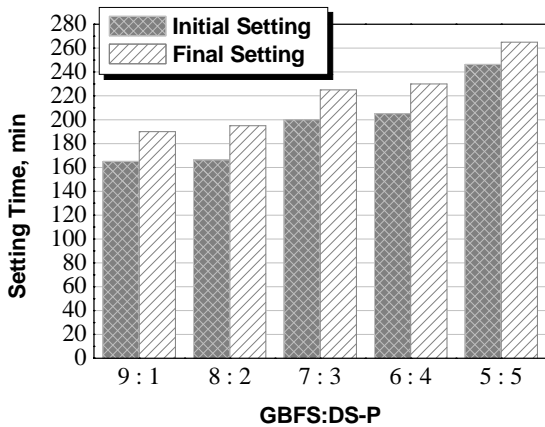

Figure 3 Setting time of various GBFS/DS-P mixing ratios

3.2.2 Flowability

The required W/B ratio for the flow test of each GBFS/DS-P mortar is shown in Figures 4. The results of standard flow value indicate that there is roughly a linear proportion in between the W/B and GBFS/DS-P ratio with $R^2 = 0.99$. In particular, the required W/B ratio increases by 0.028~0.044 as GBFS decreases by 10% (i.e. DS-P increases by 10%). The particle structures as well as the water absorption of the binders are primarily responsible for the mortar flowability when pozzolanic materials other than Portland cement are used. In this study, the SEM images in Figure 1 show irregular structures for both the GBFS and DS-P particles; while GBFS are with much flatter and smoother surfaces than DS-P. Based on the observations, we have concluded the increased W/B ratio with

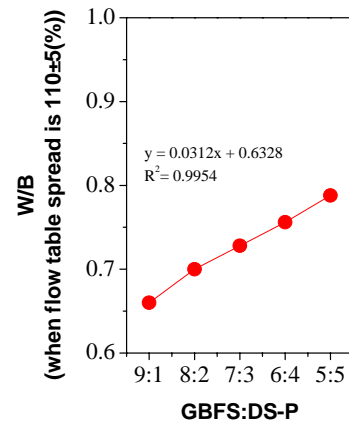GBFD/DS-P is attributed to the porous structures of the DS-P crystals.

Figure 4 Required W/B ratio for standard flow value (110±5%) of each mortar mixture

3.2.3 Compressive Strength

For the compressive strength tests, this study uses GBFS/DS-P binders and river sands to cast the mortar specimens. The mixing ratio of binder and sand is 1:2.75, and the W/B ratios are 0.6 and 0.8, respectively. The mortar specimens are then cured in 100% RH and 23±2°C for 1, 3, 7, 28, 56, 90, and 120 days.

GBFS is referred as the oxide system of R_2O-RO-R_2O_3-SiO_2-H_2O [1] or RO-R_2O-SiO_2, and the simplified vitreous structure system of CaO-Al_2O_3-SiO_2. Its dense molecular structure is attributed to the nature of low basicity, low ionic bonding, and high covalent bonding. As a result, high pH agents such as alkali metal compounds are required to dissociate OH^- ions, crush the covalent bonding of GBFS, and enforce the hydration process. The highly concentrated CaO in DS-P could efficiently raise the solution pH by generating OH^- ions with the presence of water, and thus, provide a high alkali condition for the hydration of GBFS.

Figure 5 shows compressive strength growth of the mortar specimens with various mixing proportions. Specimens with 8:2 and 7:3 mixing ratios show the highest compressive strength before the 28th day; while are surpassed by the 9:1 mixing ratio after the 56th day. Except for the extraordinary growth of mixing ratio 9:1, all the other groups shows a regular trend as lower GBFS ratio would result in a slower growth of compressive strength. The alkali DS-P plays the role as the catalyst in the hydration of GBFS; however, mixing ratio 9:1 suffers from insufficient OH^- for this chemical reaction, leading to restricted strength development at the early age. The spontaneous pozzolanic reaction of GBFS is then the primary source of strength, which grows more significantly and continuously at the later age [7, 8]. This applies to W/B of both 0.6 and 0.8.
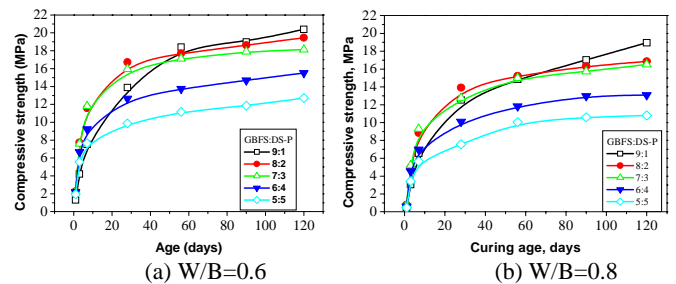

(a) W/B=0.6 (b) W/B=0.8

Figure 5 Compressive strength of mortar with various mixing ratios

3.3 Microstructural Features of GBFS/DS-P Mortar

Figure 6 shows the SEM images of GBFS/DS-P binder of the mixing ratio 9:1 after 7, 28, and 90 days of curing, respectively. The microstructure appears to be mainly composed of spherical vaterite and calcite crystals ($CaCO_3$) accompanied with small amount of

magnesium aluminium calcium silicate and reticular C-S-H colloids. It should be noted and can be observed from the SEM images that reticular C-S-H colloids become more dominant of the binder microstructure as the curing age increases.
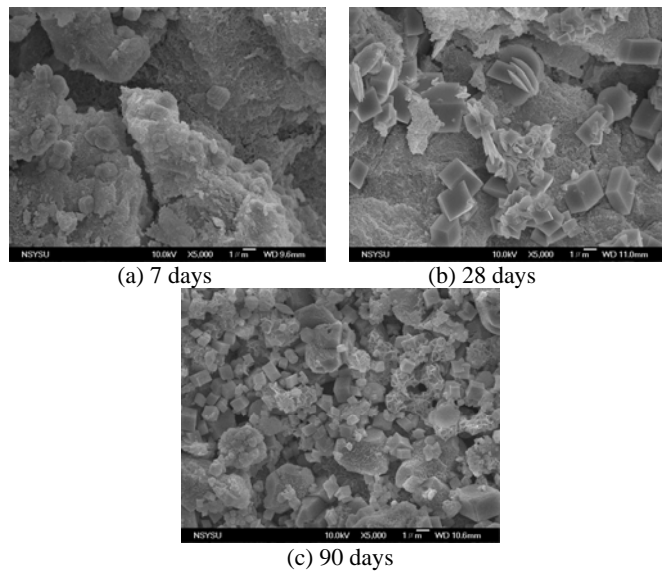

(a) 7 days

(b) 28 days

(c) 90 days

Figure 6 SEM images of GBFS/DS-P (9:1) binder(×5000)

The XRD analyses of GBFS/DS-P binders of various mixing ratios at the 7 and 28 days are illustrated in Figure 7. The spectra indicate that the primary hydration products are $Ca(OH)_2$, $CaCO_3$, $CaSiO_3$, and CaO. Among those, the characteristic peaks of $Ca(OH)_2$, $CaCO_3$, and CaO gain more prominence as the DS-P ratio increases. This feature is attributed to the heavy content of CaO in DS-P, which would turn into $Ca(OH)_2$ and $CaCO_3$ with the presence of water and carbon dioxide. The XRD spectra also indicate that the amounts of $Ca(OH)_2$ and $CaCO_3$ are not influenced by the binder age, but CaO and $CaSiO_3$ are. This phenomenon is inferred that $CaSiO_3$ is indirectly produced by the dissipated CaO. In addition, the characteristic peaks of each hydration product have reached a plateau as the GBFS ratio increases. For example, the vitreous expansion band of the 9:1 ratio binder is very similar to that of GBFS. Since the SEM analysis also reveals that there exists a small amount of magnesium and aluminium in the calcium silicate, it suggests that $CaSiO_3$ would eventually turn into a vitreous structure similar to GBFS, such as C-A-S, C-M-2S, or C-S-H colloids, so as to develop the mechanical strength.
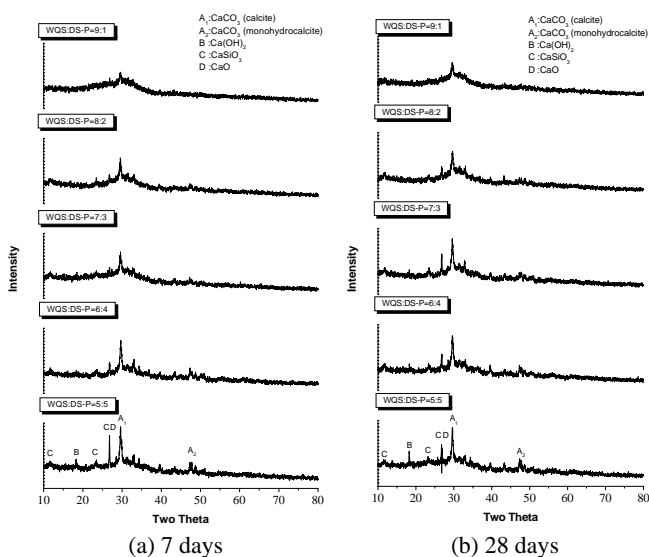

(a) 7 days   (b) 28 days

Figure 7 XRD spectra of GBFS/DS-P binders at 7 and 28 days

4.   CONCLUSION

Based on the investigations of material properties, fresh behaviors, hardening properties, and compressive strength of GBFS/DS-P binder and mortar, the following conclusions can be made:

1.   Our study results have suggested that molten iron desulphurization slag is a harmless industrial waste. Its high alkali contents could provide sufficient conditions for the hydration process of granulated blast furnace slag so as to develop mechanical strength.

2.   Increasing the GBFS mixing ratio would shorten the setting time of mortar; while increasing the DS-P mixing ratio would result in rapid setting and shrink the time interval between the initial and final setting of mortar.

3.   The mortar specimens composed of river sand aggregates and GBFS/DS-P binders of the ratio 8:2 and 7:3 gain the highest compressive strength (17MPa) before 28 days of curing; while surpassed by those of the ratio 9:1 after 28 days.

4.   The hydration products of GBFS/DS-P binder are primarily composed of calcium carbonate, magnesium aluminium calcium silicate, and reticular C-S-H colloids. The strength development is restricted by the amount of $Ca(OH)_2$ and the transition of C-S-H colloids from hydration products.

5.   REFERENCES

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