

Effect of Fine Steel Slag Powder on the Early Hydration Process of Portland Cement*

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Abstract: Hydration heat evolution, non-evaporative water, setting time and SEM tests were performed to investigate the effect of fine steel slag powder on the hydration process of Portland cement and its mechanism. The results show that the effect of fine steel slag powder on the hydration process of Portland cement is closely related to its chemical composition, mineral phases, fineness, etc. Fine steel slag powder retards the hydration of portland cement at early age. The major reason for this phenomenon is the relative high content of MgO, MnO₂, P₂O₅ in steel slag, and MgO solid solved in C₃S contained in steel slag.

Key words: steel slag powder; portland cement; early hydration process

1 Introduction

Steel slag is the waste residue of fluxing minerals used in the process of steel producing. Its discharge amount is about 10% of the production of steel. Steel slag hasn't been utilized widely and effectively in a long period of time^[1]. Hundreds of million tons of steel slag are deposited, and the amount is still increasing with tens of million tons every year. The deposited steel slag occupies great amounts of farm lands and induces serious environment problems. The main chemical compositions of steel slag are CaO, SiO₂, Fe₂O₃, FeO, MgO and MnO. And the main mineral phases of steel slag are C₃S, β-C₂S, C₄AF, C₂F, RO phase (CaO-FeO-MnO-MgO solid solution), *f*-CaO, olivine and merwinite etc. The C₃S, β-C₂S, C₄AF, C₂F phases contained in steel slag have some hydration activity, and steel slag can be regarded as a kind of weak clinker. Investigating the hydration process of steel slag powder in the hydration system of portland cement and clarifying its hydration characteristic will contribute to utilize steel slag as a kind of active admixture in the field of cement and concrete, realize its potential value, and alleviate economic, social and environmental problems caused by steel slag.

2 Experimental

2.1 Raw materials

2.1.1 Cement: 52.5[#] P.I cement, produced by Lafarge Cement Company, Beijing, China. Its chemical composition is listed in Table 1.

2.1.2 Steel slag powder: produced by Wuhan Green Metallurgy Residue Company, China. The Blaine fineness of the steel slag is 5 000 cm²/g and its chemical composition is listed in Table 2.

Table 1 Chemical composition of cement/%

Composition	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Loss
Content/%	21.3	4.4	2.5	63.4	2.3	/

Table 2 Chemical composition of steel slag/%

Composition	SiO ₂	CaO	<i>f</i> -CaO	Al ₂ O ₃	Fe ₂ O ₃ + FeO	MgO	MnO	P ₂ O ₅	others
Content/%	13.5	44.3	1.7	2.5	20.8	7.9	0.78	1.8	6.72

2.2 Preparation of specimens

Mix the raw materials according to Table 3 with forced mixer, and then cast the paste into 4 cm × 4 cm × 4 cm molds. Demold the specimens after 1 d standard curing, and cure them still under the standard curing condition. At a corresponding age, cut the central part of the specimens with a sharp tool into small granule, and then put them into absolute ethyl alcohol to terminate their hydration.

2.3 Testing method of non-evaporable water

Weight 3 specimens of which hydration has been terminated and desiccate them under vacuum condition to about 1 g each, with the precision of 0.0001 g. Dry the specimens at 105 °C for 3h, and then put the specimens into an oven and heat them up to 950 °C. Keep the specimens at 950 °C for 1 h, then cool them in an exsiccator to room temperature; Weight the specimen and calculate the non-evaporable water. To eliminate the incomparability caused by the decrease of the amount of clinker due to the steel slag powder replace part of cement, a physical quantity, equivalent non-evaporable water quantity W_{ne} , which is deduced on the basis of non-evaporable water W_n , was proposed:

$$W_{ne} = W_n / (1 - \beta) \quad (1)$$

β is the percentage of steel slag powder in the whole amount of binding materials.

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2.4 Testing method of hydration heat

The testing method of hydration heat was according to Chinese standard GB2022-80, Testing Method of Cement Hydration Heat (direct method).

Table 3 The mixture of cement paste

Cement/%	Specimens	Steel slag powder/%	Water/binder ratio
100	LS0	0	0.3
90	LS1	10	0.3
80	LS2	20	0.3
70	LS3	30	0.3

Table 4 The setting time of the cement paste mixed with steel slag powder

Specimens	Initial setting time/min	Final setting time/min
LS0	138	185
LS1	129	182
LS2	145	191
LS3	157	203

Table 5 Quantity of non-evaporable water and equivalent non-evaporable water/%

Specimens	1 h	3 h	6 h	12 h	24 h	7 d	28 d
LS0	0.42(0.42)	0.52(0.52)	1.69(1.69)	3.49(3.49)	7.16(7.16)	11.90(11.90)	14.10(14.11)
LS1	0.20(0.22)	0.47(0.52)	1.18(1.31)	2.95(3.28)	8.45(9.39)	12.53(13.92)	13.67(15.19)
LS2	0.20(0.25)	0.40(0.50)	1.03(1.28)	2.60(3.25)	7.30(9.13)	10.49(13.11)	11.35(14.19)
LS3	0.05(0.07)	0.14(0.20)	0.91(1.30)	2.29(3.27)	6.20(8.86)	9.92(14.17)	11.59(16.56)

Note: the value in the brackets is the quantity of equivalent non-evaporable water.

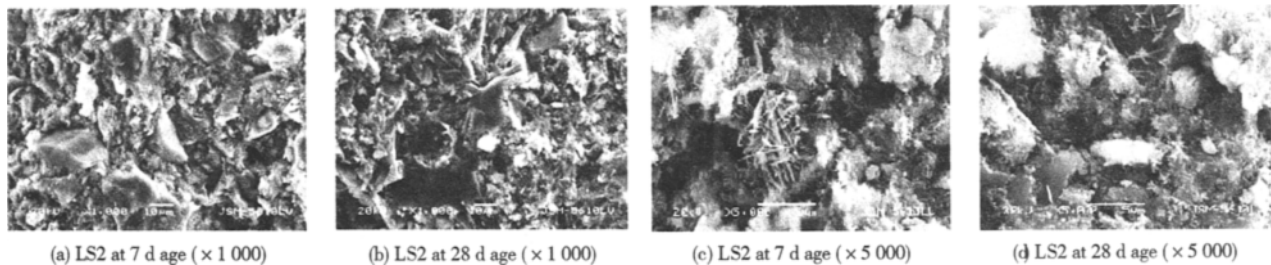


Fig.2 SEM images of LS2 at 7d and 28d age

In this experiment, the initial and final setting time of blended cement paste mixed with ground steel slag powder are similar to those of pure cement paste respectively, but they are delayed to different degree, the greater the percentage of steel slag powder, the later both the emerge of initial setting time and final setting time.

Fig. 1 shows that the hydration heat-releasing diagram of blended cement paste mixed with steel slag is similar to that of pure cement paste. But the heat-releasing peak is lowered in the diagram of blended cement, and at the same time the emergence of the peak is later. With the increase of the percentage of steel slag, the peak value of the hydration heat-releasing peak is much lower, and the emergence of the peak is much later.

The data in Table 5 show that the quantities of both the non-evaporable water and equivalent non-evaporable water of specimen LS0, LS1, LS2, LS3 increase with the

3 Results and Discussion

The quantity of non-evaporable water and the quantity of equivalent non-evaporable water of the blended cement paste mixed with ground steel slag powder at different ages are listed in Table 5.

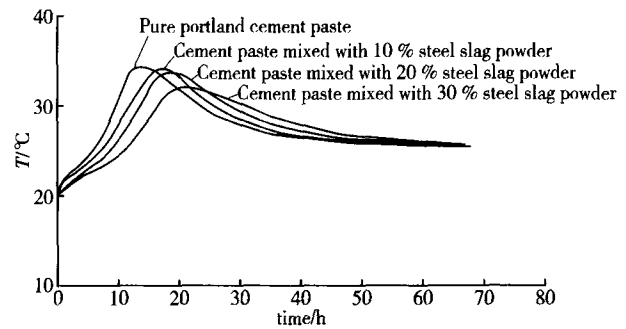


Fig.1 Temperature-time diagram of hydration heat releasing

increasing of the hydration age. At 1 h, 3 h, 6 h, 12 h age, the quantities of non-evaporable water and equivalent non-evaporable water of specimen LS1, LS2, LS3 are both lower than those of pure cement specimen. At 24 h age, the quantities of non-evaporable water and equivalent non-evaporable water of LS1 are both higher than those of LS0. At the same time, the quantity of non-evaporable water of LS2, LS3 is lower than that of LS0, however, the quantity of equivalent non-evaporable water of LS2, LS3 is higher than that of LS0. The hydration process of clinker and active mineral admixtures is in fact a water-binding and hydrate producing process, and the quantity of non-evaporable water of the hydrates at different ages in some degree indicates the hydration activity of clinker and active mineral admixture and the hydration degree. The quantity of non-evaporable water of LS2, LS3 at different ages, and that of LS1 before 6 h age are lower than that of

pure cement specimens at corresponding ages, which indicates that at this ages, the amount of the hydrates of blended cement pastes mixed with steel slag is less than that of pure Portland cement paste. However, this phenomena may be caused by the lower activity of steel slag contrasting with clinker, and, therefore, the hydrate of the blended cement system is less than that of pure cement system. So we can not deduce directly from this phenomenon that steel slag retards the hydration process of clinker and reduces the amount of hydrates at these ages. Therefore, the concept of equivalent non-evaporable water is introduced to indicate the hydrate-producing ability of clinker minerals. If the equivalent non-evaporable water of blended cement specimen at certain age is higher than that of pure cement specimen, then steel slag powders accelerate the hydration of clinker at this age, or else on the contrary. So it can be concluded from the data in Table 5 that steel slag retards the hydration of clinker before 1 d age.

Fig.2 shows the SEM images of specimen LS2 at 7 d and 28 d ages. The images show that at 7 d age, there was some relatively large, unreacted and irregular-shaped steel slag powder, with a dimension of about 10 μm -20 μm . But when it lasted to 28 d age, the amount of unreacted steel slag powder reduced, and the hydrate products became denser, containing less big pore.

Considering the experiment phenomena and the results above synthetically, it can be regarded that ground steel slag powders retard the hydration of Portland cement before 1 d age. The effect of ground steel slag powder on the hydration system of Portland cement is closely related to its mineral phases, fineness and surface shape. As described above, steel slag powder can be regarded as a kind of weak clinker, and there are C_3S , $\beta\text{-C}_2\text{S}$ and C_4AF mineral phases *etc.*, in steel slag powder. However, compared with clinker produced in strictly controlled process, steel slag contains lots of other components, such as C_2F , RO phase (CaO-FeO-MnO-MgO solid solution), olivine, merwinite, and $f\text{-CaO}$, MgO , MnO , P_2O_5 *etc.* In the hydration process of the blended cement paste mixed with ground steel slag powder, parts of these components participate in or influence the hydration system and make it possess the characteristics different from the hydration system of pure cement. The retarding effect of steel slag on the early hydration process of cement is due to its high content of MgO , MnO_2 , and P_2O_5 . Research works of İ Ak1n Altun, İsmail Y1lmaz^[2] and L Zheng^[3] indicate that the presence of MgO can retard the early hydration process of clinker. And the experiments of Pera^[4] show that the presence of MnO_2 weakens the early hydration activity and strength of blended cement mixed with

ground blast-furnace slag, but it has no obvious effect on the long-term performance. At the same time, some materials produced by the relatively high content of P_2O_5 retard the early hydration process of clinker too. Therefore, the setting time of the blended cement paste mixed with steel slag is later than that of pure cement paste, and the arise of hydration heat peak appears later and with a lower value. With the same reason, the amount of equivalent non-evaporable water of the blended cement at early age is lower. Additionally, the relative low content of AL phase is perhaps another reason for the delayed setting time. Furthermore, the research work of I G Luginina^[5] shows that a part of the MgO may be solid solved in the process of forming Alite and ferro-aluminate phases in steel slag, and its content in these phases increases steadily with the increase of its content in steel slag. N K Katyal^[6] regarded that 1% of MgO solid solved in Alite would retard its hydration before 20 h age, but the hydration speed of the Alite phase solid solved with MgO exceeded that of pure C_3S later, getting almost completely hydrated at the age of about 28 d.

4 Conclusions

- a) Ground steel slag powder affects the hydration process of portland cement.
- b) Fine steel slag powder retards the hydration of portland cement at early age. The major reason for this phenomenon is the relative high content of MgO , MnO_2 , P_2O_5 in steel slag, and MgO solid solved in C_3S contained in steel slag.

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