THE LATE-AGE STRENGTH AND MICROSTRUCTURE OF MORTAR CONTAINING STEEL SLAG

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Abstract
Steel slag has high contents of $f$-CaO and RO phase which may subsequently react with cement or water resulting in physical expansion, so the stability of steel slag is bad. The influence of steel slag on the late-age strength and microstructure of mortar was investigated in this study. The results show that the compressive strengths of mortars containing steel slag increase with hydration age, and they become closer to the compressive strength of pure cement mortar as the hydration age increases. The bad stability of steel slag does not have adverse effect on the late-age strength of mortar. The hardened cement-steel slag paste is very dense, and no obvious crack exists in the microstructure of mortar containing steel slag at late ages. RO phase and free CaO are the main factors that endow the steel slag bad stability. The unreacted RO phase particles are very easily to be observed in the hardened paste even at the age of 51 month. Part of free CaO in steel slag can react with water at very early ages. The RO phase with ultra low activity and free CaO with high activity do not have adverse effect on the volume stability of mortar.

Key words: steel slag; mortar; compressive strength; microstructure; stability

1. INTRODUCTION
Steel slag is an industrial byproduct produced from the processing of iron to steel. The steel slag emission makes up a portion of 10-15% of the steel output. About 80 million tons of steel slag was discharged in China at 2010. The steel slag dump occupies much land and results in many serious environmental problems.

The chemical compositions of steel slag conclude: CaO 45-60%, SiO₂ 10-15%, Al₂O₃ 1-5%, F₂O₃ 3-9%, MgO 3-13%, FeO 7-20%, and P₂O₅ 1-4 % [1, 2]. The main mineral compositions of steel slag conclude: silicates (e.g. C₂S and C₃S), aluminates (e.g. C₁₂A₇), ferrites (e.g. C₂F), and RO phase (CaO-MgO-MnO-FeO solid solution) [3-5]. In the meanwhile, steel slag contains some free CaO, and the free CaO content is generally higher than that in Portland cement.

During the process of cement production, the cement takes a sharp cooling manner-quench, so the minerals of cement exist in a metastable state. But steel slag is cooled naturally. The cooling process of steel slag is long enough to allow the lattice rearrangement,
so the activity of minerals in steel slag is much lower than that of minerals in cement [3, 6]. The exothermic process of steel slag is similar to that of Portland cement, which can be divided into five stages: rapid heat release period, dormant period, acceleration period, deceleration period, and steady period [7, 8]. But the second exothermic peak formed at the end of acceleration period of steel slag is only about $1 \text{ J} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$, which is much lower than that of Portland cement [7]. Li et al. [9] modified the steel slag by adding adjusting minerals during the discharging process, obtaining a new kind of steel slag with high cementitious activity. Alkaline condition can merely promote the early hydration of steel slag to a small extent [10]. Up to now, no efficient activator for steel slag has been developed.

Some researchers studied the influence of steel slag as a mineral admixture on the properties of cement or concrete, such as the setting time, fluidity, hydration heat, and strength [11-15]. Few papers reported the influence of fly ash on the durability of concrete or mortar. Besides the traditional durability problems such as carbonation, shrinkage, permeability and so on, concrete (or mortar) containing steel slag faces a particular problem: some components (e.g. RO phase and free CaO) of steel slag may react with cement or water subsequently, which will lead to physical expansion and thus cause the microstructure damage. In this paper, the late-age strength and microstructure of mortar containing steel slag were studied.

2. EXPERIMENTAL

2.1 Raw materials

The cement used was Portland cement with the strength grade of 42.5 which complies with the Chinese National Standard GB 175-1999. The chemical compositions of the cement used include: 21.86% SiO$_2$, 63.59% CaO, 4.25% Al$_2$O$_3$, 2.66% Fe$_2$O$_3$, 2.19% MgO, and 2.42% SO$_3$. The steel slag used was basic oxygen furnace steel slag which was the most common one in China. The chemical compositions of steel slag used include: 18.09% SiO$_2$, 42.55% CaO, 6.27% Al$_2$O$_3$, 18.47% Fe$_2$O$_3$, 10.04% MgO, and 1.29% SO$_3$. The specific surface areas of steel slag and cement were 512 and 312 m$^2$/kg, respectively.

2.2 Testing methods

Mortars of $40 \times 40 \times 160$ mm were prepared. ISO standard sand was used. The sand-to-binder ratio of mortar was 3.0. Two curing conditions were adopted: mortars were cured at 20$^\circ$C until testing ages (curing condition 1); mortars were first cured at 65$^\circ$C for 14 days and then at 20$^\circ$C for the remaining ages (curing condition 2). The relative humidity of curing condition is 95%. The mix proportions of mortars were shown in Table 1. At the age of 1, 3, and 51 months, the compressive strengths were tested according to the Chinese National Standards GB/T1-1999.

Table 1: mix proportions of mortars

<table>
<thead>
<tr>
<th>No.</th>
<th>Composition of binder/ %</th>
<th>W/B</th>
<th>Curing condition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cement Steel slag</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-0.50-standard</td>
<td>100 0</td>
<td>0.50</td>
<td>Condition 1</td>
</tr>
<tr>
<td>S1-0.50-standard</td>
<td>85 15</td>
<td>0.50</td>
<td>Condition 1</td>
</tr>
<tr>
<td>S2-0.50-standard</td>
<td>70 30</td>
<td>0.50</td>
<td>Condition 1</td>
</tr>
<tr>
<td>S3-0.50-standard</td>
<td>55 45</td>
<td>0.50</td>
<td>Condition 1</td>
</tr>
<tr>
<td>C-0.42-standard</td>
<td>100 0</td>
<td>0.42</td>
<td>Condition 1</td>
</tr>
</tbody>
</table>
The microstructure of hardened mortar was observed using a FEI Quanta200F scanning electron microscope under a high vacuum condition. The element distributions of the hydration products were detected by EDS.

The rate of heat evolution during the hydration of cement and steel slag was measured by a Toni7338 isothermal calorimeter with an accuracy of 0.2J/g under a constant temperature of 25°C.

3. RESULTS AND DISCUSSION

3.1 Compressive strength

The compressive strength of mortar under curing condition 1 is shown in Fig.1. As expected, the compressive strength of pure cement mortar increases along with the hydration age (Fig.1). The compressive strength of mortar containing steel slag also gains a steady growth with hydration age. It is an indication that the bad stability of steel slag does not do damage to the structure of mortar even at the age of 51 months.

The compressive strength of mortar under curing condition 2 is shown in Fig.2. Similar to results of Fig.1, for each mortar, its compressive strength at the age of 51 months is higher than that at the age of 1 month. It is an indication that the bad stability of steel slag does not do damage to the structure of mortar even under high temperature curing condition.

The pure cement mortar is adopted as the reference sample, and the percentages of the compressive strength of other samples accounting for the reference sample are presented in Fig.1 and Fig.2. Fig.1 and Fig.2 show that the presence of steel slag results in decrease of compressive strength. What’s more, the compressive strength decreases with the increase of the proportion of steel slag. For most mortars containing steel slag, their compressive strengths become closer to that of pure cement mortar as the hydration age increases.
Figure 1: Compressive strength of mortar under curing condition 1
3.2 Microstructure

Mortar S3-0.42-standard at the age of 51 months was adopted as the sample for microstructure observation. Fig.3 shows the typical morphology of the interface between hardened paste and sand. The sand combines well with hardened paste, and no obvious crack exists in the mortar. Fig.4 shows the morphology of hardened paste. A large amount of C-S-H gel is produced in 51 month, and the hardened paste is very dense. The element distribution of the C-S-H gel is shown in Fig.5. It shows that the element distribution of C-S-H gel produced by the hydration of complex binder is very similar to that of pure cement. This is because the active components of steel slag are similar to those of Portland cement.

The Fe$_2$O$_3$ content is 18.74% in the composition of the steel slag used, which is much higher than that of Portland cement. But Fig.5 shows that the Fe content in the C-S-H gel is not so high. It is an indication that the minerals containing Fe of the steel slag have a very low activity. C$_2$F and RO phase are the main minerals containing Fe. The hydration of C$_2$F makes some contributions to the microstructure. But the reaction of RO phase may cause physical
expansion because it contains MgO. Fig. 6 shows that a large unreacted particle is wrapped by the C-S-H gel. The unreacted particle is RO phase, which can be confirmed by EDS result. The unreacted RO phase particles are very easily to be observed in the hardened paste.

![EDX result 1](image1)
![EDX result 2](image2)
![EDX result 3](image3)
![EDX result 4](image4)

Figure 5: Element distribution of C-S-H gel

![SEM photo](image5)
![EDS results](image6)

Figure 6: Morphology of hardened paste

3.3 Reaction of free CaO

Free CaO is a potential threat to the structure of concrete or mortar. The early reaction activity of ordinary lime is very high. But the free CaO in steel slag has been over-burnt...
during the steel making process, so its reaction activity retards and its hydration may take place even long after the concrete or mortar has hardened. The volume of Ca(OH)$_2$ is 1.98 times of the reactant CaO volume, so the retarded hydration of free CaO may cause cracking to the concrete or mortar. Fig. 7 shows the heat evolutions during the hydration of cement and steel slag within 12 hours. The first exothermic peak of steel slag is much higher than that of Portland cement. It is believed that the early reaction of some free CaO makes a considerable contribution to the early hydration heat of steel slag. The results of Ref [7] showed that the diffraction peak of free CaO could not be detected by XRD after the steel slag hydrated for 3 days. Therefore, part of free CaO in steel slag can react with water at very early ages, which not only does not have adverse effect on the volume stability of concrete, but also reduces the early shrinkage of concrete.

![Figure 7: Heat evolutions during the hydration of cement and steel slag](water-to-cement ratio is 0.42, water-to-steel slag ratio is 0.30)

4. CONCLUSIONS

1) Though the stability of steel slag is bad, the compressive strengths of mortars containing steel slag do not decline at late ages.

2) No obvious crack exists in the microstructure of mortar containing steel slag at late ages.

3) The unreacted RO phase particles are very easily to be observed in the hardened paste even at the age of 51 month.

4) Part of free CaO in steel slag can react with water at very early ages.

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