Excitation mechanism of alkaline condition on the hydration activity of steel slag

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Abstract: Steel slag is a potential source of mineral admixture for concrete due to its certain cementitious properties. The use of slag as a cementing component should be preferentially considered. The aim of this research is to investigate the excitation mechanism of alkaline condition on the hydration activity of steel slag. The results show that the activity of RO phase (CaO-FeO-MnO-MgO solid solution) and Fe$_3$O$_4$ is very low, and these phases still show ultra low reaction extent even under strong alkaline condition. Silicates and aluminates are the main cementitious phases in steel slag, but their activity is much lower than that of Portland cement, especially at the early ages. OH$^{-}$ is helpful to disintegrate vitreous composition in steel slag. Thus alkalinity condition is able to excite the early activity of silicates and aluminates. The excitation effect is more obvious with the increase of pH value of alkalinity condition within 28 days. However, at late ages, the excitation effect of alkalinity condition on steel slag decreases. The enhancement of increasing pH value to excitation effect is not very important.

Keywords: steel slag; alkalinity condition; activity

1 Introduction

Steel slag is an industrial byproduct produced during the conversion of iron to steel either from the basic oxygen steel making furnace (BOF) process or the electric arc furnace (EAF) process. Most steel slags have similar chemical compositions with as Portland cement. The contents of Ca and Si are lower, but the contents of Fe and Mg are higher in steel slag than in Portland cement (Shi and Qian, 2000; Tufekci, et al, 1997). The steel slag can be simply treated as a CaO-MgO-SiO$_2$-FeO quaternary system (Shi, 2004). Olivine, merwinite, C$_3$S, C$_2$S, C$_4$AF, C$_2$F, RO phase (CaO-FeO-MgO-MnO solid solution), and free CaO are the common minerals in steel slag (Shi, 2004; Kourounis et al, 2007). C$_3$S, C$_2$S and C$_4$AF endorse steel slag some cementitious properties. Compared with BOF slag, the EAF slag has lower CaO content in chemical compositions (Qian et al, 2002; Qasrawi et al, 2009). In comparison with EAF slag, BOF slag is more appropriate to be used in blended cement production or concrete production.

Now most steel slag is used as a filling material in civil engineering. Some researchers conducted some researches on the utilization of steel slag as aggregate in concrete. Qasrawi et al. (2009) carried out a research to evaluate the effect of using steel slag as fine aggregate on hardened concrete. Experimental results indicated that the use of steel slag in concrete would enhance the strength of concrete, especially the tensile strength. Maslehuddin et al. (2003) conducted a comparative study about crushed limestone aggregate concrete and steel slag aggregate concrete. The results showed that the compressive strength of steel slag aggregate concrete was higher than that of crushed limestone aggregate concrete, but the tensile strengths
of these two concretes were close to each other.

Shi (2004) holds that the use of steel slag as a cementing component in cement or concrete industry should be given a priority from technical, economical, and environmental considerations. Tsakiris et al. (2008) carried out a research on using steel slag as a raw material in cement production. The results showed that the addition of steel slag did not negatively affect the quality of cement with the adding amount of 10.5%. Monshi and Asgarani (1999) found that the cement with 8% steel slag could satisfy the requirement on compressive strength for type I Portland cement. Wu et al. (1999) produced a kind of cement made of clinker, steel slag (with 30% adding amount), and fly ash, which complied with Chinese national standard for composite Portland cement. Some researchers (Sun, 2003; Wang et al, 2003) reported the use of steel slag as a cement replacement material for concrete manufacture. Their experimental results showed that a small adding amount of steel slag has limited influence on the strength and durability of concrete, however the early strength of concrete decreases sharply if the adding amount of steel slag is large.

There are some methods to improve the cementitious properties of steel slag. Li et al. (2010) modified the steel slag by adding adjusting minerals during the discharging process, obtaining a new kind of steel slag with high cementitious activity. Wang et al. (2010) suggested that a new kind of steel slag with more cementitious phase and less RO phase can be obtained by removing some large particles. The hydration rate of steel slag at the early age could be accelerated by raising the fineness of particles and curing temperature (Wang and Yan, 2010). During the hydration process of cement-steel slag complex binder, the hydration of steel slag is influenced by the alkaline condition caused by the prior hydration of cement. Wang and Yan (2010) conducted a research on the influence of alkaline condition (pH=13.0) on the hydration activity of steel slag. The results showed that increasing the pH value of hydration condition can promote the hydration rate of steel slag within 28 days, however the effectiveness decreases thereafter.

In this study, we focused on investigating the influences of alkaline conditions with different pH values on the hydration properties of steel slag, aiming to reveal the excitation mechanism of alkaline condition on the hydration activity of steel slag.

2 Experimental

2.1 Raw material

The XRD results and chemical compositions of steel slag used were given in our previous publication (Wang and Yan, 2010). The main mineral phases of steel slag used are C₃S, C₄S, and RO phase. It also contains C₂F, Fe₂O₄, C₁₂A, Ca₂Al₂Si₃O₁₂, and f-CaO. According to the alkalinity (CaO/(SiO₂+P₂O₅) proposed by Mason (1994), the steel slag’s alkalinity is 2.37. The specific surface area of the steel slag used was 458 m²/kg.

2.2 Test methods

Pure steel slag paste (denoted by S1) was prepared by mixing steel slag with water at the water-to-steel slag ratio of 0.30 (mass ratio). Alkali-activated steel slag pastes were prepared by mixing steel slag with NaOH solutions at pH value of 13.0, 13.4, and 13.8 at the solution-to-steel slag ratio of 0.30, which were denoted by S2, S3, and S4, respectively. The
pastes were cast into plastic centrifuge tubes after being stirred uniformly. Then they were cured at the temperature of 20±1°C to testing ages. At the age of 3, 28, and 90 days, the samples were placed in acetone to stop the hydration process. Before testing, the samples were dried at room temperature.

The hydration products were mineralogically determined by X-ray diffraction. XRD measurements were conducted with a TTR III diffractometer using nickel-filtered Cu Kα1 radiation (λ = 1.5405Å), 45kV voltage and 200mA current.

The pore characteristics of hardened binder pastes was measured using an AutoPoreIV9510 Mercury Intrusion Porosimeter (MIP) with an operating pressure up to 60000 psi, which could intrude mercury into pores as small as 3.2 nm in diameter.

The non-evaporable water (wn) content of paste was obtained as the difference in mass between the sample heated at 105°C and 1000°C normalized by the mass after heating 1000°C, and correcting for the loss on ignition of unhydrated samples (Lam et al, 2000; Sarita et al, 2006).

The microstructure of hydration products was observed using a FEI Quanta200F scanning electron microscope under a high vacuum condition (SEM).

3 Results and discussion

3.1 XRD results

The XRD results of pastes (S1, S2, S3, and S4) hydrated for 3, 28, and 90 days are shown in figures 1, 2, and 3, respectively. At any hydration age, the diffraction peak intensity of AFt and AFm is very weak in all samples. Figure 4 shows the morphology of steel slag paste (sample S1) hydrated for 90 days. Crystalline AFt can be observed in Figure 4. But it should be noted that the amount of AFt is very little by SEM observation. So AFt and AFm are not the main hydration products of aluminates of steel slag. It can be seen from figures 1-3 that Ca2Al(OH)7 is a main hydration product of aluminates. A qualitative analysis of the XRD patterns based on peak intensity changes indicates that increasing pH value of hydration condition can promote the formation of Ca2Al(OH)7 at early ages.

![X-ray diffraction patterns of the hydration products at the age of 3 days](image)

Figure 1. X-ray diffraction patterns of the hydration products at the age of 3 d
Figure 2. X-ray diffraction patterns of the hydration products at the age of 28 d

Figure 3. X-ray diffraction patterns of the hydration products at the age of 90 d

Figure 4. Morphology of steel slag paste (sample S1) hydrated for 90 days

C-S-H gel and Ca(OH)₂ are the main hydration products of C₂S and C₃S. The C-S-H gel doesn’t have diffraction peaks in the XRD spectrum because it is amorphous. Figure 1 shows that the peak intensity of Ca(OH)₂ in all pastes is very weak at the age of 3 days. It is an indication that the early hydration rate of C₃S and C₂S in steel slag is very low even under strong alkaline condition. This is because the cooling rate of steel slag is much lower than that
of Portland cement, so the active components of steel slag crystallize more perfectly.

Following the hydration progress, the peaks of silicates and aluminates phases diminish. However, the RO phase and Fe$_3$O$_4$ exhibit rather poor hydration activity. It is believed that the structure of RO phase and Fe$_3$O$_4$ is stable under alkaline condition.

3.2 MIP results

The pore size distributions of the four pastes at the age of 28 and 90 days are shown in Figure 5 and Figure 6, respectively. From figure 5, it is clearly seen that the total intrusion volume of mercury decreases with the increase of pH value of hydration condition at the age of 28 days. Moreover, the proportion of large pores (> 100 nm) decreases with the increase of pH value. This phenomenon is due to the hydration production especially the C-S-H gel which makes the pore finer by filling it. The C-S-H gel is produced more with the increase of pH value.

At the age of 90 days, the total intrusion volume of mercury of S1 is a little smaller than that of S2. The total intrusion volume of mercury of S3 is the smallest, even smaller than that of S4. The pre and post order of the total intrusion volume of mercury of the four pastes at the age of 90 days is different from that at the age of 28 days. The largest gaps of the total intrusion volume of mercury among the four pastes at the age of 28 and 90 days are 0.0654 ml/g and 0.0361 ml/g, respectively. It is clear that the gap becomes smaller with the hydration age.

Figure 5. Pore size distribution of pastes at 28 d

Figure 6. Pore size distribution of pastes at 90 d

Figure 7 shows the change of pore size distribution of each paste from 28 to 90 days. The biggest change occurs in paste S1. The total intrusion volume of mercury of S1 decreases by 0.044 ml/g from 28 to 90 days. Moreover, the proportion of large pores (> 100 nm) of S1 becomes much smaller from 28 to 90 days. As for paste S4, the change of its pore structure is
obviously the smallest from 28 to 90 days. This is because the early hydration rate of steel slag in S1 is the lowest, and its later hydration makes considerable contribution to the pore structure. Alkaline condition accelerates the early hydration rate of steel slag, but its excitation effect on the later hydration of steel slag decreases.

3.3 $w_n$ content results

$w_n$ content can be used as a semiquantitative indicator of the hydration products. For a specific binder, the more the amount of hydration products, the bigger the $w_n$ content. Figure 8 shows the $w_n$ contents of four pastes at the age of 3, 28, and 90 days. As expected, the $w_n$ content of each sample increases with hydration age. At any age, the pre and post order of $w_n$ content of pastes is S4 > S3 > S2 > S1. The alkaline excitation effect becomes better with the increase of pH value.

The gaps of $w_n$ content between S1 and S2 at the age of 3, 28, and 90 days are 0.86%, 1.49%, and 0.70%, respectively. The gaps of $w_n$ content between S1 and S3 at the age of 3, 28, and 90 days are 1.27%, 2.05%, and 0.83%, respectively. The gaps of $w_n$ content between S1 and S4 at the age of 3, 28, and 90 days are 1.92%, 2.89%, and 1.14%, respectively. Therefore, the alkaline excitation effect is not so obvious at late ages. The alkaline excitation effect at the age of 90 days is much poorer than that at the age of 28 days, and it is even poorer than that at the age of 3 days.

Figure 8. Non-evaporable water content of pastes

3.4 Discussion

RO phase is a solid solution of CaO, FeO, MnO, and MgO. It is a main phase of steel slag. The XRD results indicate that the hydration activity of RO phase is rather low even in the alkali environment with pH value of 13.8. Fe$_3$O$_4$ is almost inert in the alkali environment. Ca$_2$Al(OH)$_7$ is a main hydration product of aluminates, and alkaline excitation is helpful to its formation at the early ages. C$_2$S and C$_3$S are the main cementitious phases of steel slag. Their activity is much lower than that of silicates in cement. The $w_n$ content results show that the $w_n$ content of steel slag paste increases with the increase of pH value of hydration condition at the age of 3 days. It is believed that OH$^-$ is helpful to disintegrate vitreous composition and thus accelerate the hydration of C$_2$S and C$_3$S. However, the XRD results show that the diffraction peak intensity of Ca(OH)$_2$ of steel slag pastes, with or without alkaline excitation, is very weak at the age of 3 days. Therefore, though increasing the pH value of hydration condition can excite the early
hydration activity of C2S and C3S in steel slag, the alkaline excitation effect is not significant.

The $w_p$ content results show that the 28-day excitation effect is the best for each alkaline excitation condition. The 90-day excitation effect is very poor, and it is even poorer than the 3-day excitation effect. Moreover, the effect of increasing pH value becomes less important at the age of 90 days. The MIP results show that the 28-day pore structure of hardened steel slag paste is improved with the increase of pH value of hydration condition. However, the pore structure of hardened steel slag paste under alkaline condition is improved less than that of the reference sample from 28 to 90 days. Therefore, it can be concluded that the excitation effect of alkali on steel slag is a slow and continuous process within 28 days, and increasing pH value enhances the excitation effect at this period. Thereafter, alkaline excitation effect turns poorer and poorer, and the enhancement of increasing pH value to excitation effect becomes less important.

The hydration activity of RO phase and Fe3O4 in steel slag is very low. The silicates and aluminates phases in steel slag can hydrate slowly. Alkaline excitation has little influence on the hydration activity of RO phase and Fe3O4, and merely accelerates the hydration of silicates and aluminates phases to some extent at early and middle ages (in 28 days). Alkaline excitation increases the amount of hydration products at early and middle ages by accelerating the hydration rate of silicates and aluminates phases, but can not excite the activity of other phases. The excitation effect is not very important at late ages.

4 Conclusions
1) Ca2Al(OH)7 is a main hydration product of aluminates in steel slag. Alkaline excitation is helpful to its formation at early ages. Alkaline excitation has little influence on the hydration activity of RO phase and Fe3O4.
2) Increasing the pH value of hydration condition can excite the early hydration activity of C2S and C3S in steel slag. But the alkaline excitation effect is not significant.
3) The excitation effect of alkaline condition on steel slag is a slow and continuous process within 28 days. Increasing pH value enhances the excitation effect at this period. However, after 28 days, alkaline excitation effect decreases. The enhancement of increasing pH value to excitation effect is not very important.

Acknowledgment
Authors would like to acknowledge National Basic Research Program of China Grant (No. 2009CB623106) and China Postdoctoral Science Foundation (No. 20100480322).

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