The influence of steel slag on the hydration of cement during the hydration process of complex binder

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The influence of steel slag, a by-product from the processing of iron to steel, on the hydration of cement during the hydration process of complex binder was studied by calorimetry, X-ray diffraction analysis, and $Ca(OH)_2$ content determination. The results show that steel slag and cement affect each other's hydration by changing the hydration environment. Steel slag does not react with the hydration products of cement. The dormant period of cement-steel slag complex binder during the hydration is longer than that of cement. The more the adding amount of steel slag is, the longer the dormant period of complex binder will be. The steel slag decreases the early hydration rate of cement. This phenomenon is more obvious with the increment of steel slag addition. However, the steel slag can promote the hydration degree of cement at later ages and the promoting effect becomes more obvious with the increment of steel slag addition and the hydration ages.

steel slag, cement, complex binder, hydration

1   Introduction

Steel slag is a by-product from the processing of iron to steel, the amount of which produced during the process is about 15% of the steel production [1]. The utilization ratio of steel slag in America is almost 100% [2]. Most of the steel slag in Europe is utilized efficiently [3]. In contrast, the utilization ratio of steel slag in China is low, which is lower than 45% [4]. The amount of waste steel slag in China is over 300 million tons, and the total amount increases by tens of million tons per year. The steel slag dump occupies large area of land and leads to many serious environmental problems. Now most steel slag is used as filling material in civil engineering and some is also used as aggregates for concrete and asphaltic paving [5–7]. Different from common aggregates, steel slag can exhibit certain cementing property. So the properties (e.g., mechanical properties and durability) of cement concrete and asphalt concrete can be improved by using steel slag as aggregates [8–11]. A small amount of steel slag is used as raw material in brick production [12], to remove impurity agent [13, 14] and neutralizing agent [15].

The chemical composition of steel slag includes CaO 45%-60%, SiO_2 10%-15%, Al_2O_3 1%-5%, F_2O_3 3%-9%, MgO 3%-13%, FeO 7%-20%, and P_2O_5 1%-4 % [16]. Steel slag is richer in Mg and Fe contents, but it is lower in Ca and Si contents than cement. The alkalinity $M = w(CaO)/[w(SiO_2)+w(P_2O_5)]$, proposed by Mason [17], is commonly used to evaluate the activity of steel slag. Steel slag is classified into three grades based on alkalinity in China: low alkalinity slag ($M < 1.8$), intermediate alkalinity slag ($1.8 < M < 2.5$), and high alkalinity slag ($M > 2.5$). Dicalcium silicate (C_2S), tricalcium silicate (C_3S), RO phase (CaO-FeO-MnO-MgO solid solution), olivine, merwinite,

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tetracalcium aluminoferrite (C_4AF), free-CaO, and elemental Fe are common mineral phases of steel slag [18, 19]. The presence of C_2S and C_3S indorses steel slag certain cementitious properties.

Steel slag can be used as additive in cement and concrete production if its specific surface area is raised near or over that of cement. The cement with a small amount (e.g., 10% percent) of steel slag is easy to meet the requirements of related standards [20, 21]. If the adding amount of steel slag is high, the strength grade of cement is low. 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 [22–24]. High performance and "green" are the main characteristics of modern concrete, which are related closely to mineral admixtures. The study of mineral admixture is an important research direction of modern concrete [25]. Ground granulated blast-furnace slag and fly ash are the most common mineral admixtures for concrete and many researches on them have been carried out. Now these two mineral admixtures are scarcity in many regions of China. Therefore, raising the utilization of steel slag is beneficial to environmental protection and provides more mineral admixtures for concrete.

Ca^{2+} and OH^- can be released from the surface of C_3S immediately after the cement contacts with water, which can make the pH value of the pore solution exceed 12.0 within a few minutes. $Ca(OH)_2$ crystallizes constantly with the hydration of cement and the pH value of the pore solution is a little higher than 13.0 in a short time [26]. Even for concrete with a large amount of mineral admixture, the pH value of its pore solution is higher than 12.0 [27, 28]. So the reaction of steel slag is affected by the alkaline condition produced by cement during the hydration of cement-steel slag complex binder. Some researches showed that alkaline condition can promote the hydration of steel slag [19, 29]. Though the hydration properties of steel slag has some influence on the hydration properties of cement-steel slag complex binder, the hydration properties of cement play a decisive role in the hydration of the complex binder. Therefore, the influence of steel slag on the hydration of cement cannot be neglected. In this study, the influence of steel slag on the hydration properties of cement during the hydration of cement-steel slag complex binder was investigated.

2 Raw materials and experimental methods

2.1 Raw materials

The cement used was pure Portland cement with the strength grade of 42.5, which complies with the Chinese National Standard GB 175-1999. The specific surface area of cement was 312 m^2/kg. The steel slag used was basic oxygen furnace steel slag which was not processed by water braising. The specific surface area of steel slag was 458 m^2/kg. The chemical compositions of cement and steel slag are shown in Table 1. The free CaO content in steel slag was 1.16%. Figure 1 shows the XRD results of steel slag. As shown in Figure 1, the main mineral phases of steel slag were C_2S, C_3S, and RO phase.
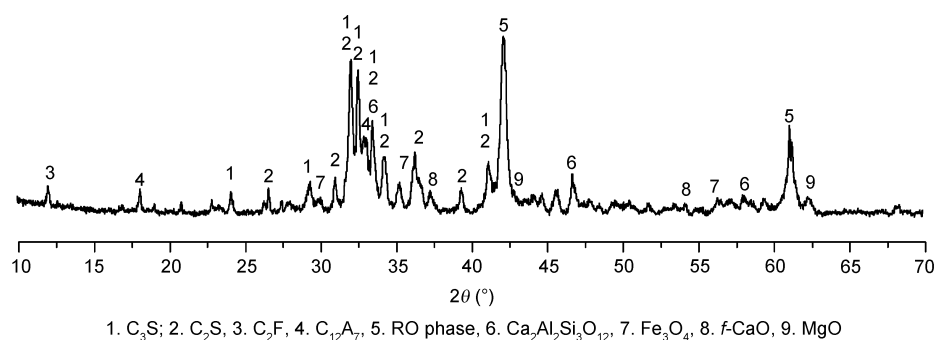
2.2 Experimental methods

Table 2 shows the mix proportions of cement paste, steel slag pastes, and cement-steel slag pastes. Sample SS was prepared by mixing steel slag with NaOH solution at pH value of 13.0. All the pastes were cast into plastic centrifuge tubes immediately after being stirred uniformly and then cured at 20°C±1°C to testing ages. At the testing ages, the hydration was stopped by soaking the samples in acetone.

Table 1 Chemical compositions of cement and steel slag

Composition	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O_{eq}	MnO	Loss on ignition
Cement	21.86	4.25	2.66	63.59	2.19	2.42	0.55	0	1.75
Steel slag	17.03	5.64	22.69	43.38	5.98	0	0.45	1.70	1.86

Note: $Na_2O_{eq}=Na_2O+0.658K_2O$

1. C_3S; 2. C_2S, 3. C_2F, 4. $C_{12}A_7$, 5. RO phase, 6. $Ca_2Al_2Si_3O_{12}$, 7. Fe_3O_4, 8. *f*-CaO, 9. MgO

Figure 1 XRD results of steel slag.

Table 2   Mix proportions of different binders

Sample	Cement	Steel slag	Water
S	-	100	30
SS	-	100	30
C	100	-	42
CS1	77.5	22.5	42
CS2	55	45	42

The samples were taken out of acetone and dried before they were tested.

The rate of heat evolution during the hydration of binder was measured by an isothermal calorimeter under a constant temperature of 25°C. The hydration products of binder were determined by X-ray diffraction with a TTR III diffractometer using 50 kV voltages and 200 mA current. The TG/DTG curves of hydration products were obtained by using a TA-Q5000 instrument with a heating rate of 10°C/min in nitrogen atmosphere.
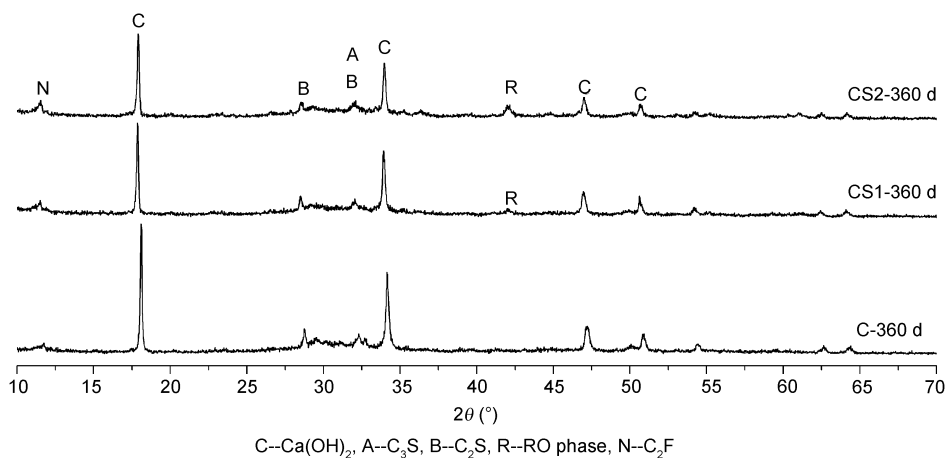
3   Results and discussion

3.1   Hydration products of cement-steel slag complex binder

Figure 2 shows the X-ray diffraction patterns of sample S hydrated for 3, 90, and 360 days and sample SS hydrated for 360 days. As shown in Figure 2, steel slag itself can hydrate after it contacts with water. C_2S, C_3S, $C_{12}A$, and $Ca_2Al_2SiO_{12}$ in steel slag diminish with age. However, the peaks of RO phase, Fe_3O_4, and C_2F remain almost unchanged, indicating that the hydration degree of these phases is very low. It can be seen from the diffraction peaks in samples S and SS at the age of 360 days that the species of their hydration products are the same, indicating that the hydration activity of RO phase, Fe_3O_4, and C_2F is very low even under the alkaline condition. Therefore, the hydration products of steel slag, either with or without alkaline-activation, are C-S-H gel which has no diffraction peaks due to its amorphous state, $Ca(OH)_2$, unhydrated C_2S, C_3S, $C_{12}A$, and $Ca_2Al_2SiO_{12}$, and inert RO phase, Fe_3O_4, and C_2F.

From above analysis, it can be seen that steel slag consists of cementitious phases (C_2S, C_3S, $C_{12}A$, and $Ca_2Al_2SiO_{12}$) and inert phases (RO phase, Fe_3O_4, and C_2F). The cementitious phases of steel slag are similar to the silicate phases and aluminate phases of cement. Steel slag is cooled naturally, but cement is quenched. The cementitious phases of steel slag crystallize much better than those of cement, and thus their activity is much lower than that of cement clinkers. So the steel slag can be regarded as the mixture of poor-quality cement and inert substances. Figure 3

A--C_3S, B--C_2S, C-$Ca(OH)_2$, N--C_2F, R--RO phase, F--Fe_3O_4
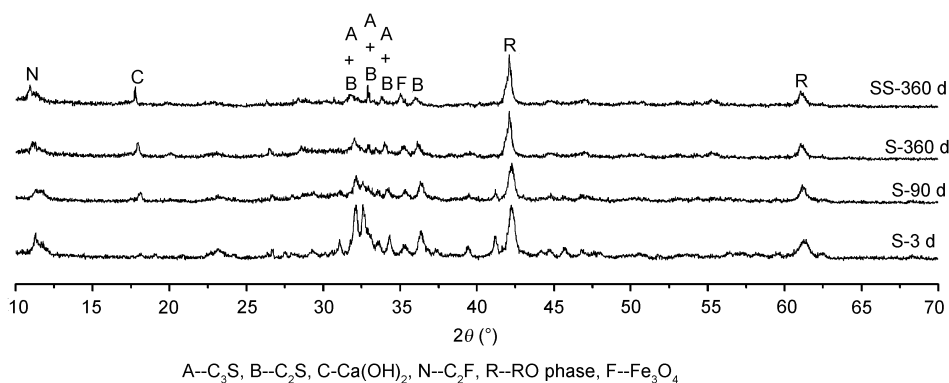
Figure 2   X-ray diffraction patterns of steel slag hydrated at various ages.

C--$Ca(OH)_2$, A--C_3S, B--C_2S, R--RO phase, N--C_2F

Figure 3   X-ray diffraction patterns of different binder pastes hydrated for 360 days.

shows the hydration products of cement-steel slag complex binders and cement. It can be seen from Figure 3 that the main hydration products of complex binders and cement are the same: C-S-H gel and $Ca(OH)_2$. RO phase, Fe_3O_4, and C_2F in the hydration products of complex binders increase with the increment of the adding amount of steel slag.

As is well known, ground granulated blast-furnace slag and fly ash react with $Ca(OH)_2$ produced by cement during the hydration of complex binder, which is called pozzolanic reaction. However, steel slag does not react with the hydration products of cement, and cement does not react with the hydration products of steel slag either. Thus, cement and steel slag simply affect each other's hydration (e.g., hydration rate and degree) by changing each other's hydration environment during the hydration of cement-steel slag complex binder.

3.2 The influence of steel slag on the early hydration of cement

Figure 4 shows the exothermic rates during the hydration of cement (W/C=0.42) and steel slag (W/S=0.30). As can be seen in Figure 4, the whole hydration process of steel slag is similar to that of cement, which can be divided into 5 stages: rapid heat release period, dormant period, acceleration period, deceleration period, and steady period. An exothermic peak whose value is 30–40 J g^{-1} h^{-1} forms very quickly at the first stage, which is mainly due to the release of surface energy of particles. In order to reflect the whole process more clearly, the maximum value of ordinate is set at 10 J g^{-1} h^{-1}. Hydration products $Ca(OH)_2$ and C-S-H gel start to crystallize only when the concentration of Ca^{2+} reaches the saturation state. So the hydration enters the dormant period after the first stage. The dormant period of steel slag is much longer than that of cement. As a result, the formation of the second exothermic peak of steel slag is about 12 h later than that of cement. The exothermic rate of steel slag in the acceleration period, deceleration period, and steady period is much lower than that of cement in the corresponding period. The accumulative hydration heat of steel
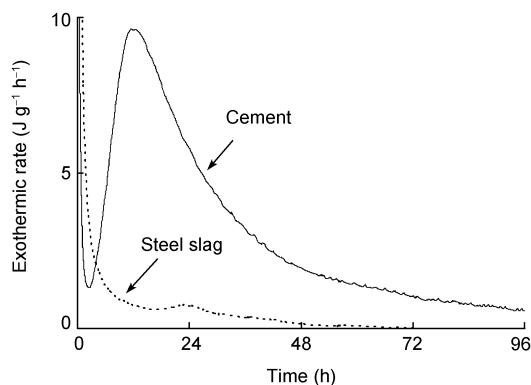
slag is 60.74 J g^{-1} in 96 h, which is much lower than that of cement.

Figure 5 shows the exothermic rates during the hydration of cement-steel slag complex binders and cement. The water-to-binder ratios of all the three samples were 0.42, and the adding amounts of steel slag in complex binder 1 and complex binder 2 were 22.5% and 45%, respectively. It can be seen from Figure 5 that the dormant period of complex binder becomes longer with the increment of steel slag adding amount. Moreover, the more the steel slag addition is, the later the second exothermic peak forms. Some researches showed that the setting time of cement and concrete became longer by replacing part of cement with steel slag, and the more the replacement the longer the setting time [18, 30, 31]. Obviously, one of the main reasons for the long setting time of cement-steel slag complex binder is its long dormant period.

The hydration condition of steel slag during the hydration process of cement-steel slag complex binder is alkaline. In this study, the alkaline condition was simulated by NaOH solution at a pH value of 13.0. Figure 6 shows the exothermic rate of steel slag hydrating under alkaline condition. The accumulative hydration heat of steel slag is 69.78 J g^{-1} in 96 h, which is higher than that of the steel slag without alkaline activation. Therefore, alkaline condition is beneficial to the activity of steel slag. The hydration heat of cement
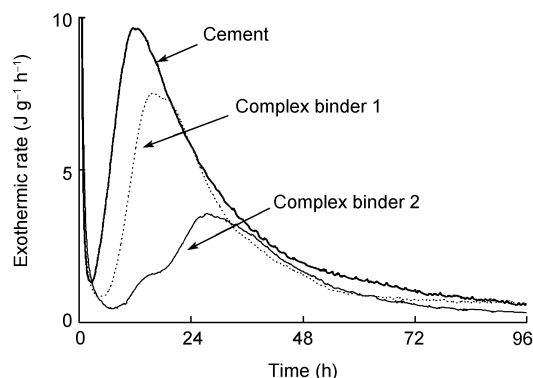

Figure 5 Exothermic rates of complex binder and cement during hydration.

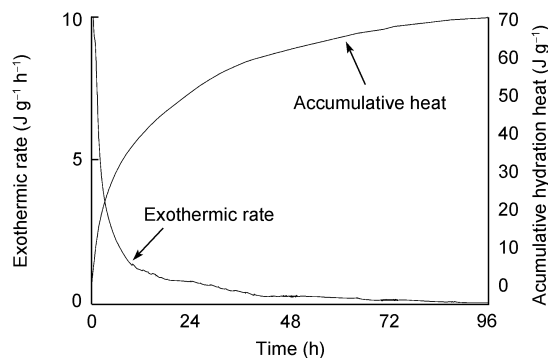**Figure 4** Exothermic rates of steel slag and cement during hydration.

Figure 6 Hydration heat curves of steel slag under the condition of alkali environment.

per unit mass in the complex binder can be described by

$$\frac{Q_B(t) - Q_S(t) \cdot p}{1 - p}, \quad (1)$$

where $Q_S(t)$ denotes the hydration heat of steel slag in time t in Figure 6, $Q_B(t)$ denotes the hydration heat of cement in time t in Figure 5, and p is the adding amount of steel slag.

Figure 7 shows the accumulative hydration heat of cement and cement in complex binder per unit mass. In Figure 7, cement 1 and cement 2 denote the hydration heat of cement in complex binder 1 and the hydration heat of complex binder 2 calculated based on eq. (1), respectively. It can be seen from Figure 7 that the hydration heat of cement per unit mass in complex binders is less than that of pure cement. Therefore, the hydration of cement is delayed by replacing part of cement with steel slag. Moreover, the effect is more obvious with the higher steel slag adding amount. This is mainly because steel slag can lead to a longer dormant period of cement-steel slag complex binder, which delays the hydration of the complex binder as well as cement.

3.3 The influence of steel slag on the late hydration of cement

The TG curves of the hydration products of samples SS, C, CS1 and CS2 at the ages of 90 and 360 days were determined in this study. Figures 8–10 show the TG/DTG curves of the hydration products of samples C, CS2 and SS at the age of 360 days, respectively. It can be seen from Figures 8–10 that the hydration products of all the three binders have three main endothermic peaks within 900°C: initial decomposition of C-S-H gel and hydrated aluminate phases (50–200°C); decomposition of $Ca(OH)_2$ (400–550°C); further decomposition of C-S-H gel and hydrated aluminate phases (550–770°C). The TG curves can further prove that the main hydration products of steel slag are similar to those of cement. However, as can be seen by comparing Figure 8 with Figure 10, the $Ca(OH)_2$ content of the hydration products of steel slag is lower than that of cement.

Table 3 shows the $Ca(OH)_2$ contents of the hydration products of different binders calculated by TG curves. The reactions of steel slag and cement don't cross mutually during the hydration of cement-steel slag complex binder, so the $Ca(OH)_2$ in the hydration products of complex binder is the sum of the $Ca(OH)_2$ contents produced by cement and steel slag respectively. The hydration condition of steel slag in sample SS is alkaline, which is to consider the influence of cement on the hydration of steel slag during the hydration of cement-steel slag complex binder. The $Ca(OH)_2$ content of the hydration products of the cement per unit mass in cement-steel slag complex binder can be described by
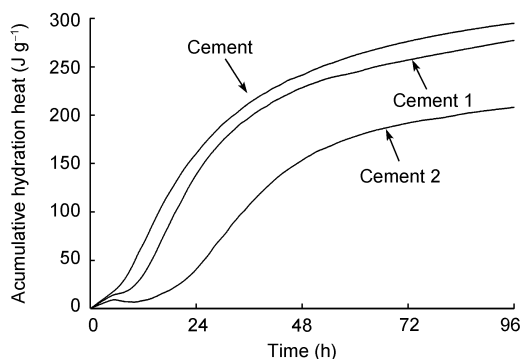
$$\frac{p - nw}{1 - p}, \quad (2)$$

Figure 7 The hydration heat of pure cement and cement in complex binder per unit mass.
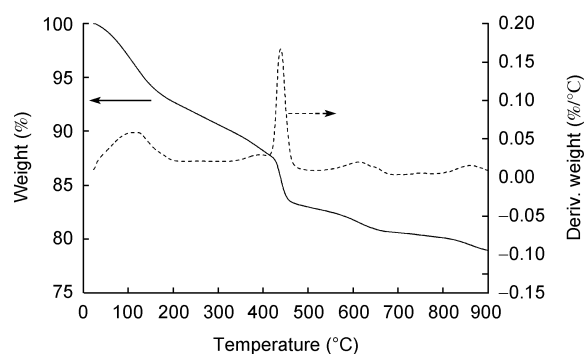

Figure 8 TG curves of the hydration products of cement hydrated for 360 days.
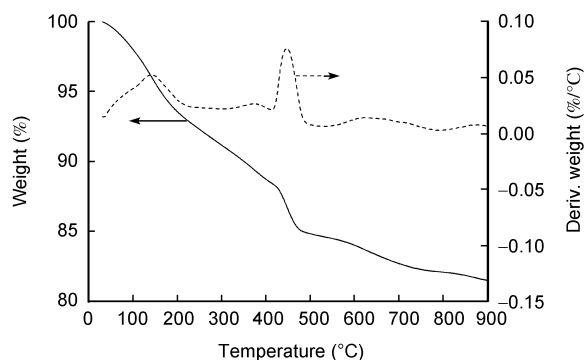

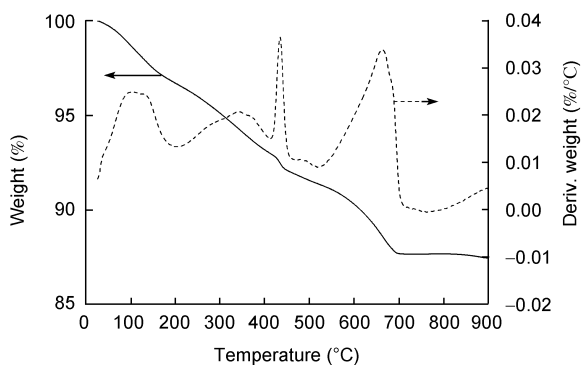**Figure 9** TG curves of the hydration products of CS2 hydrated for 360 days.

Figure 10 TG curves of the hydration products of steel slag hydrated for 360 days.

Table 3 Ca(OH)$_2$ contents of hydration products

Samples	Ages (d)	
	90	360
SS	3.54	5.82
C	18.38	20.08
CS1	15.77	18.59
CS2	13.27	16.34

where *n* denotes the Ca(OH)$_2$ content of the hydration products of steel slag per unit mass in time *t*, *p* denotes the Ca(OH)$_2$ content of the hydration products of complex binder per unit mass in time *t*, and *w* is the adding amount of steel slag.

The hydration condition of cement is changed by steel slag during the hydration of cement-steel slag complex binder to result in the change of hydration degree of cement. Eq. (3) can be used to describe the change amplitude of hydration degree of cement.

$$K(t) = \frac{\dfrac{p-nw}{1-w}-m}{m} \times 100\%, \qquad (3)$$

where *m* denotes the Ca(OH)$_2$ content of the hydration products of pure cement per unit mass in time *t*. Obviously, if $K(t)>0$, the hydration of cement is promoted by steel slag; if $K(t)<0$, the hydration of cement is hindered by steel slag. The more the absolute value of $K(t)$ is, the greater the effect of steel slag on cement will be.

The following results can be obtained by introducing the values in Table 3 to eq. (3): If the adding amount of steel slag is 22.5%, then $K(90\text{ d})=5.11\%$, and $K(360\text{ d})=11.04\%$; if the adding amount of steel slag is 45%, then $K(90\text{ d})=15.51\%$, and $K(90\text{ d})=24.24\%$. It can be seen from these results that the late hydration of cement is promoted by steel slag, and the promoting effect becomes more obvious with the increment of steel slag addition and the hydration ages.

Generally speaking, the hydration of C$_2$S and C$_3$S can be respectively described by [32]:

$$C_2S+2H=0.5C_3S_2H_3+0.5CH \qquad (4)$$

$$C_3S+3H=0.5C_3S_2H_3+1.5CH \qquad (5)$$
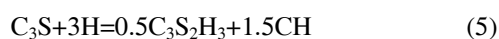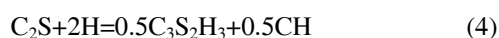
where H denotes H$_2$O, CH denotes Ca(OH)$_2$, and C$_3$S$_2$H$_3$ is the hydration product of C$_2$S and C$_3$S. The hydration of 1 mol C$_2$S consumes 2 mol H$_2$O, whereas the hydration of 1 mol C$_3$S consumes 3 mol H$_2$O. C$_3$S is the main cementitious phase of cement, but C$_2$S is the main cementitious phase of steel slag [18, 24]. What's more, the inert phases of steel slag do not consume any H$_2$O. So the hydration of steel slag consumes less water than that of cement. The actual water-to-cement ratio increases by replacing part of cement with steel slag on the premise of keeping the water-to-binder ratio unchanged. At the late hydration age of cement, the particles of cement are wrapped by thick C-S-H

gel. The hydration rate of cement at this stage depends on the difficult degree of water permeating into the C-S-H layers. The inert phases of steel slag, wrapped by C-S-H gel, play a role of nucleation, indirectly reducing the thickness of C-S-H layer around cement particles. Therefore, steel slag improves the hydration condition of cement and promotes the hydration of cement in late ages.

4   Conclusions

(I) Steel slag can be divided into two parts: cementitious phases and inert phases. The cementitious phases of steel slag are similar to those of cement, and their main hydration products are Ca(OH)$_2$ and C-S-H gel. Steel slag and cement do not react with the hydration products of each other. They affect each other's hydration by changing the hydration environment of each other.

(II) The dormant period of cement-steel slag complex binder is longer than that of cement. The dormant period of cement-steel slag complex binder becomes longer with the increment of steel slag. Steel slag decreases the early hydration rate of cement, and this phenomenon is more obvious with the increment of steel slag.

(III) Steel slag improves the hydration condition of cement and promotes the hydration of cement in late ages. The promoting effect becomes greater with the increment of steel slag addition and the hydration ages.

1 Dong B P. Treatment and Utilization of Solid Wastes. Beijing: Metallurgical Industry Press, 1999. 22–34

2 Motz H, Geiseler J. Products of steel slags an opportunity to save natural resources. Waste Manage, 2001, 21: 285–293

3 Shi Q. The development situation of steel slag industry in America (in Chinese). Constr Conserv Energy, 1980, 4: 31–35

4 Zhu G L. The utilization status and development of solid waste in China (in Chinese). Waste Steel, 2003, 3: 34–41

5 Hendrik G. Iron and Steel Slag. U.S. Geological Survey, Mineral Commodity Summaries, 2009

6 Murphy J N, Meadowcroft T R, Barr P V. Enhancement of the cementitious properties of steelmaking slag. Can Metall Quart, 1997, 36: 315–331

7 Shi C J. Steel slag-Its production, processing, characteristics, and cementitious properties. J Mater Civil Eng, 2004, 16: 230–236

8 Wu S P, Xue Y J, Ye Q S, et al. Utilization of steel slag as aggregates for stone mastic asphalt (SMA) mixtures. Bldg Environ, 2007, 42: 2580–2585

9 Asi I M, Qasrawi H Y, Shalabi F I. Use of steel slag aggregate in asphalt concrete mixes. Can J Civil Eng, 2007, 34: 902–911

10 Beshr H, Almusallam A A, Maslehuddin M. Effect of coarse aggregate quality on the mechanical properties of high strength concrete. Constr Build Mater, 2003, 17: 97–103

11 Maslehuddin M, Alfarabi M, Shameem M, et al. Comparison of properties of steel slag and crushed limestone aggregate concretes. Constr Build Mater, 2003, 17: 105–112

12 Shih P H, Wu Z Z, Chiang H L. Characteristics of bricks made from

waste steel slag. Waste Manage, 2004, 24: 1043–1047

13 Dimitrova S V. Metal sorption on blast-furnace slag. Water Res, 1996, 30: 228–332

14 Kang H J, An K G, Kim D S. Utilization of steel slag as an adsorbent of ionic lead in waste water. J Environ Sci Health A, 2004, 39: 15–28

15 Gahan C S, Cunha M L, Sandstrom A. Comparative study on different steel slags as neutralizing agent in bioleaching. Hydrometall, 2009, 95: 190–197

16 Shi C J, Qian J S. High performance cementing materials from industrial slags—a review. Resour Conserv Recy, 2000, 29: 195–207

17 Mason B. The constitution of some open-hearth slag. J Iron Steel Inst, 1994, 11: 69–80

18 Kourounis S, Tsivilis S, Tsakiridis P E, et al. Properties and hydration of blended cements with steelmaking slag. Cem Concr Res, 2007, 37: 815–822

19 Shi C J. Characteristics and cementitious properties of ladle slag fines from steel production. Cem Concr Res, 2002, 32: 459–462

20 Tsakiridis P E, Papadimitriou G D, Tsivilis S, et al. Utilization of steel slag for Portland cement clinker production. J Hazar Mater, 2008, 152: 805–811

21 Ahmad M, Masoud K A. Producing Portland cement from iron and steel slags and limestone. Cem Concr Res, 1999, 29: 1373–1377

22 Sun J Y. Study of effects of ground steel slag on mechanical performance and soundness of concrete (in Chinese). Fly Ash, 2003, 5: 7–9

23 Wang B, Dai L P, Zhou M H. Experimental investigation on high performance concrete with fine grinded steel slag (in Chinese). J Shenyang Archit Civil Eng Inst, 2003, 19: 148–149

24 Li Y X. Study on Composition, Structure, and Properties of Cement and Concrete with Steel-making Slag Powder Mineral Additive (in Chinese). Beijing: China Building Materials Academy, 2003

25 Wu Z W, Lian H Z. High Performance Concrete (in Chinese). Beijing: China Railway Press, 1999

26 Taylor H F M. Cement Chemistry. 2nd ed. London: Thomas Telford, 1997

27 Pu X C. A study on cement with addition of large amount of fly ash (in Chinese). House Mater Appl, 1996, 3: 4–12

28 Resheeduzaafar, Ehteshan H. Effect of microsilica and blast furnace slag on pore solution composition and alkali-silica reaction. Cem Concr Res, 1991, 21: 219–235

29 Wang Q, Yan P Y. Hydration properties of basic oxygen furnace steel slag. Constr Build Mater, 2010, 24: 1134–1140

30 Altun A, Yılmaz S. Study on steel furnace slags with high MgO as additive in Portland cement. Cem Concr Res, 2002, 32: 1247–1249

31 Rai A, Prabakar J, Raju C B, et al. Metallurgical slag as a component in blended cement. Constr Build Mater, 2002, 16: 489–494

32 Lea F M. The Chemistry of Cement and Concrete. 3rd ed. New York: Edward Arnold, 1974