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Cementing properties of steel slag activated by sodium silicates and sodium hydroxide

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Abstract: Steel slag which is mainly composed of γ-Ca_2SiO_4 and other silicates or alumino-silicates is activated by sodium silicates and sodium hydroxide. The powders of such steel slag are usually inert to hydrate and subsequently have very low ability of cementing. But when sodium silicates and sodium hydroxide are used as activators the steel slag shows very good properties of cementing. When activated with NaOH solution the hardened slurry of the steel slag has a compressive strength of 11.13 MPa after being cured for 28 days. When activated with Na_2SiO_3 solution the samples after being cured for 28 days have an average compressive strength of 40.23 MPa. While the steel slag slurry which is only mixed with water has a compressive of 0.88 MPa after being cured for 28 days.

Key words: steel slag; sodium silicate; sodium hydroxide; cement; binding material

1 Introduction

The steel slag is a kind of solid wastes produced during steel production. This waste mostly comes from converters which produce approximately 80wt% steel in China. Other furnaces produce approximately 20wt% steel including electric furnaces and open hearth furnaces. Ladles and other liquid steel containers also contribute little amount of steel slag. The total production of steel slag is about 40 million tons in China in the year 2002. In most iron and steel enterprises, steel slag is only treated for the recovery of steel knots. After that steel slag is mostly left to heap up. Even though little amount of steel slag has been used as a mixer to produce cement and concrete [1-3] or as pebbles in road pavement [4], but the most is still costing a large area of land and large sum of money to manage.

It has been noticed that most steel slag has $Ca_2SiO_4(C_2S)$ or both $Ca_2SiO_4(C_2S)$ and $Ca_3SiO_5(C_3S)$ as their major phases. But due to the difficulties in cooling the slag very quickly, the dicalcium silicates formed in the slag are mainly γ-C_2S which is relatively inert to react with water compared to α-C_2S which occurs as one of the major mineral phases in cement clinkers. Many studies have intended to activate γ-C_2S. The activators having been used include cement clinkers, gypsum and other similarities [5-7]. But no satisfied results have been reported. Many silicates and alumino-silicates have been tested for their dissolution and geopolymerization behavior in the solution of NaOH, KOH, Na_2SiO_3 or their mixtures [8]. The results showed that nearly all of the silicates tested can be dissolved and geopolymerized on some extent, and all of the samples can be cemented. The strength can be developed for all of the samples, even though some of the samples have very low strength. It was known that steel slag is composed of mainly calcium silicates or calcium alumino-silicate or other silicates. It is possible that these silicates can be activated by a similar dissolution and geopolymerization process when contacted with alkaline solution or alkaline silicate solution. With such a possibility, the cementing properties of steel slag activated by sodium silicate solution and sodium hydroxide solution were investigated.

2 Experimental

2.1 Raw materials

The steel slag powder was provided by Shougang Group in Beijing. The powder was produced by milling the primary steel slag which mainly come from converters. The slag has been heaped up in the out-door condition for several years before milling. The chemical analysis and some physical characters are shown in **table 1.**

The major crystalline phases detected by XRD as shown in **figure 1** are γ-C_2S, RO phase (a solid solu-

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tion of MgO, FeO and MnO), merwinite and olivine, but with γ-C_2S as a dominate phase. The sodium silicate solution was provided by Huairou Muhu Additives Co. Ltd, the original solution has a SiO_2/Na_2O ratio of 3.3. The solution was diluted and extra sodium hydroxide (NaOH) was added to adjust the SiO_2/NaOH ratio to 1. The new solution was aged for 24 h before being used, so the solution could reach a equilibrium state.

Table 1 Chemical analysis and some physical characters of steel slag

Composition /wt%						Physical character	
FeO	CaO	MgO	SiO_2	MnO	Al_2O_3	Specific surface area/ ($m^2 \cdot kg^{-1}$)	Density /($g \cdot cm^{-3}$)
15.47	48.01	8.27	16.06	1.55	1.93	350	3.22

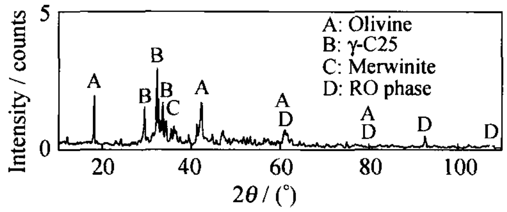

Figure 1 XRD pattern of the steel slag.

The sodium hydroxide used in this experiment was a chemical reagent provided by Tianjin Dengzhong Chemistry Co. Ltd.

2.2 Method and equipment

In order to compare the cementing properties affected by the addition of activators, three groups of samples were prepared. Group 1 samples were prepared with steel slag powder and water. Group 2 samples were prepared with steel slag powder and sodium hydroxide solution. Group 3 samples were prepared with steel slag powder and sodium silicate solution. The compositions of the three group samples are shown in **table 2.**

Table 2 Compositions of the tested samples g

Ingredient	Group 1	Group 2	Group 3
Steel slag ground powder	300	300	300
Sodium hydroxide*	0	20	0
Sodium silicate*	0	0	30.5
Water	66	66	66

Note: Solutions were used to prepare samples, but the percentage was calculated on a water-free base.

In designing the compositions in the above three group samples, two principles were kept. One is that water content is equal for all of the samples, the other is that the amount of substance of Na^+ is kept to be same for group 2 and group 3 samples.

The ingredients as shown in table 2 were mixed in a cement slurry mixer in a condition of ISO standard. The resulted slurry was poured into 30 mm× 30mm×50 mm moulds and cured in the condition of 20°C and 90% relative humidity for 24 h. Then the samples were demoulded for a continue curing in the same condition until the strength test was made. Three samples were tested for compressive strength of 3, 7 and 28 days in each group. The presented data are the average of the three samples.

XRD spectra were obtained from a Philips APD-10 type X-ray Diffractometer, with $Cu\text{-}K_\alpha$ target, the working voltage is 50 kV. The morphology and microstructure of the samples were observed by a Cambridge S250 Scanning Electron Microscope with a Link NA1000 Energy Dispersive Spectroscope. The working voltage is 20 kV.

3 Results and discussion

3.1 Compressive strength

After the samples were cured for 3, 7 and 28 days, their compressive strengths were tested. The results are shown in **table** 3.

Table 3 Compressive strength of the tested samples

MPa

Samples	Cure time /d		
	3	7	28
Group 1	2.99	3.00	0.88
Group 2	7.33	9.21	11.13
Group 3	30.66	35.40	40.23

As shown in table 3, the compressive strength of the group 1 samples is very low. Such a low strength, not significant for any building construction purpose, indicates that most of the minerals in the steel slag are nearly inert to react with water at room temperature without the presence of activators (or additives). It is expected that a small portion of ultra fine grains (for example, the grains with a diameter less than 2 μm) could be produced during the milling of the steel slag powders. Such ultra fine grains would probably be active to react with water, which contributes the early strength (3 and 7 days) of group 1 samples. The compressive strength of group 1 samples after being cured for 28 days is much lower than those after being cured for 3 days and 7days. This is probably due to the continue hydrate of residue CaO, MgO and other RO phases. It is possible that small amount of CaO and MgO could be left unhydrated in the steel slag powder but undetected by XRD, even though the steel slag had been heaped up in the out-door condition for several years before milling. If such phases (periclase and crystallized CaO) might be hydrated after 7days, a destruction force to the cemented structure was expected, which resulted in the lower strength after being cured 28 days than those after being cured for 3 days and 7 days. This destruction force comes from the expansion of hydrated grains. Group 2 samples have a much higher compressive strength than group 1 samples. This suggests that the activity of the steel slag largely increases by the addition of NaOH. Larger amount of steel slag powder can react with NaOH solution than with water to produce more cementing materials (gelling materials). Group 3 samples have the highest compressive strength among the three groups. Their strength nearly reaches the strength level of traditional cements. Groups 3 samples not only have a high strength in early days, but also their strength increases continuously from 3 days to 28 days. This suggest that intensive reactions happen between steel slag powder and sodium silicate solution in early days, such reactions would continue beyond 28 days when cured in a humid condition.

Comparing the compressive strength of the three groups, it is clear that both sodium hydroxide solution and sodium silicate solution have an activating effect on the steel slag powder. But the activating mechanism is very complicated. It is postulated here that the higher content of OH^- or high pH value in the solution is favourable to the dissolution of the minerals in the steel slag powder. This trend has been evidenced by Phair and Deventer *et al.* on the study of several other silicate minerals [9]. But apparently the higher OH^- content in the solution is not the dominant factor which promotes cementing reactions. Because in the case of group 3, the OH^- content is obviously lower than that in the case of group 2. But the compressive strength of group 3 samples is much higher than that of the group 2 samples. It is suggested that the silicate ions which may exist as monomers, dimmers, trimers or other forms, may play a dominant role in promoting the cementing reactions. But how they act needs to be further clarified by some more fundamental studies.

3.2 **XRD** analysis **and** SEM **observation of group 3 samples**

To better understand the results of the compressive strength tests, XRD analysis and SEM observations of group 3 samples were made. Figure 1 is the XRD spectrum of unreacted steel slag power. **Figure** 2 is a comparison of XRD spectra of group 3 samples in different ages. By comparing figure 1 and figure 2, it is shown that the dominant minerals in original steel slag powder are unhydrated dicalcium silicate phases (γ-C_2S), while the mineral phases in the samples cured for 3 days are dominated by hydrated dicalcium silicates and calcium hydroxide. In addition the spectra shows a high background and low peaks, this means that most of the crystalline phases in the original steel slag powder have been transformed into amorphous phases or semi-crystalline phases. These phases may be attributed to C-S-H gels which are frequently encountered in normal cement products [10] or as geopolymer described by Davidovits [11] and other researchers [12-14]. The XRD spectra obtained from the samples cured for 7 days have much higher background than the samples cured for 3 days, particularly in the area where the peaks occur frequently. Similarly, the samples cured for 28 days have higher background in the area where the peaks concentrate than the samples cured for 7 days. These probably suggest that along with the increase of curing days, the amount of amorphous phases and semicrystalline phases increase. This cooperates well with the increase in compressive strength of the same group samples.

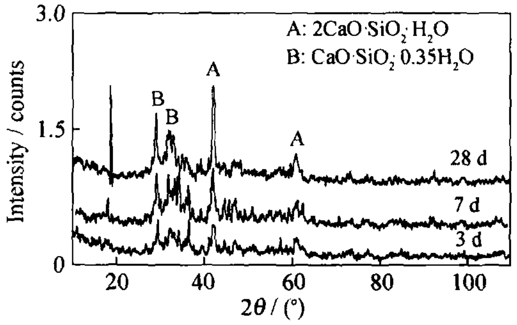

Figure 2 XRD patterns of group 3 at different ages.

Figures 3, 4 **and** 5 are the SEM photographs of group 3 samples cured for 3, 7 and 28 days. It is clear that a large amount of gels have been formed in all of group 3 samples. Among them, the samples cured for 28 days have the most abundant content of the gels and these samples also have the most dense structure which is formed by the cementing of the gels. **Figure**

6 is a spectrum of the Energy Dispersive Spectroscopy (EDS) linked with the SEM. The spectrum semi-quantitatively shows the chemical composition of point A in figure 5, where a typical newly formed amorphous or semicrystalline phase exist. As shown in figure 6, the major composition is CaO and SiO_2 at this point. Such a composition is very similar with that of the typical C-S-H gels phase frequently encountered in the traditional cement products.

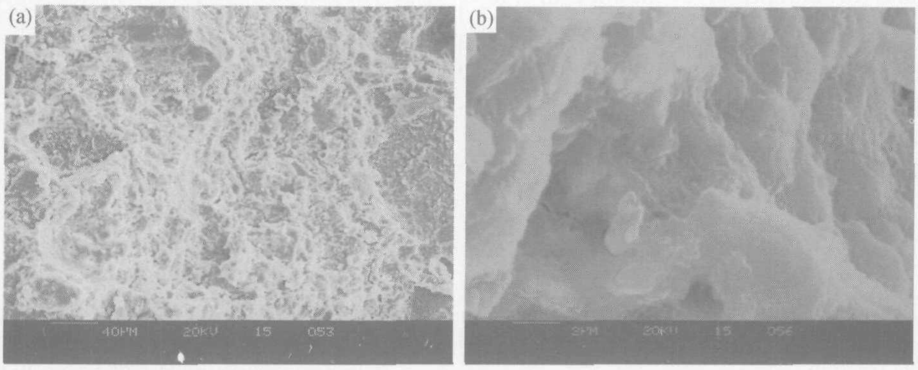

Figure 3 SEM photographs of group 3 samples cured for 3 days: (a) low magnification; (b) high magnification.

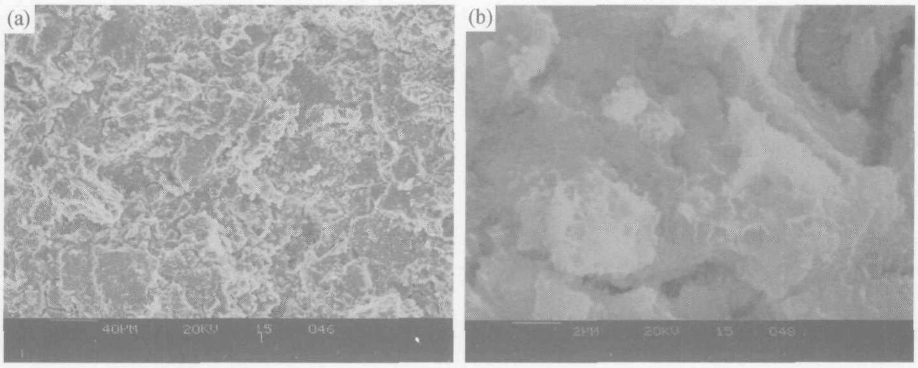

Figure 4 SEM photographs of group 3 samples cured for 7 days: (a) low magnification; (b) high magnification.

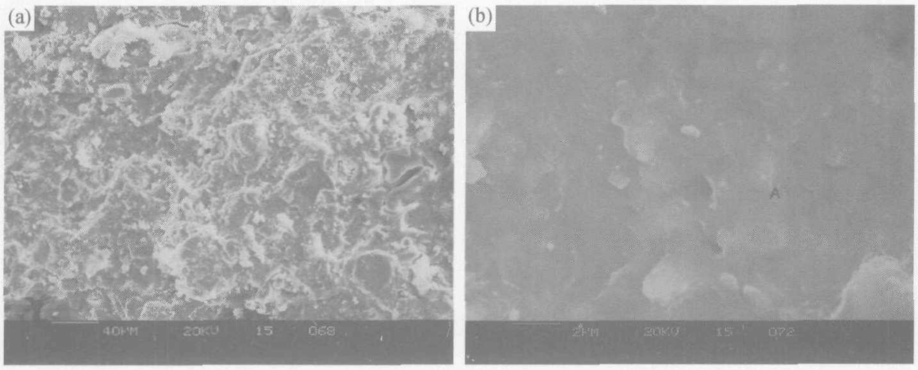

Figure 5 SEM photographs of group 3 samples cured for 28 days: (a) low magnification; (b) high magnification.

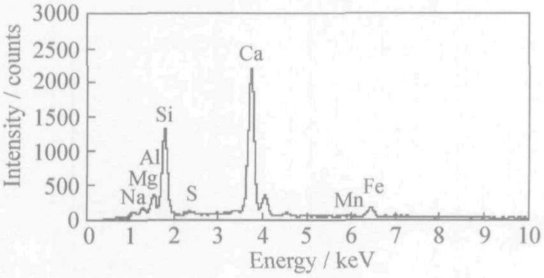

Figure 6 Spectrum of Energy Dispersive Spectroscopy linked with SEM, point A in figure 5.

4 Conclusions

The steel slag powder has a very weak tendency to react with water to form cementing gels at room temperature. This results in a very low compressive strength of the samples prepared with only steel slag powder and water. Sodium hydroxide solution has an ability to activate the steel slag powder. But the compressive strength of the samples prepared with steel slag powder and sodium hydroxide (NaOH) solution is much lower than that of the samples prepared with steel slag powder and sodium silicate (Na_2SiO_3) solution. The samples prepared with the steel slag powder and the sodium silicate solution have an average compressive strength of 40.23 MPa after curing for 28 days. XRD analysis, SEM observations and EDS analysis indicate that most of the original minerals phases have been hydrated, large amount of cementing gels have been formed in these samples.

The comparison of compressive strength of the three group samples suggests that silicate ions which may exist in the forms of monomers, dimmers, trimers and others may play very important roles in promoting the cementing reactions. But how they act needs to be further clarified by more fundamental studies.

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