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Communication

# Study on steel slag and fly ash composite Portland cement

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## Abstract

A new kind of cement made of clinker, steel slag, fly ash, and certain admixtures has been developed. The total amount of steel slag and fly ash is 50%, and the grade of cement reaches 425 or even 525 according to Chinese national standard for composite Portland cement. The optimum formulation of such cement was studied. Besides setting time and strength, the drying shrinkage, sulfate resistance, carbonation, and restriction of expansion due to alkali-aggregate reaction were also determined. 

*Keywords:* Seel slag; Fly ash; Admixture; Composite Portland cement

Steel slag (SS) is a kind of industrial waste resulting from the steel-refining process in a conversion furnace. Based on the raw materials and process used, its chemical compositions consists of CaO 45–60%, $SiO_2$ 10–15%, $Al_2O_3$ 1–5%, $Fe_2O_3$ 3–9%, FeO 7–20%, MgO 3–13%, and $P_2O_5$ 1–4%, and the mineral compositions are composed of $C_3S$, $C_2S$, CMS, $C_3MS_2$, RO phase (a solid solution of MgO, FeO, and MnO), free lime, and others. According to the alkalinity $A = CaO/(SiO_2 + P_2O_5)$, SS could be classified into four groups, such as olivine group (A = 0.9–1.4), merwinite group (A = 1.4–1.6), dicalcium silicate group (A = 1.6–2.4), and tricalcium silicate group ($A > 2.4$). Among them, only the SS with $A > 1.8$ could be used as a cementitious material [1]. From the theoretical point of view, SS can be regarded as a clinker with lower quality and can be used to substitute partially as clinker for producing composite Portland cement (CPC). Fly ash (FA) is also an industrial waste with a pozzolanic nature, which has been used to make fly ash Portland cement in many countries. However, the utilization of both SS and FA for producing CPC has not been reported. The production and application of steel slag and fly ash composite portland cement (SFCPC) have at least the following advantages:

1. It can reduce the cost of cement production as well as enhance the utilization factor of SS and FA.
2. The reduction of clinker can decrease air pollution compounds, such as $CO_2$, $SO_2$, NOx, during clinker processing.

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## 1. Experimental

### 1.1. Materials

Clinker was from Dongshan Cement Plant (Taiyuan, P.R. China), steel slag from Taiyuan Steel and Iron Company (Taiyuan, P.R. China), fly ash from Taiyuan Second Power Station (Taiyuan, P.R. China), gypsum from Taiyuan Dongshan Gypsum Mine (Taiyuan, P.R. China), alunite from Shandong Zhucheng Alunite Mine (Zhucheng, P.R. China), and high-alumina cement from Guojiazhai Cement Plant (Jiaocheng, P.R. China). Calcined gypsum and calcined alunite were made of the above raw material at 700°C and 650°C, respectively. Table 1 shows the chemical composition of these materials.

The alkalinity of SS used was 3.60 and the main minerals of SS used were $C_3S$, $C_2S$, RO phase, free lime, and others confirmed by X-ray diffraction. The samples of SFCPC were made of clinker, SS, FA, and certain admixtures. The total amount of SS and FA was 50%, which is the maximum according to Chinese national standard for CPC, and the amount of SS and FA was fixed at 30 and 20% respectively, based on the previous works. The samples were ground to the fineness of 2–4% of the residue on a 0.08-mm sieve.

### 1.2. Methods

The mortar strength was measured as per Chinese standard GB177-85. Mortar bars ($4 \times 4 \times 16$ cm) were made of cement, sand, and water (1:2.5:0.44), which were first cured in a fog room at 20°C for 24 h, and then demoulded and cured in water at 20 ± 3°C until the desired age.

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Table 1
Chemical composition of materials (wt%)

| Item | Loss on Ignition | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | MgO | $SO_3$ | $P_2O_5$ |
|---|---|---|---|---|---|---|---|---|
| Clinker | 0.53 | 20.49 | 7.53 | 4.72 | 62.12 | 1.98 | — | — |
| Steel slag | — | 12.12 | 2.58 | 8.52 | 48.19 | 6.44 | 0.43 | 1.27 |
| Fly ash | 10.20 | 48.45 | 31.30 | 5.62 | 2.23 | 0.61 | — | — |
| Gypsum | 22.98 | 0.67 | 0.21 | 0.24 | 32.34 | 2.20 | 40.56 | — |
| Calcined gypsum | 12.04 | — | 0.09 | 0.12 | 37.89 | 2.36 | 46.55 | — |
| Alunite | 18.22 | 49.16 | 14.53 | 2.14 | 1.30 | 1.58 | 10.05 | — |
| Calcined alunite | 1.08 | 59.95 | 17.72 | 2.61 | 1.58 | 1.93 | 12.25 | — |

The drying shrinkage was examined according to GB751-81. Mortar bars (2.5 × 2.5 × 28 cm) with the above proportions were cured in a fog room for 1 day and in water for 6 days, and then placed in a box (20 ± 3°C, 60 ± 5% relative humidity) for another 7, 14, 28, 60, and 90 days. The length of specimen before and after drying was measured.

The sulfate resistance was tested in accordance with GB2420-81. Mortar bars (1 × 1 × 6 cm) with the proportion of cement:sand:water = 1:2.5:0.5 were cured in a fog room for 1 day and in 50°C water for 7 days. After that the specimens were divided into three groups and cured in a water, 3% $Na_2SO_4$, and 3% $MgSO_4$ solution respectively at 20°C for another 28 days. The flexural strength of the specimen cured in sulfate solution was compared to that cured in water.

The carbonation test was carried out as follows: Mortar bars using the same type specimen as in the strength measurement were cured in a fog room for 1 day and in water for 12 days. After drying in an oven at 60 ± 5°C for 1 day, the specimens were put in a cabinet with 100% $CO_2$ and 52% relative humidity for 12 days at room temperature. The depth of carbonation and strength after carbonation were determined compared to that cured in water for the same age.

The mortar expansion due to alkali-aggregate reaction (AAR) was examined by using autoclave-curing fast method [2]. Mortar bars (1 × 1 × 6 cm) were made of the cement tested, reactive silica glass, sand (0.15–0.63 mm in size), and water with the proportion of 1:2:0.3. After curing in a fog room for 1 day, the initial length of specimen was measured. The specimens were cured in 100°C steam for 4 hours and then put into an autoclave immersed in 10% KOH solution at 150°C for 6 hours. The final length was measured after cooling, and the expansion was calculated and compared to that of control cement.

## 2. Results and discussion

### 2.1. Mortar strength

The formulations of SFCPC and their mortar strength are shown in Table 2. Number one is portland cement, which is used as a control. Numbers 10 and 11 are the strength requests for 425 and 525 grade of CPC, respectively.

It can be seen from Table 2 that all the specimens of SFCPC could reach the strength request for 425 grade of CPC. The effect of calcined gypsum on strength is better than that of gypsum. The amount of gypsum or calcined gypsum ranging from 3–6% does not exhibit very different effects on strength. The setting time is relatively long for the requirement of construction work, which may be related to the low-alumina content of SS. In the view of this judgment, another admixture rich in alumina, such as alunite (A), cal-

Table 2
Mortar strength (MPa)

| Specimen no. | Clinker (%) | Gypsum (%) | Calcined gypsum (%) | Setting time (hour:minutes) | Compressive strength | | | Flexural strength | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | 3 days | 7 days | 28 days | 3 days | 7 days | 28 days |
| 1 | 93 | 7 | — | 1:40/2:25[a] | 23.4 | 39.6 | 51.6 | 4.7 | 7.0 | 8.4 |
| 2 | 47 | 3 | — | 4:45/6:06 | 20.5 | 27.5 | 43.8 | 4.3 | 5.8 | 7.4 |
| 3 | 46 | 4 | — | 4:14/5:33 | 21.4 | 29.0 | 44.2 | 4.3 | 5.9 | 8.1 |
| 4 | 45 | 5 | — | 3:26/5:59 | 20.8 | 28.5 | 44.7 | 4.4 | 5.7 | 8.0 |
| 5 | 44 | 6 | — | 3:13/4:53 | 20.8 | 28.5 | 45.9 | 4.4 | 5.9 | 8.2 |
| 6 | 47 | — | 3 | 4:44/5:50 | 22.1 | 31.0 | 45.3 | 4.5 | 6.0 | 8.0 |
| 7 | 46 | — | 4 | 4:02/5:34 | 21.4 | 32.2 | 46.2 | 4.5 | 6.0 | 8.4 |
| 8 | 45 | — | 5 | 4:03/4:58 | 22.0 | 31.6 | 46.2 | 3.9 | 5.5 | 8.5 |
| 9 | 44 | — | 6 | 3:19/5:09 | 16.3 | 31.9 | 46.3 | 3.1 | 6.0 | 8.1 |
| 10 | | | | >0:45/<10:00 | — | 24.5 | 42.5 | — | 4.5 | 6.5 |
| | | | | >0:45/<10:00 | — | 31.5 | 52.5 | — | 5.5 | 7.0 |

[a] The left and right represent initial setting and final setting, respectively.

Table 3
Mortar strength (MPa)

| Specimen no. | Clinker (%) | Alunite (%) | Calcined alunite (%) | High-alumina cement | Setting time (hours:minutes) | Compressive strength | | | Flexural strength | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | 3 days | 7 days | 28 days | 3 days | 7 days | 28 days |
| 6 | 47 | — | — | — | 4:44/5:50 | 22.1 | 31.0 | 45.3 | 4.5 | 6.0 | 8.0 |
| 12 | 45 | 2 | — | — | 2:00/3:20 | 23.6 | 30.2 | 50.7 | 4.5 | 6.0 | 7.8 |
| 13 | 46 | — | 1 | — | 1:55/2:22 | 22.6 | 37.6 | 53.1 | 5.1 | 6.5 | 8.8 |
| 14 | 45 | — | — | 2 | 1:05/2:42 | 26.8 | 38.5 | 57.1 | 5.4 | 7.0 | 8.8 |

cined alunite (CA), and high-alumina cement, was added in specimen number six to replace clinker. The best results by adding these admixtures with different amounts were chosen and are listed in Table 3.

It is obvious that those admixtures can improve the performance to a certain degree, while specimen number 14 shows the greatest effect on both setting and strength. It is noted that a cement containing 50% SS and FA could reach 425 or even 525 grade in spite of the fact that the strength of grading of clinker was only 51.6 MPa and the ignition loss of FA used was 10.20%, which may be related to the higher $C_3S$ content of SS and the higher fineness of the components of the specimen, as well as to the fact that suitable admixtures used resulted in more C-S-H gel and ettringite being formed during hydration.

### *2.2. Drying shrinkage*

The drying shrinkage values of specimens number 14 and 1 are shown in Table 4. The drying shrinkage obviously increases before 14 days, but becomes stable between 14–90 days. It is found that the drying shrinkage of SFCPC is much lower than that of Portland cement at all ages, which may be explained in that the expansion due to the formation of ettringite for SFCPC could offset higher drying shrinkage than that of PC.

### *2.3. Sulfate resistance*

The flexural strength values of specimens number 14 and 1 cured in different solutions are listed in Table 5. The ratio of strength cured in sulfate solution to that in water is expressed in the denominator.

The sulfate resistance of SFCPC is lower than that of portland cement, especially cured in $MgSO_4$ solution, although the absolute flexural strength of SFCPC is higher cured in water and $Na_2SO_4$ solution.

Table 4
Drying shinkage (1/10000)

| Specimen no. | 7 days | 14 days | 28 days | 60 days | 90 days |
|---|---|---|---|---|---|
| 14 | 0.80 | 4.08 | 4.58 | 4.92 | 5.21 |
| 1 | 2.44 | 6.62 | 6.68 | 6.98 | 7.80 |

### *2.4. Carbonation*

Table 6 shows the results of carbonation test for specimens number 14 and 1. The carbonation resistance of SFCPC is lower than that of Portland cement, and the depth of carbonation for SFCPC is almost twice of that of Portland cement, which may be a consequence of lower alkalinity of pore solution for SFCPC due to a lower clinker content.

### *2.5. Mortar expansion*

The mortar expansion due to AAR for specimens number 14 and 1 is 0.4 and 0.84%, respectively, which means that SFCPC exhibits excellent restriction ability of expansion. In the case of similar test conditions and same reactive aggregate, the expansion is controlled by the alkali content of cement as well as the consumption of alkali in the hydration process.

The original equivalent $Na_2O$ contents of specimens number 14 and 1 were 1.94 and 2.64%, respectively. There was 30% SS and 20% FA in specimen number 14, which could consume part of the alkali during hydration, resulting in the reduction of expansion due to AAR.

## 3. Conclusion

1. The utilization of both SS and FA for producing composite Portland cement is possible. The total amount of SS and FA could reach 50% and the grade of cement could reach 425 or even 525 determined by the

Table 5
Sulfate resistance (MPa/%)

| Specimen no. | Water | 3% $Na_2SO_4$ | 3% $MgSO_4$ |
|---|---|---|---|
| 14 | 12.4/100 | 11.5/93 | 10.3/83 |
| 11 | 10.9/100 | 11.3/104 | 12.4/113 |

Table 6
Carbonation resistance

| Item | Specimen no. | |
|---|---|---|
| | 14 | 1 |
| Depth of carbonation (mm) | 6.7 | 3.4 |
| Compressive strength cured in water (MPa) | 54.1 | 55.3 |
| Compressive strength after carbonation (MPa) | 49.1 | 61.5 |
| Flexural strength cured in water (MPa) | 8.0 | 8.7 |
| Flexural strength after carbonation (MPa) | 5.9 | 6.5 |

quality of clinker, SS, and FA, as well as the use of suitable admixtures. The fineness of cement is also an important factor.

2. Specimen number 14 represents an optimum formulation of SFCPC in this study and shows fast setting, higher strength, and better restriction ability of expansion due to AAR. However, its carbonation and sulfate resistance is lower than that of portland cement (specimen number 1).
3. The mechanism of hydration for SFCPC needs to be studied further.

## References

[1] Chinese standard YB/T022-92, Steel slag used in cement, 1992.
[2] Chinese standard CECS48:93, A rapid test method for determining the alkali reactivity of sands and rocks, 1993.