Study on the Performance of Green Cement with Large Amount of Steel Slag Addition

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Abstract: In this paper, the experimental study of steel slag cement is carried out. The waste steel slag is used as one of the raw materials for cement production. According to the chemical composition and physical properties, the optimum admixture ratio of steel slag for cement production is 20%. Active SiO₂ as additive can improve the strength, shrinkage, stability and concrete performance of steel slag cement. The utilization of waste steel slag is beneficial to environmental protection and achieving the goal of turning waste into treasure.

1. Introduction
Steel slag is a by-product in steel making process which is formed from the combination of molten silicate in ores, fuels and fluxes. Its recycling has always been an important part of sustainable development strategy and one of the important research directions in the world building materials. As one of the main solid waste in the world, steel slag is about 15% or 20% of steel output[1]. With the increasing demand for iron and steel in the world, the discharge of steel slag will increase year by year. If the steel slag with potential hydraulic hardness is not used reasonably and efficiently, it will inevitably cause a large amount of steel slag to be dumped and accumulated. It will not only occupy the land, but also cause a certain degree of pollution to the surrounding environment. Unreasonable utilization of steel slag is a waste of building materials. In China, the comprehensive utilization ratio of steel slag is still low, and there is still considerable room for recycling and utilization.

The investigation found that many cement factories have used steel slag as raw material for cement production. The content of steel slag is generally 5~10%, and the utilization ratio is very low[2]. By analyzing the chemical composition of steel slag, using the rich and similar chemical composition of steel slag admixture in cement production, the inert composition of steel slag and the strength of cement are stimulated by using active SiO₂ as additive[3].

2. Chemical composition analysis of steel slag
The chemical composition of steel slag fluctuates greatly due to the difference of production process, steel-making equipment and raw mineral, but the main chemical composition is basically the same. Four groups of samples digestion time for 3 to 6 months were selected for chemical analysis of steel slag. The test results are shown in Table 1.

| Table 1. Chemical composition Analysis of Steel Slag (%) |
|--------------------------------------------------------|
| Chemical composition | SiO₂ | Fe₂O₃ | Al₂O₃ | CaO | MgO | P₂O₅ | f-CaO |
|-----------------------|------|-------|-------|-----|-----|------|-------|

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It can be seen from the test results that the composition content of the four groups of steel slag samples is very similar, in which the maximum CaO content is about 42.23%, which is caused by the need to extract impurities with quicklime in the steel-making process. Based on MasonB’s calculation formula of basicity value for chemical composition of steel slag \( M = \frac{\omega (\text{CaO})}{[\omega (\text{SiO}_2)+\omega (\text{P}_2\text{O}_5)]} \) and basicity partition of steel slag: high alkali \( M > 2.5 \), moderate alkali \( M = 1.8-2.5 \), low alkali \( M < 1.8 \). The alkalinity of steel slag is 2.84 > 2.5, which belongs to high alkalinity and has higher activity, which is beneficial to increase the strength of cement\(^{[4-5]}\). At the same time, SiO\(_2\),Fe\(_2\)O\(_3\),Al\(_2\)O\(_3\),CaO is an important product of tricalcium silicate (C\(_3\)S), dicalcium silicate (C\(_2\)S), tricalcium aluminate (C\(_3\)A) and tetracalcium ferric aluminate (C\(_4\)AF). Considered the similarity between the chemical composition of steel slag and cement clinker, the proportion of steel slag addition ratio could be increased and the amount of clinker could be reduced during the cement production process. So the cost of cement production could be reduced.

3. Experimental program

The cement used in this research is P.O 42.5 which contained clinker (60~70%), steel slag (15~20%), fly ash, gypsum and silica fume (0~1%). The cementitious product can be improved by using active silica fume as additive, while alkaline activator (NaOH,Na\(_2\)CO\(_3\), etc.) will precipitate in the later curing period or in the presence of water curing. The salt crystals formed on the surface of the structure and the precipitated composition lead to internal pores of the structure which will affect the internal compactness of the structure and decrease the strength of the structure\(^{[6]}\). The ratio of steel slag cement test and the strength of cement sand are shown in Table 2.

| test number | clinker | steel slag | fly ash | gypsum | SiO\(_2\) | flexural strength (Mpa) | compressive strength (Mpa) |
|-------------|---------|------------|---------|--------|----------|------------------------|--------------------------|
| 1#          | 70      | 15         | 10      | 5      | 0        | 5.7                    | 7.7                      |
| 2#          | 70      | 15         | 10      | 4.5    | 0.5      | 5.5                    | 7.4                      |
| 3#          | 70      | 15         | 10      | 4      | 1        | 5.0                    | 7.5                      |
| 4#          | 65      | 20         | 10      | 5      | 0        | 5.1                    | 6.8                      |
| 5#          | 65      | 20         | 10      | 4.5    | 0.5      | 5.3                    | 7.1                      |
| 6#          | 65      | 20         | 10      | 4      | 1        | 4.5                    | 6.9                      |
| 7#          | 60      | 25         | 10      | 5      | 0        | 4.7                    | 6.6                      |
| 8#          | 60      | 25         | 10      | 4.5    | 0.5      | 5.0                    | 6.8                      |
| 9#          | 60      | 25         | 10      | 4      | 1        | 5.0                    | 6.5                      |

4. Results and discussion

In Fig.1 a) showed the flexural strength of 3 days and 28 days of cement mortar, which was higher than that 4.0Mpa and 6.5 Mpa, and the compressive strength of 3 days and 28 days of cement mortar was higher than that 22.0Mpa and 42.5Mpa in Fig. 2 b). The results showed that the ratio of 9 groups of steel slag cement could meet the requirements of ordinary Portland cement at different ages and reach PO 42.5 cement strength standard. However, the residual compressive strength of steel slag is low (about 3%) when steel slag ratio is 25% (test No. 7#,8#,9#), and the 28 days flexural strength just meets the 6.5Mpa requirement in Fig.1 a). When the strength surplus is too low, the strength index may be lower than P.O 42.5 cement standard due to the difference of raw materials in mass cement.
production, so the strength surplus is required to reach 10%. The compressive strength and flexural strength of 3 days and 28 days are higher than that of the control group when the content of steel slag is 15% (test No. 1#,2#,3#), 20% (test No. 4#,5#,6#). In particular, the residual compressive strength of 28 days reached 13% (steel slag 15%) and 10% (steel slag 20%). Considering comprehensively the utilization ratio and strength index of steel slag, the experimental No.5 (steel slag 20%) was selected for production application and related research. The strength surplus of this proportion is 12.5% which the high efficiency utilization of steel slag can be realized and cement strength can also be guaranteed.

![Flexural strength and compressive strength](image)

Figure 1. The flexural strength and compressive strength of cement mortar

In the experiment, the change of different steel slag content in test No. 2#,5#,8# was analyzed by measuring the dry shrinkage strain. Fig.2 showed the dry shrinkage strain increased linearly before 21 days, and decreased after 21 days. The dry shrinkage rates of 2#,5#,8# in 28 days were 0.06%, 0.05% and 0.05% which were much less than 0.1%. This was the hydration expansion of a small amount of f-CaO,MgO in steel slag, which is superimposed on the dry shrinkage effect. The complementary effect of dry shrinkage and expansion is formed, then the shrinkage rate of steel slag cement is smaller. Comparing with different steel slag content, it could be seen that the greater the clinker ratio, the greater the dry shrinkage rate was. That was caused by the C\textsubscript{3}A formation in clinker. Fig.2 showed that the largest shrinkage sample was 2# and the smallest was 8#, the dry shrinkage variation of 5# was closed to 8#, which showed that the strength and shrinkage deformation of steel slag content of 20% could obtain a good performance.

![Dry shrinkage strain curve](image)

Figure 2. Dry shrinkage strain curve

The high content of f-CaO in steel slag and SO\textsubscript{3} in gypsum lead to poor stability. These substances continued to react with water or surrounded reaction media after cement paste hardening, which will cause the uneven volume change in cement paste\cite{1}. Therefor, the content of f-CaO, MgO and SO\textsubscript{3} in 5 groups was determined at random and the stability was detected by boiling method for test No.5#. The chemical contents of 5 groups in Fig. 3 showed that the content of f-CaO was about 0.9%, the content of f-CaO was about 3.5% (less than 5%) and the content of SO\textsubscript{3} was about 1.4% (less than 3.5%). At the same time, it is observed in Fig. 4 that after boiling, the bottom of the test cake was closely contacted with no bending deformation or crack.
According to the Inorganic Nonmetallic atlas, the steel slag cement (test No.5#) and ordinary Portland cement were analyzed by FT-IR. Fig. 5 showed that the intensity of the characteristic peak was the tricalcium silicate and dicalcium silicate groups at peak 876 cm⁻¹, tetracalcium ferric aluminate at peak 1128 cm⁻¹, tricalcium aluminate at peak 1410 cm⁻¹ and a small amount of other oxides doped in the range of 2300~2400cm⁻¹ were tricalcium silicate. At the same time, it could be observed that each characteristic peak of steel slag cement is stronger than that of ordinary Portland cement, which indicates that SiO₂, Fe₂O₃, Al₂O₃, CaO and the addition of active SiO₂ in steel slag can be effectively transformed into chemical constituents such as C₃S, C₂S, C₃A and C₄AF with high temperature grinding. By calculating the area of 750~1550 cm⁻¹ wave peak of the four major components, the steel slag cement is about 60263, while the ordinary Portland cement is about 54516. The former is 5747 larger than the latter, which showed that the steel slag cement has more active components and played an important role in hydration cementing.
The aggregate was made of natural sand graveled in good gradation. The prefabricated strength was C30 and W/C was 0.5. Table 3 showed that the compressive and flexural strength of steel slag cement concrete was higher than that of ordinary Portland cement concrete for 7 days and 28 days, especially the compressive strength of steel slag cement concrete was 3 Mpa higher. The cementing property of steel slag cement was better than that of ordinary Portland cement with the same test conditions. The durability of steel slag cement and Portland cement was analyzed by freeze-thaw cycle test. Fig. 6 showed that the two kinds of cement concrete can reach F50 (withstanding 50 freeze-thaw cycles) standard without air entraining agent, but the loss rate of dynamic elastic modulus of steel slag cement concrete was obviously lower than ordinary Portland cement concrete. And after more than 20 freeze-thaw cycles, the loss rate of dynamic modulus of ordinary Portland cement was increased, and the loss of strength was serious. The above data show that the strength and durability of steel slag cement concrete showed excellent performance.

| Cement type          | Compressive strength (Mpa) | Flexural strength (Mpa) |
|----------------------|-----------------------------|-------------------------|
|                      | 7 days | 28 days | 7 days | 28 days |
| Ordinary Portland cement | 19.8  | 33.2    | 3.7    | 4.9     |
| Steel slag cement     | 20.5   | 36.2    | 3.9    | 5.4     |

Figure 6. Freeze-thaw cycle curve

5. Conclusion
1. The alkalinity of steel slag is 2.84 > 2.5, which belongs to high alkalinity and has higher activity, which is beneficial to increasing the strength of cement. At the same time, SiO₂, Fe₂O₃, Al₂O₃, CaO are important components for tricalcium silicate (C₃S), dicalcium silicate (C₂S), tricalcium aluminate (C₃A) and tetracalcium ferric aluminate (C₄AF) formation. The properties of ordinary Portland cement can be improved by using the similarity between the chemical composition of steel slag and cement.

2. According to the test of different ratio, the best content ratio is 65% clinker, 20% steel slag, 10% fly ash, 4.5% gypsum and active 0.5% SiO₂. The strength and dry shrinkage of steel slag cement can be optimized to realize the large-scale recycling of waste steel slag.

3. The hydration and gelation reaction of steel slag can be enhanced by using active SiO₂ as an additive. The active composition of steel slag cement is larger than that of ordinary Portland cement by FT-IR analysis, and the strength of cement mortar and concrete is higher than that of ordinary Portland cement. The dry shrinkage and stability index are excellent and have good durability.

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