Effect of Al$_2$O$_3$–SiO$_2$ Addition on Gehlenite Growth and the Mechanical Performance of Steel Slag

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Abstract: Steel slag, as industrial solid waste, is difficult to recycle owing to its complex components and poor mechanical properties. However, steel slag can be modified by adding Al$_2$O$_3$–SiO$_2$ through high temperature sintering, which would improve the mechanical properties and expand the scope of its application. The phase changing, morphology evolution and the mechanical properties of the modified steel slag were investigated. The results indicate that the main phase changes to gehlenite occur with increasing temperature. The compressive strength increases to 115 MPa at 1350 °C. The relationship of the quantity of gehlenite and the compressive strength were explored.

Keywords: steel slag; sintering; gehlenite; solid phase modification

1. Introduction

Recycling and utilization of industrial waste is a current problem, and it is also a research hotspot in solid waste utilization [1]. Steel slag, as an industrial solid waste, is the main by-product in the steelmaking process, and it contains tricalcium silicate, dicalcium silicate, and some metal oxides [2,3]. According to statistics, the amount of steel slag generated is 8–15% of the crude steel output. In China, steel slag output was 149 million tons in 2019. However, the recycle rate was only 10–20% [4], indicating a large amount of steel slag was not used. Steel slag is extremely harmful because it not only occupies land but also causes environmental pollution, which poses a threat to human health [5]. Therefore, it is important to recycle steel slag in order to meet the requirements of green industry development [6].

Currently, most steel slag is used in construction field and road projects [7]. Yan et al. prepared reactive powder concrete using fly ash and steel slag powder [8]. Wang et al. improved the strength of steel slag to produce building materials by the carbonization of steel slag and gypsum [9]. Liao et al. investigated the effect of steel slag on the hydration and strength development of calcium sulfoaluminate cement [10]. Thanakorn et al. used high-calcium fly ash and steel slag to prepare pavement materials [11]. Ladle furnace steel slag was used to prepare asphalt mortar sand by Marco Pasetto [12]. Zulfiqar Ali Jattak et al. investigated the characteristics of steel slag and bottom ash, which has been used as aggregates for asphalt pavement [13].

High value-added ceramic is another efficient method for the use of steel slag. He et al. prepared steel slag ceramic by mixing with fly ash, microsilica, and quartz, and the main phases were diopside and anorthite [14]. Tang et al. successfully prepared high strength foam ceramics by mixing steel slag with other sand shale [15]. Zong et al. achieved pyroxene ceramics by the mixture of red muds and steel slag at high temperature [16]. Mymrin et al. used printed circuit, board red mud, and steel slag to prepare new ceramic; the flexural strength of the resulting ceramic was 75.39 MPa [17]. The chemical component
has a great effect on steel slag ceramics, so there have been many investigations into this area. Luo et al. investigated the effect of fluoride content on the phase formation and mechanical properties and showed that, with a high content of fluoride, the major crystalline phases of Nepheline and Cuspidine are feasible to form [18]. The effects of Fe$_2$O$_3$ on the properties of steel slag ceramics were studied by Li et al.; the results indicate that an increase in Fe$_2$O$_3$ can reduce the sintering temperature and improve the mechanical properties of the ceramics [19]. Kamal-Tabit et al. analysed the effect of CaO/SiO$_2$ ration on the phase transition and mechanical properties. The main phase of anorthite was detected at the range from 0.12 to 0.56, and gehlenite generated more above 0.8 [20]. Deng et al. investigated the effect of SiO$_2$/MgO ratio on the phase transformation and properties of wollastonite–augite glass-ceramic through the sintering of steel slag [21]. The effect of MgO/Al$_2$O$_3$ on steel slag ceramics has also been studied. With a decrease in MgO/Al$_2$O$_3$ ratio, the main phase transforms from a quartz and pyroxene phase to a quartz and anorthite phase [22]. There are few studies on gehlenite found in steel slag, which needs further research. In this study, we add Al$_2$O$_3$–SiO$_2$ system to form the main phase of gehlenite from steel slag; the growth law of the gehlenite phase was analyzed, and the relationship between the growth of the gehlenite phase and the compression resistance of the modified steel slag was investigated.

2. Experiment

2.1. Raw Material Analysis

The raw material of Shougang steel slag was used in this experiment. The chemical element compositions of steel slag were analyzed by X-ray fluorescence spectroscopy (XRF). Table 1 is the element composition ratio.

| Element | Ca   | Fe    | Si    | Mn   | Mg   | Al  | P    | V    | Ti   | Cr   |
|---------|------|-------|-------|------|------|-----|------|------|------|------|
| proportion/% | 51.87 | 32.09 | 7.67  | 2.65 | 2.39 | 0.87| 0.76 | 0.65 | 0.58 | 0.15 |

It can be seen from Table 1 that the highest content of steel slag is Ca, which can provide a sufficient source of Ca for the generation of gehlenite. Fe and Si account for 32.09% and 7.67%, respectively.

In order to determine the range of test temperature, the DTA/TG was performed on the steel slag. The DTA/TG curve from room temperature to 1450 °C is shown in Figure 1.

![Figure 1. The DTA/TG curves of steel slag.](image-url)
It can be seen from the DTA/TG curve that the steel slag showed an overall weight gain trend during the heating process. This may have been due to some low-valence ions or simple substances transformed into high-valence ions during sintering, for example, Fe and FeO may have converted to Fe₂O₃. Weight loss occurred at 440 °C and 640 °C, and corresponding endothermic peaks appeared, which may be due to the decomposition reactions of Ca(OH)₂ and CaCO₃, respectively. An obvious endothermic peak emerged at 1200 °C, which belonged to the melting of the steel slag. When the temperature increased to 1280 °C, it was difficult to keep the shape of the steel slag, therefore, it was unable to be tested. Hence, the steel slag sintering temperature was set at 1270 °C for firing.

Figure 2 shows the XRD patterns of steel slags without and with sintering. The XRD of the unfired sample indicated poor crystallinity. The raw materials of steel slag mainly contain Ca₂Fe₂O₅, Ca₂SiO₄, and Ca₃SiO₅. Some other impurity phases were also observed. This may be due to quenching when some unstable phases appeared during cooling. In order to obtain a stable phase, steel slag was sintered over 1200 °C with furnace cooling. When the steel slag is sintered at 1270 °C, the sample mainly contains Ca₂Fe₂O₅ and Ca₂SiO₄; the Ca₃SiO₅ and amorphous phase disappear, which is unstable at room temperature.

![Figure 2](image_url)

**Figure 2.** XRD patterns of unfired steel slag (a) and 1270 °C fired steel slag (b).

2.2. Thermodynamics

It can be seen from the XRD patterns of the steel slag that most of the Ca in the steel slag exists in Ca₂Fe₂O₅, Ca₂SiO₄, and Ca₃SiO₅. If Al₂O₃ and SiO₂ are added, the reaction for generating gehlenite is as Formulas (1) and (2).

\[
\text{Ca}_2\text{SiO}_4 + \text{Al}_2\text{O}_3 = \text{Ca}_2\text{Al}_2\text{SiO}_7 \tag{1}
\]

\[
2\text{CaO} + \text{SiO}_2 + \text{Al}_2\text{O}_3 = \text{Ca}_2\text{Al}_2\text{SiO}_7 \tag{2}
\]

At the same time, CaO and SiO₂ can also generate Ca₂SiO₄, the reaction formula is Formula (3).

\[
2\text{CaO} + \text{SiO}_2 = \text{Ca}_2\text{SiO}_4 \tag{3}
\]

The change curves of ΔG with temperature of Formulas (1)–(3) are shown in Figure 3.
It can be seen from Figure 3 that when the temperature is below 1000 °C, the $\Delta G$ of Formula (2) is smaller than that of Formula (1); therefore, Formula (2) is the main way to generate gehlenite. When the temperature is beyond 1000 °C, the $\Delta G$ of Formula (1) is smaller; therefore, Formula (1) is the main way to generate gehlenite. The $\Delta G$ of Formula (3) shows an upward trend, exceeding 0 kJ at 1000 °C, indicating that Formula (3) is difficult to react beyond 1000 °C.

Through thermodynamic calculations, it can be inferred that the reactions of steel slag during the sintering process after adding Al$_2$O$_3$–SiO$_2$ system are as follows. When the temperature is lower than 1000 °C, gehlenite is mainly formed by CaO, SiO$_2$, and Al$_2$O$_3$. At the same time, CaO and SiO$_2$ can also form Ca$_2$SiO$_4$, which can promote the reaction of Formula (1). When the temperature is higher than 1000 °C, the formation of gehlenite by Ca$_2$SiO$_4$ and Al$_2$O$_3$ is easier to achieve. From this point of view, it is feasible to grow gehlenite crystals by adding Al$_2$O$_3$–SiO$_2$ onto steel slag and sintering in the theoretical calculation range.

### 2.3. Calculate Ingredients

In order to determine the amount of CaO, Al$_2$O$_3$, and SiO$_2$, the proportion of the components in the steel slag was calculated. The molar ratio of Ca, Al, and Si in gehlenite is 2:2:1. However, Ca cannot be completely converted into gehlenite in the actual reaction, so the ratio of Al$_2$O$_3$ and SiO$_2$ should be increased appropriately. The mass ratio of CaO, Al$_2$O$_3$, and SiO$_2$ was determined as 6:5:4. The element Ca in steel slag accounts for 51.87%, Si accounts for 7.67%, and Al only contains for 0.76%. The Ca$_2$SiO$_4$, Ca$_3$SiO$_5$, and Ca$_2$Fe$_2$O$_5$ in the steel slag can provide CaO and SiO$_2$ for the formation of gehlenite. However, the content of SiO$_2$ and Al$_2$O$_3$ is obviously insufficient. The final ratio can be calculated by Formula (4).

$$ m(\text{CaO}) = \frac{m_1 \times \theta(\text{CaO})}{m_1 \times \theta(\text{CaO}) + m(\text{Al}_2\text{O}_3) + [m_1 \times \theta(\text{SiO}_2) + m(\text{SiO}_2)]} $$

$$ m(\text{Al}_2\text{O}_3) = \frac{m(\text{Al}_2\text{O}_3)}{m_1 \times \theta(\text{CaO}) + m(\text{Al}_2\text{O}_3) + [m_1 \times \theta(\text{SiO}_2) + m(\text{SiO}_2)]} $$

$$ m(\text{SiO}_2) = \frac{m_1 \times \theta(\text{SiO}_2) + m(\text{SiO}_2)}{m_1 \times \theta(\text{CaO}) + m(\text{Al}_2\text{O}_3) + [m_1 \times \theta(\text{SiO}_2) + m(\text{SiO}_2)]} $$

(4)
By calculation, \( m_1:m(\text{Al}_2\text{O}_3):m(\text{SiO}_2) = 4.8:2:1; \)

Among them: \( m_1 \) is the quantity ratio of steel slag;
\( m(\text{Al}_2\text{O}_3) \) is the quantity ratio of \( \text{Al}_2\text{O}_3; \)
\( m(\text{SiO}_2) \) is the quantity ratio of \( \text{SiO}_2; \)
\( \theta(\text{CaO}) \) is the mass fraction of \( \text{CaO} \) in steel slag;
\( \theta(\text{SiO}_2) \) is the mass fraction of \( \text{SiO}_2 \) in the steel slag.

### 2.4. Sample Preparation

According to Formula (4), the steel slag, \( \text{Al}_2\text{O}_3, \) and \( \text{SiO}_2 \) powder were mixed in a ratio of 4.8:2:1, and the PVA solution was added as a binder. The composite powder slurries were obtained by stir and mix. The slurries were vacuum dried at 110 °C, samples with dimensions of \( \Phi \) 7 mm \( \times \) 6 mm cylinder were cast for compressive strength testing. Finally, the samples were sintered in a muffle furnace.

### 2.5. Sintering System

In order to determine the sintering system, the DTA/TG was performed on the sample, the result of which is shown in Figure 4. An endothermic peak appeared at 1200 °C, which corresponded to the melting of the steel slag. Zhang et al. generated gehlenite at a sintering temperature range from 1100 to 1500 °C. With the increase of the sintering temperature, the crystallinity of the gehlenite material significantly improved, and the compressive strength also increased [23]. Combined with the DTA curve, the sintering temperature was set between 1200–1500 °C. When the sintering temperature exceeded 1370 °C, the shape of the sample changed, and it was not easy to carry out the compression test. Therefore, the sintering temperature range was set between 1200–1360 °C.

![Figure 4. The DTA/TG curves of steel slag with \( \text{Al}_2\text{O}_3-\text{SiO}_2 \) system.](image)

Based on the above analysis, the sintering temperature system was set as follows: Raise the temperature to 1200 °C at 10 °C /min and keep it for 1 h so that the gehlenite has enough time for crystal growth. Then, raise the temperature to sintering temperature at 5 °C /min, keep it for 2 h, and finally cool with the furnace. The final sintering temperatures are 1200 °C, 1235 °C, 1270 °C, 1305 °C, 1340 °C, 1350 °C, 1360 °C.
3. Results and Analysis

3.1. Phase Analysis

Figure 5 shows the XRD patterns of steel slag with the $\text{Al}_2\text{O}_3$–$\text{SiO}_2$ system sintering at different temperatures. The main phase of gehlenite appeared at 1200 °C and there were also many other impurity phases observed. With the temperature increasing, the amount of gehlenite increases and the impurity peaks gradually decreased, indicating that most of the Ca in the steel slag combined with Al and Si to form gehlenite crystals. In addition, the width of gehlenite peaks changed to become narrow revealing that the crystallinity improved, which may affect the mechanical properties.

![XRD patterns of steel slag with $\text{Al}_2\text{O}_3$–$\text{SiO}_2$ system sintering at different temperatures.](image)

3.2. Microstructure Analysis

Figure 6 shows the SEM images of $\text{Al}_2\text{O}_3$–$\text{SiO}_2$ sintering with steel slag at different temperatures. It can be seen from Figure 6a that there was only a small part of the cubic crystals growing and forming at 1200 °C, and the crystal grain size was small: the width is less than 5 μm. When the sintering temperature reached 1235 °C, the cubic crystal grains began to increase. After firing at 1270 °C, more cubic crystal grains appeared and the width of the particles gradually increased but irregular amorphous regions still existed. The width of the cubic crystal grains was mostly 20 μm. When the sintering temperature increased to 1305 °C, the grain boundary became fuzzy, which indicates local melting-recrystallization. With the increase of the sintering temperature to 1340–1350 °C, a number of cubic particles appeared and the particle size become large, indicating the amount and crystalline nature of gehlenite change. The gaps between the crystals of crystalline gehlenite reduced, and a staggered stacking structure appeared between crystals. The staggered packing of crystals increases the compressive strength of the sample [24]. When the temperature increased to 1360 °C, micro-melting appeared, and most of the edges of the crystals became unclear. It may be that, due to sintering at a higher temperature, the gehlenite crystal was over-burned. When over burning occurs, the main crystalline phase does not change, but the strength decreases [25].
Figure 6. SEM observation of steel slag added with Al₂O₃–SiO₂ system at different sintering temperatures (a–g) and the EDS spectrum of point 1 to 4 (h) in (a,c).
In order to determine the element composition, EDS was performed on the sample of 1200 °C and 1270 °C. The locations of points are shown in Figure 6a,c. The analysis result is shown in (h) of Figure 6. In the cube part, the content of Ca was higher than that of the non-cube part, and the content ratio of Ca, Al, and Si was close to that of gehlenite. The same result of gehlenite appeared in the research of Pan [26]. Combined with the XRD results, it can be inferred that the modified steel slag formed gehlenite with cubic crystals at high temperature.

3.3. Mechanical Performance Analysis

The mechanical performances of the fired samples were analyzed with a mechanical testing machine. The compressive strength is calculated according to Formula (5).

\[ p = \frac{F}{A} \]  

where \( p \) is the compressive strength, MPa; \( F \) is the axial loading load, N; \( A \) is the cross-sectional area of the sample, mm\(^2\).

When the sample without Al\(_2\)O\(_3\)–SiO\(_2\) is under pressure, it breaks immediately, and the dynamic load is poor. The maximum compressive force is 1319 N, and the compressive strength is 20 MPa.

Figure 7 shows the compressive strength and bearing pressure of the modified steel slag after sintering at different temperatures. When the sintering temperature was 1200 °C, the sample was in a loose state, the maximum compressive force was 452 N, and the compressive strength was only 5 MPa. In tests it broke immediately and became powder. When the sintering temperature increased to 1270 °C, the sample was relatively dense; the maximum compressive force was 2715 N and the compressive strength reached 40 MPa. Meanwhile, the modified sample could be kept for a long time without deformation, which is more than the pure steel slag sample sintering at the same temperature. With the increase in the sintering temperature, the compressive strength and the maximum compressive force of the modified steel slag kept increasing. When the temperature reached 1340 °C, the compressive strength reached 90 MPa, which is close to the results of anorthite–cordierite-based binary ceramics. The excellent mechanical properties of modified steel slag appeared at 1350 °C. The maximum compressive force was 5182 N, and the compressive strength was 115 MPa. When the temperature increased to 1360 °C, the maximum pressure and compressive strength began to decrease. This may be due to the phenomenon of over burning which causes the grain boundary of the gehlenite crystal to change and melting to appear resulting in a reduction in compressive strength [27]. To compare the results, the compressive strength properties of other steel slag ceramics are shown in Table 2. This indicates that Al\(_2\)O\(_3\)–SiO\(_2\) has great potential in improving the mechanical proprieties of steel slag.
Figure 7. Influence of temperature on the compressive strength and bearing pressure of the modified steel slag.

Table 2. Comparison of the mechanical properties for different materials prepared by adding ingredients to steel slag.

| No. | Raw Material                  | Sintering Temperature | Main Phase         | Compressive Strength | Suggested Application                | Refs.   |
|-----|-------------------------------|-----------------------|--------------------|----------------------|--------------------------------------|---------|
| 1   | Steel slag Coal fly ash       | 1188 °C               | Anorthite          | 41 MPa               | Anorthite-based ceramics             | [20]    |
| 2   | Steel slag Coal fly ash Cordierite Precursor | 1200 °C                      | α-cordierite       | 80 MPa               | Clean glass-ceramics                 | [28]    |
| 3   | Silica sand Tailing Steel slag Coal gangue | 1150–1170 °C                  | Hematite Magnetite | 72.39 MPa            | Permeable ceramics                   | [29]    |
| 4   | Harbor sediment Steel slag    | 1175 °C               | Glass phase        | 23.2 MPa             | Lightweight aggregates               | [30]    |
|     | Samples Steel slag Alumina Silica | 1350 °C                      | Gehlenite          | 115 MPa              | Ceramics                             | -       |

4. Conclusions

1. After the Al₂O₃–SiO₂ system is added to the steel slag for modification, gehlenite crystals are formed at high temperatures, and its compressive strength is also be significantly enhanced.

2. Gehlenite crystals are formed at 1200 °C, and the size gradually increases as the temperature rises; meanwhile, the sample becomes denser. When the sintering temperature increases to 1360 °C, the sample appears to melt, which is caused by over burning.

3. The compressive strength of modified steel slag is much greater than that of steel slag. There is a great correlation between the growth of gehlenite and the compressive strength of the modified steel slag. The more gehlenite grows, the higher compressive strength achieves. The optimal temperature is 1350 °C and the compressive strength is 115 MPa.
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