Study on the Effect of Ash-Slag Ratio on Mechanical Properties of Magnesium Slag Cementitious Material

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Abstract: Magnesium slag is a kind of industrial waste slag with silicate mineral as the main component when smelting magnesium metal. Its main component is similar to Portland cement clinker and can be used as cementitious material. In this paper, the mechanical properties of magnesium slag cementitious materials under different ash-slag ratios are studied and analysed. Magnesium slag and fly ash are prepared by composite method. The flexural and compressive tests are carried out. The effects of different ash-slag ratios on the mechanical properties of magnesium slag cementitious materials are studied. The experimental data are analysed and theoretical studies are carried out, and the conclusion is drawn on: (1) When the ash-slag ratio is between 0.43 and 0.8, the forming effect of Mg-slag cementitious material specimen is better; (2) When the ash-slag ratio changes from large to small, the properties of Mg-slag cementitious material will change greatly, from curable to powdered after curing, unable to form, and the critical value of the ash-slag ratio is between 0.25 and 0.43; (3) When the ash-slag ratio is in the range of 0.43-1.2, the mechanical strength of magnesium slag cementitious material is higher, the maximum flexural strength can reach 10 MPa, and the maximum compressive strength can reach 50 MPa.

1. Introduction
Magnesium slag is a kind of industrial waste which is mainly composed of silicate minerals when smelting magnesium metal. Magnesium slag produced in the smelting of magnesium metal in our country is not less than 5 million tons every year. If we cannot effectively utilize such a large amount of magnesium slag, it will not only waste a lot of precious land resources, but also a huge waste of production resources, and the magnesium slag will dissolve harmful substances such as fluorine after washing by rainwater. It makes the environment worse. Magnesium slag emissions have begun to affect and restrict the development of magnesium. If the smelting industry of magnesium metal wants to be stronger and bigger and become a sustainable industry, it is necessary to find an environmentally way to use magnesium slag.

Magnesium slag can be used as cementitious material because its main composition is similar to Portland cement clinker. Magnesium slag can not only improve the strength and durability of cementitious materials, but also improve the workability of cementitious materials. Magnesium slag contains a large number of oxides of calcium, iron, silicon, magnesium and other elements. Among them, the content of silicon dioxide is also high, which has certain hydration activity. These components can react with calcium hydroxide under autoclaved conditions and moderate temperature and water environment. The main products are fibrous crystals or gelatinous state, which consist of calcium aluminate hydrate and calcium silicate hydrate. Other products also enhance the cohesion...
between particles of the mixture, such as calcium carbonate and calcium hydroxide crystals. With the formation of hydrates, the resistance of magnesium slag cementitious materials to load increases, and the magnitude of this ability depends on the formation of calcium silicate hydrate, including the quantity and quality of formation.

However, magnesium slag has obvious hydration inertia in practical application, and its strength is low when it is used as cementitious material alone. However, increasing the fineness of magnesium slag by grinding and compounding magnesium slag with fly ash can improve the activity of magnesium slag. On the one hand, magnesium slag can improve its activity after fine grinding. On the other hand, magnesium slag has high alkalinity coefficient and low activity coefficient, while fly ash has high activity coefficient and low alkalinity coefficient. The combination of the two can complement and promote each other.

2. Experimental materials and instruments

2.1. Experimental materials
The raw materials used in this chapter are as follows: Magnesium slag produced by Fugu Taida Coal Chemical Co., Ltd. in magnesium smelting, whose composition is shown in Table 1; fly ash produced by Fugu Taida Coal Chemical Co., Ltd. in Fugu County; tap water.

Table 1. Chemical Composition Content of Magnesium Slag.

| Chemical Composition | SiO₂ | CaO | MgO | Al₂O₃ | Fe₂O₃ |
|----------------------|------|-----|-----|-------|-------|
| Content (%)          | 21.89| 60.07| 3.86| 3.56  | 8.14  |

2.2. Experimental instruments
The instruments used in the test include: electronic scale, mill, 0.5 mm square hole screen, planetary mixer, 40 mm×40 mm×160 mm mould, demoulding air gun and autoclave.

3. Experimental scheme

3.1. Raw material ratio
By changing the ash-slag ratio and water-ash ratio, the mixing ratios of different groups were determined to improve the strength of magnesium slag cementitious material matrix itself. Because the properties of magnesia slag cementitious materials are not clear, the span of ash-slag ratio and water-ash ratio is large when designing mix ratio. In the process of specimen preparation, the water-ash ratio is redesigned according to the actual situation, and the water-ash ratio is gradually improved. At the beginning of the experiment, the ash-slag ratio and water-ash ratio were selected as follows:

Ash-slag ratio: 7:3, 6:4, 5:5, 4:6, 3:7, 2:8
Water-ash ratio: 0.25, 0.275, 0.3, 0.325, 0.35, 0.375, 0.4, 0.425, 0.45, 0.5

3.2. Preparation, forming and maintenance of cementitious materials
In this chapter, only magnesium slag, fly ash and water are used as raw materials. The properties of the specimens are similar to those of cement mortar specimens. Referring to GB/T 17671-1999, the size of the specimens should be prisms of 40 mm×40 mm×160 mm, as shown in Table 2, in terms of the size, mixing and pouring methods of the specimens.

Mix ingredients according to the table. After weighing the fly ash and magnesium slag, they are placed in the mill for 10 minutes, then sifted, mixed with the corresponding quality of water, and stirred in the mixer. Next, the slurry is poured into the corresponding mould to vibrate and stamp and paste the strip number. After placing the test block at room temperature for two days, take out the mould and remove it. After removing the mould, the sample was autoclaved in an autoclave and maintained for 12 hours (heating for 3 hours, constant temperature for 6 hours and cooling for 3 hours) at 185°C and 1.2 MPa.
Table 2. Size and quantity of specimens.

| Test type                        | Specimen size      | Number of groups | Number / group |
|----------------------------------|--------------------|------------------|----------------|
| Flexural and compressive test of rubber sand | 40 mm×40 mm×160 mm | 39               | 3              |

3.3. Performance test

3.3.1. Formability test
By observing the forming condition of the cured specimens, the specimens with better forming effect were selected for the next mechanical properties experiment.

3.3.2. Flexural strength test
After the specimen is maintained at room temperature for 30 days, an electro-hydraulic servo bending and compression tester is used. The loading mode is three-point loading, and the distance between supports is 100 mm. Loading at a speed of 50N/s, cracks were observed during loading, and test data were recorded. The data processing of flexural strength test refers to the stipulation of "Test Method of Cement Mortar Strength (ISO Method)".

3.3.3. Compressive strength test
The compressive test specimens are half of the broken specimens in each group of flexural strength tests. The loading test is also carried out by the electro-hydraulic servo flexural and compressive test machine with the loading speed of 2.4 kN per second. Data Processing of Compressive Strength Test Refers to the Regulation of "Testing Method of Cement Mortar Strength (ISO Method)".

4. Results and discussions

4.1. Specimen Maintenance Result Analysis
According to the condition of specimen making and the result of specimen maintenance, the properties of magnesia slag cementitious material can be judged as follows:

1) From the point of view of the sample making process, with the increase of the ash-slag ratio, the water-ash ratio in the sample making process also increases, otherwise there will be some problems such as forming difficulties. In other words, considering the fluidity, the demand of fly ash for water is higher than that of magnesium slag with the same quality;

2) From the maintenance results of the specimens, the greater the water-ash ratio of the materials, the easier the specimens crack during the maintenance process;

3) When the ash-slag ratio is between 0.43 (3:7) and 0.8 (4:5), the forming effect of the specimens is better;

4) When the ash-slag ratio is 0.25 (2:8), the specimens cannot be formed during the curing process, so the critical value of the ash-slag ratio for the specimens to be cured is between 0.25 (2:8) - 0.43 (3:7).

4.2. Analysis of mechanical strength test results
Table 3 and Table 4 are the summary of strength test results.

Table 3. Summary of flexural strength test results (MPa)

| Water-ash ratio | 0.25 | 0.275 | 0.3 | 0.325 | 0.35 | 0.375 | 0.4 | 0.425 | 0.45 | 0.5 |
|-----------------|------|-------|-----|-------|------|-------|-----|-------|------|-----|
| Ash-slag ratio  |      |       |     |       |      |       |     |       |      |     |
| 3:7             | 7.9  | 6.9   | 6.8(8.9) | 0.4(8.9) | 2.3(6.9) |  |
| 4:6             | 7.4  | 7.5   | 7   | 5.3   | 5.4  |  |
| 4:5             | 6.7  | 10    | 8.2 | 7.2   | 5.2  |  |
| 5:5             | 7.4  | /     | 5.4 | /     |      |  |
Table 4. Summary of compressive strength test results (MPa).

| Ash-slag ratio | Water-ash ratio | 0.25  | 0.275 | 0.3   | 0.325 | 0.35  | 0.375 | 0.4   | 0.425 | 0.45  | 0.5   |
|----------------|-----------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| 3:7            | 50              | 45.8  | 45.3  | 12.2  | 23.5  |       |       |       |       |       |       |
|                |                 |       |       | (51.4)| (52.7)| (40.2)|       |       |       |       |       |
| 4:6            | 42.4            | 45.1  | 42.9  | 38.6  | 34.2  |       |       |       |       |       |       |
| 4:5            | 43.8            | 43.2  | 52.1  | 42.2  | 41    |       |       |       |       |       |       |
| 5:5            | 41.9            |       | 42    |       |       |       |       |       |       |       |       |
| 5:4            | 49.8            | 46    |       |       |       |       |       |       |       |       |       |
| 6:4            |                 |       |       |       |       |       |       |       |       |       |       |
| 7:3            | 29.5            |       |       |       |       |       |       |       |       |       |       |

Note: During the test process, the specimen with an ash-slag ratio of 3:7 has poor maintenance effect due to other factors. Subsequently, a batch of supplementary tests were carried out. After demoulding, the specimen was maintained under autoclave pressure for about 2 days at room temperature.

Fig.1 and Fig.2 show that the mechanical strength of magnesium slag cementitious material varies with the ash-slag ratio at the optimum water-ash ratio, respectively:

![Figure 1. Mechanical strength of magnesium slag cementitious material (Maximum compressive strength)](image)

Figure 1. Mechanical strength of magnesium slag cementitious material (Maximum compressive strength)
Fig. 1 and Fig. 2 show the mechanical strength of magnesium slag cementitious material under the optimum water-ash ratio when the ash-slag ratio is 2:8, 3:7, 4:6, 4:5, 5:5, 5:4 and 7:3, respectively. Among them, the mechanical strength of ash-slag ratio is higher in the range of 3:7 to 5:4, but the change trend is not obvious enough. Its strength reaches its peak value when the ash-slag ratio is about 3:7, 4:5 and 5:4 respectively.

5. Conclusions
In this paper, 40 mm×40 mm×160 mm specimens with magnesia slag, fly ash and water as raw materials are preliminarily designed, and the flexural and compressive tests are carried out. The properties of specimens with different ash-slag ratios and different water-ash ratios are analysed and compared through the maintenance and mechanical test results of specimens. The conclusions are as follows:

1. In the steam curing process, the higher the water-ash ratio, the higher the possibility of failure;
2. When the ash-slag ratio is between 0.43 (3:7) and 0.8 (4:5), the forming effect of magnesium slag cementitious material specimen is better;
3. The properties of magnesia slag cementitious materials will change greatly when the ash-slag ratio changes from large to small, from curable to powdered, and cannot be formed. The critical value of the ash-slag ratio is between 0.25 (2:8) - 0.43 (3:7);
4. The optimum water-ash ratio of magnesia slag cementitious materials varies with the ash-slag ratio, but the overall water-ash ratio is between 0.3 and 0.325;
5. The mechanical strength of magnesia slag cementitious material is higher when the ash-slag ratio is between 0.43 (3:7) and 1.2 (5:4), but the change trend is not obvious enough. The peak value can be reached when the ash-slag ratio is about 0.43 (3:7), 0.8 (4:5) and 1.2 (5:4), respectively. The maximum flexural strength can reach 10 MPa and the maximum compressive strength can reach 52.7 MPa.

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