Research on mining filling material prepared by high titanium metallurgy waste residue

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Abstract: Using the vanadium titano-magnetite for iron-making, the steel enterprises have discharged water-quenched Ti-bearing slag. Due to the high titanium content, low activity and difficult-to-use characteristic, there are vast amount of high titanium slags, which not only occupies the land, but also causes resources wasting and environment polluted. This paper analyzed the chemical component, microstructure, grindability, activity index and other factors of high titanium slag and studied the mining filling material prepared by high titanium slag. The results show that the main chemical components of high titanium slag are similar with the ordinary slag. Both of them consist of CaO, SiO₂ and Al₂O₃, all of which account for about 80% of the total weight. However, the content of TiO₂ accounts for 8.4%, which is much higher than that of ordinary slag. Therefore, the grindability of TiO₂ is poor. The solid waste cementitious material was prepared by slag, flue gas desulfurization gypsum and high titanium slag, whose specific surface area was 530 m²/kg. After the maintenance for 28 hours, the compressive strength of this material reaches 3MPa.

1. Introduction

With the rapid development of nation's industrialization progress, the consumption of natural resources increases continuously. During the process of exploiting and smelting, natural resources produce a large amount of waste residue. If those waste residues cannot be solved reasonably, lots of lands and resources will be wasted. Once the harmful substance in the waste residue penetrates the ground with surface water, the serious harm to soil, groundwater, surface water and organisms that depend on the environment will be caused.

China has abundant resource reserve of vanadium titano-magnetite, which accounts for 38.85% of the world's total reserves[1-2]. The reserve of Chengde area reaches 7.825 billion tons, ranking second in China[3]. The waste residue produced in the blast furnace ironmaking is called high titanium slag, whose original material is vanadium titano-magnetite. The chemical components of high titanium slag are similar with that of common slag, mainly including CaO, SiO₂, Al₂O₃ and MgO. However, the TiO₂ content of vanadium-titanium slag is high and the content of CaO is relatively low. Therefore, the polymerization degree of silicon oxygen tetrahedron in the high titanium content is high, the ratio between microlite and glass is large and its activity is less than the original slag, which limits the application of high titanium slag[4].

This paper used high titanium metallurgy waste residue, fgd gypsum and other industrial solid wastes to prepare cementing material for mine filling, studied the hydration mechanism of
cementitious materials in high titanium metallurgical slag and desulphurization gypsum system, which proves the potential using value. Additionally, this paper provides a new way and theoretical basis for the utilization of high titanium metallurgy waste residue and makes high titanium metallurgy waste residue into treasure.

2. Test

2.1 Raw material
The high titanium metallurgy waste residue is the water-quenching blast furnace slag provided by HBIS Group Chengsteel Company. After drying and grinding, the high titanium slag powder was produced, which was called high titanium mineral powder. The main chemical components of high titanium slag powder are shown in Table 1 and the XRD spectrogram of high titanium mineral powder is shown in Figure 1. The flue gas desulfurization gypsum is offered by HBIS Group Chengsteel Company, whose main high titanium slag powder is shown in Table 2 and XRD analysis result is shown in Figure 2.

Table 1. Chemical composition of high titanium metallurgy waste residue (wt%)

| Components | CaO | Fe₂O₃ | SiO₂ | MgO | Al₂O₃ | MnO | TiO₂ | SO₃ | Na₂O |
|------------|-----|-------|------|-----|-------|-----|------|-----|------|
| Content    | 37.33 | 1.91  | 27.54 | 8.36 | 12.89 | 0.44 | 8.18 | 1.47 | 0.97 |

Fig 1. XRD analysis of high titanium metallurgy waste residue

Table 2. Chemical composition of desulfurization gypsum

| Components | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO | MgO | SO₃ |
|------------|------|-------|-------|-----|-----|-----|
| Content    | 3.72 | 1.29  | 0.71  | 45.31 | 0.58 | 47.26 |

Fig 2. XRD analysis of desulfurization gypsum
2.2 Test method
The ball mill adopted in the test is grinding test with SMφ500×500mm and the medium of grind is the factory standard configuration. Firstly, the raw material was stoved, whose water content was 1%. Then 5kg high titanium metallurgy waste residue was put into the little mill. After grinding for 100 minutes, the superfine slag powder of high titanium was obtained, whose specific surface area was 530 m²/kg. The 5kg flue gas desulfurization gypsum was selected for small mill and ground for 15 minutes. Therefore, flue gas desulfurization gypsum powder was obtained, whose specific surface area was 550 m²/kg.

The steps of preparing high titanium filling material were as follows: (1) blending high titanium powder, desulphurization gypsum and cement clinker in a total of 259g at 7:2:1; (2) putting 1036g iron ore tailings, 259g mixed powder and 540g water into the mixing pot and stirring uniformly with JJ-5 cement mortar stirring machine; (3) putting the glue sand into the 40mm×40mm×160mm trigeminy stainless steel mold test, vibrating, scraping surface and putting the test block into the designed temperature for 28 days to test its compressive strength.

2.3 Performance test and characterization
After 28 days, the compressive strength and flexural strength of the test block were measured based on examining methods for ISO cementation sand strength (GB/T 17671-1999). The filling mining material was analyzed by XRD and the microstructure of filling material was analyzed by SEM.

3. Results and discussions
Based on the ratio above, the test block was measured after 28-day maintenance and its results were shown in Table 3.

| high titanium metallurgy (g) | desulfurization gypsum (g) | cement clinker (g) | 7d (MPa) | 28d (MPa) |
|-----------------------------|---------------------------|-------------------|--------|--------|
| 181.3                       | 51.8                      | 25.9              | 0.98   | 3.16   |

3.1 XRD analysis of test block of high titanium filling material
The XRD map of high titanium filling material is shown in Figure 3. With the age of 3 days, 7 days and 28 days, the main mineral of high titanium powder based cementitious material system includes CaSO₄·2H₂O, C₂S, AFt and RO phase. With the increase of age, diffraction peak of gypsum and C₂S decreases, which indicates that gypsum and C₂S in raw materials are involved in hydration reaction. With the increase of age, the diffraction peak of AFt is strengthened, which indicates that AFt is formed in the process of hydration. As the maintenance age increases, the hydration products AFt and C-S-H hydrogel increase constantly, which guarantees the increase of strength.

![Fig3.XRD analysis of strength of different ages](image)

3.2 SEM-EDS analysis of test block of high titanium filling material
Figures 4-6 are the SEM results of the high titanium filling material, Figure 4 and Table 4 are the test results of EDS. Figure 4 is the SEM diagram of the test block at the age of 3 days and at the magnification of 10 k and 30 k, respectively.
From the left picture of Figure 4, it is found that after 3 days, a certain number of hydration products appears, but there are many pores between the particles and the structure is loose. From the right picture of Figure 4, the needle-like and amorphous product appears on the surface of the raw material particles when the sample is cured for 3 days. Although the hydration products are not connected closely, the needle hydration products on the surface of some particles are interlaced with each other, which makes the system have certain strength.

Figure 5 is the SEM figure of test block at 10k and 150k magnification at 7-day age. From the left picture, it is seen that there are still unreacted slag particles in the system when the test block is cured for 7 days. Compared with the SEM figure of the left test block at the age of 3 days, the pointer crystals of the samples grow significantly at 7-day age in Figure 5 and the surrounding amorphous gel also grows to a certain extent. Therefore, the strength at 7-day age is significantly higher than that at 3-day age. In the right picture of Figure 5, the hydration product of the test block is interleaved with the age of 7 days and there are amorphous gels around the crystal. The gel fills the voids in the net pulp test block. However, those gels have not been completely bonded into large blocks, but they have the cluster dispersion structure. Their particles are relatively loose and there are still a large number of voids in the system.

Figure 6 is the SEM figure of paste test block at 10k and 100k magnification at 28-day age. It is found that with the increase of age, the number of hydration products in the system in the left picture in Figure 6 is large. The acicular crystal increases continuously and the overlap between crystals is more compact. The number of amorphous gels increase significantly and they are surrounded by AFt crystal and filled in the gap in the system. The gel is tightly combined with the rod-shaped crystal of the needle, so that the system has a more compact structure and the strength is improved greatly. The amorphous gel at 28-day age is shown in right picture in the Figure 5. By comparing the right picture in the Figure 5, it is seen that the C-S-H gel is grown from the dispersed clusters to the relatively dense
The results of the energy spectrum analysis of the midpoint in Figure 6 are shown in Figure 7 and Table 4. The table has demonstrated the atomic percent of element O, Al, S, Si and Ca.

Table 4. SEM-EDS spectrum analysis of strength at 28 day (Atom%)

| Components | O   | Ca  | S   | Si  | Al  | Mg  | C   |
|------------|-----|-----|-----|-----|-----|-----|-----|
| a          | 57.89 | 17.33 | 8.32 | 1.07 | 5.25 | --  | 10.14 |
| b          | 52.87 | 14.68 | --  | 7.16 | 3.30 | 1.64 | 20.35 |

The ratio of Ca:S:Al of the midpoint a is about 17:8:5 and the chemical formula of ettringite (AFt) is $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$. The ettringite is hexagonal crystal in space and its chemical formula Ca:S:Al=20:10:7 shows that the acicular crystal is ettringite crystal.

From relative references, it is known that the C-S-H gel ($x\text{CaO} \cdot y\text{SiO}_2 \cdot n\text{H}_2\text{O}$) is amorphous colloid with low crystallization. The shape and element types of point b are in accordance with the characteristics of C-S-H gel. Therefore, point b is C-S-H gel and its calcium-silicate ratio is 2.05.

4. Conclusions
The mining filling material was prepared by high titanium metallurgy waste residue, flue gas desulfurization gypsum and other industrial solid waste and the microcosmic mechanism analysis of the filling material was carried out. The conclusions were made as follows:

(1) The mechanical activated high titanium metallurgy waste residue has certain activity. When specific surface area is 530 m$^2$/kg, the activity index of high titanium mineral powder is highest. Therefore, the high titanium mineral powder with specific surface area of 530 m$^2$/kg is selected for the preparation of mining filling material.

(2) The XRD spectrogram of high titanium mineral powder filling material shows that as the hydration age increases, ettringite and C-S-H gel were formed by the interaction and synergistic hydration among the raw materials, which guarantees the increase of the strength of the test block.

(3) The SEM picture of the high titanium mineral powder filling material demonstrates that with the increase of age, the ettringite crystal in the test block grows continuously, part of the ettringite crystal is included by a large amount of C-S-H gel and the compaction rate of the system obviously increases.

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