Experimental Study on Physical Excitation of Cementation Activity of Lead-zinc Smelting Slag

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Abstract. In recent years, it is a hot research direction to improve the internal structure and properties of smelting slag by physical grinding and to prepare filling cementitious materials suitable for mining. The paper starts from the test of physical and chemical properties of the smelting slag of a lead-zinc mine, the relationship between the density and specific surface area of lead-zinc smelting slag and the different grinding time was obtained by analyzing the chemical elements of the smelting slag filled with lead-zinc, the density and specific surface area of the smelting slag with different grinding time, and the potential gelling activity of lead-zinc smelting slag were effectively evaluated. It provides a theoretical basis for lead-zinc smelting slag as a new filling material for mines.

1. Introduction

In recent years, with the continuous development and growth of metallurgical industry, many mining enterprises have a large number of smelting slags for storage which resulting in environmental pollution and waste of mineral resources. If the cementitious properties of smelting slag can be stimulated, the smelting slag will be comprehensively utilized, which can not only reduce the environmental pollution caused by the accumulation of waste slag, but also reduce the cost of using cementitious materials for mining[1-3]. In this paper, the lead-zinc smelting slag used in the experiment is taken from a lead-zinc mine in Guangdong Province. The long-term storage of lead-zinc smelting slag in this mine not only occupies a large amount of land, but also has a certain impact on the environment. Comprehensive utilization of lead and zinc smelting slag to turn waste into treasure is an urgent problem to be solved in this mine.

Generally, lead-zinc smelting slag contains silicate, aluminate and ferrialuminate minerals, and its chemical composition contains a large number of oxides, mainly in the form of CaO, Al₂O₃ and FeO, so it has certain potential gelling activity[4,5]. Chemical and physical excitations are main ways to improve the cementitious properties of smelting slag. Chemical excitation is the method to increase the alkalinity of liquid phase by adding chemical activator to accelerate hydration and hardening. Physical excitation is to grind tailings and smelting slag by physical method to improve the fineness of smelting slag. Physical abrasion can improve the fineness of particles, change the lattice structure of minerals and produce defects, which can make the surface of minerals form amorphous structure easily soluble in water[6-9]. When the contact area is between minerals and water increases, the contact...
area of reactants increases, and the extrusion probability of activated molecules increases, thus hydration reaction is accelerated.

The lead-zinc smelting slag was screened and grinded at different times. The density and specific surface area of the slag were tested. The physical activation and gelling mechanism of the slag were analyzed[9].

2. Chemical Elements Analysis of Lead-zinc Smelting Slag

Chemical element analysis of lead and zinc smelting slag is carried out. The analysis results are shown in Table 1.

| Component | CaO | Al₂O₃ | MgO | SiO₂ | Fe₂O₃ |
|------------|-----|-------|-----|------|-------|
| Content%   | 13.76 | 12.02 | 6.12 | 26.92 | 1.69  |
| Component  | MnO | P₂O₅ | K₂O | TiO₂ | FeO   |
| Content%   | 1.79 | 0.12  | 1.12 | 0.60 | 24.88 |
| Component  | Zn  | Na₂O | H₂O⁻ | Pb   | S     |
| Content%   | 3.20 | 3.35  | 0.00 | 0.92 | 2.15  |

The main metal oxides in lead-zinc smelting slag are FeO, CaO, Al₂O₃, MgO, MnO and K₂O, and the contents are 24.88%, 13.76%, 12.02%, 6.12%, 1.79% and 1.12% respectively. The main non-metallic oxide is SiO₂ with a content of 26.92%. The content of sulphur and sulphide in lead-zinc smelting slag is 2.15%, so the strength of filling body will not be affected by sulphur and sulphide.

3. Particle Size Distribution Characteristics of Lead-zinc Smelting Slag

Fraunhofer’s theory of diffraction and Mie's theory of light scattering show that when the laser is projected on the particles, the interaction between them will produce light scattering, thus the particle size and its distribution can be obtained[10]. In this paper, the particle size of lead-zinc tailings is measured by Malvern Laser Particle Size Tester.

Particle size distributions data of lead-zinc smelting slag are shown in Table 2, the particle size distribution of lead-zinc smelting slag is shown in Figure 1. The data show that the particle sizes of lead-zinc smelting slag is all available. The particle size of lead-zinc smelting slag is quite large. The particles of 200-250um is 13.92% of the total number of particles, and 250-300um particles is 10.98% of the total number of particles. We also can see that, the particles of 400-700um is 11.17% of the total number of particles. For this kind of particle, hydration reaction is hardly occurred.

Because of the large particle size and small specific surface area of lead-zinc smelting slag, it is difficult for these particles to hydrate. Theoretically, the untreated lead-zinc smelting slag can hardly self-cementing, so physical activation of lead-zinc smelting slag is necessary.
Table 2. Particle size distribution of lead-zinc smelting slag.

| Particle size (μm) | Sub sieving (%) | Cumulative under sieve (%) |
|-------------------|-----------------|---------------------------|
| 1                 | 0.07            | 0.07                      |
| 1.5               | 0.28            | 0.35                      |
| 2.5               | 0.22            | 0.8                       |
| 3                 | 0.22            | 1.02                      |
| 4                 | 0.21            | 1.45                      |
| 4.5               | 0.2             | 1.65                      |
| 5.5               | 0.17            | 2                         |
| 6                 | 0.16            | 2.16                      |
| 8                 | 0.23            | 2.66                      |
| 10                | 0.17            | 3.04                      |
| 15                | 0.71            | 3.75                      |
| 20                | 0.61            | 4.36                      |
| 40                | 1.3             | 6.92                      |
| 60                | 1.54            | 9.85                      |
| 70                | 1.77            | 11.62                     |
| 74                | 0.78            | 12.4                      |
| 80                | 1.25            | 13.65                     |
| 100               | 2.55            | 18.5                      |
| 110               | 2.78            | 21.28                     |
| 130               | 3.09            | 27.33                     |
| 140               | 3.2             | 30.53                     |
| 160               | 3.26            | 37.04                     |
| 170               | 3.27            | 40.31                     |
| 190               | 3.17            | 46.7                      |
| 250               | 13.92           | 63.71                     |
| 300               | 10.98           | 74.69                     |
| 350               | 8.21            | 82.9                      |
| 500               | 2.89            | 95.9                      |
| 600               | 1.25            | 99.09                     |
| 700               | 0.91            | 100                       |

Figure 1. Particle size distribution of lead-zinc smelting slag.
4. Effect of Physical Activation on Cementitious Properties of Lead-zinc Smelting Slag

The particles in lead-zinc slag are relatively coarse, so it is necessary to grind lead-zinc slag in advance. Physical activation is one of the ways to stimulate the activity of lead-zinc slag\textsuperscript{[11,12]}. Through grinding, the conversion from mechanical energy to surface energy of lead-zinc slag is realized, thus improving its activity. The flow chart of physical activation experiment is shown in Figure 2.

![Figure 2. Flow chart of physical activation experiment](image)

4.1. Mechanical Grinding

The equipment for grinding raw materials is the standard test mill of 500×500mm. The lead-zinc smelting slag was ground by experimental mill, it was shown in Figure 3, and the density and specific surface area of the slag were tested. Taking grinding time as variable, the relationship between grinding time and density and specific surface area of lead-zinc smelting slag was explored\textsuperscript{[13]}.

![Figure 3. Diagram of experimental mill](image)

The density and specific surface area of raw materials after grinding were tested in accordance with 《GB.T208-1994 Cement Density Measurement Method》 and 《GB/T8074-2008 Brinell Method for Measuring Specific Surface Area of Cement》 respectively. The test results are shown in Table 3.

| Grinding time | Specific surface area /m²/kg | Density /g/cm³ |
|---------------|-----------------------------|---------------|
| 30min         | 181.21                      | 3.353         |
| 50min         | 330.81                      | 3.325         |
| 60min         | 442.25                      | 3.435         |
| 70min         | 527.61                      | 3.471         |
| 90min         | 734.89                      | 3.481         |
4.2. Effect of Mechanical Activation Time on the Density of Lead-Zinc Smelting Slag

From table 3 we can see that the regularity of the density of lead-zinc smelting slag changing with grinding time is not obvious. Figure 4 shows the relationship between grinding time and density of lead-zinc slag and lead-zinc slag\textsuperscript{[14,15]}. From Figure 4, it can be seen that the density of lead-zinc slag remains almost unchanged with the increase of grinding time, between 3.3-3.5g/cm\textsuperscript{3}. This is because the lead-zinc smelting slag contains coarse particles, and the density and hardness of these particles are relatively large, grinding can change the fineness of lead-zinc smelting slag to a certain extent, but the effect is limited.

![Figure 4. Graph of relationship between grinding time and density of lead-zinc slag](image)

4.3. Effect of Mechanical Activation Time on Specific Surface Area of Lead-Zinc Smelting Slag

The analysis of specific surface area of lead-zinc smelting slag with different grinding time shows that there is a regularity between specific surface area and grinding time, as shown in Figure 5. In order to explore the specific numerical relationship, the quadratic curve fitting of the numerical value was carried out, and the equation was obtained as follows:

\[ Y = 23.63 + 5.87x + 0.029x^2 \]  

(1)

In formula: \( y \) is specific surface area, \( \text{m}^2/\text{kg} \); \( x \) is grinding time, min. It can be seen from Fig. 4 that The specific surface area increases with the lapping time and Initial data always tends to increase monotonously, so it leads to the increase of \( Y \) when \( x \) is greater than 0.
With the increase of grinding time, the specific surface area of lead-zinc slag increases continuously. When grinding time reaches 90 minutes, the specific surface area of lead-zinc slag reaches 735.81 m$^2$/kg. This indicates that the prolongation of grinding time can increase the specific surface area of lead-zinc smelting slag and increase the number of defects or active centers. The more defects or active centers, the higher the activity of lead-zinc smelting slags. The grinding test results of lead-zinc smelting slag show that the grinding time is proportional to the specific surface area, the greater the specific surface area, the higher the mineral activity. But the increase of grinding time will greatly increase the cost, so it is very important to choose the right grinding time.

On the premise of properly improving material activity and considering the practical problems of longer grinding time and higher cost, according to the requirements of the new national standard GBT18046-2008 for slag powder in cement for grinding fineness interval, the suitable grinding time of lead-zinc smelting slag is 70 minutes, and the corresponding fineness is 526.64 m$^2$/kg.

5. Conclusion
In this paper, the phase characteristics of a lead-zinc mine's smelting slag under natural gradation are analyzed, the activation of the slag by physical activation is studied, and the optimum mechanical grinding time is explored. The conclusions are as follows:

1) The main metal elements and their oxides in lead-zinc smelting slag are FeO, CaO, Al$_2$O$_3$, MgO, and the main non-metallic elements and their oxides are SiO$_2$. The main mineral compositions of the slag are glass phase, mainly consisting of hydrates of alpha-quartz, siderite and calcium-alumina oxides, which are potential hydraulics materials; the content of sulfur and sulfide in lead zinc smelting slag is less than 3% in natural gradation.

2) The particle size distribution of lead-zinc smelting slag was studied. It was concluded that the content of large particles in lead-zinc smelting slag was higher, and the particle size in the range of hydrable particle size was relatively small, so physical activation was necessary.

3) The grinding experiment of lead-zinc smelting slag shows that the longer the physical activation grinding time is, the larger the specific surface area is. Considering the cost and the requirements of the national standard, the suitable grinding time is 70 minutes, and the corresponding fineness is 526.64 m$^2$/kg.

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