Research on properties of alkali activated lead-zinc mineral powder cementitious materials

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Abstract. Cement has long been used as the main cementing material of the artesian paste filling material in the goaf of a mine, giving a generally high strength. However, the cement ‘two grinding and one burning’ process consumes a lot of energy, which aggravates the greenhouse effect. Therefore, a new type of cementitious material with lower energy consumption and lower emissions is needed. Solid wastes are useless by-products after mining and beneficiation, which are often dry piled in the open air, wasting land resources and polluting the environment. This project studied an alkali-activated mineral powder cementitious material, delineated its internal structure and morphology, and tested its mechanical properties. In a gelling system with 70% mineral powder, 30% Portland cement, 1% sodium silicate and a water-cement ratio of 0.4, the hydration reaction commenced the earliest and the early strength of the test block was the highest. In addition, further increasement in proportion of mineral powder or sodium silicate could not have a positive effect on the early strength of the system.

1. Introduction

Cement has long been widely used as the main component of artesian paste gelling materials in mines [1]. In the industrial application of artesian filling in underground mines, the filling can form support to its surrounding rock and soil structure in a relatively fast pace, as a result improves the structural stability of the hollow structure after mining.

However, using Portland cement to cement the tailings, especially the fine tailings (with a particle size below 100μm) [2], there are still troubles in its early coagulation [3] and sulfate erosion [4]. Meanwhile, the ”two grinding and one burning” process of cement production produces a considerable amount of greenhouse gases, which will result in massive pollution to the atmosphere. In some mines, filling costs account for as much as 1/3 to 2/3 of the total mining costs, which makes the backfilling technic hard to implement in some mines, thereby restricting the economic development of mines. To solve the problem, reducing the filling cost is the primary task of adopting this technic. The main factor affecting the filling cost is the cost of cementing materials [5,6]. Under the background policy of eliminating excessive...
capacity, there was a sharp reduction in the overcapacity industry represented by field of cement, which boosts the price of cement in the market and increased production costs for downstream mining enterprises that use cement as the main cementing material.

The tailings filling process of the industrial and mining industry urgently needs a new cementitious material with a lower ash-sand ratio, effective cementing of fine tailings, high efficiency for full tailings artesian paste filling, higher filling pressure, and a significant reduction in overall filling costs. Previous studies on solid waste materials as a substitute for cement as filling materials [7] focused on single solid waste. Various cementitious materials have good technical effects in the practical application of industrial filling. However, in the selection of the overall solid waste and the adjustment of the ratio of cementitious materials, the supply of materials, the choice of regions, the surrounding radius of the mine, the conditions of solid waste resources, and the corresponding logistics costs should be put at the top in the evaluation standard of the optimal solution.

To address this condition, this research aims at making an experimental system through alkali activated cementitious materials [8] using the multiple geographical resources of a lead-zinc mine in southern China, including local solid sodium silicate and mineral powder produced by a steel plant within a radius of 120km of the mine. Studied the possibilities of using a high proportion of geo-solid waste materials instead of cement to prepare tailings fillings, achieved high early strength (slurry coagulation, high pressure), high fluidity (self-flowing) and other indicators of underground filling, reduced cement consumption and greenhouses gas emissions, optimized the overall economic cost of cementitious materials.

2. Materials and Methods

2.1. Materials

Hailuo brand P.O 42.5 cement, with a density of 3.11g/cm³, fulfils National Standard ‘General Purpose Portland Cement’ (GB175-2007) requirements (Table 1). Finely ground slag (GGBS) produced by Shaoguan Steel Plant (SGS) near Lead-zinc mining area, with a density of 2.9g/cm³, specific surface area (BET) 443 m²/kg, fulfils National Standard requirements (Table 2). Sodium silicate alkali activator, a product with selected from Shijiazhuang, Hebei province, M2.0 white powder fast dissolving sodium silicate (Table 3). Using naphthalene FDN-C cement and concrete as high-range water-reducer, water reducing ratio is 18%~28%.

2.2. Preparation of alkali-activated slag silicate cementitious material

Industrial waste, granulated blast furnace was utilized to partially replace cement. With proper ratio of alkali activator (solid Na₂SiO₃), the content of vitreous body was stimulated to synthesize alkali-

| Table1 Content of cement oxide(wt%) |
|------------------------------------|
| Oxide | Na₂O | MgO | Al₂O₃ | SiO₂ |
|-------|------|-----|-------|------|
| Cement | 0.20 | 1.72 | 7.15 | 23.41 |
| Oxide | 2.66 | 58.05 | 3.09 | 2.24 |

| Table2 Technical properties of Portland cement |
|-----------------------------------------------|
| Category | BET (m²/kg) | Water consumption for standard consistency (g) | Setting time (min) |
|----------|-------------|-----------------------------------------------|-------------------|
| P.O 42.5 | 338         | 123                                           | Initial 180       |

| Table3 Properties of sodium silicate |
|--------------------------------------|
| Index | Na₂O₂ | SiO₂ | Modulus | Dissolution Rate | Proportion g/ml | Fineness(120 mesh sieving ratio% ) |
|-------|-------|------|---------|-----------------|----------------|----------------------------------|
| SM 2.00 | 26.0  | 49.0 | 2.00±0.05 | 50              | 0.30-0.60      | ≥98                              |

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activated slag silicate cementitious material for mine filling.

2.3. Content of cementing material

2.3.1. Content of non-alkaline activator cementing material.

| No. | Cement (%) | Mineral powder (%) | Water cement ratio |
|-----|------------|--------------------|-------------------|
| A1  | 50         | 50                 | 0.4               |
| A2  | 30         | 70                 |                   |
| A3  | 10         | 90                 |                   |

2.3.2. Content of fixed alkaline activator content cementing material

| No. | Cement (%) | Mineral powder (%) | Alkali activator (%) | Water cement ratio |
|-----|------------|--------------------|----------------------|-------------------|
| A4  | 50         | 50                 | 1                    | 0.4               |
| A5  | 30         | 70                 |                      |                   |
| A6  | 10         | 90                 |                      |                   |

2.3.3. Content of cementing materials with different proportion of alkaline activator

| No. | Cement (%) | Mineral powder (%) | Alkali activator (%) | Water cement ratio |
|-----|------------|--------------------|----------------------|-------------------|
| B14 | 30         | 70                 | 2                    | 0.4               |
| B16 | 30         | 70                 |                      | 0.6               |
| B18 | 30         | 70                 |                      | 0.8               |
| B24 | 30         | 70                 |                      | 0.4               |
| B26 | 30         | 70                 |                      | 0.6               |
| B28 | 30         | 70                 |                      | 0.8               |
| B34 | 30         | 70                 |                      | 0.4               |
| B36 | 30         | 70                 |                      | 0.6               |
| B38 | 30         | 70                 |                      | 0.8               |

2.4. Methods

2.4.1. X-ray Fluorescence Spectroscopy
Hailuo brand P.O 42.5 cement and mineral powder are dried and roasted to remove organic matter, crystal water, CO$_3^{2-}$, etc., to gain loss. Then the sample was mixed and ground in an agate mortar until there was no graininess. After the tablet was formed, the sample was put into the sample cup to start the test. It was characterized by a Zetium X-ray fluorescence spectrometer of PANalytical B.V (Netherlands).

2.4.2. X-ray diffraction analysis
The mineral powder is dried and roasted to remove organic matter, crystal water, CO$_3^{2-}$, etc. Then mixed and ground in an agate mortar until no graininess. An X-ray diffractometer (XRD) model D8 Advanced produced by Bruker (Germany) was utilized to characterize the sample.

2.4.3. Scanning electron microscopy
The sample was characterized by JSM-5610LV scanning electron microscope (SEM) produced by JEOL, with the accelerating voltage of 25kV.
2.4.4. Thermogravimetric analysis
Thermal analysis using Schleibinger CDF Test thermogravimetric analyze.

2.4.5. Porosity analysis
AutoPore IV95/0 mercury porosimeter was used for pore analysis.

3. Results & Discussions
There are three main reasons for choosing alkali activator for this cementitious material: (1) most of the alkali activated systems have a short hardening period with high intensity in its early stage. This characteristic is especially useful for filling Lead-zinc mine. In addition, with proper raw material and adjustment in types of alkali activators, Alkali activated backfill body could have significant increase in strength and durability than traditional cement [9-13]. (2) The main purpose of cementitious material is to solidify tailing. However, some of the feldspar tailings were also studied for its alkali activating ability, such as potassium feldspar. In this way, alkali activated cementitious material is certainly to have effects in activity of tailings. (3) There is prodigious amount of waste residue around mines where is fairly accessible. Besides, alkali activated slag is a proven technique with widespread applications [14-16].

3.1. Characteristics of mineral powder

| Oxide   | SiO₂  | Al₂O₃ | Fe₂O₃ | CaO  |
|---------|-------|-------|-------|------|
| Mineral powder | 33.04 | 14.56 | 0.98  | 40.16 |

The determination formula of mineral powder activity is the quality coefficient K determination. K is determined by:

\[ K = \frac{(\text{CaO} + \text{MgO} + \text{Al}_2\text{O}_3)}{(\text{SiO}_2 + \text{MnO} + \text{TiO}_2)} \]

The higher K is, the higher activity the powders are. According to the calculation of GGBS oxide content, the experimental mineral powder reaches the activity index of S95 mineral powder. Using XRD to test the composition of mineral powder (Figure 1a), it is notable that there are no palpable characteristic peaks in the mineral powder, indicating that it contains a lot of vitreous material and has high potential activity.

Figure 1(a) XRD patterns of SGS mineral powder

Observing the morphology of the mineral powder particles with SEM (Figure 1b), it can be seen that the surface of the mineral powder is irregular in shape, relatively smooth and vitreous.
3.2. Performance analysis

Compressive strength measurement was carried out via comparisons of various ratio of cementitious material solidified body using WAY-300 Automatic Bending and Compression Testing Machine. At the same mineral powder content, the 3d, 7d and 28d compressive strength of the test block without alkaline activator sodium silicate (SS) is lower than the test block mixed with alkaline activator under the same conditions. Without alkali activator, the 3d, 7d and 28d compressive strength of the test blocks decreased as the increase of mineral powder in replace of cement. When the mineral powder content is 70%, mixing with 1% alkaline activator, improvements of strength in test blocks are the most obvious (Figure2).

With different water-cement ratios, changing the proportion of alkaline activator had effects on 3d compressive strength of the test block. As water-cement ratio increased, the compressive strength of the test block declined rapidly. Under different water-cement ratios, the amount of alkaline activator added had little effect on compressive strength of the test block. After adding 3% alkaline activator, the compressive strength of the test block even decreased to a certain extent (Figure3).

Under the same mineral powder-cement ratio, using the new TAM AIR micro-calorimeter to test the slurry hydration exotherm activated by different amount of alkaline activator. Before adding the alkaline activator (sodium silicate) (A2), the hydration exothermic peak of Portland slag cement appeared after about 13 hours, and after adding 1% alkaline activator sodium silicate (B14), The exothermic peak of hydration was advanced to about 10h, and at the same time the peak increased significantly. The
hydration reaction became more intense. After adding 2% alkaline activator (sodium silicate) (B24), the exothermic peak of hydration was advanced to about 8h, the peak increased significantly. The hydration reaction became more intense (Figure 4). At the same time, the total heat of the cementitious material mixed with alkaline activator was also significantly increased (Figure 5), indicating that the incorporation of alkaline activator sodium silicate accelerated the early hydration process of slag Portland cement and strengthened the hydration reaction. Strength, promoted the formation of hydration products.

![Figure 4 Influence of sodium silicate content on heat release of slag Portland cement hydration](image1)

![Figure 5 Influence of sodium silicate content on total heat release of slag Portland cement](image2)

XRD was used to analyze the 3d hydration products of the alkali activated system and the non-alkali activated system (Figure 6). Schleibinger CDF Test Thermogravimetric Analyzer was utilized for thermal analysis of the alkali-activated hydration products (Figure 7). The CSH gel phase was formed in the alkali-activated system. This is because in the alkali-activated slag system, solid sodium silicate was dissolved in water forming hydrous sodium silicate, which is then hydrolyzed to NaOH and hydrated silica gel. After superimposing activation with Portland cement, glassy silica network structure in slag was disintegrated, in result, promotes the reaction; while the hydrous silica gel reacts with Ca$^{2+}$ and Al$^{3+}$ dissolved in water such as cement and mineral powder to generate C-S-H gel and hydrated calcium aluminosilicate etc.
Figure 6 3d XRD patterns of non-alkaline activated system and alkali activated system. A2 is the non-alkali activated system with 70% mineral powder content, A5 is 70% mineral powder content with 1% sodium silicate alkali activated system. Water cement ratio is 0.4.

Figure 7 A5 3d thermogravimetric analysis spectrum of alkali activated system

Cured in a standard curing room for 3 days, then using mercury intrusion method (MIP) to analyze the pore structure of the test block, plotted the pore size distribution curves and cumulative porosity of different ratio systems. From the figure 8, the water-cement ratio had the most obvious influence on the porosity of the sample. The pore size and total porosity of the samples A4 and A5 (water-cement ratio of 0.4) with smaller water-cement ratio were significantly lower than other samples (water-cement ratio of 0.8). Because the larger the water-cement ratio, the more water-containing channels and system free water. When the solidified product of the hydration reaction is formed, the more gaps the product will have. Comparing the A4 and A5 systems, when the water-cement ratio is 0.4 and proportion of alkali activators is fixed at 1%, the total porosity of the sample with the mineral powder content of 70% (A5) is less than the content of 50% (A4). The pore size distribution of the sample is similar. Comparing the B18, B28 and B38 sample systems, it is notable that in the high water-cement ratio system, when solid sodium silicate content increases, the sample pore size becomes larger, and the total porosity increases. In the experiment, because cement also has a certain alkali stimulating effect on mineral powder, when the amount of sodium silicate is higher than 1%, the facilitation on the hydration reaction of the system is not obvious.
The morphology of the hydration products of the cementitious material was analyzed by JSM-5610LV scanning electron microscope. Comparing the 3d scanning electron micrographs of the A2 and A5 samples, it can be seen (Figure 9(a)) that C-S-H gel appears around the mineral powder particles, but there is no obvious needle-shaped ettringite. Besides, the surface of the mineral powder particles in A2 is smooth, with only a few micro holes and no signs of reaction. The mineral powder particles in A5 mixed with alkaline activator (ammonium silicate) have been corroded. The C-S-H gel on the surface extended and grew continuously, filling the system holes, bonding the particles, and ensuring strength. B14, B24 and B34 were mixed with 1%, 2% and 3% sodium silicate to stimulate the system. With comparison and observation of the SEM spectrum (Figure 9(b)), the structure of the sample with 1% sodium silicate was more compact. The increase in sodium silicate dosage did not affect C-S-H gel production, which may be due to the increase in content of alkali activator, for impeding the further stimulation of mineral powder by Portland cement. Therefore, in this experiment, the addition of 1% alkaline activator sodium silicate has the best stimulation effect on the cementitious system.
4. Conclusions
In brief, the study uses S95 mineral powder to partially replace cement while adding sodium silicate as an alkali activator for cementing material. While using mineral powder instead of cement, if certain types of alkali activators were not added during the process, the powder would partially react, and the strength is not sufficient enough. After stimulated by appropriate amount of sodium silicate, the early stage of hydration reaction in cement-mineral powder gelling system was greatly accelerated with more hydration products produced, therefore providing strength to the system. In a gelling system with 70% of mineral powder, 30% of different Portland cement/silicate cement, 1% of sodium silicate and a water-cement ratio of 0.4, the hydration reaction appeared the earliest and the early strength of the test block was the highest. In addition, increasing the content of mineral powder or sodium silicate again have no positive effect on the early strength of the system. This is of great significance for lower energy consumption and carbon emissions by stimulating solid waste to partially replace cement, and for exploring more active activators and solid waste to replace cement as cementing materials.

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