The Latest Research Progress of Green Building Materials in Lead and Zinc Tailings

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Abstract: In recent years, researchers at home and abroad have used lead-zinc tailings to prepare green building materials for analysis. The main discussion on the preparation of geopolymers and foamed ceramics from lead-zinc tailings is given. The heavy metal curing and radiation-proofing ability of lead-zinc tailings-based building materials are briefly introduced. The results show that the lead-zinc tailings-based green building materials have High strength, heavy metal curing and radiation protection. Finally, the application and prospects of lead-zinc tailings in the field of building materials are analyzed, which provides a theoretical basis for the researchers in the field.

1. Introduction

The tailings produced during the lead-zinc mining process contain heavy metal ions such as lead, zinc, copper and cadmium. Long-term open-air accumulation not only occupies land resources, but also pollutes the surrounding atmosphere, water, soil and other environment, and reduces the quality of life of the residents. Security risks [1-4]. Lead-zinc tailings have good burnability and chemical characteristics similar to those of cement and clay. Therefore, the use of lead-zinc tailings to make building materials (such as cement, concrete, wallboard) has received the attention of people from all walks of life, and the related fields are developing rapidly [5-7]. According to the physical and chemical properties of lead-zinc tailings, researchers used lead-zinc tailings to prepare green building materials such as geopolymers and ceramics, and had achieved remarkable result. The main reasons for the application of lead-zinc tailings in the preparation of green building materials include:

(1) High early strength of geopolymer [8], High temperature resistance [9], Preservative [10], Radiation resistant [11], Strong heavy metal curing ability [12], The preparation of building materials has low energy consumption, low cost and low carbon dioxide emissions;

(2) The content of silicon-aluminum elements required for the preparation of ceramics in lead-zinc tailings is high (Table 1); high ceramic strength [13], can fix heavy metal ions in tailings (Table 2).

This paper mainly discusses the preparation of geopolymers and ceramics from lead-zinc tailings, and introduces the radiation protection and heavy metal curing ability of lead-zinc tailings-based green building materials. This review predicts the development trend of lead-zinc tailings in new green building materials, and provide theoretical basis for researchers in this field.
Table 1. Chemical composition of lead and zinc tailings raw materials/%

| Source of raw materials | CaO | SiO₂ | Al₂O₃ | Fe₂O₃ | MgO | Na₂O | K₂O | MnO | TiO₂ |
|------------------------|-----|------|-------|-------|-----|------|-----|-----|------|
| Mining company in Nanjing [8] | 36.95 | 22.85 | 4.57  | 9.62  | 2.67 | 14.03 |     |     |      |
| Mining company in Jiangxi [14] | 2.97  | 48.25 | 14.4  | 9.89  | 1.06 | 0.08 | 2.44 |     |      |
| Mining company in Guangdong [15] | 5.04  | 64.56 | 11.21 | 1.91  | 1.39 | 0.56 | 2.18 | 0.61 | 0.57 |

Table 2. Heavy metal content in soil of lead-zinc tailings mining area (unit: mg/kg)

| Source of raw materials | Pb   | Zn   | Cu   | Cd   | Cr   | As   | Ni   | Mn   |
|------------------------|------|------|------|------|------|------|------|------|
| Southern Shaanxi lead-zinc tailings area [2] | 69.43 | 223.99 | 196.04 | 0.37 | 37.36 | 937.48 |
| Hunan Qiaokou Lead-zinc Mine Tailings Reservoir [3] | 2773.5 | 58.8 | 124  | 3579 |
| Jinyuan Mining Area, Datian County, Fujian Province [4] | 879   | 12480 | 132  | 20   | 11   | 23   | 3    | 21400 |

2. Application of lead and zinc tailings in geopolymers

The geopolymer forms a three-dimensional network structure of amorphous silicon tetraoxide and aluminosilicate tetrahedron by polycondensation and chain reaction, which was first developed by French scientist Davidovits, J. [16]. Davidovits, J. mixes the basic alkaline activator solvent with solid waste containing silicon-aluminum raw materials such as fly ash, slag, kaolin, and then prepares it with high strength, high temperature resistance and corrosion resistance by pouring, compression molding or ultrasonic assist. Radiation resistant to radiation and strong metal ion curing ability. In recent years, with the continuous development of geopolymers, the effective treatment of solid wastes with high levels of heavy metals has attracted enough attention from many researchers and enterprises at home and abroad. There are few studies on the preparation of geopolymers from lead-zinc tailings, but some results have been achieved in theory.

The replacement of cement by lead-zinc tailings or the mixing of lead-zinc tailings with solid waste to prepare geopolymers can enhance the gelation effect and improve the density and strength properties of the geopolymer. For example, when using the alkali-impregnated lead-zinc slag geopolymer mortar test block, when the modulus, alkali activator content, and slag content are 1.2, 65%, and 45%, respectively, the polycondensation reaction of the geopolymer occurs after 28 days of curing at room temperature. Na₂Al₂Si₃O₁₀·2H₂O and Na₅Si₈O₁₉, the compressive strength is up to 49.6 MPa, and the structural strength and stability of the material are obvious. Enhance [17]. Li Beixing, etc. [15] used 70% lead-zinc tailings, 30% mineral powder (Wugang S95 grade) as catalyst. The water glass modulus is 1.0 and the alkali content is 9%, under 50 °C curing, preparing a high-strength geopolymer with a compressive strength of about 55 MPa for 28 days. The mineral powder can not only effectively improve the compactness of the lead-zinc tailings geopolymer, but also increase the high silicon and aluminum oxide content of the lead-zinc tailings and promote the alkali-excited reaction. The final product microstructure is three-dimensional network (aluminum oxide The body and the silicon tetrahedron are alternately bonded).

Mechanical grinding and high temperature calcination can improve the slag activation degree and improve the structural density and structural strength of the geopolymer. Sun Shuangyue [18] On the basis of the test, desulfurization gypsum was added. The effects of pre-grinding time, mixing time, desulfurization gypsum content and water glass content were studied. XRD and SEM analysis showed that the gelatinous material structure of the standard curing for 28 days contained a large number of gels, interposed with acicular ettringite, which reduced the porosity and improved the structural compactness. The increase in compaction is due in part to the addition of desulfurized gypsum and, on the other hand, to changes in the particle size of the lead and zinc waste. For example, adding 4wt% desulfurization gypsum, 9wt% water glass, pre-grinding for 60 min, mixing for 70 min, the compressive strength of the geopolymer at the age of 28 d reaches 36.48 MPa.
Lead-zinc tailings base polymer has good heavy metal curing ability. Guo Bin prepares fly ash base polymer from lead-zinc waste residue and studies its curing effect on Pb and Cd [19]. The results of TCLP leaching toxicity indicated that the leaching concentrations of Pb and Cd in the geopolymer were in compliance with the standard. In the geopolymer, there is only physical coating of Cd, and in addition to physical coating, Pb also has an "alkali-gelling network bonding" curing mechanism, so the geopolymer has a better curing effect on Pb.

3. Application of lead-zinc tailings in foamed ceramics
Foamed ceramics have the advantages of lightweight, sound insulation, high temperature resistance and corrosion resistance, and are widely used in construction, national defense and chemical industry. According to different foaming agents, it is divided into high temperature foamed ceramics and low temperature foamed ceramics [20]. The researchers used solid waste containing silicon-aluminum oxide as a blend to prepare low-cost, high-performance foamed ceramics [21]. The use of lead-zinc tailings to prepare foamed ceramics has achieved good results, and related research has become a hot topic.

Increasing the sintering temperature can improve the closed porosity, thermal conductivity and mechanical properties of foamed ceramics. Taoyong Liu and others used powder metallurgy technology to prepare foam ceramic materials with lead and zinc tailings, red mud and silica sand as main raw materials, and sodium borate (Na$_2$B$_4$O$_7$) as flux. The results show that the proper sintering temperature can promote the formation of closed pores inside the foamed ceramic. When the sintering temperature is increased to 970 °C, the foamed ceramic has the advantages of porous, low thermal conductivity and good heat insulation effect. Due to its low thermal conductivity and wide pore distribution, the prepared foamed ceramic materials are widely used in insulated building boards [22]. Taoyong Liu, etc. [23] The lead-zinc tailings (also used as a foaming agent), red mud and fly ash were used as the main raw materials, and the porous foamed ceramic material was prepared by using Na$_2$B$_4$O$_7$ as a flux. Through characterization and crystallization phase analysis, the best performance porous ceramics can be prepared by incorporating 18wt% lead-zinc tailings and sintering temperature of 980 °C. The test results show that the bulk density and porosity of the material are 0.67 g/cm$^3$ and 69.2%, respectively; the compressive strength is above 7 MPa, and the flexural strength exceeds 6 MPa.

4. Heavy metal curing and radiation protection of lead-zinc tailings-based building materials
The large amount of lead-zinc tailings produced lacks the short board of construction materials. Considering the high content of heavy metals in lead-zinc tailings, before applying it to building materials, theoretical research on heavy metal solidification must be carried out to explore the feasibility of using lead and zinc tailings in building materials. Secondly, building materials containing heavy metal elements High-energy ray shielding effect, γ-ray shielding effect is more significant [24]. The following is a detailed description of the heavy metal curing and radiation protection properties of lead-zinc tailings-based building materials.

4.1 Heavy metal curing building materials
The calcination temperature of clinker is the main influencing factor of the solidification ability of heavy metals in lead-zinc tailings-based cement clinker. The content of heavy metals varies with the type and proportion of cement raw materials; the calcination temperature is different, the solidification rate of heavy metals in cement clinker is different; and the solidification rate refers to the change of heavy metal content after clinker calcination; The higher the curing rate, the higher the heavy metal content in the clinker; on the contrary, the lower the heavy metal content, so that the heavy metals lost during the calcination process pollute the environment. Before the lead-zinc tailings-based building materials are put into production, the experimental study on leaching toxicity must be carried out; and the concentration of each heavy metal leaching solution must meet the technical parameters of GB5085.3-2007. In order to reduce the discharge of heavy metal elements with the exhaust gas or the
infiltration of rainwater into the groundwater; the production of cement clinker with lead-zinc tailings as raw material has been initially developed (see Table 3).

Table 3. Analysis of Heavy Metal Curing Ability of Lead-Zinc Tailings Based Building Materials

| Material style | Maximum cure rate/% | Ref. |
|----------------|---------------------|------|
|               | Zn | Pb | Cu | Cd | As |      |
| cement Calcination temperature | 98.23 | 14.97 | 29.68 |      | [24]|
|               | 86.41 | 14.60 | 35.74 |      | [25]|
|               | 89.76 | 15.19 | 73.20 | 83.62 | [26]|
|               | 91.43 | 21.16 |      | 87.61 | [27]|

Lead-zinc tailings-based cement material with good Pb$^{2+}$ ion hardening performance can be prepared under alkaline environment. Dan Zhang, etc. [28] Cement-based cementitious materials were prepared by using lead-zinc smelting slag and tailings as main raw materials; the ability of pH and leaching time to cure Pb$^{2+}$ of cementitious materials was investigated. The experimental results show that Pb$^{2+}$ is easy to form a metal compound in an acidic environment, resulting in a large amount of leaching of Pb$^{2+}$ ions; in an alkaline environment (pH 12.0), the elution amount of Pb$^{2+}$ is only about 2.5 mg/g.

4.2 Radiation protection building materials

At present, the research and application fields of radiation-proof cement at home and abroad are mainly concentrated in concrete, concrete, and boron-containing cement [29]. These cements have the disadvantages of a single anti-radiation effect and poor thermal stability. Lead-zinc tailings contain heavy metal element Pb$^{2+}$. In the field of radiation-proof building materials, the utilization of lead-zinc tailings has far-reaching research significance and broad development prospects.

Lead-zinc tailings can increase the density, strength and gamma radiation shielding properties of building materials. Alwaeli M. [30] used 50wt% scaly lead-zinc waste and 50wt% granulated lead-zinc waste instead of natural sand to prepare concrete. The results show that the compressive strength of lead-zinc waste slag concrete is about 20% higher than that of ordinary concrete; and when the density increases by 30%, the linear attenuation coefficient increases by about 23%, and the γ-radiation shielding ability is significantly improved. In addition, under the same gamma radiation shielding strength, the concrete shield prepared by the lead-zinc waste slag is thinner, and is applied to the radiation-proof building material, which can effectively reduce the space. The enhancement of radiation protection is mainly due to primary lead slag and barite; Saca N, et al. studied the use of primary lead slag as admixture to prepare heavy concrete and prepared a compressive strength of 50 MPa. High-intensity gamma radiation shielding performance with linear attenuation coefficient up to 0.35 cm$^{-2}$ [31]. The apparent density of the material is closely related to the γ-ray shielding performance. The research shows that the higher the apparent density of the lead-zinc tailings radiation-proof concrete, the stronger the γ-ray shielding performance [32]. According to the strong γ-ray shielding performance of lead-zinc tailings anti-radiation concrete, it can be promoted and applied as a protective body in the field of strong radiation such as medical and nuclear industries.

5. Acknowledgments

Lead and zinc tailings have high levels of heavy metals, and non-standard stacking treatment will pose a safety hazard to residents’ quality of life. Studies have shown that the use of lead-zinc tailings to produce green building materials is one of the effective ways to deal with solid waste and turn waste into treasure. In order to further deepen the application of lead and zinc tailings in building materials and ensure that there will be no secondary pollution to the environment, the following aspects need further study:

1) Preliminary theoretical research shows that the lead-zinc tailings base polymer has superior performance; however, it lacks research on reaction mechanism, internal structure, heavy metal solidification mechanism and radiation protection performance.
(2) A more systematic study on the properties of heat insulation, thermal conductivity and corrosion resistance of porous foamed ceramics prepared by using lead-zinc tailings. High-durability inorganic porous foamed ceramics are prepared under the premise of environmentally friendly production and simple process.

(3) Lead-zinc tailings can be used to prepare radiation-proof building materials. Lead-zinc tailings with high heavy metal content have the active constituents of silicoalumina for preparing geopolymers; combined with strong solidification ability of heavy metals and little research on radiation prevention; in the new field of geopolymers, utilization Lead-zinc tailings preparation of a high-weight metal solidification rate, strong radiation protection performance, low-cost building materials to be studied.

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