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Research and Application Status and Development Trend of Alkali-Activated Binder Powder for Mine Backfill

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ABSTRACT

To improve the economic and social benefits of mining and backfill, it is necessary to find the backfill materials suitable for mineral mining, improve the various properties of the filling materials, and develop low cost, high performance new filling materials. Portland cement is neither environmentally friendly nor economical. Currently, we have begun to study and apply some industrial waste, such as slag, fly ash, and other solid wastes, with certain activities as the primary component of cementing material that will not only meet the technical requirements of filling, but also comprehensively utilize industrial waste and possess a benign, sustainable lifecycle for environmental protection. This study expounds the composition and reaction mechanism of alkali-activated binder powder used for cemented paste backfill material, summarizes the research and application status of alkali-activated binder powders, including mechanics, durability, economic and environmental, and discusses future development directions for mine binder powders. It needs to continue to expand the utilization range of solid waste and improve the utilization rate of solid waste in the future. The development and research of this binder powder plays an important role in the progress of filling technologies. Hence, the research about alkali-activated binder powder contains great development potential and broad prospects.

KEYWORDS

Mine backfill; paste; industrial waste; binder powder; green environmental protection

1 Introduction

Cemented paste backfill technology has the comprehensive advantages of safety, environmental protection, economics, and efficiency [1–4]. Among these advantages is the ability to select filling materials with reasonable ratios of material that are closely related to the filling effect, which is the critical issue of cemented paste backfill technology. A full tailings cemented paste backfill material combines a large amount of solid waste whole tailings with a certain proportion of cementing materials to prepare a toothpaste-like fluid with good fluidity, plasticity, and stability, which meets the three "no" principles, i.e., no precipitation, no segregation, and no dehydration [5]. Cementitious materials not only determine the compressive strength of backfill, but also affect the production technology and backfill cost. Ordinary Portland cement is currently the most commonly used cementing material. The cement



dosage is 180–240 kg/m³, and the cement cost accounts for 60%–80% of the filling cost [6]. Using cement as cementing material greatly increases the cost of filling and reduces the economic benefit of mining, and the cement industry consumes a significantly amount of energy and resources and creates significant pollution. The development direction goal of backfill materials is to reduce cement consumption or seek cement substitutes without reducing backfill strength.

In recent years, new cementitious materials [6-9] have been developed around low-cost cementitious materials that have primarily included alkali-activated cementitious materials, water-quenched slag, steel slag, fly ash, red mud, semi-water phosphogypsum, desulfurized gypsum, high-water materials, and coagulative stone. Amran et al. [10] showed that Ca(OH)₂ in Portland cement can stimulate the activity of blast furnace slag when the slag is used to replace part of cement. Marvila et al. [11] used blast furnace slag to prepare mortar, and the research shows that when the sodium content is in a certain range, the mortar with better performance can be prepared. Karthirvel et al. [12] prepared concrete with high compressive strength by using slag and fly ash instead of cement. Zhang et al. [13] optimized the ratio of mortar prepared by slag, fly ash, coral sand and sea water. Xiao et al. [14] showed that the direct cost of using steel slag to prepare tailings filling material is more than 100 CNY/t lower than that of using cement and slag, but its long-term performance needs to be studied. Red mud is a solid waste produced by alumina smelting in bauxite, which can be used in building materials and filling materials. However, it is difficult to develop large-scale digestion technology because of its high alkali, complex composition and radioactivity [15]. Wang et al. [16] developed green cementitious materials with desulfurized gypsum and fly ash as basic components. Calderón-Morales et al. [17] showed that it is technically feasible to produce cementitious material with phosphogypsum as raw material and has achieved satisfactory performance in some construction fields. At present, there are few research achievements on high-water materials and coagulative stone. Hamada et al. [18] showed that semi-lightweight concrete could be prepared by using nano-palm oil clinker powder. The workability of semi-lightweight concrete increased with the increase in nano-palm oil clinker powder content, but the strength of concrete decreased with the increase in nano-palm oil clinker powder content of concrete. Shahidan et al. [19] showed that using metakaolin instead of cement can improve the strength of self-compacting concrete. New materials will have absolute advantages in reducing filling costs and improving filling efficiency, but the development of new materials is still in the early stage.

Owing to the problems of full tailing fillings that contain too many fine particles and have poor adaptability of cementing materials and full tailings, and a high cement consumption and high filling cost, a green, non-toxic, and harmless alkali-activated binder powder was developed to save cement and reduce cost. Compared with cement, this binder powder has higher requirements for slurry segregation, bleeding, early setting, and early strength, and is more suitable for mine filling. The binder powder is primarily constructed of industrial waste slag, such as water quench slag from a blast furnace as the raw material. By adding a small amount of alkali, salt, or composite excitation material, the potential activity of industrial waste slag (volcanic ash material) can be activated to produce hydration cementation. The core technology is the selection of an active excitation material and a component ratio. This binder powder can use industrial waste and solid waste as much as possible, not only using the primary raw materials of slag, steel slag, and other industrial waste. In addition, its excitation material can also use phosphorus slag, alkali slag, and other industrial waste. It is also suitable for a wide range of mine filling materials and is not only able to adapt to tailings, fly ash, coal gangue, and other mine waste slag, but also can adapt to loess, silt, aeolian sand, municipal waste, and chemical solid waste. This mine binder powder has been applied to some metal mines and coal mines and is expected to become the independent cementing material development direction for industry [6].

At present, literatures on paste filling mainly focus on filling technology and filling equipment, while literatures on comprehensive research and summary of filling materials are still insufficient. Article [7] is

(8)

relatively comprehensive, but the literatures cited before 2013 are relatively old and lack of recent research summaries. Most of the literature on alkali-activated materials focuses on the experimental study of a certain kind of industrial waste, and the performance evaluation index is relatively single, lacking systematic analysis and summary of comprehensive evaluation of mechanics, durability, economic and environmental effects. Article [20] is relatively comprehensive, but it evaluates the application of alkali-activated cementitious materials in mortar and concrete rather than filling. Therefore, it is very necessary to make a systematic and comprehensive summary of the research on alkali-activated cementing materials for mine filling in recent years. In this study the present research situation and application of different proportions of mineral binder powder are described and summarized, including mechanics, durability, economic and environmental, and the future development direction of mineral binder powder is then discussed. It is helpful to deeply understand the reaction mechanism of alkali-activated binder powder and provide a theoretical basis and technical support for the preparation of high performance and low cost environmental protection cementitious materials for mining and toe improve the solid waste resource utilization rate.

2 Reaction Mechanism of Alkali-Activated Binder Powder

Research that investigates the activation mechanism of solid waste cementing is conducive to the development of new cementing materials with higher performance and lower cost and to strengthen the synergistic development of cementing materials and filling technologies [2]. The reaction mechanism of different wastes is different, including alkali activation, sulfate activation and pozzolanic effect. It may be a combination of one or more mechanisms of them. Slag can react with hydration products of steel slag (mainly Ca(OH)₂), that is, pozzolanic effect [21,22], Gypsum can react with calcium aluminate hydrate to form ettringite, which is sulfate activation [23]. Xiao et al. [14] summarized the main hydration reactions of steel slag and slag system, as shown in Eqs. (1)–(8), among them C = CaO, S = SiO₂, H = H₂O, A = Al₂O₃, F = Fe₂O₃, S = SO₄²⁻. The main hydration products include calcium silicate hydrate (C-S-H), calcium hydroxide (CH), ettringite (AFt) and aluminoferrite hydrates. Since Eqs. (1), (2), (4) and (8) produce CH and Eqs. (5)–(7) consume CH, CH is uncertain. This balance of supply and demand is crucial to alleviate the slag expansion problem.

$$C_3S + nH \rightarrow C - S - H + (3 - x)CH \tag{1}$$

$$C_2S + mH \rightarrow C - S - H + (2 - x)CH$$
⁽²⁾

$$C_3A + 6H \to C - A - H \tag{3}$$

$$C - A - H + 3C S H_2 + 14H \rightarrow C_3 A \cdot 3C S \cdot H_{32} + CH$$
(4)

$$C_4AF + 2CH + 6C\bar{S}H_2 + 50H \rightarrow 2C_3(A, F) \cdot 3C\bar{S} \cdot H_{32}$$
(5)

$$3CH + 2S \rightarrow C - S - H \tag{6}$$

$$3CH + A + 3H \rightarrow C - A - H \tag{7}$$

 $C + H \rightarrow CH$

Feng et al. [24] summarized and elaborated the reaction mechanism of binder powder contaminated with fluorine as Eqs. (9)–(18). First, the activator in a binder powder causes a hydrolyzed reaction, the formation of network crystalline compounds, and the slurry will begin to have strength. The reaction equation can be written as Eqs. (9) and (10):

$$2(Na_2nSiO_2) + Na_2nSiF_2 + mH_2O \rightarrow NaF + (2n+1)SiO_2 \cdot mH_2O$$
(9)

 $(2n+1)SiO_2 \cdot mH_2O \rightarrow (2n+1)SiO_2 + mH_2O$ ⁽¹⁰⁾

With the hydrolysis of the activator, SiO_2 , Al_2O_3 , and other oxides in the binder powder dissolved under the action of OH⁻ in the solution. This is divided into three stages. Stage 1: The silicon-oxygen bond in the vitreous is subjected to OH⁻ to generate two transition compounds, -Si-OH and -Si-O-, as Eq. (11):

$$H - O - H + OH^{-} + -Si - O - Si \rightarrow Si(OH)_{4} + HO - Si - +H - O - H + OH^{-}$$
(11)

A similar reaction occurs to the -Si-O-Al-O bond. In addition, HO-Si- anions may undergo polymerization reactions that slow down the bond breaking reaction. If the bond breaking reaction in an alkaline solution, because there exists a significant amount of OH^- , the probability of a polymerization reaction is reduced, as Eq. (12):

$$-Si - O - + Na^{+} \rightarrow -Si - O - Na$$
⁽¹²⁾

The -Si-O-Na continued reaction as Eqs. (13) and (14):

$$-Si - O - Na + OH^{-} \rightarrow -Si - O - Na, \dots OH$$
⁽¹³⁾

$$-Si - O - Na(-) - OH + Ca^{2+} \rightarrow -Si - O - Ca - OH + Na^{+}$$
(14)

 Na^+ and OH^- in the reaction can catalyze the formation of calcium silicate crystal water, and OH^- is also directly involved in the formation of calcium silicate, as Eq. (15):

$$-Si - O - + Ca^{2+} + OH^{-} \rightarrow -Si - O - Ca - OH$$
⁽¹⁵⁾

Stage 2: This stage is the stage where alkali metal ions are involved in the reaction. The disintegrated -Si-O-Si- will repolymerize to form an unstable pentagonal Si central ion according to NaOH and SiO₂ in the liquid phase. The ratio depends on the formation of a different C/S ratio and the structure of different hydrates. It also produces low-alkalinity C-S-H gels and zeolite minerals.

Stage 3: The solid phase and colloidal particles formed in the former stage form crystals, and these form the hardened body structure. When the alkalinity is higher, primarily low-alkalinity C-S-H gels and mixtures of alkali-alkaline earth compounds are formed, and some of the unstable phases also convert to relatively stable zeolite and mica mineral. These minerals have very little solubility in water. Therefore, the corrosion resistance of the material can be improved.

There exist significant amounts of SiO₂, Al₂O₃, and other oxides in the tailings and binder powder, and when it meets water, the binder powder hydrates to produce OH^- , Na^+ , and other molecules that will react with SiO₂ and Al₂O₃ to generate alumina-silicon vitreous. Then this will further the volcanic ash reaction that occurs with Ca(OH)₂, as Eqs. (16)–(18):

$$\operatorname{CaO} + \operatorname{H_2O} \to \operatorname{Ca(OH)}_2 + Q \uparrow$$
 (16)

$$xCa(OH)_2 + ySiO_2 + nH_2O \rightarrow xCaO \cdot ySiO_2 \cdot nH_2O$$
⁽¹⁷⁾

$$xCa(OH)_2 + yAl_2O_3 + nH_2O \rightarrow xCaO \cdot yAl_2O_3 \cdot nH_2O$$
⁽¹⁸⁾

Calcium silicate aluminate is a type of crystalline water compound with high bond energy. Calcium silicate hydrate is an unstable compound in the reaction, but with the action of the additive, it will gradually form a high-strength network structure over time and interact with ettringite and eventually make the slurry into a hardened body with a certain strength [24].

3 Research and Application Status of Binder Powder

Around 1980, the former Soviet Union, the former West Germany, the United States, and other countries conducted several studies on alkali-activated cementing materials and achieved initial achievements. Around 1950, China conducted research on gypsum slag cement, lime slag cement, wet slag concrete, and wet ground slag concrete and applied them in practical construction projects. In 1990, on the basis of the research conducted in other countries, application research of granulated blast furnace slag powder began, and it was first used in an airport expansion project and subway construction project in 1996 [25,26]. Li et al. [27,28] utilized a mixing ratio test using full tailings and demonstrated that the 28-d compressive strength of backfill could be increased three to five times using binder powder instead of cement. In addition, the improvement in the strength of the backfill was more obvious by increasing the amount of binder powder, and the binder powder has more cost advantages than cement. A large number of studies have found that the cementitious materials that formed after activation and the activation of wastes with certain activities had the advantages of high efficiency, low cost, good performance and could meet the requirements of tailings cementation. The raw materials used for the binder powders were slag, steel slag, fly ash, desulfurized gypsum, phosphogypsum, calcium carbide slag, and other materials.

3.1 Influence of Slag on the Binder Powder Properties

Water quenched slag is granulated blast furnace slag with a specified fineness and particle size distribution that meets the requirements of the corresponding activity indexes after being treated by drying, grinding, and other processes using high-temperature dissolved slag discharged from water quenching treatment. It is also called slag micro powder. The activity of a slag primarily depends on the in vitreous composition content ratio of CaO and SiO₂. The higher the vitreous content in a slag, the higher the ratio of CaO and SiO₂, the lower the degree of polymerization in the vitreous, and the higher the activity. The vitreous contents of most slags in China are greater than 80%, and the content ratio of CaO, and SiO₂ is approximately 1.0 [5]. Using slag powder as filling material can not only replace cement with its potential activity, but also solve the environmental pollution caused by surface accumulation. The activation of slag primarily includes mechanical activation and chemical activation. Under the action of mechanical force [14]. Studies and physical and chemical properties change with an increase in the mechanical force [14]. Studies and applications in many countries have shown that blast furnace slag can replace a portion of cement. For fine tailing particles, the cementing ability of a slag-based composite cement is stronger than that of pure Portland cement and composite silicate cement [29].

Using industrial waste slag as the base material, a suitable filling binder powder was developed in the Daizhuang Mine using laboratory testing and field verification. The filling binder powder reacts to generate acicular ettringite crystals at the early stage of hydration to achieve rapid setting and early strength effects. In the middle and late stage of hydration, volcanic ash activity in industrial waste slag, such as slag, is stimulated to generate cementitious substances, such as calcium silicate gel, to achieve the effect of sustained strength growth at a later stage. After the cemented paste backfill material is made, it takes approximately 8 h to achieve self-stability and proper support for direct roofing after solidification. In practical application, different filling cementing materials can be added to meet the needs of different engineering strengths [4]. Xu et al. [30] studied the strength properties of filling materials prepared using different cementing agent and obtained the compressive strength values shown in Fig. 1. Binder B1 and binder B2 in the figure are slags with different activators, and it can be seen that the strength of the slag group was higher than that of the cement group. Cihangir et al. [31] researched the mechanical properties of filling materials prepared with slags stimulated using different alkalis (LSS-S and SH-S), and the different tailings were studied. The compressive strength values were obtained and are shown in Fig. 2. In the figure, FT and DT were full tailings and desilted tailings, respectively, and their particle size distributions are shown in Fig. 3. It can be seen that no matter what type of tailing, the compressive

strength of the slag group was higher than that of the cement group. Marvila et al. [11] showed that the workability of mortar prepared by alkali activated slag decreases with the increase in sodium content due to the high viscosity of alkaline solution.



Figure 1: Compressive strength of backfill materials prepared using different cementing agents [30]



Figure 2: Compressive strength of filling materials prepared using different cementing agents and tailings [31]

3.2 Influence of Steel Slag on the Binder Powder Properties

Steel slag is the waste slag produced during steelmaking, and the discharge of steel slag is approximately 10%–15% of the steel output. This is the largest solid waste in the iron and steel industry. The utilization rate of steel slag in Europe has reached 65%, and the steel slag in the United States has reached a balance with the discharge. China's steel output accounts for approximately 1/5 of the world's total steel output, but the utilization rate of steel slag is only 44%. Most enterprises only extract slag steel with particle sizes less than 10 mm, and the dumped tail slag accounts for approximately 90% of the total steel slag. The research shows that hydraulic cementitious materials made by grinding steel slag with the micro-expansibility and hydraulic properties and adding the slag and desulfurized gypsum as the activator can generate calcium hydroxide, calcium silicate hydrate, calcium aluminate hydrate, and other new hardening bodies under the action of an activator and hydration medium. With high strength and stability, this material can completely

replace cement as a cementing agent, and a steel slag system full tailings mine filling material can be prepared by adding a large amount of full tailings. This type of filling material has micro-expansion performance and permeability resistance and can be widely used in mine filling [32].



Figure 3: Particle size distribution of the different tailings [31]

Dong et al. [26] used industrial wastes, such as water quenchable slag, steel slag, and a salt activator from the metallurgical industry of Angang and its surroundings, to develop a new low-cost green filling binder powder instead of cement. Guo et al. [33] developed a filling binder powder with good suspension using steel mill waste, an activator, an early strength agent, and a dispersant that effectively increased the fluidity of the filling slurry. Binder powder, instead of cement, can not only meet the requirements in the early stage, but also has the advantages of dry shrinkage, low cost, and resistance to sulfate erosion. Zhao et al. [34] studied the influence of different steel slag contents on the strength of filling materials, and the compressive strength values are shown in Fig. 4. It can be seen that when the content of steel slag was appropriate, the 3-day strength of the steel slag group was lower than that of the cement group, the 7-d strength was similar to that of the cement ground, and the 28-d strength was much higher than that of the cement group, which was similar to the law of fly ash on binder powder [6]. Both steel slag and fly ash have great influence on the later strength of filling materials.



Figure 4: Compressive strength of filling materials prepared with different steel slag contents [34]

3.3 Influence of Fly Ash on the Binder Powder Properties

Fly ash refers to the matter discharged from the flue of a power plant and collected by a dust collector after pulverized coal is burned. It has been widely used in concrete admixtures. The primary phase of fly ash are aluminosilicate vitreous and a small amount of quartz, mullite, and other minerals. A large amount of vitreous material is the main source of the gelation activity of fly ash. Fly ash can improve the fluidity of the filling slurry, the filling concentration, and the pipe artesian transport performance, and make a great contribution to the strength of the filling body during the later period [6]. Chen et al. [35] researched the influence of fly ash on the hydration performance of binder powder. Under the condition of the same age, the compressive strength of the fly ash of the 30% dosage group was the largest compared with other dosage groups. However, fly ash will delay the hydration process of binder powder, so it is necessary to add an appropriate amount of alkaline substances into the cementitious material system to assist the fly ash hydration process.

3.4 Influence of Desulfurized Gypsum on the Binder Powder Properties

Desulfurized gypsum is a byproduct of flue gas desulfurization in power plants. It is an environmentally friendly material with a low alkali content and few harmful impurities. The microstructure of desulfurized gypsum is shown in Fig. 5 [36]. The grade of dihydrate gypsum in desulphurized gypsum can reach 90%–93%. Improving the utilization rate of desulphurized gypsum can reduce the mining amount of natural gypsum. Li et al. [25] developed an early-strength filling binder powder based on low-activity water-quenched slag and addition of desulfurized gypsum, and the compressive strength of the filling body at 3-d and 7-d reached 2.038 and 3.172 MPa, respectively. According to the results of a field filling test, the strength of the 3-d, 7-d, and 28-d backfill reached 1.765, 3.615, and 5.35 MPa, which met the requirements. Compared with cement, the cost of the early-strength filling cementitious material was reduced by 48.3 CNY/t. Remarkable economic and social benefits can be obtained by applying this developed binder powder in mining applications.



Figure 5: Electron microscopy of the microstructure of desulfurized gypsum [36]

3.5 Influence of Phosphogypsum on the Binder Powder Properties

Phosphogypsum is a byproduct of the phosphoric acid industry, and it can replace cement together with industrial waste slag with an activation effect similar to fly ash to reduce cost and pollution. The mineral composition of phosphogypsum is shown in Fig. 6 [37]. Zhang [38] developed a phosphogypsum slag-

based early-strength binder powder. Using a strength verification test, it was concluded that the compressive strength of the 3-d, 7-d, and 28-d binder powder backfilled with a 1:4 cement-tailing ratio and a 78% solid content reached 1.85, 3.06, and 8.69 MPa, respectively. The minimum compressive strengths of requirement were 1.5, 2.5, and 5.0 MPa, respectively. In addition, the cost was 66% of the cost of ordinary cement. It was found that the slag powder was hydrated under the action of phosphogypsum as the primary compound activator, and the primary hydration products were hydrated calcium silicate gel and ettringite. Calcium silicate hydrate gel acts as bond, and ettringite crystals act as a support. With an extension in the hydration age, the hydration reaction changed the composition of the backfill, absorbed the water in the backfill, compacted the structure of the backfill, and thus improved its strength.



Figure 6: Mineral composition of the phosphogypsum and the tailings [37]

3.6 Other Industrial Waste

At present, the research and application of blast furnace slag is relatively sufficient, followed by steel slag, fly ash and desulfurized gypsum, and phosphogypsum is relatively less, which is in the initial stage. Blast furnace slag can improve the strength of paste, but the fluidity is poor. Steel slag can improve the late strength of paste, but the volume is unstable and easy to expand when used alone. Fly ash can improve paste fluidity and late strength, but the reaction is slow. Desulfurized gypsum and phosphogypsum can improve the paste strength, but the former is not suitable for wet environment, the latter is radioactive. Other waste for filling are carbide slag, gypsum, limestone powder, loess, etc.

Carbide slag is an industrial waste slag generated after carbide hydrolysis. Li et al. [39] found that with an increase in the carbide slag content, the setting time of the binder powder decreased, and the compressive strength of the binder powder was relatively the highest when the carbide slag content was 1%. Chen et al. [40,41] found that when the dosage of dihydrate gypsum was 4%, it had the best excitation effect on the fly-ash based binder powder. The 3-d and 28-d compressive strength of the binder powder increased by 23.8% and 25.2%, respectively, compared with the binder powder without gypsum. With an increase in the gypsum dosage, the setting time increased. The addition of limestone powder reduced the setting time of the binder powder. When the content of the limestone powder was 6%, the compressive strength was relatively high, and the amount of the chemical binding water was the largest. In addition, the number of hydration products increased. Song et al. [42] found that the strength of loess cured using the binder powder was more than two times that of cement, and the loess cured using the binder powder did not collapse when it met water. Feng

et al. [43] determined the proportion of binder powder loess filling material using a proportion test that provided a beneficial supplement to the existing filling material system. These solid waste have certain positive effects on the paste. There are red mud, silica fume, metakaolin, waste glass, rice husk ash, etc. Red mud is alkaline, silica fume can improve durability, but it needs a lot of water.

To sum up, almost all the solid waste have certain limitations when used alone, so it is necessary to use a variety of wastes together, through adjusting the ratio, comprehensive utilization, advantages and weaknesses complement each other to achieve the best effect. In the future, more industrial wastes will be applied in the field of mine filling through activation technology.

3.7 The Durability Properties of the Alkali-Activated Materials

At present, there are many researches on the mechanics of alkali-excited cementing materials, but relatively few researches on its durability. Jindal et al. [20] showed that the durability of alkali-activated mortar and concrete could be significantly improved after the addition of mineral admixtures such as slag. Okoye et al. [44,45] found that the use of silica fume in alkali-activated concrete enhanced its durability. The concrete prepared by ordinary cement showed obvious deterioration and cracking in 2% H₂SO₄, 5% NaCl, and 5% Na₂SO₄ solution, while the alkali-activated concrete containing silica fume did not show any obvious deterioration and cracking. Ahmad et al. [46] studied the influence of admixtures such as silica fume, metakaolin, MgO and cement clinker on sulfate and acid corrosion resistance of mortar. A 270-d durability test of alkali-activated mortar was carried out with sodium sulfate and sulfuric acid solution. The results show that there is no discoloration, mass or length change of alkali-activated mortar samples during immersion in sulfate solution, and the loss range of mortar compressive strength is 1% to 17%. However, mortar samples exposed to sulfuric acid solution cracked and deteriorated, the strength loss ranges from 15% to 46%. The alkali-activated mortar containing 4.5% metakaolin has the least strength loss against sulfate and acid erosion. Alkali-activated mortar has good resistance to sulfate and acid erosion due to its high content of calcium and alumino-silicates materials, which leads to high degree of geopolymerization.

The calcium content of alkali-activated binder powder prepared from different waste is different, which can be divided into calcium-free, low-calcium and high-calcium. The representative materials are metakaolin, fly ash and blast furnace slag, respectively. The products of calcium-free or low-calcium systems are mainly zeolite gels, while the products of high-calcium systems are calcium aluminum silicate hydrate gels with a low Ca/Si ratio. Different calcium content results in different durability of materials. However, because of the inherent composition and structural characteristics of alkali-activated material, its resistance to sulfate and acid attack is superior to that of ordinary cement. As can be seen from the above literature, silica fume contributes greatly to the durability of materials. Silica fume can effectively refine pore size while increasing density, thus improving Cl[−] permeability resistance. Therefore, the durability of alkali-activated materials can be improved by increasing the degree of waste reactive polymerization and structure density and refining the pore structure. In addition, the durability of alkali-activated using the same method as cement and concrete. However, they are different in reaction mechanism, product formation and microstructure, so whether the same method can be used needs to be further verified in future studies.

3.8 Environmental and Economic Perspective of the Binder Powder

The production of Portland cement releases CO_2 and consumes a lot of energy in the heating process [47]. The use of slag, silica fume, volcanic ash, fly ash, steel slag and other industrial waste, partly replace ordinary cement, can effectively improve the environment. The influence of cement on environment can be reduced by developing alkali-activated binder powder [48]. Alkali-excited materials do not require very high temperatures during production, thus reducing high fuel consumption. They can

be used as a supplementary cementing material to ordinary cement, thereby reducing CO_2 emissions from the cement industry [49]. Alkali-activated materials as secondary raw materials provide a means of reuse and recovery of waste, avoiding waste disposal problems and associated environmental impacts. The environmental sustainability of alkali-activated materials is highly dependent on alkali-activated agents, and the type, content and curing mode of the activator are the influencing factors to determine their cost and environmental impact [50]. Abdulkareem et al. [50] studied the environmental impact and economic cost of alkali-activated mortar prepared from waste glass and rice husk ash. The results show that compared with traditional alkali-activated mortar, the emission reduction of climate change, fossil depletion, terrestrial acidification and photochemical ozone generation of alkali-activated mortar prepared by waste glass and rice husk ash can reach 62%, 61%, 76% and 56%, respectively. In conclusion, if the use of chemically modified waste-derived activators can reduce or replace traditional alkali-activators, they are a promising alternative for improving the environmental performance of alkalized materials. Cost analysis results show that compared with traditional alkali-activated mortar, the alkali-activated mortar prepared by waste glass and rice husk ash can save 19% cost. Xiao et al. [14] showed that the direct cost of using steel slag to prepare tailings filling material is more than 100 CNY/t lower than that of using ordinary cement and slag. Compared with ordinary cement, the cost of the early-strength filling material based on low-activity waterquenched slag and addition of desulfurized gypsum was reduced by 48.3 CNY/t [24]. The cost of phosphogypsum slag-based binder powder was 66% of the cost of the ordinary cement [37].

The economic benefits brought by the reuse of industrial waste include the profit from product sales, the cost saved by reducing pollutant emissions, saving water resources and reducing the use of land. The environmental and social benefits after the effective utilization of solid waste include solving the environmental problems brought by the process of waste storage and reducing the impact of human activities on the living environment. Moreover, the use of industrial waste in filling can reduce the damage to the natural environment and formation structure, and avoid man-made disasters such as collapse and pollution. The preparation cost of binder powder mainly includes the cost of industrial waste recovery and treatment, transportation cost, etc. Therefore, in the future, the cost can be further reduced by using on-site preparation, simplifying the solid waste treatment process, improving the efficiency of recovery equipment, etc. At the same time, continue to develop environmentally friendly raw materials and activators, reduce the consumption of manpower and energy and the pollution to environment in the development process, achieve the maximum utilization of resources and minimize pollution emissions, and promote the coordination and harmonious development between human and nature.

4 Development Trend of Binder Powder

With the continuous development of mineral exploitation and deep processing of ore resources, more industrial solid wastes will be generated. This will result in resource waste and environmental pollution, and the utilization rates of most solid wastes are still low. In addition, mine filling requires a large number of cementing materials and aggregate, and the cost of cement of traditional filling materials can reach more than 2/3 of the filling cost [6]. Using activation technology to recycle industrial waste not only reduces cement consumption and filling material cost, but also solves environmental problems caused by waste stockpiling, providing an important method for the efficient utilization of industrial waste. The development of a low cost, widely sourced, easy to use binder can achieve the necessary physical and mechanical properties of the active cementing materials, and additives as mine binder powder can reduce cement consumption without reducing the strength of backfill. This is the direction of binder powder development. Therefore, more industrial wastes can be used in the field of mine filling.

Full tailings cemented paste backfill material can efficiently use a large amount of tailings waste as an aggregate, and the content of fine tailings with particle sizes less than 75 µm in the full tailings is relatively high. Therefore, it is also a development trend in binder powder to improve the adaptability of binder powder

by utilizing full tailings and filling technology. Industrial waste is used to develop low-cost and highperformance new filling binder powders suitable for filling the fine aggregates of full tailings instead of cement, thus improving the strength of the cemented filling body of full tailings, reducing the amount of cementing material, and reducing the cost of the filling material.

Improving the early strength of cemented backfill is a development focus of binder powder backfill materials. First, increasing the early strength of the filling body can shorten the mining and filling cycle, shorten the time for equipment to enter the upper portion of the filling body and adjacent stopes, increase the effective time of the filling mining operation, and improve the production capacity of ore hill and ore mining efficiency. Second, improving the early strength of backfill can also improve the production environment of underground stope and achieve high efficiency and safety production [6]. In addition, increasing the early strength of the backfill can correspondingly reduce the amount of cementing material, thus reducing the cost.

Based on the above development status of mine filling binder powder, it can be concluded that the primary development trend of filling cementing materials in the future will be to expand the utilization range of solid waste, improve the utilization rate of solid waste, and study binder powders that are more suitable for mine filling instead of cement. In addition, improving the adaptability of binder powder and full tailings and promoting the synergic development of binder powder and filling technology will be important goals. These achievements will improve the early strength of the binder powder filling body, improve the material cost, and promote the development of binder powder in the direction of sustainable economic and environmental protection.

5 Conclusion and Prospect

In this study, the reaction mechanism, research and application status, and future development trend of alkali-activated binder powders were described from the perspective of the raw material composition of binder powder for mine filling. The primary conclusions and prospects are as follows:

- (1) The effective method to reduce the filling cost was to select cheap filling materials and use a reasonable slurry mixing ratio on the premise of ensuring the filling effect. The excellent cost performance of a binder powder and the resource utilization of solid waste will greatly reduce the filling cost. In addition, binder powder-based cemented paste backfill material will solve the pollution problem caused by industrial waste to the ecological environment, which is of great significance for the sustainable exploitation of resources.
- (2) The raw materials of a binder powder are currently primarily slag, steel slag, fly ash, desulfurized gypsum, phosphogypsum, and calcium carbide slag. According to laboratory testing and on-site verification, it was shown that industrial waste slag can achieve good results and can replace cement, meet engineering needs, and achieve remarkable economic and social benefits. However, the utilization rate of industrial waste remains low.
- (3) The development trend of filling cementing materials in the future is to expand the utilization range of solid waste, improve the utilization rate of solid waste, and study binder powders that are more suitable for mine filling instead of ordinary cement. These strategies will meet the requirements for high-efficiency mining technology, reduce the cost of materials, and promote the development of an alkali-activated binder powder in the direction of sustainable, economic benefits and environmental protection.
- (4) Future recommendations include research and development of more sustainable raw materials that do not require much process such as grinding, granulation and high temperature heating, and have zero or low pollution. Further study the scale of supply and demand of these materials and their feasible applications, and fully expand the scope of solid waste utilization. The other is to use XRD, SEM-EDS, FTIR, NMR and other microscopic analysis techniques to characterize the microstructure of alkali-activated materials in detail.

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References

- 1. Wu, A. X., Yang, Y., Chen, H. Y., Chen, S. M., Han, Y. (2018). Status and prospects of paste technology in China. *Chinese Journal of Engineering*, 40(5), 517–525. DOI 10.13374/j.issn2095-9389.2018.05.001.
- 2. Wang, L. H., Bao, A. Y., Luo, Y. Y. (2017). Development and outlook on the filling method in China. *Mining Research and Development*, 37(3), 1–7. DOI 10.13827/j.cnki.kyyk.2017.03.001.
- Liu, Q., Zhang, X. W. (2016). Overview of the research progress of the paste backfill technology in China. *Modern Mining*, (5), 1–5.
- 4. Yue, T., Feng, R. M., Li, X. S. (2012). Paste stowing mining technology and its application prospect. *Coal Mining Technology*, *17(6)*, 72–74. DOI 10.13532/j.cnki.cn11-3677/td.2012.06.025.
- 5. Wu, A. X., Wang, Y., Wang, H. J. (2016). Status and prospects of the paste backfill technology. Metal Mine, (7), 1-9.
- 6. Wu, A. X., Jiang, G. Z., Wang, Y. M. (2018). Review and development trend of new type filling cementing materials in mines. *Metal Mine*, (3), 1–6.
- 7. Tariq, A., Yanful, E. K. (2013). A review of binders used in cemented paste tailings for underground and surface disposal practices. *Journal of Environmental Management, 131,* 138–149. DOI 10.1016/j.jenvman.2013.09.039.
- Cihangir, F., Ercikdi, B., Kesimal, A., Turan, A., Deveci, H. (2012). Utilisation of alkali-activated blast furnace slag in paste backfill of high-sulphide mill tailings effect of binder type and dosage. *Minerals Engineering*, 30, 33–43. DOI 10.1016/j.mineng.2012.01.009.
- Cihangir, F., Ercikdi, B., Kesimal, A., Deveci, H., Erdemir, F. (2015). Paste backfill of high-sulphide mill tailings using alkali-activated blast furnace slag effect of activator nature, concentration and slag properties. *Minerals Engineering*, 83, 117–127. DOI 10.1016/j.mineng.2015.08.022.
- Amran, M., Murali, G., Khalid, N. H. A., Fediuk, R., Ozbakkaloglu, T. et al. (2021). Slag uses in making an ecofriendly and sustainable concrete: A review. *Construction and Building Materials*, 272, 121942. DOI 10.1016/j.conbuildmat.2020.121942.
- 11. Marvila, M. T., Azevedo, A. R. G., Matos, P. R., Monteiro, S. N., Vieira, C. M. F. (2021). Rheological and the fresh state properties of alkali-activated mortars by blast furnace slag. *Materials*, *14*, 2069. DOI 10.3390/ma14082069.
- Kathirvel, P., Gunasekaran, M., Sreekumaran, S., Krishna, A. (2020). Effect of partial replacement of ground granulated blast furnace slag with sugarcane bagasse ash as source material in the production of geopolymer concrete. *Material Science*, 26, 477–481. DOI 10.5755/j01.ms.26.4.23602.
- Zhang, B., Zhu, H., Shah, K. W., Feng, P., Dong, Z. (2021). Optimization of mix proportion of alkali-activated slag mortars prepared with seawater and coral sand. *Construction and Building Materials*, 284, 122805. DOI 10.1016/j. conbuildmat.2021.122805.
- Xiao, B. L., Wen, Z. J., Miao, S. J., Gao, Q. (2021). Utilization of steel slag for cemented tailings backfill: Hydration, strength, pore structure, and cost analysis. *Case Studies in Construction Materials*, 15, e00621. DOI 10.1016/j.cscm.2021.e00621.
- 15. Wang, S. H., Jin, H. X., Deng, Y., Xiao, Y. D. (2021). Comprehensive utilization status of red mud in China: A critical review. *Journal of Cleaner Production, 289,* 125136. DOI 10.1016/j.jclepro.2020.125136.
- Wang, T., Wu, K., Wu, M. (2021). Development of green binder systems based on flue gas desulfurization gypsum and fly ash incorporating slag or steel slag powders. *Construction and Building Materials*, 265, 120275. DOI 10.1016/j.conbuildmat.2020.120275.
- Calderón-Morales, B. R. S., García-Martínez, A., Pineda, P., García-Tenório, R. (2021). Valorization of phosphogypsum in cement-based materials: Limits and potential in eco-efficient construction. *Journal of Building Engineering*, 44, 102506. DOI 10.1016/j.jobe.2021.102506.

- Hamada, H. M., Alattar, A. A., Yahaya, F. M., Muthusamy, K., Tayeh, B. A. (2021). Mechanical properties of semi-lightweight concrete containing nano-palm oil clinker powder. *Physics and Chemistry of the Earth*, 121, 102977. DOI 10.1016/j.pce.2021.102977.
- Shahidan, S., Tayeh, B. A., Jamaludin, A. A., Bahari1, N. A. A. S., Mohd, S. S. et al. (2017). Physical and mechanical properties of self-compacting concrete containing superplasticizer and metakaolin. *IOP Conference Series: Materials Science and Engineering*, 271, 12004. DOI 10.1088/1757-899X/271/1/012004.
- 20. Jindal, B. B. (2019). Investigations on the properties of geopolymer mortar and concrete with mineral admixtures: A review. *Construction and Building Materials, 227*, 116644. DOI 10.1016/j.conbuildmat.2019.08.025.
- Feng, Y., Yang, Q., Chen, Q., Kero, J., Andersson, A. et al. (2019). Characterization and evaluation of the pozzolanic activity of granulated copper slag modified with CaO. *Journal of Cleaner Production*, 232, 1112– 1120. DOI 10.1016/j.jclepro.2019.06.062.
- 22. Kanchanason, V., Plank, J. (2019). Effect of calcium silicate hydrate-polycarboxylate ether (C-S-H-PCE) nanocomposite as accelerating admixture on early strength enhancement of slag and calcined clay blended cements. *Cement Concrete Research*, *119*, 44–50. DOI 10.1016/j.cemconres.2019.01.007.
- Allahverdi, A., Maleki, A., Mahinroosta, M. (2018). Chemical activation of slag-blended portland cement. *Journal of Building Engineering*, 18, 76–83. DOI 10.1016/j.jobe.2018.03.004.
- 24. Feng, C. G. (2018). *Experimental study on sand filling material in old empty area of coal mine (Ph.D. Thesis)*. China Coal Research Institute.
- 25. Li, M. H. (2015). Research on the hydration mechanism and development of early strength filing materials base on the low active slag (Ph.D. Thesis). University of Science and Technology Beijing.
- 26. Dong, P. X. (2017). Research on cementitious materials and rheological properties of the whole tailings in Angang Iron (Ph.D. Thesis). University of Science and Technology Beijing.
- Li, H., Wu, A. X., Han, B., Chen, H. (2016). Effect of a new type of binder on the strength of cemented backfill. *Metal Mine*, (1), 8–12.
- 28. Wang, A. F., Yang, Z. Q., Gao, Q., Sun, G. H. (2016). Comparison test of backfilling strength between cement and glue-powder. *Metal Mine*, (7), 109–112.
- 29. Zheng, J. R., Gu, D., Zhao, X. F. (2015). The influence of types and content of binders on the properties of cemented paste backfill. *The Journal of Nonferrous Metals*, 67(6), 83–88. DOI 10.3969/j.issn.1671-4172.2015.06.018.
- Xu, W. B., Cao, P. W., Tian, M. M. (2018). Strength development and microstructure evolution of cemented tailings backfill containing different binder types and contents. *Minerals*, 8, 167. DOI 10.3390/min8040167.
- Cihangir, F., Akyol, Y. (2018). Mechanical hydrological and microstructural assessment of the durability of cemented paste backfill containing alkali activated slag. *International Journal of Mining, Reclamation and Environment, 32,* 123–143. DOI 10.1080/17480930.2016.1242183.
- 32. Zhang, J. W. (2014). *Research on the backfilling materials of iron mine (Ph.D. Thesis)*. University of Science and Technology Beijing.
- 33. Guo, J. L., Xu, J. L., Bai, J. (2015). Test for tailings cemented filling using glue-powder. Modern Mining, (7), 45-46.
- Zhao, Y. L., Ma, Z. Y., Qiu, J. P., Sun, X. G., Gu, X. W. (2020). Experimental study on the utilization of steel slag for cemented ultra-fine tailings backfill. *Powder Technology*, 375, 284–291. DOI 10.1016/j.powtec.2020.07.052.
- Chen, H. T., Cheng, W. M., Peng, D. X., Wang, J. L., Liu, B. W. (2016). Impact of fly ash on the performance of mine filling adhesive powder. *Journal of Shandong University of Science and Technology: Natural Science*, 35(6), 37–42. DOI 0.16452/j.cnki.sdkjzk.2016.06.006.
- Ma, Y. T., Nie, Q. K., Xiao, R., Hu, W., Han, B. Y. et al. (2020). Experimental investigation of utilizing waste flue gas desulfurized gypsum as backfill materials. *Construction and Building Materials*, 245, 118393. DOI 10.1016/j. conbuildmat.2020.118393.
- Jiang, G. Z., Wu, A. X., Wang, Y. M., Lan, W. T. (2018). Low cost and high efficiency utilization of hemihydrate phosphogypsum: Used as binder to prepare filling material. *Construction and Building Materials*, 167, 263–270. DOI 10.1016/j.conbuildmat.2018.02.022.

- 38. Zhang, G. C. (2015). Development for early strength cementing material and study on filling slurry pipeline transportation characteristics in jinchuan nickel mine (Ph.D. Thesis). University of Science and Technology Beijing.
- Li, G. L., Zhang, B. Y., Zhu, A. Q., Li, Y. J., Li, B. L. et al. (2017). Research on effect of dosage of carbide slag on the performance of filling cementing powder. *Multipurpose Utilization of Mineral Resources*, (2), 89–91. DOI 10.3969/j.issn.1000-6532.2017.01.020.
- 40. Chen, H. T., Li, Y. J., Zhang, B. Y. (2016). Gypsum effect on performance of mine filling adhesive powder. *Coal Technology*, 35(3), 14–16. DOI 10.1330/j.cnki.ct.2016.03.006.
- 41. Chen, H. T., Hu, X. M., Cheng, W. M. (2016). Impact study of stone powder on properties of mine filling glue powder. *Safety in Coal Mines*, 47(3), 48–51. DOI 10.13347/j.cnki.mkaq.2016.03.014.
- 42. Song, W. P., Li, X. D. (2015). Experiment study on cement adhesive powder bound loess applied as grouting material. *2015 National Engineering Geology Conference*, pp. 567–572. Geological Society of China. Beijing: Science Press.
- Feng, C. G., Gao, G. R., Zhang, T. C. (2016). Experiment study on cement adhesive powder bound loess applied as backfill material of mine goaf. *Mine Construction Technology*, 37(6), 35–38. DOI 10.19458/j.cnki.cn11-2456/ td.2016.06.010.
- 44. Okoye, F. N., Durgaprasad, J., Singh, N. B. (2016). Effect of silica fume on the mechanical properties of fly ash based-geopolymer concrete. *Ceramics International*, 42(2), 3000–3006. DOI 10.1016/j.ceramint.2015.10.084.
- 45. Okoye, F. N., Prakash, S., Singh, N. B. (2017). Durability of fly ash based geopolymer concrete in the presence of silica fume. *Journal of Cleaner Production*, *149*, 1062–1067. DOI 10.1016/j.jclepro.2017.02.176.
- Ahmad, M. R., Chen, B., Shah, S. F. A. (2020). Influence of different admixtures on the mechanical and durability properties of one-part alkali-activated mortars. *Construction and Building Materials*, 265, 120320. DOI 10.1016/j. conbuildmat.2020.120320.
- 47. Andrew, R. M. (2018). Global CO₂ emissions from cement production. *Earth System Science Data*, *10*, 195e217. DOI 10.5194/essd-10-195-2018.
- 48. Provis, J. L. (2018). Alkali-activated materials. *Cement Concrete Research, 114,* 40e48. DOI 10.1016/j. cemconres.2017.02.009.
- 49. Luukkonen, T., Abdollahnejad, Z., Yliniemi, J., Kinnunen, P., Illikainen, M. (2018). One-part alkali-activated materials: A review. *Cement Concrete Research, 103,* 21e34. DOI 10.1016/j.cemconres.2017.10.001.
- Abdulkareem, M., Havukainen, J., Nuortila-Jokinen, J., Horttanainen, M. (2021). Environmental and economic perspective of waste-derived activators on alkali-activated mortars. *Journal of Cleaner Production*, 280, 124651. DOI 10.1016/j.jclepro.2020.124651.