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Application Strategy of Industrial Waste Gypsum in Cement Production

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Abstract: The paper primarily analyzes the application strategy of industrial waste gypsum in the cement production process, encompassing an introduction to industrial waste gypsum and its principal application strategies in cement production. According to the research, in modern cement production processes, industrial waste gypsum serves not only as a retarder and mineralizer but also for cement co-production. It is hoped that this analysis can offer valuable insights into the utilization of industrial waste gypsum and the enhancement of cement production process quality.

Keywords: Industrial waste gypsum; Cement production; Cement coagulant; Cement mineralizer; Coproduction cement

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1. Foreword

In cement production technology, industrial waste gypsum plays a crucial role. Consequently, the application strategy of industrial waste gypsum in cement production has garnered significant attention from cement production enterprises, researchers, and related personnel. In studying its application strategy, researchers should first clarify the fundamental aspects, main types, and advantages of applying industrial waste gypsum. Then, they should integrate this knowledge with the actual production requirements of cement products and apply it judiciously to the cement production process. This approach can further enhance the effectiveness of utilizing industrial waste gypsum to meet the demands of cement production technology and improve the quality of cement products.

2. Industrial waste gypsum

2.1. Basic overview

Industrial waste gypsum is a residue generated from industrial processes, primarily consisting of calcium sulfate. Typically, industrial processes yield significant amounts of industrial waste gypsum; for instance, the production of 1 ton of phosphoric acid can result in 5 tons of phosphogypsum emissions [1]. Consequently, in many countries, the emissions of waste gypsum from industrial activities have surpassed those of natural gypsum. If these waste gypsum materials are not utilized scientifically and efficiently, they will not only occupy considerable land resources for storage but also pose a risk of water and soil pollution. In severe cases, they may even pose health hazards to humans [2].

2.2. Main types

Currently, the main types of industrial waste gypsum comprise the following:

(1) Gypsum tailings: These are substances found in impurities discharged during mining operations. They primarily consist of anhydrite and dihydrate gypsum. The main chemical components include sulfur trioxide and calcium oxide.

(2) Anhydrite: This refers to impurities discharged during industrial production. The calcium carbonate content of such industrial waste gypsum can reach 80%, indicating good quality and crystallization effects. Anhydrite also boasts higher hardness compared to dihydrate gypsum.

(3) Chemical gypsum: This type of gypsum originates from impurities discharged by chemical and electric power industries. Its main component is industrial waste slag of the calcium sulfate type. Chemical gypsum generally has a finer particle size and higher quality compared to natural gypsum [3].

2.3. Application advantage

In the modern industrial production sector, industrial waste gypsum has emerged as a significant advantage in various applications. Particularly in the cement production process, its application yields remarkable results [4]. This is because industrial waste gypsum contains a considerable amount of unreacted calcium carbonate, as well as soluble sodium and potassium salts and other substances. These impurities not only enhance the hydration of cement but also stimulate the interaction among different cement mixtures [5]. Therefore, the judicious utilization of industrial waste gypsum in cement production can substantially enhance the quality of the resulting products.

3. Main application strategies of industrial waste gypsum in cement production

3.1. Application strategies of cement retarder

In the cement production process, industrial waste gypsum serves as a retarder to effectively regulate the setting time of cement products [6]. This effect stems from the reaction between C_4AF and CA_3 in the cement clinker with gypsum, resulting in the formation of hydrated calcium ferric sulfate and hydrated calcium chloride sulfate. These hydration products adhere to the surface of clinker particles, forming a film that seals the hydrated components, delaying the hydration process until a certain pressure value is reached and the film fractures, allowing cement particles to continue hydrating.

When selecting a cement retarder, gypsum tailings should be limited to 3.5% of the total SO_3 content in cement. However, the SO_3 content in gypsum should not be too low, as it may adversely affect the performance and shrinkage deformation of the cement [7]. Ideally, the SO_3 content in gypsum should exceed 35%. Practical applications have shown that qualified gypsum tailings as a retarder do not affect the volume stability or setting time of cement products, nor do they adversely affect the strength within 3 days and 28 days.

Dihydrate gypsum and anhydrite also exert a significant retarding effect on cement products. Previous practices have shown that in specific cement production processes, if the total SO_3 content in the cement product is kept at 3.5% or lower, the normal setting time of the cement product remains unaffected [8]. Currently, anhydrite is widely utilized in the production of fly ash and slag cement. This is because anhydrite and calcined anhydrite possess a dissolution rate that aligns with that of fly ash and slag. Their application in coal ash and slag cement production effectively enhances their activity, resulting in higher strength [9].

From previous practical applications, it is evident that in the cement production process, the quantities of chemical gypsum and natural gypsum are essentially the same. Through the judicious application of this type of industrial waste gypsum, the cement's setting time can conform to technical standards. Upon further investigation, it was discovered that after 3 days of cement curing, all calcium sulfate within it would combine into hydrated calcium sulfoaluminate, eliminating any free calcium sulfate within the cement. In such cases, the incorporation of any type of chemical gypsum into the cement production process to replace natural gypsum will not adversely affect the cement's strength. Based on this finding, in specific cement production processes, production enterprises can directly employ various types of chemical gypsum as a retarding agent to substitute natural gypsum [10].

To reasonably determine the application effect of industrial waste gypsum in the cement production process, researchers conducted chemical analyses on the cement under conditions involving fluogypsum, phosphogypsum, and natural dihydrate gypsum as retarders through experiments. The tests revealed that when all retardants were controlled at 4% of the total cement mass, the SO_3 content in the cement was below 3%, with clinker comprising 84% and slag 12%. Additionally, further investigation indicated that to enhance cement product quality, production enterprises should regulate the fineness of the cement powder, ensuring that the screening margin in the 0.08 mm^2 hole screen does not exceed 6%.

Comparing the test results for strength, stability, final setting time, and other indicators, it was observed that whether fluorine gypsum or phosphogypsum was used as a retarder, the strength, stability, and final setting time at 3 days and 28 days met practical application standards and industry requirements. Moreover, when phosphogypsum replaced dihydrate gypsum, the strength of cement products at 3 days and 28 days setting duration was higher. This suggests that both fluorogypsum and phosphogypsum can serve as retarders in the cement production process, replacing natural gypsum.

3.2. Application strategies of cement mineralizer

The reasonable application of industrial waste gypsum containing fluorine, phosphorus, sulfur, and other components to cement raw materials can effectively decompose $CaCO_3$. This process facilitates the premature formation of the clinker's liquid phase, thereby reducing the sintering temperature of cement and the viscosity of the liquid phase. Consequently, it promotes the crystallization of the liquid phase, facilitating the reaction between the solid and liquid phases. Ultimately, this leads to the formation of a transition phase more conducive to the creation of clinker minerals and the generation of new clinker minerals. These minerals are the result of mineralization produced by the calcination of a small amount of elements during clinker formation.

Whether it's gypsum tailings, anhydrite, or various chemical gypsum, they can serve as mineralizing agents in the cement production process [13]. As an effective mineralizer and co-solvent, gypsum can lower the liquid phase temperature by over 100°C and significantly reduce viscosity and surface tension. However, in practical applications, the amount of gypsum cannot increase the SO_3 content in cement clinker to more than 3% of the total cement. The primary mineralization of fluorogypsum comes from fluoride, which can affect the stability of the calcium carbonate rhombohedral structure and the stability of carbonate and silicate groups. Yet, in practical application, the fluoride content in cement clinker should be kept within 0.6% to effectively ensure the mechanical strength of cement products.

When phosphogypsum is used as a mineralizing agent, its phosphorus content affects the calcination process of the entire cement clinker, accelerating the reaction, facilitating the combination of lime in the solid phase, and creating favorable conditions for rapid mineral crystallization in the presence of the liquid phase [14]. Previous practice has shown that fluorogypsum and phosphogypsum are excellent mineralizing agents in the cement production process. Additionally, gypsum tailings and chemical gypsum also exhibit good mineralization properties in cement production.

Hence, in specific cement production processes, cement enterprises should consider factors such as the main chemical composition of raw materials and production process conditions to make a reasonable choice regarding the type and amount of gypsum mineralizing agent. Moreover, the ratio between industrial waste gypsum mineralizers and cement raw materials should be adjusted according to actual production circumstances to ensure the quality of cement production.

To validate the mineralization of industrial waste gypsum in the cement production process, researchers conducted a study where they specifically fired cement clinker with a strength of 70MPa in the laboratory. This clinker, characterized by its loose and porous structure and increased brittleness, is prone to grinding and crushing, yet meets industry standards for physical properties. By using fluorogypsum as a mineralizing agent, researchers effectively addressed quality issues with such cement products, increasing their output by 12% compared to the original. In the test, the selected fluorogypsum had an SO_3 content of 46.30% and a CaF_2 content of 4.76%, with its quantity added to the cement raw material accounting for 3.5% of the total cement mixture's quality.

The comparative analysis of the test results reveals a significant improvement in the mechanical properties of the cement products obtained when fluorogypsum is used as a mineralizing agent and added to the cement production process. Further experimental studies have shown that besides fluorine gypsum, other types of industrial waste gypsum used as mineralizing agents in the cement production process also lead to cement products with enhanced mechanical properties [15]. This indicates that industrial waste gypsum is highly suitable for use as mineral compounds in the cement production process. Through the judicious application of such minerals, the mechanical properties of cement products can be effectively enhanced, thereby improving the overall quality of the products.

3.3. Application strategies of cement co-production

In addition to serving as a retarder and mineralizing agent, industrial waste gypsum can also be utilized in the cement co-production process to ensure the quality of cement products. For instance, phosphogypsum, a vital phosphorus resource, undergoes modification to become anhydrous gypsum or semi-hydrous gypsum during the concrete cement co-production process. It is then dried, mixed with coke and other materials, and added to the rotary kiln for melting. This facilitates effective blending between the gypsum and cement materials, thereby facilitating cement co-production. However, due to the substantial initial investment required for this technology, many small and medium-sized cement production enterprises have yet to adopt it, thereby limiting its application to some extent. Consequently, future research on cement production processes and the application of industrial waste gypsum should include comprehensive investigations into its utilization in cement co-production, aiming to broaden its application scope.

4. Conclusion

In summary, industrial waste gypsum shares similar properties and application functions with natural gypsum, yet its output surpasses that of natural gypsum by a significant margin. With this in mind, in the concrete cement production process, production enterprises, researchers, and staff can judiciously integrate industrial waste gypsum, thereby enhancing the quality of cement products and achieving the rational application of industrial waste gypsum. This approach not only expands the options for utilizing coagulants and mineralizing agents in the cement production process, leading to cost savings but also facilitates the timely and effective recycling of industrial waste gypsum. Consequently, it helps mitigate the adverse effects of excessive accumulation of industrial waste gypsum on the environment and human health.

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Disclosure statement

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