

Pretreatment and comprehensive utilization of phosphogypsum from industrial solid waste

Baoxiang Kang¹, Qinghe Zhang², Ying Wang¹, Jiang Ma³

1. School of Transportation Engineering, Xi'an Vocational University Of Automobile, Xi'an 710600, China

2. School of Architectural Engineering, Xuzhou College of Industrial Technology, Xuzhou 221000, China

3. Shaanxi Construction Engineering Fifth Construction Group Co., LTD., Xi'an 710000, China

Abstract: Due to the special nature of industrial solid waste phosphogypsum itself, it can be effectively used in many fields such as chemical industry, agriculture, transportation and so on. For example, phosphogypsum can be used in the construction field to make gypsum board. Industrial solid waste phosphogypsum will not only have an impact on environmental quality, but also threaten people's health, so the application of the corresponding method of phosphogypsum pretreatment, not only can reduce pollution, but also can provide an important guarantee for human development and survival. Therefore, this paper analyzes the main causes of industrial solid waste phosphogypsum and the influence of impurities in industrial solid waste phosphogypsum. At the same time, it also discusses the pretreatment of industrial solid waste phosphogypsum and the comprehensive utilization of industrial solid waste phosphogypsum.

Key words: Industrial solid waste; Phosphogypsum; Pretreatment; Comprehensive utilization

At present, the rapid development of science and technology and economy in China can effectively promote the production and development of industrial industries, and the demand for phosphoric acid in various domestic industries is gradually increasing. However, in the production of phosphoric acid, more industrial solid waste phosphogypsum will be produced. If a large amount of phosphogypsum is discharged, it will not only pollute the land, but also cause great harm to the surrounding ecosystem, seriously affecting people's normal life and production. Therefore, in order to effectively realize the coordinated development of environmental protection and economy, it is necessary to do a good job in the pretreatment and comprehensive application of industrial solid waste phosphogypsum, so as to significantly improve the application efficiency of industrial solid waste phosphogypsum.

I. Industrial solid waste phosphogypsum main causes

Wet method is the main method of phosphoric acid production in our country at present, through the application of this method can produce a lot of phosphoric acid, before the use of phosphoric acid must be purified and purified, the formation of phosphate, and finally transform it into phosphogypsum based solid, so in the phosphoric acid production process will inevitably produce a large number of industrial solid waste phosphogypsum. In addition, in recent years, one of the important factors for the high production of phosphogypsum in China is the large-scale application of industrial compound fertilizer in the agricultural industry. Compared with other industrial solid wastes, the chemical properties of phosphogypsum are relatively special. The main state of phosphogypsum is white powder, which belongs to a crystal and has good crystallinity. The solid waste phosphogypsum that has not been purified and purified has more impurities, usually showing black powder or light gray powder. Most of the solid waste phosphogypsum contains 25% water, which has poor mobility and contains a small amount of other elements. Usually at 100°C the solid waste phosphogypsum shows a free water state, when the solid waste phosphogypsum temperature reaches 175°C, it will be converted into semi-aqueous gypsum, and when the temperature reaches 200°C, it will be converted into anhydrous gypsum. Although the untreated phosphogypsum has great application and development potential in many industries, it has not been developed at present. Therefore, if we want to effectively solve the problem of phosphogypsum accumulation, we must do a good job of pretreatment.

II. The impact of impurities in phosphogypsum of industrial solid waste

Due to the differences in control conditions and production processes between various production enterprises, even the same enterprises in the actual production process, due to the long-term open-air stacking of phosphogypsum or the different production years, will have a greater impact on the impurity content of phosphogypsum, especially the phosphorus content and fluorine content, will also affect the overall nature of phosphogypsum. Phosphorus can not only extend the setting time of phosphogypsum, but also reduce the strength of phosphogypsum. Precipitated phosphorus and soluble phosphorus are the main forms of phosphorus, among which soluble phosphorus has the greatest influence on its performance.

Soluble phosphorus mainly exists on the surface of dihydrate gypsum crystal, and the soluble phosphorus content will increase with the increasing of phosphogypsum particle size. Related studies show that different forms of soluble phosphorus can have different effects on the properties of phosphogypsum, among which the most significant effect is H₃PO₄. In the hydration reaction, the soluble phosphorus in phosphogypsum will form Ca₃(PO₄)₂, which is insoluble and water, and usually exists on the surface of the dihydrate crystal, which has a certain obstacle to the dissolution of the dihydrate crystal, and can prolong the condensation effect of phosphogypsum.

In addition, the influence of fluorine content on the properties of phosphogypsum can not be ignored. Fluorine is produced by phosphate rock treatment and processing, in the phosphogypsum production process, fluorine has two different forms, respectively refractory fluorine

and soluble fluorine, of which soluble fluorine can promote the condensation of phosphogypsum to a certain extent, but if the soluble phosphorus content in phosphogypsum is more than 0.3%, its overall strength will be significantly reduced.

III. Industrial solid waste phosphogypsum pretreatment

1. Chemical method

Chemical method can be applied in the treatment of industrial solid waste phosphogypsum, mainly using the principle of citric acid and lime neutralization to carry out related treatment work. Mainly because phosphogypsum and lime can produce a certain chemical reaction, resulting in the formation of calcium fluoride and calcium dihydrogen phosphate and other difficult to dissolve substances, these substances will show a precipitating state, but the actual harm is less. The application of chemical method to the treatment of industrial solid waste phosphogypsum can effectively adjust the pH value of phosphogypsum to keep it neutral. In the actual industrial production process, although phosphogypsum can be used as a retarder, if its pH value does not reach the relevant standards, it will not have a great impact on the production quality. In addition, the industrial solid waste phosphogypsum treatment process of another commonly used chemical method for citric acid method, many researchers in the phosphogypsum treatment, will try to use 4% citric acid solution to soak it, phosphogypsum after soaking can be dissolved, and used as a cementing material, in order to effectively achieve resource saving. Thus significantly reduce the cost of chemical production. In addition, the application of this method can also effectively improve the overall structure of phosphogypsum and improve the application efficiency of industrial solid waste phosphogypsum.

2. Physical method

The physical method can also be applied in the treatment of phosphogypsum, an industrial solid waste. Related research shows that with the extension of milling time can have a direct impact on the condensation of industrial solid waste phosphogypsum and particle size. Under normal circumstances, the best time for ball milling is 60-75 minutes, at this time the original shape and structure of phosphogypsum have been greatly changed, and with the continuous extension of the ball milling time, impurities will be reduced, so ball milling is a more commonly used physical method. In addition, a more commonly used physical method is water washing method. The change of industrial solid waste phosphogypsum can be effectively increased by adjusting the solid-liquid ratio in the washing process reasonably. During this period, its temperature changes little. Compared with saline washing, this method has outstanding advantages, and can effectively remove the organic matter on the surface of dihydrate gypsum from the solid waste phosphogypsum. However, the water washing method also has shortcomings in practical application, that is, it is difficult to clean up impurities such as insoluble phosphorus and eutectic phosphorus.

IV. The comprehensive utilization of industrial solid waste phosphogypsum

1. Application in gypsum building materials

When applying industrial solid waste phosphogypsum in gypsum building materials, it is necessary to dehydrate calcium sulfate dihydrate first, and produce α -type semi-hydrous gypsum and β -type semi-hydrous gypsum, and then treat and process it, and eventually form a variety of different decorative materials.

Lighter quality, lower cost, simple construction, waterproof fire and good thermal insulation and sound insulation performance are the main characteristics of gypsum board. By pretreating phosphogypsum, it can replace natural gypsum to manufacture gypsum sheet. The straw fiber gypsum board similar to natural gypsum can be made by soaking phosphogypsum, and the water resistance and bending strength of the board can be significantly improved by adding the strengthening modifier. The paper gypsum board has the characteristics of heat preservation, heat insulation, waterproof, fire prevention, etc. By adding additives and fibers to the building gypsum, a new gypsum board can be formed. At present, due to the increasing demand for gypsum board in the domestic construction industry, the demand in some areas is much higher than the supply. Therefore, phosphogypsum as the main raw material of production, is an important material to comply with the current market demand. At present, China has promulgated the relevant documents, which explicitly prohibits the use of solid clay bricks, the introduction of this policy makes our phosphogypsum treatment work to obtain good prospects for development. In 1999, a research and development center in Shandong applied phosphogypsum sintering brick technology. The technology has been applied to many building materials factories, and the products produced by this method can meet the relevant requirements and standards. In addition, some special building materials, phosphogypsum can also be used to replace, such as through special methods and processes can get a better performance of gypsum building materials, in which to add specific materials, can make it effectively meet the special building needs.

2. The application in agriculture

In the agricultural industry, the application of industrial solid waste phosphogypsum, the main principle is to highlight the application value of phosphogypsum, as a nutrient that can be absorbed by animals and plants, so as to promote the virtuous cycle of nature. Therefore, phosphate ions are made into phosphate fertilizer, in order to provide sufficient nutrients for plants and promote plant growth. However, industrial solid waste phosphogypsum in the case of untreated, its own acid, should not be applied to acid soil, so as not to affect the soil performance, thus hindering the growth of crops. Therefore, farmers in the use of phosphogypsum as the main raw material of phosphate fertilizer, must first determine the soil pH, if the acid kick can not be applied to phosphate fertilizer, if alkaline can be applied to phosphate fertilizer, in order to promote the growth and development of crops, improve the quality of crops.

3. Application in the chemical industry

In the chemical industry, the application of industrial solid waste phosphogypsum can effectively produce heat-resistant calcium sulfate

hemihydrate, or for the production of high-purity calcium carbonate. If only phosphogypsum is used for processing and production, it is difficult to get good quality calcium sulfate hemihydrate, so it is necessary to add an appropriate amount of sodium sulfate and sodium stearate to improve the quality and efficiency of calcium sulfate hemihydrate production. Through the repeated trials and verification of relevant researchers, it can be learned that adding 8% sodium oleate and 10% sodium stearate to phosphogypsum can obtain better production results. If phosphogypsum is used as the main component in the production of calcium nitrate, it is necessary to mix water with phosphogypsum, and then inject ammonia into it. Through continuous agitation of ammonia gas, phosphogypsum in water can be completely reacted. When the reaction is over, the phosphogypsum precipitating liquid that has not fully realized the chemical reaction can be obtained. At the same time, nitric acid is used as raw material to chemically react with phosphogypsum precipitates, and high quality calcium nitrate solution can be obtained. In the production of pure calcium carbonate, if the researchers use phosphogypsum as the main raw material, it is necessary to chemically react ammonia carbonate with phosphogypsum first, so as to obtain calcium carbonate. But by using a blender during the process, the researchers were able to understand that the duration of the reaction would change with changes in the blender's temperature and rotation speed, both of which would have a direct impact on the quality and purity of its production. Through continuous research and experiments, it can be understood that if the speed of rotation is maintained at 300-400rpm per minute, the reaction temperature is $120^{\circ}\text{C} \sim 130^{\circ}\text{C}$, and the reaction duration needs to be between 30 minutes and 3 hours, through this method, the purity of calcium carbonate can be significantly improved.

Concluding Remarks

In general, if there is no pretreatment and comprehensive utilization of industrial solid waste phosphogypsum, it is easy to damage and affect the ecological environment, so only the effective treatment and application of it can highlight the practical value of phosphogypsum, eliminate its impact on the ecological environment, and bring a lot of convenience to people's production and life. It can also effectively promote the production and development of a variety of enterprises, improve the economic benefits of enterprises, so as to fundamentally solve the environmental problems caused by excessive emission of phosphogypsum. Therefore, this paper for industrial solid waste phosphogypsum in the building materials, agriculture and chemical industry of the application of in-depth analysis and discussion, so as to effectively promote the development and construction of various industries.

References:

- [1] Ziyang Wang, Shuihe Shui, Tao Sun, et al. Effect of high iron Steel slag as alkali activator on setting and hardening property of perthophosphate gypsum slag [J]. *Materials Review*, 2023, 37(z1): 269-275.
- [2] Weihong Lu, Yaofang Wang, Juan Liu, et al Research Progress on innocuous modification of phosphogypsum and its application in farmland soil improvement [j] *Soil*, 2023, 55 (4): 699-707.
- [3] Zhihao Zhao, Kongwei Wang, Zhun Zhou, et al. Karst hydrogeological survey and tracing of Zhangyukeng Phosphogypsum reservoir [J]. *Carsologica Sinica*, 2023, 42(3): 413-424.
- [4] Jinhui Xu, Longyi Shao, Haihai Hou, et al. Research status of environmental impact under the background of comprehensive utilization of phosphogypsum [J]. *Journal of Mining Science*, 2023, 8(1): 115-126.

Project Fund: 2019 General Special Scientific Research Project of Shaanxi Provincial Education Department (19JK0642).

Remarks: Project participant: Dexu Li, Mengdi He, School of Transportation Engineering, Xi'an Vocational University Of Automobile.

About the author: Baoxiang Kang (1989 -), male, master degree, engineer, mainly engaged in the testing of construction engineering materials, tunnel and underground engineering research and teaching work.