ISSN: 2414-1895 DOI: 10.6919/ICJE.202107_7(7).0027

Present Situation and Development of Building Material Utilization of Phosphogypsum

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Abstract

The impurity components of phosphogypsum in China are complex and the accumulation is large. Due to its low utilization rate, the sustainable development of phosphogypsum industry in China is limited. How to effectively digest large amounts of phosphogypsum has become an urgent world problem to be solved. Therefore, according to the application status of phosphogypsum all over the world, in this paper, the characteristics and utilization difficulties of phosphogypsum in China are summarized and analyzed, the application of partial phosphogypsum in building materials is explained, and the future research trend of phosphogypsum utilization is prospected.

Keywords

Phosphogypsum; Building Materials; Application; Prospect.

1. Introduction

Phosphogypsum is a solid waste produced by phosphate fertilizer process, which is gray-white or gray-black powder. About 4.5-5t phosphogypsum is produced per 1t phosphoric acid. It is an acid by-product. Due to the complex and harmful impurity components, phosphogypsum cannot be directly used. At present, the global phosphogypsum accumulation has reached 6 billion tons and is still growing at 150 million tons per year. China is a by-product country of phosphogypsum. How to use phosphogypsum efficiently has become a big problem in China. Phosphogypsum stacking not only occupies land resources, but also pollutes the environment. Therefore, seeking low cost and high utilization of phosphogypsum application is an urgent problem to be solved, which is not only of great significance to the sustainable development of the phosphate industry, but also of great practical significance to China' s green environmental protection.

2. Characteristics of phosphogypsum and analysis of main difficulties in its application

2.1 Characteristics of phosphogypsum

Dihydrate gypsum ($CaSO_4 \cdot 2H_2O$) is the main component of phosphogypsum, its pH value is about 1.5~4.5, and its water content is high. Because phosphogypsum contains a small amount of impurities such as undegradable phosphate rock, unwashed phosphoric acid, calcium fluoride, iron aluminum oxide, acid insoluble matter, organic matter, etc., it is soluble in acid, ammonium salt and glycerin, slightly soluble in water, and insoluble in ethanol. When calcined to 128℃, dehydrated gypsum ($CaSO_4 \cdot 1/2H_2O$), calcined to 160℃, completely dehydrated into anhydrous gypsum. Researchers at home and abroad have done a lot of basic research for the utilization of phosphogypsum, invested a lot of manpower and material resources and opened up some relatively efficient utilization methods.

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However, due to the inherent characteristics of phosphogypsum, it is difficult to be consumed in large quantities. The main application difficulties of phosphogypsum are briefly analyzed below.

2.2 Adverse Effects of Eutectic Phosphorus Impurities on Application of Phosphogypsum Building Materials

There are certain differences in the source, composition and production process conditions of phosphogypsum, resulting in the complex impurity components. At the same time, it contains harmful impurities and cannot be directly used as building materials. It is one of the key problems in building material application of phosphogypsum to study and record the influence of impurities on the properties of phosphogypsum, find reasonable and effective pretreatment methods, and reduce or even eliminate the adverse effects of harmful impurities. Phosphogypsum mainly consists of soluble phosphorus, eutectic phosphorus and precipitated phosphorus. Among them, eutectic phosphorus has a great influence on the bonding performance of gypsum. The study shows that eutectic phosphorus cannot be removed by simple washing. This is because the eutectic phosphorus in phosphogypsum is HPO, which is released from the crystal lattice during the hydration process and converted into HPO soluble phosphorus. It is dissolved in the slurry, and the ionized PO is combines with a large amount of free Ca^{2+} in the solution to form insoluble Ca $(PO)_2$ that is covered on the crystal surface. The gypsum cannot be further hydrated, thus affecting the hydration performance of gypsum.

2.3 Effect of phosphogypsum crystal shape on its performance

The crystal form of phosphogypsum is one of the factors affecting the performance of phosphogypsum. The main factors affecting the strength of phosphogypsum curing agent are the shape and size of phosphogypsum crystals, the strength of contact points between crystals, impurities in crystals and the number of pores in the curing agent. How to improve the performance of phosphogypsum bonding materials by controlling the crystallization morphology of phosphogypsum is also one of the research priorities to improve the performance of phosphogypsum.

3. Application status of phosphogypsum at home and abroad

3.1 Application status of phosphogypsum abroad

Studies on phosphogypsum applications date back to 1960. In 2000, the cumulative amount of phosphogypsum in the United States reached 900 million tons, mostly used for stacking, roadbed construction, landfill, etc. Approximately 140 million tons of phosphogypsum were used for roadbed construction in 2010. Europe is the most active country in the plaster market. Brazil is one of the earliest countries in the world to carry out phosphogypsum comprehensive application research, and has made many leading achievements in the field of building materials and soil improvement. Japan attaches great importance to the rational utilization of phosphate rock and the comprehensive processing of phosphogypsum, and has advanced comprehensive utilization technology of phosphogypsum [1]. At the same time, due to the lack of phosphate rock resources, the utilization rate of phosphogypsum in Japan is very high, up to 95 %, which is mainly used in the production of gypsum powder and gypsum building materials.

3.2 Application of phosphogypsum in China

With the rapid development of China's phosphate fertilizer industry, the emissions of phosphogypsum increased exponentially. At present, the total annual growth of phosphogypsum in China has reached about 20 million tons. Due to the bottleneck problem in application technology, the cumulative total stock in China exceeds 500 million tons [2]. The utilization rate of phosphogypsum in China, most of the piled phosphogypsum in disposal may cause pollution to the surrounding environment, and contain acidic substances and other harmful substances, not only occupies land resources, but also is a waste in resource application.

Figure 1 and 2 are the annual emissions and annual total utilization of phosphogypsum in China.

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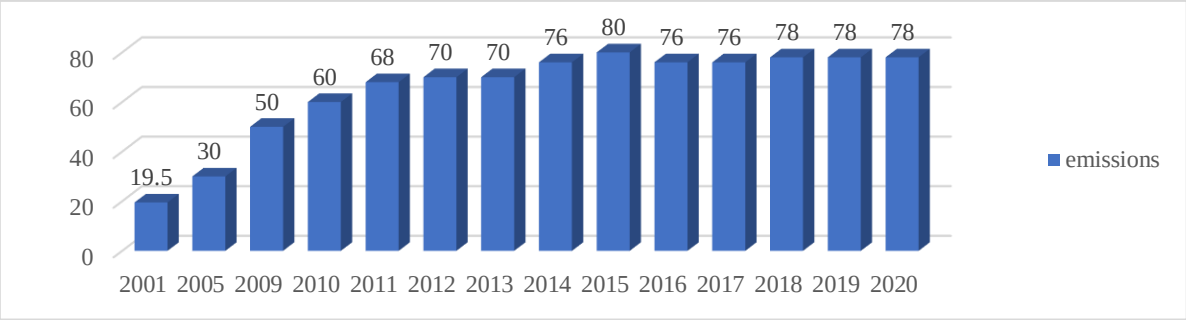

Figure 1. Annual emissions of phosphogypsum in China

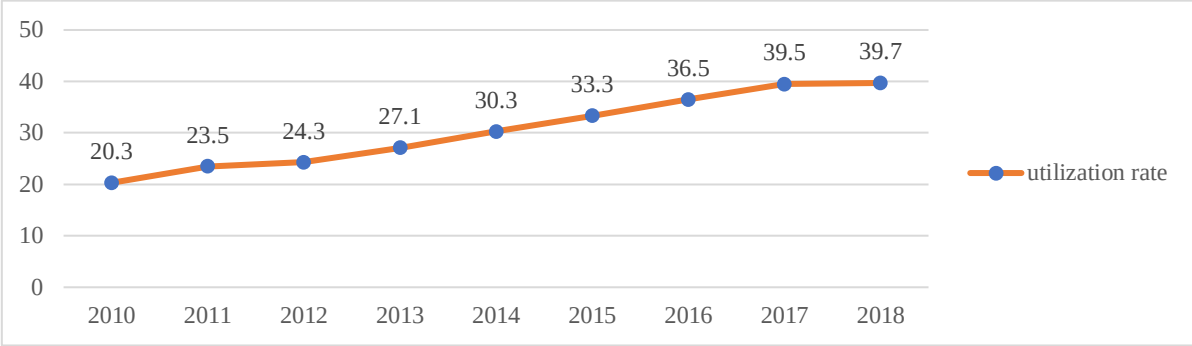

Figure 2. Annual utilization rate of phosphogypsum in China

It can be seen from the above figure that at present, China' s phosphogypsum emissions are about 78 million tons, and will maintain this level for a long time in the future. In 2018, the total utilization of phosphogypsum through various means was about 31 million tons, with an annual utilization rate of about 39.7%. Although the utilization rate is increasing year by year, the overall comprehensive utilization rate is low [3]. In China, in addition to hoarding and disposal, phosphogypsum as building materials, is the main way of disposal. Therefore, China has done a lot of research and practical production in this area, including cement retarder, gypsum block, paper gypsum board and so on.

4. Application of phosphogypsum in building materials

4.1 Phosphogypsum as cement retarder

At present, the domestic cement retarder is mainly natural gypsum and desulfurization gypsum. With the increase of cement production, domestic demand for cement retarder is also increasing. In addition, with the increasing cost of natural gypsum mining in China, the reduction of the number of high-quality gypsum ores has also created opportunities for the use of phosphogypsum as cement retarder. The biggest problem of phosphogypsum as cement retarder is that impurities in phosphogypsum will affect the setting time of cement and reduce the strength of cement. Therefore, phosphogypsum must be properly purified so that it does not contain impurities, mainly to remove phosphorus, fluorine and other acidic substances contained in phosphogypsum [4]. At present, washing, separation, neutralization, drying and calcination are commonly used purification and decontamination processes. Through the existing technology, under the premise of ensuring quality, reduce the production cost of phosphogypsum as cement retarder, to speed up the replacement rate of phosphogypsum and natural gypsum and the desulfurization rate of gypsum as cement retarder.

4.2 Phosphogypsum blocks

Gypsum block is a global recognized sustainable development building material product. Phosphogypsum obtained by pretreatment is used as the main raw material to prepare lightweight block wall material through stirring, molding and drying. Various filling materials, foaming agents and other auxiliary materials can also be added in the production process [5]. There are no three-

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wastes in the production process, so it is very beneficial to environmental protection. Phosphogypsum block has excellent fire resistance, thermal insulation performance. At the same time, due to the characteristics of phosphogypsum, gypsum block has breathability, can adjust indoor humidity and temperature, improve the comfort of residential.

4.3 Phosphogypsum paper gypsum board

Paper gypsum board is a new lightweight board material for building decoration, which is the closest substitute to wood veneer and the best material for protecting forest resources and trees [6]. It has the characteristics of light weight, sound insulation, heat insulation, seismic resistance, low shrinkage, high strength, automatic adjustment of indoor humidity, strong processing performance, and simple construction method of paper gypsum board. In recent years, there are more and more gypsum plasterboard project in China, mainly using natural gypsum and desulfurization gypsum as raw materials. With the improvement of phosphogypsum purification and impurity removal technology in China, many enterprises have begun to build new phosphogypsum paper gypsum board projects.

5. Conclusions and Prospective

It has important practical significance to seek the architectural utilization of phosphogypsum which is in line with the development strategy of national environmental protection and rational utilization of resources. Under the high pressure of environmental protection and cost increase, the quality of phosphogypsum is improved from the source. According to the quality of phosphate rock, we can improve the technical process and route, strengthening the management of the whole production process, reducing the emissions of phosphogypsum to the atmosphere and it's impurities, to improve the quality of phosphogypsum, and create conditions for the use of phosphate fertilizer. Focus on the development of new gypsum building materials with energy saving and environmental protection characteristics. In the future, some scientific research achievements such as the low-temperature decomposition of sulfur phosphogypsum to sulfuric acid technology and the preparation of new environmentally friendly green building materials by phosphogypsum will become the trend of phosphogypsum application, and a low-cost and multi-channel comprehensive application market pattern of phosphogypsum will be formed. At present, there are still some difficulties in the low-cost pretreatment technology of phosphogypsum and the energy-saving and high-efficiency decomposition technology of phosphogypsum, which scientific and technical personnel still be required to study and open up new ways for the utilization of phosphogypsum building materials.

Acknowledgements

This study was supported by Chongqing University Student Innovation and Entrepreneurship Project "Development and Application of Respirable Wall" (project number: S202010647024).

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