

A Review of the Current Status of Resource Utilization of Phosphate Slag

Yunxi Nan, Jiayi Yang, Hao Pi, Shuang Yao*, Liang Zhao, Jing Dong, Hong Jiang
School of Civil and Architectural Engineering, Yangtze Normal University, Chongqing 408100, China

Abstract

As by-products in the production of phosphoric acid and phosphate fertilizers, the main components of phosphate slag are dolomite and phosphogypsum. At present, the resource utilization of phosphate slag at home and abroad mainly focuses on the use of dolomite and phosphogypsum, and there has been some progress. This paper systematically introduces the current application progress of dolomite and phosphogypsum based on the relevant reports and literature on the application of dolomite and phosphogypsum in the fields of building materials preparation, new refractories, ceramics, catalysts, etc. The idea of phosphogypsum intermixed with Portland cement for making new wall insulation materials.

Keywords

Dolomite; Phosphogypsum; Silicate Cement; Compound Mix; Wall Insulation Material.

1. Introduction

In the history of human beings for thousands of years, the continuous progress of society and high-speed development have entered the era of industrialization. The development of industrialization has also quickly promoted the progress of human civilization and the advancement of society. While humans are enjoying the social advancement and high-quality life brought about by industrial development. The waste and pollutants produced by industrialization development are also incorporated pollution and destruction of the environment that we live in. As a big energy country, China's increasingly serious industrialization development brought about the problem of environmental pollution should be solved.

Dolomite has been widely distributed in my country. The chemical composition, crystal structure, physical activity and chemical activity of dolomite have been studied by many scholars at home and abroad. However, in order to improve the effective utilization rate of dolomite and extend the development of the Dolomite Industry Chain to the high-end industry, based on the original research and experiments, it still needs more detailed and bold research. Therefore, by analyzing the research status of dolomite and phosphogypsum, this paper expects to get the significance of the composite effect of dolomite - phosphogypsum intermixing on the performance of Portland cement, and through this article to provide technical methods and basis for future developers.

2. Research on Dolomite and Phosphogypsum

2.1 Environmental Background

China is the second largest energy producer country in the world today. China has also ranked among the 2007 list of carbon dioxide emissions in the world. While Chinese energy mining and production. Obvious problems have also occurred due to the insufficient utilization of energy and some waste of energy. The greenhouse effects, frequent sour rain, severe urban haze, and severe desertification have

become the main problems facing today. In order to ensure the environmental safety of national security, further achieve sustainable development and solve the problem of environmental pollution caused by industrial production, our society needs to face the problems and considerations, but also need to improve people's living environment and quality. "Lucid waters and lush mountains are invaluable assets." and "A good ecological environment is the fairest public product and the most inclusive people's well-being." Also further reflects that our country attaches importance to ecological environmental protection, and has become China's long-term adherence to the basic national policy. Currently in China, there are many industrial pollution problems that need to be dealt with urgently.

On November 30, 2016, the environmental pollution incident of Sinochem Group's Chongqing Fuling Chemical Plant was reported by the "Economic Half Hour" column of the Central Financial Channel, and it was pointed out that the corresponding environmental pollution problems caused by the chemical plant were pointed out. Through unannounced visits by reporters, reporters were found that Shuanggui Village, Longqiao Town, Fuling District, Chongqing, China was seriously polluted by phosphate slag produced by chemical plants. These phosphate slags lead to "depletion of crops, fumigation of livestock, and frequent acid rain", which greatly affected the lives of the villagers. After that, the Fuling District Party Committee and the District Government took a series of rectification measures. For example, the overall relocation of Sinochem's Fuling chemical plant, and the launch of an ecological restoration project for the severely polluted phosphate slag tailings mine. By 2021, the soil-covering and greening work of the tail mine has been realized. In the position where the overlying soil is shallow, the green plants can hardly grow. There are still a lot of pollutants in the surface water under the tail mine. Overland greening failed to fundamentally eliminate the effects of chemical pollution, and these problems were discovered in a recent survey. In addition, the Fuling District of Chongqing City has abundant precipitation, the mines located along the Yangtze River are bound to continue to cause serious pollution to groundwater and the Yangtze River system. Therefore, it is urgent to deal with waste pollutants in tailing mines, and resource utilization is a prerequisite for fundamentally dealing with waste pollutants. In the recent field investigation of tailings mines, the team found a large amount of phosphogypsum, and a considerable part of dolomite slag. So how to make phosphogypsum and dolomite be effectively co-resourced is the significance of this research.

2.2 Material Performance Background

2.2.1 Basic Situation of Dolomite

As a category of carbonate mineral categories, dolomite is also an important calcium and magnesium resource. Its branch can be subdivided into iron containing and manganese -containing dolomite. Dolomite is based on iron -containing dolomite as the main mineral formed by the ingredients, the main mineral composition of dolomite is manganese -containing dolomite. Dolomite mineral resources are very rich in China. Dolomite mainly distributed in northeast, southwest and other regions in China.

2.2.2 Study of Dolomite Properties

When dolomite is heated to further explore its properties, we can know that when the external temperature reaches about 800 degrees Celsius, dolomite will form some solid and gaseous products after adding hydrochloric acid, which are magnesium oxide, oxide calcium and carbon dioxide [1]. Under normal temperature, when the dolomite reacts with dilute hydrochloric acid a small amount of gases will be generated. Dolomite's structure is similar to the crystal structure of calcite, and mostly rhombus. Dolomite has the characteristics of large specific surface area, remarkable adsorption, thermal insulation and fire resistance. Dolomite has been widely used in these aspects in the fields of metallurgy, building materials, agriculture, forestry, glass, ceramics, chemical and environmental protection. In the process of building construction, dolomite can be processed into magnesium cement; dolomite ash produced by heating can be used as internal and external wall paint.

However, the high-quality resources of dolomite are limited, and the dolomite in many chemical products cannot be effectively utilized. At present, dolomite is mainly used to produce primary products, such as being crushed and processed into dolomite powder, lightly burned and used as a

metallurgical flux and used in the environmental protection industry [2]. The added value of the product is low. Therefore, there are many issues that people need to consider deeply, such as how to extend the dolomite industry chain and improve the effective utilization rate of dolomite mineral resources while solving the problem of chemical waste pollutants in tailings, how to produce more higher-end products than before.

2.2.3 Dolomite Research Status Summary at Home and Abroad

The strong adsorption of dolomite makes it partially used in the field of environmental protection and rectification. In terms of environmental protection, phosphogypsum has the characteristics of strong filtration, cheap and low pollution. Chen Miao, Ni Hao, Xiao Liping, etc. studied the adsorption performance of dolomite for heavy metals such as Cd^{2+} , Cu^{2+} and Pb^{2+} respectively [3-5]. Gan Fangqun and Mei Xiang studied the adsorption performance of dolomite on phosphorus, their research provided experimental basis for solving the problem of phosphorus pollution problems and sustainable use of phosphorus resources [6-7]. Firing dolomite is used by Wei Zunli and others to adsorb boron in wastewater, and the adsorption of boron in water by firing dolomite can reach about 90% [8]. The wastewater was treated by burning dolomite, which can meet the standard of daily use and drinking. In the field of environmental protection in dolomite, many domestic and foreign scholars have studied its adsorption properties such as adsorption properties of printing and dyeing wastewater, excess sludge, carbon dioxide, *Escherichia coli*, etc.

In the field of raw material preparation, the content of calcium oxide and magnesium oxide is higher in dolomite. Dolomite is also used to produce raw materials containing magnesium and calcium elements. Zhang Hua, Guo Xiaoshui, Fu Rui and others used different processes to prepare magnesium oxide with high raw materials with dolomite, the product had strong insulation, thermal conductivity, and extremely high thermal expansion coefficient and light transmission performance [9-10]. Changjiang and Ren Shuang, made inorganic flame retardants $Mg(OH)_2$, the produce had the characteristics of low cost, good thermal stability, simple craftsmanship, environment -friendly and other characteristics [11-12].

In terms of refractory materials, Dolomite is roasted at a high temperature of 1500 degrees to form a high-density crystalline calcium oxide. Because dolomite has good fire resistance and can withstand high temperature of 2300 ° C, it is often used as a raw material for making refractory panels. For example, the flame retardant performance of the $MgO-CaO$ fire resistant agent is good; the product has good residual resistance and good heat resistance impact performance, and can replace the application of $MgO-Cr_2O_3$ in the environment. Pan Bo and others used dolomite sand, calcium-bearing magnesia, magnesia and graphite to make non-burned magnesia-calcium sand and silicon carbide bricks [13]. The products not only had the characteristics of $MgO-CaO$ bricks, but also show good performance in vacuum and thermal shock. Zhang Wangnian and others used dolomite powder as the main raw material, and produced magnesia-calcium sand through the secondary roasting method [14]. Some scientific researchers in India used dolomite waste residue and roasting method to produce a new type of composite, and then used the new composite to produce high spar-calcium aluminate refractory material, the produce has low thermal conductivity and is not easy to be wetted. It can replace the current phosphate aluminum silicate board.

In the field of ceramic production and preparation, dolomite can be used as a raw material for glazes and embryonic bodies, and it can also be used as a raw material in some ceramics that are quite different from ordinary ceramics, dolomite acted as a catalyst part of the role, or as a catalyst carrier.

Further research on dolomite: Xie Xiaoli, Yan Yun, Hu Zhihua, etc. added an appropriate amount of dolomite to cement-based materials. They came to the following conclusions: some of the cementitious materials made of two materials as the main raw materials, after adding dolomite, the material's ability to withstand mechanical properties such as pressure, shear force and other mechanical properties for a period of time is better than that only adding active MgO powdered limestone [15]. Therefore, the mechanical properties were analyzed by adding only fly ash or only light-burning dolomite, and adding both fly ash and light-burning dolomite into the material.

Combining fly ash and light-burning dolomite has better mechanical strength than when it is mixed alone. Different firing time and firing temperature will produce more active powdery CaCO_3 and MgO for lightly fired dolomite.

2.3 Basic Situation of Phosphogypsum

In China's current industrial wet-process phosphoric acid production process, more or less solid wastes such as phosphogypsum are generated. Its main ingredients are $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, the produce are relatively complicated. The composition of phosphogypsum contains a variety of impurities that are harmful to the environment and materials, such as a small amount of phosphate and fluoride, soluble P_2O_5 , and multiple organic matter [16]. These substances will cause great damage to the environment and limit the resource utilization of phosphogypsum.

2.3.1 Research on the Performance of Phosphogypsum

Before the use of phosphogypsum for research experiments, the first step is to carry out the cleaning work. There are many ways to remove impurities, but it is very important to choose the most economical, environmentally friendly and efficient way. Among the current pollution problems of the ecological environment in China, one of the problems that cannot be ignored is the pollution of groundwater resources caused by the discharge and accumulation of phosphogypsum; not only that, unreasonable stacking the phosphogypsum also causes waste of land resources; It restricted the production and sustainable development of wet-process phosphoric acid, phosphate fertilizer and other industries. How to find a reasonable way to make full use of the generated phosphogypsum, it is necessary to deal with it according to the characteristics and composition of the phosphogypsum, as well as the internal and external structure. Compared with natural gypsum, phosphogypsum has many differences, such as structure and composition, etc. Therefore, it is necessary to choose a suitable way of utilization according to the characteristics of phosphogypsum. At present, the main application fields of phosphogypsum are in agriculture, industry, and construction.

2.3.2 Study in Phosphogypsum

Phosphogypsum used in construction as an effective material has a very good development prospect at home and abroad, and the technology is relatively mature. Adding phosphogypsum to gypsum board and mixing phosphogypsum in wall plastering materials are also one of the effective ways to use phosphogypsum today.

With the improvement of building energy conservation requirements. China's wall insulation materials have also developed by leaps and bounds. However, the focus of research on wall insulation materials is still new raw materials and new processes, and phosphogypsum has great potential in this regard. Because phosphogypsum contains chemical components such as calcium sulfate dihydrate, they cross the combination of the overall structure of phosphogypsum, calcium sulfate dihydrate also leads to pores in the phosphogypsum, so phosphogypsum has a high pore rate. Introducing the impurity-removed phosphogypsum into the cement-based wall thermal insulation material can effectively improve the thermal insulation performance of the wall, and at the same time, it can adjust the indoor humidity to a certain extent and improve the comfort of the indoor living environment. At the same time, with the in-depth implementation of the policy of building an environment-friendly society, the exploitation of natural gypsum resources is also restricted, which provides opportunities for the resource utilization of phosphogypsum. Therefore, the use of phosphogypsum to develop wall insulation materials can not only solve the pollution problem caused by phosphogypsum tailings, but also promote the development of new types of walls. The utilization of phosphogypsum is of great significance for environmental protection and effective utilization of resources.

3. A Conjecture on Further Effective Utilization of Dolomite Phosphogypsum

According to the world's carbon dioxide emission testing data, it can be inferred that the production and release of carbon dioxide in the production of cement has reached about 5% of the global carbon dioxide production. At present, the most widely used materials in construction in the world are

cement-based building materials. From the perspective of construction development and the need for materials, the demand for cement will not decline significantly. Therefore, how to use cement reasonably to achieve more efficient utilization and obtain higher economic value and reduce the impact of cement on the environment, without increasing the economic budget, adding other materials to cement for substitution. If the performance of cement can be improved, and the effect of reducing production and use costs and increasing output can be achieved, it will be a very effective method.

4. Conclusion

Through the analysis of the existing research status of dolomite at home and abroad, it is concluded that although dolomite is widely distributed in nature, its high-quality resources are limited, and the dolomite in many chemical products cannot be effectively utilized. At present, dolomite is mainly used to produce primary products, such as crushed and processed into dolomite powder, lightly burned as metallurgical flux and environmental protection industry, and the added value of products is low. Therefore, when solving the problem of chemical waste pollutants in tail mines, the factory cannot improve the effective utilization rate of dolomite mineral resources, extend the dolomite industry chain, carry out deep processing of dolomite, develop to the high end of the industry, and produce and process high-end products. Through research and analysis, it is found that the unique crystal structure of phosphogypsum can effectively improve the thermal insulation performance of the wall. Phosphogypsum can also adjust indoor humidity to a certain extent, so as to improve the comfort of indoor living environment.

Therefore, the team proposed an idea of mixing dolomite and phosphogypsum into cement-based materials, in order to provide technical and theoretical basis for future developers.

Acknowledgments

This paper was supported by University Student Innovation and Entrepreneurship Project of Chongqing (Grant No. S202110647022).

References

- [1] LIU Yi-ming, YU Xin-ping. Comprehensive Development and Utilization of Dolomite[J]. Yunnan Chemical Technology, 2003, 30(1): 5-6.
- [2] WANG Lin. Study on the production of stable Magnesia-calcium refractories from dolomite and asbestos tailings[J]. Non-Metallic Mine, 2003, 26(4): 19-21.
- [3] CHEN Miao, WU Yong-gui. Adsorption and desorption of cadmium (II) by two natural carbonate minerals in waste water[N]. Journal of Guilin University of Technology, 2014, 34(1): 94-98.
- [4] Ni Hao, Li Yilian, Cui Ruiping, et al. Kinetics and thermodynamics of Cu²⁺ and Pb²⁺ adsorption from aqueous solutions onto dolomite adsorbent[N]. Chinese Journal of Environmental Engineering, 2016, 10(6): 3077-3083.
- [5] XIAO Li-ping, PEI Ge, GAO Xiao-yu, et al. The Adsorption Regularity of Modified Bentonite-dolomite to Fe²⁺, Mn²⁺ Heavy Metal Ions[J]. Earth and Environment, 2014, 42(5): 669-676.
- [6] GAN Fang-qun, QIN Pin-zhu, TANG Rong, et al. CHARACTERIZATION AND MECHANISM OF PHOSPHATE ADSORPTION ONTO DOLOMITIC ATTAPULGITE[J]. Mineralogy and Petrology, 2015, 35(2): 10-14.
- [7] Mei Xiang, Yang Xu, Zhang Tao. Phosphorus recovery from anaerobic digestion supernatant of sewage sludge using dolomite[J]. Chinese Journal of Environmental Engineering, 2012, 6(11): 3809-3816.
- [8] WEI Zun-li, JIANG Yi-ying, LU An-huai. Disposal of Boron-Containing Wastewater by Lightly-Burnt Dolomite[J]. Acta Mineralogica Sinica, 2010, 30(03): 349-354.
- [9] Zhang Hua, Nie Pengfei, Xu Chunhel, et al. Preparation of high purity magnesium oxide from dolomite[J]. Inorganic Chemicals Industry, 2012, 44(04): 22-24.
- [10] FU Rui. Research on Synthesis of High-pure MgO by Dolomite Primary Carbonization Method[J]. Coal and Chemical Industry, 2013, 36(3): 58-61.

- [11] CHANG Jiang, FAN Tian-bo, LI Xue, et al. Preparation of Magnesium Hydroxide Flame Retardant with Brine and Dolomite[J]. Journal of Shenyang University of Chemical Technology, 2014, 28(01): 20-23+46.
- [12] Ren Shuang, Wang Xiaojuan, Wu Yanni, et al. Preparation of nano-sized magnesia by brine-dolomite process[J]. Inorganic Chemicals Industry, 2010, 42(04): 30-32.
- [13] Pan Bo, Yin Guoxiang, Zhang Cuimin, et al. Effect of synthesis process of dolomite clinker on corrosion resistance of MgO-CaO brick[J]. Naihuo Cailiao, 2009, 43(5): 328-330+334.
- [14] Zhang Wangnian, Xu Huan, Wang Xitang, et al. The Research on the New Sintering Technology of Dolomite[J]. Non-Metallic Mines, 2020, 43(02): 19-22.
- [15] XIE Xiao-li, YAN Yun, HU Zhi-hua. Synergy Between Light-burnt Dolomite and Fly Ash in Ternary Cements[J]. Journal of Wuhan University of Technology, 2015, 37(10): 27-31+36.
- [16] CHEN He-quan. Comprehensive utilization of phosphogypsum--the by-product from WPA production[J]. Phosphate & Compound Fertilizer, 2009, 24(04): 68-69.