Brief introduction of Resourcification Utilization Routes for Carbide Slag

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Abstract. According to the characteristics of the carbide slag, the resourcification utilization routes for carbide slag is summarized, such as building materials, chemical products, environmental governance, etc. Through the investigation to the condition of the carbide slag, the feasibility of resourcification utilization routes for carbide slag is analysed. The concept is put forward that resourcification utilization for carbide slag should conform to situ transformation and comprehensive utilization, in order to dispose carbide slag resourcefully and harmlessly.

Keywords: carbide slag; resourcification; calcium oxide; construction materials

1. Introduction

Based on granular limestone and coke as raw material, calcium carbide (CaC_2) is produced under high temperature molten state. A large amount of waste will be produced in the calcium carbide production process, and 1.2 tons of calcium carbide slag will be produced per ton of calcium carbide [1]. Calcium carbide slag is alkaline, it will cause serious impact on the environment when thrown directly. It belongs to difficult industrial waste.

Due to the high alkalinity, carbide slag is regarded as a harmful substance. The traditional storage method will occupy a large amount of land and cause environmental pollution, and it requires extra caution when handling. The comprehensive utilization of calcium carbide slag has important benefits for turning waste into profit and improving the environment.

2. The characteristics of the carbide slag

Carbide slag is a by-product of hydrolysis reaction in the production of calcium carbide, which is a kind of industrial waste residue. The main composition of $Ca(OH)_2$, accounting for more than 80% of the calcium carbide slag. It also contains Fe_2O_3, SiO_2, Al_2O_3 metal oxide, hydroxide and a small amount of organic matter. Except Fe_2O_3, SiO_2, Al_2O_3 common silicate components, a small amount of $CaCO_3$ formed due to the $Ca(OH)_2$ on the surface of calcium carbide slag long-term contact with CO_2 in air[2]. The water content of the calcium carbide slag is about 85% to 90% when it is discharged. The carbide slag are grayish white after drying, the particles are fine and uniform, the specific gravity is small, the structure is loose, and the general particle size is between 0.05 and 0.01 mm. The chemical composition content range are shown in table 1[3].

Table 1. The main components of calcium carbide slag (%)

component	CaO	SiO_2	MgO	AI_2O_3	Fe_2O_3
(%)	65～71	2～5	0.22～1.68	1.5～4	0.2～1.4

3. The application of calcium carbide slag resources

3.1. Carbide slag produces building materials

3.1.1. Production of cement. The main component $Ca(OH)_2$ of calcium carbide slag is calcined to form CaO, which can replace limestone with other raw materials to produce cement. Production of cement is one of the important ways to comprehensive utilization of calcium carbide slag. Compared with the decomposition of limestone and calcium carbide slag. The heat is low, the calcium content is high, and the heat consumption per unit clinker is reduced by about 1/3. The use of calcium carbide slag to produce cement has the following advantages:

(1) The CaO content is high and the particle size is fine, which improves the burnability of the raw material.

(2) The decomposition temperature of $Ca(OH)_2$ is lower than the decomposition temperature of $CaCO_3$, and the heat loss of firing is low.

(3) The use of calcium carbide slag can reduce the amount of limestone and save resources.

Domestic application of calcium carbide slag to cement production began in the 1970s. The main technologies used were wet long kiln and vertical kiln calcined cement clinker. The disadvantage of adopting the wet process is that the energy consumption is large and the environment is polluted, and the addition amount of the carbide slag is only about 9% (mass fraction). With the development of preheating decomposition technology, dry production process, wet grinding dry burning production process and dry grinding dry burning production process were used to produce cement clinker.

3.1.2. Production of carbonized bricks. In addition to producing cement, carbonized bricks can be produced from industrial solid waste such as calcium carbide slag, fly ash, and slag. In addition to the production of cement, industrial solid waste such as calcium carbide slag, fly ash, slag, etc., can be carbonized by carbon dioxide in the waste gas of calcium carbide to produce carbonized bricks. The carbonization mechanism of carbonized bricks is that Ca(OH)2 is formed after adding lime (CaO), and the calcium carbide slag is just rich in Ca(OH)2. The carbonization reaction refers to the reaction of calcium carbide slag and carbon dioxide gas. The reaction process is as follows:

$$Ca(OH)_2+CO_2+H_2O=CaCO_3+2H_2O \tag{1}$$

Calcium carbide slag reacts with carbon dioxide gas to form calcium carbonate under the action of water, calcium carbonate further formation calcite crystals. The cohesive force generated by the crystals during development develops high strength, and the carbide slag can be used to produce carbonized bricks.

3.1.3. Production of non-burning bricks. Calcium carbide slag can be used as a calcareous raw material mixed with cinder to produce burn-free bricks [4]. The use of calcium carbide slag, pulverized coal (or cinder, coal research stone) and other production of non-burning bricks, non-load-bearing building blocks and other building materials have good environmental and social economic benefits, product durability, high compression and flexural strength, Meet the requirements of national non-sintered brick standards. In the production process of non-burnt bricks, wet calcium carbide slag, cement, fly ash, coal slag, etc. may be added according to strength requirements, after being metered and proportioned, crushed, the ingredients are mixed and evenly mixed, and the raw material is prepared, pressed and steamed or cured.

3.1.4. Production of other building materials. The calcium carbide slag can be used as a raw material for porcelain light wall coatings and putty for building interiors after solid-liquid separation, impurity removal, and decolorization. The modified calcium carbide slag is used as the main filler, and a certain film-forming substance, film-forming auxiliary agent and pigment are added to prepare a coating with good waterproof performance [5]. Fly ash-calcium carbide slag can be used as roadbed material for highway construction. The use of calcium carbide slag and fly ash to produce roadbed materials has the characteristics of short construction period and high efficiency, and realizes the comprehensive utilization of solid waste such as calcium carbide slag and fly ash. , reducing the cost of municipal construction [6].

3.2. Alternative limestone to prepare chemical products

The calcium carbide slag can replace limestone to produce a variety of chemical products, such as calcium chloride, potassium chlorate, various calcium carbonate products, etc[7].

3.2.1. Production of calcium chloride. Calcium chloride can be made by calcium carbide slag instead of stone powder and hydrochloric acid by reaction, filtration, concentration and crystallization, dehydration, drying, etc. Calcium chloride is widely used in coolants, infrastructure antifreeze, road spray and protective agent, medicine and water. The main processes for the production of calcium chloride are neutralization, solid-liquid separation, concentrated evaporation and drying. The chemical reaction of calcium carbide slag to produce calcium chloride is as follows:

$$Ca(OH)_2+2HCl=CaCl_2+2H_2O \tag{2}$$

$$CaO+2HCl=CaCl_2+H_2O \tag{3}$$

3.2.2. Production of potassium chlorate. The calcium carbide slag can be used as a raw material to produce potassium chlorate. The potassium chlorate solution is obtained by a series of processes such as evaporation, crystallization, dehydration, drying, pulverization, and packaging. The principle of calcium slag production of potassium chlorate is as follows:

$$6Ca(OH)_2+6Cl_2= Ca(ClO_3)_2+5CaCl_2+6H_2O \tag{4}$$

$$Ca(ClO_3)_2+2KCl = 2KClO_3+CaCl_2 \tag{5}$$

3.2.3. Production of calcium carbonate products. The calcium carbide slag is used as raw material to produce calcium carbonate. The main process is to carbonize the pretreated calcium carbide slag by CO_2, then separate, dry and pulverize, without calcination, which greatly reduces energy consumption. The calcium carbonate series products have Light calcium carbonate, activated calcium carbonate, high-purity industrial calcium carbonate, ultra-fine calcium carbonate.

The use of calcium carbide slag to prepare calcium carbonate can be divided into three methods according to the carbonization method:

(1) Drying and calcining the calcium carbide slag, adding water, and carbonizing with carbon dioxide;

(2) Using ammonium chloride as an extract to convert $Ca(OH)_2$ into Ca^{2+} ions, separating from impurities and then carbonizing with carbon dioxide;

(3) Extracting Ca^{2+} ions with ammonium chloride as an extract, adding carbonate, and preparing calcium carbonate by liquid-liquid continuous carbonization.

3.2.4. Production of other chemical products. Carbide slag can be used to produce soda ash, calcium peroxide, ethylene oxide, propylene oxide, bleaching powder, bleach, high purity calcium oxide, chloroform, citric acid and other chemical products. Due to the high transportation cost of carbide slag, the production of chemical products is a low grade, making it difficult to achieve large-scale production.

3.3. Using calcium carbide slag to improve the environment

3.3.1. Production of desulfurizer or sulfur-fixing agent. Sulfur dioxide is the main atmospheric pollutant emitted by coal-fired power plants and is the chief culprit in the formation of acid rain. Carbide slag is an alkaline solid that can remove various acid gases from industrial waste gases. Using calcium carbide slag as a sulfur-fixing agent, the desulfurization absorbent of boiler flue gas can not only reduce SO_2 emissions in coal-fired flue gas, but also make comprehensive utilization of industrial waste to achieve waste treatment.

The main reaction equation for desulfurization agent sulfur fixation is as follows:

$$Ca(OH)_2=CaO + H_2O \tag{6}$$

$$SO_2+CaO=CaSO_3 \tag{7}$$

$$2CaSO_3+O_2=2CaSO_4 \tag{8}$$

$$2CaO+2SO_2+O_2=2CaSO_4 \tag{9}$$

When the temperature is higher than 850°C, $CaSO_3$ is unstable, so CaO is less likely to react with SO_2 to form $CaSO_3$ during desulfurization.

3.3.2. Treatment of acid waste water and waste residue. The main component of calcium carbide slag can form alkaline compounds with heavy metal ions in waste water. The neutralization method can be used to treat acid waste water from chemical fiber plants, smelters, sulfuric acid plants, etc. In addition, carbide slag can also act as a precipitant or coagulant for certain waste water. It is excellent for neutralizing acidic waste water, but the disadvantage is that some waste is produced.

4. Resource direction of calcium carbide slag

The utilization of calcium carbide slag has certain difficulties in the implementation process. The resource utilization method of calcium carbide slag requires it to achieve environmental and economic benefits. The treatment technology of carbide slag not only focuses on sulfur fixation, road construction and production for construction. Materials should also focus on high value-added product development. Calcium carbide slag is not convenient for long-distance transportation and centralized treatment, it must be resourced and utilized according to local conditions.

Quicklime (CaO) is the main raw material in the production of calcium carbide. It is an effective way to realize the recycling of calcium carbide slag to produce high-purity CaO in the process of removing impurities and calcination by using the high content of $Ca(OH)_2$ in calcium carbide slag. On the one hand, calcium oxide can be used as a chemical raw material, mainly used in rubber, plastics, food, sewage treatment and other industries. It is widely used as a raw material, desulfurizer, auxiliary agent or dehydrating agent. On the other hand, it can also be used as calcium carbide production of raw materials. The key to recovering calcium oxide from calcium carbide slag is to solve the problem of purity and activity of calcium oxide. The purity problem mainly involves the removal of chemical components contained in calcium carbide slag. The activity problem mainly involves the formation and transformation of calcium oxide crystal form during the decomposition of calcium carbide slag.

5. Conclusion

(1) The resource utilization of calcium carbide slag should be adapted to local conditions, and the rational use of calcium carbide slag can bring good environmental and economic benefits.

(2) Since the water content of calcium carbide slag is extremely high, it should be dried as much as possible by the waste heat in production before production and recovery, to improve the efficiency of energy use and reduce costs.

(3) Calcium carbide slag is used in the production of general chemical products with low added value and poor economic benefits. It can be used in the field of environmental protection. It can be used for waste treatment, but its dosage is limited. It is used as a raw material for the production of calcium oxide to realize large-scale treatment of calcium carbide.

Acknowledgments

Project supported by the University Natural Science Foundation of Jiangsu Province, China (Grant No.18KJD450002).

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