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REVIEW

Resource utilization of solid waste carbide slag: a brief review of application technologies in various scenes

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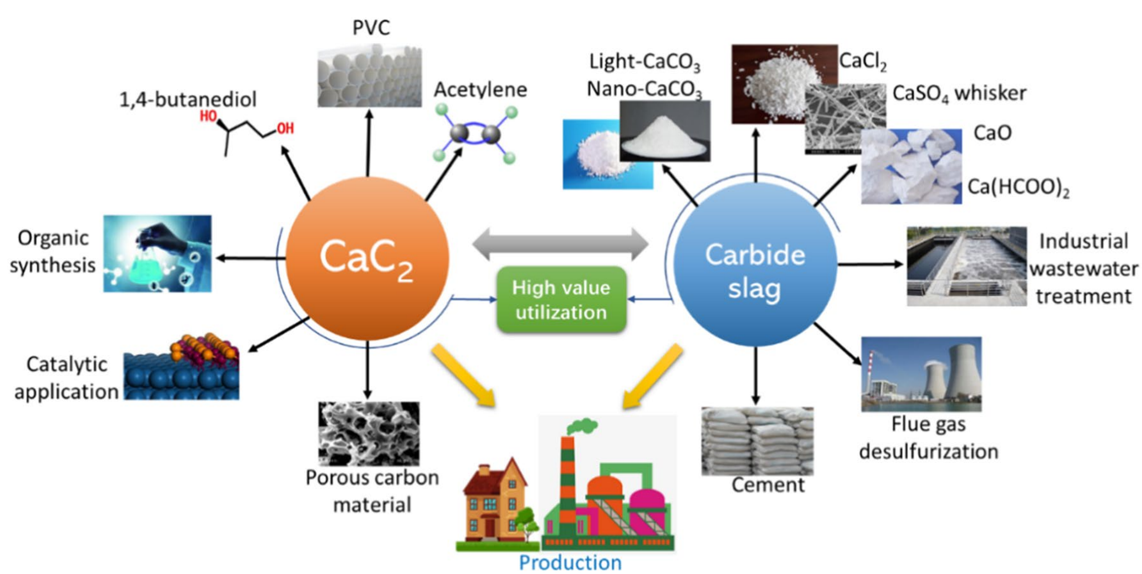
Abstract
China is the largest producer and consumer of calcium carbide in the world. The calcium carbide industry is an indispensable industry to support the basic life of people. The huge production capacity of calcium carbide is accompanied by a large number of solid waste carbide slag. Due to the immature treatment technology of carbide slag, a large number of carbide slag are stacked on-site, resulting in land occupation, air-drying, easy take-off ash, and pollution of the environment and water resources. In China, calcium carbide is mainly used to produce acetylene and further utilized, 80% of which is used to produce polyvinyl chloride (PVC). A large amount of carbide slag is not used, while only a small part is used in the traditional building materials industry, flue gas desulfurization, sewage treatment, etc., however, the economic benefits are poor. Therefore, converting the solid waste carbide slag produced by the calcium carbide industry into high value-added $CaCO_3$, $CaCl_2$, $CaSO_4$ whiskers, etc. has become a potential way to expand the development field of the calcium carbide industry and is environmentally friendly. This paper focuses on summarizing the traditional and emerging high value-added utilization technologies of carbide slag, and then introduces the application research of carbide slag in carbon emission reduction. Finally, the defects of these technologies are summarized and further research directions are prospected. This study provides basic guidance for the diversified development of efficient resource utilization of carbide slag.

Graphical abstract
Diversified development of calcium carbide industry, resource utilization of solid waste carbide slag and its application of carbon emission reduction have been fully reviewed.



Keywords Calcium carbide · Carbide slag · Application research · High added value · Carbon emission reduction

Extended author information available on the last page of the article

Introduction

In 2020, the Chinese government proposed to strive to reach the peak of CO_2 emissions by 2030 and achieve carbon neutrality by 2060. Therefore, in the next few decades, carbon peaking and carbon neutrality will become the prerequisites and goals for the development of industrial economy. As the largest producer and consumer of calcium carbide in the world, China's carbon emission and solid waste resource utilization caused by calcium carbide industry are urgent problems to be solved. CaC_2, the main component of calcium carbide, is an important basic chemical raw material. It is mainly used to produce acetylene gas, organic synthesis, oxyacetylene welding, etc. [1]. By the end of 2020, the output of calcium carbide in China reached 28 million tons, and the total amount of carbide slag discharged was nearly 33 million tons, while the utilization rate of carbide slag is less than 30% [2, 3].

Carbide slag is a kind of waste residue with calcium hydroxide which is the main component after acetylene gas produced by hydrolysis of calcium carbide [4]. Generally, a large amount of carbide slag is produced in the process of using calcium carbide to produce acetylene, polyvinyl chloride, acetone, and other chemical products. Conventional utilization methods only solved 40% of the discharge problem of carbide slag, while the recycling disposal of most discharged carbide slag has not been solved and can only be discarded and stacked, which results in serious environmental pollution and resource waste [5–7]. In particular, the amount of carbide slag produced by Chlor-alkali industry is huge, and due to the immature treatment technology and high treatment cost, most manufacturers stack the untreated carbide slag near the production place which leads to the problems of land occupation, easy take-off ash, pollution of environment and water resources [8, 9]. It can be seen that it is extremely urgent to increase the development of industrial solid waste carbide slag resource utilization technology. In particular, as the alkaline solid waste, carbide slag is more suitable for CO_2 mineralization due to its relatively high reactivity and inherent alkalinity, while the generated $CaCO_3$ can continue to be used in the production of calcium carbide. Therefore, the CO_2 emissions of the process are reduced [10, 11]. Furthermore, carbide slag is also expected to be used in the production of high value-added fine chemical products, such as calcium chloride and nano-calcium carbonate [12–16]. Taking the resource utilization and circular economy of calcium carbide and carbide slag as the development concept, strengthening technology research and development, and forming a circular economy industrial chain adapted to local conditions are effective measures to respond to global carbon peaks and carbon neutrality.

Formation of calcium carbide and carbide slag

Formation of calcium carbide

The calcium carbide production technology in the industry was invented in 1892. Its production principle is that calcium oxide and coke react at a high temperature above 2000 °C generated by an arc to produce molten calcium carbide (CaC_2). This process is called the electro-thermal method or arc method [17] that is shown in Eq. (1). Due to the high operating temperature for calcium carbide production and the huge amount of heat in the absorption reaction, the electro-thermal method for production of calcium carbide has disadvantages of high energy consumption, high material consumption, and high pollution. Accordingly, the oxy-thermal method for the calcium carbide production process is invented which can directly use the combustion heat for the production of calcium carbide to avoid the energy consumption of electricity. The oxy-thermal method is the development direction toward the calcium carbide production technology which is innovative and energy saving, however, it is still at the experimental stage [18–20].

$$CaO + 3C \rightarrow CaC_2 + CO - 465.7\ \mathrm{kJ/mol} \tag{1}$$

At present, oil and natural gas have become the main fossil fuels consumed in the world, but the amount of the available oil and natural gas reserves are only 10% of the amount of the known coal reserves [19]. Calcium carbide is an important bulk coal chemical product. Considering China's energy structure that riching in coal and lack of oil, nearly 80% of calcium carbide in China is used to produce PVC (polyvinyl chloride) while PVC abroad mainly comes from petroleum ethylene synthesis [21–23]. Compared with the petroleum ethylene route, the coal-based calcium carbide route has the characteristics of low cost, simple process, short construction period, and low investment. In this case, the world's calcium carbide production mainly concentrated in China [24]. China's annual output of calcium carbide increased rapidly in 1996, reaching 28.88 million tons in 2020, as shown in Fig. 1. China has a large demand for calcium carbide, so the position of the calcium carbide industry in China's coal chemical industry will keep increasing in a short time [25].

Formation of carbide slag

Carbide slag is a kind of industrial waste residue produced during the reaction of calcium carbide and water to produce acetylene [26]. This process is often carried out in a wet reactor. The main hydrolysis reaction equation is expressed as:

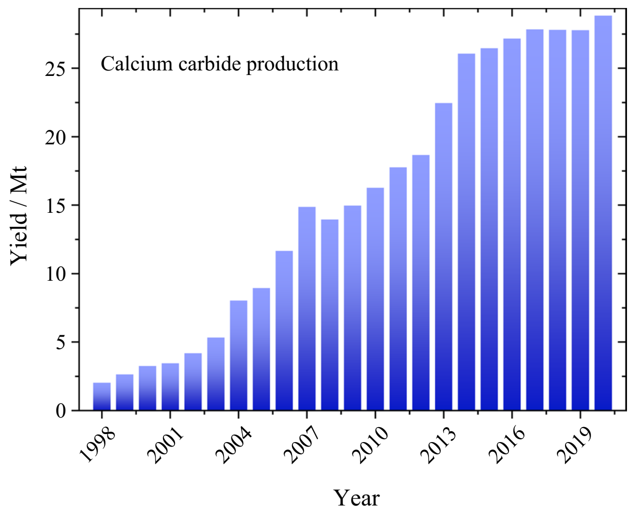


Fig. 1 The annual output of calcium carbide in China [24]

Table 1 The mass percentage of the main components of carbide slag

Component	$Ca(OH)_2$	Al_2O_3	SiO_2	Fe_2O_3	MgO
Carbide slag (%)	86–94	1.5–4	2–5	0.14–0.2	0.22–1.68

$$CaC_2 + 2H_2O \rightarrow C_2H_2 + Ca(OH)_2 + 130\ \mathrm{kJ/mol} \quad (2)$$

It can be seen from the Eq. (2) that for every mol of acetylene produced, 1 mol of calcium hydroxide is bound to be produced. As the solubility of $Ca(OH)_2$ in water is small, and the solid $Ca(OH)_2$ particles gradually precipitate out of the solution. In the actual production process, the acetylene generator first discharges the liquid carbide slag slurry with a water content of 5% to 95%. After treatment, it becomes a thick substance with slightly water. After natural stacking, it becomes a paste with about 50% water content. If it is finally dried, the particles of carbide slag will become much fine [27]. Because there is a large amount of calcium hydroxide in carbide slag, the alkalinity is high which is about 3000 mmo1/L [28]. The mass fraction range of main components of carbide slag is shown in Table 1 [29].

Carbide slag slurry is a gray–brown turbid liquid. After standing still, it is divided into three parts, the clear liquid, the solid sedimentary layer and the intermediate colloidal transition layer, as shown in Fig. 2. The ratio of the three parts changes reversibly with the change of resting time and environmental conditions. The solid sediment is calcium carbide waste residue. The accumulation of carbide slag occupies a large amount of cultivated land. The long-term storage will cause serious calcification of the soil which will be difficult to re-cultivate. At the same time, there is a risk of damaging the ecological environment and air quality. Therefore, the resource utilization of carbide slag is particularly important, which can not only create economic value but also reduce the impact on the environment.

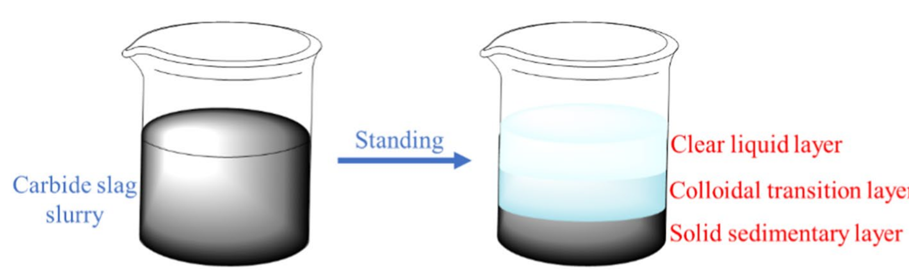
Calcium carbide utilization technology

The generation of a large number of carbide waste slag in China is due to the rapid development of the calcium carbide industry. China's calcium carbide production capacity accounts for more than 90% of the world's total production capacity. The main consumption industries of calcium carbide are productions of acetylene and its derivatives. The acetylene gas produced by calcium carbide can be used for other organic synthesis and oxyacetylene welding [30–34]. The products of these traditional industries are widely used and the industrial production and residents' life are inseparable from it.

As shown in Fig. 3, calcium carbide reacts with water to form acetylene [35] which was discovered in the middle of the nineteenth century. The acetylene has very rich chemical properties because of its active carbon–carbon triple bond. The most mature application of acetylene is PVC and 1,4-butanediol production. Calcium carbide–PVC production has accounted for more than 60% of the total domestic output, and dry acetylene technology has been promoted to reduce environmental pollution [36, 37]. 1,4-butanediol is an important fine chemical product. At present, the northwest part of China is the main production area of 1,4-butanediol in China [38].

In addition to being used in traditional industries, such as acetylene, PVC, and 1,4-butanediol, calcium carbide can also be used in new areas, such as organic

Fig. 2 Schematic diagram of precipitated carbide slag slurry



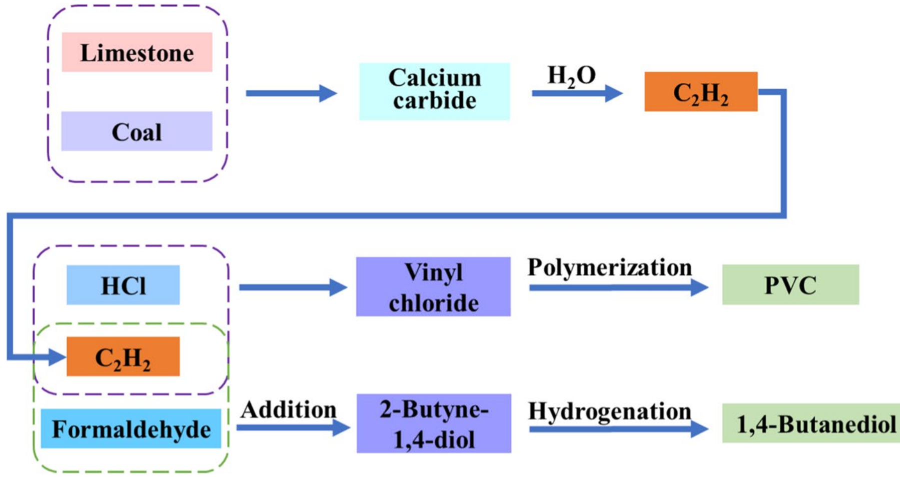


Fig. 3 Schematic diagram of the application process of calcium carbide and acetylene. *PVC* polyvinyl chloride

synthesis, catalysis, and conversion into porous carbon materials, as shown in Fig. 4. Among them, calcium carbide has become a viable raw material for organic synthesis due to its active triple bonds and ends [30, 39–41]. For example, calcium carbide is used as a source of alkyne to synthesize Propen-2-yl Sulfone which provides unique characteristic for drug design and medicinal chemistry [42]. New research suggests that CaC_2 can be used as an efficient catalyst for biomass and organic conversion due to its stability and active triple bonds [43–48]. CaC_2 is also an important carbide which can be used to prepare porous carbon materials (PCM) such as calcium carbide-derived carbon (CaC_2-CDC). It has broad application prospects in adsorbents, lithium–sodium-ion battery negative materials, etc. because of its high specific surface and diverse structural characteristics [49, 50].

Traditional applications of carbide slag

Generally, carbide slag is mainly used for building materials production, such as cement, block, thermal insulation materials, and other chemical products [7]. It is also employed for flue gas desulfurization, industrial wastewater treatment, and other environmental management. However, these methods usually have high investment, high operation intensity, and high pollution, and are easy to be restricted by market supply, demand and objective environmental factors, resulting in poor economic benefits.

Cement production with carbide slag

With the development of the domestic calcium carbide process, the comprehensive utilization of carbide slag has become the key factor restricting the sustainable

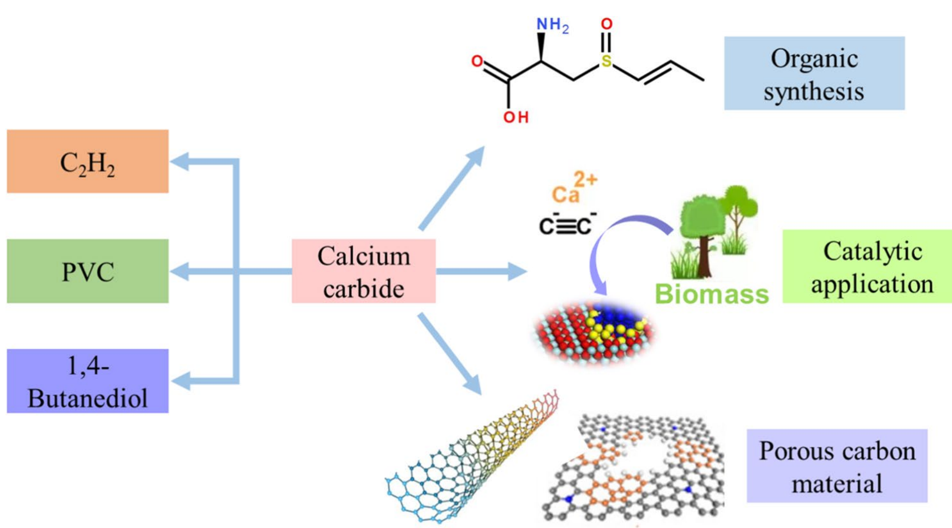


Fig. 4 Review of traditional and new technology applications of calcium carbide

development of the PVC industry in scale. Carbide slag is a high quality cement raw material with uniform composition and high calcium content. In China, the production of cement clinker from carbide slag began in the 1970s. There are four kinds of main processes, namely wet process, semi-wet rotary kiln process, wet grinding and dry burning process, and dry grinding and dry burning process.

In 2005, Xinjiang Tianye (Group) Co., Ltd. (Xinjiang, China) built the first 350000 tons/year carbide slag cement production plant in China, which marked a breakthrough of the domestic cement technology of carbide slag [51]. Compared with the traditional limestone cement production process, the carbide slag cement production process can reduce 0.6 tons of carbon dioxide emissions for each ton of cement, and reduce the limestone mining capacity by about 1 ton per ton of cement [2]. Regarding the imbalance of dry and wet carbide slag in enterprises that use both dry and wet carbide slag as raw materials to produce cement clinker, the first-line wet carbide slag has high moisture (about 30%) and is easy to stick while the dry carbide slag has a low moisture content (about 6%) and is easy to raise dust. Li and Xiong [52, 53] used dry and wet carbide slag to replace limestone to produce cement, which reduced energy consumption, cost, and CO_2 emissions. Lin et al. [54] conducted a comprehensive comparison between the carbide slag cement clinker system and the traditional Portland cement clinker system, and quantitatively analyzed the environmental impact and environmental benefits of the comprehensive utilization of carbide slag in cement kilns. According to the life cycle assessment (LCA) method [54], it is concluded that the carbide slag cement clinker system has a better effect in saving materials and reducing carbon emissions. It was also observed that the carbide slag cement clinker system shows little Global Warming Potential (GWP), Acidification potential (AP), and Eutrophication potential (EP).

Although the development of the cement industry has been very mature, its economic price is relatively low and market attractiveness has declined. The use of carbide slag in the production of other high economic value products, such as $CaCO_3$, $CaCl_2$, $CaSO_4$ whisker, and $Ca(HCOO)_2$, attracts much investment attention. Its market sales price is shown in Table 2. The cement price is much lower than that of $CaCO_3$, $CaSO_4$ whistler, and $Ca(HCOO)_2$. Therefore, more researchers are currently committed to using solid waste carbide slag to produce high value-added products.

Table 2 Market price comparison [55, 56]

Material	Price RMB¥/t
Cement	192–511
CaO	300–350
$CaCl_2$	400–900
Nano/light $CaCO_3$	2000–12000
$Ca(HCOO)_2$	3050
$CaSO_4$ whistler	4500–6500

Application of carbide slag in flue gas desulfurization

At present, more than 95% of domestic large-scale coal-fired boiler flue gas desulfurization processes use limestone or quicklime as desulfurizers. This process has strict requirements on the particle size and calcium purity of the desulfurizer. The conventional requirements of desulfurizer are that the particle size is less than 0.044 mm, calcium purity is greater than 85%, and the solid content of the slurry is 15%–20%. The price of limestone and quicklime is relatively high, and the operating cost accounts for 30%–35% of the desulfurization process [8, 57]. To reduce operating costs and save resources, many researchers have turned their attention to alkaline solid waste carbide slag as a desulfurizing agent to realize waste treatment [58, 59]. For the carbide slag-wet desulfurization system, the flue gas enters the desulfurization tower where the flue gas and the carbide slag slurry are in gas–liquid reverse contact to form calcium sulfite. which is further oxidized by the air directed by the oxidation fan to form calcium sulfate, and then gypsum is generated through crystallization. The gypsum slurry generated by desulfurization is directly sent to the pressure filter for treatment, and the main reactions are as Eqs. (3–5), and obviously, the desulfurization efficiency of carbide slag is much higher than that of traditional limestone, as shown in Table 3.

Absorption reaction:

$$SO_2 + H_2O \rightarrow SO_3^{2-} + 2H^+ \tag{3}$$

Oxidation reaction:

$$SO_3^{2-} + 2H^+ + 1/2O_2 \rightarrow SO_4^{2-} + 2H^+ \tag{4}$$

Neutralization reaction:

$$SO_4^{2-} + 2H^+ + Ca^{2+} + 2OH^- \rightarrow CaSO_4 \cdot 2H_2O \tag{5}$$

Although using carbide slag instead of limestone as a flue gas desulfurizer improves the desulfurization efficiency, it still faces the following problems like using limestone as desulfurizer [66, 67]:

1. To ensure the efficiency of desulfurization, the pH value of the slurry needs to be controlled during the production process at 7.0–8.5. Due to the characteristics of strong alkalinity, it is actually difficult to control the pH value. Most of the time, the pH value fluctuates frequently between 3 and 9.

Table 3 Comparison of wet flue gas desulfurization efficiency between carbide slag–gypsum and limestone–gypsum in some domestic enterprises

Carbide slag–Gypsum wet desulfurization		Limestone–Gypsum wet desulfurization	
Company	Desulfurization efficiency	Company	Desulfurization efficiency
Tianjin Dagu Chemical Co., Ltd	90% [60]	Xi'an Thermal Power Research Institute Co., Ltd	70%–90% [61]
Xinjiang Tianye	95% [62]	East China University of Science and Technology	86.4%–92.9% [63]
Ningxia Younglight Chemicals Co., Ltd	≥ 95% [8]	Beijing General Research Institute of Mining and Metallurgy	≥ 90% [64]
Ningxia West PVC company	96.6% [62]	Kunming University of Science and Technology	94% [65]
Jilantai Salt Chemical Co., Ltd	99.54% [62]	Jilantai Salt Chemical Co., Ltd	80% [62]

2. Carbide slag is used as the absorbent for desulfurization. If the belt dehydrator is still used to dehydrate the by-products, the parameters are difficult to control and uncertainties occur in long-term stable operation. To meet environmental protection requirements, it is necessary to conduct more in-depth research on the dehydration method of by-products.
3. The composition of carbide slag is very complex and the quality is unstable. The solid particulate content is very high. The equipment maintenance costs caused by abrasion and other reasons increased significantly. Besides, due to the unstable operation, the equipment stops frequently and the comprehensive desulfurization efficiency decreases which will increase the sewage costs.

Therefore, the low cost of the carbide slag is the main motivation for replacing limestone with carbide slag in some domestic power plants. However, considering the above problems, it is not appropriate to simply use carbide slag instead of limestone as an absorbent for flue gas desulfurization to pursue low operating costs. It is a much meaningful research direction to improve the existing carbide slag–gypsum desulfurization technology to overcome the above problems. For example, we can learn from Yu et al. [61] to study limestone–gypsum desulfurization double-tower series system. The first and second desulfurization towers adopt different flue gas velocities, liquid–gas ratios and slurry circulation residence time, respectively, which can effectively improve the large pH fluctuation and operation stability.

Treatment of industrial wastewater with carbide slag

The acidic wastewater produced from papermaking, printing, chemical industry, textile process, electroplating, steel, and other industries must be neutralized before discharge. In the past few years, China's industrial wastewater treatment costs have risen by more than 70%, and the use of carbide slag for wastewater treatment can greatly reduce wastewater treatment costs and environmental pollution [2]. In the treatment of fluorine-containing wastewater, the combination of carbide slag and polyacrylamide has also achieved better treatment effects [68].

Newly developed carbide slag utilization technology

As mentioned above, carbide slag was mainly used in the production of ordinary cement, refractory bricks, and other building materials in the early days. However, it consumes a lot of carbide slag and the added value of the product was low. Therefore, the researchers proposed some new resource utilization technologies to realize the high added value utilization of carbide slag.

Production of light/nano-calcium carbonate from carbide slag

The preparation of calcium carbonate from carbide slag can realize the high value-added utilization of carbide slag [69]. As an important fine chemical product, calcium carbonate is widely used. Limestone ore is used as a raw material in the carbonization process for the production of calcium carbonate at the industrial level. But the limestones cannot meet the market demands due to some demerits like environmental impacts, few mineral resources. On the other hand, calcium carbonate production using carbide slag as a raw material has so many advantages in comparison with limestone ore. For example, carbide slag turns waste into treasure, protects the environment, saves mineral resources, and has good economic and environmental benefits.

To prepare calcium carbonate using carbide slag as raw material, first, the carbide slag is processed to obtain a $Ca(OH)_2$ suspension or a soluble calcium ion solution, then, it carbonized to obtain calcium carbonate as shown in Fig. 5.

Light calcium carbonate and nano-calcium carbonate can be prepared by controlling the process. Light calcium carbonate is a precipitated calcium carbonate which is different from heavy calcium carbonate. It has a fine particle size and high purity, which can be widely used in rubber, plastics, paint, water-based coatings, and other industries. Shu et al. [70] and Tian et al. [71] used carbide slag as raw material and adopted ammonium chloride leaching and CO_2 carbonization process. The purity of the product is more than 98%, and the calcium conversion rate of carbide slag can reach 84.3%. This technology has realized industrial production. Guo et al. [72] used water-soluble method to extract calcium ions. Due to the small solubility of calcium hydroxide, the utilization rate of carbide slag is low which is not conducive to industrial production.

Moreover, Nano calcium carbonate is a high value-added fine chemical product. Due to the ultra refinement of particles, it produces excellent properties that ordinary calcium carbonate does not have. Nano calcium carbonate is easy to agglomerate because of its small size and large specific surface area. Increasing the dispersion of nano-calcium carbonate in organic polymers, such as rubber and plastics, through surface modification is the key technology of its application. At present, there are many studies on the production of calcium carbonate from carbide slag. Wang et al. [73], Zhang et al. [74], and Wang et al. [75] used carbide slag as raw material, NH_4Cl as leaching agent, CO_2 as precipitant, and added composite additives to prepare calcium carbonate with nano activity, uniform particle size, and high dispersion. Shuai et al. [76] leached carbide slag with NH_4Cl and the calcium ion conversion rate was 88%. The particle size of nano-calcium carbonate D90 was 2.78 μm and the whiteness was 97.51%.

At present, some research achievements have been made in the preparation of light calcium carbonate, nano-calcium carbonate, surface modification, and crystal form control of carbide slag. In the future, the recycling process should be further improved for the preparation of calcium carbonate from carbide slag, and research on superfine, surface modification, and crystal control of calcium carbonate should be carried out.

Calcium chloride production from carbide slag

Calcium chloride can be prepared by the processes of reacting stone powder or lime with hydrochloric acid, filtering, concentrating and crystallization, dehydrating, drying, and other processes. Common applications include brine used in refrigeration equipment, road ice melting agents, and desiccants. Calcium chloride and its hydrates and solutions have important applications in food manufacturing, building materials, medicine, and biology. The use of carbide slag instead of stone powder or lime to produce industrial calcium chloride is suitable for the chlor-alkali industry [77, 78].

Tang et al. [79] invented a process for preparing high-grade ammonia and calcium chloride using ammonium chloride and carbide slag as shown in Fig. 6. The ammonia gas is dried and dehydrated to obtain anhydrous ammonia gas, or passes into a water absorption tower and absorbed into ammonia water. After the calcium chloride slurry is crystallized and separated, it is dried at 150–380 °C to obtain high-grade anhydrous calcium chloride. The mother liquor is filtered and recycled for use in the preparation of ammonium chloride and calcium hydroxide slurry. Zeng et al. [80] prepared $CaCl_2$ with high yield (90.26%) and high purity

Fig. 5 Schematic diagram of calcium carbonate preparation from carbide slag

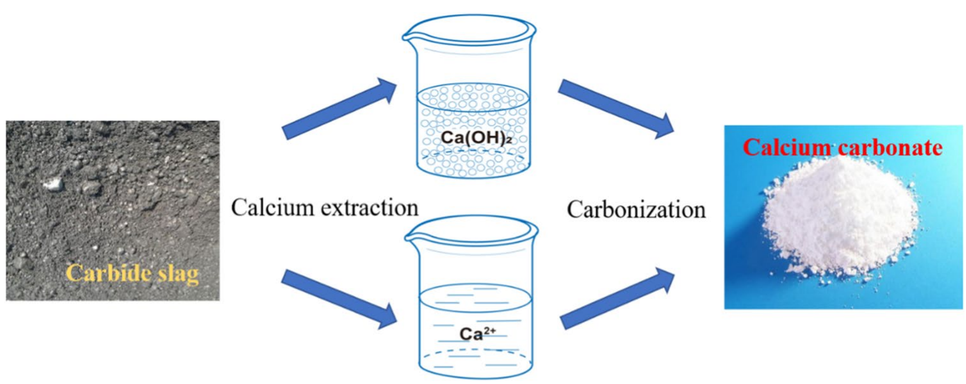
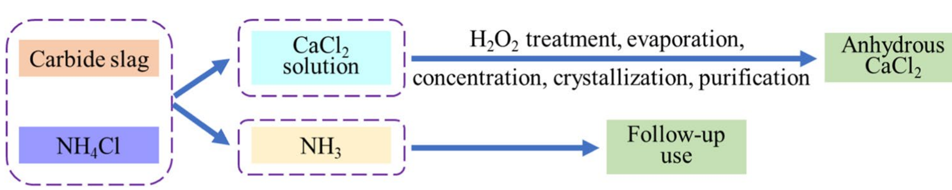


Fig. 6 Schematic diagram of preparing calcium chloride



(95.25%) by the reaction of carbide slag with NH_4Cl after pretreatment. The optimum reaction conditions were as follows: the molar ratio of carbide slag to ammonium chloride was 1:1.7, the amount of water was 30 mL, the reaction time was 40 min, the reaction temperature was 20 °C, and the stirring speed was 200 r/min. Ma et al. [81] also used the same process as Fig. 6 to prepare industrial-grade anhydrous calcium chloride, and ammonia gas was recycled.

It can be seen from the above that the carbide slag/ammonium chloride system is an environmentally friendly process for the production of high-value calcium chloride and ammonia recovery from industrial solid waste, and is a potential way for the resource utilization of carbide slag.

Preparation of calcium sulfate whisker from carbide slag

Whiskers are fibrous single crystals with high strength, high elongation, and high modulus, which are mainly used for the manufacture of high-strength composite materials and reinforcements for composite materials. Calcium sulfate whisker, also known as gypsum whisker or gypsum fiber, is a fibrous needle-like single crystal of calcium sulfate. It can be used as a reinforcing component and inorganic filling material in composite materials. Calcium sulfate whisker has strong market competitiveness because of its low price and excellent performance as a green environmental protection material.

With the advancement of industrial technology, many industrial wastes, such as citric acid waste residue, phosphogypsum, and salt mud of phosphate compound fertilizer industry, can be used to prepare calcium sulfate whiskers, for example, carbide slag can also be used to prepare high-value calcium sulfate whiskers that turns waste into treasure [3, 82]. The preparation process of calcium sulfate whiskers generally includes three steps: dissolution → crystallization → dehydration. The reaction process is shown in Fig. 7.

Li et al. [83] synthesized calcium sulfate whiskers with a length of 10–3000 μm, an aspect ratio of 10–300, and whiteness of 96 using carbide slag as raw material. Lv et al. [84] used industrial waste carbide slag as raw material and pretreated carbide slag with hydrochloric acid. The synthesized calcium sulfate whisker has a length of 80–250 μm, a diameter of 1–4 μm, and an average length diameter ratio of 95–110. Wang et al. [85] used carbide slag that provided by a factory in Inner Mongolia as raw material, after high-temperature pretreatment, mixed with a certain concentration of dilute sulfuric acid to prepare calcium sulfate whiskers with uniform morphology, high aspect ratio, and good dispersion.

Some researchers [86, 87] have used the carbide slag, waste hydrochloric acid, and mirabilite to make calcium sulfate whiskers. The reaction principle is shown in Eqs. (6–7). First of all, the crude $CaCl_2$ solution was prepared by the reaction of carbide slag and hydrochloric acid, and so, the refined $CaCl_2$ solution was obtained by adjusting pH value and pressure filtration. Then mirabilite crystal ($Na_2SO_4 \cdot 10H_2O$) was added to the reaction to obtain white crystal $CaSO_4 \cdot 2H_2O$. Finally, calcium sulfate whisker was obtained by high-pressure treatment with saturated steam. It can be seen from the above that it is necessary to go through a series of complicated procedures to produce calcium sulfate whiskers with high added value and excellent performance.

$$Ca(OH)_2 + 2HCl = CaC_2 + H_2O \tag{6}$$

$$Na_2SO_4 \cdot 10H_2O + CaCl_2 = CaSO_4 \cdot 2H_2O \downarrow + 2NaCl + 8H_2O \tag{7}$$

Carbide slag produces lime as raw material for calcium carbide

Lump quicklime (CaO) is the main raw material for the production of calcium carbide. Taking advantage of the high content of $Ca(OH)_2$ in carbide slag, high-purity CaO is produced as a calcium carbide raw material through processes, such as impurity removal, extrusion molding, and calcination. Carbide slag provides a source of calcium and can reduce energy consumption and carbon emissions caused by limestone mining and calcination. It is an effective way for the current recycling of carbide slag as shown in Fig. 8.

China National Salt-Hunan Zhuzhou Chemical Industry Group Co., Ltd. (Hunan, China) has built a set of

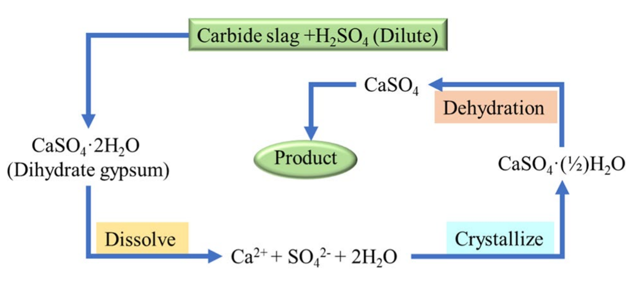


Fig. 7 Preparation mechanism diagram of calcium sulfate whisker

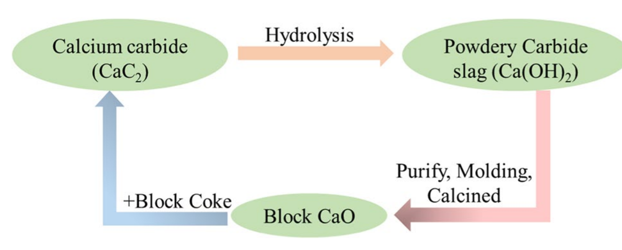


Fig. 8 Recycle route of carbide slag for generating CaC_2

10000 tons/year carbide slag production units. The main processes include raw material pretreatment, impurity separation, calcination, and decomposition of carbide slag. The mass fraction of calcium oxide product can reach to more than 85% by calcination process at a temperature of 900 °C for 5 h [56].

Lump CaO must have a certain strength when used as raw material for calcium carbide, and direct calcination of carbide slag usually only obtains powdered CaO. Zhang et al. [88] adjusted the strength of powdered CaO by adding inorganic adhesive H_3PO_4. Zhang et al. [26] prepared high-purity calcium oxide by a two-step method with carbide slag as raw material. The purity of the product was as high as 99.05%, and the recovery rate of calcium oxide in carbide slag was 84.02%. However, this method only stayed at the laboratory stage and has not been applied in the industry. Fan et al. [89] adopted the wet process of "carbide slag slurry preparation → rotary liquid slag removal → impurity removal and purification → washing and filtration → extrusion molding → calcination → CaO". It was found that the content of effective calcium oxide in lime products reached to more than 95%. They also performed feasibility analysis which was in line with the industrial policy of energy conservation, environmental protection, and circular economy at the present stage, and has good promotion value.

Preparation of feed-grade calcium formate from carbide slag

In 2016, investigators from Xi'an Jiaotong University have discovered a new environmental cleaning technology, that is, preparation of feed-grade calcium formate from calcium carbide residue [90]. Calcium formate has been widely concerned as a feed additive, food additive, or industrial and building material additive. This new technology is to produce calcium formate by the reaction of carbide slag and CO through carbonylation synthesis as shown in Fig. 9. And an industrial exhaust gas, the yellow phosphorus tail gas is used as a source of CO in this new finding. As the results show, using calcium carbide residue as raw material will give a higher conversion rate and the product quality is as good as that obtained from hydrated lime.

Preparation of new type cementitious materials from carbide slag

The production of cementitious materials is the most common and mature resource utilization way of carbide slag. For example, carbide slag is used in the production of cement as described in Section "Cement production with carbide slag". Its products can replace Portland cement as concrete raw materials which can not only reduce production energy consumption and a large amount of CO_2 emitted in the process of calcining limestone but also inhibit the self-shrinkage of cement paste. Therefore, researchers have carried out a large number of research on the modification of carbide slag in the production of new cementitious materials.

Sun et al. [91] synthesized a new cement material with carbide slag and silica fume (SiO_2 = 94 wt%), its specific surface area is very similar to that of Portland cement and shows better porous properties. The contents of $2CaO{\cdot}SiO_2$, $Ca(OH)_2$, and $Ca_3Si_3O_8(OH)_2$ in the material are 40.6%, 34.2%, and 13.6%, respectively, which are potential active components of the new cement material. In addition, the preparation of new cementitious materials from carbide slag and fly ash (SiO_2 + $A1_2O_3$ >70 wt%) is also a hot topic in recent years [92, 93]. Yi et al. [94] studied the use of carbide slag and reactive magnesia (MgO) activated ground granulated blast furnace slag (GGBS) to stabilize soft clay subjected to accelerated magnesium sulfate ($MgSO_4$). The results showed that carbide slag GGBS stabilized clay has a higher resistance to magnesium sulfate corrosion with no additional carbon dioxide emissions or related energy consumption. Lang et al. [95]. studied the use of lime and 25%–30% carbide slag to activate ground granulated blast-furnace slag, which can replace Portland cement to stabilize dredged sludge and achieve the highest unconfined compressive strength. Li et al. [96] studied that carbide slag can be used to activate ground granular blast furnace slag instead of hydrated lime. The compressive strength of the slurry is similar to that of hydrated lime-based slurry. Guo et al. [97] developed a new multi-strength level binder system. The 28 days strength of the new binder system is 17.5–43.2 MPa. This system can be applied to concrete blocks, pavement bricks, slope protection concrete, and other unreinforced products.

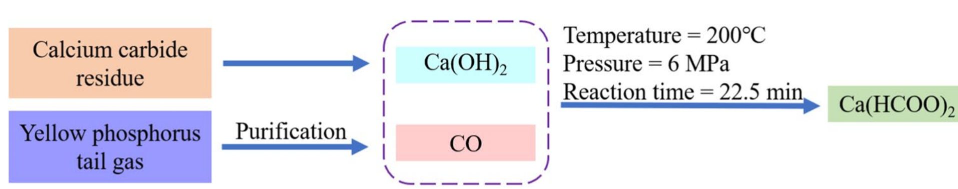


Fig. 9 Schematic diagram of preparing feed-grade calcium formate

Application research on carbon emission reduction of carbide slag

With the increasingly stringent environmental governance and the implementation of dual-carbon goals, the carbon emission reduction efforts of the calcium carbide industry are also gradually increased. Using the solid waste carbide slag produced by the calcium carbide industry to absorb CO_2 and convert it into useful products not only improves the utilization value of carbide slag but also helps to control and reduce CO_2 emission, and truly realizes the purpose of treating waste and turning waste into treasure. The carbon emission reduction applications and effects of carbide slag are shown in Table 4.

Carbide slag is rich in $Ca(OH)_2$ and has low decomposition heat. It can replace limestone to produce cement and other building materials by calcination or other means, which not only realizes the multiple resource recycling utilization of carbide slag but also reduces the CO_2 emission during the limestone calcination [100, 101]. Besides, the limited exploitation of raw limestone is one of the important factors restricting the long-term stable operation of the calcium carbide industry [102, 103]. Therefore, the researchers propose that carbide slag mineralizes CO_2 to prepare nano and light calcium carbonate, and the generated $CaCO_3$ can replace part of limestone [104, 105]. Furthermore, feed-grade calcium formate is synthesized with $Ca(OH)_2$ and CO as raw materials. The product has high purity with low cost, and reduces greenhouse gas emissions caused by CO combustion. In addition, the solubility of limestone is 10000 times lower than that of $Ca(OH)_2$ [57]. When carbide slag is used as a desulfurizer, its main component $Ca(OH)_2$ has high activity, which makes the absorption rate of SO_2 higher than that of limestone method, and achieves the effect of carbon emission reduction [99, 106, 107].

In summary, the rational use of solid waste carbide slag can not only turn waste into treasure but also promote the carbon emission reduction of the calcium carbide industry.

Perspectives

China's special coal-based energy structure determines the important position of calcium carbide as an intermediate product of the coal chemical industry. It is an important raw material for plastics, fibers, and other products that are indispensable in life and industry. At the same time, with the massive production of solid waste carbide slag and its inefficient utilization, it has caused an urgent environmental pollution problem. At present, to maximize economic and environmental benefits, enterprises and research institutes have improved the existing technologies and developed new technologies in terms of calcium carbide and carbide slag, which is summarized in Fig. 10.

It should be noted that as industrial solid waste, carbide slag is conducive to the healthy development of the whole industry only by seeking breakthroughs in process technology, comprehensive utilization, and turning waste into treasure. Although there are many comprehensive utilization methods of carbide slag, most of these technologies are still at the laboratory development stage, such as calcium chloride, calcium oxide, and nano-calcium carbonate. However, due to the huge amount of carbide slag produced, these methods only consume a small amount of carbide slag, and the main comprehensive utilization method is to prepare the cement. Besides, it is recommended to increase the development of closed-loop technology, especially for the production of calcium oxide from carbide slag which is directly used for the production of calcium carbide, so as to achieve efficient cycle conversion of calcium carbide production and reduce direct CO_2 emissions in the process [108–110]. Furthermore, vigorously promoting the carbon emission reduction application of carbide slag is also an important measure in response to the current dual-carbon goal [111–117]. For example, Yang et al. [118–120] used carbide slag as a carbon capture agent to realize the negative carbon pyrolysis of coal or biomass. Hu et al. [13, 107, 121–127] have done a lot of research on the absorption of CO_2 by modified carbide slag. Ma et al. [123] used Mn/Mg to co-precipitation carbide slag, and the CO_2 capture

Table 4 Application of carbide slag in carbon emission reduction

Application type	Carbon emission reduction effect
Cement	The production of 1 ton of cement can reduce about 0.6 tons of CO_2 emissions and reduce the amount of limestone mining by about 1 ton [2]
Nano/light $CaCO_3$	1 ton of carbide slag can replace 1.28 tons of limestone and reduce the emission of 0.56 tons of CO_2 [98]
$Ca(HCOO)_2$	Synthesizing 1 ton of $Ca(HCOO)_2$ consumes about 1.36 tons of calcium carbide slag and more than 344 Nm^3 CO [90]
Desulfurizer	Carbide slag replaces limestone for desulfurization. Every 1 ton of SO_2 removal will reduce the emission of 0.57 tons of CO_2 [99]

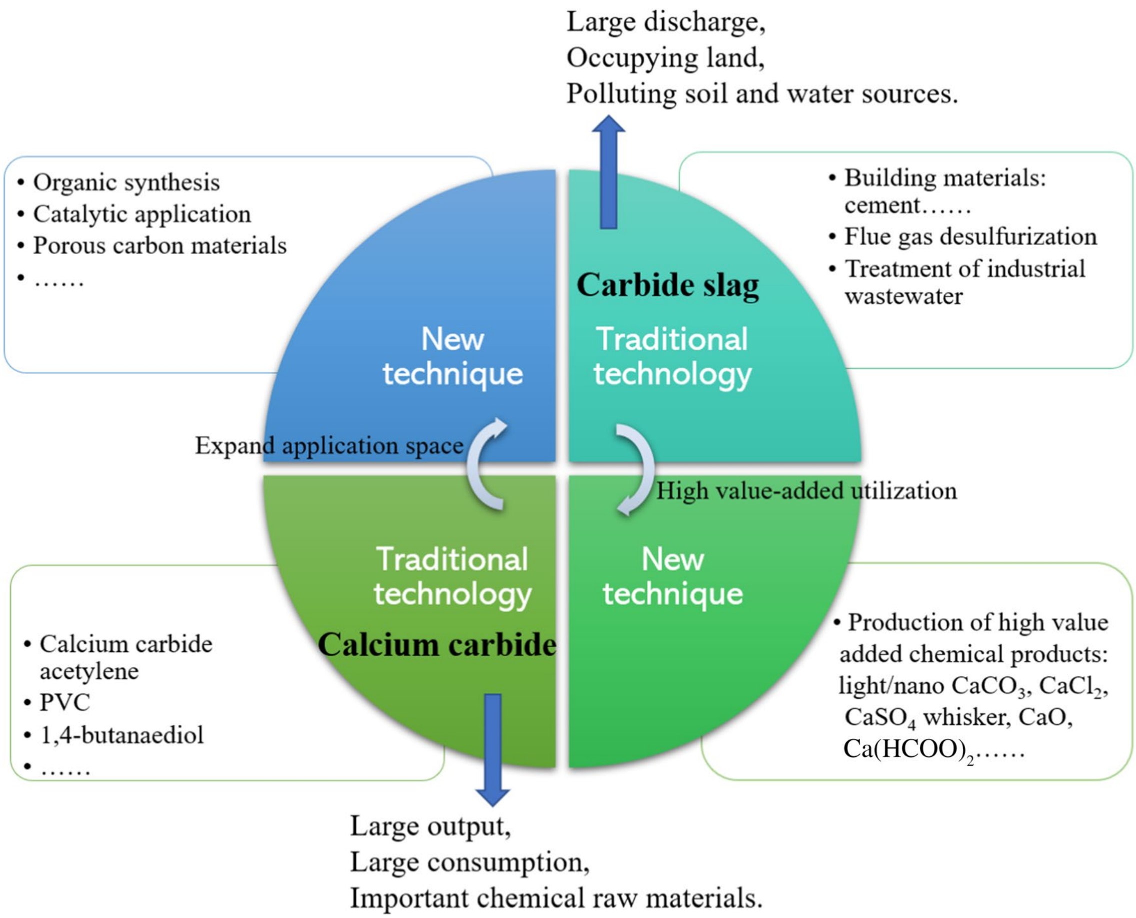


Fig. 10 Summary of the application fields of calcium carbide and carbide slag

capacity of carbide slag after 10 cycles is 0.52 g CO_2/g. Liu et al. [125] adopted carbide slag to synthesize CaO-based adsorbent. After 1 cycle and 15 cycles, the CO_2 adsorption capacity are 619.8 mg/g and 542.6 mg/g, which are 6.6% and 33.9% higher than the original carbide slag. Cai et al. [124] synthesized binary-doped carbide slag by liquid-phase precipitation method. The CO_2 capture capacity was 0.32 g CO_2/g after 20 cycles, and the CO_2 capture performance degradation rate was 67.75% lower than that of the original carbide slag. In summary, with the in-depth understanding of carbide slag, the carbide slag recovery process of CaO and carbon emission reduction process technology are gradually improved, and industrial application is possible. Large-scale utilization of industrial solid waste resources will produce obvious social and economic benefits.

Conclusion

In summary, the calcium carbide industry is an indispensable industry to support the basic life of the people, and the comprehensive utilization of carbide slag is to achieve maximum economic benefit under the premise of ensuring environmental benefits. Future research could focus on the following issues:

1. Calcium carbide has a high production capacity, which is accompanied by large investment and large water consumption. The prominent problems are that more energy saving and emission reduction measures should be addressed to improve the economy and protect the environment. Moreover, calcium carbide can be used in organic synthesis as a catalytic in the biological transformation process, and can produce porous carbon materials. These new technologies open up a new situation for the vigorous development of calcium carbide chemistry.
2. The traditional utilization of carbide slag, such as cement building materials, flue gas desulfurization, and waste water treatment, can only be used at a large industrial scale, needs large investment, low efficiency, and slightly insufficient profit creation. It is a new way to use carbide slag to produce light, nano-calcium carbonate, calcium chloride, calcium sulfate whisker, and other chemical products. Carbide slag has strong profitability

in the production of these chemical products which can actively develop high value-added downstream products of carbide slag.

3. Calcium oxide or calcium carbonate prepared from carbide slag is further used in calcium carbide production. On the one hand, it can get rid of the dependence of calcium carbide production on lime resources, and on the other hand, it can realize the recycling of calcium sources and reduce carbon emissions. It is the most valuable and significant means of recycling carbide slag, which needs large-scale promotion and industrialized production.
4. The conversation of solid waste carbide slag into useful products, such as cement, calcium carbonate, and calcium formate, is worthy of key research which not only improves the utilization value of carbide slag but also helps to control and reduce CO_2 emission.

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Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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