

Review

Sustainable Utilization of Steel Slag from Traditional Industry and Agriculture to Catalysis

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Abstract: Steel slag is a large amount of residual material produced in the process of steel manufacturing. With the requirements of sustainable development in China, the utilization of steel slag has become a hot issue. Through an in-depth study on steel slag, it is apparent that it has been widely used in various fields in recent years. The resource utilization of steel slag is not only conducive to resource conservation, but also conducive to sustainable production and environmental protection. In this paper, the common ways of resource utilization of steel slag in construction, agriculture, industry, and catalysis are reviewed. Steel slag as a solid waste with great development potential and large output is expected to be widely developed into high value-added products such as catalytic material in the future.

Keywords: steel slag; resource utilization; utilization of solid waste; sustainable development; high value-added

1. Introduction

With the rapid development of China's steel industry, rising rates of steel production have led to the increase of steel slag emissions. Steel slag is a kind of industrial solid waste produced in the process of iron and steel smelting, and its emission is about 15 wt%–20 wt% of crude steel output [1]. According to the data released by the World Iron and Steel Association, China's crude steel output in 2019 was 996 million tons, which meant that the emission of steel slag was as high as 100 million tons, while the comprehensive utilization rate of steel slag in China was only about 25% [2]. The comprehensive utilization rate of steel slag in developed countries such as the United States, Japan, and Germany was almost 100% [3]. Compared with developed countries, there was a lot of exploration space in the resource utilization of steel slag in China. Improving the utilization rate of steel slag and reducing the side effects of steel slag on environmental protection was the premise to ensure the green, stable, and sustainable development of the metallurgical industry [4].

In the process of iron and steel production, steel slag is mainly produced in the smelting process of raw metal ore, which is the slag discharged from the smelting process of converter, electric furnace, or refining furnace, and is mainly composed of oxides generated after the oxidation of various elements in the furnace charge, eroded lining materials, and added slagging materials [5]. Because of the different steel production processes and various raw materials, there are some differences in the composition of steel slag. Steel slag contains a variety of useful components: calcium oxide (CaO), magnesium oxide (MgO), silicon dioxide (SiO₂), alumina (Al₂O₃), ferrous oxide (FeO), iron oxide (Fe₂O₃), manganese dioxide (MnO₂), free calcium oxide (f-CaO), and free magnesium oxide (f-MgO). The main mineral phases are solid solutions of calcium silicate, dicalcium silicate, auroilite, calcium aluminoferrite, and oxides of silicon, magnesium, iron, manganese, and phosphorus, and also a small amount of free calcium oxide and metallic iron [6,7].

In summary, the complex composition and structure of steel slag determine the diversity of steel slag characteristics, so that steel slag can be used in many fields, such as cement, concrete aggregate, road paving, fertilizer production, and so on, and some achievements have been made, though the application of steel slag is limited in these aspects because of some negative factors. The catalytic performance of steel slag could be developed, which opens up a new way for the resource utilization of steel slag.

2. Resource Utilization of Steel Slab

2.1. Production of Building Material

Steel slag has the characteristics of high density, high strength, many pits on the surface, strong wear resistance, and gel property [8]. Therefore, steel slag can be used to prepare cement and steel slag bricks with little or no clinker, steel slag brick, concrete aggregate, and other building materials.

Steel slag contains a large number of active materials, such as $3\text{CaO}\cdot\text{SiO}_2$ and $2\text{CaO}\cdot\text{SiO}_2$, which are similar to the main components of a Portland cement clinker [9]. Therefore, in cement production, steel slag can be mixed into cement clinkers in a certain proportion to obtain steel slag cement, steel slag Portland cement, steel slag white cement, and other products [10]. Shan et al. used the principle that steel slag and blast furnace slag can activate each other to promote hydration and added a 25% steel slag and 25% blast furnace powder as an admixture to increase the strength of the cement, with results showing that the 28 day bending strength and compressive strength of cement was 21.2 MPa and 55.0 MPa, respectively, which recently met the strength requirement of 52.5 grade Portland slag cement in GB/T175-2007 [11].

Liu et al. successfully prepared a new type of permeable brick for walkway-steel slag base permeable brick (SSPB) by liquid phase sintering and systematically studied the effect of sintering temperature on the properties of SSPB [12]. The results showed that SSPB had excellent permeability, high mechanical strength, bending strength, and excellent chemical stability at the optimum sintering temperature of 1270 °C/1 h. This study provides a kind of environmental protection permeable brick with high added value and provides an important guide for the utilization of industrial steel slag waste.

Steel slag contains more iron particles, loose structure, less pores, hard and dense texture, so that the steel slag has good compressive strength and rough surface. As coarse aggregate, it can make the bond between aggregate and cement stone better [13]. When the steel slag was used as the binder of the concrete, the fluidity among mud particles was improved, and the micro-aggregate effect was added so that the void ratio in the concrete was reduced, penetrating pores were difficult to form, and the impermeability of the concrete was improved. The latter strength, chloride ion permeability resistance, and carbonization resistance were all improved. Liu et al. used steel slag as a gel material, mixed 30%, 50%, and 70% steel slag into concrete by volume and tested the mechanical properties and durability of the mixture. When the cement content was 4% and the steel slag content was 50%, its strength and stiffness were the largest [14]. As a kind of high activity admixture, steel slag powder played an important role in the preparation of high-performance concrete. Compared with limestone mixture, steel slag mixture had good economic benefits and potentially huge environmental benefits [15].

2.2. Extraction of Various Valuable Components

Steel slag is rich in the heavy metal element chromium, from which the separation of chromium is conducive to the realization of steel slag recycling and environmental protection, while alleviating the demand for chromium in China [16]. Mochizuki et al. studied the separation and recovery of metal elements from steel slag through a combination of chlorination and carbon chlorination, with their results showing that the combined method was effective for separating Fe, Ti, and P from steel slag [17].

2.3. Agricultural Fertilizer Production

Steel slag could also be used as a raw material for soil improvement and fertilizer production. The chemical composition of CaO, SiO₂, and MgO in steel slag was the same as that of the raw inorganic fertilizer material, in terms of composition and also contained effective components such as FeO, MnO, and P₂O₅ [18,19]. The solubility of steel slag was improved by the high-temperature calcination that resulted from the process of smelting, so that the easily soluble amount of the main components reached 1/3–1/2 of the total amount, part of which was even higher, and more easily absorbed by plants. Thus, steel slag was a fast and powerful compound mineral fertilizer [20] and was used to prepare phosphate fertilizer and silicon fertilizer.

Silicon could promote the yield of plants. There was a lot of active silicon in steel slag that could be absorbed by crops, so many researchers used steel slag as raw material to produce steel slag silicon fertilizer, which was mainly applicable to wheat, rice, corn, and sugarcane, among which rice was the most significant [21]. Steel slag was a good raw material for silicon–calcium fertilizer and acid soil amendment because of its large specific surface area and porosity [22]. Ning et al. studied the application of steel slag in soil, and their results suggested that it not only improved the pH value of soil but also increased the availability of silicon in soil, both of which were conducive to reducing the accumulation of Cd (cadmium) in rice buds or grains, helped to reduce the effective concentration of heavy metals, reduced the mobility of metals, and combined metals into more stable components [23].

Phosphorus could greatly promote the growth of crops. Steel slag phosphate fertilizer was made from basic steel slag by crushing and grinding. Its main components were Ca₄(PO₄)₂, Ca₂SiO₄, and some metal elements such as magnesium, iron, and manganese. For acid soil, steel slag phosphate fertilizer was an excellent base fertilizer, which could improve soil fertility. The release of steel slag phosphate fertilizer in soil was relatively slow and the after-effect was very good. When steel slag was selected as the additive of fused calcium-magnesium phosphate (FCMP), the content of soluble SiO₂ and alkali in steel slag exceeded the requirement of the national standard, added to FCMP is good [24]. The application of steel slag could increase rice yield because it contained CaO, MgO, P₂O₅, and other elements, which effectively promoted the synthesis of rice [25].

Phosphate fertilizer with steel slag could be used for remediation of lead contaminated soil, which reduces the concentration of lead in soil by changing pH, available phosphorus content, and chemical reaction [26]. The repair mechanism of phosphate fertilizer with steel slag included precipitation/coprecipitation and ion exchange adsorption. The Ca²⁺ in the steel slag phosphate fertilizer was replaced by Pb²⁺, and the formed lead phosphate precipitate had low solubility, good acid and alkali resistance, good chemical repair, and was extremely difficult to be decomposed under natural environments [27]. Zhang et al. preferred the kind of acid to be added by testing the pH value, resistivity, and Ca²⁺ dissolution of differently modified steel slag phosphate fertilizers [28]. In view of the low content of soluble phosphorus in ordinary steel slag phosphate fertilizers and the poor effect on the remediation of heavy metal pollutants, they modified the steel slag phosphate fertilizer to improve its remediation effect. When the initial concentration of Pb in the soil was not higher than 1000 mg/kg, the remedying soil, with 15% and 20% of A-TP and N-TP, respectively, could meet the requirements after 7 days of curing. The use of A-TP is small and its economy is good.

2.4. Terial

Steel slag as metallurgical raw material, and its main value, was reflected in the sintering flux, blast furnace flux, and the return slag in the process of steel making. The flux of blast furnace and steel making was mostly limestone (CaO) [29]. Steel slag separated by magnetic separation contained a large amount of iron and magnetic iron oxide, which could be directly returned to the blast furnace to be smelted into steel, thus greatly saving the consumption of lime, shortening the slag-forming time of steel slag, and improving the fluidity of molten slag. Developed countries, such as the USA, Japan, and Germany, use steel slag as sintering material to be returned to blast furnace for reuse, and the effect is considerable, accounting for 24%–75% of the comprehensive utilization of steel slag [30]. Steel slag

replaced limestone as a metallurgical raw material, thus reducing metallurgical fuel consumption and metallurgical production costs, and improving blast furnace operation status [31].

With the development of the economy and the increase of steel production, the discharge of steel slag is increasing. Under the current mode of steel slag utilization, the development and application of domestic steel slag resource technology has made some achievements, and the effective utilization of steel slag has been realized to a certain degree. At present, steel slag is mainly used as a cement concrete admixture, soil improvement fertilizer, and for building materials in China, but the utilization rate is only about 25%, which is far behind that of other developed countries. The main reasons why China's steel slag resources have not been used on a large scale and with high efficiency are as follows: (i) There is f-CaO (free calcium oxide) and a small amount of f-MgO (free magnesium oxide) in steel slag. These substances cause a hydration reaction, resulting in volume expansion, thus greatly limiting the utilization of steel slag for building materials. In order to eliminate the volume stability problems caused by f-CaO and f-MgO, it is necessary to modify the steel slag, which greatly increases the cost [32,33]; (ii) because there are a large number of micron-sized metallic iron particles in steel slag, it causes a high energy consumption of steel slag grinding. At the same time, steel slag has low activity, which greatly limits the application of steel slag in cement or gel [34]; (iii) When steel slag is used as a soil conditioner and as a chemical fertilizer, some heavy metal elements contained in steel slag may cause secondary pollution of the soil.

2.5. Pyrolysis

The experiment of CO₂ catalytic pyrolysis of polystyrene on steel slag was carried out by Lee et al. In the presence of a steel slag catalyst, the ability of dehydrogenation of hydrocarbons to H₂ was greatly improved. Since CO₂ could be used as an oxidant in the presence of steel slag, the synergistic effect of steel slag and CO₂ resulted in a more than 300-fold increase in CO production and a doubling of H₂ production [35]. Cho et al. used scrap tire (ST) as raw material to pyrolyze ST in a CO₂ atmosphere, and the effect was significantly enhanced (about 400% at 400 °C). In the presence of steel slag, CO₂ enhanced the pyrolysis of volatile pyrolysis compounds and promoted the formation of H₂ [36]. Lee et al. used pine sawdust as the carbonaceous material for pyrolysis and controlled the pyrolysis of carbon from a liquid state to a gas state through gas phase reactions (GPRS). Using steel slag as a catalyst, the slow reaction kinetics of CO₂ with GPRS of volatile pyrolysis products was obviously accelerated, resulting in the enhancement of CO and the formation of CH₄ and H₂ [37]. Kim et al. carried out a pyrolysis of biogas residue under the condition of CO₂. The metal elements in the steel slag accelerated the homogeneous reaction in the catalysis, which significantly accelerated the reaction kinetics, and increased the production of CO, thus promoting the rapid increase of H₂ and CH₄ production and producing more pyrolysis gas [38]. Kapird et al. used steel slag derived zeolite (FAU-SL) to catalyze the pyrolysis of oil palm mesocarp fiber (OPMF) in a slow heating fixed bed reactor. At 550 °C, the maximum yield of bio oil was 47 wt%, the relative abundance of peak area was 48.02%, and the peak area of phenolic compounds was 12.03%. Compared with other common zeolites, the activity of the catalyst narrowed the distribution range of organic compounds in bio oil [39].

2.6. Tar Cracking

Metal oxides such as Fe₂O₃, MgO and Al₂O₃ in steel slag may promote the catalytic tar reforming process. Guo et al. used steel slag calcined with a small amount of nickel at 900 °C and then carried out biomass catalytic reforming experiments to pyrolyze pine sawdust to produce primary tar [40]. The calcined steel slag formed granular NiO particles that were dispersed on the surface of nickel bearing steel slag to form a porous catalyst, which provided conditions for a long-term and effective application of a steel slag supported catalyst in the biomass tar reforming process. Li et al. proposed a method of coupling a catalytic thermochemical conversion of oily sludge with a high-temperature reduction of steel slag [41]. The results showed that temperature, slag addition, and slag particle fineness were positively correlated with gas production rate, iron reduction rate, and carbon conversion

rate. With the addition of steel slag, the carbon conversion rate increased from 76.6% to 90.1%, and the reduced iron efficiency increased from 38.5% to 70.6%. As an effective catalyst for a cracking/reforming reaction, iron particles in situ could produce significant fuel gas, which improved the reduction rate of steel slag and the catalytic cracking/reforming rate of oily sludge. Song et al. studied whether steel slag could be used as a catalyst for oil sludge pyrolysis. Their results showed that steel slag as a catalyst could increase the H₂ content in the pyrolysis of oil sludge pyrolysis process [42]. The addition of steel slag promoted the fracture of macromolecules and reduced the activation energy of oil sludge pyrolysis, which played a good role in promoting pyrolysis.

In conclusion, through the process of biomass pyrolysis, metal elements rich in steel slag could form effective active structures after modification, so as to prevent the formation of a stable chemical structure in hydrocarbon and accelerate hydrocarbon degradation. As a catalyst, steel slag could promote the decomposition of tar by weakening the C–C bond, thus reducing the activation energy of a complex pyrolysis reaction. Furthermore, it may have a good catalytic effect on the pyrolysis of biomass tar.

2.7. Optical Induction

Steel slag could be used as photocatalyst to degrade organic matter. Kang et al. synthesized a new porous steel slag-based cementitious material photocatalyst by a CeO₂ impregnation method [43]. Adding a pore-forming agent to change the pore structure, the mass transfer rate of water molecules increased, and the coupling semiconductor formed by the highly dispersed active CeO₂ component and FeO in the carrier promoted the efficient separation of photogenerated electron and hole pairs, thus improving the catalytic activity of the whole photocatalytic system. Sarkar et al. synthesized a MIL-53 (FE)/SiO₂ nanocomposite photocatalyst with a simple solvothermal method using steel slag as raw material and carried out photodegradation experiments of methylene blue (MB) under different conditions [44]. The UV-Vis absorption spectra and PL spectra showed that it had a good photocatalytic activity in the UV region. Under UV irradiation, the degradation rate reached 66.3% when the amount of photocatalyst was 0.5 g/L, which was much higher than that of similar catalysts. Zhang et al. reported a new type of nickel calcium cementitious material through alkali steel slag polymerization and ion exchange reactions and carried out a photocatalytic degradation of MB [45]. In the process of photocatalytic oxidation and degradation, Ni²⁺ ions played an important role in the transfer of photo-induced electrons, while iron oxide was responsible for the transfer of a photogenerated electron-hole, thus improving the separation efficiency of electron hole pairs and improving the photocatalytic efficiency. Shao et al. reported a steel slag derivative of calcium silicate hydrate (CSH) with a hierarchical structure and amorphous phase using an alkali activation method, which is used for in situ photodegradation of the organic pollutant MB [46]. The adsorption capacity of all heavy metals was higher than 100 mg/g, and the photodegradation efficiency of MB under low-power visible light was 63%. The results showed that CSH, a derivative of steel slag, had excellent chemical adsorption and in situ photodegradation of organic pollutants.

2.8. Electrocatalysis

Wang et al. made a new particle electrode with steel slag. The results showed that the new particle electrode had good catalytic activity for the degradation of rhodamine B (RhB) in three-dimensional electrolytic cells [47]. In 60 min, 82.4% and 65.54% of RhB were removed with and without aeration, respectively, which was much higher than 42.4% of RhB in the same time and had good circulation performance. It was feasible and economical to use steel slag as a particle electrode. Zhang et al. prepared a kind of Sn/Mn loaded steel slag zeolite particle electrode and applied it to the three-dimensional electrocatalytic system (TDE) degradation of RhB. Under the optimal conditions, the degradation rate of RhB in TDE reached 95.0% [48]. Wang et al. prepared a reactor with a saturation magnetic field of 1.6389 emu/g. Magnetic steel slag particles were used as particle electrodes to promote the degradation of organic matter, and 85% of total organic carbon (TOC) could be removed in 2 h

under the optimal conditions [49]. The magnetic particle electrode maintained a high TOC removal efficiency in the novel continuous three-dimensional reactor and had a good practical application potential. Song et al. prepared particle electrodes with kaolin/steel slag as raw materials to degrade methylene blue (MB) [50]. Under the optimum conditions, the degradation rate of MB decreased from 87.0% to 81.2%. The results showed that the electrocatalytic activity of three-dimensional electrodes was much better than that of two-dimensional electrochemical reactors. In addition, it was proved that the kaolin/steel slag particle electrode had good cycle performance. Teng et al. prepared a kind of particle electrode to degrade MB. Under the best combination of pH 3, voltage 12 V, initial MB concentration 15 mg/L, electrolyte concentration 0.3 mol/L, the removal rate of MB reached 91.41% [51]. The results showed that the removal efficiency of MB by three-dimensional electrodes was 23.48% higher than that by two-dimensional electrode, and energy consumption was reduced by 36.2%.

3. Conclusions

At present, steel slag is mainly used in construction, agriculture, and other fields. In the field of construction, steel slag is often used in cement, steel slag brick, and concrete aggregate due to its poor stability, low activity, and other adverse factors. According to a certain proportion and other materials mixed to achieve the use of the standard, there are certain restrictions. In agriculture and other fields, soil improvement and fertilizer production have achieved some results, but the problem of secondary pollution caused by heavy metals needs to be further solved. Compared with other developed countries, the application of industrial recycling has yet to be further explored. Steel slag as a catalyst has a broad prospect in the field of catalytic pyrolysis, tar cracking, photocatalysis, and electrocatalysis, and other aspects have shown high efficiency catalytic performance. In some catalytic aspects used for pyrolysis and tar cracking, steel slag can synergistically interact with some substances to form a virtuous cycle, and its catalytic performance is greatly improved.

In conclusion, steel slag as a catalyst has the characteristics of high efficiency, economy, and reusability and will not be affected by the bad factors. In addition to construction, the agricultural industry, and other fields, application of steel slag in catalysis has great potential, which provides more development space for the green sustainable utilization of steel slag in China.

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