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An overview of utilization of steel slag

Huang Yi*, Guoping Xu, Huigao Cheng, Junshi Wang, Yinfeng Wan, Hui Chen

Sinosteel Wuhan Safety & Environmental Protection Research Institute, Wuhan 430081, PR China

Abstract

The current utilization rate of steel slag is only 22% in china, far behind the developed countries. At present, the amount of slag deposited in storage yard adds up to 30Mt, leading to the occupation of farm land and serious pollution to the environment. Improving the slag utilization is an important way to resolve these problems. The physical and chemical characteristics of steel slag were analyzed and then the research progress of steel slag utilization at home and abroad as recycled raw material in steel enterprise interior, aggregate of road and hydraulic construction, cement additive and concrete admixture, materials for waste water or gas treatment, construction materials and fertilizer in agriculture production were introduced respectively. At last, the important routes and critical problems for large-scale utilization of steel slag were proposed.

Keywords: Steel slag; Composition and Charactesrics ; Recycle; Utilization

1. Introduction

Steel slag is a solid waste from steel production. It can be categorized as carbon steel slag and stainless steel slag according to the type of steel, and as pretreatment slag, basic oxygen furnace slag (BOFS), electrical arc furnace slag(EAFS), ladle refining slag (LFS）and casting residue according to the steelmaking process [1]. Steel and steel slag annual output of 2010 in China reached to 626.7 million tons and 90 million tons respectively [2]. However, the current utilization rate of steel slag in china is only 22%, far behind the developed countries like USA, Japan, German and France, of which the rates have been close to 100%. In these developed countries, 50% of slag has been used for the road project directly, with the remaining part for sintering and iron-making recycling in plant [3]. The amount of deposited steel slag (mainly BOFS) in china has been accumulated to more than 300 million tons, which leads to the occupation of farm land and pollution of groundwater and soil [1]. Therefore, improving the utilization

* Corresponding author.
E-mail address: jeremyme@163.com

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rate of steel slag is an imperative way for the steel enterprise to realize sustainable development. The research progress of steel slag utilization is overviewed in the present paper.

2. Physical and chemical characteristics of steel slag

The density of steel slag lies between 3.3-3.6g/cm^3. In appearance, steel slag looks slag a loose collection, and appears hard and wear-resistant due do its high Fe content. The grindability index of steel slag is 0.7, in contrast with the value of 0.96 and 1.0 for blast furnae slag and standard sand respectively [4].The steel slag mainly consists of SiO_2、CaO、Fe_2O_3、FeO、Al_2O_3、MgO、MnO、P_2O_5 [5].The chemical component of steel slag varies with the furnace type, steel grades and pretreatment method. Table 1 summarizes the chemical composition of BOFSand EAFS [6, 7]. The main mineral phases contained in steel slag are dicalcium silicate (C_2S), tricalcium silicate (C_3S), RO phase (CaO-FeO-MnO-MgO solid solution), tetra-calcium aluminoferrite (C_4AF), olivine, merwinite and free-CaO [8]. The utilization way of steel slag is closely related to its chemical and physical characteristics. Table 2 lists the relationship between the characteristics and application fields of steel slag.

Table 1. Chemical composition of steel slag

Oxides/%	CaO	SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	MnO	P_2O_5
BOFS	45-60	10-15	1-5	3-9	7-20	3-13	2-6	1-4
EAFS	30-50	11-20	10-18	5-6	8-22	8-13	5-10	2-5

Table 2. Characteristics and applications of steel slag

Characteristics	Applications
Hard, wear-resistant, adhesive, rough	Aggregates for road and hydraulic construction
Porous, alkaline	Waste water treatment
FeO_x, Fe components	Iron reclamation
CaO,MgO,FeO,MgO,MnO componets	Fluxing agent
Cementitious components (C_3S, C_2S and C_4AF)	Cement and concrete production
CaO, MgO components	CO_2 capture and flue gas desulfurization
FeO, CaO, SiO_2 components	Raw material for cement clinker
Fertilizer components (CaO, SiO_2, MgO, FeO)	Fertilizer and soil improvement

3. Research progress of steel slag utilization

3.1. Utilization in steel enterprise interior

3.1.1. Reclamation of waste steel

Steel slag contains approximately 10% waste steel, which can be reclaimed through crushing, sorting, magnetic separation and screening process. The developed countries carried out the research of recycling waste steel from steel slag earlier than other counties. For example, USA reclaimed approximately 3.5 Million tons steel scrap from 1970 to 1972 and Nippon magenetic dressing Co., Ltd in Japan has annual slag treatment capacity of 2 Million tons, reclaiming 0.18 Million tons iron particles with more than 95% Fe content yearly. In China, Anshan Iron and Steel Company recycles 0.28 Million tons of grained steel with 60%-65% Fe content and 0.4 Million tons of iron concentrate with approximately 50% Fe content yearly from steel slag through the combination of sorting, magnetic separation and gravity concentration processes[9]. Benxi Iron and Steel Company produces 78,000 tons of slag steel and 89,000 tons of iron concentrate with the advanced slag hot disintegrating treatment technique and crusing-screeing-bar mill purification-magnetic separation combined process [10]. The University of Science and Technology Beijing [3] developed a sorting-grinding-precise reduction-magnetic separation process of waste steel reclamation, through which 29.8kg iron particle and 152.1kg iron-rich material could be obtained from one ton of slag. However, the current reclaiming ratio of waste steel in China is still low due to lack of advanced slag treatment equipment and technology.

3.1.2. Utilization as sinter material

Steel slag with CaO content above 50% can be used as sinter ore fluxing agent, partially replacing the commercial lime. The slag addition can improve the quality, reduce fuel consumption due to the heat liberation of Fe and FeO oxidation reaction, and decrease the cost of sinter ore [11]. More than 56% and 24% of the produced steel slag have been utilized as sinter material in USA and German respectively [12]. In China, Baoshan Iron and Steel Group(Bao Steel) began to reused steel slag for sintering in 1996, now having a stable reusing amount of 15,000 tons[13]. Lianyuan Iron and Steel Company (Lianyuan Steel) have been utilizing steel slag as sinter material while in recent years the amount for sintering has deceased because of either the increase of phosphorus content in iron ore and hot metal or the decrease of CaO and Fe content in steel slag [14].

3.1.3 Utilization for hot metal dephosphorization

Nippon Steel Corporation (NSC) [15] has developed the MURC (Multi-Refining Converte) process, in which dephosphorization and decarbonization are conducted in the same converter. In this process, approximately 50% of decarbonization slag stays in the converter after the decarbonization process and hot recycled as dephosphorization and desiliconization slag of the next charge, resulting in increased dephosphorization efficiency and decreased CaO consumption. Muroran Iron And Steel Plant and Oita Iron And Steel Plant of NSC takes this process. Sumitomo Metal Industries, Ltd., invented a duplex process, called SRP (Simple Refining Process), in which dephosphorization and decarbonization tasks are assigned to be carried out by two converters. In this process, decarbonization slag and LDS are recycled and applied to dephosphorization (Fig.2). In China, Northeastern University [16] and Xian University of Architecture and Technology [17] have researched the basic theories of hot metal dephosphorization with

BOFS. Bao Steel was the first steel enterprises that successfully developed the duplex process in China, named BRP (BOF Refining Process) where steel slag is reused for dephosphorization and less slag is discharged [13].

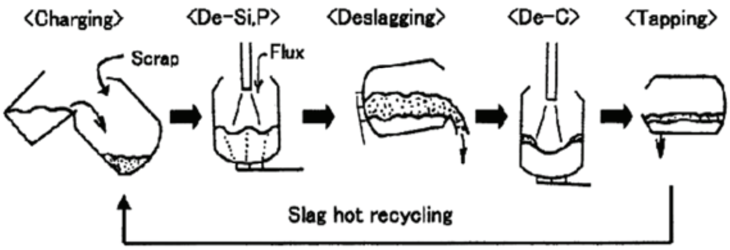

Fig. 1. Outline of MURC (Multi-Refining Converter) process [15]

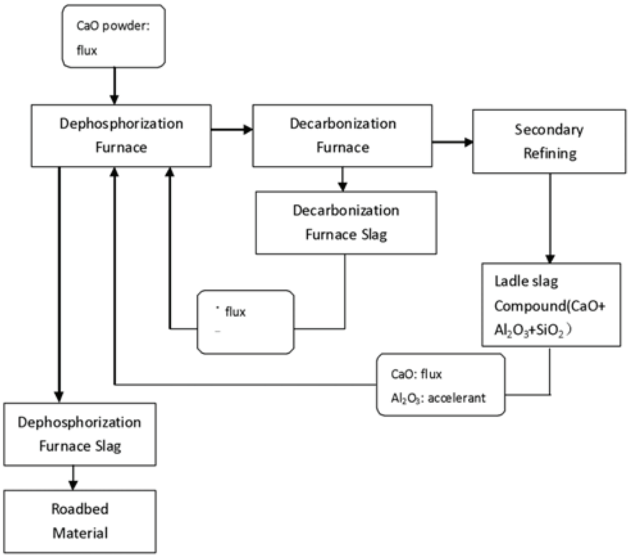

Fig. 2. Kashima steel works' recycling and application of steel slag in steelmaking

3.2. Utilization for road and hydraulic construction

Steel slag, due to its high strength and durability, can be processed to aggregates of high quality comparable with those of natural aggregates. The high bulk density, the high level of strength and abrasion as well as the rough texture qualify steel slag as a construction material for hydraulic engineering purposes. In Germany, about 400,000 tons per year is used as aggregate for the stabilization of rive bankers and river beds against erosion [5]. Nippon Slag Association in Japan has since 1993 been involved in application technology research for the use of steelmaking slag as a material for ground improvement in port and harbour construction [18] and in 2008 published the Guide to the use in port and

Harbour Construction. JFE steel corporation in Japan [19] manufactured artificial reefs for seawood/coral breeding (Marine block) using carbonated steel slag. The Artificial reefs show a high stability in seawater due to the fact that it consists of $CaCO_3$, like shells and coral, and they act as great breeding habitats for seaweeds and coral. In China, Xu [20] manufactured concrete armour blocks for sea coast projects, partially replacing sand with steel slag and cement with fine slag powder, and the concrete blocks has been applied practically in East China sea coast reclamation works and Luchao port project. Li, et al.[21] prepared high strength of artificial reefs concrete with 79% granulated high furnace slag ,15% steel slag , 5% flue gas desulphurization gypsum and 1% mixture as cementitious material and steel slag grains as its fine and coarse aggregates.

Also, based on high level of strength, high binder adhesion as well as high frictional and abrasion resistance, steel slag can be used as an aggregate not only in surface layers of the pavement but also in unbound bases and subbases, especially in asphaltic surface layers [5]. Approximately 60% of slag is used for road engineering in Japan and European countries, and even 98% of that is utilized as aggregates of cement and bituminous pavement in UK. More than 25 years ago in Germany test roads were built using steel slag as an aggregate for unbound and bituminous bound mixtures [5]. Ahmedzadea [22] investigated the influences of the utilization of steel slag as a coarse aggregate on the properties of hot mix asphalt. The results showed that steel slag used as a coarse aggregate improved the mechanical properties of asphalt mixtures. Moreover, volume resistivity values demonstrated that the electrical conductivity of steel slag asphalt mixtures were better than that of limestone asphalt mixtures. Asi [23] observed that asphalt concrete mixes containing 30% steel slag had the highest skid number followed by Superpave, SMA(Stone Mastic Asphalt), and Marshall mixes, respectively. Ameri, et al. [24] evaluated the effectiveness of steel slag as a substitute for virgin aggregates on mechanical properties of cold mix recycling asphalt pavement. The results showed that the use of steel slag could enhance Marshall stability, resilient modulus, tensile strength, resistance to moisture damage and resistance to permanent deformation of CIR (Cold In Place Recycling) mixes.

China began the application of steel slag in road construction in early days. The Ministry of Construction in 1990 issued the standard 'Technical specification for construction of steel slag and lime mixture used as base course' (CJJ35), and Ministry of Metallurgical Industry issued standard 'Technical specification for construction of steel slag mixture used as base course' (YBJ230) in 1991 and 'Steel slag for road'(YBT803) in 1993, which were substituted by YBT4184 in 2009 and GBT25824 in 2010 respectively. Up to 2009, standards 'Steel slag for pervious asphalt pave' (GBT24766) and 'Steel slag for wearing asphalt pave' (GBT24766) were published. In recent years, Chinese researches have made extensive works on the steel slag asphalt pavement. Xue [25] found that steel slag SMA pavement was comparable with conventional asphalt pavement, even superior to the later in some aspects. Test road was paved on the old expressway asphalt surface as skid resistance and abrasion resistance layer with 2 km long and 24m wide. Near 2 years service, the steel slag test road appeared excellent performance, without coming into being the rutting, cracking, and stripping which render the asphalt pavement early damage. Wu [26] also investigated the utilization of steel slag as aggregates for SMA mixtures. Two test sections of steel slag SMA mix were constructed as surface friction course on the asphalt overlay upon old cement concrete pavement of Wuhan–Huangshi expressway, and after 2 years services, the test roads showed excellent performances. With reference to the Chinese enterprise, Bao steel built a test road with steel slag as base materials and the road presented levelled and no cracking after one year service. Lianyuan Steel in 1997[14] and Wuhan Iron and Steel Group (Wuhan Steel) in 2002[27] paved an asphalt pavement with steel slag as aggregates in their plants respectively. The roads were substantially levelled and observed no cracking, bump and asymmetric settlement during the service. In 2009, steel slag was used as a substitute for basalt stone in Chang'an street major maintenance work of asphalt pavement [28].

Volume instability and heavy metal leaching are two considerable unsafe factors for steel slag using as aggregates in road and hydraulic engineering. In contact with water, free CaO and MgO in steel slag will react to hydroxides. Depending on the rate of free lime and/or free MgO this reaction causes a volume increase of the slag mostly combined with a disintegration of the slag pieces and a loss of strength [5]. Therefore, the volume stability is a key criterion for using steel slags as a construction material. Immersion expansion ratio is used to evaluate the volume stability of steel slag in USA and Japan [29], while in Germany, steam test is taken to measure that of steel slag used for road construction and boiling test for hydraulic construction. In China, the national standard 'Steel slag Stability test Method' was published in 2009 with immersion expansion test as evaluation method. The immersion expansion ratio is limited to 2% for road construction according to the specifications of relative standards. In Germany, experience has found that steel slags with a free lime content up to 7% may be used in unbound layers and up to 4% in asphaltic layers [5].The heavy metal leaching is mostly related to the stainless slag because it contains a higher amount of Cr and Ni than the ordinary. In Germany steel slag processed to aggregates for road construction and hydraulic structures have to be analysed by leaching tests twice a year. The concentration of Cr_{total} is limited to 3 mg/L [5]. Zhang [30] insisted that the pollution risks of the heavy metals in the stainless steel slag were very low and could only treat as the common wastes, not the hazardous through the leaching test. Manso [31] also performed the leaching test of the concrete with EAF as aggregates and found that Cr_{total} concentration was under the maximum limits stipulated by local legislation.

3.3. Utilization for production of cement and concrete

The presence of C_3S, C_2S and C_4AF endorse steel slag cementitious properties. It is generally agreed that the cementitious properties of steel slag increases with its basicity. Therefore, steel slag ground into fine powder can be used as cement additives and concrete admixtures [32]. Feng [33] used the mixture of fly ash, steel slag powder and cement clinker to prepare composite cement and observed that a certain amount of steel slag admixture in cement could reduce the porosity, improve pore distribution and increase the consistency of cement. The observation by Altun, et al. [34] showed that the cement with 30% steel slag fine powder addition qualified the Turkish standard requirements for Portland cement. Huang, et al. [35] prepared a cementitious material by utilizing phosphogypsum(PG), steel slag (SS), granulated blast-furnace slag (GGBFS) and limestone(LS). The results showed that the 28 days compressive strength of a mixture of 45% PG, 10% SS, 35% GGBFS and 10% LS exceeded 40 MPa and the main hydration products were ettringite and C–S–H gel. Wen, et al. [36] found that concrete mixed with steel slag had a compressive strength of 100 MPa and an excellent anti-chloride ion penetration performance. Chen, et al., [37] observed that, through experimental investigation, ground EAFS addition in concrete performed an excellent water-reducing effect. However, it should be noticed that the β-C_2S and C_3S formed in BOFS are proved less activity compared with those in cement clinker due to their large crystal size and the amount of cementitious minerals in BOFS is much lower relative to that in cement clinker, sometimes β-C_2S, having no cementitious activity, is a predominant mineral of BOFS. All of above mentioned factors lead to a low cementitious activity of BOFS, therefore blended cements with BOFS usually present low strengths, especially for early strengths [8]. In order to resolve this problem, Luo, et al. [38] experimented the effect of accelerators on the early strength of steel slag cementitious materials and found that a combination of inorganic and organic early strength agent could improve the early strength but no influence on the 28 days compressive strength. Wanga et al. [39] believed that in the steel slag treatment process, increasing the cooling rate and alkalinity of steel slag could improve the activity of cementitious phase in steel slag. Liang, et al. [40] observed that compared to the uncarbonated steel slag, the 3 days and 28 days activity indexes of carbonated steel slag could be increased by 97% and 16% at the initial water content of 19%. The fineness of slag is also an important factors influencing the activity, and the potential cementitious property of slag fines significantly increases with their fineness [39]. The highly efficient and energy-saving pulverizing mill equipment should be developed because steel slag is hard and have a low grindability index.

Steel slag can also be used an aggregate for high-strength and refractory concrete. Qasrawi,et al.[41] found that the compressive strength of concrete using steel slag as fine aggregates was 1.1 to 1.3 times of common concrete. Papayianni, et al. [42] prepared a high-strength (>70MPa) concrete utilizing EAFS as aggregates. Ducman,et al.[43] investigated the feasibility of the refractory concrete production using EAFS as aggregates and the results showed that when slag was heated up to a temperature of 1000 °C prior to its use for refractory concrete, the final products exhibited mechanical properties which are comparable to concrete with conventional refractory aggregate, e.g. bauxite. The research results by Netinger, et al. [44] showed that steel slag concrete exhibited similar fire resistance to the river aggregate mixture up to 400 ℃, and much improved fire resistance at high-temperature ranges.

In China, the standards of different types of steel slag cement have been issued including steel slag cement for road, steel slag masonry cement, Portland steel slag cement, and so on.

In addition, steel slag can be a raw material for Portland cement [45] and belite cement production [46].

3.4. Utilization for other construction materials

Both Guo [47] and Khater[48] applied the steel slag into preparing glass ceramics. Zhang [49] believed steel slag was a potential material for ceramic production. Shih, et al. [50] found that an appropriate addition of steel slag could reduce the firing temperature needed of clay bricks. For steel enterprise, Wuhan steel used steel slag to produce colored pavior bricks and tiles [27]; Lianyuan steel invented the steel slag baking free load-bearing tile [14]. In 2010, the Chinese national standard 'Steel slag for concrete perforated brick and concrete pavior brick' was issued.

3.5. Utilization for materials of waste water treatment

Steel slag presents porous structure and large surface area; in addition, it is easy to separate from water due to its high density. Therefore, the application of steel slag in industrial waste water treatment has received intensive attention in recent years. Shi, et al. [51] studied the treatment of mercury-containing sea water with steel slag and the high adsorption capacity of steel slag for mercury was observed. Chamteut [52] used steel slag as a low-cost adsorbent for arsenic in aqueous system, showing 95-100% removal efficiency near initial pH=2. The removal mechanism included the coprecipitation and adsorption of CaCO3. Kim, et al. [53] investigated the removal mechanism of copper using steel slag and the results confirmed that the major mechanisms were adsorption and precipitation. In addition, steel slag as a separated adsorbent can be used to remove aqueous ammonium nitrogen [54], phosphorous[55], and phenol [56]. The combined use of steel slag and H_2O_2 can decompose organic pollutions due to the ferrous ion produced from FeO in steel slag reacting with hydrogen peroxide to form Fenton's reagent that has strong oxidation [57]. Steel slag can also be used as raw material for coagulant preparation [58].

3.6 Application in CO_2 capture and flue gas desulfurization

CO_2 is one of the primary green house gases, which gives great contribution to the climate change. Therefore, carbon capture and storage (CCS) research has been the focus of CO_2 reduce technology. Among current popular CO_2 sequestration routes, the mineral CO_2 sequestration is regarded as a potential important technology due to its benefits such as environmentally benign, permanent trapping CO_2 in form of carbonate, and without the need of post-storage surveillance for CO_2 leakage [59]. In mineral carbonation, CO_2 gas is stored by promoting magnesium or calcium oxides in silicate minerals to react with carbon dioxide and form carbonates [60]. Steel slag contains a large amount of CaO so it is possible to store CO_2 in carbonates forms using steel slag slurry with mild conditions of temperature and CO_2 pressure [61]. Chang, et al. [62] investigated the technological condition of CO_2 sequestration with steel slag slurry, including reaction time, liquid-to-solid ratio (L/S), temperature, CO_2 pressure, and initial pH. The results of experiment conducted by Sun, et al.[59] showed that the maximum CO_2 capture capacity could reach to 211kg CO_2/ton steel slag with consideration of the contribution of $Mg(HCO_3)_2$ in capturing CO_2 and the precipitate obtained under optimized carbonation condition was rich in $CaCO_3$ with composition percentage reaching up to 96 ± 2 wt%. Huijgen [63] has evaluated the cost of CO_2 sequestration by aqueous mineral carbonation using steel slag as feedstock and the results is 77 €/ton CO_2, which seems expensive relative to other CO_2 storage technologies. The find by Eloneva, et al. [64] showed that CO_2 sequestration using steel slag could obtain high quality $CaCO_3$. It was calculated that 4.7 tons of steel slag were consumed for one ton CO_2 capture and the end products were 2.3 tons of $CaCO_3$ and 3.4 tons of residual slag. Although CO_2 capture with steel slag in laboratory has been successful, there is no industrialization case reported up to now. In order to realize industrialization, future work should be concentrated on scale-up equipments design and built-up, material recycle, residue treatment and suitability of $CaCO_3$ obtained as a paper filler.

The method of flue gas desulfurization includes wet process, dry process and semi-dry process, among which wet limestone/lime method is most widely used. Steel slag can be used for desulfurization due to its high CaO, especially free-CaO content. Feng [65] confirmed that aglomeration gas desulfurization with steel slag was practicable through theory research. Ding,et al.[66] carried out the experiment study on wet flue gas desulfurization with scrap slag powder residue and the results showed that by a reasonable design and suitable operation, the steel slag used in wet desulfurization rate could reach more than 60%. But, this technology is still limited in the laboratory research stage.

3.7. Application in agriculture

Steel slag contains fertilizer components CaO, SiO_2, and MgO. In addition to these three components, it also contains components such as FeO, MnO, and P_2O_5, so it has been used for a broad range of agricultural purposes. Its alkaline property remedies soil acidity [67]. In developed countries such as Germany, USA, France and Japan, converter slag is used to produce siliceous fertilizer, phosphorus fertilizer and micronutrient fertilizer [68]. In China, the first steel slag fertilizer program invested by Taiyuan Steel Group and Harsco Corporation of USA started building in 2011.

4. Conclusion and Prospect

Compared to the developed countries, the utilization rate of steel slag is still very low in China. Therefore, large-scale utilization is a substantial resolution to the environmental problems arisen by steel slag dump. The author believes that there are two important routs for steel slag large-scale utilization in China where industrialization is accelerating: one is to produce cement and concrete using the steel slag fine powder after reclaiming waste steel; the second is direct application in road and hydraulic construction. When the technology of CO_2 capture and flue gas desulfurization become reliable in the future, the two technologies will be selective before utilization in other ways. In addition, the database establishment of steel slag characteristics and applications is a substantial task for steel utilization.

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