Chapter 12
Energy Saving and Emission Reduction from the Steel Industry: Heat Recovery from High Temperature Slags

Yongqi Sun and Zuotai Zhang

Abstract The steel industry is an energy-intensive and CO_2-intensive industry and the greenhouse gas (GHG) emission in the steel industry was more than 2.95 billion tons in 2012, which faces the great challenge of energy saving and CO_2 emission reduction in the context of global warming. The heat recovery from high temperature slags (1450–1650 °C) from the metallurgical process represents one of the greatest potential to reduce the carbon emission in the steel industry (460 million tons of blast furnace slags (BFS) and 150 million tons of steel slags (SS) in 2012). The basic constraints of slag heat recovery include the low thermal conductivity and the easy crystallization trend. To meet these constraints and achieve the aim of heat recovery, many methods have been proposed and investigated during the past few decades, which could be divided into physical method, chemical method, and other method based on the working mechanism. The fundamental property of the hot slags that the cooling path of the slags could be composed of three regions, namely the liquid region, the crystallization region and the solid region, determined that a two-step physical method composed of a granulation atomizer and a fluidized bed for heat transfer and a two-stage process combined with physical dry granulation and chemical reaction are theoretically reasonable, which represents the research trend nowadays. The combination of the phase change material (PCM) heat storage and chemical methods could make up another research trend in the future especially when the crystallization behavior of the molten slags could be ignored. Besides, in the integrated system proposed recently, the obtained glassy blast furnace slags could be utilized in the cement industry because of the severe challenge of GHG emission reduction in the cement industry (3.7 billion tons of CO_2 in 2013). Only

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by employing a reasonable and efficient method, could the waste heat in the high temperature slags be effectively recovered and target of the GHG emission reduction in the steel industry be achieved.

Keywords Energy saving · Emission reduction · Heat recovery · High temperature slag · Physical method · Chemical method · Integrated system

Abbreviations

ARM	Alternative raw materials
BFS	Blast furnace slag
CCS	Carbon capture and storage
CFD	Computational fluid dynamics
DRI	Direct reduced iron
EAF	Electric arc furnace
GHG	Greenhouse gases
IPCC	Intergovernmental panel on climate change
MCF	Material CO_2 footprint
MSR	Methane steam reforming
MSW	Municipal solid waste
NKK	Nippon kokan KK
PCB	Printed circuit boards
PCF	Process CO_2 footprint
PCM	Phase change materials
RCA	Rotary cup atomizer
RCLA	Rotary cylinder atomizer
RMCA	Rotary multi-nozzle cup atomizer
SCPS	Selective crystallization and phase separation
SDA	Spinning disk atomizer
SS	Steel slag
TRT	Blast furnace top gas recovery turbine unit

1 Introduction

The metallurgical industry, especially the steel industry, as one of the most energy-intensive and CO_2-intensive industries, is responsible for around 4–5 % of total world energy consumption [1] and 9 % of process CO_2 emissions [2, 3], which is thus faced with the severe challenges of energy saving and emission reduction [4]. Actually, during the past decades, many advanced technologies have been introduced in the steel industry including the continuous casting operation [5, 6], the direct reduced iron (DRI) technique [7, 8] and the heat recovery from the process off gas [9, 10] and therefore the energy consumption per ton of crude steel has been greatly reduced; however, the results of energy consumption and greenhouse gases (GHG) emission are still quite unsatisfactory, especially in the context that targets set by the Intergovernmental Panel on Climate Change (IPCC) require that global emissions should be cut to less than 50 % of 2000 levels by 2050 [2, 3]. For example, Fruehan et al. [11] estimated that there was an opportunity to further reduce the energy consumption by around 25 % in the steel industry, indicating that the potential of energy saving is still great in the steel industry in the near future.

In 2013, the global output of crude steel reached as high as 1.55 billion tons [12]. With the CO_2 emission ratio of 1.9 ton per ton of crude steel production [1, 13], the GHG emission in the steel industry was thus more than 2.95 billion tons, which caused substantial impact on the acceleration of global warming. If the GHG emission target could be uniformly addressed, the steel industry should emit less than 1 billion tons of CO_2 per year by 2050 [2, 3], despite the population growth and economic development in many developing countries. Using scenario analysis method, Milford et al. [2] predicted that the last required blast furnace will be built by 2020. Therefore, it can be seen that there exists great challenges in the iron and steel sector to reduce GHG emission and specific energy consumption. Accordingly lots of measures from technological and policy prospects should be designed and introduced in the steel industry. Overall, these measures could be conventionally classified into two main strategies, i.e., material efficiency strategy and energy efficiency strategy [2, 14]. In a separate study on the energy intensity and greenhouse gases footprint of metallurgical processes, Barati [15] defined two new parameters to character the CO_2 footprint in the steel industry, i.e., material CO_2 footprint (MCF) and process CO_2 footprint (PCF), which were actually in consistent with these two strategies.

As for the material efficiency, Allwood et al. [14, 16] identify six potential material efficiency options: (1) increase of product life spans; (2) using existing goods more intensely; (3) lightweight product design; (4) updated manufacturing processes; (5) reuses of the fabrication scrap; (6) reuses of the components from unwanted products and buildings. The implementation of these material efficiency strategies not only requires the technological innovation but also requires the policy support, which would bring up great progress in the GHG emission reduction in the steel industry and further the achievement of the whole emission reduction target. In addition to these material efficiency methods, there are extensive energy efficiency strategies required to be employed in the iron and steel sector including the commercial applications of the less emissions intensive electric arc furnace (EAF) [17, 18] and the continuous casting technology [5, 6]. Another important energy efficiency strategy is to recover the utmost waste heat from the iron and steel industry, which has already attracted the attentions of the researchers worldwide. Furthermore, the transport cost could be compensated once the recovered waste heat could be reused or recycled in the iron and steel plant. Generally, the waste heat falls into three groups, namely outlet products, high temperature slags, and waste gases [1, 19]. In fact, the waste heat stored in the products and waste gases has been effectively recovered in the steel industry with the development of many advanced technologies including the thermoelectric power generation [20, 21] and the Blast Furnace Top Gas Recovery Turbine Unit (TRT) power generation [22, 23].

Hence it is generally believed that the heat recovery from the high temperature slags represents the last undeveloped potential to remarkably reduce the specific energy consumption in the steel industry [15, 19]. The molten slags are in common discharged at the high temperatures up to 1450–1650 °C, which carry a high-grade energy according to the second law of thermodynamics. Many investigations were performed in the 1970–1980s in the wake of energy crisis and a series of heat recovery technologies were exploited in the steel industry in Europe and Japan, which were focused on the physical granulation of the molten slags. However, unfortunately, quite few of these methods have been realized commercial application because of the fundamental properties of the molten slags and the immature technologies. Conventionally, the molten slags could be classified into ferrous slags and nonferrous slags [15] and the latter one involves the production of some specific metals such as the copper slags and the nickel slags, etc. The energy tapped in the ferrous slags alone accounts for over 90 % of the waste energy in the molten slags [15], which mainly comprises of blast furnace slags (BFS) and steelmaking slags (SS) and therefore the previous studies were mainly concentered on those two kinds of slags.

Generally around 0.3 ton of BFS and 0.1 ton of SS could be produced per ton of crude steel [24], and accordingly it could be calculated that the global output of the BFS and SS in 2012 were about 460 million tons and 150 million tons, respectively. The waste heat in these molten slags is corresponding to the heat of around 32 million tons of standard coal, which was a numerous energy capacity required to be recovered. However, much of the high grade energy at 1450–1650 °C was wasted because the molten slags were directly discharged into the slag yard. For example, the recovery ratio of the slag waste heat was less than 2 % in China [25] because of the present nonscientific disposal methods, which accounted for a significant potential of energy saving and GHG emission reduction in the steel industry. Traditionally, there were two kinds of widely used slag disposal methods, i.e., water quenching methods and naturally cooling method; through either of these methods the heat in the slags could not be recovered. The deep understanding of the properties and the development of novel recovery methods contribute to the crucial steps to effectively recover the waste from the slags, which was, actually, the initial objective of this paper. Moreover, we reviewed the technological methods previously and nowadays developed and characterized them in order to predict some possibly promising methods in the future.

2 Properties of the High Temperature Slags

As aforementioned, the constraints that restrict the industrial application of the heat recovery methods result from the fundamental properties of the slags including the basic physical and chemical properties of the molten slags and the specific hot process of these slags. A deep insight of these basic properties of the high temperature slags is the key to select and design a reasonable heat recovery method.

The first dominant property of the high temperature slags is the exactly low thermal conductivities [1, 15, 19] especially the liquid slags, which brings up the great difficulties of heat exchange between work medium and the liquid slags. Many studies measured the thermal conductivities of the slags using a series of methods such as the square wave pulse heat method [26], the hot strip method [27], and the hot wire method [28–30] and it was found that the thermal conductivity of the slags showed a regular variation trend, i.e., the thermal conductivity of the liquid slags was in the range of 0.1–0.3 W/(m K) while that of the glassy slags was in the range of 1–3 W/(m K). There was a great transition of the thermal conductivity of the slags near the glass forming temperature and it generally increased with increasing temperature with a constant slag state. However, the thermal conductivity of the crystalline slags remarkably increased up to 7 W/(m K) [19].

The low thermal conductivity of the slags increased the resistance of heat transfer and could thus cause a great temperature difference between the core and the surface of slags during the cooling path. For example, it was found that a slag ladle that has been left to cool in the air could remain liquid in the core for days [19]. In addition, through computational fluid dynamics (CFD) simulation, we found that the temperature difference differences could be more than 100 °C between core and surface of a BFS droplet with 3 mm in diameter [31], which was also proved by a few previous studies [32–34]. The low thermal conductivity and the big temperature difference between slag core and surface could decrease the inside cooling rate of the slags and therefore cause another property of the slags, i.e., easy crystallization trend inside the slags, which could increase the difficulties of further disposal of the slags and reduce the commercial value of the obtained solid slags. The basic constraints of the slag heat recovery were summarized in Table 1. As for the SS, because of the higher basicity (mass ratio of CaO/SiO_2) in the slags [35], the crystalline trend is stronger and even the crystallization behavior could not be avoided. The common hot processes of the molten slags are depicted in Fig. 1.

Once the liquid slags are discharged in the slag pool or yard and naturally cooled by the ambient air, crystals could form in the slags (BFS and SS) and the obtained slags with inside crystallizations could be utilized as roads/railways ballast and aggregates for concrete, etc. [1, 15] Actually, this accounts for one of the most

Table 1 The basic constraints of slag heat recovery

Constraints	Details	Meeting solutions	Refs.
Low thermal conductivity	1 W/(m K) for solid slags; 0.1 W/(m K) for liquid slags	Dry granulation into small particles/droplets	[1, 15, 19, 26–30]
Easy crystallization trend	Large temperature difference → Easy inside crystallization trend	Small particles; Water quenching	[31–35, 42, 43]

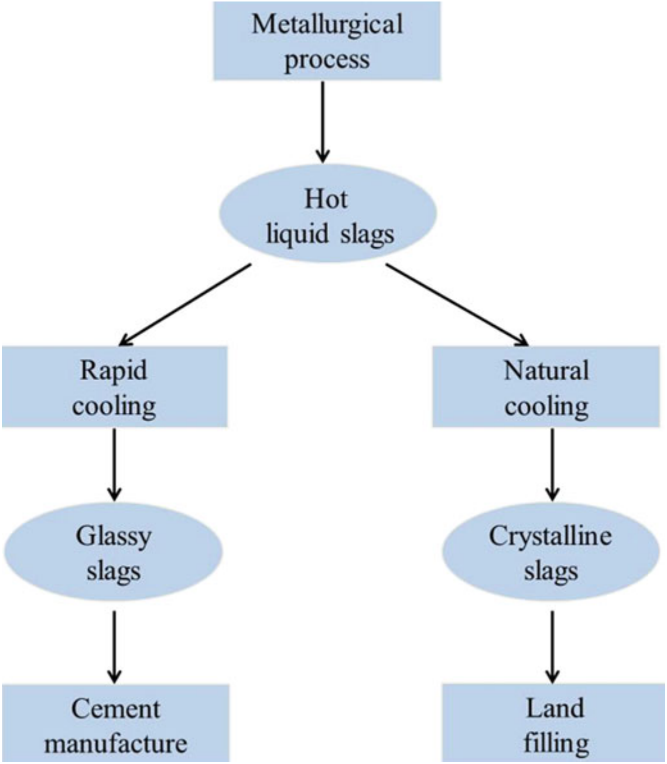

Fig. 1 Hot processes of the high temperature slags

traditional method to deal with the slags. Recently, more and more BFS is utilized as the alternative raw materials (ARM) in the cement industry because the main chemical compositions of the BFS (CaO, SiO_2, and Al_2O_3) are similar to those of Portland cement, whereas the employed slags should be in the glassy state because of the required hydraulic activity of the cement used for concrete [36, 37]. Actually, like the steel industry, the cement industry is an energy-intensive and CO_2-intensive industry, which also faces the great problem of emission reduction because of the substantial calcination of the limestone ($CaCO_3$) [38–40]. In 2013, the global output of cement was around 4 billion tons [41] and with the CO_2 emission ratio of 0.91–0.96 ton per ton of cement [24], the discharged CO_2 emission in the cement industry was in the range of 3.64–3.84 billion tons, which was pronouncedly more than that in the steel industry. In order to avoid the crystalline formation and confirm the amorphous state of the slags, the liquid slags must be rapidly quenched at a relatively high cooling rate, i.e., often more than 10 °C/s [42, 43], and two technological strategies could be conducted to realize this object, i.e., water quenching method and dry granulation method.

Nowadays water quenching method has been increasingly used because of the high value of the obtained glassy slags. However, there are many issues to be addressed during the water quenching process, which could be divided into the following three types: (1) the great water consumption and waste (1–1.2 ton of water per ton of slags [1, 44, 45]), actually the water shortage has been a serious problem in many developing countries; (2) environmental pollution, i.e., the leached alkaline from the slags could contaminate the ground water and the emitted H_2S and SO_2 could pollute the air [1, 45]; (3) energy consumption, i.e., the high-grade thermal heat in the molten slags is wasted and in addition the obtained wet slags require to be re-dried before used as the ASM in the cement industry. In order to deal with the foregoing problems and recover the waste heat from the high temperature slags, dry granulation method has been proposed and many technologies have been developed during the few past decades; these technologies, in fact, make up a significant type in the technological method family of slag heat recovery, i.e., physical method, which would be discussed in the following section in detail. The low thermal conductivity suppresses the heat exchange between the slags and the work medium and causes the inside crystallization behavior of the BFS; thus the slags should be granulated into small droplets or particles in order to increase the specific surface area of slags and thus the contact between the slags and the working medium and finally the heat transfer efficiency and the heat recovery ratio are increased.

3 Physical Method

As for the physical method, the slags should be first granulated into small particles and then the thermal heat of the droplets is transferred to the working medium such as air or steam [15, 19] and therefore the physical method is focused on the development of various granulation methods, which could be divided into several types based on the granulation mechanism. In a previous study by Zhang et al. [1], these different physical methods could be classified into three types, i.e., mechanical crushing granulation method, air blast granulation method, and centrifugal granulation method.

3.1 Mechanical Crushing Granulation Method

Mechanical crushing granulation method as a relatively traditional method was proposed to granulate the liquid slags, which included some specific technologies such as mechanical stirring, solid slag impingement and rotary drum process, etc. (1) Mechanical stirring method was first designed by Japanese Kawasaki steel corporation in 1980 [46–49], during which the operational process could be divided into two individual steps, i.e., the liquid slags were first crushed and granulated into

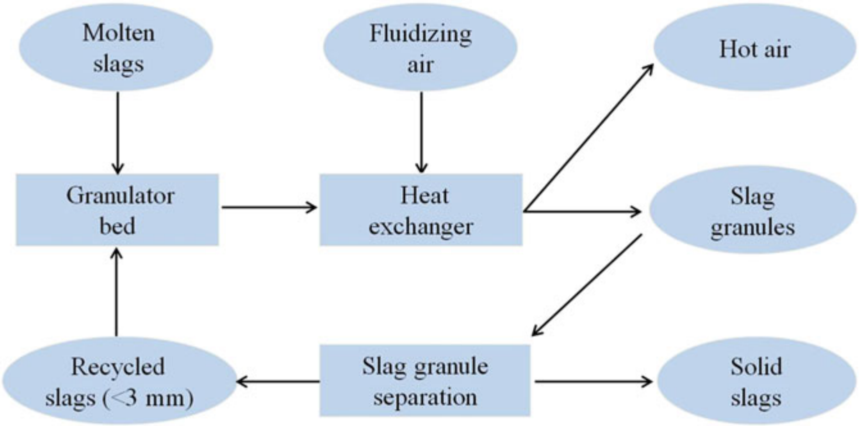

Fig. 2 Process of solid slag impingement method

small particles using rotary stick in a container and part of the sensible heat was transferred into the cool wall with flowing water; then the residual heat in the granulated slags were further exchanged into the cool air a fluidized bed. The heat recovery of mechanical stirring method was around 59 %. (2) Solid slag impingement method was first developed by Swedish group Merotec (a steel corporation) in 1979–1981 [47], as shown in Fig. 2, which could also divided into two related steps, i.e., the liquid slags were first impinged and granulated into granules by the previously small solid slag particles (<3 mm) and then the obtained granulated slags were fully contacted with the air in a multiple-step fluidized bed and the thermal heat were further exchanged; in addition, posttreatment was performed that the solid slags less than 3 mm were separated and recycled into the former granulator. The heat recovery of solid slag impingement method was around 75 %. (3) Rotary drumming method was first designed by Japanese Ishikawajima-Harima Heavy Industries and Sumitomo Metal in early 1980s [48] and then a twin-drum technique was developed by Nippon Kokan KK (NKK) in 1980s [49], which was also composed of two related steps, i.e., the liquid BFS was first impinged by the rotary drum and granulated into small particles and then the granulated slags was placed in the fluidized bed and fully reacted with the cool air to fulfill the heat exchange process. It has been reported the heat recoveries of the rotary single-drum and the twin-drum methods were 50–60 % and 40 %, respectively.

It should be pointed out that these mechanical crushing methods failed to realize industrial application especially nowadays because of the existed drawbacks [1]: (1) the heat recovery ratios of these methods were relatively low because of the relatively high temperature of the discharged solid slags; (2) the great energy consumption during the mechanical process, which lowered the recovery ratio of these methods [46–49]; (3) most importantly, the glass content in the obtained solid slags was not high enough for cement manufacturing and the diameter of the slag particles could not be effectively controlled, which increased the difficulties of the post use of these slags. However, as an important technological method, mechanical crushing method provided important clues of the further development of granulation methods; for example, the rotary single-drum shared some similar mechanism to some centrifugal granulation methods.

3.2 Air Blast Granulation Method

Air blast granulation method was a better method than the mechanical crushing method because of its recovery ratio and glass content in the slags, which was first developed by Mitsubishi Heavy Industries and NKK in 1970 and 1980s [50–53] because of the energy crisis. As displayed in Fig. 3, in this method, both air and cool water were used as working medium, i.e., the liquid slags were first broken up and granulated into small particles by the high velocity air ($\sim$100 m/s) ejected from a series of nozzles and partial heat of the slags were exchanged into the hot air; then the solid slags were taken successively into the heat boiler by the air and the second embedded boiler and the heat were extracted to the cool water tubes to form steam. Thus it could be concluded that the air blast method was composed of two successive steps, namely initial granulation by air and second heat exchange in the boiler by cool water. It was reported the heat recovery ratio of air blast method could be around 80 % and the slag particles were discharged in the range of <3 mm and at the temperatures of 200–300 °C. However, air blast granulated method were still faced with a series drawbacks such as the utilization of the high velocity air consumes a substantial energy and the liquid slags used should be pre modified to adjust its composition and the viscosity. Despite these shortcomings, nowadays air blast method is still in development and industrial trial in China, especially for the heat recovery from the SS [54, 55].

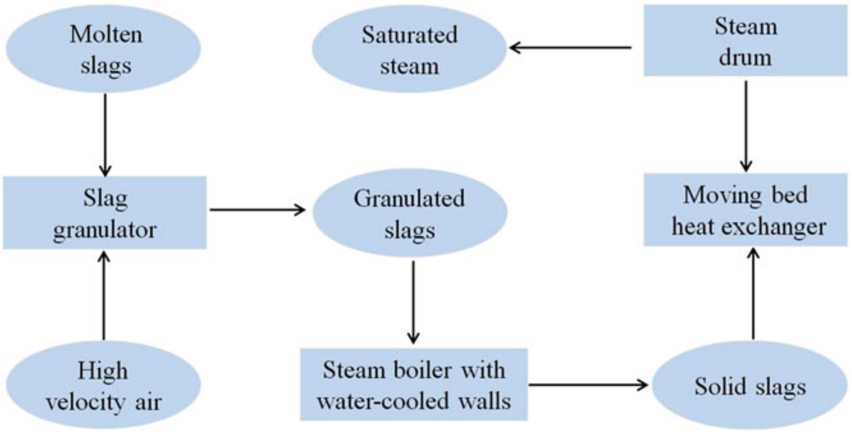

Fig. 3 Process of air blast method

3.3 Centrifugal Granulation Method

Another important type of physical methods is centrifugal granulation method and numerous techniques including the rotary cup atomizer (RCA) method and the further rotary cylinder atomizer (RCLA) method and spinning disk atomizer (SDA) method, have been developed in the past few decades due to its specific advantages. (1) Rotary cup atomizer was first developed by Pickering al. in 1985 [56], which was actually a combination of air blast method and centrifugal method, and many studies have been performed on this method [57–60]. The basic idea of RCA method is shown in Fig. 4. In this method, the granulation of liquid slags and the heat transfer between the slags and the air made up to divided steps, i.e., the liquid slags was poured into a rotary cup air blast atomizer located in the center of a vessel, ejected radially outwards into the space in the vessel because of the centrifugal force and granulated into small droplets due to the surface tension; then the granulated slags contacted with the vessel wall and fell onto two successive fluidized beds and the sensible heat of the slags were fully extracted to the cool air. The obtained slag particles were less than 2 mm and contained more than 95 % glassy phase, which were exactly suitable as the raw materials applied in the cement industry. Besides, the diameter distribution of the slag particles could be effectively controlled by changing the size of the outlet of the RCA and the rotating speed of the atomizer cup. The original recovery ratio of this method was around 59 % and on the other hand, the main shortcomings of RCA method were the formation of the slag wool and the degradation of the atomizer cup [1]. (2) Following the idea of RCA method, Kashiwaya et al. developed the RCLA method in a lab scale in 2010 [61, 62], the apparatus of which could be divided into a rotary cylinder with several nozzles and a graphite crucible. In this method, the cylinder was rotated in an individual speed and the liquid slags were squeezed from the nozzles and then

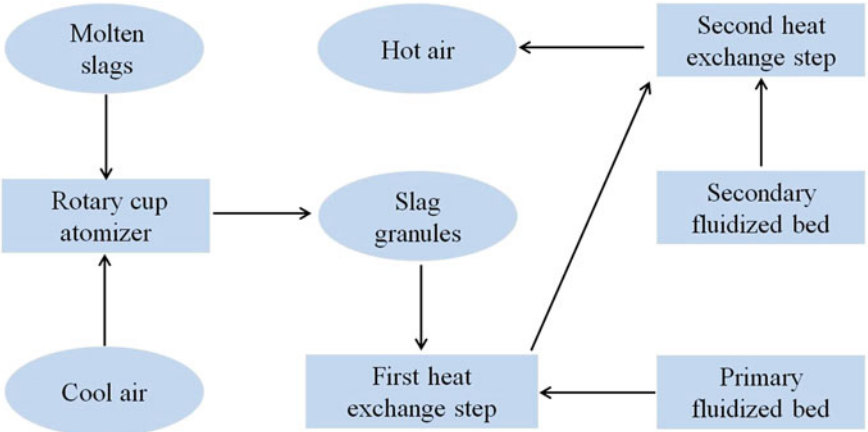

Fig. 4 Process of RCA method for slag heat recovery

granulated into small particles; in addition, the reasonable selective of the nozzle size and the rotation speed of atomizer cylinder is the key step. In a further study by Kashiwaya et al. [63], the RCLA method was even combined with the phase change material (PCM) heat storage, i.e., the glassy slag particles obtained by RCLA methods were utilized as a phase changing material.

Compared with RCA and RCLA methods, a rotating disk was employed to granulate the liquid slags in the SDA method, which was first developed in Japan by Sumitomo Metal Industries in 1980s [64]. The spinning disk process was composed of two related steps, i.e., the liquid slags were first fed on the rotating disk, impinged by the disk and granulated into small particle by the centrifugal force during which the temperature of the slags fell below 900 °C and the liquid slags transformed into glassy state; then the solid slag particles were dropped onto a packed bed and the secondary heat exchange fully occurred between the slags and the cool air [64–68]. This method showed the advantages of small particle size (1–1.5 mm), high glassy content and simple operations, so that a series of scale-up experiments are underway nowadays.

Through the foregoing numerous physical granulation methods, the liquid slags could be broken into small particles or droplets and the sensible heat were exchanged to the hot air or steam, which could be further used for the combustion in the blast furnace or for power generation. Actually physical granulation method contributes to a significant step of the slag heat recovery. All these methods could be categorized into the first generation in the technological method family of slag heat recovery and recently, heat recovery by chemical reactions has been extensively investigated because of the specific advantages.

4 Chemical Method

As aforementioned, many chemical methods for heat recovery from high temperature slags were exploited, which could be divided into three types, i.e., methane reforming reaction (MSR), a series of gasification and pyrolysis reaction (coal, biomass, and sewage sludge) and the utilization of the effective compositions in the slags. Furthermore, based on the thermodynamics calculation, it was predicted that the decomposition of limestone, reforming of methane and gasification of carbon are the most promising ways in the future [69]. The main advantages of chemical methods consisted of the combination of the various industries including the steel industry, cement industry, and the chemical engineering industry and the production of the high-value fuel gas. Actually, one of the dominant objectives of these methods was to collect the produced syngas composed of H_2 and/or CO.

4.1 Methane Reforming Reaction Method

MSR method was a typical chemical reaction for H_2 production [70, 71] and one of most investigated chemical reactions for the slag heat recovery, which was first proposed by Kasai et al. [72] in 1997. The concept of MSR using the waste heat from slags is shown in Fig. 5. The MSR heat recovery process could be divided into two parts, i.e., first the reaction of $CH_4 + H_2O = CO + H_2$ occurred in the steam reformer using the waste heat in the slags and second the chemical heat in the produced gases was released in the metalation reactor through the reversible reaction for steam production and CH_4 regeneration. The proposed concept was actually a single stage method, which was verified by a series of experiments since then. It was even found that the slags could act as an effective catalyst for MSR similar to that of Ni-base catalyst [73, 74] in addition to heat carrier [72, 75]. Furthermore, based on the concept of MSR, a combined system composed of a RCA system and a MSR system was designed by Maruoka et al. in 2004 [76], as displayed in Fig. 6. The liquid slags were first granulated using a RCA system and then a packed bed full of solid hot slags was used to perform the MSR.

In addition to steam, CO_2 could also be employed to conduct the methane reforming reactions [77, 78], especially from the view of point of carbon capture and storage (CCS). Moreover, the possibility of this combined system was proved in lab scale by Purwanto et al. in 2006 [79] using the biogas (CH_4) and CO_2 and the

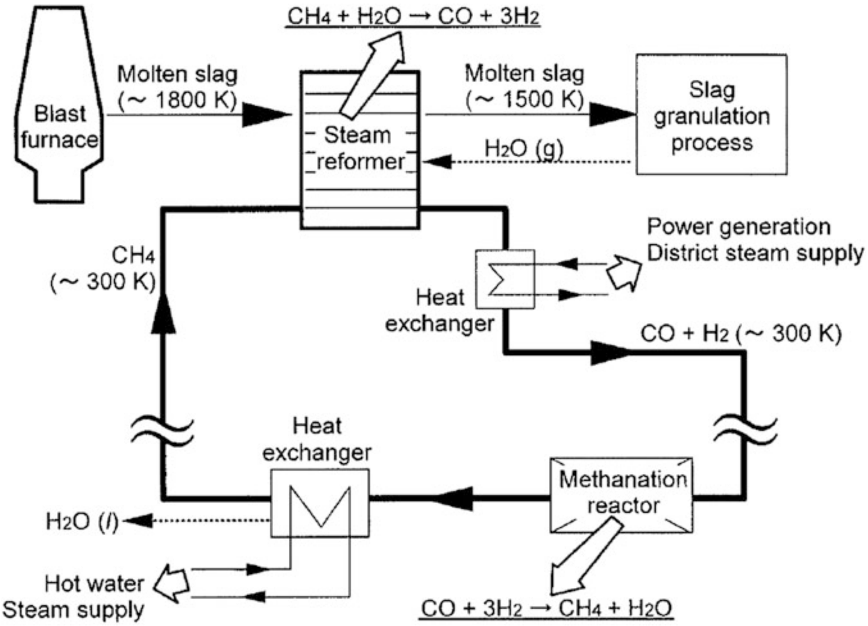

Fig. 5 Schematic diagram of the concept for MSR method [72]

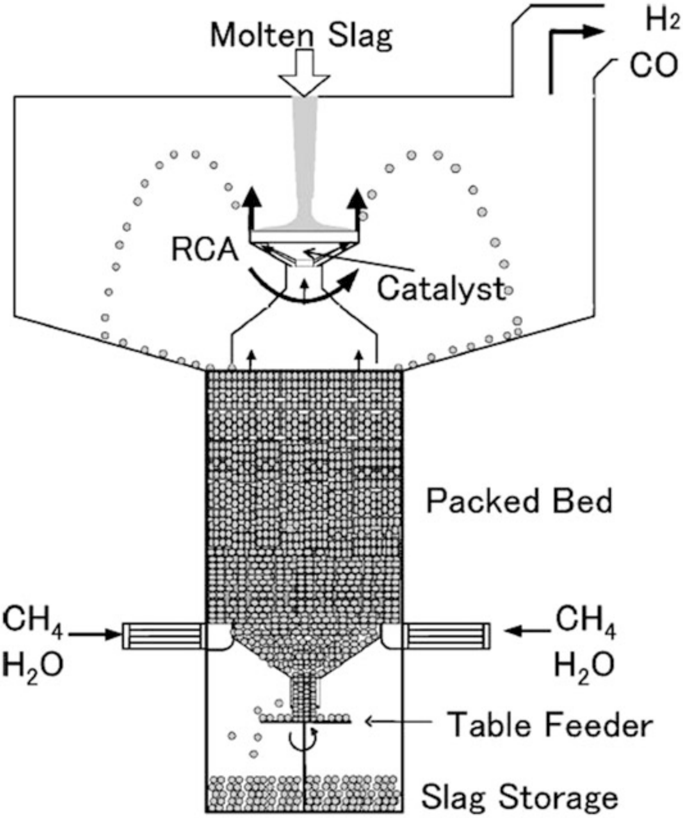

Fig. 6 Schematic diagram of the concept comprising RCA and MSR [76]

catalytic effect of the BFS was meanwhile identified in this study [79]. In addition to the MSR and methane-CO_2 decomposing, the waste heat in the molten slags could be used for the CH_4 thermal decomposition reaction by means of $CH_4 = C + 2H_2$. This concept was explored by Kashiwaya et al. [80] in 2012 through the CH_4 injection experiments into molten slag at 1500 °C and it was found that the CH_4 decomposition was enhanced by the existence of slag melts.

4.2 Pyrolysis and Gasification Reaction

Another significant chemical method was to utilize the sensible heat in the slags to perform the pyrolysis and gasification reaction of the organic materials in the fault coal, biomass, or the solid wastes such as waste printed circuit boards (PCB) [81], municipal solid waste (MSW) [82] and sewage sludge [83].

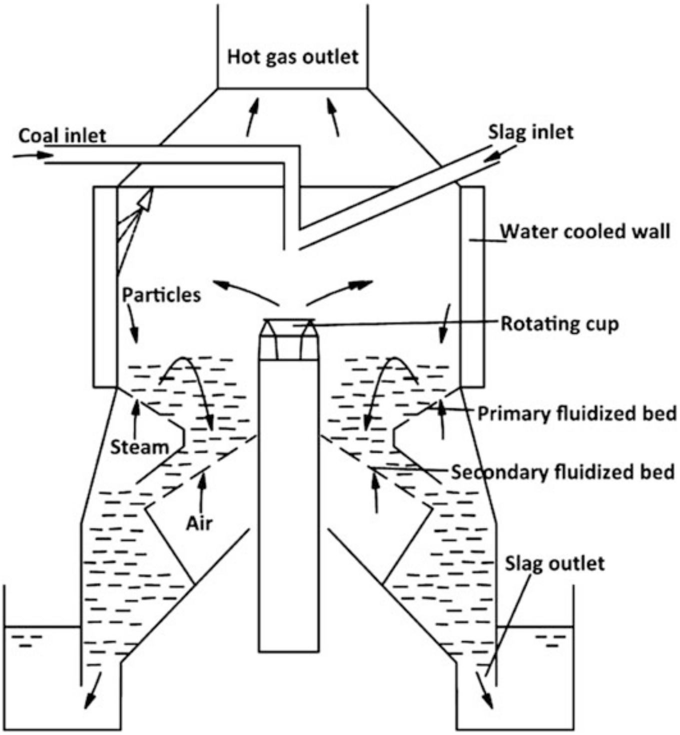

Fig. 7 Schematic of coal gasification process [1, 86]

(1) Generally, the heat for coal gasification was supplied by the partial combustion of the feed coal [84, 85] and the sensible heat in the hot slags showed potential to supply the required energy, the concept of which was first proposed by Liu et al. in 2004 [86], as displayed in Fig. 7. Similar to MSR method [72, 75], this system mainly consisted of a RCA system and a coal gasification system, i.e., the liquid slags were first granulated into small granules and then the solid hot slags was contacted with the fault coal and the coal gasification reaction occurred in two-stage fluidized bed. In order to explore the feasibility of this concept, the Yu Group not only designed a series of experiments in lab scale using CO_2 agent or waste gas from blast furnace [87–90] but also performed some thermodynamic calculations of coal gasification using hot slags [90, 91]; the catalytic effect of the slags on coal gasification was clarified and the combination of RCA and coal gasification was further proposed in a previous study [90]. Recently, the feasibility was also explored of coal pyrolysis using the waste heat from slags. Shatokha et al. [92] and Cahyono et al. [93] separately performed the researches on the combination of coal pyrolysis and slag heat recovery for the purpose of char production and tar reforming using BFS and SS, respectively. A more porous char

was obtained by Shatokha et al. [92] and it was found that the existed metal oxides in the slags effectively enhanced the tar decomposing reaction and thus the fuel gas production by Cahyono et al. [93].

(2) As a CO_2-neuteral resource, the gasification and pyrolysis of biomass was one of the most important ways of hydrogen production [94, 95]. Similar to coal gasification, the energy for biomass gasification and pyrolysis could be supplied by the high temperature slags, the concept of which was verified by Luo et al. in 2012 [96, 97]. A moving bed reactor was used to conduct the gasification (800–1200 °C) and pyrolysis (500–750 °C) using hot BFS and it was proved that BFS as a good catalyst for tar cracking and syngas production. However, these methods mainly contained a single stage of biomass thermal–chemical treatment and the further slag treatment was not discussed enough. Then in 2014, Sun et al. [98] designed a low temperature biomass gasification method using the hot slags (250–500 °C) and proposed an integrated system composed of several sectors including the steel industry, the cement industry, the chemical engineering industry and the agricultural sector, as displayed in Fig. 8. Most importantly, the produced syngas could be separated and used in the iron-making process [99–101] in order to reduce the carbon footprint in the steel industry. One significant problem of the biomass gasification pointed out was the contamination of the biomass ash on the BFS especially the Cl element and the alkali metal and thus the possible impact on the cement production, which should be reasonably controlled.

(3) With the continuous urbanization and the population growth in many developing countries, substantial solid wastes were discharged in the modern cities, the disposal of which became an important environmental issue [102–104].

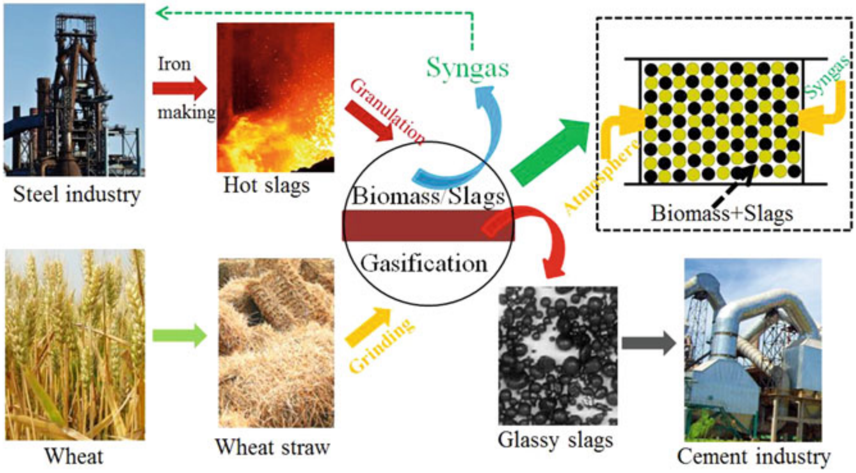

Fig. 8 An integrated prototype based on low temperature biomass gasification composed of multiple sectors [98]

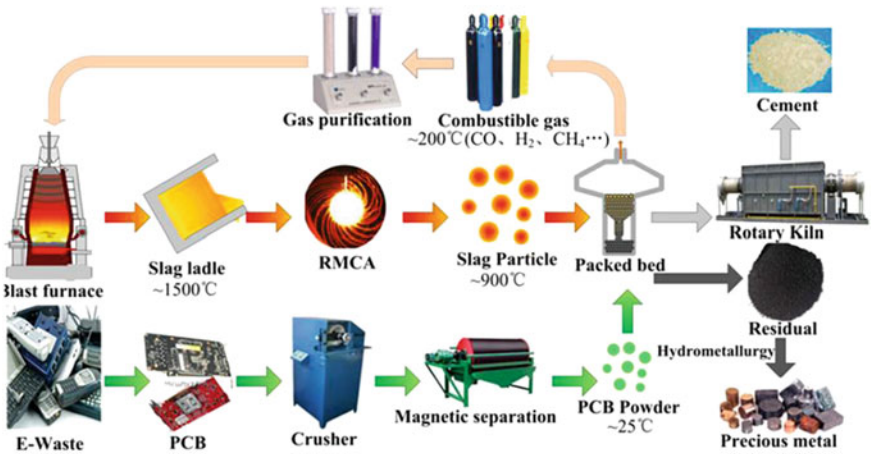

Fig. 9 Schematic of PCB pyrolysis using hot slags [81]

The thermal heat in the hot slags showed some potential to treat these solid wastes, the idea of which has been tried by a series lab scale experiments recently. In 2010, Luo et al. [82] explored the feasibility of MSW steam gasification using hot slags and they found that the BFS could act as not only heat carrier but also effective catalyst. In 2012, Qin et al. [81] proposed a novel method of waste PCB pyrolysis using the waste heat in the slags, the process of which could be divided into two stages, i.e., a slag granulation system in a rotary multi-nozzle cup atomizer (RMCA) and a PCB pyrolysis system, as displayed in Fig. 9. However, the recovery ratio of this method was less than 12 % because of the limited contact between the slags and the PCB and the heat loss of the system, which should be further optimized. In 2014, we proposed an integrated method consisting of the sludge/CO_2 gasification and the slag heat recovery using a fixed bed system [83]. The experiments were carried out at 500–950 °C using both BFS and SS and it was found that the solid BFS and SS acted as not only a heat carrier but also an effective SO_2 fixation because of the present CaO in the chemical composition of the slags.

4.3 Reduction Reaction Method

In addition to the foregoing slag heat recovery through the typical gasification and pyrolysis reactions, there were other chemical methods developed for fuel gas production. Theoretically speaking, the development of the CO and H_2 production method was a way of pursuit of reductant to reduce the H and C elements in H_2O and CO_2. On the one hand, the reductants could be the organics in natural materials such as biomass and sludge and the fixed carbon in the coal. On the other hand, the specific chemical compositions especially the metal oxide with low valence state in the hot slags could also be the possible alternative reductants. (1) The SS contains high content of FeO, which could be used as a potential reductant to reduce the steam to generate H_2 by the traditional means of $2FeO + H_2O = Fe_2O_3 + H_2$ [105, 106]. In 2012, Matsuura et al. [107] and Sato et al. [108] separately investigated this concept using thermodynamic calculations at (1600–1700 °C) and lab scale experiments at (1450 °C), respectively. The reaction could be conducted using the FeO-containing SS and the H_2O-Ar mixture gases and it was found that an increase in gas temperature (200–1000 °C) and FeO content in SS increased the H_2 production. As the crystallization ability of SS was much stronger than BFS due to a higher basicity, thus this single stage method could be effectively realized in the future because the SS contained abundant FeO [109] and the inside crystallization behaviors of slags could be exactly ignored. (2) Another potential metal oxide with low valence state was V_2O_3 in the V_2O_3-rich gasifier slag; and in 2014, Nakano et al. [110] designed a method of CO/H_2 production using the reaction of molten CaO-rich metallurgical slag and V_2O_3-rich gasifier slag by means of $3CaO + V_2O_3 + 2CO_2 = (CaO)3V_2O5 + 2CO$ and $3CaO + V_2O_3 + 2H_2O = (CaO)3V_2O_5 + 2H_2$. It was discovered that around 97 % CO_2 was converted into the CO at the temperatures of 1405–1460 °C and based on this efficiency it could be estimated that the a steel plant with the steel output of 7680 tons per day could consumed 970 tons of CO_2 and produced 620 tons of CO, which showed a great potential of CO_2 emission reduction. Besides the aforementioned metal oxides, there exist some other candidate low valence state metal oxides such as Ti_2O_3 in the titanium bearing slags [111], the utilization of which may be explored in the future.

5 Other Methods of the Heat Recovery from Slags

In the technological method family of heat recovery from hot slags, there were several other kinds of strategies, i.e., slag wool production, selective crystalline and phase separation (SCPS) and direct electricity generation, which cannot be simply categorized into the physical methods or chemical methods. The former two methods have already been widely used in the metallurgical industry because of the large treatment capacity and the development of latter method was just in infancy.

5.1 Selective Crystalline and Phase Separation Method

SCPS method was one of the most important methods to extract the valuable elements in the individual types of molten slags such as the titanium bearing slags [111–115], the vanadium bearing slags [116, 117] and the phosphorus bearing slags [118, 119] in the metallurgical industry. Actually, the achievement of SCPS could

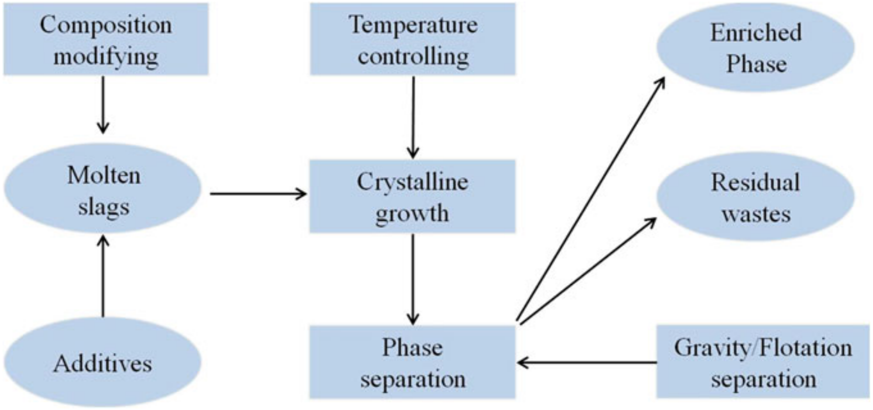

Fig. 10 Process of the SCPS method

also be divided into multiple steps, the concept of which is presented in Fig. 10. First, the chemical compositions of the liquid slags were modified by the additives in the direction that the crystallization behavior of the target crystalline phase was enhanced and thus the physical properties of the slags were changed such as the viscosity and the crystallization behaviors. Second the cooling path of the molten slags was reasonably controlled and the enriched crystalline phase fully grew and evolved with large size. After that, the enriched phase could be separated from other phases by various phase separation methods such as gravity separation method and flotation separation method. For example, during the extraction of titanium from titanium bearing BFS, it has been reported that the additives of SiO_2 [111, 115], B_2O_3 [114] and P_2O_5 [113] could be used for slag modification. It should be pointed out that SCPS method was exactly suitable for some specific kinds of hot slags and during the process of composition modification, part of the waste heat of the slags could be used to melt the added raw materials, from viewpoint of which, the waste heat in the slags was recovered.

5.2 Slag Wool Production Method

With the continuous development and urbanization, the demand for thermal insulation material is greatly increased in many countries. Compared with the organic insulation materials, slag wool showed the dominant advantage of fireproof [120–123], as a kind of inorganic insulation material. Similar to the SCPS, the mechanism of slag wool production was also focused on the modification of the chemical composition and the temperature control of the liquid slags, the concept of which is presented in Fig. 11. While different from the SCPS method, the aim of the composition of the slags was mainly to change the viscosities of the liquid slags in favor

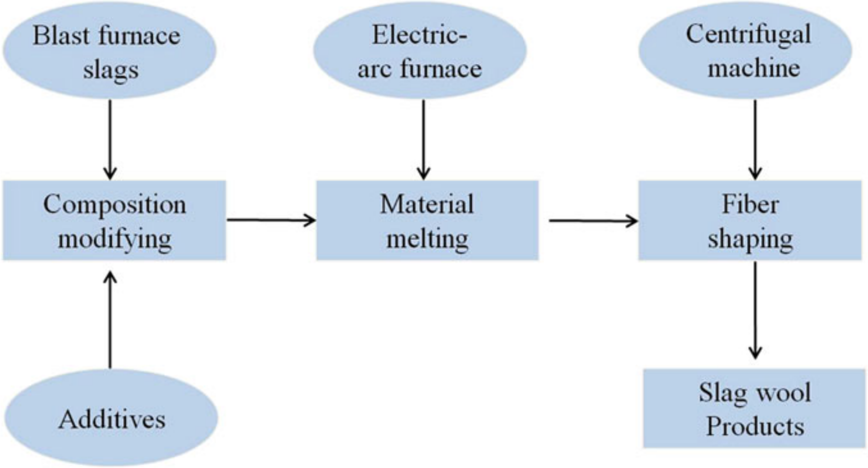

Fig. 11 Process of the production of slag wool

of the fiber shaping. The sensible heat in the slags could be used for additive melting and the hot air obtained from the fiber shaping process could be further recovered. Recently, Zhao et al. [122] and Li et al. [123] separately investigated the slag wool production using BFS modified by coal ash in China whereas the industrial application has already realized in Shanxi province, China. It was reported that the energy saving was more than 70 % through this new method compared with the traditional methods. In fact, utilization of the glassy slags (BFS) into the cement industry shared some similar characteristics to the slag wool production method. First, it was calculated that the heat release of glassy slags was 17 % less than the solidification slags during the cooling process [56] and this part of energy was utilized in the cement industry in order to confirm the hydraulic activity. Second, during both the slag wool production and the cement manufacturing processes, the whole compositions of the obtained slags were utilized as the raw materials despite that the content of the slags was different.

5.3 *Other Novel Methods*

In addition to the foregoing methods that directly disposed the slags, there were other novel methods mentioned in the recent studies. One environmentally friendly and reliable method was direct electricity generation through the Seeback effect to recover the waste heat from slags, which was first proposed by Rowe et al. in 2006 [124]. With the development of modern semiconductor materials with large Seeback coefficient [15, 125], this concept could be realized in the future, which is also tentatively employed in the heat recovery of waste gas nowadays. However,

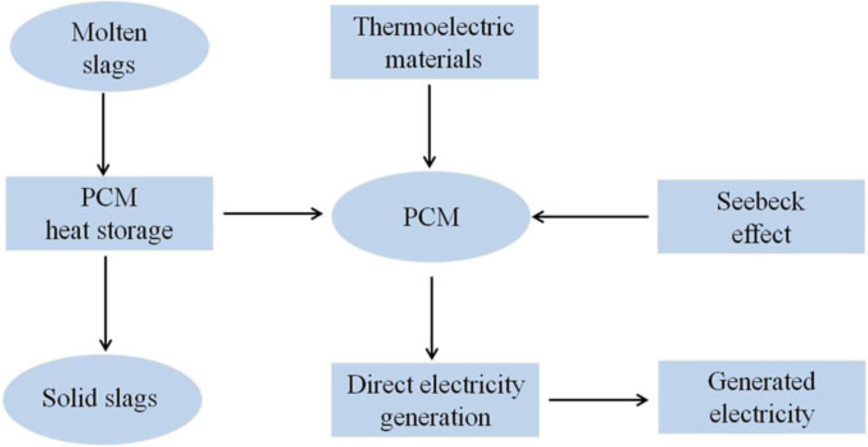

Fig. 12 Concept of two stages of PCM heat storage and direct electricity generation

the effective match of the slag temperature and the temperature range of semiconductor materials accounted for a great challenge to realize this process. A possible idea was that, similar to the foregoing methods, a two-stage method was designed, i.e., the heat of the high temperature slags was first extracted into the PCM [126–128] and then the reaction between the PCM and the thermoelectric materials occurred for power generation the concept of which is presented in Fig. 12. This two-stage method required the emergence of the high temperature PCM and the first step of this method provided important clues of many other heat recovery methods, for example, the waste heat of the SS could be first stored in the PCM and then the chemical reactions could occurred using the heat of PCM, which actually, could enhance the stability of the whole system.

6 Summary and Conclusions

As aforementioned, it is believed that the waste heat recovery from the high temperature slags and the waste off gas represents the last potential to reduce the energy consumption in the steel industry. However, the results of the heat recovery from the molten slags are not satisfactory nowadays because of the specific properties of the slags. Meanwhile, in order to meet the fundamental constraint and achieve the heat recovery, numerous methods have been proposed and verified during the past few decades. A deep understanding of the basic properties and the mechanism of the various methods is the key step to design and select a feasible method to effectively recover the substantial waste heat, which is, actually, the aim of this study.

The basic constraint that resisted the heat recovery ratio was the low thermal conductivity of the slags. For the common BFS from iron-making process, the low thermal conductivity caused a low cooling rate of the slags and therefore the inside crystallization behavior, which reduced the value of the BFS. In order to ensure the formation of the glassy state and the further utilization of the slags as the raw materials in the cement industry, the hot slags should be quickly cooled and therefore water quenching method and physical granulation method are generally used to achieve this target. Because of drawbacks of the water quenched method, many dry granulation methods have been exploited, which make up the physical method family of slag heat recovery. The basic property of the liquid slags determined that the slags should be granulated into small particles in order to quickly extract the thermal heat of the slags into the working medium.

As for the physical method family of heat recovery, the developed methods could be classified into three typical kinds according to the specific mechanism, i.e., mechanical crushing granulation method, air blast granulation method and centrifugal granulation method, which are summarized in Table 2 in detail. The mechanical crushing granulation method has been ceased because of the drawbacks such as energy consumption and system complexity. On the opposite, the air blast method is still under development in China. Furthermore, the recently extensive

Table 2 Summary of the various physical methods for heat recovery

Physical granulation method	Mechanism for heat recovery	Recovery ratio	The time first proposed	Refs.
Mechanical stirring	First step: granulation (rotary stick); Second step: heat exchange (fluidized bed)	59 %	1980	[47–50]
Solid slag impingement	First step: granulation (impinged by small solid slags); Second step: heat exchange (fluidized bed)	75 %	1979–1981	[48]
Rotary drumming	First step: granulation (impinged by rotary drum); Second step: heat exchange (fluidized bed)	<60 %	1980s	[49, 50]
Air blast	First step: granulation (high velocity air); Second step: heat exchange (two step boiler)	80 %	1970s	[51–56]
Rotary cup atomizer	First step: granulation (Rotary cup air atomizer); Second step: heat exchange (fluidized bed)	59 %	1985	[57–61]
Rotary cylinder atomizer	Granulation using a rotary cylinder with several nozzles	–	2010	[62–64]
Spinning disk atomizer	First step: granulation (Spinning disk atomize); Second step: heat exchange (packed bed)	–	1980	[65–69]

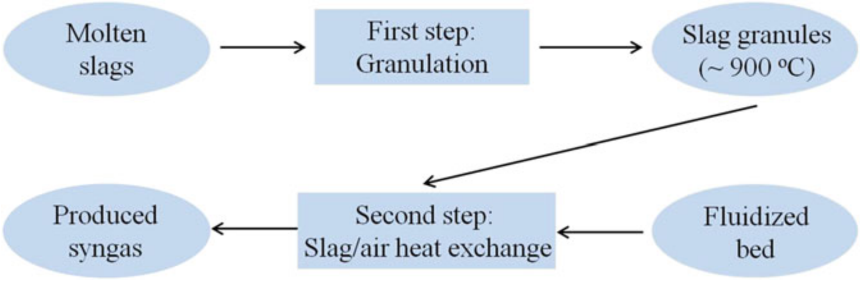

Fig. 13 Concept of two steps of physical granulation method

investigations of centrifugal methods including RCA methods and RCLA methods are mainly focused on a two-step process. The liquid slags were first granulated into small granules to form the glassy state and part of the thermal energy was recovered during which the temperatures fell to around 900 °C in the atomizer and then the obtained solid granules were further contacted with the cool air in the fluidized beds and the residual heat were fully exchanged. The crucial point of these physical methods was the full heat recovery of the slags and the avoidance of the crystallization behavior and therefore a two-step physical method was theoretically reasonable, which, actually, represented the research trend of the development of physical methods. The basic concept of two-step physical method is shown in Fig. 13.

As for the chemical method family of slag heat recovery, syngas production accounted for the main research trend recently such as the MSR method, biomass and coal gasification and pyrolysis and the gasification reactions of a series of solid wastes including the MSW and sewage sludge, which are summarized in Table 3 in detail. Through these reactions, the high value fuel gas composed of CO and H_2 were collected. Another basic idea of chemical methods were the pursuit of reductants to reduce the C and H elements in CO_2 and H_2O into CO and H_2 and the effective components in the slags could also be used, following which a series of metal oxides with low valence state were employed including FeO in SS and V_2O_3 in V_2O_3-rich gasifier slag. Moreover, for the heat recovery from BFS using chemical methods, the process were generally divided into two stages, i.e., the liquid slags were first granulated into small particles below 900 °C to obtain the glassy phase and then the chemical reactions between the solid slags and other materials occurred, which contributed to an important research trend of chemical methods. The basic concept of two-stage process is shown in Fig. 14.

As for other methods in the technological method family of slag heat recovery, the SCPS method and slag wool production method showed the similar mechanism, which was also shared by the idea that the glassy BFS were used as raw materials in the cement industry. A concept of multiple stages was employed, i.e., the liquid slags were first modified by the additives, then the temperature of the slags was effectively controlled and finally the enriched crystalline phase fully evolved or the

Table 3 Summary of the various chemical methods for heat recovery

Reaction type	Reaction equation	Slag type	Reaction role of slag	The time first proposed	Refs.
Methane steam gasification	$CH_4 + H_2O = CO + 3H_2$	Blast furnace slag	Heat carrier, catalyst	1997	[69, 72, 75, 76]
Methane–CO_2 decomposition	$CH_4 + CO_2 = 2CO + 2H_2$	Blast furnace slag	Heat carrier, catalyst	2006	[79]
Methane thermal decomposition	$CH_4 = C+2H_2$	Blast furnace slag	Heat carrier	2012	[80]
Coal pyrolysis	Tar $\rightarrow H_2 + CO + CO_2$ + other light hydrocarbon	Blast furnace slag, steel slag	Heat carrier, catalyst	2012	[92, 93]
Coal–steam gasification	$C + H_2O = CO + H_2$	Blast furnace slag	Heat carrier	2014	[91]
Coal–CO_2 gasification	$C + CO_2 = 2CO$	Blast furnace slag	Heat carrier, catalyst	2004	[86–90]
Gasification of municipal solid waste		Blast furnace slag	Heat carrier, catalyst	2010	[82]
Pyrolysis of printed circuit boards	$C_mH_nO \rightarrow C_aH_bO_c + CO + H_2 + CH_4 + CO_2$	Blast furnace slag	Heat carrier	2012	[81]
Gasification of sewage sludge	$C_mH_nO + CO_2 \rightarrow aCO + bH_2 + cCH_4$	Blast furnace slag, steel slag	Heat carrier	2014	[83]

(continued)

Table 3 (continued)

Reaction type	Reaction equation	Slag type	Reaction role of slag	The time first proposed	Refs.
Biomass pyrolysis	$C_mH_nO_x \rightarrow aCO_2 + bH_2O + cCO + dCH_4 + fC_{2+}$	Blast furnace slag	Heat carrier	2012	[96]
Biomass gasification	$C_mH_nO_x + H_2O \rightarrow$ $aCO_2 + bH_2O + cCO + dCH_4 + fC_{2+}$	Blast furnace slag	Heat carrier, catalyst	2012	[97, 98]
FeO reduction	$2FeO + H_2O = Fe_2O_3 + H_2$ $3FeO + H_2O = Fe_3O_4 + H_2$	Steel slag	Heat carrier, reactant	2012	[107, 108]
V_2O_3 reduction	$3CaO + V_2O_3 + 2CO_2 = (CaO)_3(V_2O_5) + 2CO$ $3CaO + V_2O_3 + 2H_2O = (CaO)_3(V_2O_5) + 2H_2$	CaO-rich metallurgical slag; V_2O_3-rich gasifier slag	Heat carrier, reactant	2014	[110]

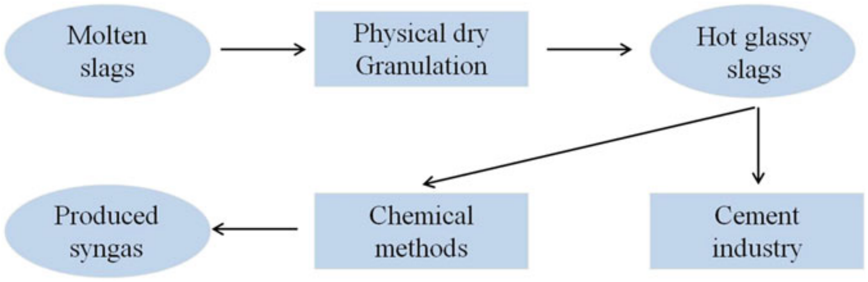

Fig. 14 Concept of two stages of physical granulation and chemical reactions

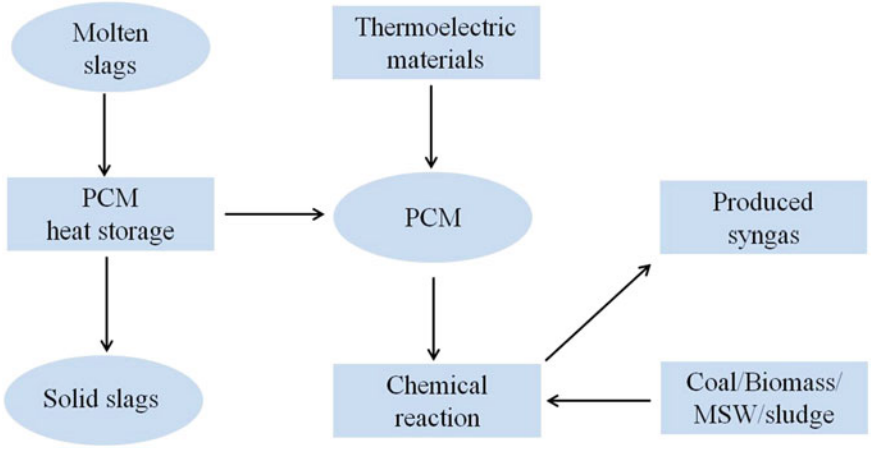

Fig. 15 Concept of two stages of PCM heat storage and chemical reactions

slag fiber was shaped and produced. In addition, the direct electricity generation method based on the See beck effect using modern thermoelectric materials could be combined with the PCM heat storage, which was also indicated a two-stage idea and could make up a novel research trend. Furthermore, the PCM heat storage could be the first stage of slag heat recovery and then acted as the stable heat source to supply the heat for the gasification reaction using chemical methods especially when the crystallization behavior of the slags could be ignored, which was also suggesting a concept of two stages, as depicted in Fig. 15.

From the aforementioned analysis, it could be concluded that, logically speaking, the two-step physical granulation method, the two-stage process combined of physical granulation and chemical reaction and the two-stage method combined of PCM heat storage and chemical reaction composed the main research trends in the heat recovery from high temperature slags. The reason lies in not only the basic properties of the hot slags such as low thermal conductivity and the easy inside crystallization trend but also the initial objective of a specific method such as the production of the high value CO or H_2 and the confirmation of the post use of the solid slags. Theoretically, the cooling path of the hot slags could be divided into liquid region, crystallization region and the solid region with the individual temperature ranges [129], which indicated that the temperature schedule of the hot slags should be composed of multiple stages and consequently a two-step or two-stage heat recovery method was determined.

Furthermore, the combination of multiple sectors to design an integrated system made up another characteristic of the research trend of the slag heat recovery including the steel industry, cement industry, chemical engineering industry, urban municipal sector and agricultural sector. Only by designing and employing a reasonable method, could the waste heat in the high temperature slags be effectively recovered and the GHG emission reduction and energy saving in the steel industry be achieved in time. Most importantly, the achievement of the heat recovery and the integrated system required not only the technological innovations but also the necessary roadmaps of city plan and policy support [130–132].

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References

1. Zhang H, Wang H, Zhu X, Qiu YJ, Li K, Chen R, Liao Q (2013) A review of waste heat recovery technologies towards molten slag in steel industry. Appl Energy 112:956–966
2. Milford RL, Pauliuk S, Allwood JM, Müller DB (2013) The roles of energy and material efficiency in meeting steel industry CO_2 targets. Environ Sci Technol 47:3455–3462
3. Allwood JM, Cullen JM, Milford RL (2010) Options for achieving a 50 % cut in industrial carbon emissions by 2050. Environ Sci Technol 44:1888–1894
4. Cullen JM, Allwood JM, Bambach MD (2012) Mapping the global flow of steel: from steelmaking to end-use goods. Environ Sci Technol 46:13048–13055
5. United Nations, Economic Commission for Europe (1979) The increasing use of continuous processes in the iron and steel industry and their techno-economic aspects. United Nations, New York
6. Warner NA (2003) Towards coal based continuous steelmaking. Part 1: iron ore fines and scrap to low carbon steel via melt circulation. Ironmaking Steelmaking 30:429–434
7. Inaba S (2001) Overview of new direct reduced iron technology. Tetsu-to-Hagane (J Iron Steel Inst Jpn) 87:221–227
8. Kawatra SK, Anameric B (2007) Properties and features of direct reduced iron. Miner Process Extr M28:59–116
9. Pardo N, Moya JA (2013) Prospective scenarios on energy efficiency and CO_2 emissions in the European iron and steel industry. Energy 54:113–128
10. Hasanbeigi A, Morrow W, Sathaye J, Masanet E, Xu TF (2013) A bottom-up model to estimate the energy efficiency improvement and CO_2 emission reduction potentials in the Chinese iron and steel industry. Energy 50:315–325

11. Fruehan RJ, Paxton HW, Fortini O, Brindle R (2000) Theoretical minimum energies to produce steel for selected conditions. U.S. Department of Energy, Washington, DC
12. Steel Statistical Yearbook (2013) World steel association. http://www.worldsteel.org/publications/bookshop/product-details.~Steel-Statistical-Yearbook-2013~PRODUCT~SSY2013~.html. Accessed 10 Mar 2015
13. Zhang X, Zhou S (2009) The prospect of sensible heat recovery of blast furnace slag. In: The 7th China iron and steel annual meeting proceedings, Beijing, China, 11–13 Nov 2009, vol 7, pp 175–178
14. Allwood JM, Gutowski TG, Ashby MF, Worrell E (2010) Material efficiency: a white paper. Resour Conserv Recyc 55:362–381
15. Barati M (2010) Energy intensity and greenhouse gases footprint of metallurgical processes: a continuous steelmaking case study. Energy 35:3731–3737
16. Allwood JM, Cullen JM, Carruth MA, Cooper DR, McBrien M, Milford RL, Moynihan M, Patel ACH (2012) Sustainable materials: with both eyes open. UIT, Cambridge
17. Abu-Eishah SI, El-Dieb AS, Bedir MS (2012) Performance of concrete mixtures made with electric arc furnace (EAF) steel slag aggregate produced in the Arabian gulf region. Constr Build Mater 34:249–256
18. Bakkar A (2014) Recycling of electric arc furnace dust through dissolution in deep eutectic ionic liquids and electro winning. J Hazard Mater 280:191–199
19. Bisio G (1997) Energy recovery from molten slag and exploitation of the recovered energy. Energy 22:501–509
20. Sahin AZ, Yilbas BS (2013) The thermoelement as thermoelectric power generator: effect of leg geometry on the efficiency and power generation. Energ Convers Manag 65:26–32
21. Date A, Dixon C, Akbarzadeh A (2013) Progress of thermoelectric power generation systems: prospect for small to medium scale power generation. Renew Sust Energy Rev 33:371–381
22. Wu P, Yang CJ (2012) Identification and control of blast furnace gas top pressure recovery turbine unit. ISIJ Int 52:96–100
23. Arens M, Worrell E, Schleich J (2012) Energy intensity development of the German iron and steel industry between 1991 and 2007. Energy 45:786–797
24. Hendrik GVO (2010) Slag, iron and steel. US geological survey minerals yearbook. http://minerals.usgs.gov/minerals/pubs/commodity/iron_&_steel_slag/index.html#myb. Accessed 10 Mar 2015
25. Cai J, Wang J, Chen C, Lu Z (2007) Recovery of residual heat integrated steelworks. Iron Steel 42:1–6
26. Nishioka K, Maeda T, Shimizu M (2006) Application of square-wave pulse heat method to thermal properties measurement of $CaO\text{-}SiO_2\text{-}Al2O_3$ system fluxes. ISIJ Int 46:427–433
27. Li F, Susa M, Nagata K (1991) Temperature and composition dependence of thermal conductivity, thermal diffusivity and specific heat of the $PbO\text{-}SiO_2$ system. J Jpn Inst Met 55:194–203
28. Kang Y, Morita K (2006) Thermal conductivity of the $CaO\text{-}Al_2O_3\text{-}SiO_2$ system. ISIJ Int 46:420–426
29. NagataK SM, Goto KS (1983) Thermal conductivities of slags for iron making and steelmaking. Tetsu-to-Hagané 69:1417–1424
30. Goto KS, Linder KH (1985) Thermal conductivities of blast furnace slags and continuous casting powders in the temperature range 100–1550 °C. Stahl U Eisen 105:1387–1391
31. Sun Y, Shen H, Wang H, Wang X, Zhang Z (2014) Experimental investigation and modeling of cooling processes of high temperature slags. Energy 76:761–767
32. Yoshinaga M, Fujii K, Shigematsu T, Nakata T (1981) Method of dry granulation and solidification of molten blast furnace slag. Tetsu-To-Hagané 67:917–924
33. Yoshinaga M, Fujii K, Shigematsu T, Nakata T (1982) Dry granulation and solidification of molten blast furnace slag. Tetsu-To-Hagané 22:823–829
34. Meng Y, Thomas BG (2003) Heat-transfer and solidification model of continuous slab casting: CON1D. Metall Mater Trans B 34:685–705

35. Li Q, Meng A, Zhang Y (2009) Recovery status and prospect of low-grade waste energy in China. In: International conference on sustainable power generation and supply, Nanjing, China, 6–7 April 2009, pp 2024–2029
36. Nakada T, Nakayama H, Fujii K, Iwahashi T (1983) Heat recovery in dry granulation of molten blast furnace slag. Energy Dev Jpn 55:287–309
37. Liu J, Yu Q, Dou C, Li R (2010) Experimental study on heat transfer characteristics of apparatus for recovering the waste heat of blast furnace slag. Adv Mater Res 97:2343–2346
38. Worrell E, Price L, Martin N, Hendriks C, Meida LO (2001) Carbon dioxide emissions from the global cement industry. Ann Rev Energy Environ 26:303–329
39. Monshi A, Asgarani MK (1999) Producing Portland cement from iron and steel slags and limestone. Cem Concrete Res 29:1373–1377
40. Schneider M, Romer M, Tschudin M, Bolio H (2011) Sustainable cement production-present and future. Cem Concrete Res 41:642–650
41. The statistics portal, world cement production (2010–2013) http://www.statista.com/statistics/219343/cement-production-worldwide/
42. Ryu HG, Zhang ZT, Cho JW, Wen GH, Sridhar S (2010) Crystallization behaviors of slags through a heat flux simulator. ISIJ Int 50:1142–1150
43. Kashiwaya Y, Nakauchi T, Pham KS, Akiyama S, Ishii K (2007) Crystallization behaviors concerned with TTT and CCT diagrams of blast furnace slag using hot thermocouple technique. ISIJ Int 47:44–52
44. Guo H, Zhou S (2010) Discussion about heat recovery technology of blast furnace slag. In: The proceeding of iron making technology conference and iron making academic annual meeting, Beijing, China, 26–28 May 2010, pp 1044–1048
45. Qin Y, Lv X, Zhang J, Hao J, Bai C (2014) Determination of optimum blast furnace slag cooling rate for slag recycling in cement manufacture. Ironmaking Steelmaking 42(5):395–400
46. Fujii K et al (1981) Apparatus for heat recovery from molten slag. United States patent, 4,350,326. https://www.google.com/patents/US4350326. Accessed 21 Sept 1982
47. Li S (2009) Heat recovery from B.F. Slag at home and abroad. Ind Heating 38:23–25
48. Dai X, Qi Y, Zhang C (2008) Development of molten slag dry granulation and heat recovery in steel industry. J Iron Steel Res 20:1–6
49. Xu Y, Ding Y, Cai Z, Liu Q, Ye S (2007) Development of heat recovery from blast furnace slag using dry granulation methods. China Metall 17:23–25
50. Yoshida H, Nara Y, Nakatani G, Anazi T, Sato H (1984) The technology of slag heat recovery at NKK SEAISI conference of energy utilization in the iron and steel industry, Singapore, 10–13 Sept 1984, pp 1–21
51. Mitsubishi Heavy Industries Ltd. and Nippon Kokan K.K. (1982) Granulating apparatus for slag melts. Japan Patent 5, 915, Japan
52. Fukuyama Works (1983). Blast granulation system of BOF slag and its products. Nippon Kokan Technical report No. 38
53. Ando J, Nakahar T, Onous H, Tchimura S, Kondo M (1985) Development of slag blast granulation plant characterized by innovation of the slag treatment method, heat recovery, and recovery of slag as resources. Mitsubishi Heavy Industries technical review, pp 136–142
54. Chen G et al (2010) The development of steel slag quenching with wind technology and energy saving. In: National conference of energy and environmental protection technologies, Jiujiang, China, 22–24 June 2010, pp 494–499
55. Industry and Information Technology Department of Hebei province. <http://www.ii.gov.cn/news/qyfc/2010/10/101029102248929.html>
56. Pickering SJ, Hay N, Roylance TF, Thomas GH (1985) New process for dry granulation and heat recovery from molten blast furnace slag. Ironmaking Steelmaking 12:14–21
57. Mizuochi T, Akiyama T, Shimada T, Kasai E, Yagi JI (2001) Feasibility of rotary cup atomizer for slag granulation. ISIJ Int 41:1423–1428
58. Liu J, Yu Q, Li P, Duan W (2012) Cold experiments on ligament formation for blast furnace slag granulation. Appl Therm Eng 40:351–357

59. Liu J, Yu Q, Duan W, Qin Q (2014) Experimental investigation on ligament formation for molten slag granulation. Appl Therm Eng 73:886–891
60. Qu Y, Mao Y, Zhang D, Wang Z (2011) Progress on granulation for blast furnace slag by rotary cup atomizer at home and abroad. Energy Metall Ind 30:23–25
61. Kashiwaya Y, In-Nami Y, Akiyama T (2010) Development of a rotary cylinder atomizing method of slag for the production of amorphous slag particles. ISIJ Int 50:1245–1451
62. Kashiwaya Y, In-Nami Y, Akiyama T (2010) Mechanism of the formation of slag particles by the rotary cylinder atomization. ISIJ Int 50:1252–1258
63. Kashiwaya Y, Akiyama T, In-Nami Y (2010) Latent heat of amorphous slags and their utilization as a high temperature PCM. ISIJ Int 50:1259–1264
64. Yoshinaga M, Fujii K, Shigematsu T, Nakata T (1982) Dry granulation and solidification of molten blast furnace slag. Trans Iron Steel Inst Jpn 22:823–829
65. Xie D, Jahanshahi S (2008) Waste heat recovery from molten slags. In: 4th international congress on science and technology of steelmaking, Gifu, pp 674–677. Iron and Steel Institute of Japan, Japan
66. Akiyama T, Mizuochi T, Yagi J, Nogami H (2004) Feasibility study of hydrogen generator with molten slag granulation. Steel Res Int 75:122
67. Xie D, Washington B, Norgate T, Jahanshahi S (2005) Dry granulation of slags turning waste into valuable cement binder. CAMP-ISIJ 18:1088–1091
68. Xie D et al (2007) Heat recovery from slag through dry granulation. In: Jahanshahi S, Rickards T (eds) 1st CSRP annual conference. CSIRO Minerals, Melbourne, pp 29–30
69. Akiyama T, Oikawa K, Shimada T, Kasai E, Yagi JI (2000) Thermodynamic analysis of thermochemical recovery of high temperature wastes. ISIJ Int 40:288–291
70. Xu J, Froment GF (1989) Methane steam reforming, methanation and water-gas shift: I. Intrinsic kinetics. Aiche J35:88–96
71. Gallucci F, Paturzo L, Famà A, Basile A (2004) Experimental study of the methane steam reforming reaction in a dense Pd/Ag membrane reactor. Ind Eng Chem Res 43:928–933
72. Kasai E, Kitajima T, Akiyama T, Yagi JI, Saito F (1997) Rate of methane-steam reforming reaction on the surface of molten BF slag: for heat recovery from molten slag by using a chemical reaction. ISIJ Int 37:1031–1036
73. Hou K, Hughes R (2001) The kinetics of methane steam reforming over a Ni/α-Al_2O catalyst. Chem Eng J 82:311–328
74. Laosiripojana N, Assabumrungrat S (2005) Methane steam reforming over Ni/Ce-ZrO_2 catalyst: influences of Ce–ZrO_2 support on reactivity, resistance toward carbon formation, and intrinsic reaction kinetics. App Catal Gen 290:200–211
75. Shimada T, Kochura V, Akiyama T, Kasai E, Yagi JI (2000) Effects of slag compositions on the rate of methane-steam reaction. ISIJ Int 41:111–115
76. Maruoka N, Mizuochi T, Purwanto H, Akiyama T (2004) Feasibility study for recovering waste heat in the steelmaking industry using a chemical recuperator. ISIJ Int 44:257–262
77. Rostrupnielsen JR, Hansen JB (1993) CO_2-reforming of methane over transition metals. J Catal 144:38–49
78. Ruckenstein E, Hu YH (1998) Combination of CO_2 reforming and partial oxidation of methane over NiO/MgO solid solution catalysts. Ind Eng Chem Res 37:1744–1747
79. Purwanto H, Akiyama T (2006) Hydrogen production from biogas using hot slag. Int J Hydrogen Energy 31:491–495
80. Kashiwaya Y, Watanabe M (2012) Kinetic analysis of the decomposition reaction of CH_4 injecting into molten slag. ISIJ Int 52:1394–1403
81. Qin Y, Lv X, Bai C, Qiu G, Chen P (2012) Waste heat recovery from blast furnace slag by chemical reactions. Jom 64:997–1001
82. Zhao L, Wang H, Qing S, Liu H (2010) Characteristics of gaseous product from municipal solid waste gasification with hot blast furnace slag. J Nat Gas Chem 19:403–408
83. Sun Y, Zhang Z, Liu L, Wang X (2015) Integrated carbon dioxide/sludge gasification using waste heat from hot slags: syngas production and sulfur dioxide fixation. Bioresour Technol 181:174–182

84. Irfan MF, Usman MR, Kusakabe K (2011) Coal gasification in CO_2 atmosphere and its kinetics since 1948: a brief review. Energy 36:12–40
85. Higman C, Tam S (2013) Advances in coal gasification, hydrogenation, and gas treating for the production of chemicals and fuels. Chem Rev 114:1673–1708
86. Liu HX (2004) Investigation of coal gasification using blast furnace molten slag as heat carrier. Energy Conserv 6:41–43
87. Li P, Yu Q, Qin Q, Lei W (2012) Kinetics of CO_2/Coal gasification in molten blast furnace slag. Ind Eng Chem Res 51:15872–15883
88. Li P, Yu Q, Qin Q, Liu J (2011) Adaptability of coal gasification in molten blast furnace slag on coal samples and granularities. Energy Fuels 25:5678–5682
89. Li P, Yu Q, Xie H, Qin Q, Wang K (2013) CO_2 gasification rate analysis of datong coal using slag granules as heat carrier for heat recovery from blast furnace slag by using a chemical reaction. Energy Fuels 27:4810–4817
90. Duan W, Yu Q, Zuo Z, Qin Q, Li P, Liu J (2014) The technological calculation for synergistic system of BF slag waste heat recovery and carbon resources reduction. Energy Conv Manag 87:185–190
91. Duan W, Yu Q, Xie H, Qin Q, Zuo Z (2014) Thermodynamic analysis of hydrogen-rich gas generation from coal/steam gasification using blast furnace slag as heat carrier. Int J Hydrogen Energy 39:11611–11619
92. Shatokha VI, Sokolovskaya IV (2012) Study on effect of coal treatment with blast furnace slag on char reactivity in air. Ironmaking Steelmaking 39:439–445
93. Cahyono RB, Rozhan AN, Yasuda N, Nomura T, Hosokai S, Kashiwaya Y, Akiyama T (2013) Integrated coal-pyrolysis tar reforming using steelmaking slag for carbon composite and hydrogen production. Fuel 109:439–444
94. Ahrenfeldt J, Thomsen TP, Henriksen U, Clausen LR (2013) Biomass gasification cogeneration–a review of state of the art technology and near future perspectives. Appl Therm Eng 50:1407–1417
95. Bridgwater AV (1995) The technical and economic feasibility of biomass gasification for power generation. Fuel 74:631–653
96. Luo S, Zhou Y, Yi C (2012) Hydrogen-rich gas production from biomass catalytic gasification using hot blast furnace slag as heat carrier and catalyst in moving-bed reactor. Int J Hydrogen Energy 37:15081–15085
97. Luo S, Yi C, Zhou Y (2013) Bio-oil production by pyrolysis of biomass using hot blast furnace slag. Renew Energy 50:373–377
98. Sun Y, Zhang Z, Seetharaman S, Liu L, Wang X (2014) Characteristics of low temperature biomass gasification and syngas release behavior using hot slag. RSC Adv 4:62105–62114
99. Lin H, Van Wagner E, Freeman BD, Toy LG, Gupta RP (2006) Plasticization-enhanced hydrogen purification using polymeric membranes. Science 311:639–642
100. Yang T, Chung TS (2013) High performance ZIF-8/PBI nano-composite membranes for high temperature hydrogen separation consisting of carbon monoxide and water vapor. Int J Hydrogen Energy 38:229–239
101. Denys RV, Poletaev AA, Solberg JK, Tarasov BP, Yartys VA (2010) LaMg11 with a giant unit cell synthesized by hydrogen metallurgy: crystal structure and hydrogenation behavior. Acta Mater 58:2510–2519
102. Kelessidis A, Stasinakis AS (2012) Comparative study of the methods used for treatment and final disposal of sewage sludge in European countries. Waste Manag 32:1186–1195
103. Yang T, Xu Z, Wen J, Yang L (2009) Factors influencing bioleaching copper from waste printed circuit boards by Acidithiobacillus ferrooxidans. Hydrometallurgy 97:29–32
104. Arena U (2012) Process and technological aspects of municipal solid waste gasification: a review. Waste Manag 32:625–639
105. Hacker V, Fankhauser R, Faleschini G, Fuchs H, Friedrich K, Muhr M, Kordesch K (2000) Hydrogen production by steam-iron process. J Power Sources 86:531–535

106. Rydén M, Arjmand M (2012) Continuous hydrogen production via the steam-iron reaction by chemical looping in a circulating fluidized-bed reactor. Int J Hydrogen Energy 37:4843–4854
107. Matsuura H, Tsukihashi F (2012) Thermodynamic calculation of generation of H_2 gas by reaction between FeO in steelmaking slag and water vapor. ISIJ Int 52:1503–1512
108. Sato M, Matsuura H, Tsukihashif F (2012) Generation behavior of H_2 gas by reaction between FeO-containing slag and H_2O-Ar gas. ISIJ Int 52:1500–1502
109. Dippenaar R (2005) Industrial uses of slag (the use and re-use of iron and steelmaking slags). Ironmaking Steelmaking 32:35–46
110. Nakano J, Bennett J (2014) CO_2 and H_2O gas conversion into CO and H_2 using highly exothermic reactions induced by mixed industrial slags. Int J Hydrogen Energy 39:4954–4958
111. Li J, Zhang Z, Zhang M, Guo M, Wang X (2011) The influence of SiO_2 on the extraction of Ti element from Ti—bearing blast furnace slag. Steel Res Int 82:607–614
112. Zhang L, Zhang LN, Wang MY, Li GQ, Sui ZT (2007) Recovery of titanium compounds from molten Ti-bearing blast furnace slag under the dynamic oxidation condition. Miner Eng 20:684–693
113. Sun Y, Li J, Wang X, Zhang Z (2014) The effect of P_2O_5 on the crystallization behaviors of Ti-bearing blast furnace slags using single hot thermocouple technique. Metall Mater Trans B45:1446–1455
114. Sun Y, Li Z, Liu L, Wang X, Zhang Z (2015) Co-modification and crystalline-control of Ti-bearing blast furnace slags. ISIJ Int 55:158–165
115. Li J, Wang X, Zhang Z (2011) Crystallization behavior of rutile in the synthesized Ti-bearing blast furnace slag using single hot thermocouple technique. ISIJ Int 51:1396–1402
116. Wu X, Li L, Dong Y (2011) Enrichment and crystallization of vanadium in factory steel slag. Metallurgist 55:401–409
117. Monakhov IN, Khromov SV, Chernousov PI, Yusfin YS (2004) The flow of vanadium-bearing materials in industry. Metallurgist 48:381–385
118. Basu S, Lahiri AK, Seetharaman S (2007) Phosphorus partition between liquid steel and $CaO\text{-}SiO_2\text{-}P_2O_5\text{-}MgO$ slag containing low FeO. Metall Mater Trans B 38:357–366
119. Diao J, Xie B, Wang YH, Guo X (2012) Recovery of phosphorus from dephosphorization slag produced by duplex high phosphorus hot metal refining. ISIJ Int 52:955–959
120. Yang H (2003) A new one-step technology of mineral wool production by using the sensible heat of industrial BF slag high-efficiently. Patent No. 02152584, Property Office of the People's Republic of China
121. Ji R, Zhang Z, Liu L, Wang X (2013) Numerical modeling and experimental study of heat transfer in ceramic fiberboard. Text Res J 84:411–421. 0040517513485630
122. Zhao D, Zhang Z, Tang X, Liu L, Wang X (2014) Preparation of slag wool by integrated waste-heat recovery and resource recycling of molten blast furnace slags: from fundamental to industrial application. Energies 7:3121–3135
123. Li J, Liu W, Zhang Y, Yang A, Zhao K (2014) Research on modifying blast furnace slag as a raw of slag fiber. Mater Manuf Process. doi:10.1080/10426914.2014.973597
124. Rowe DM (2006) Thermoelectric waste heat recovery as a renewable energy source. Int J Innov Energy Syst Power 1:13–23
125. Ismail Basel I, Ahmed Wael H (2009) Thermoelectric power generation using waste heat energy as an alternative green technology. Recent Pat Electr Eng 2:27–39
126. Nomura T, Okinaka N, Akiyama T (2010) Technology of latent heat storage for high temperature application: a review. ISIJ Int 50:1229–1239
127. Pandiyarajan V, Pandian MC, Malan E, Velraj R, Seeniraj RV (2011) Experimental investigation on heat recovery from diesel engine exhaust using finned shell and tube heat exchanger and thermal storage system. Appl Energy 88:77–87
128. Pitié F, Zhao CY, Baeyens J, Degrève J, Zhang HL (2013) Circulating fluidized bed heat recovery/storage and its potential to use coated phase-change-material (PCM) particles. Appl Energy 109:505–513

129. Sun Y, Zhang Z, Liu L, Wang X (2014) Multi-stage control of waste heat recovery from high temperature slags based on time temperature transformation curves. Energies 7:1673–1684
130. City plan of Beijing (2004–2020). http://www.china.com.cn/aboutchina/zhuanti/09dfgl/2009-03/04/content_17371797.htm
131. Dong L et al (2014) Promoting low-carbon city through industrial symbiosis: a case in China by applying HPIMO model. Energy Policy 61:864–873
132. Joss S, Molella AP (2013) The eco-city as urban technology: perspectives on Caofeidian international Eco-City (China). J Urban Technol 20:115–137