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Review

Modifying hot slag and converting it into value-added materials: A review

Yu Li [a,*], Wen-Bin Dai [a,b]

[a] State Key Laboratory of Advanced Metallurgy, University of Science and Technology Beijing, No.30 Xueyuan Road, Haidian District, Beijing 100083, China
[b] Beijing Building Materials Academy of Sciences Research Co. Ltd, No.69 North Road Jinding Street, Shijingshan District, Beijing 100041, China

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ABSTRACT

Waste heat of metallurgic slags at 1450–1650 °C are the largest secondary energy which are still not reused in iron and steel industry. How to reuse such huge slag and its waste heat have become a great challenge for constructing a greener iron and steel industry. A method for directly modifying hot slag and converting it into value-added materials has been developed in recent years. Two kind of hot slag modification technologies are firstly reviewed in this paper. Crude modification of hot slag was conducted to enhance its properties such as disintegration, volume expansion, cementitious reactivity, heavy metal leaching, iron component recovery, etc. Fine modification of hot slag has been developed to prepare high value-added products, such as glass-ceramics, mineral wool and fertilizers. Moreover, dispose of hazardous solid waste and recovery of valuable metals by hot slag modification method were introduced as two significant research trends from the economic and environment point of view. Finally, many bottleneck problems on application of hot slag modification technologies are proposed. Related researches in this areas will construct a green industrial chain among metallurgy, silicate and environmental industry in the future, and hot slag modification technologies as a core has a broader development perspective.

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* Corresponding author.
E-mail address: leeuu00@sina.com (Y. Li).

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1. Introduction

The iron and steel industry is an energy-intensive industry that consumes the largest manufacturing energy, accounting for approximately 6.7% of the world's total CO_2 gas emissions (Watson et al., 2005; Wu et al., 2016) and 18% of the world's total industry final energy consumption in 2013 (International Energy Agency (IEA), 2015). Global crude steel output had reached 1665 Million tons in 2014 with an average annual growth rate of 6.85% from 2000 to 2014 (World Steel Association, 2015). Accordingly, energy consumption in the iron & steel sector increase rapidly.

Improving energy efficiency is one way for manufacturing industries to reduce costs, and energy-saving technologies can be attractive from a business point of view (Johansson, 2015). In iron and steel industry, Fruehan et al. (2000). estimated that there is an opportunity to further reduce the energy consumption for making liquid steel by about 20–30%. Waste heat of high temperature (1450–1650 °C) slags tapped from blast-furnace (BF), converter and electric-furnace (BOF and EAF) are the largest secondary energy which still were not reused (Barati et al., 2011; Bisio, 1997; Dai et al., 2008). In China, 250 million tons of BF slag at about 1450 °C with heat of 15 × 10^6 tons standard coal equivalency (tce) and 100 million tons of steel slag (including BOF and EAF slag) at about 1650 °C with heat of 6.8 × 10^6 tce were produced in 2014, but almost all of their waste heat dissipated in the air. How to utilize hot slag and its waste heat is an urgent and meaningful research works.

In industry, methods of utilizing waste heat for hot solid and for hot liquid are different. As shown in Fig. 1 (a), taking coke dry quenching (CDQ) process as example, heat and mass of hot solid were separated and then utilized respectively. In CDQ chamber, heat is transferred into gas from hot coke, and then cold coke with improved quality is conveyed for iron-making process while heat of heated gas is further transferred to water and steam for electricity generation. Beside hot coke, heat recover of hot sintering mine and clinker belong to this method. For the three hot solid, enhancement of their quality by quenching of cold gas is the most primary goal at the first stage even without any heat recovery. With development of energy saving technologies, recovering heat of flue gas become feasible and popular both in economy and environment and has been applied into practices at the present stages.

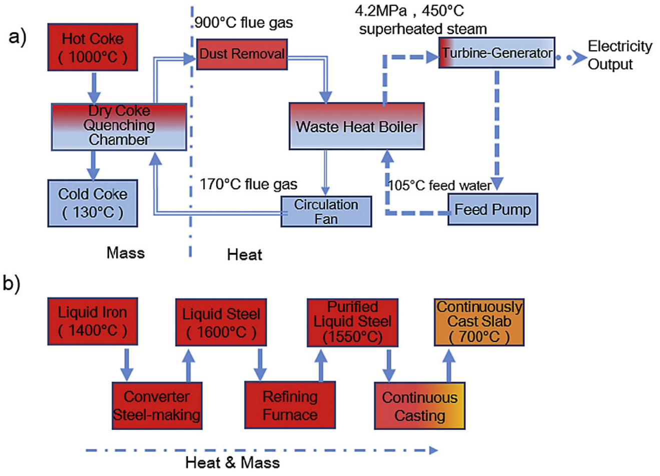

Fig. 1. Comparison of typical method of utilizing waste heat between hot solid and hot liquid, a) Separate utilization of heat and mass for hot solid taking cake dry quenching process as example; b) Integrated utilization of heat and mass for hot liquid taking steel making process as example.

Liquid iron is a typical hot liquid tapped after iron making process. Fig. 1 (b) showed its change in a traditional steel making process. Heat and mass of liquid iron are integrated utilized to produce liquid steel, purified liquid steel and continuously cast slabs respectively after converter (basic oxygen furnace), refining furnace and continuous casting process. Value from liquid iron to cast slabs improved from $300/ton to $550/ton and even more. Because hot liquid was used directly to prepare new higher value-added materials at the same high temperature, energy and exergy of hot liquid could almost completely utilized in subsequent process for preparation of the materials.

With respect to hot slag, two methods, traditional route and improved route were developed and shown in Fig. 2, which respectively corresponded to separate utilization of heat and mass for hot solid and integrated utilization of heat and mass for hot liquid.

Traditional routes (Barati et al., 2011; Bisio, 1997; Dai et al., 2008; Fruehan et al., 2000; Johansson, 2015) are generally composed of two steps: physical or chemical methods to recover heat after dry granulation, and utilization of cooled granulated slag (Fruehan et al., 2000; Li et al., 2013a, b; Qin et al., 2012; Yoshinaga et al., 1981). For both physical and chemical method, dry granulation is necessary for heat transfer, but difference between them is thermal medium of heat transfer in subsequently heat recovery process. For the former method, air, N_2 or steam gas are often used as thermal medium for finally generating electricity. While for the latter, reactants are as thermal medium for its chemical reaction whose heat could be supplied by transfer of heat from hot slag particles.

However, thermal conductivity in slag melts is from only 1–2 kcal/(m·h·°C)$^{-1}$, and the temperature difference between the core and surface of a slag particle of 5 mm in diameter could exceed 200 °C (Yoshinaga et al., 1981). The very low thermal conductivity of slag makes it difficult to improve heat transfer efficiency between slag particles and different thermal media. Recent researches (Qin et al., 2012) on chemical method showed that the heat recovery ratio achieved was only 7%–12%. As for physical method, summary (Li et al., 2013a, b; Qi et al., 2012) about heat recovery efficiency of seven industrially test processes for the hot BF slag shows that exergy recovery efficiency of the seven processes ranged from 9.5% to 41.5%, which was significantly less than that of CDQ process, 73%. So, the largest problem for heat recovery from molten slag is how to recover energy at a high quality level.

Moreover, quality of BF slag would be degraded when dry granulation method was applied into it. A large cooling rate is hard to obtain for the slag particle especially in its inner parts, which would result in precipitation of crystals in it, deterioration of its potential cementitious reactivity and finally its rejection by cement industry (Mizuochi et al., 2001).

Though many researches (Fruehan et al., 2000; Johansson, 2015; Li et al., 2013a, b; Qi et al., 2012; Xu et al., 2007) on BF slag have made progress, those methods are still not put into practice.