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CURRENT DEVELOPMENT OF SLAG VALORISATION IN CHINA

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Abstract

The current state of ironmaking and steelmaking slags valorisation in China is reviewed in this paper. The hot stage processing processes with respect to BF slag granulation and steel slag pyrolytic self-slaking have made progress and are applied in a number of large steelmaking companies in China. Current researches and developments are focusing on the dry granulation of molten BF slag with high efficiency of heat recovery. In this paper, the dry granulation process flow and semi-industrial experiment results are described.

Introduction

The crude steel and pig iron production in China are 626.65 and 590.21 million tonnes, respectively, in 2010. Meanwhile, the steel slags and blast furnace slags have reached 81.47 and 200.67 million tonnes, respectively.[1] The ratios of utilisation or valorisation are 21% for steel slags and 76% for blast furnace slags. Both values are still far from the previous planned target. Realising "zero" dumping of iron and steelmaking slag has been an urgent task to save energy, to reduce the emission, to protect the environment and to develop a recycling economy in the steel industry. The better understanding of the importance of the resource and energy conservation actively forced slag recycling towards the development of application technologies and publicity activities. During the last period of the "five years plan" (2006 to 2010), under the exerted pressure of the Chinese government by law and policy and through the efforts of Chinese industrial society with technology innovations, a series of technical routes, management modes, valorisation standards and environmental regulations for the utilisation of iron and steelmaking slags were established in China. The fundamental researches with mathematical modelling and laboratory experiments were also carried out in the research institutes and universities in China and got significant progress. In this work, the current state including application developments and fundamental researches with respect to ironmaking and steelmaking slags valorisation in China is reviewed.

Current State of Ironmaking and Steelmaking Slags Valorisation in China

From 2005 to 2010, the quantity of iron and steelmaking slags generated and the un-utilised piled slags were increasing year by year (see left diagram of Figure 1), although the ratio of slags valorised (or utilised) was increasing gradually (see right diagram of Figure 1). Here the utilisation or valorisation ratio is defined as the percentage of slags which were reused as a resource or material after dressing of steel particles and iron oxides. The slag valorisation routes and their ratio are listed in Table 1. [1]

Table 1: Slag valorisation routes and their ratio

Type of slags		Main valorisation routes	Ratio(%)
BF slag	Water granulated	Ground granulated BF slag powder as cement and concrete material	48.5
		Cement mortar material	46.5
	Air cooled	Blinding	5.0
Steel slags		Ground granulated steel slag powder as cement and concrete material	5.4
		A series of Portland cements grades	30.1
		Bricks	1.1
		Road construction and backfilling	63.4

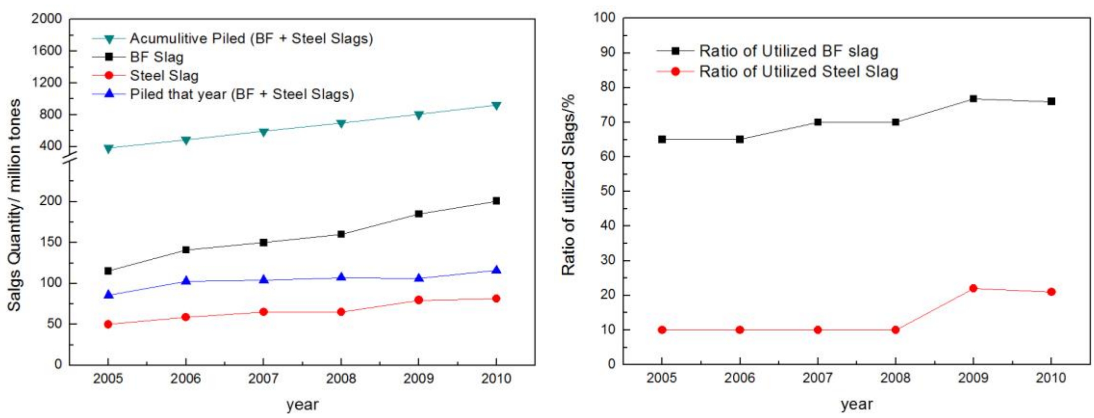

Figure 1: Changes in the quantity of iron and steelmaking slags (left) and ratio of the utilised slag to total slag (right) during 2005 to 2010 in China

It should be pointed out that the re-use of steel slag in the ironmaking and steelmaking process is not included in Table 1 and that the data for steel slag valorisation indicates the percentage of the slag which was utilised as the specified construction material after dressing of steel particles and iron oxides.

Main hot stage slag valorisation processes for Ironmaking and Steelmaking Slags in China

The hot stage processing for BF slags

In China, different methodologies are used to granulate the BF slags. These mainly include INBA, TYNA, SG-MTC, and Jiaheng processes. These processes involve pouring the molten slag through a high-pressure water jet or a rotation drum and then with water cooling in close proximity to the blast furnace. The slag undergoes accelerated cooling under controlled water flow, thus forming vitreous solidified slag sand. The most popular process for hot stage slag treatment of large scale blast furnace is the INBA or modified INBA. The INBA process was developed by SIDMAR and Paul Wurth in 1981. Due to its reliability, low sulphur emissions, and limited water consumption, the INBA process was first introduced in 1991 by Baosteel for No. 2 Blast furnace (4063 m^3).[2] After that, Wuhan, Ma'anshan, Benxi, and Taiyuan Steel companies adopted the INBA process. WISDRI Engineering & Research Incorporation Limited Company developed a modified INBA process called IDE (Impact, Drum improved and Environmental friendly). The distance from the granulation box to the process tank is lengthened by a channel which is 7 meter long to allow the hot slag to adequately react with the water stream. The filtering capacity of the drum was improved greatly and suitable for 10t/min to a maximum of 14 t/min. The condensing ability for steam was also enhanced to minimise the emission of steam outside. The water flowrate for slag granulation is 2000 m^3/h. Granulated BF slag contains more than 95% vitreous phases and less than 15% water. Up till June 2012, 9 sets of IDE units were employed in practice, thereby operating in 6 blast furnaces ranging from 1800 m^3 to 5800 m^3, and 6 sets are under construction. [3]

The hot stage processing for BOF slags

About seven process types are being used in Steel works for BOF slag stabilisation treatment in China. These had been described in the 1st international slag valorisation symposium.[4]

The pyrolytic Self-slaking process is one of the seven processes and widely employed in China. The hot molten slag is poured into a tank with a cover, while water is sprayed into the tank, resulting in steam generation. This water steam reacts with the free lime and magnesia in the slag to obtain a stabilised BOF slag. This stabilised slag is subjected to size reduction for different utilisations. This process was designed by China Jingye Eng. Corporation Ltd. Due to the good stability, the wide suitability of the treated slag and the high recovery yield of steel grains from the residual slag, the pyrolytic self-slaking process is generally used in China. From 2007 to 2010, this process has been adopted by more than 30 steel companies such as Bayuquan works of Ansteel Group, Jingtang Caofeidian works of Shougang Group, Benxi Steel, Xinyu Steel, Jiujiang Steel, Rizhao Steel, *etc*.. The treatment ability of these installations ranges from 0.25 to 1.7 million tonnes slag/year. During 2008 to 2010, 31 million tonnes steel slags were treated and recovered iron increased 496 thousand tonnes by the newly installed Pyrolytic Self-slaking processing units which increased the valorisation ratio of steel slags from 10% to 21%. [1]

The magnetic component (mainly metallic iron and iron oxides) which is about 40% of the slag weight can be separated and recycled to metallurgy processes. Other 60% of the slag is applied as construction material. The ratio and T. Fe (metallic iron and iron in iron oxide) content of the magnetic components separated from the treated slag is listed in Table 2[5].

Table 2: The ratio and T. Fe content of the magnetic components recovered from steel slag

Items	T. Fe (%)	Grain Size (mm)	Ratio in slag (%)
Steel block	>80	> 50 mm	10
Steel granule	>62	10~50 mm	10
Magnetic powder	>40	0~10 mm	20

Slag valorisation in China

The treated steelmaking slag by the Pyrolytic Self-slaking process is then ground and the steel particles and magnetic iron oxides are separated by magnetic dressing. The recovered metallic phase contains more than 85% iron which can be reused as scrap in BOF for steelmaking. The recovered magnetic powders contain more than 60% iron which is then used as sintering material. The remaining slag after dressing contains less than 2% iron which can be used in construction materials production.

According to the national standards, slag powder production for cement and concrete industry has been generalised in China. The basicity of ground granulated BF slag powder is low, which will result in the corrosion of the steel bars and in the carbonation of concrete if the ratio of BF slag powder in cement is too high. Thus an appropriate addition of fine ground basic steel slag powder for cement production can improve the property of cement made of BF slag powder. Better strength and wearing resistance of the concrete can be obtained by using the cement with this basic steel slag powder addition.

Since the ground granulated blast furnace slag has a high specific surface area (420 m^2/kg), it not only can be used to substitute 10 - 40% of cement equivalently in concrete, but also serves as a necessary mineral additive to high performance concrete.[6] A national standard for "the ground granulated blast furnace slag powder used for cement and concrete" was issued (GB18046-2008). Since then, the application of ground granulated blast furnace slag is generalised. From 2000, China began to build production lines to produce the ground granulated blast furnace slag powder with an annual output of 0.6 million tonnes only. In 2010, China has more than 100 production lines for the slag powder preparation and the annual output reached 61 million tonnes. Meanwhile, the annual production of ground steel slag powder increased from 0.6 in 2000 to 4 million tonnes in 2010.[1]

Equipment for slag valorisation such as BF slag vertical mills, horizontal rolling mills and rod mills for steel slag crashing and grinding before final magnetic dressing, can be made domestically and the technical quality of these slag valorisation facilities can satisfy the requirements of slag recycling in China.

Standard system

Since 2005, in order to expand slag applications, the Chinese national steel standardisation committee together with the Chinese metallurgical and standardisation institute and the Central Research Institute of Building and Construction MCC Group, has started to establish a standard system for metallurgical industry solid wastes utilisation. A temporary standard system has been constructed, which includes 18 product standards, 7 analysis and test method standards, and 4 technical specifications related with slag valorisation, as shown in Table 3.[1]

Current development and fundamental research activities

Even though a certain part of ironmaking and steelmaking slags could be valorised as resources, the sensible heat in all kinds of molten slags was not recovered. Based on the industrial data in 2005 and 2006, Wang and his co-authors[7] estimated the total waste heat energy of Chinese steel industry to be 243.8 kgCE (kilogram of coal equivalent) per tonne of steel production. The recovery ratio was less than 15.1%. The waste sensible heat of the molten BF slag at 1500°C and that of the molten steel slag at 1550°C reached respectively 18.5 and 5.1 kgCE per tonne of steel production. Furthermore, the recovery ratio of sensible heat for the molten BF slags was only 2.16% and that for steel slag was zero. A simple estimation shows 2.7×10^8 GJ heat energy, i.e. 9.2 million tonne CE (coal equivalent) was wasted in 2010 by BF slag. The energy consumption ratio of steel industry is about 10 to 15% of the total energy consumption in China. Therefore, the heat recovery of the BF slag is of significant importance for energy saving and emission reduction of Chinese steel industry.

The current widely used process for BF slag treatment is the water granulation method, such as INBA which can obtain vitreous slag product as cement chamotte. This method shows high added value and environmental benefit. However, the water granulation transforms the high temperature sensible heat in the molten BF slag into the low temperature heat of the granulating water. The high quality heat in molten BF slag cannot be well utilised.

There were a number of studies aiming at recovery of heat with respect to the BF slag granulation. As shown in Table 4,[8] Qi and co-authors summarised the technical data (or specifications) of seven industrially tested slag heat recovery processes for the hot stage BF slag treatment. The problem of heat recovery from molten slag is the lower exergy recovery efficiency. As can be seen from Table 4, most of the heat recovery efficiency in various industrial scale tests was higher than 60%, even to 80%, but the exergy recovery efficiency was only about 40%. Comparing with CDQ (coke dry quenching), the quality of energy recovered from molten slag is poor. To realise the commercial operation of heat recovery from molten slag, the exergy recovery efficiency must be improved.

The key issue is that it is necessary to recover heat in a closed system with simultaneously the valorisation of the slag products. In the current dry granulation process the emphasis is on a high heat recovery efficiency and the optimisation of the utilisation of recovered heat. The water granulation process aims at high value slag products related with other industries. The priority selection (with respect to heat recovery and high added value slag product) depends on the social and economical conditions of the steel companies.

Recently, Chinese researchers are interested in using the Rotary Cup atomisation process to recover heat from BF slag.[10] With this topic, several projects have been conducted respectively by the Central Iron and Steel Research Institute (CISRI), Shougang Group, Ansteel, Northeastern University, Qingdao University, Chongqing University and Wuhan University of Science and Technology.[11] The present authors designed a 5 kg Rotary Cup atomisation unit for molten BF slag. By using our 5 kg Rotary Cup atomisation unit, the influence of process parameters such as rotary speed, slag temperature, slag flow rate, disc materials and geometry, falling height of slag from nozzle to disc, and the glass wool formation phenomenon was systematically studied. The experimental results show that the best disc material was graphite and the most suitable rotation speed was in the range of 1500 to 2300 rpm; the vitreous content of granulated slag was more than 88%, which was comparable to that of water granulated BF slag. The higher the molten slag temperature and the rougher the surface of the rotation disc, the better the results in the slag wool

Table 3: Standards for ironmaking and steelmaking slag valorisation

Category	No	Title	Serial No.
Product standard	1	Portland steel slag cement	GB 13590-2006
	2	Steel slag powder used for cement and concrete	GB/T20491-2006
	3	Low heat Portland steel slag cement	JC/T1082-2008
	4	Steel slag cement for road	JC/T1087-2008
	5	Steel slag masonry cement	JC/T1090-2008
	6	Steel slag cement for road	GB 25029-2010
	7	Low heat BF slag and steel slag cement	report for approval
	8	BF slag and steel slag powder	report for approval
	9	steel slag sand for road	YB/T 4187-2009
	10	Ground granulated blast furnace slag powder used for cement and concrete	GB/T 18046-2008
	11	Crushed air-cooled blast furnace slag for concrete	YB/T 4178-2008
	12	Ground Silicon-manganese slag used for cement and concrete	YB/T 4229-2010
	13	Ground lithium slag used for cement and concrete	YB/T 4230-2010
	14	Steel slag used for cement	YB/T 022-2008
	15	Steel slag for engineering backfill	YB/T 801-2008
	16	Steel slag for metallurgical burden	YB/T 802-2009
	17	Steel slag for roads	GB/T 25824-2010
	18	Steel slag for concrete perforated brick and concrete pavior brick	YB/T 4228-2010
Basic standard	19	Terminology for iron and steel slag & treatment and utilisation	YB/T 804-2009
Methodology standard	20	Test method for stability of steel slag	GB/T 24175-2009
	21	Methods for chemical analysis of steel slag	YB/T 140-2009
	22	Method for the determination of content of magnetic metallic iron in steel slag	YB/T 4188-2009
	23	Methods for the determination of total iron content in steel slag	YB/T 148-2009
	24	Test method for grindability of smelting slag	YB/T 4186-2009
	25	Method for the determination of particle size of smelting slag by using powder laser diffraction	YB/T 4183-2009
	26	Method for estimation of the metal content in stainless steel slag	YB/T 4227-2010
Technical specification	27	Technical specification for iron and steel slag concrete application	Under working
	28	Code for construction of the mass concrete	GB 50496-2009
	29	Technical specification for the construction of steel slag mixture used as base course	YB/T 4184-2009
	30	Technical specification of the tailings mortar	YB/T 4185-2009

Table 4: Summary of the technical data (or specifications) of slag heat recovery processes

No.	Developer or process name	Slag temp. (°C)	Industrial test scale (t/h)	Process functions and characteristics	Recovered media	Heat recovery (%)*	Exergy recovery (%)**	Slag product
1	NKK, Mitsubishi Heavy Industry	BOF slag 1600	80	Air-atomisation, Heat exchanger generates steam	500°C air and 270 kPa saturated steam	Hot air: 39.95 Steam: 41.4; Total: 81.35	39.9	Easy to be weathering dusted
2	Sumitomo Metal, Ishikawajima-Harima Heavy Industries	BF slag 1400	50	Rotary Cup atomiser, Fluid bed and packed bed heat exchange	600°C air	55	38.9	Fine aggregate for concrete
3	MEROTEC	BF slag 1450	40	Cooled slag fluid bed Granulation, fluid bed Heat exchanger recover steam	400 kPa saturated steam	65	38.8	Un-known
4	NKK	BF slag 1400	Unknown	Drum quenching, Recovering heat	250°C high boiling point organic liquid	40	16.3	Vitreous ratio >95%
5	NSC	BF slag 1400	7	Molten slag poured into mould, heat exchange through mould wall	Hot water	60~70	<12	Fine aggregate for concrete
6	NSC	BF slag 1450	100	Air-atomisation, First heat exchange by wind tunnel, Second heat exchange by multi fluid bed	510°C air (first heat exchange); 650°C air (second heat exchange)	First: 47.8; Second: 14.8 Total: 62.6	41.5	Cement material
7	Conventional water granulation	BF slag 1450	N. A	High pressure water granulation, 5 t water /per tonne slag, Circulation water Temp. 30°C	80°C hot water	73	9.5	Cement material
8	CDQ gas-solid heat exchange process	Red hot Coke 1000	N. A	Coke packed heat exchange	800°C nitrogen	80	73.0	N. A

* 25°C as reference temperature

**calculated according to the references reporting heat recovery effects, Exergy calculation refers to reference 9.

formation. The slag composition has also influence on the slag wool formation. The heat recovery was not measured in this experiment because the experiment scale was small and the continuous experimental time was short, for which the heat balance could not be reached.

Wang and his co-authors in the Central Iron and Steel Research Institute (CISRI) proposed a quantitative analysis method to determine the ratio of non-crystalline to crystalline solids in BF slag by using X-ray diffraction. They also analysed the crystallisation process of non-crystalline BF slag. Based on model simulations and laboratory experiments, the SKLP (State Key Laboratory of Advanced Steel Process and Products of the CISRI in China) developed a Dry Slag Granulation Technology. The process flowsheet is shown in Fig. 2.[8] In this system the molten slag is first poured in the center of the disk and atomised by centrifugal force. Then the particles are dispersed onto drums which are located parallel to the disc, from there the granulated slag particles are moved into a fluidised bed heat exchanger and rapidly cooled by upstream blowing air. In this process, molten BF slag flow rate is controlled by a slide gate to keep a constant slag level in the slag tundish so that the molten slag can be stably and continuously poured onto the rotating cup, and then partially granulated and dropped to the rolling crusher. There are two lines rollers in the process system. The up line is for crushing the solidified slag and the lower line is for discharging the granulated slag particles. The rollers' inner chambers are forcibly cooled by water and their surface temperature can be kept below 300°C. High speed air jets mixed with part of circular air are injected into this atomising chamber to quickly cool the slag to a temperature below 750°C. The air temperature after first heat exchange is about 500°C. This hot air mixed with new cooling air (at room temperature) is then passed through the hot cyclone dust collector. The granulated slag is gas-tight and discharged into the vertical heat exchanger. The final temperature of the granulated slag is lower than 150°C, and the final air temperature after secondary heat exchange reaches 700°C. The temperature of the exhausted air from the boiler is lower than 150°C.

Based on the above data, a pilot scale experiment was designed and carried out. The size of the slag tank was 1 meter in diameter and 1.3 meter in height with a volume of 1 m^3. The slag tundish size was 0.56 meter in diameter and 1.5 meter in height with a volume of 0.05 m^3. The inner diameter of the slag outlet nozzle (in the bottom of the slag tundish) was 30 mm. During the test, the above slag tank and tundish were heated to a constant temperature. The diameter of the heat resistant steel rotary cup was 250 mm and the rotating power of the rotary cup was 1.5 kW. The diameter of the heat resistant steel rollers was 150 mm, and the rotating power of the steel roller was 2.2 kW. Rotary cup and rollers were inner cooled by water. The

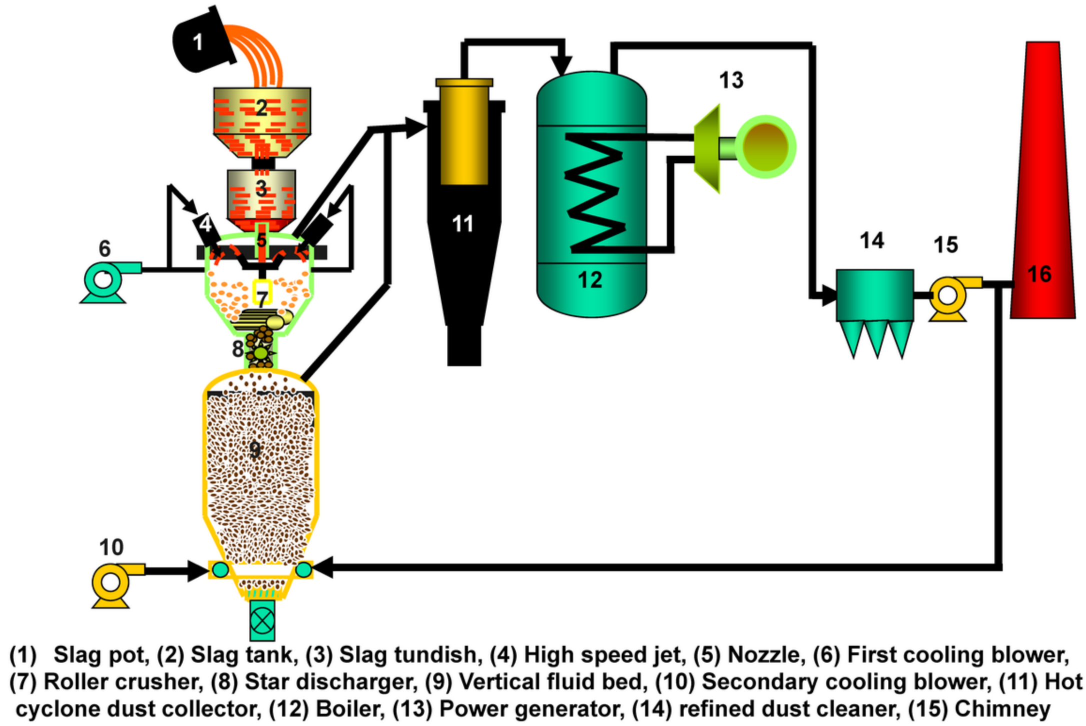

Figure 2: Process flowsheet of BF slag dry granulation and heat recovery developed by the Central Iron and Steel Research Institute (CISRI), China

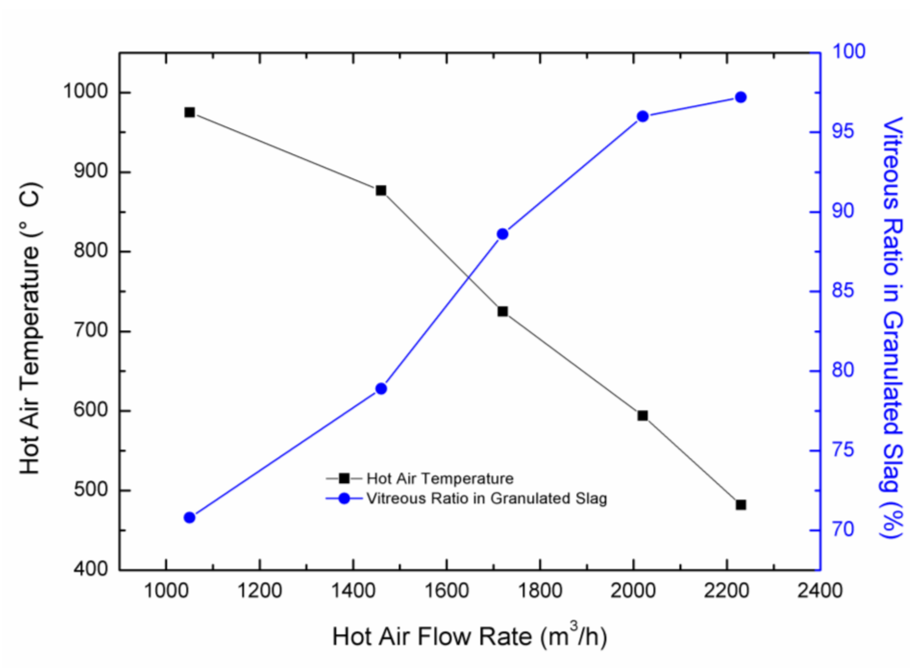

Figure 3: The recovered hot air temperature and vitreous ratio of the granulated BF slag as a function of the air flow rate in the experiment

BF slag quantity treated was 1.2 tonne; the line speed of slag flow was 0.2m/s; slag flowed 1 hour in the experiment. As a result, 2020 m^3 hot air with temperature of 594°C was recovered from 1.2 tonne molten slag theoretically containing 2.1 GJ heat. The recovered heat was 1.6 GJ and the electricity consumed in this process was 38.5 MJ, accounting for 2.4% of the recovered heat. The heat recovery efficiency by the heat exchange between molten slag and cooling air was 77%. The recovered hot air temperature and the vitreous ratio of granulated BF slag changed with the cooling air flow rate in the experiment, as shown in Figure 3. About 96% vitreous components in the dry granulated BF slag could be obtained when the cooling air flow rate was higher than 2200 m^3 per hour. This is similar to the level of water granulated BF slag. The maximum particle size of the dry granulated BF slag was 3.1 mm. Further studies, however, are needed concerning to the issues of slag crusting and heterogeneous size distribution, and to the phenomenon of glass wool formation in the process.

Conclusions

The state of the art of ironmaking and steelmaking slags valorisation in China is reviewed. The slag valorisation in China improved gradually during the recent past years. This was not only in quantity but also in quality, thereby increasing the economical and environmental benefits. The hot stage processing processes with respect to BF slag granulation and steel slag pyrolytic self-slaking have made progress and are applied in a number of large steelmaking companies in China. The fundamental researches and process developments are mainly focusing on the dry granulation of molten BF slag with both heat recovery and improvement of the slag product quality.

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