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Recent progress of hot stage processing for steelmaking slags in China considering stability and heat recovery

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Abstract

The recent progress of hot stage processing for steelmaking slags in China considering stability and heat recovery is reported and discussed. In industry, several projects are being constructed based on air or rotor granulation, including recovery of part of the slag's sensible heat. Composition modification of molten slag is very important both for continuous granulation and the utilisation of treated steel slag products. Fundamental studies focus on process simulation and exploration of new processes.

Introduction

The recovery and converting of heat energy in the steel industry has been a target of metallurgists all over the world. In 2005, the total waste heat energy of China's steel industry was 288 kgCE (kilogram of coal equivalent) per tonne of steel. The average recovery ratio was less than 26%. Furthermore, the recovery ratio of sensible heat in all kinds of molten slags was only 1.6%. In 2009, the total quantity of steelmaking slag was 90 million tonnes in China. The development of sensible heat recovery from high temperature molten slag is becoming a major point of attention. The hot stage treatment processes for BF slag and BOF slag in China were reported in the First International Slag Valorisation Symposium in April 2009.[1] For BOF slag treatment, pyrolytic self-slaking, Wheel-granulation process (HK), and Baosteel's Slag Short Flow (BSSF) are commonplace. Until now there are no large scale processes available in China that can recover heat energy from molten slag. Several companies, institutes, and universities are, however, developing technologies to realise this. This paper will introduce the ideas, research and engineering progress in China with respect to the hot stage processing of steelmaking slags, considering both stability and heat recovery.

Treating and heat recovery system for steelmaking slag

As a subject of the state science and technology support program, the Sugang Group started a research project for steelmaking slag treatment, which uses a dry granulation method with heat recovery.[2] The targets of this project are: recovery of the heat energy of molten slag, recycling of metal, fast stabilisation of free lime and utilisation of the remaining slag.

The flow chart is shown in Figure 1. The molten slag is transported in a slag pot from the steelmaking workshop to the slag treatment yard. A turn-over unit pours the slag into a hopper in which there are several rotors to granulate the molten slag. This unit is the primary granulation. It acts as a buffering and first heat exchange system, in which the liquid slag is cooled down to solid grains by air and then continuously proceeds to the second granulation and heat exchange system. In this system, the solid slag grains are crushed and further cooled by air. In the stabilising system, slag grains react with steam and CO_2, free lime is stabilised quickly, while steel grains are separated from the slag by a magnetic dressing machine. The tailings are used to make construction materials such as bricks or additives for concrete. The hot air is used to generate steam to run a turbine. The advantages of this technique are:

1. The heat energy of molten slag can be recovered efficiently and slag can be stabilised quickly, the metal can be recycled and the tailings can be utilised;
2. Either a liquid slag with good fluidity or a liquid/solid slag mixture can be treated;
3. There is no danger as the molten slag does not contact water directly;
4. Gas (air, CO_2 and steam) is only used as heat exchange medium and lime stabiliser but not as granulating energy, thereby lowering the energy consumption.

Currently, a testing line for steelmaking slag treatment and energy recovery is being built in the Sougang Group. It has the capacity to treat 1 million tonne of slag per year.

Dry treating method based on steelmaking slag composition modification

The Wuhan Research Institute of Metallurgical Construction developed another slag granulation method.[3] They considered that the tailings of conventionally treated slag cannot be fully utilised due to the lower cementitious activity caused by water treatment. The sequences of this process are: (1) Homogenising the molten slag; (2)

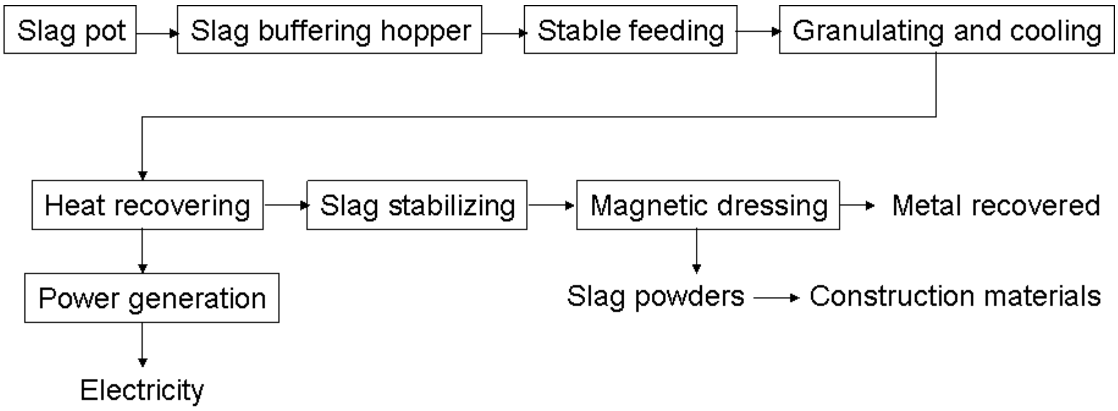

Figure 1: Schematic diagram of the slag treatment and energy recovery flowsheet for steelmaking slag

Water quenching and granulation; (3) The high temperature steam obtained by heat exchange during water quenching and granulation is used to heat dry air and to dry the granulated slag powders; (4) Dry magnetic dressing to separate metal; (5) Utilisation of slag powders.

Homogenising the molten slag

Because some unreacted solid lime, refractory particles, and unmelted flux are contained in the molten slag, the fluidity of steelmaking slag may be poor and depends on the refining status. This will result in a lower ratio of slag granulation so that not all molten slag can be utilised well. In order to obtain slag with good fluidity and suitable mineral composition for consequent utilisation, crushed waste clay bricks, glass cullet, coke, mineralisation agent, and stabilisation agent was mixed and blown into the molten slag in a tundish. After a period of reaction, the adjusted slag was granulated by water. In the process of the compositional modification of the slag, ferrous oxide is oxidised to ferric oxide, which reacts with calcium oxide, aluminium oxide in slag to form cementitious minerals:

$$4FeO + O_2 = 2Fe_2O_3 \quad (1)$$
$$Fe_2O_3 + nCaO = nCaO \cdot Fe_2O_3 \quad (2)$$
$$4CaO \cdot FeO + O_2 = 4CaO \cdot Fe_2O_3 \quad (3)$$
$$4CaO \cdot Fe_2O_3 + Al_2O_3 = 4CaO \cdot Al_2O_3 \cdot Fe_2O_3 \ (C_4AF) \quad (4)$$

Silica and alumina contained in waste clay bricks or glass cullet also react with free lime in the slag to form cementitious minerals:

$$2CaO + SiO_2 = 2CaO \cdot SiO_2 \ (C_2S) \quad (5)$$
$$2CaO \cdot SiO_2 + CaO = 3CaO \cdot SiO_2 \ (C_3S) \quad (6)$$
$$3CaO + Al_2O_3 = 3CaO \cdot Al_2O_3 \ (C_3A) \quad (7)$$

The analysis confirmed that the quantity of main high early strength minerals such as C_4AF, C_3A and C_3S increased, while the quantity of free lime and free magnesia obviously decreased. Hence, the slag after compositional modification becomes a Portland cement clinker with high early strength and stable properties.

Granulation and dressing

The modified molten slag is poured into a blast groove and granulated by rotors. subsequently, the granulated slag grains are quenched by water in the pool below the rotors. The slag grains in the pool are lifted by a screw lifter and then dried. The maximum size of dried granulated slag grains is 10 mm, and most of them are smaller than 5 mm. The dried water granulated slag grains are crushed and grounded by ball milling. After classification and magnetic dressing, four kinds of products can be obtained, as shown in Table 1.

Table 1: Separated products of steelmaking slags

Products	Diameter (mm)	T. Fe (wt %)	Magnetic Fe (wt %)	Ratio (%)	Water (%)	Application
Steel powder	< 1	> 50	--	10~14	< 2	Sintering
Steel grain	1~10	> 90	--	3~7	< 1	Steelmaking
Slag powder	< 0.1	--	< 2	68~78	< 2	Construction material
Slag grain	0.1~5	--	< 2	5~15	< 1	

The slag powder (containing magnetic iron oxide: less than 2 wt% calculated as Fe), which has a surface area of 300 m^2/kg, can be directly used in construction materials, for example, as additive for cement. As the slag grain fraction contains less magnetic iron oxide (< 2%) and the grain size is small (< 5 mm), it can be used as fine aggregate in concrete.

The advantages of this process

The advantages of this process are: continuous production; small number of processing steps, low investment and space requirement; low energy requirement and environmental-friendly, and an expanded range of applications. The energy recovered in this process is used to dry the water quenched slag thus decreasing the energy input of the slag treatment. The investment and space requirements are 30% lower than conventional slag treatment processing. The cementitious activity of steelmaking slag treated by this process can be improved effectively by compositional modification and dry granulation. The content of free lime and other unbeneficial components is lowered to less than 1%. As the strength of construction materials made of treated slag powders are improved over 40%, these slag powder products can be applied in a wider range.

Fundamental Studies

Several groups in China focus on hot stage processing for steelmaking slags. Cang Daqiang's group in University of Science and Technology Beijing (USTB) initiated a key project under the support by the National Natural Science Foundation of China (NSFC) from 2011. The title of this project is "Fundamental study on key techniques for the preparation of high value products by utilisation of both heat and slag". The process they proposed targets the modification of the slag composition by carbothermic reduction to reduce iron oxides in the molten slag. Meanwhile, waste refractory materials containing silica and alumina are added into the molten slag to lower the viscosity and adjust the slag composition making it suitable for making glass ceramics. Subsequently, the liquid slag is air granulated and heat can be recovered. As a part of their research project, the component modification of steelmaking slag in an air quenching process to improve grindability was reported.[4] One tonne as-received BOF slag at 1923 K was reacted with 50 kg fly ash placed at the bottom of a tundish with a 3.5 tonne slag capacity. After air quenching, the properties of treated slag are evaluated. The composition of the modification agents and original BOF slag is shown in Table 2.

Table 2: Composition of modification agents and original BOF slag (wt%)

Component	T. Fe	CaO	MgO	Al_2O_3	SiO_2	S	f-CaO	FeO	M-Fe	C
Fly ash	1.53	5.3	0.78	21.53	67.27	0.47	--	--	--	3.59
Mill tailings	15.79	--	--	--	63.42	1.53	--	0.71	--	--
Steel slag	17.28	44.73	8.46	4.6	14.53	0.045	9.54	21	8.45	--

Their results showed that the mineral phases of the slag after modification changed. Metal iron was generated due to reduction by carbon, the ratio of C_3S and free lime decreased and that of C_2S increased, while CS formed as a new phase due to the addition of SiO_2 and Al_2O_3 by fly ash. A small amount of a vitreous phase was also observed. The grindability of modified slag was obviously improved.

Granularity and reactivity of molten slag quenched and atomised by a high pressure water jet

A method of quenching and atomising the molten slag simultaneously under a high pressure water jet was investigated by Cang's group.[5] Experiments about cooling and pulverising the molten steel slag and blast furnace (BF) slag by a high pressure water jet of 8 to 10 MPa were conducted on a self-made slag melting and high pressure water cooling system. The results show that the atomised steel slag can be pulverised with an average particle size of 94.3 µm and a phase constitution of glass phase and Ca_2SiO_4. The slag's reactivity is increased and the compressive strength of its cement samples aged for 28 days is 33.96 MPa, which is 8 MPa higher than that of cement samples from original steel slag. The quenched BF slag forms a flocculent structure, with degraded reactivity. The proposed method is more suitable for steel slag treating processes than BF slag. The cooling speed of slag was estimated as 1000 K/s to 5000 K/s. To ensure the fluidity of steel slag, 4% CaF_2 (expressed with reference the total weight of the slag mixture). The particle size distribution of jetted steel slag is shown in Figure 2, while the compressive strength of cement samples from jetted and original steel slag powders is shown in Figure 3.

No direct energy was recovered in this process. However, as the energy of the high pressure water jet is focused on the liquid slag and as the surface tension of liquid slag is smaller than that of the solid, the process can be considered to be more energy efficient as the alternative process of crushing the solid slag. It may also be considered that the sensible heat of molten slag was utilised adequately as part of it

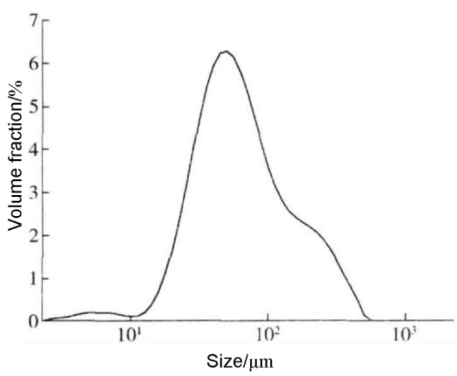

Figure 2: Particle size distribution of jetted steel slag

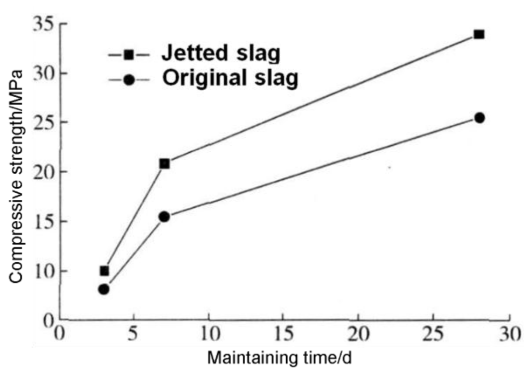

Figure 3: Comparison of compressive strength of cement samples from jetted and original steel slag

was converted to chemical energy of the vitreous phase in the treated slag particles. Their results corroborate that a high pressure water jet can result in fine steel slag powder and improve the cementitious activity simultaneously.

Preparation of glass-ceramics from liquid steel slag

Zhang and his co-authors reported on an approach of direct utilisation of liquid steel slag as a raw material and heat for preparation of glass-ceramics.[6] 40% EAF slag was melted at 1724 K and then mixed with 60% melting additives (containing silica, alumina and sodium oxide), subsequently heated to 1773 k for 1 hour. Then the modified slag was cast, annealed and transformed to glass–ceramics. The results show that the dominant crystalline phase is diopside ($CaFe(SiO_3)_2$) and the crystal shape is like the granule with a diameter between 0.2 to 0.6 µm. The glass-ceramic with nucleation at 968 K for 2 hours and crystallisation at 1166 K for 1 hour and 1463 K for 0.5 hour exhibited an optimum combination of properties. The XRD patterns and SEM image of glass-ceramic are shown in Figure 4 and Figure 5, respectively. The properties of developed glass-ceramics can satisfy the industrial standard well.

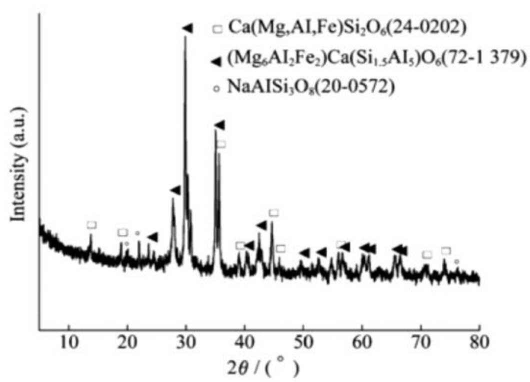

Figure 4: XRD patterns of glass-ceramics

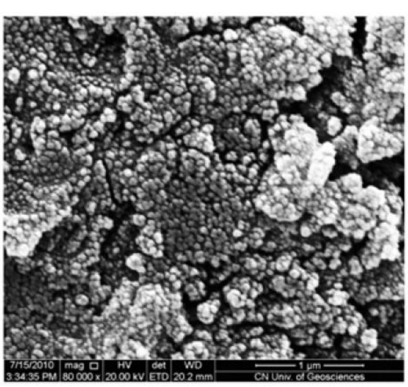

Figure 5: SEM image of glass-ceramics

Simulation on heat recovery in dry granulation process of steelmaking slag

Wang and his co-authors simulated the heat recovery condition for the dry granulation system of steelmaking slag described previously by ANSYS software.[7] According to their results, the average pressure drop of the blown air is 100 Pa, with the maximum pressure drop being 300 Pa. This pressure drop is suitable for a heat exchange system. The temperature of output granulated slag will be 900 K if the input slag temperature is 1673 K. The temperature of room temperature blown air was increased to 693 K after heat exchange with molten slag. The flow rate of air in the range of 80000 to 100000 m^3/h results in slag cooling and heat recovery efficiently. The simulated average temperature of output slag and air are shown in Figure 6 and Figure 7, respectively.

Xing *et al.*[8] established physical and mathematical models of solidification processes of spherical molten steel slag granules. The temperature fields of slag grains and its outer gas was calculated using FLUENT. The solidification time of slag spheres with different diameter was obtained. It is believed that the numerical simulated results would provide the theoretical basis for granulating molten slag and heat recovery equipment. The numerical simulation results showed that the liquid slag sphere could release more than 80% of the phase transformation heat in 2 seconds with the initial conditions as follows: the temperature of molten slag being 1823 K, the

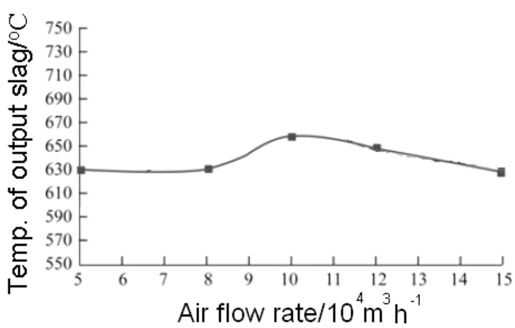

Figure 6: The average temperature of output slag as a function of the air flow rate

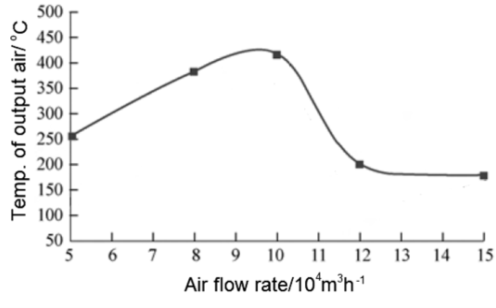

Figure 7: The average temperature of output air as a function of the air flow rate

granule diameter between 1 and 3 mm, the inlet temperature of cooling gas at 373 K, the velocity of gas flow in the range between 1 and 20 m/s. It is concluded that there is no agglomeration between slag spheres after a certain cooling period if the molten steel slag has been granulated to 1 to 3 mm particles.

Conclusions

According to the pilot-scale experiments and fundamental studies on hot stage steelmaking slag treatment recently carried out in China, heat recovery from molten slag in the slag granulating process must consider the massive application of treated slag products and engineering possibility of the process. No matter what process is selected, molten slag with suitable fluidity is essential for smooth and continuous processing. For this reason, slag modification in composition and temperature are necessary in some cases. Slag modification in composition is also a measure to enlarge the application areas of steel slag products. Completely dry treatment is impossible to eliminate free lime. Therefore, water quenching, steam treatment, or wet milling must be included in the process. Making use of the sensible heat of molten slag and decreasing the energy input during molten slag treatment should be acceptable instead of net energy recovery.

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