Article

Multi-Stage Control of Waste Heat Recovery from High Temperature Slags Based on Time Temperature Transformation Curves

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Abstract: This paper presents a significant method and a basic idea of waste heat recovery from high temperature slags based on Time Temperature Transformation (TTT) curves. Three samples with a fixed CaO/SiO_2 ratio of 1.05 and different levels of Al_2O_3 were designed and isothermal experiments were performed using a Single Hot Thermocouple Technique (SHTT). The TTT curves established through SHTT experiments described well the variation of slag properties during isothermal processes. In this study, we propose a multi-stage control method for waste heat recovery from high temperature slags, in which the whole temperature range from 1500 °C to 25 °C was divided into three regions, *i.e.*, Liquid region, Crystallization region and Solid region, based on the TTT curves. Accordingly, we put forward an industrial prototype plant for the purpose of waste heat recovery and the potential of waste heat recovery was then calculated. The multi-stage control method provided not only a significant prototype, but also a basic idea to simultaneously extract high quality waste heat and obtain glassy phases on high temperature slags, which may fill the gap between slag properties and practical waste heat recovery processes.

Keywords: multi-stage control; high temperature slags; TTT curves; waste heat recovery

1. Introduction

It is well known that the steel industry is energy intensive, consuming around 9% of anthropogenic energy [1] and emitting large quantities of CO_2 into the atmosphere [2]. With the acceleration of global warming nowadays, energy saving and CO_2 emission reduction in the steel industry is attracting more and more attention, although the energy efficiency has already been substantially improved by implementing extensive advanced technologies. According to the previous estimations [3,4], high temperature (1450–1550 °C) slags, carrying a substantial amount of high quality heat, represent the last potential source for energy reduction in the steel industry. In China, the steel industry's output of crude steel was more than 710 million tons in 2012 [5], and accordingly around 200 million tons of high temperature blast furnace slags (BF slags) and 70 million tons of steel slags were produced [6] and the total waste heat was more than 4.80×10^{19} J, equivalent to 16 million tons of standard coal, whereas less than 2% of that was recovered, according to the estimation of Cai *et al.* [7], so there is a great potential of waste heat recovery. BF slags alone accounted for more than 70% of the waste heat of the slags in the steel industry, and therefore the previous studies were mainly focused on BF slags [8].

Conventionally, BF slags can be treated through two methods: gradually cooled by air in a slag pit [9] or rapidly quenched by water [10]. Air-gradually-cooled slags have low utilization values because of their weak hydraulicity due to the high content of crystalline phases [11], while water quenched BF slags are increasingly utilized as cementitious materials because of the glassy phases [11] and the similarity between the components of slags and Portland cement, high content of calcium silicates [12]. However, the water quenched method faces a series of problems, such as water consumption and pollution, SO_2 and H_2S emissions and energy consumption and waste [13,14]. To solve the aforementioned problems and realize the recovery of waste heat, a dry granulation method has been proposed, through which the liquid slags are granulated into small droplets with the diameter of several millimeters using different waterless granulation technologies, such as rotary cup atomizer [15–18], rotating drum [19,20], air blasts [21,22] and so on. Recently the combination of dry granulation with other waste heat utilization methods, such as hydrogen production from biogas [18,23], coal gasification [24,25] and heat storage of phase change materials (PCM) [26] has been intensively studied, and is expected to be a promising method in the future. Whatever the utilization method applied, the understanding of the variation of slag properties during cooling processes and the control of heat transfer are fundamental for simultaneously realizing waste heat recovery and slag recycling. Considering the large amount of BF slags, the present study was focused on BF slags. Meanwhile, iron ore has been degraded and Al_2O_3 content in gangues has been increasing in the past decades [27], which has led to variations in the chemical composition of BF slags, such as an increase of Al_2O_3 content. With the variation of chemical compositions of slags, the slag properties, including crystallization properties could be changed, which could influence the waste heat recovery of high temperature slags. Three samples containing different levels of Al_2O_3 were therefore designed in this study.

The investigation was carried out using a Single Hot Thermocouple Technique (SHTT) for visualizing phase changes in the slag melts, through which Time Temperature Transformation (TTT) curves were established. TTT curves described well the variation of slag properties, based on which a multi-stage control method was proposed in this paper. The potential of waste heat recovery at different stages was accordingly calculated.
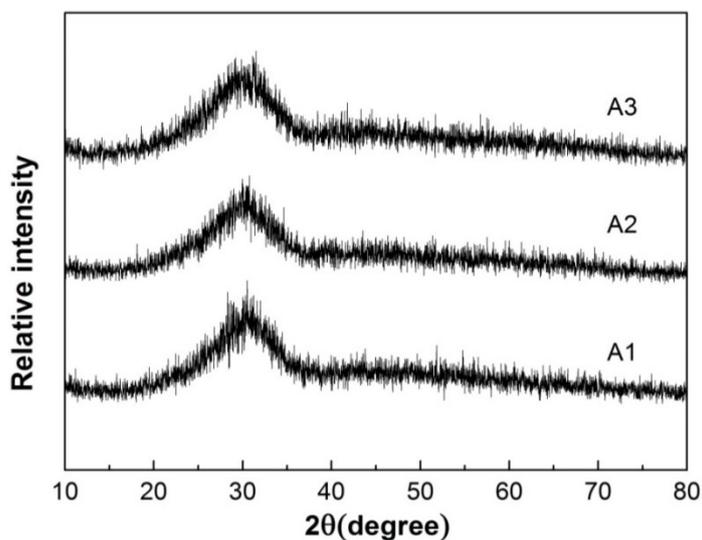
2. Materials and Methods

2.1. Sample Preparation

In the present study, three slag samples with a CaO/SiO$_2$ ratio of 1.05 and Al$_2$O$_3$ contents of 10–25 wt% were prepared using analytically regent (AR) pure oxides. These oxides were mixed and pre-melted in a molybdenum (Mo) crucible (Φ40 mm × 45 mm × H40 mm) under an argon atmosphere at 1500 °C for 2 h to homogenize the chemical compositions. Then the liquid slags were rapidly poured into the cold water to obtain glassy phases. Subsequently, the solid slags were dried at 120 °C for 12 h, crushed and ground to 300 mesh size for compositional analysis and SHTT experiments. The chemical compositions were measured by the X-Ray fluoroscopy (XRF) technique and the results are listed in Table 1. To confirm the glassy phases of slags and the accuracy of SHTT experiments, X-ray diffraction (XRD) tests were carried out and the results are shown in Figure 1.

Table 1. Chemical compositions of samples (wt%)

Samples	Basicity (B)	CaO	SiO$_2$	MgO	Al$_2$O$_3$
A1(XRF)	1.05	40.7%	38.9%	9.2%	11.3%
A2(XRF)	1.02	35.8%	35.1%	9.1%	20.0%
A3(XRF)	1.02	34.3%	33.5%	9.0%	23.1%

Figure 1. XRD results of the pre-melted slags.

2.2. Apparatus and Procedure

Experiments in this study were carried out using SHTT for visualizing the phase transformations and measuring the incubation time of these slags. SHTT combines the advantages of *in-situ* optical observation and the low inertia of the system, with a maximum cooling rate of 200 °C/s. The work mechanism of SHTT has been described in detail elsewhere [28,29] and is only briefly outlined here. As schematically shown in Figure 2, a Pt-Rh thermocouple was used to heat the sample and simultaneously measure the temperature, which was controlled by a computer program. A microscope equipped with a video camera was used to observe and capture images of the slag melts. The isothermal experiments by

SHTT were performed following several steps as below. Firstly, the temperature of thermocouple was calibrated using pure K_2SO_4 with a constant melting point 1067 °C. Secondly, about 10 mg sample was mounted on the top of the thermocouple, heated to 1500 °C, and held for 120 s to eliminate the bubbles and homogenize the chemical composition. Thirdly, the liquid slags were rapidly quenched at a cooling rate of 50 °C/s to a given temperature and held for a long time at this temperature. Then the evolution of crystallization with time in the slag melts was observed and the sample images were captured by the video camera, shown in Figure 3 as an example. The crystalline phases precipitated in the melts were identified by the XRD technique.

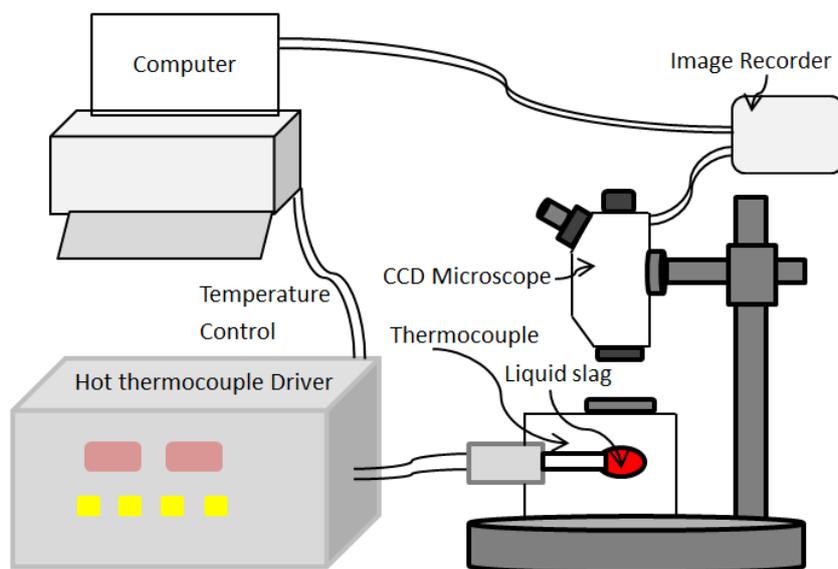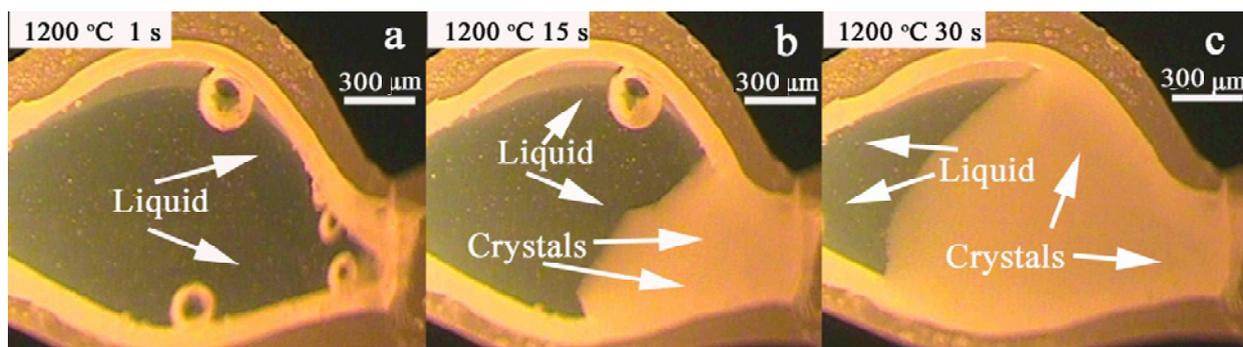**Figure 2.** Schematic diagram of the SHTT instrument.

Figure 3. Schematic diagrams of SHTT images for sample A1 at 1200 °C.

After the liquid slag was rapidly quenched to a given temperature, it may take some time to crystallize, *i.e.*, there is a certain incubation time. To reduce measurement errors, the incubation time at each temperature point was measured at least three times and the average value was used. The obtained incubation time can help to design a waste heat recovery process in a reasonable time to avoid crystal formation. The variation of incubation time with isothermal experiments was presented in TTT curves. The crystalline phases precipitated in slags were confirmed by Factsage software calculation and the latent heat of phase transformation was calculated [30].
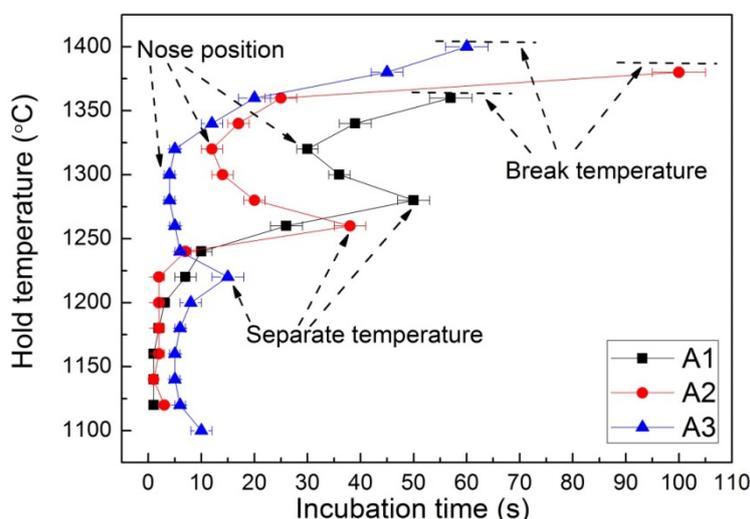
3. Results and Discussion

3.1. Multi-Stage Control of Waste Heat Recovery Based on TTT Curves

3.1.1. TTT Curves

The TTT curves of different samples were presented in Figure 4. As can be seen, these TTT curves showed a similar shape, that is a double "C" from high temperature to low temperature, which suggested that two different crystallization events occurred. As the slag melt was quenched from 1500 °C, the crystallization was not observed when it was higher than the break temperature (the highest temperature at which crystallization could appear), indicating that the waste heat recovery from the slags can last a long time during this temperature interval. It can be seen that the break temperature increased from sample A1 to A3, which suggested that the crystallization was enhanced by Al_2O_3 addition.

Figure 4. TTT curves of the different samples.

As the temperature decreased lower than the break temperature, crystals may precipitate after an incubation time. The incubation time decreased with the decrease of isothermal temperature until the nose position, then it increased with further decreasing temperature to the separate temperature between these two "C" shapes. With the decrease of temperature, the undercooling degree was increased, which was beneficial for crystal formation, whereas the viscosity increased at the same time, which suppressed the crystal formation. These two factors caused by temperature decrease influenced the crystal precipitation in opposite directions and caused the appearance of a shortest incubation time, *i.e.*, at the nose position. The shortest incubation time at the nose position suggested that the waste heat recovery time with medium must be very quick at this temperature in order to avoid crystallization.

With further decreasing temperature, a similar variation tendency as with the first "C" shape was observed in the crystallization temperature range. Finally the temperature was decreased to a low temperature zone where no crystallization was observed due to the high resistance of mass transfer caused by the higher viscosity. These results indicated that the waste heat recovery time from slags could be set up with temperature, and the cooling process was therefore determined based on the TTT curves. An apparent trend was observed in that the TTT curves moved to the left side in high temperature zones

with increasing Al_2O_3 content, which indicated that the crystallization was enhanced by Al_2O_3. This suggested that an increasing Al_2O_3 content resulted in a lower waste heat recovery time in this temperature interval. It is also noted that the second "C" shape in low temperature zones did not show an apparent variation tendency for different samples, which might be because that the effect of undercooling on the crystallization was greater than that of the Al_2O_3 content [31].

3.1.2. Multi-Stage Control Method

Based on the aforementioned findings, a multi-stage control method of waste heat recovery from high temperature slags was proposed here, a general schematic diagram of which is shown in Figure 5. During stage 1, as the temperature was higher than the break temperature, no crystallization was observed and the heat exchange could continue for a long time to fully extract the waste heat. Slags in this temperature zone could be slowly cooled and the high quality waste heat could be fully exchanged to PCM [26] and stored for further utilization. This stage was located in the temperature range where slags were liquid, defined as Liquid region. During stage 2, with the temperature decreasing to the first "C" and the second "C" shapes, the heat exchange time should be adjusted according to the incubation time. The cooling rate during this stage must be larger than the critical cooling rate, which was a cooling rate larger than which crystallization does not appear. The critical cooling rate can be calculated by the following expression [32]:
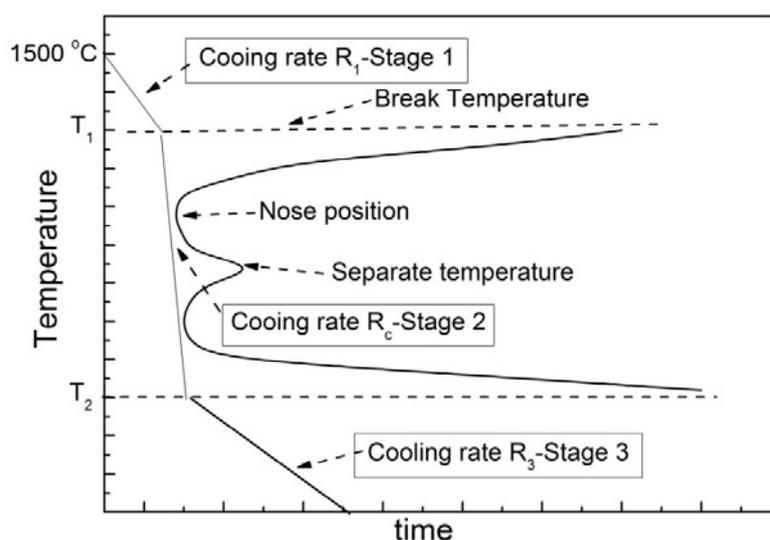
$$R_c = \frac{1500 - T_0}{\tau} \tag{1}$$

where R_c is the critical cooling rate; T_0 and τ are the crystallization temperature and incubation time of nose position. The calculated values of R_c were 6 °C/s, 15 °C/s and 50 °C/s for samples A1, A2 and A3, respectively. As can be seen, the variation of Al_2O_3 content greatly influenced the critical cooling rate and these increasing critical cooling rates could bring new challenges for waste heat recovery of high temperature slags, which must be considered in any practical waste heat recovery process. In this stage, the liquid slags should be rapidly quenched at a cooling rate larger than critical cooling rate to avoid crystal formation. This stage was located in the crystallization temperature range, defined as Crystallization region. During stage 3, as the temperature further decreased, crystallization was not found in the slag melt due to the high transfer resistance of ions, *i.e.*, the slag started to solidify under this temperature, and therefore there was enough time to extract the waste heat from the slags. This stage was suitable for combination of waste heat recovery from high temperature slags with other new heat utilization methods, such as H_2 production, coal gasification and heat storage in PCM because the slags have been totally solidified. Purwanto *et al.* [23] have studied the hydrogen production using biogas and hot slags and the temperature range in their study was from 973 K to 1273 K, which was located in the temperature zone of solidified slags. They found that the slag acted not only as a good thermal media but also as a good catalyst for H_2 production. The possibility of CO_2/coal gasification has been studied by Li *et al.* [24,25] using slag granules as heat carries for waste heat recovery from BF slags in the temperature range of 1223 and 1423 K and they found that the added BF slags greatly enhanced the gasification reaction, which might be a development trend for waste heat recovery form high temperature slags in the future. This stage was located in the temperature range where only solidified slags existed, defined as the Solid region. However, it should be pointed out that attention should be paid

to the recrystallization from the solidified glassy slags during this stage. Recrystallization caused the increase of the content of crystalline phases in slags and finally reduced the utilization value of solid slags.

In this section, the whole temperature range during waste heat recovery process was divided into three regions, *i.e.*, Liquid region, Crystallization region and Solid region, and the technological parameters of heat exchange can be therefore designed according to the TTT curves, as shown in Figure 5.

Figure 5. Schematic diagram of the multi-stage control of waste heat recovery.

3.2. Fitting of TTT Curves

To realize a continuous control of waste heat recovery from high temperature slags, it is necessary to obtain a fitting of the TTT curves for a practical waste heat recovery process. The polynomial expressions could be used to fit the TTT curves, from which the incubation time at a given temperature could be deduced [33]. The following equation gave acceptable calculation results that fitted the measured incubation time for samples in this study:

For sample A1:

$$\tau = 31146.8458T - 35.41T^2 + 0.01789T^3 - 3.38\times10^{-6}T^4$$
$$1280\ ^\circ C \leq T \leq 1360\ ^\circ C,\ R^2 = 0.999 \tag{2.1}$$

$$\tau = 546787.44 - 1871.79T - 2.40T^2 - 0.00137T^3 + 2.93\times10^{-7}T^4$$
$$1120\ ^\circ C \leq T \leq 1280\ ^\circ C,\ R^2 = 0.994 \tag{2.2}$$

For sample A2:

$$\tau = 1.41\times10^7 - 43010.47T + 49.25T^2 - 0.02506T^3 + 4.78\times10^{-6}T^4$$
$$1260\ ^\circ C \leq T \leq 1380\ ^\circ C,\ R^2 = 0.975 \tag{3.1}$$

$$\tau = 2.34\times10^6 - 7964.41T + 10.16T^2 - 0.00576T^3 + 1.23\times10^{-6}T^4$$
$$1120\ ^\circ C \leq T \leq 1260\ ^\circ C,\ R^2 = 0.987 \tag{3.2}$$

For sample A3:

$$\tau = 11178.25 - 47.15T + 0.0726T^2 - 4.85\times10^{-5}T^3 + 1.18\times10^{-8}T^4$$
$$1220\ ^\circ C \leq T \leq 1400\ ^\circ C,\ R^2 = 0.970 \tag{4.1}$$

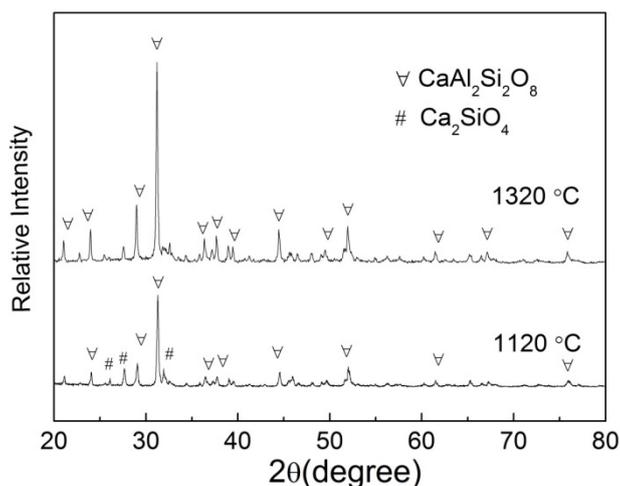$$\tau = 761414.07 - 2633.75T + 3.42T^2 - 0.00197T^3 + 4.26 \times 10^{-7} T^4$$
$$1100 \text{ °C} \leq T \leq 1220 \text{ °C}, R^2 = 0.997 \tag{4.2}$$

where τ was incubation time and T was the holding temperature. These calculated polynomial expressions well matched the TTT curves, which could provide significant information for tailoring the technological parameters for waste heat recovery.

3.3. Phase Change of Slags

Conventionally, solidified slags containing less than 5% crystalline phase are applicable as raw materials for the cement manufacturing industry. The primary crystalline phase in these slag melts was examined by XRD tests and the results are shown in Figure 6. It can be seen that the primary phase was $CaAl_2Si_2O_8$, and Ca_2SiO_4 was precipitated upon further decreasing the temperature, which agreed with the Factsage phase diagrams. The latent heat of phase change ($CaAl_2Si_2O_8$) was around 421.81 KJ/mol referred to Factsage software data [30]. The small amount of crystals (5%) formed in the melts could result in the increase of waste heat recovery due to the heat release from phase transformation, but it was difficult to control the crystallization degree in practical operation processes. It is therefore proposed that the liquid slags should be rapidly cooled to avoid crystallization according to the TTT curves.
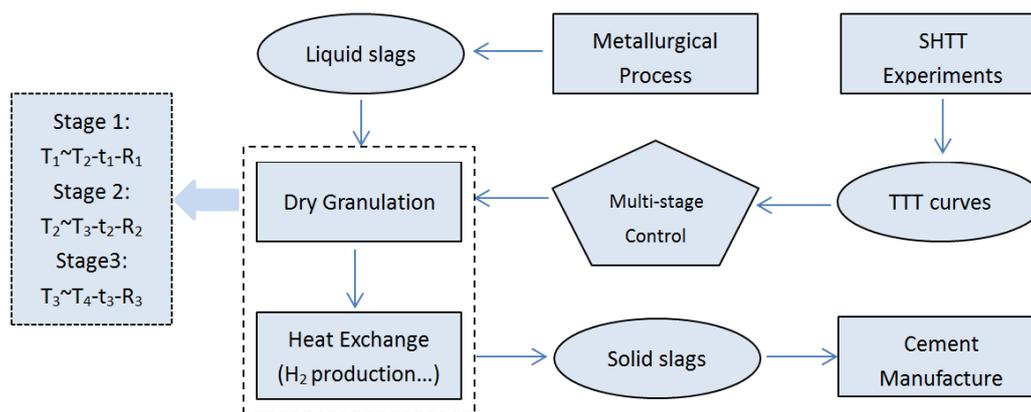
Figure 6. XRD patterns of quenched sample A2 from 1320 °C and 1120 °C.

3.4. Industrial Prototype Plant

Based on the aforementioned analysis, an industrial prototype plant was proposed for the purpose of recovering the high quality waste heat from high temperature slags, and the process flow is shown in Figure 7. The whole process flow could be divided into several parts. Firstly, SHTT experiments were carried out for a slag sample and the TTT curves were obtained. Secondly, the waste heat of the high temperature slags produced in steel industry was extracted with the dry granulation based on a multi-stage control method and the integrated heat was used by coal gasification, hydrogen production or heat storage in PCM. Then the solidified glassy slags could be utilized as cementitious material and finally both the waste heat and slag resources were recovered.

Figure 7. Process flow for the proposed prototype plant.

The possible recovered energy of this prototype plant based on multi-stage control method was calculated and listed in Table 2, in which average heat capacity of slags was referred to Factsage software data [30], the crystal content was assumed as 1% and the slags were assumed to be cooled to ambient temperature (25 °C). As can be seen, the calculation was divided into three stages based on the multi-stage control method. Accordingly the extraction of the high quality energy of slags could be divided into three stages, during which several operational parameters were controlled including heat exchange time and cooling rates; and finally different quantities of waste heat was recovered. For example, the possible extracted waste heat for sample A1 was 160.94 MJ, 198.91 MJ and 1235.86 MJ per ton of slags in the temperature range of 1500–1360 °C (Stage 1), 1360–1100 °C (Stage 2) and 1100–25 °C (Stage 3), respectively, and the total extracted waste heat could be up to 1695.71 MJ per ton of slags without phase change. Accordingly, the cooling rate and heat exchange time during stage 1 and 3 could be adjusted and that during stage 2 should be controlled larger than 6 °C/s and less than 43.3 s. With the heat release of 151.73 MJ per ton of slags from 1% crystal precipitation, the potential of total extracted waste heat could be more than 1847 MJ per ton of slags. In a similar way, the potential extracted waste heat during different stages for samples A2 and A3 could be calculated and the total extracted waste heat for samples A2 and A3 without phase transformation was 1793.82 MJ and 1828.82 MJ per ton of slags, respectively, as listed in Table 2.

Table 2. Energy accounting of waste heat recovery based on multi-stage control.

Sample	Stage	Temperature range (°C)	Heat exchange time (s)	Cooling rate (°C/s)	Heat capacity (J/mol/K)	Possible recovered waste heat (MJ/t)	Phase change heat (MJ/t)	Total extracted heat (MJ/t)
A1	1	1500–1360	-	-		160.94	Crystals: 1%	Non-Crystallization: 1695.71
	2	1360–1100	43.3	6	69.99	298.91	151.73	Crystallization: 1847.44
	3	1100–25	-	-		1235.86		
A2	1	1500–1380	-	-		145.94	Crystals: 1%	Non-Crystallization: 1793.82
	2	1380–1100	18.7	15	78.32	340.52	151.73	Crystallization: 1945.55
	3	1100–25	-	-		1307.36		
A3	1	1500–1400	-	-		123.99	Crystals: 1%	Non-Crystallization: 1828.82
	2	1400–1080	6.4	50	81.51	396.76	151.73	Crystallization: 1980.55
	3	1080–25	-	-		1308.07		

4. Conclusions

The present study provided an analysis of high temperature slags for the purpose of recovering both the high quality waste heat and the slag resources. Three samples were designed containing different levels of Al_2O_3 at a fixed CaO/SiO_2 ratio of 1.05. A Single Hot Thermocouple Technique (SHTT) was used to investigate the slag properties during isothermal experiments and Time Temperature Transformation (TTT) curves were therefore obtained. The main conclusions were summarized as below:

(1) A multi-stage control method of waste heat recovery from high temperature slags was proposed based on TTT curves, in which the whole temperature range was divided into three regions, *i.e.*, Liquid region, Crystallization region and Solid region. Some significant technological parameters, including heat exchange time and cooling rate should be effectively controlled during these stages;

(2) The polynomial expressions fitted the TTT curves well and could be used to deduce the incubation time at any temperature;

(3) An industrial prototype plant was put forward aiming to recover the high quality waste heat of high temperature slags, and accordingly the potential of the extracted waste heat was calculated.

Author Contribution

The work presented here was carried out in collaboration between all authors. Zuotai Zhang and Yongqi Sun conceived and designed the study. Yongqi Sun performed the experiments and wrote the paper. Zuotai Zhang edited the manuscript. Lili Liu and Xidong Wang discussed and reviewed the manuscript. All authors read and approved the manuscript.

Conflicts of Interest

The authors declare no conflicts of interest.

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