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ORIGINAL PAPER

Characterization and Valorization of Kanbara Reactor Desulfurization Waste Slag of Hot Metal Pretreatment

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Abstract The desulfurization waste slag from hot metal pretreatment process is a typical solid waste generated in the integrated steel company. About 7- to 9-kg waste slag is produced per ton hot metal treated in the Kanbara Reactor (KR) desulfurization process, and the waste slag contains approximately 40–60 % CaO and large amounts of iron. Therefore, effectively valorization of these waste slags is significant for resources reutilization and environmental protection. A novel valorization process of KR desulfurization waste slag into iron-containing substances and desulfurization agent for hot metal pretreatment was investigated. Magnetic separation method was conducted to recovery iron-containing substances from the KR waste slag. Various techniques such as XRD, TG-DSC, SEM–EDS were used to characterize the non-magnetic (NM) waste slag. The pyrometallurgical recycling experiments of NM waste slag were performed in a tube furnace after considering various parameters, such as reaction temperature, ratio of slag volume and slag composition. The results show that ~56 wt% of the KR slag can potentially be recycled as an iron-bearing raw material for steelmaking process. The major components of NM KR waste slag are calcium, silicon and iron oxides, and ~70 vol% of NM waste slag particles are <100 μm. The major crystalline phases present in NM waste slag are C, Ca $(OH)_2$, $CaSO_4$, CaF_2, $CaCO_3$, CaS and Ca_2SiO_4. A mass loss of ~20 wt% from room temperature to 1573 K is possibly due to the vaporization of moisture, water of crystallization and fluoride, decomposition of carbonates and $CaSO_4$. The desulfurization ratio in pig iron increases with reaction time, which indicates that the NM waste slag still has desulfurization ability. Moreover, the desulfurization ratio increases with temperature and ratio of slag volume. It is also found that the apparent desulfurization rate constants are in the range between 0.007 and 0.016 min^{-1}.

Keywords Waste · Valorization · Recycling · Desulfurization slag · Hot metal pretreatment

Introduction

Sulfur is generally considered to be of no value in the steel except for some grades of free-cutting steel, and it causes the hot shortness of steel through precipitation of sulfide at the grain boundaries of steel [1]. Hot metal desulfurization pretreatment is a typical process to improve the purity of pig iron between the blast furnace (BF) ironmaking process and basic oxygen furnace (BOF) steelmaking process in the integrated steel companies for its high efficiency, lower cost and lower consumption for refractories. In China, it has been estimated that approximately 70 wt% of hot metal would be pretreated through desulfurization processes in 2015 [2].

Currently, the predominant desulfurization processes for hot metal include the Kanbara Reactor (KR) process and injection processes of passivated Mg powder, or mixtures of passivated Mg powder and lime or calcium carbide. In the KR process, the refractory impeller rotates in the hot metal ladle with charged reagents of burnt lime and fluorite for 6–9 min, and approximately 7 to 9 kg t^{-1} slag by-product would be generated per ton hot metal treated [3]. The valuables present in the KR hot metal pretreatment slag are mainly CaO and iron (typically 50–60 wt%) [4].

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On the other hand, pulverized slag powder and generation of CO during cooling stage of KR slag will cause potential environment issues and be harmful to the workers [4]. Therefore, valorization of these waste slags is of great significance for zero slag emission, which would contribute to resource utilization, environmental protection and developing a recycling economy [5].

A variety of comprehensive utilization processes of waste steelmaking slag have been developed, such as recovering the residual metal in the waste slag, or directly feeding back to the sintering process, recycling as a raw material for cement industry and reutilizing as a fertilizer in agricultural industry [6]. However, only limited studies focus on the utilization of hot metal pretreatment desulfurization waste slag. Han et al. reported that the recoverable iron in the waste desulfurization slag is more than 50 wt% of slag, and mainly present as the crystalline phases of metallic iron, magnetite and metal ferrites [7]. A process combined gravity separation and magnetic separation process has therefore developed to recover the iron in the slag [7]. The obtained iron-containing fines contain up to 86 wt% Fe, and 78 wt% of total iron in the waste slag can be recovered through the process. Moreover, simple ball milling and magnetic separation process can be used to recycle iron in the desulfurization waste slag [8]. During the recycling process, the waste slag is ground with balls and then magnetically separated. More than 15–20 wt% of iron can be recovered as iron nuggets containing ~85 wt% Fe, and 30 wt% of iron can be recovered as fines with ~50 wt% Fe. However, the tailings of these processes still require further treatment.

Sheng et al. developed a process which uses lime in KR waste slag to neutralize acidic mine drainage (AMD) [9]. It is reported that the waste slag can treat AMD efficiently, less toxic heavy metals would be dissolved, and parts of graphite in the slag can simultaneously be recycled. Nakai and Takehama [10, 11] employed a small KR device to determine the desulfurization ability of the waste slag containing CaO and CaF_2 at 1573 K. They found that the desulfurization ability of the water-quenched waste slag is lower than that of the slag with natural cooling, while the particle size of waste slag has little effects on its desulfurization ability. However, large amounts of iron-containing components in the waste slag which can be recycled are not reported in these studies.

In basic slag–metal systems, the desulfurization reactions in the presence of C and Si can be written as [1]:

$$[\mathrm{S}] + (\mathrm{CaO}) + [\mathrm{C}] = (\mathrm{CaS}) + \{\mathrm{CO}\} \tag{1}$$

$$[\mathrm{S}] + 2(\mathrm{CaO}) + 1/2[\mathrm{Si}] = (\mathrm{CaS}) + 1/2(2\mathrm{CaO} \cdot \mathrm{SiO_2}) \tag{2}$$

Based on the thermodynamic analysis of the desulfurization process, the favorable factors for desulfurization by solid reactants include high lime content, low iron oxide content, low temperature, high carbon, silicon and phosphorus content, high fluidity slag, CaF_2 addition and stirring in the molten bath [1]. Niedringhaus and Fruehan [12] indicated that there is no limitation for desulfurization with lime thermodynamically. According to Ward [1], the sulfur equilibrium content of slag–metal is theoretically lower than 0.0015 wt% for reactions (1) and (2) at 1573 K. However, the formation of solid reaction products layer of CaS will stifle the desulfurization reactions [1, 13, 14]. Due to the limitation of kinetics condition, the desulfurization reactions will not reach equilibrium. Therefore, large amounts of unreacted lime and calcium-containing substances in the KR waste slag exist and can be potentially recycled to desulfurize the hot metal.

The basic concept of recycling process in this study is shown in Fig. 1. A combination process of magnetic separation and direct recycling of KR waste slag is developed. The valuables, such as iron-containing substances and lime in the KR waste slag, would be reutilized. The KR waste slag is naturally cooled and magnetically separated, the iron-containing products can be potentially utilized as a raw material for steelmaking, the waste residual slag, i.e., non-magnetic parts, is recycled back to the hot metal pretreatment process to form a closed materials loop for the waste slag. In the present study, the KR waste residual slag was characterized and the potential use of the slag for hot metal desulfurization was also evaluated.

Experimental

Materials

The KR desulfurization waste slag and pig iron used in this study were collected from a local integrated steel plant.

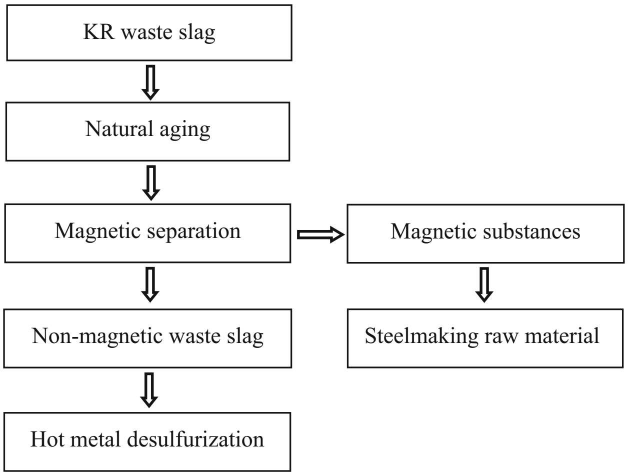

Fig. 1 Flow sheet of comprehensive utilization of KR waste slag

The pig iron used in this study contains mainly 4.75 wt% C, 0.33 wt% Si, 0.22 wt% Mn, 0.078 wt% P, 0.056 wt% S, small amounts of trace elements and balance iron. The slag sample was naturally aged for ~2 months and dried in an oven at 110 °C for 4 h, and then, it was magnetically separated by hand at ~0.2T without being precrushed or ground. The non-magnetic slag parts are used for further experiment.

Slag Characterization of Non-Magnetic KR Waste Slag

The particle size distribution of non-magnetic KR (NM) waste slag was analyzed using Malvern Mastersizer 2000. Chemical analysis for the NM waste slag was conducted with IRIS advantage ER/S inductively coupled plasma atomic emission spectrometry (ICP-AES). The effective calcium content in the NM slag was measured with the standard method for the determination of effective calcium oxide in lime (Chinese standards T0811-1994). The crystalline phases of the waste slag were determined using an X'Pert PRO MPD X-ray diffractometer with Cu Kα radiation (tube voltage of 40 kV and current of 40 mA) and 2θ scanning ranging from 10° to 70°. A scanning electron microscopy with energy-dispersive spectrometer (SEM–EDS) (PHILIPS XL30 TMP) was used to examine the microstructure of the NM waste slag.

Thermogravimetric tests on the NM waste slag were conducted on a Netzsch STA 449C TGA/DSC thermogravimetric analyzer. During the experiment, 30 mg powder slag sample was loaded in an alumina crucible, and nitrogen gas (99.99 % purity) purged. The powder sample was heated from 298 to 1573 K at a heating rate of 15 K min^{-1}.

Waste Slag Recycling for Hot Metal Desulfurization

The NM waste slag recycling experiments were carried out in a high-temperature furnace with heating elements of $MoSi_2$ bar (as shown in Fig. 2). In the experiment, the weighed pig iron sample (325 ± 20 g) was placed in the graphite crucible with inner diameter of 5 cm and height of 10 cm. The crucible was then set on the alumina support inside the furnace tube. The high-purity argon gas was purged into the tube furnace to keep an inert atmosphere in order to avoid oxidation of the molten sample.

During the experiments, the heating rate of the furnace was set as 5 K min^{-1}. After the temperature of the furnace reached the set temperature, it was kept for about 10 min to homogenize the chemical composition of pig iron. Then, the weighed desulfurization agent was added and stirred with quartz rod. The pig iron samples (~3 g) were taken from the melt at certain reaction time intervals by using a sucker quartz glass pipe. The sampled pig iron was quenched and crushed, and the sulfur content in the pig iron was determined using a CS-8800 carbon sulfur analyzer.

The experimental parameters are shown in Table 1. It can be seen from Table 1 that the effects of reaction temperature (1573 and 1673 K), slag volume (5 and 10 wt%) and addition ratios of fresh desulfurization agent (FDA) on the desulfurization ability of NM waste slag were considered. The FDA was prepared by using CaO and CaF_2 (AR grade) with a mixture ratio of 9:1. The addition ratio of FDA was set as 40 wt% of total slag weight.

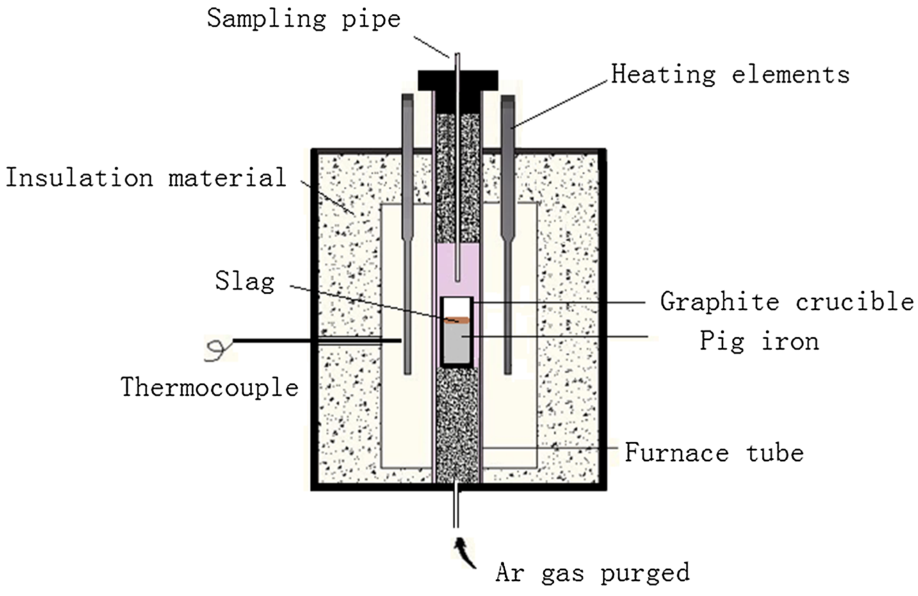

Fig. 2 Schematic of the experimental apparatus

Table 1 The experimental parameters of recycling the NM waste slag

No.	T/K	Mass of pig iron/g	Mass of slag/g	Desulfurization agent ratio/wt%	With or without FDA	Ratio of FDA/wt%
1	1573	332.45	16.62	5	Without	0
2	1573	338.12	33.81	10	Without	0
3	1573	327.84	32.72	10	With	40 ($CaO:CaF_2 = 9:1$)
4	1673	307.54	30.75	10	Without	0

FDA fresh desulfurization agent

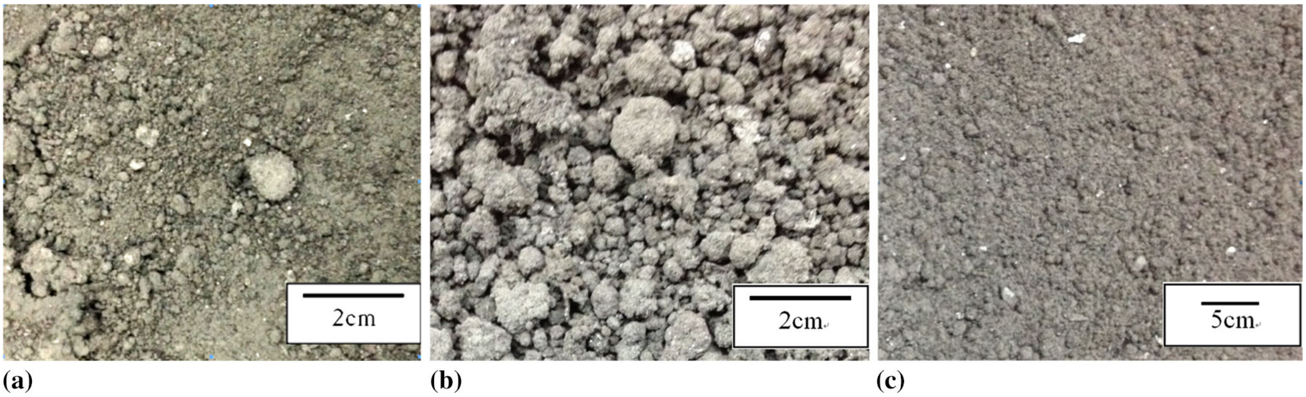

Fig. 3 Photographs of KR waste slag samples before and after magnetic separation. **a** Original KR slag. **b** Magnetic substances. **c** Non-magnetic waste slag

Table 2 The chemical composition of NM KR waste slag/wt%

Composition	SiO_2	Al_2O_3	FeO	CaO	MgO	MnO	S	CaO_{eff}
NM KR waste slag	8.94	0.35	15.15	61.06	0.94	0.09	2.2	38.5

Results and Discussion

Separation of KR Waste Slag

The aged KR waste slag was magnetically separated manually. Figure 3 shows the photographs of the waste KR slag sample before and after magnetic separation. It clearly shows that the original slag contains a wide range of particles (Fig. 3a). However, most of the coarse particles (Fig. 3b) in the KR slag are magnetic substances, which share 56 wt% of the total weight of KR slag and can potentially be used as iron-containing raw material for steelmaking. This is similar to the results reported by Bu et al. [15] that ~50 wt% of the desulfurization slag can be recycled as iron-containing resources.

The fine particles are non-magnetic (Fig. 3c). White particles (possibly unreacted lime) can also be found in these slags. According to Zou et al. [16], the waste desulfurization slag with lime typically has a three layers of shell structure from outside to inner, i.e., CaS, $2CaO{\cdot}SiO_2$ and CaO. The unreacted lime particles (white particles) are either from the virgin lime or appearance of the inner layer of desulfurization slag particles after pulverization of $2CaO{\cdot}SiO_2$ from α-$2CaO{\cdot}SiO_2$ to γ-$2CaO{\cdot}SiO_2$ with volume expansion in the aging period.

Characterization of Non-Magnetic KR Waste Slag

The chemical composition of NM waste slag is shown in Table 2. It indicates that the major components of waste slag are calcium, silicon and iron oxides (~85.2 wt%), and small concentrations of sulfur (2.2 wt%) are also present in the slag. Moreover, calcium-containing substances possibly present as oxide, sulfide and fluoride (~61.06 wt% converted into CaO as shown in Table 2), which mainly originates from the unreacted desulfurization agent and the product of desulfurization. The effective lime content (free CaO) in the NM waste slag is up to 38.5 wt%, which indicates that the waste slag can potentially be used as a desulfurization agent.

Figure 4 shows the particle size distribution of NM waste slag. ~70 vol% of slag particles are <100 μm in diameter. Zou et al. [16] reported that the desulfurization agent with small particle size (<0.5 mm) has large desulfurization ratio and apparent desulfurization rate constant. As the surface area increases with a decrease in the particle size, it will be beneficial to the desulfurization process to have small particle sizes. It is pointed out that the fine desulfurization agent could be sucked by off-gas system during the treatment process and therefore, increase the consumption of desulfurization agent, if it is not injected into the melt.

Microstructurally, the NM waste slag mainly consists of CaS (Fig. 5A), Ca–Si–O-S (Fig. 5B) and CaO. The X-ray diffraction pattern of the NM waste slag is shown in Fig. 6. It can be seen that the major crystalline phases presented in waste slag are C, $Ca(OH)_2$, $CaSO_4$, CaF_2, $CaCO_3$, CaS and $2CaO{\cdot}SiO_2$. This is partially consistent with the results of SEM analysis. Carbon originates from the precipitation of the carbon-saturated pig iron during the cooling processes of waste slag. The existence of $Ca(OH)_2$ and $CaCO_3$ is possibly due to the reaction of lime with moisture and carbon dioxide in the atmosphere, respectively, while the oxidation of CaS forms $CaSO_4$ [17, 18]. Small amounts of $2CaO{\cdot}SiO_2$ are formed as the desulfurization product through reaction (2).

The TG–DSC curves of NM waste slag are presented in Fig. 7. It shows a mass loss of 2.5 wt% from room temperature to 400 °C, which is mainly from the moisture in the slag. The calcium hydroxide dehydrates (~10 wt% weight loss) between 400 and 500 °C with an endothermic peak in the DSC curve [19]. A 5 wt% weight loss is associated with the decomposition of carbonates at 600–800 °C [20]. Only about 2.5 wt% of the weight loss occurs at temperatures above 800 °C, which probably originated from the decomposition of $CaSO_4$ and vaporization of fluoride in the slag sample [19, 21].

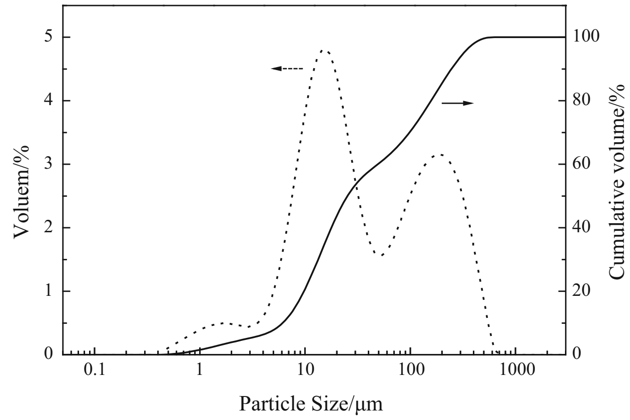

Fig. 4 Particle size distribution of NM KR waste slag

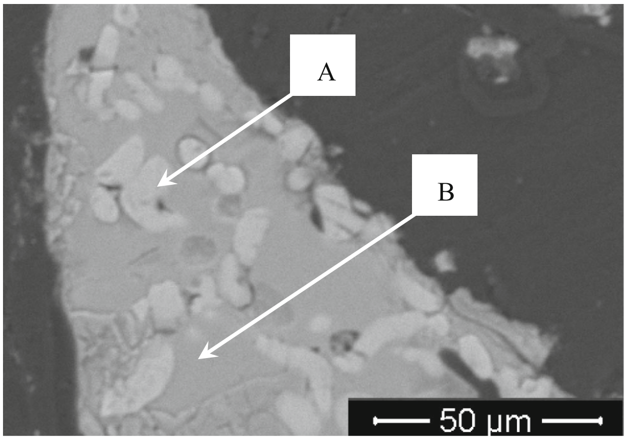

Fig. 5 SEM image of NM KR waste slag

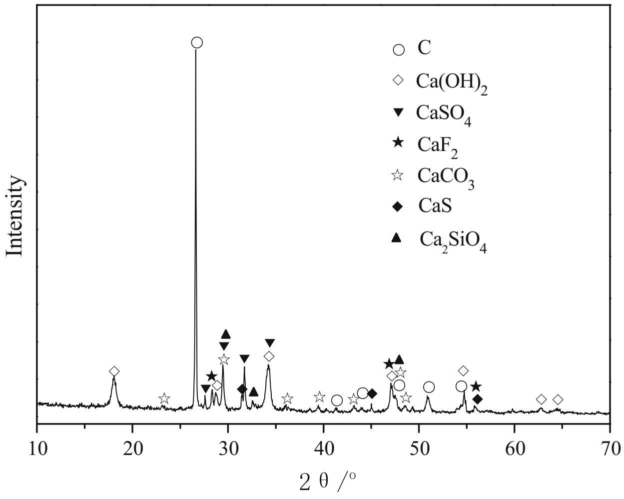

Fig. 6 XRD pattern of KR waste slag (Cu Kα)

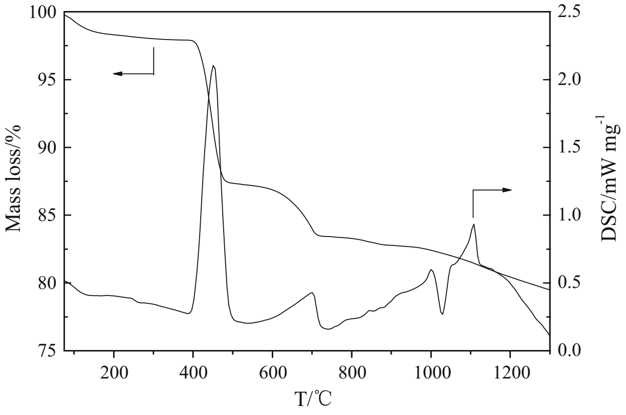

Fig. 7 TG–DSC analysis of NM KR waste slag

Recycling of Waste Slag for Hot Metal Desulfurization

During the desulfurization experiment, the fractional desulfurization can be used to characterize the desulfurization efficiency according to Eq. (3) [11]:

$$\eta_s = \left([\%\mathrm{S}]_{\mathrm{ini}} - [\%\mathrm{S}]_{\mathrm{t}}\right)/[\%\mathrm{S}]_{\mathrm{ini}} \times 100\,\% \qquad (3)$$

where η_s is the desulfurization ratio of slag, $[\%\mathrm{S}]_{\mathrm{ini}}$ is the initial sulfur concentration in the pig iron, and $[\%\mathrm{S}]_{\mathrm{t}}$ is the sulfur concentration in the pig iron at certain time interval. It is assumed that %S in the final metal approaches zero.

The results of desulfurization experiment are shown in Table 3. It shows the sulfur content in liquid iron and relative fractional desulfurization with variation of the reaction time. The effects of slag volume and composition (with or without FDA), reaction temperature and time on the fractional desulfurization in pig iron based on Table 3 are illustrated in Fig. 8. It indicates that increasing volume of desulfurization agent (i.e., NM waste slag) benefits the desulfurization process at 1573 K, since large slag volume can provide more lime and fluoride particles. The desulfurization ratios with desulfurization agent volumes of 5 and 10 wt% can be obtained as 16.3 and 20.5 wt% after 25-min reaction at 1573 K, respectively. This shows that the NM waste slag has potential capability for hot metal desulfurization. In addition, it can be speculated that the desulfurization ratio increases with an increase in reaction time.

With the same amount of slag addition, the desulfurization ratio in pig iron increases with reaction temperatures, and it can be up to 34.5 wt% after 25 min reaction at 1673 K. Although lower temperatures thermodynamically favor desulfurization, it is generally recognized that CaF_2 addition will form liquid phases above 1633 K according to the phase diagram of CaO–CaF_2 [1, 22]. The presence of liquid phases will eliminate the solid reaction products layer of CaS formed through reactions of (1) and (2), and possibly increase the reaction rate of desulfurization. Furthermore, the existence of SiO_2 in the NM waste slag would also provide more liquid phases, and benefits the transfer of CaS. Therefore, it is helpful for the desulfurization reactions [13, 14]. However, the desulfurization distribution ratio increases with an decrease in the FeO content in desulfurization agent [1]. The NM waste slag contains 15.15 wt% FeO, and it is harmful to desulfurization reaction. Therefore, it is suggested to use mixture of fresh desulfurization agent and the NM waste slag to desulfurize in order to minimize the impact of FeO.

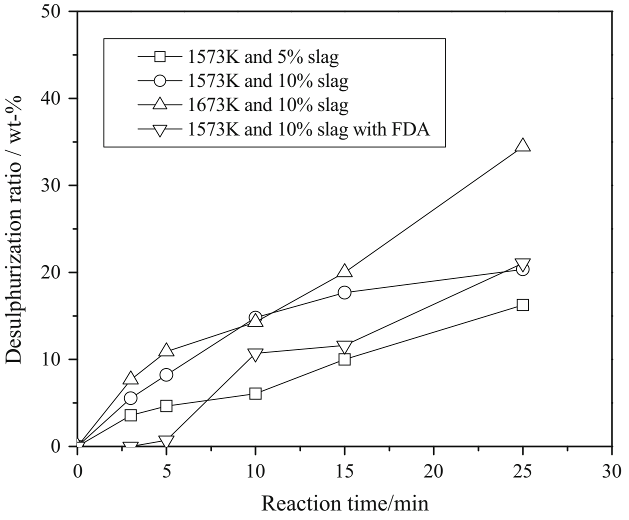

Fig. 8 Effects of slag volume and composition, reaction temperature and time on the fractional desulfurization of pig iron

Table 3 and Fig. 8 also show that the fractional desulfurization in pig iron with 40 wt% fresh desulfurization agent (FDA) (21.1 wt%) is slightly higher than that without FDA (20.4 wt%) after 25-min reaction at 1573 K. Since addition of FDA into the NM waste slag would bring more CaO and CaF_2 and dilute the impact of FeO in the NM waste slag, it therefore increases the desulfurization ability.

Desulfurization reaction can be regarded as the first-order reversible reaction [24]. The limitation step of the desulfurization rate is either the diffusion of sulfur from the boundary of the molten iron to surface of lime particles or the solid diffusion of sulfur in lime particles [24]. The relationship of log $[\mathrm{S}]/[\mathrm{S}]_{\mathrm{ini}}$ and reaction time based on the

Table 3 Sulfur in liquid iron and relative fractional desulfurization with variation of the reaction time

Reaction time (min) no. S or FDS	Sulfur in liquid iron %				Fractional desulfurization %			
	1	2	3	4	1	2	3	4
0	0.0560	0.0560	0.0560	0.0560	0	0	0	0
3	0.0540	0.0529	0.0560	0.0517	3.6	5.5	0	7.7
5	0.0534	0.0514	0.0556	0.0499	4.6	8.2	0.7	10.9
10	0.0526	0.0477	0.0500	0.0480	6.1	14.8	10.7	14.3
15	0.0504	0.0461	0.0495	0.0448	10.0	17.7	11.6	20.0
25	0.0469	0.0446	0.0442	0.0367	16.3	20.4	21.1	34.5

FDS fractional desulfurization

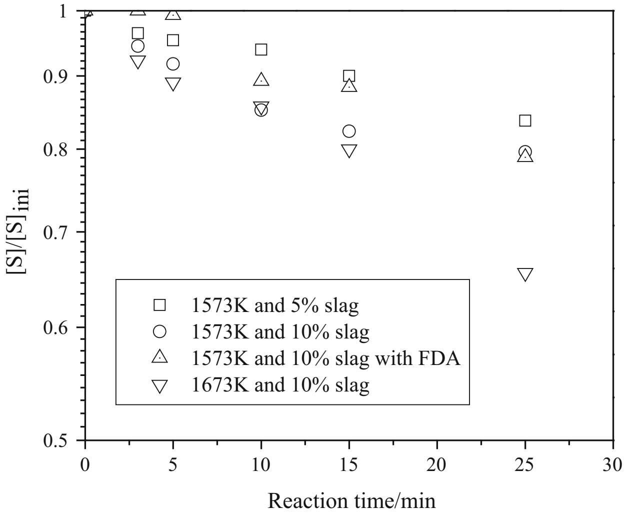

Fig. 9 The relationship between log $[S]/[S]_{ini}$ and reaction time for different experiments

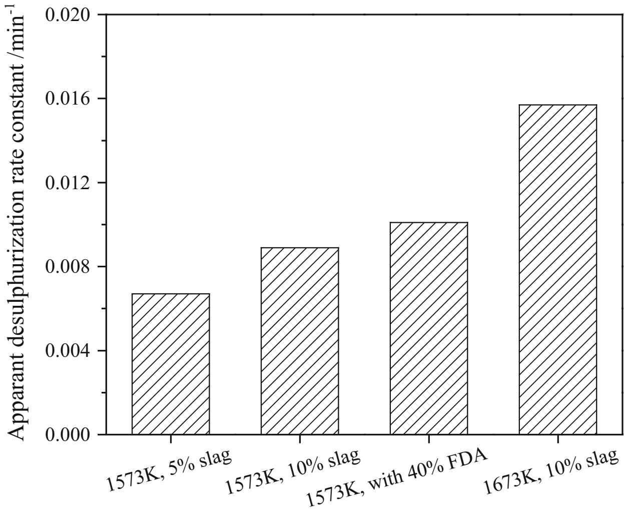

Fig. 10 Desulfurization rate constants at various experimental conditions

data from Table 3 shows linear (Fig. 9). Thus, the desulfurization rate constant can be used to evaluate the desulfurization ability of slag through assuming that the equilibrium sulfur in metal is zero [11]. In this study, the desulfurization rate constant can be calculated using Eq. (4) [24]:

$$\ln\left([\mathrm{S}]/[\mathrm{S}]_{\mathrm{ini}}\right)/\mathrm{d}t = -kt \tag{4}$$

where k is the desulfurization rate constant, min^{-1}.

Figure 10 indicates that the desulfurization rate constants of desulfurizer are in the range between 0.007 and 0.016 min^{-1}. Combined with Table 3, it is found that the desulfurization rate constants have positive relationship with fractional desulfurization after 25-min reaction, i.e., the larger the apparent desulfurization rate constants are, the greater the desulfurization effects are. It is also noted that the desulfurization rate constants in this study are similar to the results of Xu et al. [23], who reported that the desulfurization rate constants of Al_2O_3-containing KR desulfurizers varied from 0.006 to 0.021 min^{-1} with Al_2O_3 contents of 0–30 % at 1648 ± 5 K (3 % of slag to metal ratio and 500 g ± 10 g iron per experiment).

Conclusions

1. A novel valorization process of KR waste slag for iron-containing substances and residual waste slag as a desulfurization agent for hot metal pretreatment was developed. About 56 wt% of the total weight of KR slag can potentially be used as an iron-bearing raw material for steelmaking process. The non-magnetic KR waste slag still has desulfurization ability.
2. The major components of non-magnetic KR waste slag are calcium, silicon and iron oxides, the effective lime content is 38.5 wt%, and ~70 vol% of slag particles are <100 μm.
3. The major crystalline phases presented in the waste slag are C, $Ca(OH)_2$, $CaSO_4$, CaF_2, $CaCO_3$, CaS and $2CaO{\cdot}SiO_2$. A mass loss of ~20 wt% from room temperature to 1573 K is possibly due to the vaporization of moisture, crystal water and fluoride, decomposition of carbonates and $CaSO_4$.
4. The fractional desulfurization in pig iron increases with reaction time, temperature and slag volumes. It is also found that the apparent desulfurization rate constants are in the range between 0.007 and 0.016 min^{-1}, and the fractional desulfurization can be 34.5 % after 25-min reaction with 10 wt% of slag at 1673 K.

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