Journal of Cleaner Production xxx (2016) 1–9

Contents lists available at ScienceDirect

Journal of Cleaner Production

journal homepage: www.elsevier.com/locate/jclepro

System assessment of recycling of steel slag in converter steelmaking

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ARTICLE INFO

Article history:
Received 18 July 2015
Received in revised form
8 March 2016
Accepted 8 March 2016
Available online xxx

Keywords:
Steel slag
Recycling
Steelmaking
Dephosphorization
Temperature drop

ABSTRACT

Aimed to utilize useful components and reduce the environmental impacts, the present study investigated the recycling of steel slag in converter steelmaking. A mathematical model based on the regular solution model was firstly developed to calculate the activities of calcium oxide and ferrous oxide and the substitution ratio of steel slag. The dephosphorization experiments were conducted in an induction furnace. In addition, theoretical analysis of the detailed heat expenditure items of dephosphorization agent was carried out. The heat enthalpy of unit mass slag was measured by differential scanning calorimetry. The results of dephosphorization experiments indicate that there is a sharp drop in phosphorus content in hot metal at the initial stage of dephosphorization. It was found that the optimal proportion of steel slag in dephosphorization agent is 20%. The heat enthalpy of unit mass slag No.1 and No.2 are 1164 kJ/kg and 1131 kJ/kg, respectively. The cooling capacity of steel slags are lower than the reference dephosphorization agent. One ton of reference dephosphorization agent made of 42% lime, 50% scale and 8% soda, could reduce the temperature of 80 ton of hot metals by up to 83.60 °C. The corresponding temperature drop by using No.1 and No.2 steel slags are 56.01 and 55.99 °C, respectively. For each increase of 5% substitution ratio with No.1 slag, the temperature drop of hot metal increases by 5.80 °C; for each increase of 5% substitution ratio with No.2 slag, the temperature drop of hot metal increases by 2.70 °C. The main factor that influences the temperature drop is the slag amount.

1. Introduction

Integrated steel plants utilize large amounts of slag former such as lime and dolomite to produce steel. During the production of steel, 2–4 t of wastes are being generated per tonne of steel produced (Das et al., 2007). The various solids wastes exist in the form of slags, sludges, dusts, mill scales, etc. Amongst the numerous solid wastes, steel slag is a byproduct of steelmaking industry, which comes from hot metal refining processing using basic oxygen furnace or electric arc furnace. The amount of steel slags from different steel industries are 100–150 kgs/t of steel output (Gao et al., 2015; Proctor et al., 2000). According to the statistical data of Worldsteel Association, China's crude steel output is 822.7 million tons in 2014, which means the generation of steel slag is over 80 million tons per annum. Compared with the developed countries, the comprehensive utilization ratio of steel slag in China is relatively low. The conventional method for disposal of steel slags is dumping. As the fly ash in open-air slag yard would pollute the air and the harmful components like chromium, arsenic, and phosphorus, etc. would dissolve in water, which are highly objectionable from the pollution point of view. Therefore, the increasing accumulation of steel slags not only occupies plenty of land, but also pollutes the environment and water. It becomes a seriously problem of both the society and the industry itself (Dippenaar, 2005).

Various efforts have been made on the utilization of steel slags. Steel slags have been applied in many areas, such as cement production, road construction, civil engineering, landfill daily cover, fertilizer production, and so on. In general, the main application can be divided into two ways (Shen and Forssberg, 2003). One is the direct application of steel slag in the ironmaking and steelmaking process; the other includes recovery of metals from steel slag and then the application of the remaining slag outside the iron and steel making process.

For the first way, as the main components in the steel slags are calcium oxide (CaO), iron (Fe), ferrous oxide (FeO), silicon dioxide (SiO_2), magnesium oxide (MgO) and manganese oxide (MnO), it can be used as fluxing material in sintering, ironmaking or steelmaking

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http://dx.doi.org/10.1016/j.jclepro.2016.03.040
0959-6526/

process for substitution of a part of limestone, dolomite and manganese ore so as to reduce the material cost. In this utilization way, Fe in steel slag is also recovered. For the other way, as steel slags usually contain a quantity of valuable metals, they are actually a secondary resource of metals. Particularly, the iron and steel industry has applied mineral processing technology to recover steel scrap (Fe: 90%) and iron oxide concentrate (Fe $\geq$ 55%) from steel slag and use them as feed materials for sintering, ironmaking and steelmaking (Shen and Forssberg, 2003). Some steel slags contain high amounts of transition metal elements, such as Cr, Ni, Mn, Ti, V, Mo, etc. It is desirable to recover the valuable metals from steel slags in judicious manners. For example, converter slags are always used to extract V in some countries (Lundkvist et al., 2013; Park et al., 1994). In addition, steel slags can be used to produce precipitated calcium carbonate or remove phosphate from aqueous solution (Mattila et al., 2014; Eloneva et al., 2010, 2012; Bao et al., 2010; Xue et al., 2009). For some applications, steel slags have comparable or even better properties than their competitive materials like lime, dolomite and so on.

Steel slag has many useful components and high fluxing capacity. It is usually being recycled in the iron and steel industry due to easy melt and better utilization of CaO. Fig. 1 shows the schematic of recycling of steel slag in converter steelmaking. Particularly, according to the concept of circular economy, recycling of steel slag in dephosphorization process in converter steelmaking not only improves the slag formation due to the exists of the premelted substances, but also saves the iron resource. However, recycling of steel slag in converter steelmaking may encounter some problems. Since some steel slags contain a notable amount of P and S, which are harmful to the process of dephosphorization and mechanical property of steels (Mohammed et al., 2014). It was reported that the FeO and phosphorus pentoxide (P_2O_5) in steel slag could be separated by capillary action. After separation, the recovered CaO concentrated phase, which includes a FeO rich liquid phase, may be used as Fe source or dephosphorization agent, and the dicalcium silicate ($2CaO{\cdot}SiO_2$) phase, which includes P_2O_5, may be used as P source (Miki and Kaneko, 2015). Our previous studies also investigated the separation of Fe concentrated phase and P concentrated phase by slag modification or magnetic separation (Jiang et al., 2015; Diao et al., 2012). A recycling technology of weak magnetic separation coupled with selective particle size screening has been developed at ArcelorMittal Global R&D-EastChicago Laboratories, targeted at solving the problem in a cost-effective way (Ma and Houser, 2014). These studies aimed to separate P and Fe in steel slag, and obtain cleaner iron-rich products with sufficiently high iron contents and low levels of impurities to be reused or recover P-rich phase to produce phosphate fertilizer. When steel slag is being recycled in steelmaking process to substitute the original dephosphorization agent, the substitution grade is a key parameter. The purpose of the present study aims to investigate the

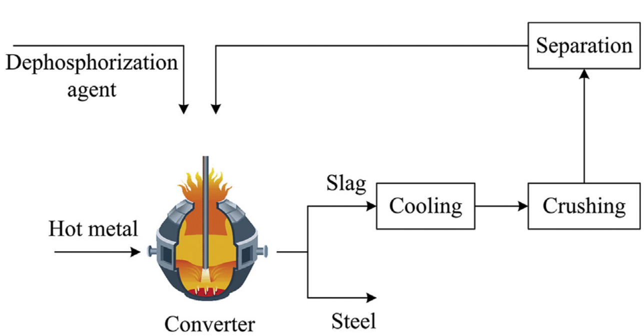

Fig. 1. Schematic of recycling of steel slag in converter steelmaking.

relationship between dephosphorization effect, thermal effect and substitution ratio of steel slag.

Following sections describe the development of a mathematical method for estimation of substitution grade of dephosphorization agent. It is expected to establish a correlation between the composition of substituted dephosphorization agent and activities of CaO plus FeO, then the substitution ratio can be calculated. The laboratory dephosphorization experiments were conducted to investigate the impact of recycling of steel slag on dephosphorization. Furthermore, as the temperature drop of hot metal are strongly dependent on the composition and amount of slagging agents in steelmaking process, therefore, the quantitative relationship between the temperature drop of hot metal and the substitution ratio of recycled steel slag was also studied.

2. Mathematical model for slag substitution

2.1. Activity calculation

As steel slags contain various components, the oxygen potential and the proportion of alkaline oxides may donot meet the requirements of current dephosphorization agents. Therefore, when steel slag was used as a substitute of the dephosphorization agent, we cannot making simple equivalent substitution with the mass concentration of iron oxide and calcium oxide in the steel slag. To keep the dephosphorization efficiency, a mathematical model must be developed to calculate the substitution ratio of dephosphorization agent by steel slag. A previous study reported that the activities of FeO and CaO in the slags have been obtained from the iso-activity diagrams of (CaO + MgO + MnO)-(SiO_2 + P_2O_5)-FeO_n system (Hu et al., 2002). In the present work, we use the regular solution model to calculate the activities of the slag (Huang, 2002).

It was assumed that the slag was composed by simple cations such as Ca^{2+}, Fe^{2+}, Mn^{2+}, Mg^{2+}, Si^{4+}, P^{5+}, etc., and simple anion O^{2-}. The polymerization of silicates can be ignored. The activity coefficient of component, *i*, in regular solution is expressed by the following equations:

$$RT\ \ln\gamma_i = \sum_j a_{ij}x_j^2 + \sum_j \sum_k \left(a_{ij} + a_{ik} - a_{jk}\right)x_j x_k \tag{1}$$

where, α_{ij} is the interaction energy between cation *i*-O-cation *j*. x_i is the cation fraction of the component *j* in slag. $i \neq j$ or *k*.

The activities of CaO and FeO in the slag can be calculated as follows:

$$a_{CaO} = \gamma_{Ca^{2+}}\gamma_{O^{2-}}x_{Ca^{2+}}x_{O^{2-}} = \gamma_{Ca^{2+}}x_{Ca^{2+}} \tag{2}$$

$$a_{FeO} = \gamma_{Fe^{2+}}\gamma_{O^{2-}}x_{Fe^{2+}}x_{O^{2-}} = \gamma_{Fe^{2+}}x_{Fe^{2+}} \tag{3}$$

where, $\gamma_{O^{2-}} = x_{O^{2-}} = 1$.

2.2. The formulas of dephosphorization agents

As the composition of steel slag differ from the dephosphorization agent, appropriate amount of calcium oxide or iron oxide must be added to balance the effective components. The slag amount is to be calculated according to substitution of fixing agent (CaO) or oxidant (FeO) respectively, then choose the minimum slag amount in accordance with the principle of minimization slag amount and add the rest of lime or oxidant.

It must be emphasized that the present work concentrated on the dephosphorization in high phosphorus hot metal refining. Therefore, to keep a higher slag solubility and obtain phosphate

Please cite this article in press as: Diao, J., et al., System assessment of recycling of steel slag in converter steelmaking, Journal of Cleaner Production (2016), http://dx.doi.org/10.1016/j.jclepro.2016.03.040