Recovery of Phosphorus from Dephosphorization Slag Produced by Duplex High Phosphorus Hot Metal Refining

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(Received on September 16, 2011; accepted on January 30, 2012)

Phosphate rock is a vital nonrenewable resource. In order to find new source of phosphorus, the recovery of phosphorus from dephosphorization slag produced by duplex steelmaking process (De–P_De–C steelmaking process) was investigated in the present paper. It was demonstrated that the P-rich phase in dephosphorization slag is difficult to recover effectively by magnetic separation as the reason of P enriched phase inlay in the Fe enriched phase in the slag. The relationship between P recovery ratio and magnetic intensity and slag particle size were also obtained. A series of slag modification experiments were designed to investigate the recovery of phosphorus from high P 2O 5 content dephosphorization slag produced by duplex high phosphorus hot metal refining. It was found that the addition of SiO 2, Al 2O 3 and TiO 2 has a positive influence on the P recovery ratio. However, the P recovery ratio and the concentration of P 2O 5 in unmagnetized slag showed a reciprocal relationship with increasing SiO 2 and Al 2O 3 content. The P recovery ratio was little affected by the addition of Fe 2O 3 and MnO. Furthermore, the P recovery ratio increased under the stirring condition. 74% and 87% P were recovered in the unmagnetized phases with adding 10% SiO 2 and Al 2O 3, respectively. The results demonstrated that most of the phosphorus in the slag could be recovered through slag modification and magnetic separation.

KEY WORDS: phosphorus; dephosphorization slag; recovery; duplex; magnetic separation; slag modification.

1. Introduction

Phosphorus is an important element, making a major contribution to agricultural and industrial development. Phosphate rock minerals are the only significant global resources of phosphorus. However, phosphate rock is neither substitutable nor recyclable in agricultural applications.1) In a previous report,2) it was stated that the phosphorus used in fertilizer and industry were 82% and 12%, respectively, and numerous articles have suggested phosphate rock maybe exhausted in the 21st century. Hence, interest in phosphorus recycling and substituting is steadily increasing in the industrialized world. One possibility is to recycle the phosphorus in steelmaking slags. We all know that phosphorus is one of the most detrimental impurities in steels and very considerable quantities of phosphorus are eliminated into the steelmaking slags.

Many previous studies have concentrated on the removal of phosphorus from steelmaking slag. Ono et al.3) developed a method for removal of phosphorus by floating separation of dicalcium silicate during slow solidification. Li et al.4) proposed a slag regeneration process to reduce the BOF slag in an iron bath furnace, and then the high phosphorus hot metal obtained from the reduction process was dephosphorized to get high P 2O 5 content slag for the use of fertilizer. Ishikawa5) investigated the reduction behaviors of each element in the slag regeneration process. Yokoyama et al.6,7) used a simulated dephosphorization slag to recover phosphorus by magnetic separation. In addition, there are many other methods on recovery of phosphorus have also been summarized in these papers, including electrolytic dephosphorization, dual liquid phase separation, and floatation etc. Moreover, these methods have inspired us a lot to recover the phosphorus from dephosphorization slag.

Usually, the typical BOF slag has 1–3% P 2O 5. The content is too low to be used as phosphate fertilizer. A previous study8) indicated that the duplex steelmaking process originated in Japan is favorable to dephosphorization. Briefly, the duplex steelmaking process is characterized by treating the hot metal with two LD converters; i.e. one for dephosphorization and the other for decarburization. A flow sheet of typical duplex steelmaking process is given in Fig. 1. For normal hot metal ([P]~0.1%), the P 2O 5 content in dephosphorization slag is about 5%. When the phosphorus concen-
tration in hot metal is adjusted to 0.15–0.25%, the P2O5 content in dephosphorization slag exceeds 10%. The NingXiang-type iron ore deposits in China is a typical high phosphorus (Pave 0.8%) iron ore deposits, which has a large reserves of 3.72 billion tons and has not been exploited until now.\(^9,10\) If high phosphorus hot metal refining in duplex process become technically feasible, the utilization problems of high phosphorus iron ore were to be resolved, and the high P2O5 content dephosphorization slag could be obtained and used as raw material in fertilizer production. With this background, this paper mainly studied the separation and recovery of phosphorus from dephosphorization slag.

2. Experimental

2.1. Magnetic Separation Experiment

Yokoyama\(^{11}\) found the absolute values of magnetization of the phosphorus-containing phases in BOF slag are as little as 1/100th of phosphorus-free phases. Because of the different magnetic property in the two phases, it should be possible to separate and recover the phosphorus enriched phases if a magnetic field is applied to the crushed slag. A dephosphorization slag came from a duplex steelmaking trial was used in present study. The reason for the low P2O5 content is that the [Si] in hot metal is too high (≥0.5%) in the trial. The lump slag samples were milled with steel balls in a globe mill to produce particles less than 74 μm mesh. Chemical composition of the slag powder was analyzed by X-ray fluorescence spectroscopy and given in Table 1. 30 g slag powder was applied for a magnetic separation experiment with a Davis Magnetic Tube Tester (XCGS, Tangshan Hongda, China). The experimental apparatus is schematically illustrated in Fig. 2. Specifically, the tube was positioned between the poles of the magnet at an angle of approximately 45 degrees and vibrated with an oscillation stroke of 40 mm at a vibration frequency of 70 per minute. During the operation, the water-filled glass tube moves forward and backward while it rotates simultaneously. The magnetized particles in slag were congregated in the zone of intense magnetism, and the unmagnetized particles were flushed from the tube. Both the magnetized and unmagnetized particles were collected and analyzed.

2.2. Slag Modification Experiment

The slag phase could be changed greatly by adding modifying agents. To enrich and concentrate the vanadium in V-bearing steelmaking slags, a number of previous studies pointed out that different oxides such as SiO\(_2\), Al\(_2\)O\(_3\) and TiO\(_2\) can be used as slag modifying agents.\(^{12–17}\) As phosphorus resembles vanadium, we have reason to believe that the phosphorus in dephosphorization slag could also be concentrated in P-rich phases by slag modification. The slags used in this study were synthesized by analytic reagents and the composition is listed in Table 2. In a typical experimental run, the sample was heated to 1 823 K in a magnesia crucible that was put in an electric resistance furnace. The temperature was kept constant for 30 min to melt and homogenize the slag. Thereafter, it was cooled to 1 623 K at a rate of 10 K/min and kept for 120 min to promote the precipitation of P-rich phases. Then, the system was cooled to 1 473 K at 10 K/min. The slag was taken out at 1 473 K and quenched to room temperature in air. After being pulverized to less than 48 μm, the slag powder was separated by magnetic separation.

3. Results and Discussion

3.1. Effect of Magnetic Intensity and Particle Size on Separation Behaviors

Figure 3 shows the magnetic separation results of No.0 slag with a particle size of <74 μm. The P recovery ratio and Fe recovery ratio are defined by Eqs. (1) and (2), respectively.

\[
\begin{align*}
\text{P recovery ratio} & = \frac{\text{recovered P content}}{\text{total P content}} \\
\text{Fe recovery ratio} & = \frac{\text{recovered Fe content}}{\text{total Fe content}}
\end{align*}
\]

Table 1. Composition of dephosphorization slag.

| No. | CaO  | SiO\(_2\)  | Ti-Fe | MnO | MgO | P\(_2\)O\(_5\) | Al\(_2\)O\(_3\) | TiO\(_2\) |
|-----|------|-----------|-------|-----|-----|-------------|-------------|---------|
| 0   | 40.08| 15.56     | 17.42 | 3.23| 7.24| 2.06        | 3.05        | 2.59     |

Table 2. Composition of synthetic slag samples.

| No. | CaO  | SiO\(_2\)  | FeO | P\(_2\)O\(_5\) | MnO | MgO | Al\(_2\)O\(_3\) | TiO\(_2\) |
|-----|------|-----------|-----|-------------|-----|-----|-------------|---------|
| 1   | 34.3 | 13.7      | 28.0| 10.0        | 3.0 | 8.0 | 3.0         | 3.0     |
| 2   | 29.3 | 11.7      | 28.0| 10.0        | 3.0 | 8.0 | 10.0        | /       |
| 3   | 22.1 | 8.9       | 28.0| 10.0        | 3.0 | 8.0 | 20.0        | /       |
| 4   | 28.8 | 19.2      | 28.0| 10.0        | 3.0 | 8.0 | 3.0         | /       |
| 5   | 24.0 | 24.0      | 28.0| 10.0        | 3.0 | 8.0 | 3.0         | /       |
| 6   | 27.1 | 10.9      | 28.0| 10.0        | 3.0 | 8.0 | 3.0         | 10.0    |
| 7   | 29.3 | 11.7      | 28.0| 10.0        | 10.0| 8.0 | 3.0         | /       |
| 8   | 23.6 | 9.4       | 43.0| 10.0        | 3.0 | 8.0 | 3.0         | /       |

Fig. 2. Schematic of experimental apparatus.

Fig. 3. Effect of magnetic intensity on separation behaviors.
The left ordinate indicates that the proportion of unmagnetized slag decreased gradually with the increasing of magnetic intensity. The right ordinate demonstrates that the Fe recovery ratio increased with the increasing of magnetic intensity. However, there is an obvious tendency for the P recovery ratio to decrease as the magnetic intensity increases.

Figure 4 shows the magnetic separation results of No.0 slag with the magnetic intensity of 2 800 Oe. It can be seen that the ratio of unmagnetized slag increased as the particle size decreased under a fixed magnetic intensity. From the right ordinate it also can be seen that the P recovery ratio increased and Fe recovery ratio decreased with the decreasing of particle size. There is a competition between the recovery of P and Fe element.

3.2. Difference between Dephosphorization Slag and Ordinary BOF Slag

It is well known that the ordinary BOF slag generally consists of two phases. One is P enriched 2CaO·SiO$_2$–3CaO·P$_2$O$_5$ solid solution, the other is CaO–SiO$_2$–FeO based phase.$^{18}$ Ono$^3$ suggested that when liquid BOF slag solidified slowly, most dicalcium silicate was crystallized primarily and accumulated in the top part of slags. CaO, SiO$_2$ and P$_2$O$_5$ were enriched in the top, while FeO, Fe$_2$O$_3$ and MnO in the bottom. However, this separation method by flotation requires the content of FeO + MnO to be higher than 30%. The initial cooling temperature must be higher than 1 853 K. Furthermore, slow cooling from 1 873 K to 1 723 K at an average cooling rate of less than 2 K/min is necessary. All of these limits restrict its industry application.

Figure 5(a) presents a representative SEM photomicrograph of ordinary BOF slag. For the reason of high temperature (>1 923 K) and good dynamic conditions in converter, large blocked 2CaO·SiO$_2$–3CaO·P$_2$O$_5$ phases and CaO–SiO$_2$–FeO phases were formed independently. However, the P enriched phase is not easy to aggregate and grow under the condition of low temperature (<1 673 K) and short period in dephosphorization process of duplex refining. It can be seen from the morphology of dephosphorization slag in Fig. 5(b) that the P enriched phase inlay in the Fe enriched phase. The average composition of P enriched phase was analyzed with Energy Dispersed X-Ray Spectrum (EDS) and given in Table 4. The results showed that the average content of P element in P enriched phase in No.0 dephosphorization slag is about 2.93%. The average size of P enriched phase is far less than 74 μm, which leading to difficulties in effective magnetic separation. As previous section mentioned, small particle size benefits the recovery of P. It can be interpreted as the inlay state between P enriched phase and Fe enriched phase was broken under smaller particle size condition.

3.3. Effect of Slag Modification on Separation Behaviors

In the subsequent experiments, we choose the magnetic intensity and particle size as 2 800 Oe and 48 μm, respectively. The concentrations of P$_2$O$_5$ and FeO in magnetized slag and unmagnetized slag after experiments are shown in Figs. 6–7. The dotted lines in Figs. 6 and 7 indicate the initial concentrations of P$_2$O$_5$ and FeO in the No. 1 reference slag. The P and FeO recovery ratio are shown in Fig. 8. Because of the lack of stirring in the present study, it is hard to separate P enriched phase from FeO enriched matrix. The P recovery ratio is less than 40%.

The addition of acidic oxide SiO$_2$, and amphoteric oxides Al$_2$O$_3$ and TiO$_2$ has a important effect on the P recovery ratio. It can be seen from Fig. 8 that the P recovery ratio increased noticeably with the addition of these oxides. However, the P recovery ratio was little affected by the addition of basic oxides FeO and MnO. This is because FeO and MnO present in the CaO–SiO$_2$–FeO matrix phase in the slag, which has little effect on the P enriched phases. It needs to be noted that the concentration of P$_2$O$_5$ in unmag-
netized slag is not always increase with increasing SiO2 and Al2O3 content. In fact, the P recovery ratio and the concentration of P2O5 in unmagnetized slag showed a reciprocal relationship in the present study. The reason for this phenomenon is that the proportion of unmagnetized slag increased with the increasing of SiO2 and Al2O3 content, and then resulted in a decrease in the concentration of P2O5 in unmagnetized slag. That’s also why the Fe recovery ratio is low and concentration of Fe2O3 in unmagnetized slag is high in No. 3 slag in Figs. 7–8.

From the results, we found that the addition of Al2O3 makes a significant effect on the separation behaviors. Al2O3 is an effective nucleating agent in the crystallization process of gehlenite. Seen from Eq. (1), with the addition of Al2O3 into the dephosphorization slag, Ca2SiO4 vanished gradually, Ca3P2O8 and Ca2Al2SiO7 coexisted in the slag. Most of the phosphorus has a high potential to be precipitated into the 2CaO·SiO2–3CaO·P2O5 solid solution. The separation results approved the positive effect of Al2O3 on slag modification behaviors. Similarly, TiO2 is a nucleating agent of CaTiSiO5. It also can capture the CaO and SiO2 in the 2CaO·SiO2–3CaO·P2O5 solid solution, which could heighten the concentration of P in the P enriched phases. Dong et al.12) found that the addition of SiO2 could greatly change the phase relationships in BOF slag. The high basicity of BOF slag favour the formation of dicalcium silicate and dicalcium ferrite. The addition of SiO2 would lower the basicity of the slag. Thus, both the dicalcium silicate and dicalcium ferrite would be thermodynamically unstable, leading to the formation of new P enriched phases and Fe2O3 enriched phases. In general, acidic and amphoteric oxides could change the slag phases in the dephosphorization slag, therefore, the P recovery ratio increased significantly after slag modification.

### 3.4. Effect of Stirring on Separation Behaviors

As discussed in the previous section, there is no stirring in the slag modification experiments. In order to further confirm the feasibility of recovery of phosphorus from dephosphorization slag produced by duplex high phosphorus hot metal refining and improve the separation efficiency, P2O5, SiO2 and Al2O3 were added into the No. 0 industrial dephosphorization slag. The experimental conditions are listed in Table 3.

Figure 9 shows the magnetic separation results. It can be seen that both the concentrations of P2O5 in unmagnetized slag and unmagnetized slag.

![Fig. 6. Concentrations of P2O5 in magnetized slag and unmagnetized slag.](image)

![Fig. 7. Concentrations of Fe2O3 in magnetized slag and unmagnetized slag.](image)

![Fig. 8. Effect of slag modification on separation behaviors.](image)

![Fig. 9. P recovery ratio and concentrations of P2O5 in magnetized slag and unmagnetized slag.](image)
gives to modification and separation behavior is obvious. The reason of this is attributed to the acceleration of mass transfer in the slag phases by make the slag keep moving. Further experiment and consideration may be needed to make clear this point.

4. Conclusions

In the present study, being focused on the recovery of phosphorus from dephosphorization slag produced by duplex high phosphorus hot metal refining, slag modification and magnetic separation were investigated by testing different slags under different conditions. The following conclusions can be drawn from the experiments,

(1) The proportion of unmagnetized slag decrease with increasing magnetic intensity and decreasing slag particle size. P recovery ratio decreases with increasing magnetic intensity and slag particle size. In contrast, Fe recovery ratio increases with increasing magnetic intensity and slag particle size.

(2) P enriched phase inlay in the Fe enriched phase in the dephosphorization slag produced by duplex steelmaking process. The grain size of P enriched phase is far less than that in the ordinary BOF slag. Such disadvantages lead to difficulties in effective magnetic separation.

(3) The addition of acidic oxide SiO₂ and amphoteric oxides Al₂O₃ and TiO₂ has a positive influence on the P recovery ratio. However, the P recovery ratio and the concentration of P₂O₅ in unmagnetized slag showed a reciprocal relationship with increasing SiO₂ and Al₂O₃ content. The P recovery ratio was little affected by the addition of basic oxides Fe₂O₃ and MnO.

(4) The P recovery ratio increased under the stirring condition. 74% and 87% P were recovered in the unmagnetized phases with adding 10% SiO₂ and Al₂O₃, respectively.

Acknowledgements

Financial supports from Chongqing Science and Technology Commission (CSTC, 2011BA4018) is greatly appreciated.

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