

# STUDY ON PHOSPHORUS MICROSCOPIC ENRICHMENT REGULARITY OF EARLIER AND FINAL SLAG IN DOUBLE –SLAG STEELMAKING

Received – Primljeno: 2015-11-04

Accepted – Prihvaćeno: 2016-01-15

Original Scientific Paper – Izvorni znanstveni rad

This work examined phosphorus enrichment in different micro areas of the earlier slag and the final slag in converter double-slag technology. The results show that: phosphorus has high enrichment in the micro-area the basicity of which is between 2 to 2,5; the phosphorus content is at a higher point in the micro area with a silicon (Si) content of 9% ~ 12% in the final slag or 13% ~ 14% in the earlier slag; phosphorus can reach the maximum value when the ferrum content is between 5% ~ 9%, higher phosphorus content appears in the micro zone with a low magnesium content.

*Key words:* steelmaking, convertor, double-slag operation, phosphorus enrichment, micro-area

## INTRODUCTION

For converter, dephosphorization is the one of steel-making's primary tasks [1,2]. In order to improve dephosphorization efficiency and reduce consumption, Nippon Steel Corporation developed the MURC double slag operation process in a converter [3-6]; this process was also extended and applied on a large scale in China [7]. In addition, due to cheap raw material consumption and the high dephosphorization efficiency of the limestone-slagging steelmaking process, the new process has been widely recognized. As such, some steel companies are also trying to combine the double-slag and limestone-slagging operation in order to achieve more economic and environmental benefits. The phosphorus distribution in the converter's earlier slag and the final slag sample was studied, finding phosphorus enrichment in different micro areas in the slag is not only related to slagging time, but also related to the existence of other elements in the slag. In this paper the distribution of phosphorus in the slag's micro area are discussed; we aim to provide a reference for improving converter slagging dephosphorization.

## EXPERIMENTAL WORK

The slag sample was taken from a 100 t converter that undergoes the double slag process, qualifying the end-point temperature and content. Sampling times were set at slag discharge after early dephosphorization and end-point temperature sampling. Four sampling furnaces were used in this study; one lime-slagging furnace, and three limestone-slagging. According to the

definition of steel tempering, when it reaches carbon burning temperature, the sample obtained from dephosphorization can be defined as an early slag sample, and the sample obtained from the end-point temperature can be defined as the end-point slag sample. There are total eight samples.

To undergo chemical analysis, a part of slag samples must be crushed to remove the iron, using an X ray fluorescence analysis (XRF). Through this analysis, lime-slagging or limestone-slagging doesn't influence a great deal of the sample content. What matters is whether the sample is early slag or end-point slag. As a result, this paper focuses on the difference between early slag and end-point slag.

To research the microscopic distribution of the elements, the remaining slag samples were inset without crushing; the samples were then investigated using an S-3400N scanning microscope after polishing to obtain back scattering electron images. Next, X-Max20 were used to get the content of O, Mg, Ca, Fe, Si, and P on the micro zones of different hues. For 8 samples, 130 non-ferrous zones were found, and the content data of O, Mg, Ca, Fe, Si, and P were obtained in 130 non-ferrous zones.

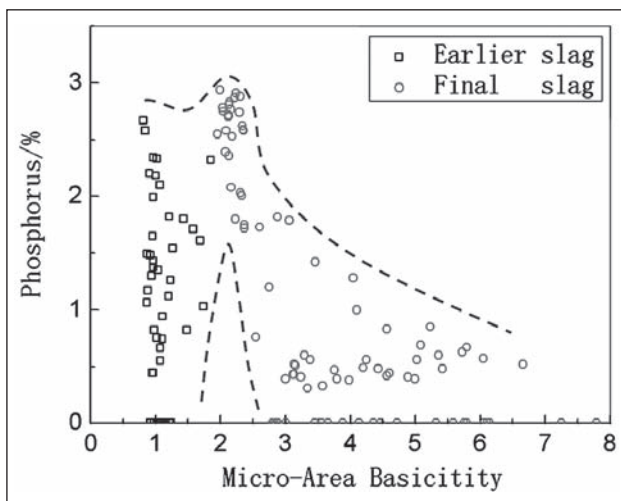
Regarding the many micro zones of early and end-point slag of experiment furnaces, this paper focuses on the influence of Fe, Ca, Si, Mg and the basicity on P contents.

## RESULTS AND DISCUSSION

### Effect of micro-area basicity on Phosphorus (P) occurrence content in micro area

Micro-area basicity refers to the quality percentage ratio of CaO and SiO<sub>2</sub> in the micro zone of slag; The micro-area basicity is not the same concept as an aver-

C. X. Li, H. Li, H. Lu, W. W. Mao: State key laboratory of advanced Metallurgy, University of Science and Technology Beijing, China



**Figure 1** Relationship between micro-area basicity with P content in micro area of earlier slag and final slag

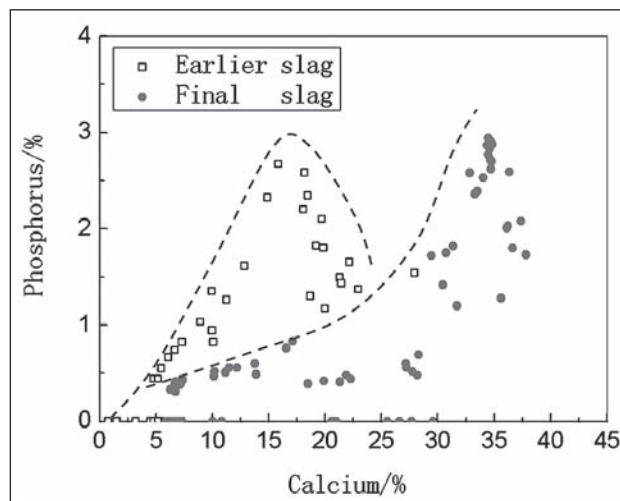
age basicity  $R$ ; The micro-area basicity are different in the slag. Figure 1 shows the influence of micro-area basicity on the P content in the micro area of slag. Figure 1 shows the micro-area basicity of earlier slag in the experiment is smaller. The micro-area basicity values are between 0,8 ~ 2, focusing around 1. The P content falls between 0 ~ 2,8; the micro-area basicity value of the final slag has a large distribution range, between 2 ~ 8. With the increase of micro-area basicity, the P content in the micro area shows a decreasing trend. Many micro zones with an micro-area basicity above 2,7 have no P. Whether in the earlier slag's micro zone or in that of the final slag, the degree of P accumulation in the same micro-area basicity value shows a wide difference, revealing significant influence on other factors.

The two curves in Figure 1 outline the P content change with the Micro-area basicity range in the earlier slag and final slag's micro area. The average basicity and the sample temperature of the earlier and final slag are different, but as a whole, when the Micro-area basicity ranges between 1,4 to 2,6, the P content in the micro area is not 0. The peak of the under curve and the above curve have roughly the same Micro-area basicity value, which means there is a small Micro-area basicity range between two vertices. Although there are influential factors, such as temperature and oxidizing, the Micro-area basicity value has the most significant effect on P concentration. The figure reveals the Micro-area basicity value of the two vertices to be roughly between 2 ~ 2,5.

### Effect of Calcium (Ca) content on P occurrence content in micro area

Figure 2 shows the influence of calcium (Ca) content on P content in micro area of slag.

Figure 2 shows that in the earlier slag's micro area, the Ca content is between 0 ~ 28 %. As the Ca content increases, the P content shows an obvious trend, reducing after first rising, with a vertex between Ca = 16 ~ 20



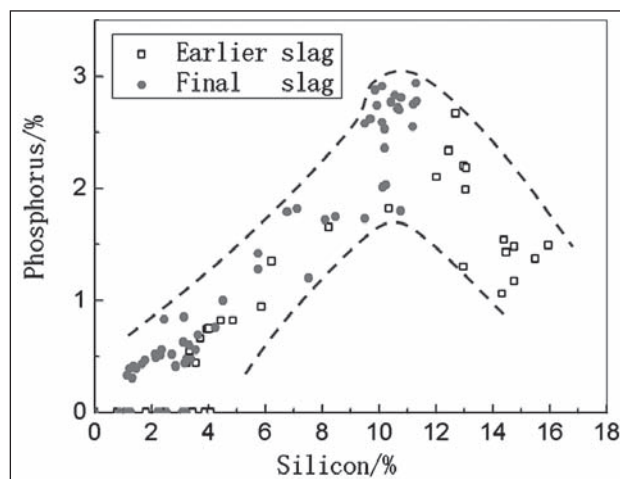
**Figure 2** Relationship between Ca content with P content in the micro area of earlier and final slag

%. In the micro area of the final slag, the Ca content ranges from 5 % to 38 %. With increases in the Ca content, the P content also increases gradually, The P content in the micro area has the highest value when the Ca content is between 33 % and 37 %. The different variation trends between the P content and the Ca content in earlier slag and final slag are caused by the influence of temperature during sampling.

### Effect of Silicon content on P occurrence content in micro area

Previous research has shown that the P element solubilizes in the calcium silicate phase, the atomic mass and atomic radius of the P element and Si element are close [8,9], and the crystal structures of the two acid radical ions are same. Consequently, the Si element has a greater influence on the occurrence of P. Figure 3 shows the influence of Si content on P content in the slag's micro area.

Figure 3 shows that in the micro area of earlier slag, the Si content is between 0 ~ 16 %, and with an increase



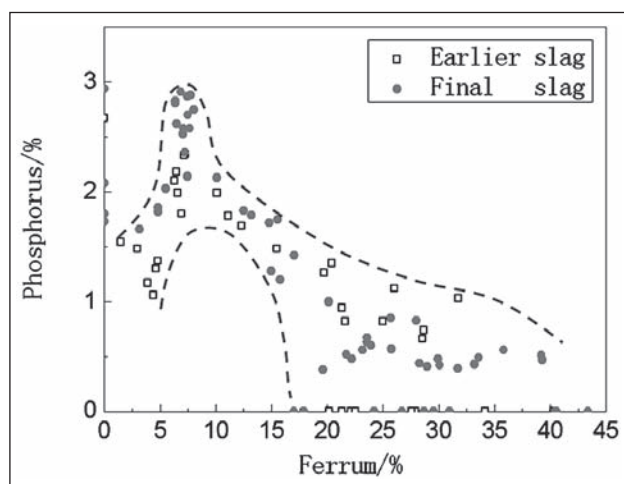
**Figure 3** Relationship between Si content with P content in micro area of earlier and final slag

in the Si content, the P content is lower after the first rising trend. When the Si content is between 13 to 14 %, the P content in the micro area at its largest. However, in the micro area of final slag, the Si content is between 0 ~ 12 %, with an increase in the Si element content, and the P content showed a gradually increasing trend. The P existence content in the micro area was at its highest position when the Si content was between 9 % and 12 %. It can be seen that the effect of the Si content on the P content micro area is concentrated, and this also proves whether the P concentration depends on the content of Si. In the final slag under high temperature conditions, the P content in the micro area was at its largest when Si = 9 ~ 12 %. In the earlier slag under low temperature conditions, the P content in the micro area was at its largest when Si = 13 ~ 14 %.

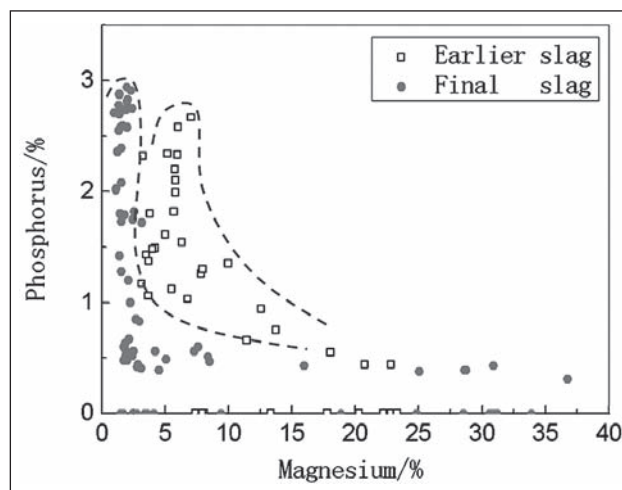
### Effect of Ferrum (Fe) content on P occurrence content in micro area

The Fe element content can reflect the slag's oxidation degree. According to the micro-area basicity-dynamic theory, the existence of  $P_2O_5$  depends on the existence of iron oxides. However, in this experiment, the relationship between Fe content and P content in the micro area of slag is thought-provoking. Figure 4 shows the influence of Fe content on P content in the micro area of

Figure 4 shows that the P content shows a "pour the V" trend with the increase in Fe content in the micro area of the converter's earlier slag and final slag; the change curve of the earlier slag and final slag is consistent, which has nothing to do with the sampling temperature. When the Fe content is less than 9 %, an increase in Fe content means the P content shows a steep rising trend. When the Fe content is greater than 9 %, the P content appears to have a downward trend with an increase in Fe content. Some micro areas with a Fe content greater than 16 % may have no P.



**Figure 4** Relationship between Fe content with P content in micro area of earlier slag and final slag



**Figure 5** Relationship between Mg content with P content in the micro area of earlier and final slag

Compared with the Si element, the peak of the Fe element in the micro area is narrower. This means that the influence of the Fe content on the P content is clearer; the P content of the micro area can reach its maximum when the Fe content ranges from 5 % to 9 %. In general, an increase in Fe content in slag can be regarded as an increase in oxygen content. As such, when the Fe content is less than 9 %, the oxygen content in the slag is low. In addition, Fe exists as FeO, which is an alkaline oxide and may reduce the activity coefficient of  $P_2O_5$ , promoting the micro-area basicity of  $3CaO \cdot PO_4$ . When the Fe content is greater than 9 %, the slag's micro area has a high oxygen content; Fe exists largely as  $Fe_2O_3$  and when the content of FeO decreases, the activity coefficient of  $P_2O_5$  increases. A high Fe content in the micro area blocks the micro-area basicity of  $3CaO \cdot PO_4$ , and a high FeO content will dilute the CaO and  $SiO_2$  content of the slag, potentially challenging the stability of the P element solution. The results are also consistent with the study of K. Ito.

### Effect of Magnesium (Mg) content on the P occurrence content in the micro area

Figure 5 shows the influence of Mg content on the P content in the slag's micro area.

Overall, earlier slag and final slag's change trend are the same; the P content in the micro zone decreased with an increase in Mg content. From the perspective of chemical properties, the Mg element exists in the micro-area basicity of MgO, which is a strong alkaline substance in slag, and can combine with  $P_2O_5$ . Consequently, the curve changes in Figure 5 are contrary to the curve in Figure 2; this embodies an alternative phenomenon between the Ca and Mg element. Figure 5 shows that the maximum value of P content appears in the low Mg area, and the P content may be high when Mg = 2 % ~ 3 % in the final slag or Mg = 6 % ~ 7 % in

earlier slag. As such, high Mg content is not conducive to P concentration.

## CONCLUSIONS

The paper researched the influence of micro-area basicity on the P occurrence content in the micro area of slag. P has high enrichment in the micro-area with micro-area basicity ranging between 2 and 2.5. The P content is higher in the slag micro area with a Ca content between 16 % and 20 %, or between 33 % and 33 % in earlier slag and final slag, respectively.

P enrichment in the micro area is closely related to the Si content; the P content is at a higher point in the micro area with a Si content between 9 % ~ 12 % in the final slag or Si = 13 % ~ 14 % in earlier slag.

The Fe content in the micro area clearly impacts P enrichment; P can get the maximum value when Fe content is between 5 % ~ 9 %. The higher P content appears in the micro zone with lower Mg content.

## Acknowledgements

Presented research was supported by Ministry of Science and Technology of the People's Republic of China, project 2012BAC27B02.

## REFERENCES

- [1] P. Fila, L. Martínek, Evaluation of super clean steels according to chemical composition, *Metalurgija* 44 (2005)3, 183-188.
- [2] M. Gojić, Current State and Development of Steelmaking Processes, *Metalurgija* 43 (2004)3, 163-168.
- [3] Y. Ogawa, M. Yano, Development of the continuous dephosphorization and decarburization earlier using BOF, *Testu-to-Hagane* 87 (2001), 21-28.
- [4] M. Iwasaki and M. Matsuo, Change and development of steel-making technology, *nippon steel technical report* 391 (2011), 88-93.
- [5] E. T. Turkdogan, Assessment of  $P_2O_5$  activity coefficients in molten slags, *ISIJ International* 40 (2000) 10, 964-970.
- [6] Kitamura S, Aoki H, Okohira K. Dephosphorization reaction of chromium containing molten iron by CaO-based flux, *ISIJ international* 34 (1994) 5, 401-407.
- [7] Qin D. P., Yang J. P., Analysis and earlier practice on steelmaking technology of 100t top-blown oxygen converter by limestone for slag making, *China Metallurgy* 24 (2014) 05, 34-40.
- [8] Yang Xiao, Matsuura, Reaction behavior of  $P_2O_5$  at the interface between solid  $2CaO$  center dot  $SiO_2$  and liquid  $CaO-SiO_2-FeO_x-P_2O_5$  slags saturated with solid  $5CaO$  center dot  $SiO_2$  center dot  $P_2O_5$  at 1573 K, *ISIJ International* 50 (2010) 05, 702-711.
- [9] J. Kijac, P. Kovac, The current status of tundish covering slags in a slab caster plant, *Metalurgija* 43 (2004)1, 59-62.

**Note:** The responsible translator for English language is Ph. D. Richard Wagner, Wilmington, Boston