

# OPTIMIZATION OF SLAG COMPOSITION IN HOT METAL DEPHOSPHORIZATION

**Shin-ya Kitamura**

Tohoku University, Japan

## ABSTRACT

*The steelmaking process in Japan has achieved a unique development owing to the use of hot metal dephosphorization.*

*This process has some advantages, i.e., decrease in the unit consumption of lime and increase in the iron and manganese yields, increase in the productivity, and easy production of high purity steel with a low phosphorus content. In addition, hot metal dephosphorization, combined with "less slag decarburization" and the recycling of the decarburization slag to the dephosphorization, can cause the drastic decrease in the disposal amount of slag.*

*Initially, dephosphorization was carried out by a flux injection process in a transportation vessel (i.e., torpedo car) after desiliconization treatment. In this process, the slag with low oxygen activity and high basicity is formed. On the other hand, the processes using the converter as the reaction vessel became common. In this process, the slag with high oxygen activity and low basicity is formed.*

*Recently, to improve the reaction efficiency, the importance of dicalcium silicate solid phase in slag becomes to be paid attention. Since tricalcium phosphate can dissolve in dicalcium silicate and form a solid solution, the phosphorus content in the liquid slag can be decreased by the precipitation of this solid solution.*

*In this paper, history and the present research activities on the hot metal dephosphorization in Japan will be discussed.*

## INTRODUCTION

The steelmaking process in Japan has achieved a unique development owing to the use of hot metal dephosphorization. Initially, dephosphorization was carried out by a flux injection process in a transportation vessel (i. e., torpedo car) after desiliconization treatment. The top slag was highly basic and had low oxygen activity. In this process, fluorspar was required to melt the top slag; however, owing to environmental problems, the use of fluorspar became to be difficult. In order to form the fluid slag at the hot metal temperature, the basicity of the slag composition was decreased and the oxygen activity was increased. A decrease in the scrap melting capacity in the steelmaking process is another disadvantage of using hot metal dephosphorization by injection process. To solve this problem, dephosphorization was carried out in a top and bottom blowing converter for the hot metal without the desiliconization treatment.

Decrease the disposal amount of slag in the steelmaking process is an important issue. The hot metal dephosphorization, combined with the *less slag decarburization* and the recycling of the decarburization slag to the dephosphorization, can cause the drastic decrease in the disposal amount of slag.

Recently, to improve the reaction efficiency, the importance of dicalcium silicate solid phase in slag becomes to be paid attention. Since tricalcium phosphate can dissolve in dicalcium silicate and form a solid solution, the phosphorus content in the liquid slag can be decreased by the precipitation of this solid solution.

In this paper, history and the present research activities on the hot metal dephosphorization in Japan will be discussed.

## PRINCIPLE OF HOT METAL DEPHOSPHORIZATION

The reason for carrying out dephosphorization under the hot metal conditions is attributed to the strong temperature dependence of the reaction.



Figure 1 shows the equilibrium relationship between the phosphorus content and the oxygen activity. The activity of  $\text{P}_2\text{O}_5$  in the slag is calculated using a regular solution model [1] and the temperatures at the end of decarburization in a basic oxygen furnace (BOF; LD) and hot metal (HM) pretreatment are assumed at 1923 K and 1623 K, respectively. It is clear that at the hot metal temperature, the oxygen activity or basicity can be decreased in order to obtain phosphorus content similar to that obtained at the end of decarburization. In other words, for carrying out the dephosphorization at the hot metal temperature, only one of the following two conditions is necessary:

- Low oxygen activity with high basicity
- High oxygen activity with low basicity.

Figure 2 shows the slag composition for each case of the hot metal dephosphorization in phase diagram for  $\text{CaO-SiO}_2\text{-Fe}_2\text{O}_3$ .

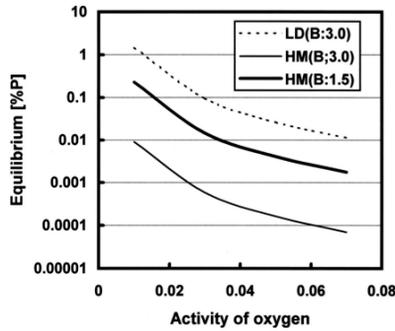


Figure 1: Relationship between the oxygen activity and the equilibrium phosphorous content

By the use of hot metal dephosphorization, the phosphorus removal need not be carried out during the decarburization process in the BOF, and the amount of slag can be minimized. This type of BOF operation is termed *less slag decarburization*. A combination of less slag decarburization with the hot metal dephosphorization process offers the following general advantages:

- Decreases the unit consumption of lime and slag generation in overall refining process
- Increases the iron and manganese yield in BOF
- Increases the productivity of steel refining process
- Enables easy production of high purity steel with a low phosphorus content.

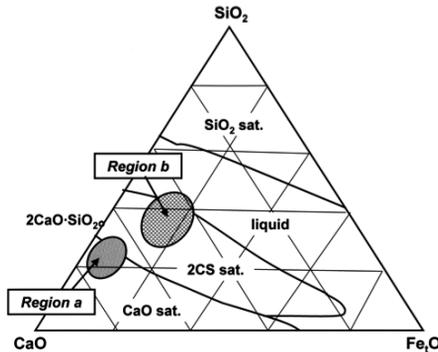


Figure 2: Top slag compositions in hot metal dephosphorization treatment

## HISTORY OF HOT METAL DEPHOSPHORIZATION PROCESS

Figure 3 shows the history of the development of the hot metal dephosphorization process [2]. The hot metal dephosphorization for the all hot metal tapped from blast furnace (BF) before decarburization was started in 1982 at Kimitsu works, Nippon Steel [3], for the first time in the world. In the 1980s, the transportation vessel that transfers the hot metal from the BF to the BOF (i. e., torpedo car or hot metal ladle) was used as a reaction vessel. In the very early stage, the processes using soda ash as the flux were developed; however, their use has been discontinued because of the high cost factor, severe refractory damage, and large temperature drop during the treatment. From the mid-1990s, the processes using the converter as the reaction vessel became common, although these processes were in use since early 1980s.

Now, hot metal dephosphorization using the top and bottom blowing converter is carried out in most steelmaking shops. In general, for the dephosphorization process using a transportation vessel, the slag with low oxygen activity and high basicity is formed. On the other hand, for the dephosphorization process using the converter, slag with high oxygen activity and low basicity is formed.

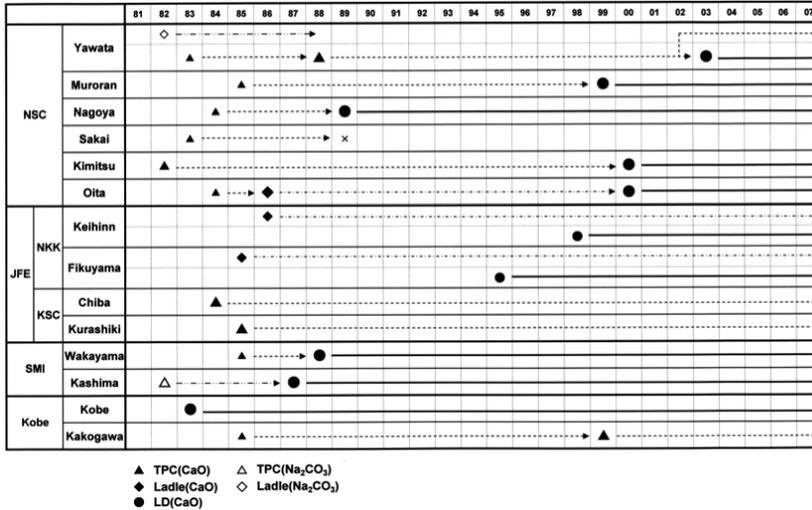


Figure 3: History of hot metal dephosphorization process in Japan

## DEPHOSPHORIZATION BY THE SLAG OF LOW OXYGEN ACTIVITY AND HIGH BASICITY

This process is developed using the flux injection process, and its characteristics are summarized in Figure 4. The flux particle with high  $P_2O_5$  content was sampled in the steel bath [4] and the reaction occurring during the floatation of the injected flux was named *transitory reaction*, and the reaction by the top slag was termed *permanent reaction* (Figure 5). The ratio of both the reactions was investigated [5], and the importance of the transitory reaction was stressed. In this process, since the transportation vessel is used, the space available for containing the slag is not sufficient. As a result, the slag volume is limited and foaming is not allowed. Owing to this limitation, hot metal desiliconization before the dephosphorization process and the slag of high basicity without foaming are imperative. The top slag composition is shown in Figure 2 (region a). As the high basicity and low  $Fe_2O_3$  content, the solid fraction of the slag is high. Hence, it is necessary to add fluorspar to the slag in order to increase the liquid fraction. This process has the following advantages:

- Increases yield of iron and manganese during the hot metal dephosphorization treatment
- Simultaneous desulphurization and dephosphorization.

On the other hand, the disadvantage of this process is that it decreases the scrap melting capacity of the decarburization process; this is because the latent heat of the oxidation reaction of silicon cannot be used and the charging temperature in the BOF is considerably decreased.

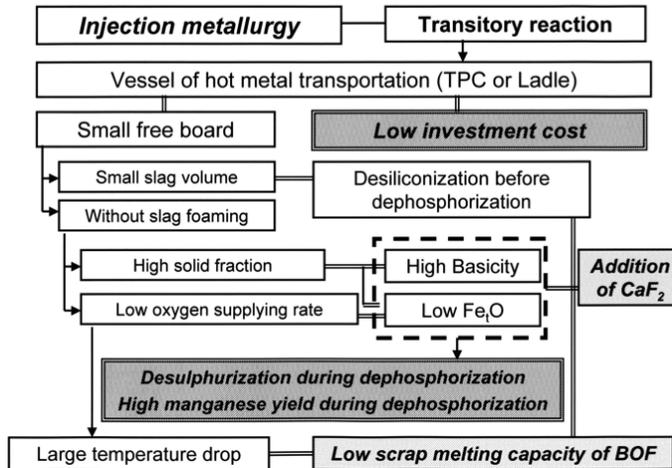


Figure 4: Characteristics of the hot metal dephosphorization treatment with low oxygen activity and high basicity condition

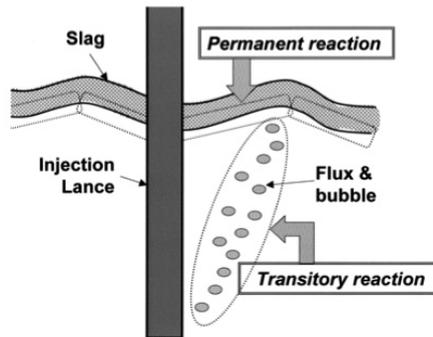


Figure 5: Concept of the transitory and the permanent reactions

## DEPHOSPHORIZATION BY THE SLAG OF HIGH OXYGEN ACTIVITY AND LOW BASICITY

Since 2001, leaching of fluorine to water is regulated by the environmental law in Japan. The abovementioned process becomes difficult to operate as fluorspar is imperative for the formation of a liquid phase in the top slag. Figure 6 shows the influence of the additive agents on the melting points of CaO and  $2\text{CaO}\cdot\text{SiO}_2$ , which are summarized by the data based on phase diagrams (ACerS-NIST Phase Equilibria diagrams, Version 3.1). In order to lower the melting points of CaO and  $2\text{CaO}\cdot\text{SiO}_2$ , increasing FeO content is considered to be an effective alternative to the addition of fluorspar.

From Figure 1, it can be found that an increase in the Fe<sub>2</sub>O<sub>3</sub> content does not need to increase the slag basicity for dephosphorization. Therefore the hot metal dephosphorization can be carried out by the high oxygen activity and low basicity slag. As the slag is very foamy under this composition, the top and bottom blowing converter is used as the reactor; this is because it is sufficiently spacious for containing the foamy slag.

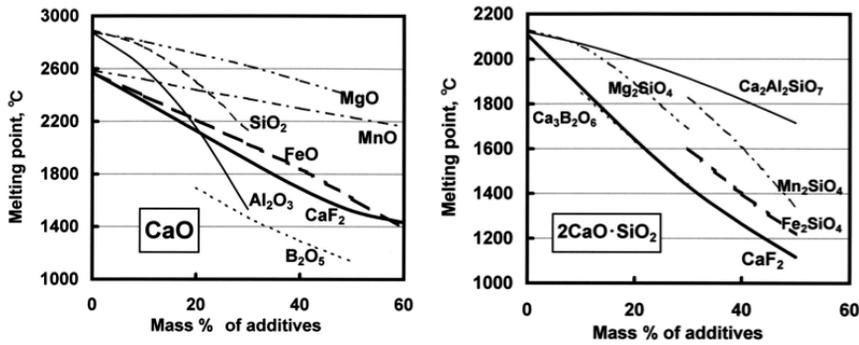


Figure 6: Influence of additive agents on the melting points of CaO and 2CaO·SiO<sub>2</sub>

The basic concept of the hot metal dephosphorization using converter is the same as a *double-slag process*. In comparison to the conventional double-slag process, the treatment is carried out at lower temperature and higher carbon content. Figure 7 shows the characteristics of this process. In this process, only the *permanent reaction* is used. Since the slag basicity is not very high, the slag composition is in the 2CaO·SiO<sub>2</sub> saturated region. Further, as the Fe<sub>t</sub>O content is high, the solid fraction of slag is less and the addition of fluorspar is not imperative (region b in Figure 2). To control the Fe<sub>t</sub>O content, the optimizations of the oxygen top blowing rate and the bottom stirring intensity are necessary. This process has the following advantages:

- Desiliconization is not necessary before the dephosphorization process
- Short treatment time and high productivity
- The scrap melting capacity does not decrease because the latent heat oxidation reaction of silicon can be used, and the scrap can be charged in the dephosphorization process
- Recycling of decarburization slag to the dephosphorization process is very easy.

On the other hand, the disadvantage of this process is that the desulphurization does not occur, and manganese yield is low in the dephosphorization process. In addition, the construction cost to build a new converter for the dephosphorization process is high. Therefore, the processes using a stand-by converter or continuous dephosphorization and decarburization processes using intermediate deslagging (MURC; multi-refining converter [6]) are operating.

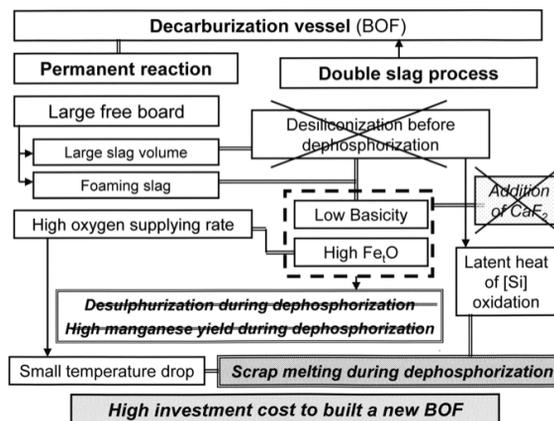


Figure 7: Characteristics of the hot metal dephosphorization treatment with high oxygen activity and low basicity condition

## RECENT RESEARCH ACTIVITIES

To date, many researches on the hot metal dephosphorization have been carried out in Japan. Recently, to improve the reaction efficiency, the importance of dicalcium silicate solid phase in slag becomes to be paid attention.

From the phase diagram of the  $\text{CaO-SiO}_2\text{-P}_2\text{O}_5$  system, it is well known that dicalcium silicate and tricalcium phosphate form a solid solution at the hot metal dephosphorization temperature in a wide composition range. This phase diagram implies that the main products of the dephosphorization reaction can be dissolved into the main solid phase in the slag. The partition ratio of phosphorus between dicalcium silicate and the liquid slag was high and depending on the liquid slag composition it varied from 7 to 70 [7]. On the basis of this result, it can be stated that phosphorus is more stable in the solid solution of dicalcium silicate and tricalcium phosphate than in the liquid slag phase.

The effect of dicalcium silicate on the reaction efficiency of hot metal dephosphorization has been studied [8], and a drastic increase in the efficiency has been reported when the slag composition is in the dicalcium silicate saturated region. The result indicates that the effect of dicalcium silicate on the dephosphorization reaction would be influenced by the method in which the slag composition is changed during the treatment.

In order to utilize dicalcium silicate, the rate of phosphorus enrichment from the liquid slag to the dicalcium silicate phase, which is influenced by the various modes of slag composition change, should be clarified. In order to satisfy this requirement, The Iron and Steel Institute of Japan (ISIJ) has launched a research project named *Development of a new refining technology using multiphase flux* in 2005. From 2005 to 2007, several fundamental researches about the influence of solid phases in the slag on various properties (i. e., reaction kinetics, viscosity, thermal conductivity etc) have been conducted. Base on these results, from 2008, this project has started to make a new kinetic simulation model of the dephosphorization process considering the effect of solid phase in the slag [9].

## CONCLUSIONS

Hot metal dephosphorization process is one of the Japanese original technologies and already had a history of more than 25 years. This process has some advantages, i. e., decrease in the unit consumption of lime and increase in the iron and manganese yields in BOF, increase in the productivity of steel refining process, and easy production of high purity steel with a low phosphorus content. In addition, hot metal dephosphorization, combined with *less slag decarburization* and the recycling of the decarburization slag to the dephosphorization, can cause the drastic decrease in the disposal amount of slag.

Initially, dephosphorization was carried out using flux injection process in a hot metal transportation vessel, for example, in a torpedo car, after the desilicization treatment. Top slag was highly basic and had low oxygen activity. After the use of fluorspar was restricted owing to the environmental law, the slag composition has changed to the conditions in the low basic and the high oxygen activity. In order to perform the treatment using this slag composition, dephosphorization has to be carried out in the top and bottom blowing converter for the hot metal without the desilicization treatment. The hot metal dephosphorization using converter can overcome the main disadvantage of the injection process; in other words, it increases the scrap melting capacity in the steelmaking process.

Researches on this process are still in progress and dicalcium silicate solid phase in the slag becomes to be paid attention. Since tricalcium phosphate can dissolve in dicalcium silicate and form a solid solution, the phosphorus content in the liquid slag can be decreased by the precipitation of this phase. ISIJ had launched a research project named *Development of a new refining technology using multiphase flux* in 2005.

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