

Improvement of Reaction Efficiency in Hot Metal Dephosphorization

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Abstract

In Japan, hot metal pretreatment process has been developed to refine hot metal under condition where each impurity can be removed most efficiently. At Nippon Steel, three types of hot metal pretreatment processes, using the torpedo car, hot metal ladle and LD converter are employed, making a great contribution to the reduction in slag volume. Recently, Nippon Steel has developed a new hot metal pretreatment process named MURC, in which dephosphorization and decarburization are continuously carried out in the same converter.

Nevertheless, as the dephosphorization efficiency of CaO is lower than 30%, CaO is now being used in far large quantities than the quantity stoichiometrically required to make $3\text{CaO}\cdot\text{P}_2\text{O}_5$.

As hot metal dephosphorization is a non-equilibrium reaction in which hot metal is in contact with slag whose oxygen activity differs greatly from that of hot metal, it is important to increase the interfacial oxygen activity.

According to the results of fundamental experiment, $2\text{CaO}\cdot\text{SiO}_2$ solid phase, in which P_2O_5 can be solved, makes a great effect on the dephosphorization reaction.

1. Introduction

The purpose of refining process is to decrease the concentration of impurities under minimum cost and minimum slag volume. In Japan, hot metal pretreatment process has been developed to refine hot metal under condition where each impurity can be removed most efficiently ¹⁾. Owing to this process, the slag volume has been gradually decreased. In recent years, as the increasing needs for environmental protection, further reduction in slag volume has becoming necessary. This paper describes the present condition of hot metal pretreatment at Nippon Steel Corporation and the result of recent research on the improvement of reaction efficiency in hot metal dephosphorization process.

2. Hot metal pretreatment process at Nippon Steel ²⁾

The thermodynamic conditions, which are suitable for the removal of impurities, are shown in Table 1. Basically, the hot metal pretreatment consists of the processes shown in Fig. 1 based on the following principles:

1) Desiliconization, dephosphorization and decarburization which are oxidation refining processes are separated from desulfurization which is a reduction refining process.

2) Decarburization is separated from dephosphorization so that low temperature condition is suitable for dephosphorization.

3) Preliminary desiliconization is carried out so that dephosphorization with basic slag can be performed under a small slag volume.

The hot metal pretreatment processes at Nippon Steel are shown in Fig. 2. Nippon Steel employs three types of processes which are based on the principles described above and utilizes existing equipment as the reaction vessel ²⁾: torpedo car (Kimitsu and Yawata Works), hot metal ladle (Oita Works) and LD converter (Nagoya Works). Furthermore, recycling the decarburization slag to dephosphorization (Kimitsu and Yawata) and the dephosphorization slag to desiliconization (Kimitsu) decreases the slag volume.

To characterize the operating condition of each process, the relation between slag basicity and (T·Fe) after treatment is shown in Fig. 3, and the relation between unit consumption of oxygen and that of lime is shown in Fig. 4. It will be seen from these figures that each process has the following features:

1) Treatment using torpedo car or hot metal ladle

As the torpedo car or hot metal ladle is a vessel for transporting hot metal, the freeboard is small and the exhaust gas treatment equipment is simple. Therefore, the basicity of slag is high and preliminary desiliconized hot metal is used to suppress slag foaming. Also, the oxygen consumption is low and iron oxide is used as oxygen source mainly to suppress decarburization. The flux injection system is adopted to ensure reactivity and desulfurization can be occurred during the dephosphorization as (T·Fe) is low.

2) Treatment using LD converter

In this treatment, the freeboard is large and the capacity of exhaust gas treatment equipment is large enough. Accordingly, the dephosphorization with low basicity and high (T·Fe) slag can be carried out and the preliminary desiliconization is not required. Also, the oxygen consumption is high and oxygen gas can be used as oxygen source mainly. As coolant, scrap can be used instead of iron oxide. However, desulfurization during the dephosphorization cannot be occurred.

Figure 5 shows a comparison of the slag volumes in the respective processes, which were calculated by making corrections for the same hot metal composition before treatment. It will be noted that the slag volume can be reduced by more than 25% in all processes compared

with the case where hot metal pretreatment is not conducted.

3. Development of a new hot metal pretreatment process

For further reduction in slag volume, recycling of decarburization slag is necessary. For this purpose, LD converter is advantageous, as the pulverization of decarburization slag is not required compare with the flux injection process. For this process, however, two converters must be used, one for dephosphorization and the other for decarburization. To overcome this drawback, Nippon Steel has developed the multi-refining converter (MURC) process in which dephosphorization and decarburization can be performed continuously in the same converter. This process is schematically shown in Fig. 6. The process has the following three features:

- 1) Continuous dephosphorization and decarburization treatment in one vessel.
- 2) Dephosphorization with low basicity and high (T·Fe) slag using hot metal without desiliconization treatment.
- 3) Intermediate slag removal after dephosphorization.
- 4) Recycling of the whole quantity of decarburization slag in high temperature condition.

Figure 7 shows an example of treatment. The operations from hot metal charging for dephosphorization to tapping after decarburization can be completed within 35 min. Figure 8 shows the relation between phosphorous distribution ratio and slag basicity after dephosphorization period. There is no difference between the case where the decarburization slag is recycled and the case where the decarburization slag is not recycled. The advantages of this process are as follows:

- a) As the existing one converter can be used to carry out MURC process, the investment cost is very small.
- b) As the decarburization slag is recycled, the total slag volume of MURC is decreased by 50% compared with the conventional process without adopting the hot metal pretreatment, and by about 30% compared with the existing hot metal pretreatment process.
- c) As scrap can be charged before the dephosphorization period, the minimum hot metal ratio of MURC is nearly the same as that in the conventional process without adopting the hot metal pretreatment, and about 10% higher than the existing flux injection type hot metal pretreatment process.
- d) As the high-basicity slag is discharged from the conventional LD converter and the flux injection type hot metal pretreatment, valuable utilization of slag was prevented by the characteristics of expansion or powdering. On the contrary, as the low-basicity dephosphorization slag is only discharged from MURC process, the valuable utilization of steelmaking slag can be conducted.

4. Improvement of CaO efficiency for dephosphorization

For further reduction in slag volume, it is necessary to increase the ratio of contribution of the lime to dephosphorization. Assuming the dephosphorization reaction as expressed by Eq. (1), the ratio of contribution of added lime (W_{CaO} ; kg/t) to dephosphorization is evaluated in terms of the CaO efficiency for dephosphorization (η_{CaO} ; %) which is defined by Eq. (2).



$$\eta_{CaO} = (27.1 \times [\%P]) \times 100 / W_{CaO} \quad \cdots (2)$$

As an index, expressing the operating condition which is shown in Fig. 4, the ratio of unit

CaO consumption to total oxygen consumption (the sum of oxygen gas and oxygen in iron oxide) which were converted into the weight (O; kg/t), i.e., CaO/O is used.

The results of calculation are shown in Fig. 9. It will be noted that the CaO efficiency can be improved by decreasing CaO/O. As the efficiency is lower than 30%, however, CaO is now being used in far large quantities than the quantity stoichiometrically required to make $3\text{CaO}\cdot\text{P}_2\text{O}_5$.

The difficulties in hot metal dephosphorization lie in the following two points:

First, the hot metal dephosphorization is a non-equilibrium reaction, in which hot metal is in contact with slag whose oxygen activity differs greatly from that of hot metal. In other words, the oxygen activity in equilibrium with (FeO) in the slag is about $10^{-2}\%$, while that in equilibrium with the hot metal which contains more than 4% of carbon is about $10^{-4}\%$, the difference being more than two digits. Figure 10 shows the relation between the equilibrium phosphorous distribution ratio and oxygen activity. As this figure shows, the dephosphorization capacity greatly varies with slight changes in oxygen activity. For the promotion of dephosphorization under a small slag volume, it is very important to increase the interfacial oxygen activity to approach the equilibrium value with the slag.

Second, the slag is multiphase, solid and liquid coexisting slag. According to the results of investigation about the structure of dephosphorization slag, four phases are generally observed: calcium-silicate phase, calcium-phosphate phase, wustite phase and other composite phase³⁾. For slag such complex structure, it is very important to elucidate the elementary step of phosphorous transfer between the hot metal, the liquid phase in slag and the solid phase in slag.

Accordingly, a fundamental experiment was conducted to clarify the mechanism of hot metal dephosphorization under multiphase, solid and liquid coexisting slag. About 1kg of hot metal was melted in a MgO crucible using a resistance furnace at about 1625K. The initial content of [P] was about 0.1% and the initial content of [Si] was changed from 0 to 0.2%. Dephosphorization was carried out by adding the premelted calcium-ferrite flux powder. After the test, the phases in the slag were identified by EPMA.

Table 2 shows the relation between the range of desiliconization during the test and the CaO efficiency for dephosphorization, which is defined by Eq. (2). When [Si] content of hot metal is high, it is generally considered that the CaO efficiency for dephosphorization decreases, because oxygen is consumed for desiliconization and the slag basicity decreases. However, it will be seen from Table 2 that the CaO efficiency in Case 2, in which [Si] content is high, is nearly the same as that in Case 1, in which [Si] content is zero.

Table 2 also shows the observed solid phase in slag, in which phosphorous is contained, after the experiments. In Case 1, $3\text{CaO}\cdot\text{P}_2\text{O}_5$ was observed, while in Case 2, P_2O_5 was observed in $2\text{CaO}\cdot\text{SiO}_2$ phase. It is well known that $2\text{CaO}\cdot\text{SiO}_2$ and $3\text{CaO}\cdot\text{P}_2\text{O}_5$ have a complete solid solution phase⁴⁾. This suggests that $2\text{CaO}\cdot\text{SiO}_2$ solid phase, in which P_2O_5 can be solved, makes a great contribution to the dephosphorization efficiency.

5. Conclusions

1) At Nippon Steel, three types of hot metal pretreatment processes, using the torpedo car, hot metal ladle and LD converter are employed, making a great contribution to the reduction in slag volume.

2) The treatment using torpedo car and hot metal ladle has low (T·Fe) and high basicity slag, while the treatment using converter has high (T·Fe) and low basicity slag. The CaO efficiency for dephosphorization is improved by decreasing CaO/O.

3) Nippon Steel has developed a MURC process in which dephosphorization and

decarburization are continuously carried out in the same converter.

4) As hot metal dephosphorization is a non-equilibrium reaction in which hot metal is in contact with slag whose oxygen activity differs greatly from that of hot metal, it is important to increase the interfacial oxygen activity.

5) According to the results of fundamental experiment, $2\text{CaO}\cdot\text{SiO}_2$ solid phase, in which P_2O_5 can be solved, makes a great effect on the dephosphorization reaction.

REFERENCES

- 1) T. Shima: Proceedings of the 6th IISC, vol.2 (1990), ISIJ, p.1.
- 2) S. Kitamura et al.: CAMP-ISIJ, 11 (1998), p.723.
- 3) T. Nagasaka et al.: private communication.
- 4) W. Fix et al.: J. Amer. Ceram. Soc., 52 (1969), p.347.

Figures



Fig. 1. Basic outline of hot metal pretreatment process.

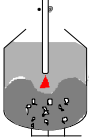
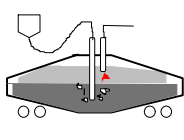
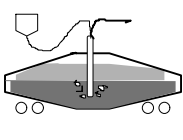
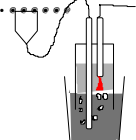
| | | LD | TPC | | Ladle |
|-------|------------------|--|--|---|--|
| | | A | B | C | D |
| | Works | Nagoya | Yawata | Kimitsu | Oita |
| De-Si | Process | - | BF Runner+TPC | BF Runner | TPC |
| | Final [Si] | - | 0.12% | 0.12% | 0.12% |
| De-P | Process | Converter  | TPC  | TPC  | Ladle  |
| | Heat Size | 270 ton | 200 - 300 ton | 250 ton | 340 ton |
| | Oxygen Gas | Top blow | Top blow | Injection | Injection |
| | Oxygen Flow Rate | 0.7-1.0 Nm ³ /t/min | 0.1-0.3 Nm ³ /t/min | -0.1 Nm ³ /t/min | 0.5 Nm ³ /t/min |
| | Oxygen Gas Ratio | ~100 % | ~50 % | ~25 % | ~30 % |
| | Flux | CaO | CaO+CaF ₂ LD slag | CaO+CaF ₂ LD slag | CaO+CaF ₂ |
| | Oxide | dust+ore | dust+sinter | dust | dust+ore |

Fig. 2. Hot metal dephosphorization processes of Nippon Steel.

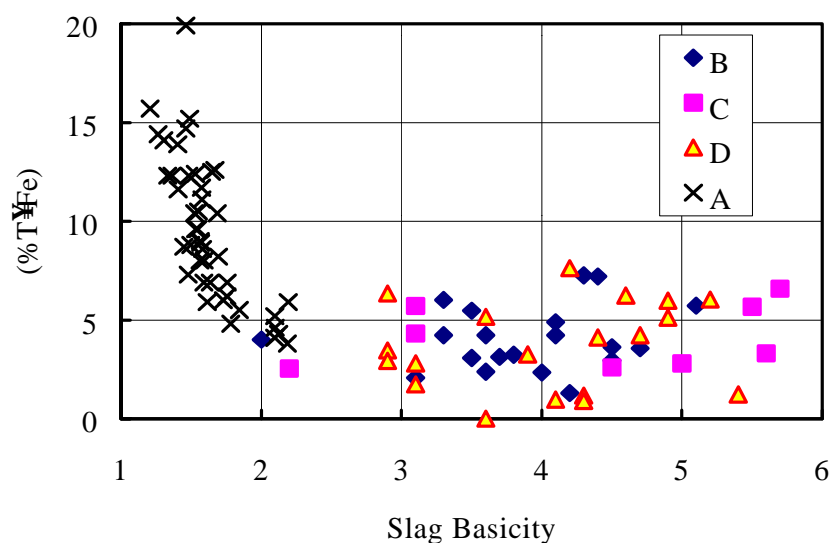


Fig. 3. Relation between slag basicity and (T-Fe) for each process.

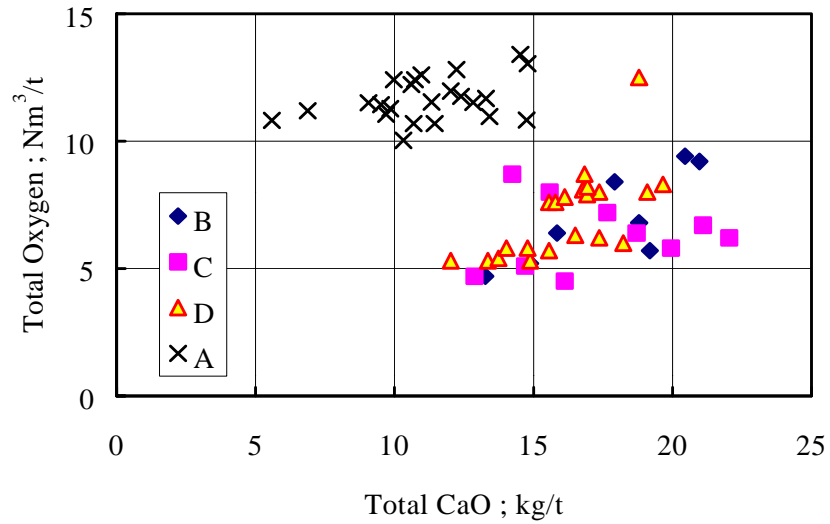


Fig. 4. Relation between total CaO and total oxygen consumption for each process.

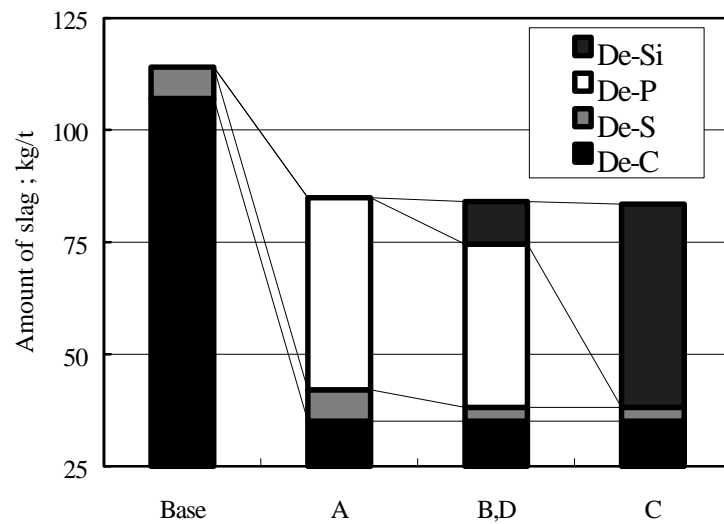


Fig. 5. Comparison of slag volume among various processes.

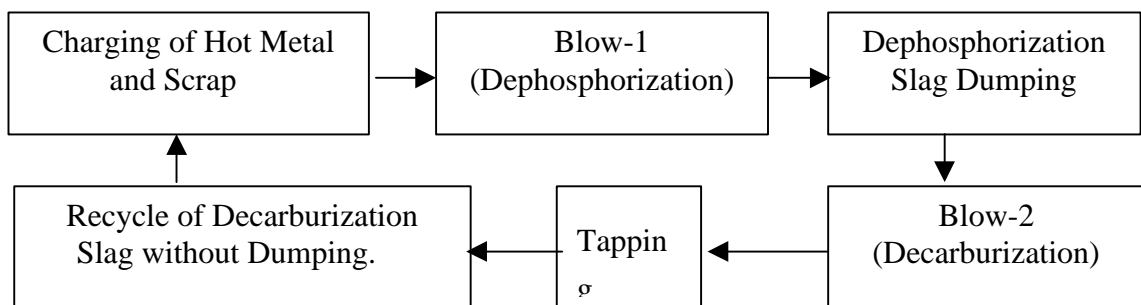


Fig. 6. Outline of MURC process.

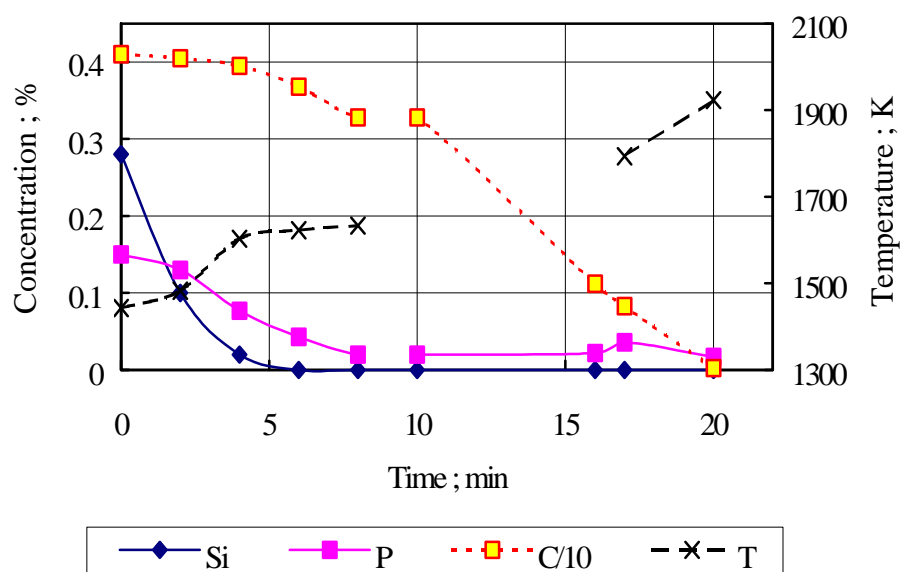


Fig. 7. Composition changes during MURC process.

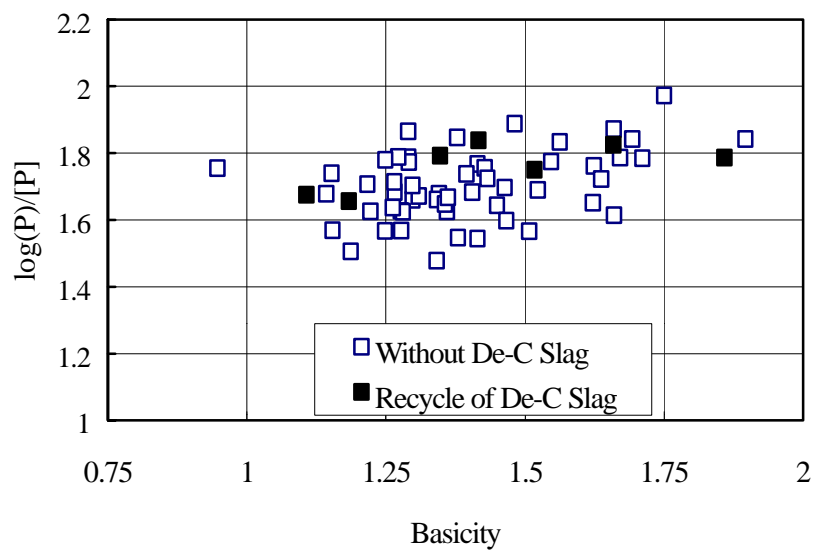


Fig. 8. Influence of slag recycle on phosphorous distribution ratio.

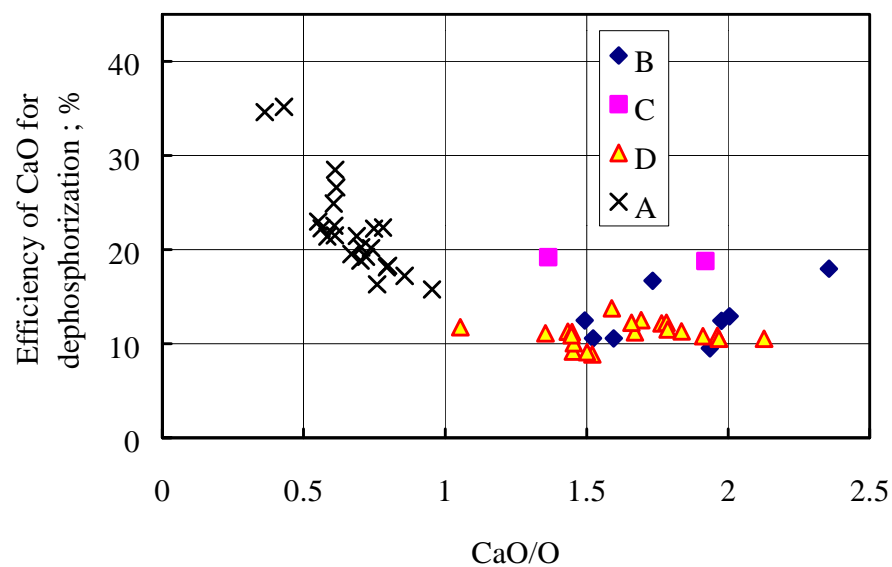


Fig. 9. Dependence of CaO efficiency for dephosphorization on CaO/O.

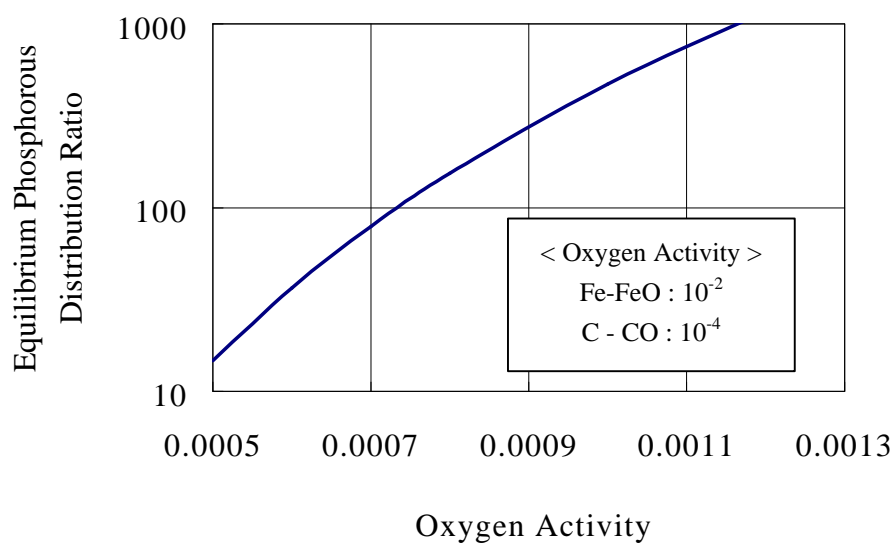


Fig. 10. Influence of oxygen activity on equilibrium phosphorous distribution ratio.

Tables

Table 1. High reaction efficiency condition for each impurity.

| | Temperature | Basicity | Oxygen Activity |
|--------------------|-------------|----------|-----------------|
| De-Phosphorization | Low | High | High |
| De-Sulfurization | High | High | Low |
| De-Siliconization | Low | High | High |

Table 2. Observed solid phases in slag by the fundamental experiments.

| Case | $\Delta[\% \text{Si}]$ | CaO Efficiency for Dephosphorization | Observed Solid Phases in Slag |
|------|------------------------|--------------------------------------|--|
| 1 | 0 | 15.4% | CaO, Calcium-Phosphate |
| 2 | 0.15 | 15.0% | Solid Solution of Calcium-Phosphate and Calcium-Silicate |