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Technical Report

Improvement of Flux Reaction Efficiency in Steel Refining

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Abstract

To meet the increasing demand for high-end products and to secure competitiveness in the world steel market, the Japanese steel industry has bent efforts to stay at the forefront in steelmaking technology. In response to increased demand for higher-grade products and consequent heavier burden on steel refining facilities, the process efficiency has been enhanced to enable their stable production in quantities. In the meantime, production costs and slag generation have been lowered owing to higher process efficiency and slag recycling. In view of new environmental standards for soil, the use of fluorine has been eliminated from steel refining. The present paper outlines the past, present, and future prospects of the improvement of flux reaction efficiency and the reduction of slag generation.

1. Introduction

The steel industry of Japan improved the process efficiency of steel refining in the 1980s in response to the urgent need for higher competitiveness in the international market, growing demand for high-end products and increasingly strict quality requirements. A significant development was the advance in hot metal pretreatment processes,[1] and as a result, the steel refining functions were divided into separate process stages. More recently, however, the loads on the refining processes have increased further because of the increase in high-grade products and increased amounts of impurity elements in pig iron owing to wider choice of material supply sources, and therefore, technology to efficiently, stably, and economically produce high-quality steels has been explored. Facing the situation, the industry has endeavored to lower steel refining costs as well as the slag discharge amount (the slag formation less the slag amount recycled in the works premises) by improving flux reaction efficiency and increasing the recycling of slag. In addition, considering the regulations on the use of fluorine in relation to the environmental quality standards for soil, steelmakers were requested to quit using fluorine for steel refining. To solve these problems, Nippon Steel & Sumitomo Metal Corporation has reviewed the primary refining processes including hot metal pre-treatment and developed new refining technologies. The present paper outlines these technical developments and their effects.

2. Technology to Improve Flux Reaction Efficiency

2.1 Viewpoints in improving flux reaction efficiency and reducing slag generation

To reduce costs and slag generation in the production of high-grade steels at high productivity, it is necessary to develop processes that enable (i) refining steel at high efficiency with less flux input to decrease slag formation, (ii) simple and economical recycling of slag, (iii) elimination of the use of fluorine to meet the environmental quality standards for soil, and (iv) wider flexibility in raw materials selection and larger thermal allowance in reaction vessels.

From these viewpoints, Nippon Steel & Sumitomo Metal reviewed the methods of hot metal pretreatment that had been established up to the 1980s, and mainly introduced the following improvements:

(i) Separating the four principal steel refining processes, i.e., desiliconization, desulfurization, dephosphorization, and decarburization (hereinafter referred to as de-Si, de-S, de-P, and de-C, respectively,) from each other, which made it possible to raise reaction efficiency and expand slag recycling; and

(ii) Selection of the converter-type method as the main hot metal de-P process, its wider application, and further enhancement of reaction efficiency.

The reaction efficiency of flux has been improved and the slag quantity reduced through these measures.

2.2 Separation of steel refining processes

As a measure to cope with increasing loads on the steel refining processes owing to the increase in high-grade products, the Compa-

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ny has reviewed the hot metal pretreatment processes. **Figure 1** shows how the steel refining processes are divided at the integrated works of the Company at present and what technologies are employed there.

The basic concept was to separate hot metal de-P from de-S, which had been done in one reaction vessel before, and to assign de-P to converters. This meant the division of the steel refining process into four separate steps, de-Si, de-S, de-P, and de-C; of these, de-Si was to be applied when the silicon content of hot metal was high. The intention here was to make it possible to adequately control each of the processes according to their respective reactions to enhance process efficiency and reduce the unit consumptions of burnt lime and other additives. Under this guideline, the Company's steelworks have taken measures to separate the refining processes, making the most of the characteristics of their existing equipment and increase the use of separate processing. The measures taken at the process separation are explained below in more detail.

2.3 Separation of hot metal desulfurization

The hot metal de-S process was originally developed such that torpedo ladle cars or hot metal ladles were used as the reaction vessel, and the processing was to be done together with de-P or immediately thereafter. However, mutually opposite conditions are required for the two processes: high temperature and low oxygen activity for de-S and low temperature and high oxygen activity for de-P. As a result, the efficiency of de-S was naturally low in the oxidizing atmosphere of de-P. Hence, to raise the efficiency of the de-S process, it was first separated from de-P to enable it at higher temperatures and under a lower oxygen partial pressure. There was another significant change: while the flux injection method using burnt lime, calcium carbide, and soda ash was the main method of de-S, the KR process, using ladles as the reaction vessel and a molten metal stirring mechanism to accelerate the reaction, which was developed at Hirohata Works in 1965[2] and also used at Kashima and Kokura (now part of Yawata), began to attract attention again due to its high reaction efficiency, and recently, was newly introduced in the Wakayama,[3] Yawata (Tobata), and Kimitsu Works.[4]

On the other hand, in relation to the flux injection method, the Company developed the use of CaO–Mg flux in appreciation of its higher reaction efficiency.[5] Thus, for hot metal de-S, the steelmaking plants of the Company have chosen either the KR process or the flux injection process using torpedo cars, ladles, or converters as the reaction vessel, considering their existing equipment.

As a result of the separation of hot metal de-S and process improvement, the efficiency has been enhanced and the slag generation has been reduced.

2.4 Separation of hot metal dephosphorization and decarburization

2.4.1 Advantages of dephosphorization in converters

Since the early days of hot metal de-P, Nippon Steel & Sumitomo Metal used torpedo ladle cars as the reaction vessel; with torpedoes, however, the free board is small, and the dephosphorizing agent blown into the hot metal is likely to flow out of the top opening, hindering the agitation of the hot metal, lowering the reaction efficiency, and as a result, making the process time longer. Another problem of the method was the low thermal allowance for the de-C in converters, which restricts the scrap ratio and decreases production flexibility. By the de-P method using hot metal ladles as the reaction vessel, on the other hand, the metal is better agitated and the process time is shorter, but the problems of the small free board and the limited scrap ratio persist.

To solve these problems, the Company developed a new de-P method using converters as the reaction vessel; with a converter, the free board is large, and it is possible to agitate the hot metal strongly by blowing oxygen gas from the top. Thanks to the strong agitation under high-speed oxygen blowing of converters, it is possible to rapidly complete the process within 10 min using slag of low-basicity (CaO/SiO_2) under high oxygen potential. In addition, this method has a high scrap melting capacity and it is possible to raise the scrap ratio. Another advantage is that, since the method allows slag mixing, it is possible to recycle hot slag, i.e., to use the slag that formed during de-C for dephosphorizing the hot metal of the succeeding charge. The hot metal de-P in converters is thus more advantageous than in other types of vessels.[6, 7]

2.4.2 Simple Refining Process (SRP) and LD-Optimized Refining Process (LD-ORP)

A version of the hot metal de-P in converters was developed at the Steelmaking Plant of Kashima Works in 1987. The new method, named the Simple Refining Process (SRP), brought about high process efficiency with less slag formation; the method comprised assigning one of two converters to de-P and the other to de-C, and transferring the slag that formed during de-C to the de-P vessel for reuse (see **Fig. 2**).[8, 9]

Another version was developed at Nagoya Works in 1989 using as the reaction vessel the converters of No. 1 Steelmaking Plant,

Works	Separation of the 4 refining processes De[Si]	De[S]	De[P]	De[C]
Muroran	Torpedo ⇒	Torpedo ⇒ (De[S] in LF)	Converter ⇒ MURC LD-ORP	Converter
Kashima		Ladle ⇒ KR	Converter ⇒ SRP	Converter
Kimitsu	Torpedo ⇒	Ladle ⇒ KR Partially Torpedo	Converter ⇒ MURC Partially LD-ORP	Converter
Nagoya	Converter ⇒	Converter ⇒ Desulfurization Furnace	Converter ⇒ LD-ORP	Converter
Wakayama		Ladle ⇒ KR	Converter ⇒ SRP	Converter
Yawata (Kokura)		Ladle ⇒ KR	Converter ⇒ SRP	Converter
Yawata (Tobata)	Torpedo ⇒	Ladle ⇒ KR Injection	Converter ⇒ MURC Partially Torpedo	Converter
Oita	Torpedo ⇒	Ladle ⇒ Injection	Converter ⇒ MURC Partially Ladle	Converter

Fig. 1 Separation of refining process in Nippon Steel & Sumitomo Metal

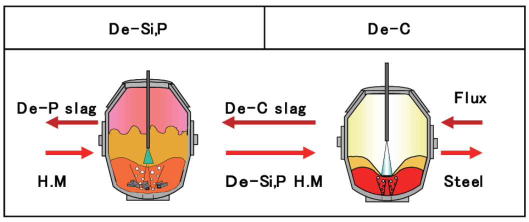

Fig. 2 Converter type hot metal dephosphorization process (SRP)

which were then working at low operating ratios (see **Fig. 3** [10])).[11, 12] The developed method, named the LD-Optimized Refining Process (LD-ORP), comprises charging hot metal into the converter assigned for de-Si and de-P, and then, after these processes, desulfurizing it in the same vessel by blowing CaO and other desulfurizing agents from the bottom, discharging the slag, and transferring the hot metal to another converter assigned for de-C.

By either the SRP or the LD-ORP, although hot metal is transferred from a converter vessel to another, the consumption of CaO is lower, the steel yield is higher, and the converter operation is made stable and quick, and hence, the Company promoted the use of either of the processes for all its steel production.

Later, in the late 1990s, facing increasingly tougher international competition and expanding demand for steel products, Nippon Steel and Sumitomo Metal, the then predecessors of the Company, rapidly expanded the application of these de-P methods in appreciation of their overwhelming advantages. In fact, a new steelmaking shop equipped with a converter-type vessel meant exclusively for de-P was constructed at Wakayama Works in 1999,[3] bringing about marked enhancement of process efficiency, decrease in burnt lime consumption, and reduction of slag generation. The method was then expanded to Kokura, and a converter-type vessel for de-P was built there in 2010.

After the commercial use at Nagoya, the LD-ORP was expanded to Kimitsu, and has been used for the production of ultra-low-P steels.

More recently, aiming at dephosphorizing hot metal at higher efficiency, de-S was separated as a step prior to de-P, and assigned to yet another converter; this method, called the ORP-II, has been commercially practiced at Nagoya, realizing higher process efficiency by slag recycling, lower burnt lime consumption and less slag generation despite an additional transfer of hot metal.[13)]

2.4.3 Multi-Refining Converter (MURC) Process

Nippon Steel & Sumitomo Metal has developed yet another version of the converter-type de-P process, the multi-refining converter (MURC) process, whereby de-P and de-C are sequentially performed, with deslagging in between, in one converter vessel (see Fig. 3 [10])).[14–16] By this process, the slag stemming from de-P is discharged immediately thereafter, keeping the hot metal in the vessel, and then, de-C is performed in the same vessel. At the tapping, the slag from the de-C is left in the vessel and used for dephosphorizing

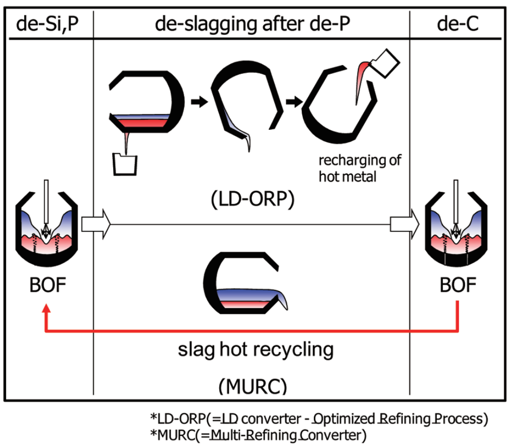

Fig. 3 Converter type hot metal dephosphorization processes (LD-ORP, MURC) [10)]

the molten pig iron of the following charge. Thanks to the slag recycling, heat loss is minimal and the amount of slag is significantly reduced.

The MURC process is effective at decreasing the burnt lime consumption, reducing slag generation and effectively using thermal allowance, which is excellent for producing ordinary carbon steels (except for ultra-low P steels), and in appreciation of these advantages, after being established at Muroran, it has been introduced to Oita, Kimitsu, and Yawata (Tobata).

The advantage of slag hot recycling is explained here using the MURC process by way of example. **Figure 4** [17)] shows the ratio between observed and calculated phosphorus distribution (L_p = P concentration in slag/same in hot metal) with and without hot recycling of de-C slag; the observed values are those of the de-P by the MURC process at Oita Works, and the calculated values are those based on slag composition. It is clear from the graph that, with slag hot recycling, the actual values of phosphorus distribution are higher and closer to the calculated figures, which means that it is possible to decrease burnt lime consumption by the amount corresponding to the excessive basicity of the recycled slag. In fact, as a result of slag hot recycling, burnt lime consumption has been decreased by 40% (see **Fig. 5** [17)]).

2.4.4 Increase in hot metal dephosphorization ratio

Figure 6 shows the historical change of the treatment amounts by different methods of hot metal de-P. To enhance competitiveness in the international market, respond to the increase in the demand for steel products, and reduce slag generation, Nippon Steel & Sumitomo Metal has expanded the application ratio of hot metal de-P, and simultaneously, considering the advantages of converters, increased the treatment share of the SRP, LD-ORP, and MURC pro-

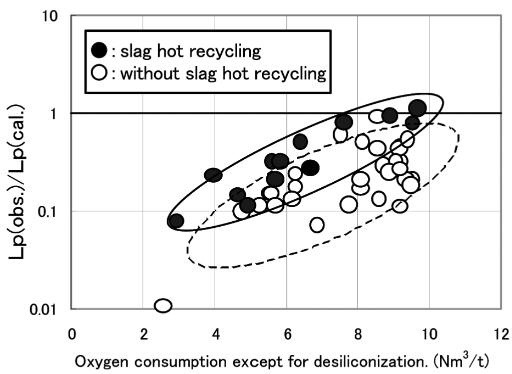

Fig. 4 Effect of slag hot recycling by MURC process (Oita Works) [17)]

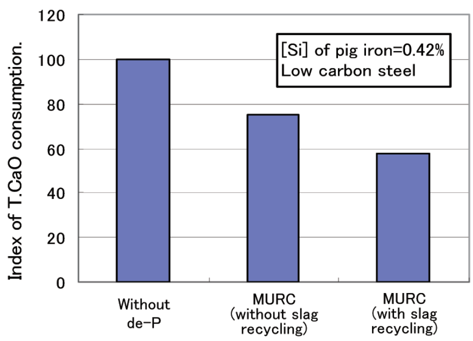

Fig. 5 Comparison of CaO consumption (Oita Works) [17)]

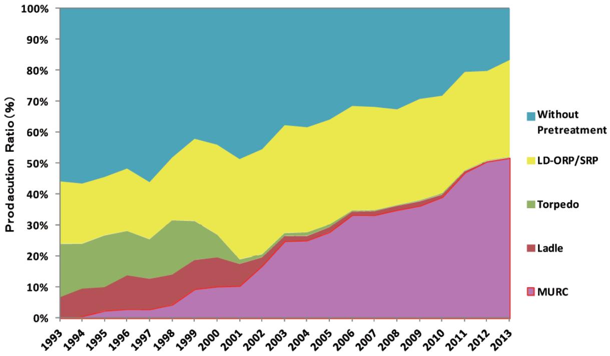

Fig. 6 Application ratios of different de-P methods

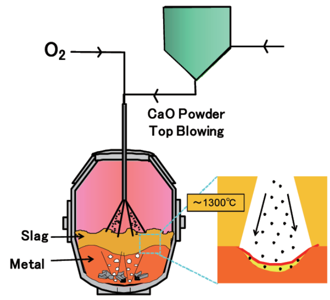

Fig. 7 Schematic illustration of CaO powder top blowing [19)]

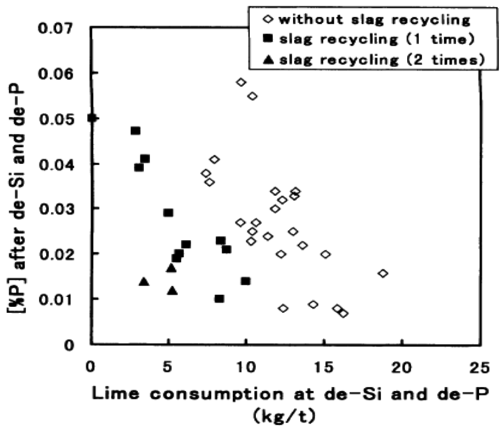

Fig. 8 Effect of slag recycling on lime consumption [16)]

cess in preference to conventionally popular methods using torpedo cars or ladles as the reaction vessel; in fact, the total application ratio of the three converter-type de-P processes reached 84% in 2013. The target application ratio at present is 100% of the whole molten pig iron the Company produces to decrease slag generation through improved flux reaction efficiency.

2.5 Hot metal desiliconization

Increase in the silicon content in molten pig iron leads to an increase in the consumption of burnt lime and a consequent increase in slag formation in steel refining.

As stated earlier, by the converter-type de-P, it is possible to remove P and Si by oxygen blowing using the slag of comparatively low basicity and melting point, owing to the large volume of the reaction vessel. This means that it is not necessary to minimize the Si content of hot metal, but there is the Si content level most suitable for de-P. The standard practice in the Company presently is to decrease slag formation by de-Si of hot metal before de-P when the Si content exceeds the most suitable level. However, the de-Si capacity is insufficient at present, and it is desirable to expand the capacity to further decrease the generation of steelmaking slag.

As stated above, Nippon Steel & Sumitomo Metal has separated the four fundamental steel refining processes, i.e., de-Si, de-S, de-P, and de-C, from each other, and concentrated the hot metal de-P methods on those using converters as the reaction vessel, and consequently, enhanced the efficiency of steel refining and reduced slag generation.

2.6 Further improvement in flux reaction efficiency

Further improvement in the reaction efficiency is aimed at in each of the separated refining processes. Some of such technical developments are outlined.

Since de-P is done at comparatively low temperatures and within a short time, the melting of burnt lime tends to be insufficient. To solve this problem and improve reaction efficiency, the melting is accelerated by increasing the flow of the bottom blowing gas to intensify the stirring of the metal bath; this is possible only in converters equipped with bottom blowing facilities.[7, 18)]

Another latest development is to blow burnt lime in powder, which is better for slag forming, than in lumps through the top blowing lance. This is a method for preventing the powder from being lost to dust collection and increasing its slag forming by blowing the powder directly to the high-temperature combustion reaction point (see **Fig. 7**).[19)]

2.7 Expansion of slag recycling

To reduce slag generation, it is essential to recycle slag as much as possible. As a result of the separation of hot metal pretreatment processes, it became possible to separately recover de-S slag and de-C slag having low contents of phosphoric acid, and use them as sinter feed. This recycling is practiced at many of the Company's works to minimize slag discharge to outside the works premises.

The Company is also bending efforts to increase the recycled use of slag. As stated before, the slag from de-C reactions is of a comparatively high basicity, but because it is left in the converter under the end-point condition at high temperatures, its phosphoric acid concentration is low. Hence, its reuse for hot-metal de-P at lower temperatures and in lower basicity is advantageous for decreasing the burnt lime consumption for de-P.

Figure 8 [16)] shows the relation between the unit consumption of burnt lime and the P concentration in slag after de-P using the MURC process. With slag recycling, the unit consumption of burnt lime is decreased by 5–10 kg/t-steel.

3. Advance of Fluorine-free Refining Technology

Regulations on the use of fluorine were included in the environmental quality standards for soil in the 2000s, and in view of the trend, Nippon Steel & Sumitomo Metal pushed forward the studies to develop a de-P process without using it. Fluorine, or fluorspar, was used for de-P in torpedo cars or hot metal ladles to lower the melting point of the slag, because it tended to be basic owing to the limited capacity of the vessel, and without F, the process efficiency drastically fell and the loads on succeeding processes increased. As the converter-type de-P became widely practiced at many works of the Company, a method not requiring F was developed taking advantage of the strong bath stirring and low-basicity slag under high oxygen potential of converters. **Figure 9** [17)] shows the relation between CaO/O and the lime utilization ratio (K_{CaO}) during de-P; the

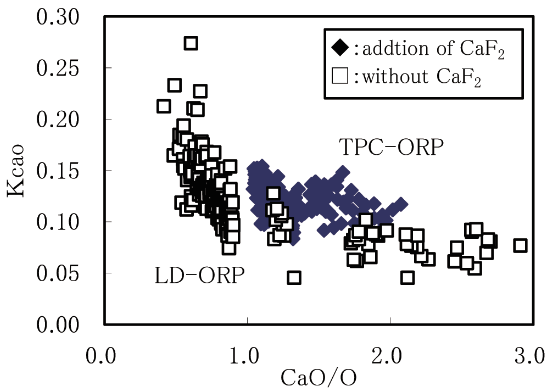

Fig. 9 Relationship between CaO/O and K_{CaO} (Yawata Works)[17]

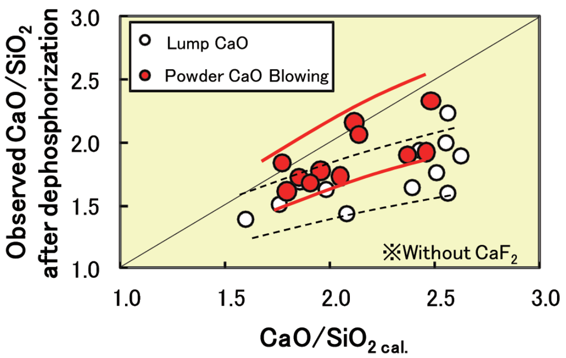

Fig. 10 Relationship between calculated and observed CO/SiO_2 after de-P[19]

graph shows that the high lime utilization ratio is obtainable even without F.

The top blowing of CaO powder mentioned earlier is also effective at accelerating the melting of burnt lime and raise the process efficiency without F because of the large surface area of the CaO powder and its direct blowing to the combustion reaction point (see **Fig. 10**[19]).

4. Reduction of Steelmaking Slag Generation

As a result of the said functional division of the steel refining processes, concentration on the converter-type de-P, and increase in the hot metal de-P ratio, the steelmaking slag generation of the Company has significantly decreased. As seen in **Fig. 11**, the slag generation of the Company has decreased by roughly 13% since 2005.

5. Future Improvement of Flux Reaction Efficiency and Reduction of Slag Generation

To further improve flux reaction efficiency and decrease slag generation, the Company will aim at 100% hot metal pretreatment and increase the capacity of hot metal de-Si as the pretreatment for de-P. In addition, the present utilization efficiency of lime in the de-S and de-P reactions still has considerable room for improvement. The Company will continue to take measures to reduce slag generation by further enhancing reaction efficiency and increasing slag recycling.

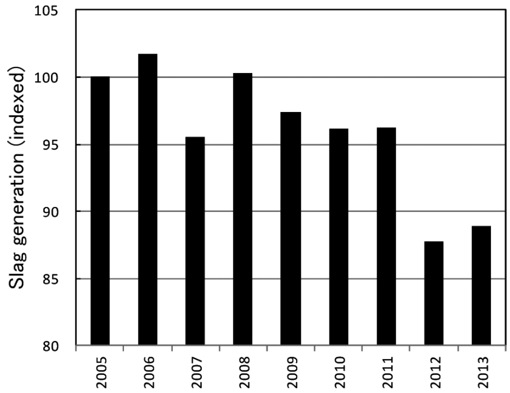

Fig. 11 Change of steelmaking slag generation

6. Closing

While the market demand for high-grade steel products increased and, consequently, more loads came to be imposed on steel refining facilities, Nippon Steel & Sumitomo Metal has decreased the generation of steelmaking slag through measures such as the separation of the four fundamental steel refining processes, i.e., removal of Si, S, P, and C, from each other, increase in hot metal pretreatment ratio, concentration on the converter-type de-P, enhancement of refining reaction efficiency, and increase in slag recycling. Efforts were also made to develop technologies to eliminate the use of fluorine for steel refining for environment conservation. The Company will continue to bend efforts to improve its technical capability and job expertise in the plants to enhance its steelmaking technology by decreasing slag generation and improving other operation parameters.

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