

# Development of High-Grade Steel Manufacturing Technology for Mass Production at Nagoya Works

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## Abstract

*Form the beginning of 1980's, demand for high corrosion resistance steel sheet for automobile were increased. In Nagoya Works, to satisfy these demands, development was focused on the improvement of productivity of IF(Interstitial Free) steel by improving RH decarburization performance and refining cycle time to match sequential casting. Skull removing equipments system and enlargement of snorkel diameter and introduction of pre-evacuation system were effective counter measures. Second issue was the development of converter type hot metal pre-treatment system, which enabled simultaneous desiliconization and dephosphorization treatment. After that, demand for mass production of low sulphur steel for high tensile strength steel for automobile elimination of weight to match CO<sub>2</sub> reduction, separated process between desulphurization and dephosphorization, ORP II process, was developed. For anti-sour steel production, such as line pipe, RH desulphurization technology was developed for ultra low sulphur steel on mass production.*

## 1. Introduction

Many of the manufacturing plants of Japanese automakers are located in the Chubu district. The Nagoya Works of the Nippon Steel Corporation was founded there as well and has made supplying automotive sheet to automakers its primary mission. Since the 1980s, in particular, reflecting a mounting cry for cars having better corrosion resistance, the demand for high-quality galvanized sheet with heavier coating weight has increased and the need for interstitial free (IF) steel has expanded. Under those conditions, Nagoya Works has carried on development of new technologies, including the converter-type mass pretreatment of hot metal and the efficient mass production of high-purity steels, specifically of extra-low carbon steels, for the refining process, and the H-shaped tundish and the application of an electromagnetic force in the mold for the casting process.

Recently, there is a growing need for high-strength steels in order to decrease automobile weight and, thereby, improve fuel effi-

ciency as a means of curbing global warming. At the same time, the steelmaking process requires greater sophistication to allow for mass production of low-sulfur steels.

In this report, we shall describe the development of the refining process carried out at the steelmaking plant of Nagoya Works.

## 2. Innovation in Refining Technology

### 2.1 Technology for mass refinement of IF steel

In order to meet the rising demand for IF steel as a material for galvanized sheet in the 1980s, strenuous efforts were made to improve the decarburization capacity of the plant's vacuum degassing equipment. To allow for "continuous casting" (sequential casting) of IF steel, it is necessary to enable the continuous processing of multiple charges by the RH (Ruhrstahl Heraeus) process vacuum degassing equipment, which must also be synchronized with the cycle time of the continuous casting (CC) machine. At Nagoya Works, in particular, two 2-strand CC machines are casting more than 400,000

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tons of steel monthly, and, hence, the cycle time is short.

Fig. 1 shows the relationship between the number of charges of IF steel subject to continuous RH treatment and the carbon concentration of the steel after treatment. It can be seen from the figure that the carbon concentration shows a tendency to decrease with an increase in the number of charges. This observation is considered to be due to the acquisition of carbon from the skull deposited inside the vacuum tank as a result of the dehydrogenation treatment of thick material having a high carbon concentration. It can also be seen that the influence of the skull deposit extends over about four charges. In order to implement reliable refining of extra-low carbon steel, therefore, it is of primary importance to reduce the amount of skull deposit inside the vacuum vessel and thereby minimize the influence of skull. To that end, we introduced oxygen lance equipment for cutting skull<sup>1)</sup> as shown in Fig. 2. In addition, we installed top-burner equipment, shown in Fig. 3, for actively maintaining a high temperature inside the vacuum vessel.<sup>2-5)</sup>

Additionally, the decarburization behavior of steel in the RH process is divided into two phases: Phase I in which the decarburization rate is high and Phase II in which the decarburization rate is low. This can be interpreted in the following manner:<sup>6)</sup> During Phase

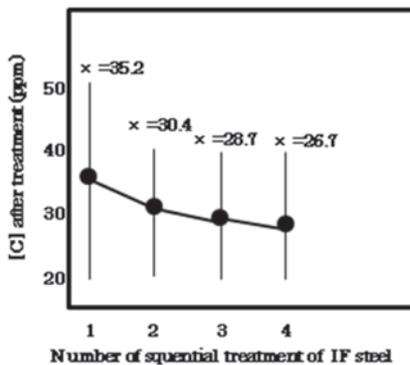


Fig. 1 Relation between number of treatment charges of IF steel and C after treatment

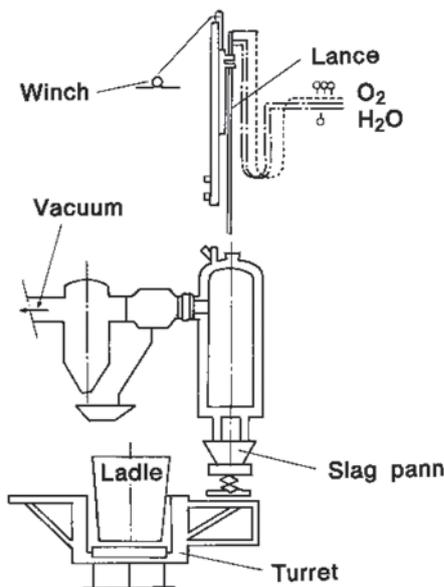


Fig. 2 Oxygen lance equipment for skull cutting<sup>1)</sup>

I, the supersaturation pressure of carbon monoxide (CO) gas bubbles is so high that the steel is decarburized mainly from the inside, whereas during Phase II, the free surface of the steel becomes the main site of the decarburization reaction. It can be imagined from a two-vessel model<sup>7)</sup> that the decarburization rate will increase when the circulation rate of molten steel<sup>8)</sup> is increased. In the No. 2 RH unit degassing equipment of Nagoya Works, the snorkel inside diameter, which was originally 600 mm, was expanded to 730 mm in 1984 for this purpose.

As a result of this expansion, as shown in Fig. 4, the apparent circulation rate of molten steel rose from 110 tons/min to 160 tons/min and the decarburization rate constant improved markedly for Phases I and II.<sup>9,10)</sup> It should be noted here that the injection of gas into the vacuum vessel increases the decarburization rate, especially in Phase II. However, gas injection needs to be optimized taking into account the deposit of skull inside the vacuum vessel and the cost of the gas. In order to increase the extent of decarburization of steel in Phase I, it is important to raise the vacuum exhaust rate. To that end, a pre-vacuum exhaust system was installed in 1993 (Fig.

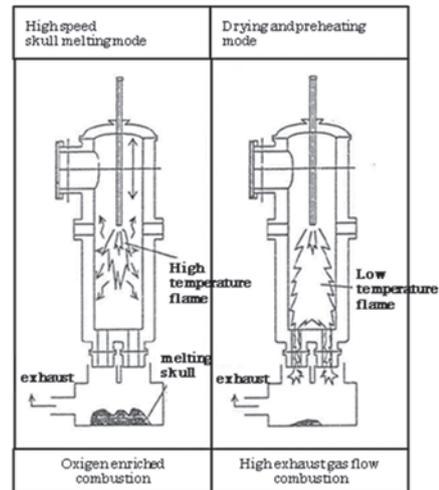


Fig. 3 Function of top burner equipment<sup>2)</sup>

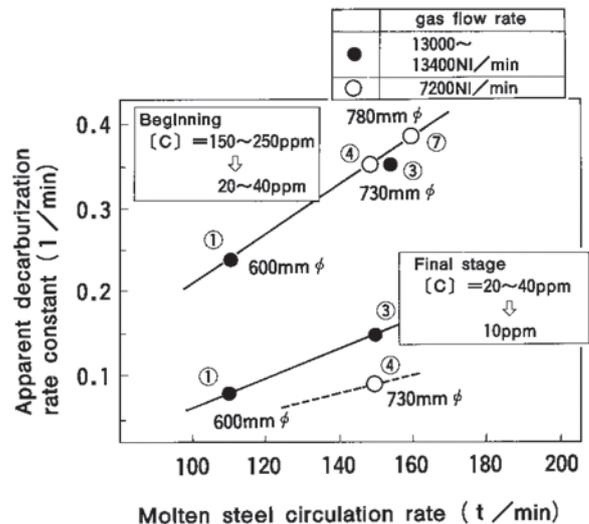


Fig. 4 Relation between molten steel circulation rate and apparent decarburization rate constant<sup>9)</sup>

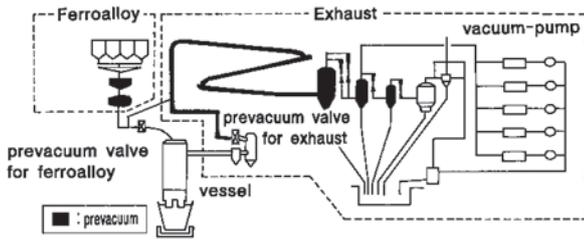


Fig. 5 Schematic illustration of prevacuum valve equipment<sup>11)</sup>

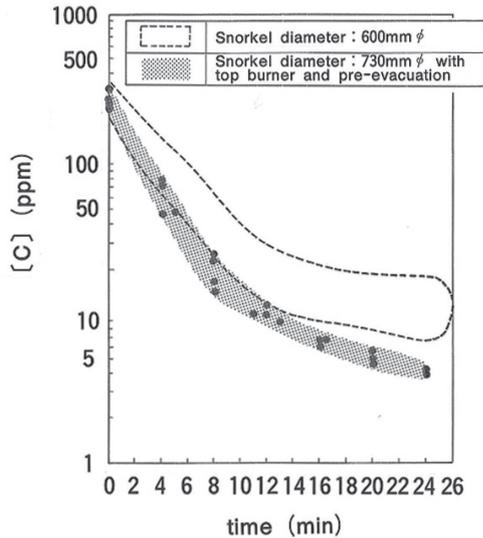


Fig. 6 Transition of carbon content during decarburization treatment at RH<sup>12)</sup>

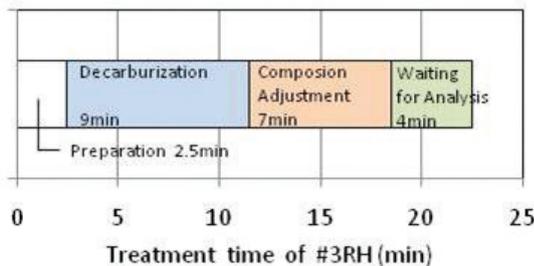


Fig. 7 Items of treatment time a No.3-RH<sup>13)</sup>

5).<sup>11)</sup> As a result, a high-speed decarburization technique was established that permits attaining a carbon concentration of 10 ppm or less in 12 minutes of treatment as shown in Fig. 6.<sup>12)</sup>

At a later date, the immersion pipe inside diameter was further expanded to 800 mm. The above described high-speed decarburization technology developed for the No. 2 RH unit was transferred to the No. 3 RH unit constructed in 2007. Although the No. 3 RH unit has only one vacuum tank as shown in Figs. 7 and 8, it permits mass-production of IF steel through sequential treatment of the steel for the No. 2 CC, which is a high-speed casting machine.<sup>13)</sup>

**2.2 Development of technology for mass pretreatment of hot metal**

At Nagoya Works, since the No. 2 CC was put into operation in 1980, in the material flow from the No. 2/No. 3 converters of the former steelmaking plant I to the No. 4/No. 5 converters of the for-

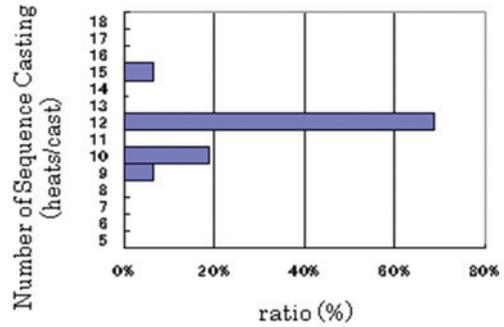


Fig. 8 Distribution of sequential casting number of IF steel at No.2CC<sup>13)</sup>

mer steelmaking plant II to the No. 1/No. 2 continuous casters, the activity rate of the No. 2 and No. 3 converters was declining because of the continual increase in the continuous casting ratio. Under this condition, a hot metal pretreatment process utilizing those two converters was developed. Specifically, the silicon concentration of the blast-furnace hot metal was found to be at the 0.2% level throughout the 1980s and, hence, a method was studied for dephosphorizing hot metal without desiliconization by utilizing the converters of the former steelmaking plant I, together with a large freeboard and powerful stirrer. In addition, since the cycle time of steel refining at Nagoya Works is short, as mentioned in 2.1, it was an important task to shorten the converter blowing time at the former steelmaking plant II and allow for high-efficiency plant operation through enhancement of the activity rate of the single converter.

Fig. 9 shows the basic concept of simultaneous processing for desiliconization and dephosphorization using a converter.<sup>14, 15)</sup> It can be expected from competing reaction models<sup>16, 17)</sup> that using a high rate of oxygen supply and vigorous stirring within the converter will make it possible to desiliconize and dephosphorize steel simultaneously since the oxygen activity at the slag-metal interface is kept high. In addition, under conditions of vigorous stirring of the hot metal, the oxygen activity at the slag-metal interface can approach the slag bulk oxygen activity. Therefore, by optimizing the rate of oxygen supply, it becomes possible to dephosphorize the hot metal with a relatively low FeO concentration even when it is of low basicity. When the FeO concentration is low, the crystallization of solid 2CaO-SiO<sub>2</sub> phase increases and the phosphorus contained in the hot metal is fixed in the form of a solid solution.<sup>18-20)</sup> Therefore, by injecting a dephosphorizing agent into the converter, it is possible to dephosphorize the hot metal while restraining the occurrence of rephosphorization without discharging the dephosphorized slag from the converter. Here, the process by which desiliconization/dephosphorization and desulfurization are performed continuously in a single converter is called the ORP I process.

This process was developed into commercial production equipment in 1989.<sup>15, 21, 22)</sup> The pretreatment furnace is an LD-PB furnace, into which CaCO<sub>3</sub> is injected from the bottom and which utilizes CO<sub>2</sub> generated by the pyrolysis of CaCO<sub>3</sub> to stir the hot metal.<sup>23, 24)</sup>

As a part of the original process, during the treatment requiring vigorous stirring of the hot metal, CaCO<sub>3</sub> was injected into the furnace from the bottom, and during the succeeding desulfurization treatment, the desulfurizing agent was injected into the furnace from the bottom. From the results of an analysis using a competing reaction model and the change in slag composition observed during dephosphorization treatment, it is confirmed that when a lump of CaO

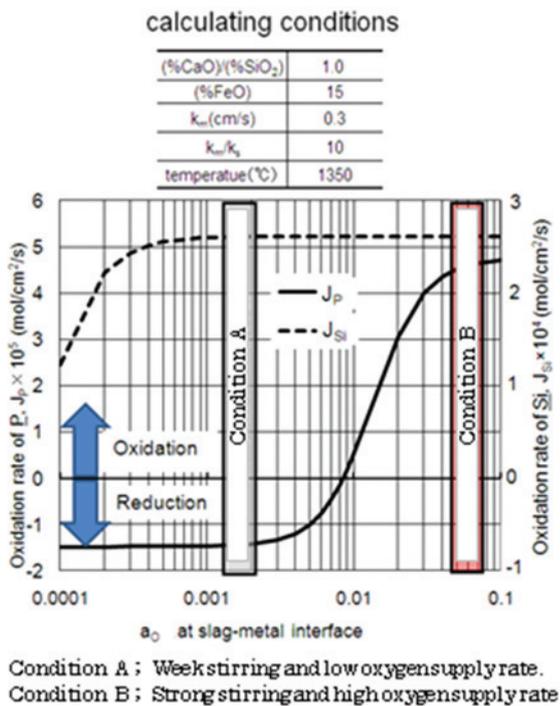


Fig. 9 Relation between oxygen activity at slag-metal interface and the rate of oxidation of Si, P<sup>14, 15)</sup>

source is put into the converter from top for dephosphorization treatment for a short time, say, about 10 minutes, the slagging rate of CaO is considered to be one of the factors governing the dephosphorization reaction, as shown in Figs. 10 and 11.<sup>19, 25)</sup> At present, therefore, hot metal is subjected to dephosphorization under low-basidity, high-FeO conditions.

Later, an increase in the proportion of high-strength steel sheet was produced and, in particular, the demand for low-sulfur steel increased. Therefore, in 2010, in order to further improve the efficiency of desulfurization reaction by performing the desulfurization and dephosphorization treatment separately, the ORP II process was developed into commercial production equipment, in which the No. 1 converter, which had previously been shut down, was modified into a hot metal desulfurization furnace and the No. 2 and No. 3 converters were used exclusively for dephosphorization of hot metal.<sup>26)</sup>

The salient characteristic of the ORP II process is that the desulfurized slag is utilized repeatedly in the desulfurization furnace, rather than being discharged as it is produced. As shown in Fig. 12, the efficiency, in the furnace, of the desulfurization reaction expressed by the following equation (1) is nearly 100% until part of the treatment.<sup>26)</sup> Under conditions where the slag formed after desulfurization treatment has a high basicity and a large solid phase ratio, numerous particles of CaS trapped in the slag can be observed.<sup>27)</sup> It can be reasonably assumed that these CaS particles come from CaO contained in the desulfurizing agent that has been injected into the converter. On the other hand, since the CaS layer formed on the surface of CaO particles as a result of reaction (1) is only tens of micrometer in thickness, the reaction efficiency of CaO in a single reaction continues to be several percent. It is estimated, however, that the repetitive use of slag in the furnace causes the thickness of the CaS layer to increase, thereby making the reaction efficiency close to 100%.

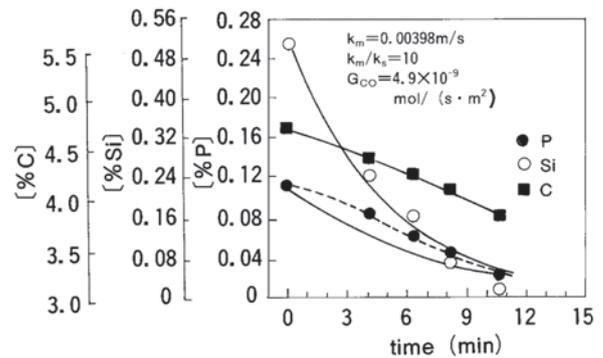


Fig. 10 Changes in hot metal composition with time<sup>25)</sup>

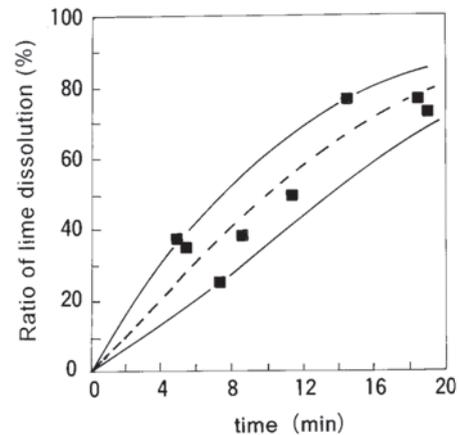


Fig. 11 Change in lime dissolution ratio with time<sup>25)</sup>

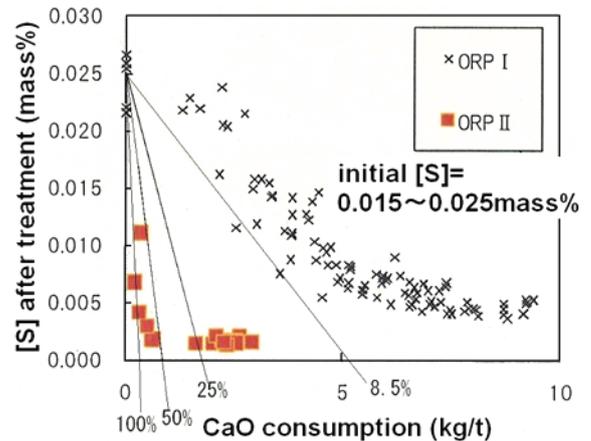


Fig. 12 Relation between lime consumption and S after treatment<sup>26)</sup>



In addition, since the desulfurization by after-blow of a desulfurizing agent into the converter is not performed, it is possible to improve the dephosphorization efficiency by lowering the hot metal temperature after dephosphorization, as is shown in Fig. 13.<sup>26)</sup>

Through the development, introduction, and modification of the LD-ORP process, it has become possible to shorten the tap-to-tap time and increase the heat size and thereby enhance the converter productivity as shown in Figs. 14<sup>28)</sup> and 15. In addition, the unit consumption of CaO has been reduced as shown in Fig. 16.

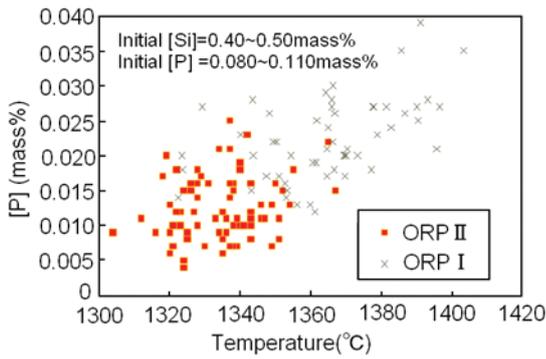


Fig. 13 Relation between temperature and P at end point<sup>26)</sup>

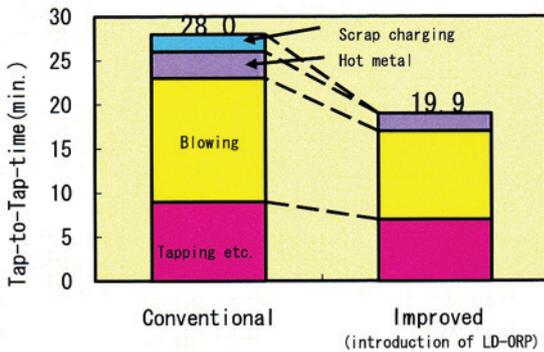


Fig. 14 Changes of tap-to-tap time at the converter by introduction of LD-ORP<sup>28)</sup>

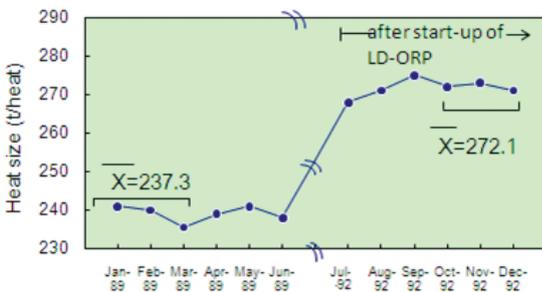


Fig. 15 Increase in heat size of the converter by introduction of LD-ORP

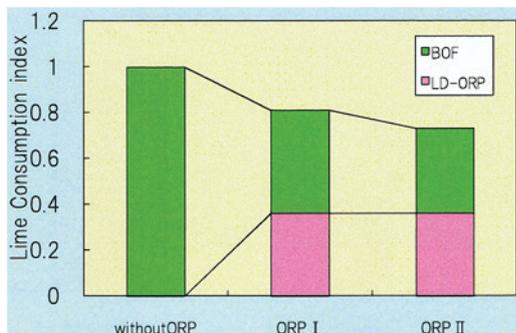


Fig. 16 Reduction of lime consumption by introduction of LD-ORP

Furthermore, because the introduction of ORP II and the installation of a furnace exclusive for desulfurization made it possible to

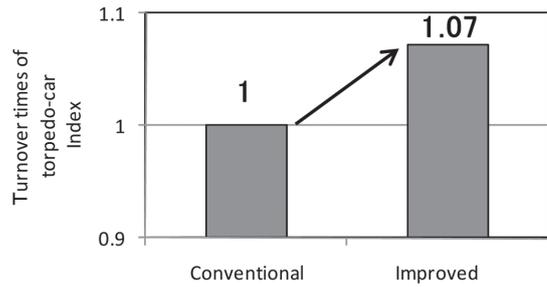


Fig. 17 Changes of turnovertimes of torpedo-car

completely omit the desulfurization treatment using torpedo cars, the turnover rate of torpedo cars has improved as shown in Fig. 17.

### 2.3 Development of technology for refining extra-low sulfur steel using the RH-PB process

At Nagoya Works, electric resistance welded (ERW) steel pipes of medium diameter are also manufactured. The steel materials for ERW pipes used in exceptionally severe environments are required to have superior sour resistance. In this case, it is necessary to reduce the sulfur concentration of steel to a level as low as 10 ppm or less in the steel refining process.

In the hot metal pretreatment process, there are cases in which the steel sulfur concentration decreases to 10 ppm or less right after the desulfurization treatment. However, as the steel goes on to the secondary refining process through the dephosphorization and decarburization processes, it picks up sulfur from the slag stuck to the converter wall and auxiliary raw materials. Therefore, it is indispensable to perform an additional desulfurization treatment in the final refining process closest to the casting process. In this case, in order to guarantee a final sulfur concentration of 10 ppm or less, it is important not only to efficiently reduce the sulfur concentration of the steel to the prescribed level in the secondary refining process but also to prevent the steel from being resulfurized by the slag.

Additionally, since many of the above steel products are so-called project goods that call for short delivery times, they need to be manufactured by sequential casting in a concentrated manner. Thus, it is necessary that it be possible to reduce the sulfur concentration of steel to the prescribed level in a mass production process. In order to establish extra-low sulfur steel manufacturing in its RH-CC process, Nagoya Works developed an RH steel refining technology for obtaining extra-low sulfur steels. At the early stages of technology development, the steel was desulfurized by putting a lump of desulfurizer into the vacuum vessel.<sup>29, 30)</sup> With the aim of further enhancing the efficiency of desulfurization, the Works went on to develop the RH-PB process by which a desulfurizer in the form of fine powder is injected directly into the molten steel through a nozzle provided at the RH lower vessel as shown in Fig. 18.<sup>31-34)</sup> The desulfurizing flux used is based on a CaO-CaF<sub>2</sub> compound.<sup>35, 36)</sup>

It has been determined that the efficiency of desulfurization differs according to the position of flux injection into the lower tank. Namely, as shown in Fig. 19, when the flux is injected into the vigorously stirred region right above the immersion pipes, the desulfurization efficiency is much higher than when the flux is injected into the weakly stirred region between the immersion pipes. It is reasonable to assume that the reason for this is that vigorous stirring of the molten steel facilitates the dispersion of flux particles in the molten steel.<sup>37)</sup>

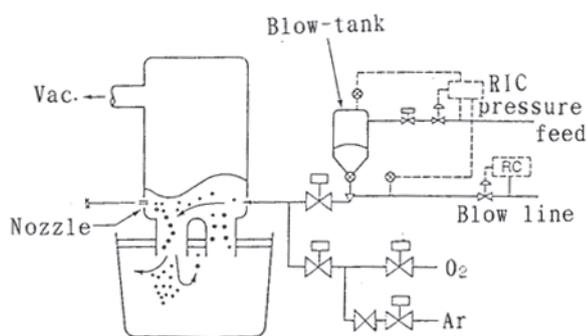


Fig. 18 Schematic illustration of RH-PB process<sup>31,37)</sup>

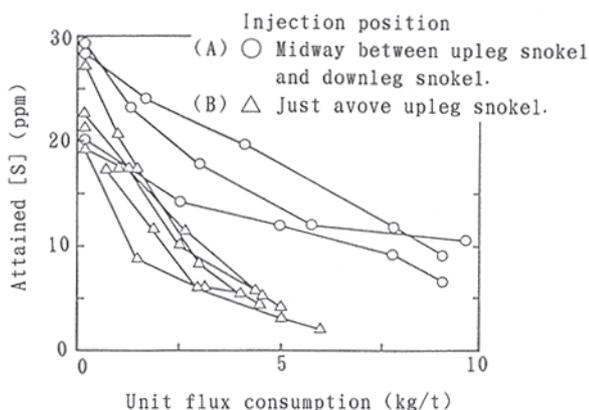


Fig. 19 Relation between unit consumption of flux and attained S<sup>31,37)</sup>

### 3. Conclusion

Since the early 1980s, Nagoya Works has continually modified and improved its steel refining processes in order to meet the need for mass production of extra-low carbon steel for automobile applications and to respond to the subsequent increase in the proportion of high strength steels produced. The representative examples are the development of an RH, high-speed continuous decarburization/desulfurization process; the introduction of a hot metal mass pre-treatment process utilizing vigorous stirring and a high oxygen feeding rate for hot metal in the converter; and the improvement of steel desulfurization efficiency.

In the future, we intend to continue making improvements and developments aimed at reducing out-of-the-system discharges of

slag, from the standpoint of environmental protection, and to further enhance the efficiencies of the existing processes.

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