

Chapter 11

Ladle Refining and Vacuum Degassing

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The treatment of steel in the ladle started approximately 45 years ago when the first ladle-to-ladle and ladle-to-ingot mold vacuum degassing processes for hydrogen removal appeared on the scene. In the late 1950s more efficient vacuum degassers such as the Dortmund Hoerder (DH) and Ruhrstahl-Heraeus (RH) processes became popular. In the middle 1960s degassing processes such as vacuum arc degassing (VAD), the ASEA-SKF process, and the vacuum oxygen decarburization (VOD) process for treating high-chromium steels were successfully implemented. Converter processes such as the argon oxygen decarburization (AOD) process were introduced in the early 1970s. The AOD process is now the preferred route in many specialty steel and stainless steel shops.

Granulated flux injection into the liquid steel, combined with argon stirring, started in the early 1970s. This was soon followed by the application of cored-wire feeding of alloying elements for better control of composition and inclusion morphology. A good overview of the various developments was given by Nijhawan¹, while an extensive review of the thermodynamic and kinetic principles underlying the various secondary steelmaking processes was prepared by Lange.³²

All the aforementioned innovations have had a pronounced effect on the steelmaking process, particularly with respect to the vessel or the furnace in which the steel is produced. For example, the implementation of ladle metallurgy and its related aspects enabled electric furnace steelmakers to use their furnaces as fast melters without the need to perform any refining in the furnace. In addition, ladle refining and degassing make it possible for the steelmaker to exert much tighter control over the properties of the final product through improved accuracy in the composition of the final product as well as its cleanliness and by being able to control inclusion morphology.

The contents of this chapter are arranged according to the sequence of operations in a steelmaking shop, i.e. starting with tapping the furnace, followed by reheating, refining, inclusion modification and degassing. Where appropriate, the underlying metallurgical principles of each operation will be discussed in terms of reaction equilibria and kinetics as well as fluid dynamics. In preparing this chapter frequent reference has been made to a recently published book by Turkdogan.²

11.1 Tapping the Steel

11.1.1 Reactions Occurring During Tapping

During tapping of the steel, air bubbles are entrained into the steel where the tap stream enters the bath in the tap ladle. The quantity of air entrained into the steel increases with the increasing free fall height of the tap stream as was demonstrated with the aid of water model studies.² The entrainment of a gas such as air into a falling stream of liquid steel has been the subject of a number of studies.³⁻⁶ However, a reliable prediction of the quantity of air entrained into a stream of liquid steel during tapping is difficult because of the assumptions that have to be made.

The nitrogen contained in the air entrained by the steel will be absorbed by the liquid steel depending on the extent to which the reaction



will proceed to the right; the symbol within the square brackets refers to nitrogen dissolved in the steel. It is well-known that surface active solutes such as oxygen and sulfur impede the kinetics of nitrogen absorption by the steel. The higher the concentration of dissolved oxygen and/or sulfur, the lower is the extent of nitrogen absorption. This is illustrated in Fig. 11.1 where the effect of deoxidation practice on the nitrogen pickup during tapping of an electric furnace is shown.⁷ For deoxidized steels the average nitrogen pickup during tap is significantly higher than for non-deoxidized steels. The same effect is shown in Fig. 11.2 where the nitrogen pickup during tapping of 220 tonne oxygen converter heats is depicted as a function of the dissolved oxygen content for steels containing approximately 0.01% sulfur.² The data in Fig. 11.1 and Fig. 11.2 are in complete accord.

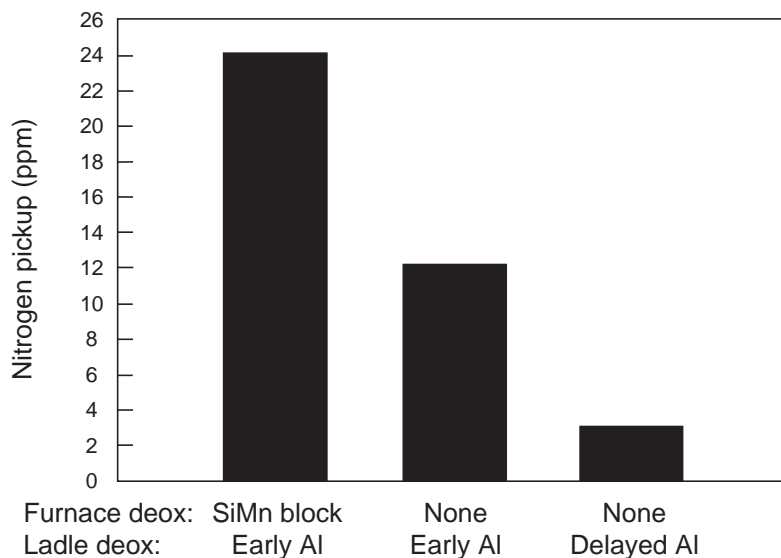


Fig. 11.1 Effect of deoxidation practice on nitrogen pickup during tap. From Ref. 7

Other sources contributing to the nitrogen pickup during or shortly after tap are: petroleum coke, when used for recarburization and various ferroalloys, particularly ferrotitanium, ferrovandium and low and medium-carbon ferrochromium.

Ladle additions often contain moisture which reacts with the liquid steel according to the following reaction:



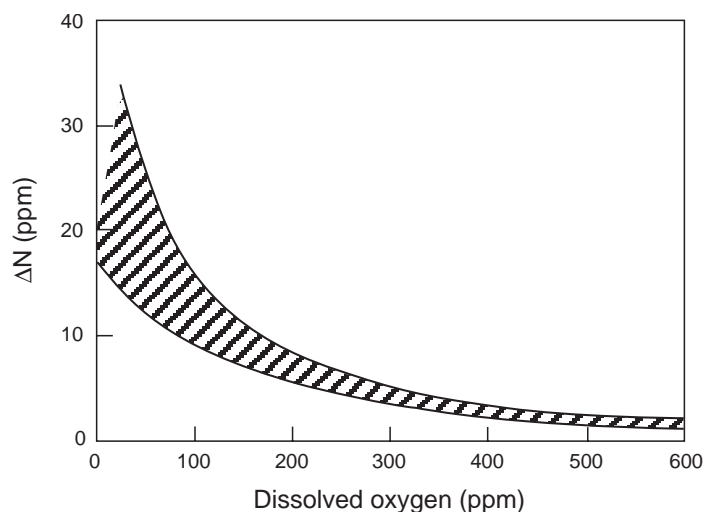


Fig. 11.2 Nitrogen pickup during tapping of 220 tonne heats as affected by the extent of deoxidation in the tap ladle. From Ref. 2.

It is seen from this equation that the extent of hydrogen pickup will be more pronounced for a fully deoxidized steel in which the dissolved oxygen content is low.

Of the various ferroalloys, ferromanganese is probably the major contributor of hydrogen.

11.1.2 Furnace Slag Carryover

It is generally unavoidable that a quantity of furnace slag is carried over into the tap ladle during tapping. The furnace slag generally contains a high concentration of FeO and MnO and

therefore (in an untreated form) is not suitable for use as a refining slag. Accordingly, methods to minimize the amount of furnace slag carryover have been developed and implemented; Szekely et al. discuss various methods for BOFs and EAFs.⁸ These include locating the taphole in the barrel of the converter sometimes in conjunction with the use of a ceramic sphere to block off the taphole towards the end of tap. In electric arc furnaces the first improvement was the use of submerged tapholes, later followed by the widespread implementation of eccentric bottom tapholes, which are now common in modern arc furnaces.

In older shops, inadequately equipped to control furnace slag carryover, slag raking is often practiced to remove the furnace slag. A good slag-free surface is attainable by careful raking. According to Hoeffken et al. raking is usually accompanied by a temperature loss of approximately 2.5°C (~5°F) per minute of treatment time and a metal loss of approximately 0.2%,⁹ raking times are typically of the order of ten minutes. For best results it is recommended that the steel be tapped open, then raked and covered with the synthetic ladle slag and finally deoxidized.

As a result of furnace slag carryover into the tap ladle, oxidation of aluminum and silicon present in the ladle additions occurs through reactions with less stable oxides (e.g. iron oxide and manganese oxide) present in the furnace slag. Another consequence of furnace slag carryover is phosphorus reversion from the slag to the steel, particularly when the steel is fully deoxidized.

To be able to predict the aluminum and silicon losses as well as the anticipated degree of phosphorus reversion, it is necessary to know the quantity of furnace slag carried over into the tap ladle. Kracich et al. describe a sensor to measure the depth of the slag layer in a ladle.¹⁰ These data provide accurate feedback to the melter and assist him in controlling the amount of furnace slag carryover.

11.1.2.1 Aluminum and Silicon Losses

The reactions of aluminum and silicon dissolved in the steel with the iron and manganese oxide in the slag and with the fallen converter skull may be represented by the following general reaction:



Using average molecular masses and assuming 80% Fe₃O₄ for the composition of the skull, Turkdogan¹¹ derived the following approximate empirical relation for the percentages of aluminum and silicon lost to the ladle slag for a 200 tonne steel bath in the ladle:

$$[\% \text{Al} + \% \text{Si}]_s \approx 1.1 \times 10^{-6} \Delta (\% \text{FeO} + \% \text{MnO}) W_{fs} + 1.1 \times 10^{-4} W_{sk} \quad (11.1.4)$$

where W_{fs} and W_{sk} are the weights (kg) of the carried over furnace slag and the fallen converter skull, respectively and $\Delta(\text{FeO} + \% \text{MnO})$ is the decrease in oxide contents of the furnace slag during tapping.

11.1.2.2 Phosphorus Reversion

Furnace slag carryover generally results in phosphorus reversion from the slag to the steel, particularly when the steel is fully deoxidized. The general relationship for the increase in steel phosphorus content, $\Delta[\% \text{P}]$, as a result of reversion from the slag is:

$$\Delta [\% \text{P}] = (\% \text{P}) (W_{fs} / W_b) \quad (11.1.5)$$

where $(\% \text{P})$ is the phosphorus content of the furnace slag and W_{fs} and W_b are the weights of the carried-over furnace slag and the steel bath in the ladle, respectively.

For OBM (Q-BOP) heats and low-carbon heats made in EAFs with oxygen injection, typical values for $(\% \text{P})$ and $\Delta[\% \text{P}]$ are approximately 0.3 and 0.003, respectively.^{11,12} Substitution of these values into equation 11.1.5 gives $W_{fs}/W_b \approx 0.01$. In other words, when proper measures are taken to prevent excessive furnace slag carryover, the average quantity of carried-over converter or furnace slag is approximately 1% of the steel tapped. This quantity of slag carried over during tapping corresponds to a slag thickness in a 200 tonne ladle of 5.5 ± 3 cm, in general agreement with plant observations.¹¹

Hoeffken et al.⁹ observed that phosphorus reversion is more likely to occur when both the basicity, $\% \text{CaO}/\% \text{SiO}_2$, of the carryover slag is approximately 2 or lower and its iron oxide content is approximately 17% or lower. For iron oxide contents of approximately 25% or higher the phosphorus reversion is noticeably less, provided the slag basicity exceeds 2–2.5.

For heats that are tapped open, to which only ferromanganese and a small amount of aluminum are added, the steel is not sufficiently deoxidized to cause phosphorus reversion. In fact, in some cases of tapping open heats to which 0.3–0.6% manganese is added, the phosphorus content of the steel decreases by approximately 0.001% due to mixing of the carried-over furnace slag with the steel during tapping.¹¹

11.1.3 Chilling Effect of Ladle Additions

Ferrous alloys and fluxes added to the steel in the tap ladle affect the temperature of the steel in the ladle, usually resulting in a decrease in temperature. The effect of various alloying additions, including coke, on the change in temperature of the steel for an average bath temperature of 1650°C (3002°F) is summarized in Table 11.1. These data were calculated from the heat capacities and heats of solution of the various solutes.

Table 11.1 Effect of Alloying Additions on the Change in Temperature of the Steel in the Tap Ladle for an Average Bath Temperature of 1650°C (3002°F).

Addition to give 1% of alloying element at 100% recovery	Change in steel temperature $\Delta T, ^\circ \text{C} (^\circ \text{F})$
Coke	-65 (-117)
FeCr (50%), high-C	-41 (-74)
FeCr (70%), low-C	-28 (-50)
FeMn, high-C	-30 (-54)
FeSi (50%)	~0 (~0)
FeSi (75%)	+14 (+25)

It can be seen from Table 11.1 that ferrosilicon is the only ferroalloy that, upon addition, does not result in a decrease in steel bath temperature; in fact, the use of FeSi (75%) results in an increase