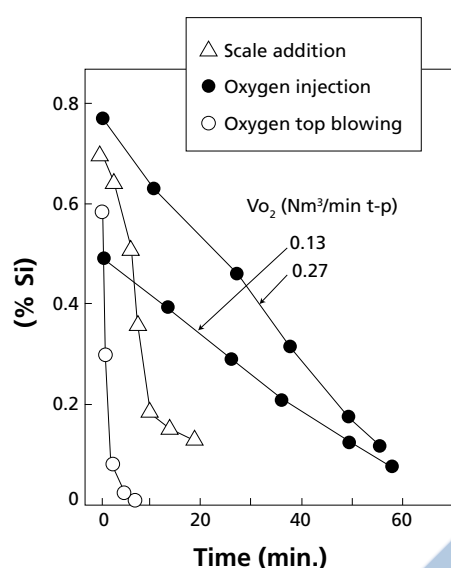
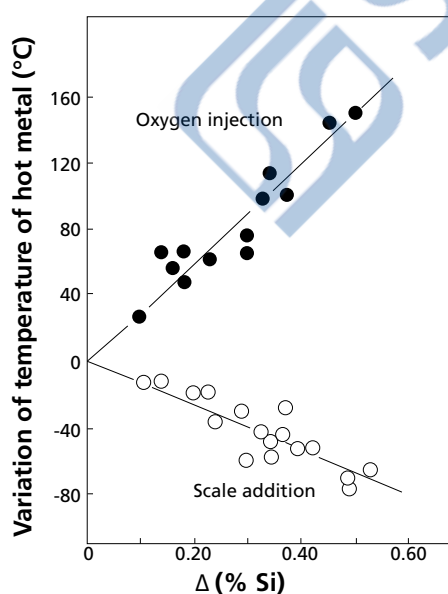


Efficient hot metal pretreatment to satisfy the requirement of low sulphur and phosphorus contents

Limited availability of high-quality ore as well as highly volatile prices of these selective qualities have inexorably influenced the conditions of ironmaking operations for some years, leading to a growing demand for hot metal pretreatment prior to further processing or ingot casting. Contents of sulphur, silicon, phosphorus and carbon are typically adjusted in hot metal pretreatments or refining facilities.



Comparison of desiliconization behaviour [5]



Desiliconization with gaseous and solid oxygen and variation of the hot metal temperature for desiliconization [5]

Since the 1980s, the quality of raw materials and fuels used in iron- and steelmaking has become increasingly worse. This global trend has led to a deteriorating hot metal quality in terms of higher contents of impurities. At the same time steelmakers have been faced with the growing demand for clean steel with low and ultra-low contents in particular of sulphur and phosphorus.

The decreasing availability of premium raw materials and fuels with low contents of unwanted and harmful elements and the growing pressure to lower production cost by purchasing cheap raw materials have led to a doom loop. In the past, western steelmakers generally responded to this challenge by optimizing their facilities, improving the degree of automation, introducing bottom stirring in BOF converters and by pushing the productivity of their production units to ever new records. But these efforts have come to an end and further progress can be only attained by alternative concepts.

In contrast, Japanese steelmakers opted for a different very radical path, focusing on intensive hot metal pretreatment taking advantage of the benefits of the low treatment temperature. As a result they established a different but competitive way of steelmaking.

It is the right time to call the concepts and results of hot metal pretreatment to mind and investigate which chances the application of these technologies to the conventional steelmaking route may provide.

Hot metal desulphurization

Sulphur in blast furnace (BF) hot metal mainly comes from fuels such

as coke, coal, and oil. With the exception of some very specific steel grades, sulphur is undesirable and has to be removed. Although the blast furnace is a very efficient facility for desulphurization and able to remove typically 85% of the total sulphur input, 15% remain in the produced hot metal. This is still too much to satisfy the requirements of steelmaking. Therefore additional desulphurization outside the BF is required [1].

Today desulphurization of hot metal is carried out by the following methods:

- injection of desulphurization agents into torpedo ladles,
 - injection of desulphurization agents into open ladles,
 - addition of desulphurization agents into open ladles using the KR impeller stirring system,
 - desulphurization in the BOF converter,
 - desulphurization in the steel ladle.
- The costs to remove 1 kg sulphur by different procedures is calculated [2] to be
- 27 US\$ if executed in the blast furnace,
 - 10.5 US\$ if done by hot metal ladle treatment,
 - 177 US\$ if done in the BOF converter,
 - 64 US\$ if done in the steel ladle.

The cost comparison clearly shows that desulphurization of hot metal is

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less costly than the effort of sulphur removal in the BF [2]. This topic has been discussed in detail [4]. The BOF converter is the most expensive unit to perform desulphurization and steel desulphurization should only be performed if necessary.

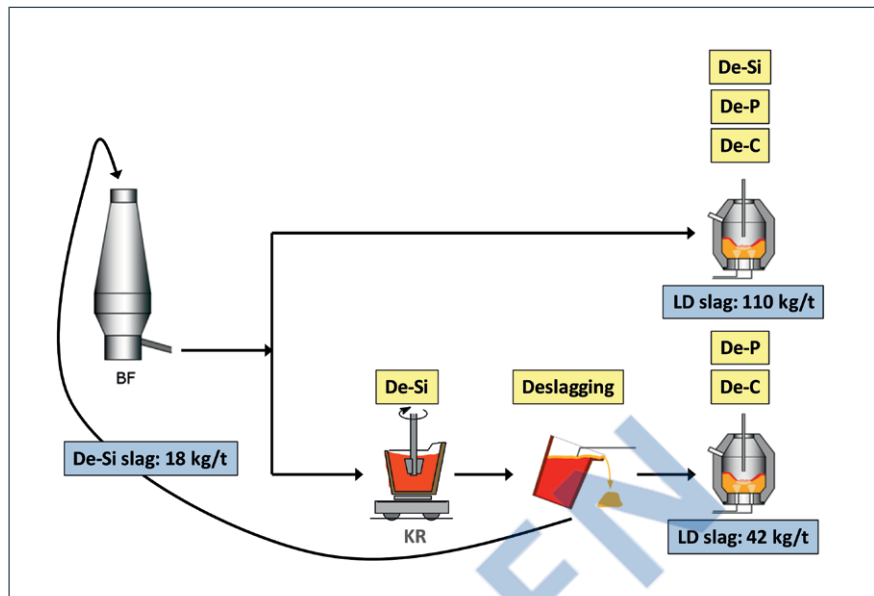
Hot metal desulphurization by injection technology is carried out by deep injection of powdery reagents like lime, calcium carbide, magnesium, soda ash, or mixtures thereof into ladles (torpedo ladles, transfer ladles, or BOF charging ladles). Refractory lined lances are immersed deep into the hot metal while the reagents are injected with high speed using mainly nitrogen as transport gas in mono-, co-, or multi-injection mode.

Efficient desulphurization requires intensive mixing of reagents, metal and slag. This is achieved with a gas/solid mixture deeply injected into a ladle. A minimum bath level of 1.5 m has to be ensured in order to maximize the residence time of the particles in the bath. Injection desulphurization in open ladles is more efficient compared to torpedo ladles due to their unfavourable shape. The consumption of reagents in torpedos is approximately 15 – 25% higher compared to open ladles.

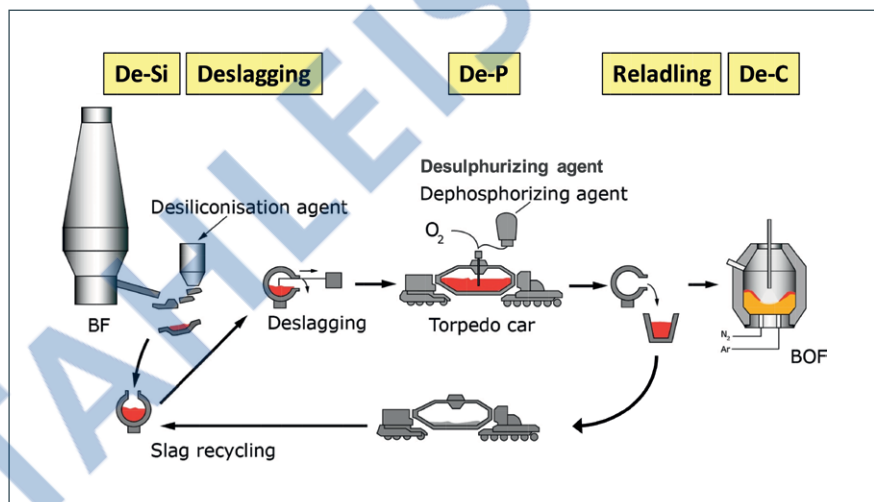
High mixing power is also achieved by mechanical stirring with an impeller. This technique is used by SPCO's KR (Kanbara Reactor) system [3]. While a refractory lined rotating impeller is immersed into the metal and thus providing a good mixing of reagent, metal and slag, cheap coarse lime is fed by a vibration feeding system as desulphurization agent. The KR system achieves very low sulphur levels at comparably low reagent cost. Investment cost and other operating cost of the KR are typically higher compared to the deep injection technology. In any case it is essential to properly remove the desulphurization process slag before the hot metal is charged into the BOF.

Hot metal desiliconization

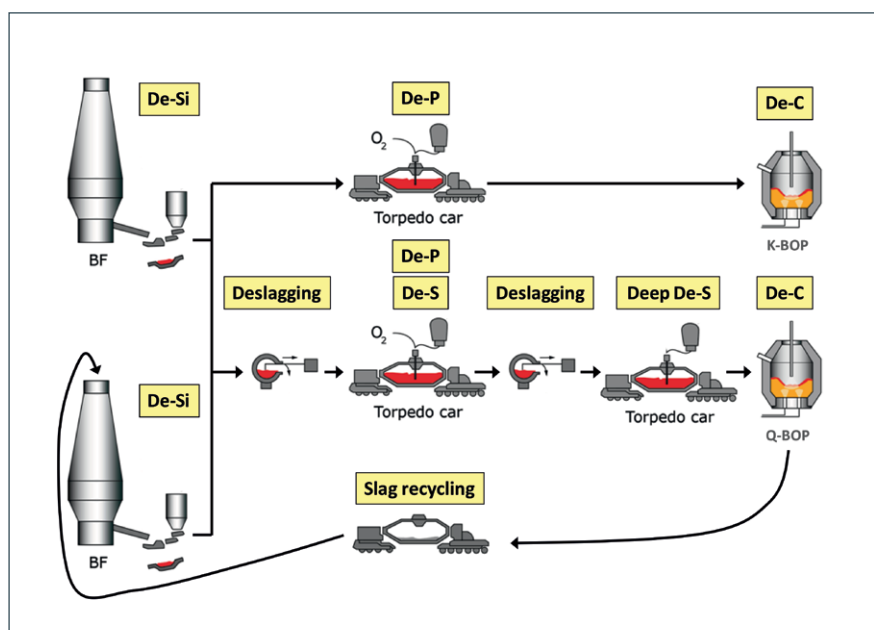
The silicon in hot metal comes mainly from the ash of the coke and the blast furnace operation. Silicon has a higher oxygen affinity than phosphorus and carbon. It is thus the first element to be oxidized during oxygen blowing in the BOF converter. The competi-



Process flow scheme of Nippon Steel's slag minimum refining process (SMP) [7]



The simple refining process (torpedo-based SMP) at Nippon Steel, Kimitsu and Yawata works [1]



Hot metal pretreatment process at Kawasaki Steel, Chiba works [8]

tive reactions of phosphorus and in particular carbon start with decreasing silicon content in the hot metal, depending on the temperature. High silicon content in hot metal of more than 0.7 – 1.0% leads to problematic oxygen blowing:

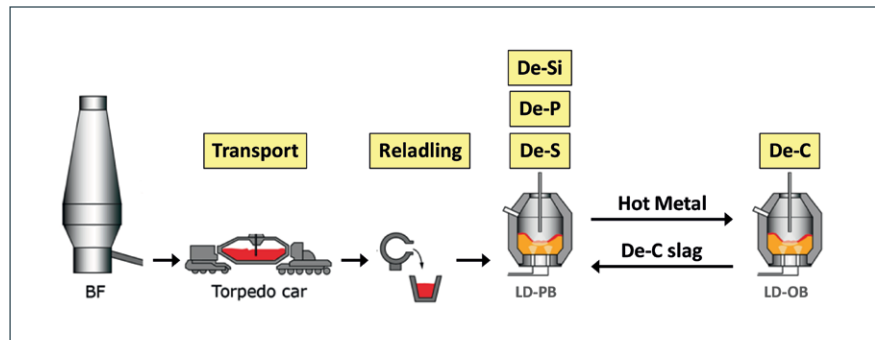
- increased consumption of lime in order to maintain a suitable basicity,
- increased iron losses in the slag,
- decreased BOF capacity due to increased slag amount,
- increased oxygen blowing time and thus decreased productivity (sometimes even a double slag practice is necessary),
- increased danger of slopping (instable blowing process).

Therefore control of the silicon content below say 0.7% is desirable and one of the benefits of hot metal desiliconization. Another reason is that a silicon content of less than 0.15% is necessary before effective dephosphorization can start.

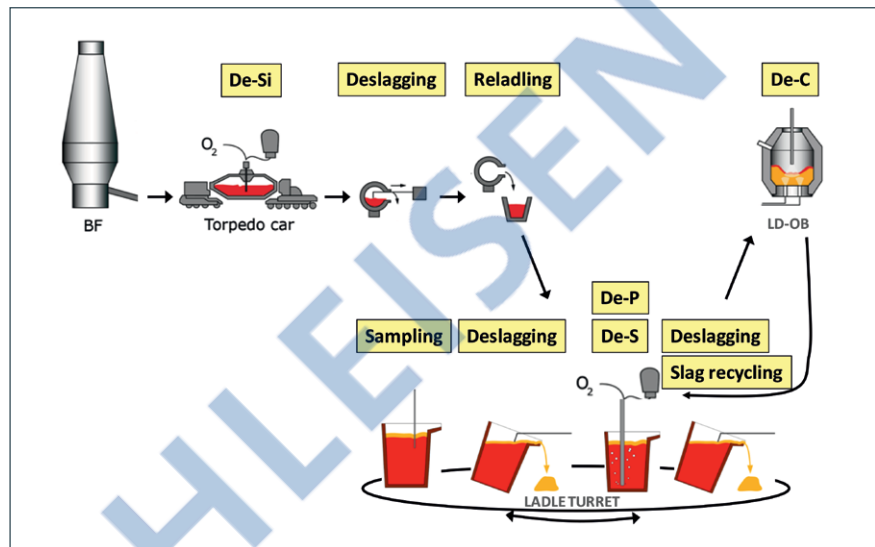
The ability to control the silicon content offers maximum flexibility regarding the hot-metal-ratio (HMR) and thus allows responding to varying scrap and raw material prices to minimize the BOF operation cost.

The process of hot metal desiliconization requires oxygen which can be supplied as gaseous oxygen or in form of iron oxides ("solid oxygen"). Hot metal desiliconization with solid oxygen drops the temperature by 10°C per 0.1% of removed silicon (e.g. using scales as source of solid oxygen). Including slag skimming this accounts for huge temperature losses in case of high initial silicon content in the hot metal. Desiliconization by means of gaseous oxygen is more effective compared to the addition of an agent. Assuming initial silicon content of 0.7%, approximately 1.4 m³ (s.t.p.) O₂ per t per 0.1% of removed silicon is required. The removal of silicon is a function of time for adding solid oxygen (here: scales), oxygen injection, and oxygen top blowing [5]. Blowing of gaseous oxygen for desiliconization is exothermic and increases the temperature by approximately 27°C per 0.1% of removed silicon. The huge amount of generated slag and fumes makes it challenging to control this process in ladles.

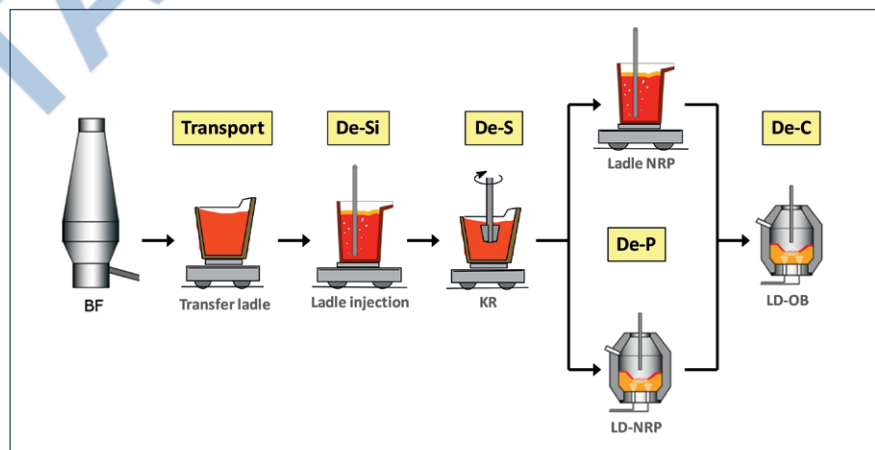
High mixing power of the desiliconization agents, metal and slag is



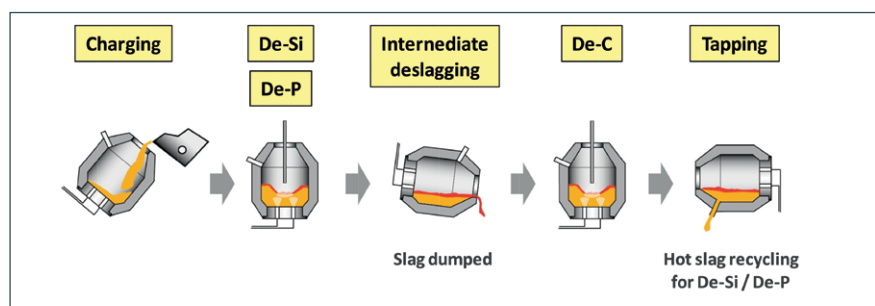
Converter-based pretreatment process LD-ORP at Nippon Steel, Nagoya works [9]



Ladle-based hot metal pretreatment process at Nippon Steel, Oita works [9]



Zero slag process (ZSP) at NKK's Fukuyama works [10]



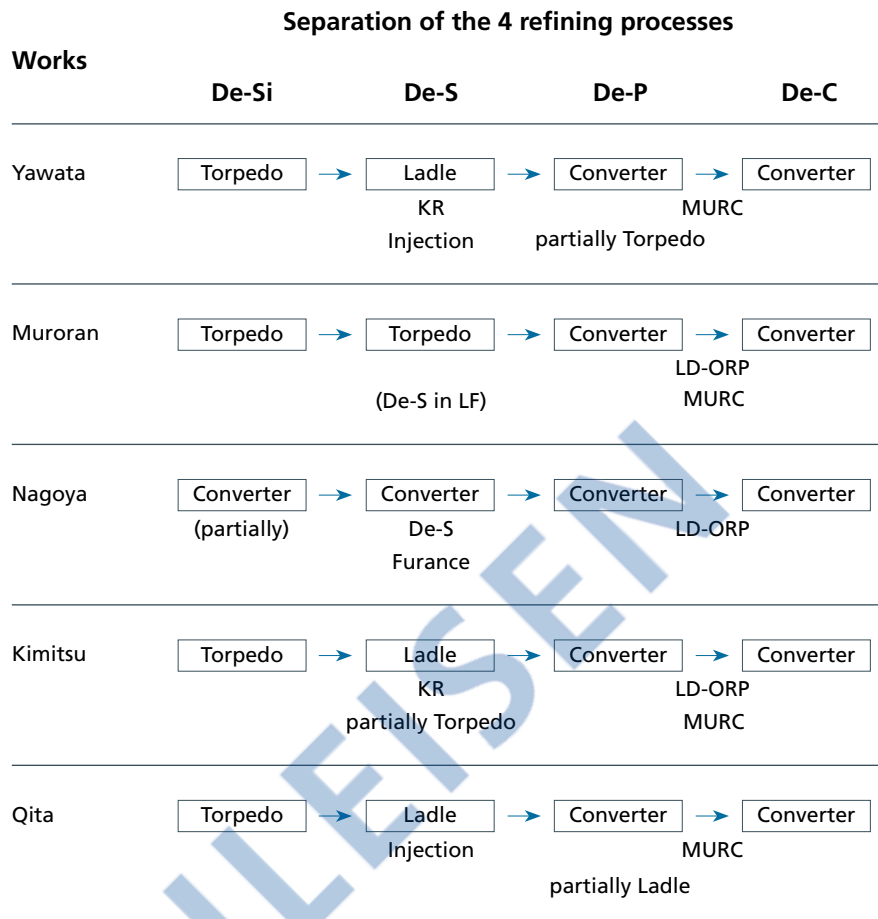
The multirefining converter process (MURC) at Nippon Steel [11, 12]

required for efficient desiliconization. This can be achieved by several methods, e.g. natural flow, gas stirring by injection, mechanical stirring with an immersed impeller. In general, the desiliconization efficiency of a process should be high enough to lower the silicon content to match with the requirements of proper oxygen blowing in the converter or to lower the silicon content to allow efficient dephosphorization.

The following methods are applied at industrial scale:

- top addition of desiliconization agents into the BF runner with or without slag separation by means of a skimmer blade or by adding the agents directly into the hot metal stream during reladling. In both cases the natural flow of the hot metal is utilized to generate mixing power.
- injection of desiliconization agents into torpedo ladles with or without simultaneous oxygen blowing,
- injection of desiliconization agents into open ladles with or without simultaneous oxygen blowing,
- top addition of desiliconization agents into open ladles using a KR impeller stirring system to provide mechanical stirring.

The first method (above) is cheap and simple as few equipment is needed but efficiency and predictability are poor. An addition of 10–20 kg sinter dust fines per t of hot metal achieves 30% removed silicon. Injecting the desiliconization reagents into the blast furnace runner increases the desiliconization rate to 40%. Nakasuga et. al. introduced a process using mechanical stirring with an impeller immersed in the hot metal runner. They report improved desiliconization rates up to 55% [6]. All these methods have fluctuations in the achieved silicon content, caused by varying temperature and varying flow velocity of the hot metal. The desiliconization rates obtained with these methods are normally sufficient to control the hot metal Si content below say 0.7% making it suitable for oxygen blowing in the BOF converter.



Overview of the hot metal treatment processes as applied at the different steelmaking works of Nippon Steel [12]

But desiliconization down to 0.15% – which is the precondition to proceed with dephosphorization – requires one of the other methods mentioned above. Injection of agents into torpedo ladles saves process time as the reactions can take place “on the road”. Due to the shape of the torpedo it is difficult to completely remove the high amounts of slag. As a result, the torpedo capacity is decreasing with every treatment as accretions accumulate inside and at the mouth.

Injection or top addition of agents into open ladles allow precise control of the final silicon content and adjustment of the temperature to a certain extent. Furthermore these methods often allow usage of existing facilities already used for desulphurization. Mill scale, magnetite fines, hematite fines or sinter dust are used as sources of solid oxygen in the desiliconization agent with similar desiliconization efficiencies. Lime and silica are added to flux the slag to adjust the basicity and prevent excessive foaming.

Figure	Desulphurization	Desiliconization	Dephosphorization
Process condition	Reducing	Oxidizing	Oxidizing
Oxygen activity	Low	High	High
Hot metal temperature	High	High	Low
Slag basicity (CaO/SiO ₂ -ratio)	High	High	High
Hot metal silicon content	High	-	Low (< 0.15%)
Hot metal carbon content	High	-	-
Mixing power of metal and slag	High	High	High

Favourable conditions for the single hot metal pretreatment steps

Hot metal dephosphorization

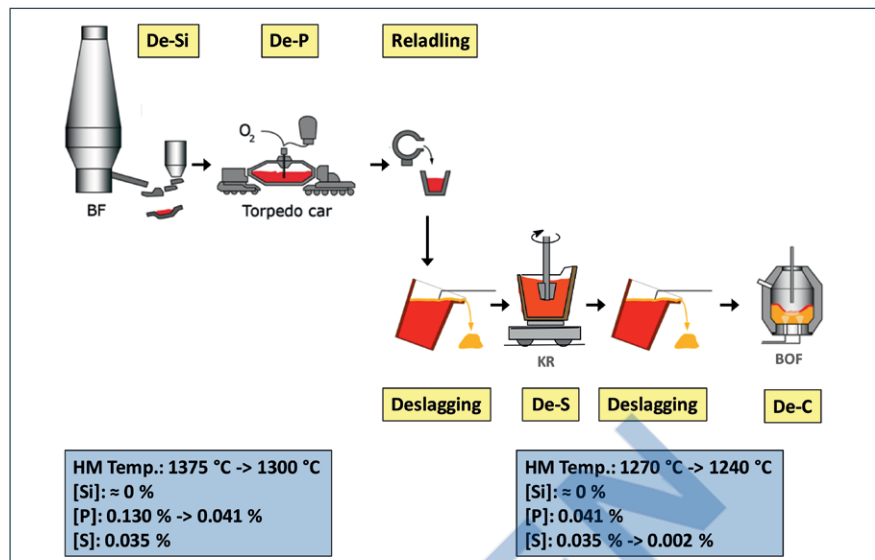
Phosphorus (P) in the iron ore fed to the blast furnace is converted into the hot metal by a rate of >90%. The only possibility to limit the phosphorus content of the hot metal is to use a low P-containing iron burden. It is thus clear, that higher P-content in hot metal requires higher efforts in steel-making operations [1].

The BOF converter is a highly efficient facility to perform dephosphorization especially when equipped with strong bottom stirring [1]. Anyhow several limitations call for alternatives like hot metal desiliconization and dephosphorization. Applying hot metal dephosphorization reduces the required slag amount during oxygen blowing, and ensures achieving consistently ultra-low phosphorus contents at the end of blowing. In this sense, hot metal pretreatment is of great help in reducing the metallurgical work load of the oxygen blowing process. Basically hot metal dephosphorization makes use of the same agents as desiliconization. Oxygen in solid and/or gaseous form is needed. Iron oxides like mill scale, sinter dust fines, iron ore fines (e.g. magnetite or hematite fines), etc. are used as sources of solid oxygen. Blowing oxygen onto or into desiliconized hot metal will simultaneously initiate strong decarburization. Due to the generation of CO gas, such a process is extremely difficult to be managed safely in an open ladle. Therefore hot metal dephosphorization is done either in ladles with the sole use of solid oxygen or in a converter which provides enough space to handle the foamy slag.

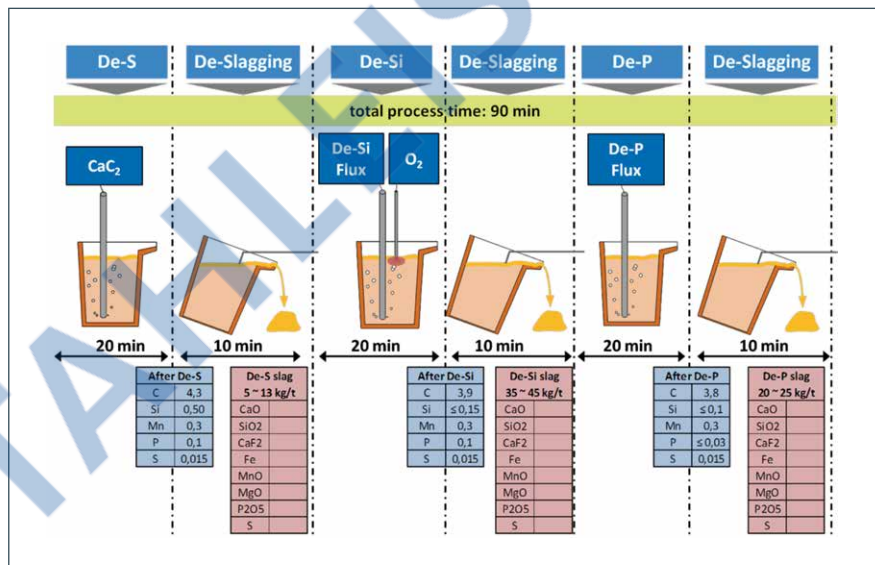
Similar to desiliconization, also dephosphorization of hot metal requires high mixing power. A simple addition of the reagent on the surface of the metal results in unacceptable long treatment time and tremendous temperature losses. Application of gas stirring via bottom bricks in the ladle improves the situation only slightly. Only deep injection of the reagents or mechanical mixing with impellers provide sufficient mixing power.

The benefits of hot metal dephosphorization can be listed as follows:

- Dephosphorization is more effective at lower hot metal temperatures than at steel temperatures.
- A lean slag BOF blowing process for decarburization can be established.



Possible process flow of hot metal pretreatment within the conventional BF-BOF route



Alternative sequence of hot metal pretreatment procedure within the conventional BF-BOF route

- Slag from a BOF process using dephosphorized hot metal contains no free CaO and allows direct utilization as construction material e.g. for road layers, etc.
- Slag from a BOF process using dephosphorized hot metal contains no P_2O_5 and can be re-utilized for hot metal dephosphorization or more easily as a feedstock for sinter plants.

Hot metal pretreatment

Process steps which are used to remove impurities from the hot metal can be summarized as hot metal pretreatment. These process steps are in-

serted between the blast furnace and the BOF converter. Main objective is the adjustment and control of the hot metal composition by removal of unwanted impurities like sulphur (desulphurization), silicon (desiliconization) and phosphorus (dephosphorization) along with their undesired inclusions (oxides, borides, nitrides, carbides, and chlorides). This is a precondition to produce clean steel. Less than 100 ppm total impurities are the standard requirement for quality steelmakers today.

Desulphurization of hot metal is a standard practice carried out in nearly all steel plants around the world while desiliconization and dephosphoriza-

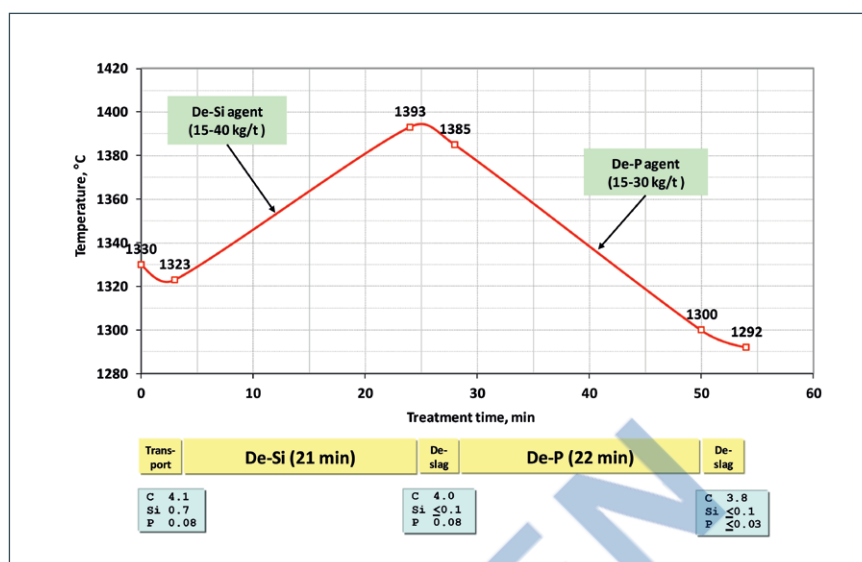
tion have so far not been in the main focus of Western steelmakers, in contrast to Japan, where steelmakers started to investigate and develop hot metal pretreatment technologies as early as 30 years ago. A variety of hot metal pretreatment processes and technologies have been developed, applied, and reported in several papers during recent years. All these processes use different vessels to carry out the metallurgical work of desiliconization, dephosphorization, and desulphurization. All kinds of combinations using different vessels and logistics have been tried and practiced over the years. The most common metallurgical vessels are the:

- blast furnace runner,
- torpedo ladle,
- open ladle (transfer or charging ladle), and
- BOF converter.

One of the early pioneers was Nippon Steel, which developed and introduced the slag minimum process (SMP) in 1983. The main idea of this process is to separate the desiliconization reaction from the dephosphorization and the decarburization reactions and separate the process slag. At industrial scale, this process consisted of hot metal desiliconization in the ladle using a KR impeller system. The BOF converter is then utilized for dephosphorization and decarburization. Advantages compared to the conventional process using the BOF converter for removal of (sulphur), silicon, phosphorus and carbon, were found to be reduced consumption of fluxes (mainly lime), reduced slag amount, and increased metallic yield. It is reported that the slag amount of this process for a hot metal silicon content of 0.15% is half compared to the conventional process [7].

Further investigations subsequently led to technologies using the injection of suitable reagents into (oversized) torpedo cars. This operation procedure offered significant benefits in terms of “less slag” production, slag recycling, etc. but it had also some disadvantages due to the excessive handling requirements and the huge temperature losses. Nippon Steel installed and operated the torpedo-based “simple refining process (SRP)” for hot metal dephosphorization in their Kimitsu and Yawata works [1].

Another Japanese steelmaker, Kawasaki Steel, installed and operated



Principle of the compensation of temperature losses by the Kuttner process

similar processes in their Mizushima and Chiba works, also using the torpedo ladle as reactor for dephosphorization. They applied the intensive pretreatment operations in dedicated hot metal pretreatment centres located between the blast furnace and the steel plant. Chiba works firstly used gaseous oxygen blowing during dephosphorization in the torpedo in order to reduce the tremendous temperature losses [8].

The huge slag generation due to oxygen blowing in the torpedo ladle during dephosphorization and a highly restricted scrap ratio led Nippon Steel's Nagoya works to modify their BOF converter into a hot metal pretreatment converter for desiliconization, dephosphorization, and desulphurization. After tapping and separation of the slag the pretreated hot metal is charged to another converter where decarburization takes place. This process was named LD-ORP (LD – optimized refining process) [9].

The first hot metal pretreatment centre using torpedo ladles for desiliconization and open ladles for dephosphorization and desulphurization was installed and operated at Nippon Steel Oita works. The process is completely based on the deep injection technology [9].

NKK's Fukuyama works (today: JFE) operated a hot metal pretreatment process where the silicon content of hot metal from the blast furnace is already lowered to 0.2%. The hot metal is then sent to the desiliconization station, where it becomes ultra-low silicon hot metal with a silicon content

of less than 0.1%. At the desiliconization station, oxygen gas is used along with sintered iron ore (iron oxide) as reagents for desiliconization. The reaction vessel is an open ladle, and the hot metal is vigorously stirred by injecting lime through an immersed lance. This method provides a highly efficient and stable supply of ultra-low silicon hot metal which improved the efficiency of lime for dephosphorization significantly. As a result, the slag generation throughout the entire steel-making process could be lowered to a minimum amount. Therefore NKK named this completely ladle-based process “zero slag process (ZSP)” [10].

A further development was the multirefining converter process (MURC) which allows desiliconization, dephosphorization and decarburization treatment in one vessel without tapping and recharging. Desiliconization and dephosphorization are carried out with a low basicity slag, high percentage of total iron content and a hot metal without previous desiliconization treatment. After dephosphorization the P-rich slag is tapped and sent for dumping. The slag of the following decarburization step is totally recycled as it remains as a hot feedstock in the converter for the next desiliconization and dephosphorization treatment [11, 12]. These converter-type hot metal pretreatment processes are today's standard operation practice in all works of Nippon Steel.

Beside the ability to produce clean steel with low and ultra-low contents of sulphur and phosphorus, there are

additional benefits of hot metal pretreatment. Benefits of hot metal desulphurization regarding blast furnace operation [1]:

- The BF can be released from some metallurgical work of desulphurization which increases BF productivity.
- Coke, coal, and flux charges to the BF can be reduced and the hot metal yield can be increased.
- The BF alkali balance can be improved due to operating at a lower basicity and a cost saving "lean slag" production becomes possible [4].

There are also benefits of hot metal desiliconization and dephosphorization regarding BOF operation, such as reduced refractory attack by the less acidic slag. Double slag technique, often applied in case of high silicon hot metal, can be avoided. This shortens the tap-to-tap time and increases productivity. The slag generated during oxygen steelmaking using dephosphorized hot metal has a low phosphorus content which allows utilization of this slag in the sinter plant as part of the feedstock for the blast furnace. Normally, the recycling of BOF slag in the blast furnace without previous hot metal dephosphorization is limited due to an enrichment of the phosphorus content in the hot metal.

Low contents of silicon, phosphorus, and sulphur in the hot metal allow operating the BOF for more or less decarburization only with minimum slag (less than 1/3 of the standard amount) and thus minimizing lime consumption. Besides the obvious saving, the so reduced slag amount leads to a smoother blowing behaviour, less slopping, and an easier control of the endpoint targets.

Converter operation with minimum slag even allows (partial) substitution of FeMn added at BOF tap by much cheaper Mn ore added as BOF (scrap) charge. Due to the small slag amount, the major portion of the manganese from the Mn ore is dissolved in the steel instead of being oxidized to the slag. This operation allows cost savings of several US\$ per t.

Anyhow, the rather smart hot metal pretreatment technologies did not have a major breakthrough outside of Japan and at some installations in Taiwan and South Korea. Today conditions have changed and there is an increasing need for steelmakers to in-

vestigate opportunities to benefit from including hot metal pretreatment steps in their existing conventional BF-BOF production route in order to relieve their production units from some metallurgical work.

Integration of hot metal pretreatment into the conventional process route

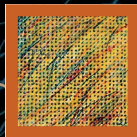
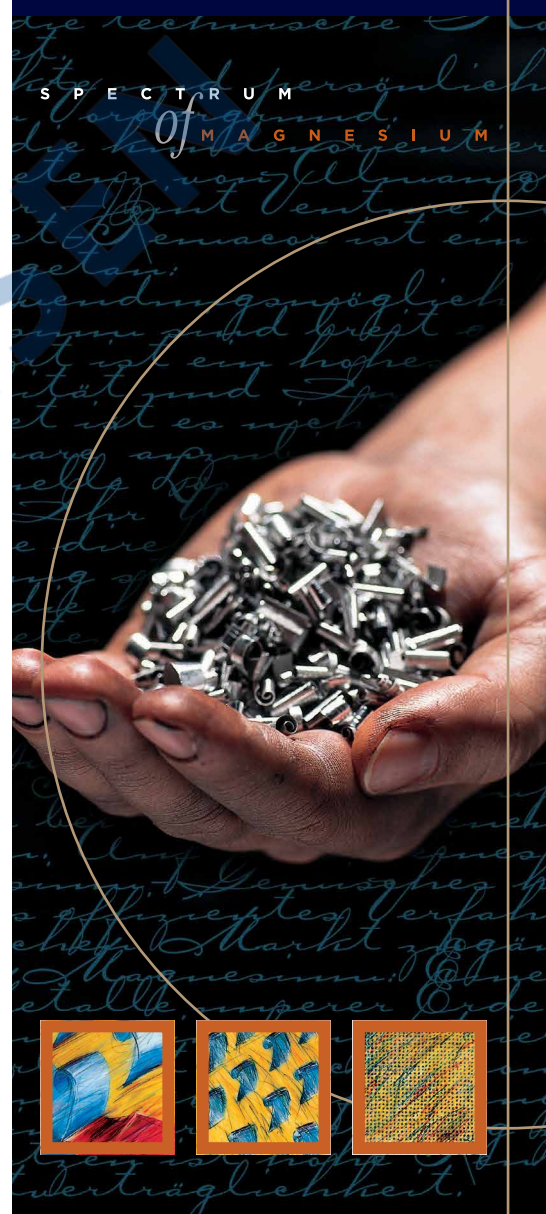
In order to evaluate the technical feasibility and the economic benefits, an optimum sequence has to be defined. Considering favourable conditions for the individual hot metal pretreatment steps and the typical logistics of the conventional BF-BOF steelmaking route, the process flow can be realized with little modifications. E.g., desiliconization can be performed in the BF runner with separation of the desiliconization slag during pouring into a torpedo ladle by means of a skimmer blade. This is followed by dephosphorization based on injection of agents into the torpedo ladle. After reladling into the BOF charging ladle, the dephosphorization slag is skimmed off. Desulphurization is then carried out by means of injection technology or a KR system. After the desulphurization slag has been removed, the hot metal is charged into the BOF converter and the decarburization process is performed by means of oxygen blowing. It is known that during desiliconization with a proper agent also a certain amount of sulphur is removed. This advantage can be utilized when desiliconization is carried out before desulphurization. Although this sequence is a "natural" sequence taking advantage of the "low cost" possibility to desiliconize in the BF runner as the first step, another sequence is often more advantageous from a thermodynamic point of view. After dephosphorization the oxygen activity of the hot metal is increased. This has a negative impact on desulphurization. In addition, desulphurization as well as desiliconization, both favour high temperature. In contrast, dephosphorization favours low temperature.

Summarizing, it can be said that an optimum sequence has to be individually selected for each installation depending on the available facilities, in particular existing vessels for desulphurization treatment, metallurgical targets, and the hot metal temperature.

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Many desulphurization stations for open ladles and torpedo ladles are in operation worldwide based on either injection technology or mechanical stirring technology (KR systems). These existing stations can be fairly easily extended to hot metal pretreatment stations, providing desiliconization and dephosphorization in addition to desulphurization when needed and beneficial. The major reasons why hot metal desiliconization and dephosphorization in open ladles did not have a real break-through in the international iron and steel industry are limited capacity of treatment facilities and huge temperature losses.

Existing treatment facilities especially for desulphurization are normally sized to meet the requirements of the converter cycle. Additional treatments in these facilities for desiliconization and/or dephosphorization lead to an increased load and thus the converter cycle can no longer be met.

Every treatment step causes a temperature drop of the hot metal: desulphurization injection, slag skimming, desiliconization injection, slag skimming, dephosphorization injection, and again slag skimming. In total this accounts for more than 100°C which often impedes the execution of all steps due to a too low final hot metal temperature. In particular the last dephosphorization step can often not be executed due to this reason.

Oxidation of carbon in a ladle process is especially critical due to the generation of CO gas and the excessive foaming of the slag. Therefore the oxidation of carbon during desiliconization and dephosphorization has to be limited and controlled to the best possible extent.

Küttner has designed a process for desiliconization and dephosphorization of hot metal which overcomes the drawback of huge temperature losses by using chemical heating with gaseous oxygen. The generated heat is tak-

en from the exothermic reaction of silicon with gaseous oxygen in contrast to the reaction of silicon with iron oxides. In order to control the temperature increase during the removal of silicon to the desired extent, a balanced supply of gaseous oxygen and injected solid oxygen from iron oxides deep into the ladle is used. As the silicon has to be removed for dephosphorization anyway, this effect can be utilized to compensate the temperature losses at least to some extent.

This process requires the injection of a mixture of CaO and iron oxide. Some additives are used to control slag composition and excessive slag foaming. The required reagents are injected as a premix in mono-injection mode or as single components using co- or multi-injection systems. At an incoming silicon content of 0.5% and 1,323°C, the consumption of desiliconization agent to achieve 0.15% [Si] is approximately 20 kg/t.

Phosphorus removal requires high mixing power to achieve a low phosphorus content. A dephosphorization rate of 70% (e.g. reduction of phosphorus from 800 ppm to 250 ppm) is achieved by injecting approximately 22 kg/t of a dephosphorization agent. It is almost impossible to achieve sufficiently high mixing power with top addition and lance stirring or bottom plug stirring. Injection of solids or mechanical stirring by an impeller are the preferred methods for hot metal dephosphorization.

Conclusions

Production of clean steel requires removal of all undesired impurities especially sulphur and phosphorus. The removal of sulphur from hot metal is already applied by most steelmakers but dephosphorization is traditionally carried out in the BOF at least by Western steelmakers. As this process is often already opti-

mized to its limits, additional incoming phosphorus contents can only be handled at the expense of increased production cost and reduced productivity. Purchasing premium iron ores with low phosphorus contents is often the only way to avoid these problems.

On the other hand, premium low phosphorus iron ores are significantly more expensive than ores with higher phosphorus contents. Therefore economic benefits can be gained by introducing selected hot metal pretreatment steps before charging the hot metal into the BOF converter.

By blowing pretreated low-P hot metal in the BOF converter, ultra low phosphorus steel grades with contents of less than 50 ppm can be easily achieved. Another benefit arises from a lean slag BOF operation which allows partial substitution of FeMn with many times cheaper Mn ore. Savings of several US\$ per t of steel can be achieved. Furthermore the generated BOF slag can be utilized as desiliconization agent or BF feedstock.

As many already existing desulphurization stations based on injection technology or mechanical stirring (KR) are suitable to be used also for desiliconization and dephosphorization, extension of desulphurization to triple-D is often just a short step. The main drawback of the ladle-based hot metal pretreatment technologies is the huge temperature drop of the hot metal with the already discussed negative effects on the downstream operations. A process concept has been described which utilizes the exothermal oxidation of silicon with gaseous oxygen in order to generate heat required to compensate the temperature losses at least partially. This process can be applied to the production sequence of nearly all plant concepts and layouts and thus helps to create capabilities of processing cheaper raw materials. ■

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