Advantages of Steel Production Quality/Cost and Operational Mechanisms with Dolomite Bricks in Steel Ladle

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Abstract

It is well known that much of the cost in steelmaking derives from ladle operation. During the ladle refining of steel the process of the dolomite refractory is a very complex and dependent many factor.

When studying the mechanisms of dolomite refractory ladle line study examined it is generally focused on below effects.

1.1-Thermal Termomecanical effects
1.2-Chemical and kinetic effects
1.3-Mechanical effects

Dolomite bricks have advantages in cost effective liquid steel production process quality improvements via below steps and subejcts.

2.1-Desulphurisation of the steel
2.2-Deoxidation and cleanliness of the steel
2.3-Improvements in the pourability of the steel
2.4-High specific heat

Our study covers the investigation of wear mechanisms of dolomite line and also the effect of dolomite bricks cost on the quality and cost processes of liquid steel production based on previous publications.

1. Introduction

1.1 Thermal Termomecanical Effects

During the operation of steel ladles in ladle metallurgy there is some thermal/termomecanical effects can brief as below:

- The wear of the slagline refractories of the ladle is initiated at the preheating station, through the redoxidation reactions.

- The degree of the decarburization process is mostly dependent on the preheating fuel. Other factors like the refractory composition and preheating time are also of great importance.

- For the refractories without antioxidants, the refractory decarburization is slower when coal gas is used during ladle preheating than when a mixture of oil and air is used.

- Ladle preheating of the refractories without antioxidants leads to a direct wear of the slagline refractories. This is due to the total loss of the matrix strength, which results in a sand-like product. This finding was found to be independent of the preheating method. [1]

- During the continuous cooling and heating of the ladle due to the operating conditions, the wear rate at the start of working with the hot metal is higher than the average wear rate at the next dies. In the Dolomite-C bricks, under the thermomechanical effects, the bricks are deformed at a higher rate and the wear rate in the form of shells is accelerating.

- The resulting thermal stresses form fine capillary cracks inward from the hot surface of the brick, creating slag on the hot surface and shell deposits resulting in steel infiltration.

- The horizontal and vertical expansion of the resin-bound Dolomite-C brick used to remove such thermomechanical effects in the steel ladle must be well calculated and spaced so as to optimize the thermal stresses. The tensile strength of the Dolomite-C bricks is lower than the compressive strength.

\[
\frac{dT_{\text{max}}}{dt} = Gf(1/p)\lambda \alpha E
\]

\( t = \text{time} \)
\( T = \text{max. temp} \)

Thermal shock resistance is directly proportional to tensile strength, poise value and thermal
Conductivity but inversely proportional with elastic modulus and thermal expansion coefficient.

Changes in the working temperature of the steel in the ponds and changes in the post-treatment temperatures of the operating conditions initiate excessive wear. Potential changes in the thermal state of the ladle prior to casting, sudden changes in temperature, thermal stress on the brick, and heterogeneous refinement become homogenous during operation, increasing the wear rate.

In heating, Dolomite-C and Mg-C bricks which are connected to the resin at 600-900 °C are waiting for a long time, resulting in C-oxides. Carbon burnout at these temperatures is the result of small pores in the Dolomite-C brick becoming larger cavities, making the slag and steel more susceptible to chemical erosion. At temperatures above 900 °C, most of C is coking and closing pores. The heat in the coking coal leads to the formation of capillary cracks. [2]

The wear of the ladle slagline refractories does not only take place during steel refining, but also at the pre-heating station through the redoxidation reactions. The degree of decarburization of the redoxidation reactions is dependent on the refractory composition as well as the preheating conditions (time and fuel). The reaction products from the burning fuel contribute to the redoxidation corrosion of the refractory as shown by reactions [1]

\[
\begin{align*}
\text{CO}_2 (g) + C(s) &= 2\text{CO} (g) \\
\text{H}_2\text{O} (g) + C (s) &= \text{CO} (g) + \text{H}_2 (g)
\end{align*}
\]

In dolomite-C bricks, the sudden thermal changes are accelerated by the end-expiratory spalling of the dolomite-C brick after completion of the operation without completion of the expansion. Thermal differentials are the result of sudden and rapid temperature fluctuations and non-linear temperature differences in the brick wall. High permanent expansion occurs as a result of spalling bricks if they have appropriate design and development as a result of releasing tension. [2]

1.2 Chemical and Kinetic Effects

In very simple terms slag engineering can be defined as the balance between the refractory oxides (CaO and MgO) and the fluxing oxides (SiO$_2$, Al$_2$O$_3$, CaF$_2$ and iron oxide) This balance is typically expressed as a basicity ratio:

\[
B_{50} = \frac{\text{Refractory Oxides} \times \%\text{CaO} + \%\text{MgO}}{\text{Fluxing Oxide} \times \%\text{SiO}_2 + \%\text{Al}_2\text{O}_3 + \%\text{CaF}_2 + \%\text{FeO})}
\]

The following simple set of figures give a graphical view of the balance between the refractory oxides and fluxing oxides. [3]

- The formation of liquid phases by the impurity oxides during service has a big effect on the high-temperature strength of the refractory and their wear resistance.

- The slags rich in iron oxide lead mostly to the oxidation of carbon in the carbon containing refractories leading to an increased porosity and wettability, and therefore a reduced corrosion resistance.

- The high contents of alumina and/or silica in the slag promote reactions between the slag components and the dolomite-carbon refractory. This leads to the formation of low-temperature melting phases such as calcium aluminates and silicates.

The corrosion of oxide-carbon refractories by slag during steel refining is a complex process involving numerous mechanisms and factors. The most important corrosion mechanisms leading to a severe wear of the slagline are:

I. Oxidation-reduction processes, caused by the reactions between the easily reducible oxides such as FeO and the main components of the refractory.

II. Dissolution/diffusion, a chemical process by which the refractory material is dissolved into slag.

III. Penetration, whereby the slag infiltrates the refractory structure leading to structural/chemical changes (or structural spalling).

IV. Erosion, which is the abrasive wear of the refractory caused by the movement in liquid steel and slag.

The steel refining slag, rich in alumina and silica, attacks the dolomite refractory mainly through reactions with CaO in the refractory. This leads to the formation of low-temperature melting phases such as calcium silicates and aluminates. These can easily be eroded by slag due to forced convection during ladle treatment. This is the possible explanation for the accelerated wear of the dolomite-carbon refractory during steel refining. [1]

Among the refractory compounds used in steel ladles, only carbon can be affected by a dissolution in steel. For example carbon (residual carbon from the binders or additional carbon in Dolomite-C bricks) can be dissolved directly into the liquid steel. The corrosion between refractory lining and slag is often controlled by a direct dissolution, chemical exchanges are controlled by a boundary layer at the liquid/refractory interface. The gradient of chemical potential, which is usually assimilated to a
composition gradient, is the driving force of the corrosion process. Two elementary steps manage the dissolution mechanism:

- a thermo chemical reaction at the solid/liquid interface
- a diffusion of species. [4]

Solid oxides (CaO + Al₂O₃ + MgO + SiO₂) in the liquid slag layer, ferro alloys and non-metallic additives directly affect the performance of the slag steel ladle. In case of contact with slag in refractory material, wear is occurring due to stable, dense, low slag and gas. The excess of FeO, MnO, SiO₂ in slag and alkali excess cause the deterioration of the brick carbon structure and the MgO / CaO matrix structure. Increasing the ratio of MgO and CaO in the slag, increases the basicity and C prevents the structure from deteriorating.

The higher the MgO / CaO ratio in the slag, chemical corrosion is reduced to the pores of the dolomite bricks. During the waiting of the steel in the ladle and slag attack when repeated operations of Dol-C brick after the extinction of formed thin film in the front surface chemical attacks reaches maximum level. [2]

Near the hot face, where more oxidising conditions prevail (PO₂ = 10−8 at), the previous gaseous species Mg, SiO and/or Si react with either CO₂ or O₂ to revert back to an oxide form. This leads to the well-known phenomenon of magnesia transport to compensate for carbon oxidation on the hot face. MgO is reduced within the brick.

MgO and CaO entering the slag during mass loss can be written as follows:

\[
\frac{-dr}{dt} = k \frac{\chi_{\text{MgO}} - (\text{MgO})_{\text{ph}}}{100\rho} \tag{7}
\]

The slag penetrates into the refractory material very quickly reacts with the MgO / CaO grains. The slag penetration is like a branch of a roots in a pore. First, the main body (large MgO / CaO grains in the surface) then reaches all its branches. (All pores of the brick) [2]

\[\text{Figure 1. Schematic of the interaction of the different corrosion mechanisms leading to the severe wear of the oxide carbon refractories during steel refining [1]}\]

Increase of chemical penetration of the slag related with the increase in pore diameter and appearent porosity and reduce of FeO concentration, basicity and temperature begins to accelerate penetration.

The state of dissolution rate in liquid slag for refractory allow for the quick depletion of the thickness of the refractory bricks. Often the transfer of solid mass to liquid steel and the rate of deterioration (mass loss) result in the following equation.

\[
\frac{-dr}{dt} = A_0 \cdot U \tag{5}
\]

\[
v = k(n_s - n_b) \tag{6}
\]

- Atmospheric oxidation (especially during preheating).
- FeO and MnO in the slag undergo brick oxidation.
- Corrosion on the surface when directly working with hot metal is directly related to steel C ratio.
1.3 Mechanical Effects

Besides the cold/hot crushing and other strengths, modulus of rupture of Dolomite-C bricks plays an important role in mechanical effects. Strength to impact and mechanical erosion is important for regional performance.

Penetration from liquid slag also reduces the mechanical strength. Siebring and Franken defined the penetration of the slag into the refractory wall with the following equation.

\[ \Delta P = \frac{4 \sigma \cos \Theta}{d} \]

where

- \( \Delta P \) = pressure differentials in capillary cracks
- \( \sigma \) = liquid-gas tension in the surface (N / M)
- \( d \) = capillary pore diameter (m)
- \( \Theta \) = slag contact angle with refract

As you can see from the equation above, pressure need to fill the pores. Horizontal slag penetration depth is related with the following equation.

\[ L^2 = \frac{6 \sigma \cos \Theta t}{\eta} \]

where

- \( L \) = penetration depth
- \( \sigma \) = liquid slag on the surface
- \( \eta \) = slag viscosity (Pa.s)
- \( t \) = time (s)

Viscosity is the most important factor in penetration. When the slag dissolves some of the refractory oxides from the brick surface, the slag viscosities increase, which in turn increases the slag resistance. Refractories with higher porosity dissolve in slag faster. The equation of analysis for vertical penetration is also below (wanibe);

\[ L = \frac{2 \sigma \cos \Theta}{R \rho g} \]

where

- \( L \) = radius of radius
- \( \rho \) = density of slag (kg / m3)
- \( g \) = stable draft (ms⁻²)

In order to reduce the penetration, it is necessary to decrease the surface tension, increase the viscosity and to have the contact angle \( \Theta > 90 \). As a result of the slag penetration, dissolved MgO / CaO materials enter the slag and break the slag structure, resulting in different stresses, cracks and crusts between the slag and the refractory.

CaO / MgO in dolomite brick content includes optimizing the costs of steel production quality processes. [2]

1.4 Desulphurisation of the Steel

The CaO/MgO present in dolomite bricks favours desulphuration Dolomitic linings are ideal for withstanding the impact of very basic slags, saturated in lime, and at the same time provide less steel oxidation, thus facilitating conditions for a rapid desulphurisation of the steel. [5]

Desulphurisation of liquid steel is obtained by metal-slag stirring in secondary metallurgy. The lime in the ladle slag reacts with the sulphur dissolved in the steel and with a deoxidation element, forming calcium sulphide and the oxide of the reduction compound. [4]

\[ CaO + S = CaS + O + Xi = XiO \rightarrow CaO + S + Xi = CaS + XiO \]

The sulfur dissolved in the steel can be removed from this by interactions between steel and slag, according to (K12)

\[ S + CaO \rightarrow O + CaS \]

In secondary steelmaking it is essential to know the composition and amount of ladle slag just after tapping in order to be able to modify the ladle slag for the purpose of deoxidation and desulphurization. Normally, lime (CaO), alumina (Al₂O₃) and slag deoxidizer are used to modify the ladle slag. For steel desulphurization it is important to reduce the mass content of FeO and MnO to a low level. The desulphurization process uses the following different steps.

Slag adjustment with respect to (i) slag deoxidation, and (ii) lime saturation
Slag homogenization and liquefying
Reduction of FeO and MnO
Intensive stirring for desulphurization

CaO is the main component. It is hygroscopic and leads to the pick-up of hydrogen (H₂) in the steel. Sulphur is thus an undesirable element in steel. Manganese actively reacts with iron sulphides during solidification of steel transforming FeS to MnS according to the following reaction.

\[ FeS (slag) + Mn (steel) = MnS (slag) + Fe \]

The melting temperature of manganese sulphide (MnS) is comparatively high (around 1610 deg C). [7]
Sulfide capacity as a function of saturated MgO It shows that for better desulfurization reaction rate, it will be very effective to decrease the MgO content. Likely effect on increasing viscosity.

**Figure 2.** Sulphide capacity as a function of CaO content of slag [5]

![Figure 2](image)

It was concluded that sulphide capacity of steel slag has a strong effect on composition of CaO of the slag. Sulphide Capacity has poor correlation with Fe concentration in slag.

Also it was seen that sulphide capacity (Cs) decreases to a much lower value with increase in MgO. This can be attributed to the fact that MgO increases the viscosity of the slag which in turn decreases the sulphur partition ratio or in other words the ability to form sulphides decreases and correspondingly increases the sulphur content of the hot metal. [5]

1.5 Deoxidation and Cleanliness of the Steel

The choice of refractory products for metal cleanliness must also take into account the metal-slag-refractory reactions which may occur during elaboration. It is indeed not rare to find often undesirable elements in the liquid steel or in the inclusions coming from impurities or even made of refractory products. [4]

The main component of sintered dolomite is lime oxide (CaO). Of all refractory oxides, it is the one that possesses least oxidisation potential, and therefore leaches less oxygen into the steel that may react with other metal elements to produce non-metallic inclusions. It is therefore the most suitable lining for the production of steel, free of inclusions such as alumina from the oxidisation of aluminium or other refractory bricks. [5]

![Figure 3](image)

Figure 3. Sulphide capacity as a function of saturated MgO It shows that for better desulfurization reaction rate, it will be very effective to decrease the MgO content. Likely effect on increasing viscosity [5]

![Figure 4](image)

Figure 4. Inclusion distribution for each diameter range (µm) (a) before and (b) after vacuum treatment. Phases: 1 - ASlag-liq + ASlag-liq#2; 2 - ASlag-liq; 3 - ASlag-liq + ASpinell; 4 - ASlag-liq + ASpinell + (a) AMonoxide, (b) Mullite; 5 - ASlag-liq + AMonoxide; 6 - ASlag-liq + AMonoxide + AMonoxide#2; 7 - ASlag-liq + AMonoxide +
AMonoxide + a-Ca$_2$SiO$_4$; 8 - ASlag-liq + AMonoxide + a-Ca$_2$SiO$_4$; 9 - ASlag-liq + Mullite; 10 - ASlag-liq + a-Ca$_2$SiO$_4$.

An important source of reoxidation is the carryover of slag from the steelmaking furnace to the ladle, which contain a high content of FeO and MnO. These liquid oxides react with the dissolved aluminum to generate solid alumina in the liquid steel, owing to the strong favorable thermodynamics of the following reactions:

$$3\text{FeO} + 2\text{Al} = \text{Al}_2\text{O}_3 + 3\text{Fe}$$ (15)

$$3\text{MnO} + 2\text{Al} = \text{Al}_2\text{O}_3 + 3\text{Mn}$$ (16)

The higher is the FeO and MnO content in the ladle slag, the greater is the potential for reoxidation and the corresponding generation of alumina inclusions. Many slivers in the final product have been traced to reoxidation that originated from FeO in the ladle slag. [10]

1.6 Improvements in the Pourability of the Steel

Nozzle clogging is a serious productivity and quality problem in continuous casting.

![Figure 5. Schematic of steel flow pattern in a submerged entry nozzle (SEN) with clogging](image)

The Al$_2$O$_3$ particles stick in the nozzle decreasing the casting velocity, and can even stop casting altogether (clogging). [6]

One of the goals of these treatments, on aluminium killed steels, is to improve the castability of these grades by transforming the alumina deoxidation inclusions into liquid lime aluminate inclusions. These liquid inclusions, contrary to alumina, do not stick to the nozzle refractories, which they even tend to dissolve when they are too rich in lime. During treatment, calcium, having a higher affinity for oxygen than most metallic elements used in iron and steel making, can reduce, at least partially, some constituents of the refractories (SiO$_2$, Cr$_2$O$_3$, Al$_2$O$_3$, ...) A notable improvement in the efficiency of a calcium addition was, for example, noted when high alumina ladle refractories were replaced by dolomite or magnesia refractories, more stable with respect to alkaline earth elements. This transformation made it possible to increase drastically the percentage of ladles cast in billets without clogging of the calibrated nozzle.

The average composition of inclusions obtained following too large an addition of SiCa to steel in a dolomite ladle. These inclusions, have a final composition of 55% MgO-35% CaO-10% Al$_2$O$_3$ after following the path shown on the figure during treatment.

They are solid at casting temperature (T$_{liq}$ > 2400 °C) and, like most solid inclusions, may stick to the refractory walls and especially participate in nozzle clogging. The reliability of calcium treatment thus requires not only an optimisation of added quantities, but also an adequate selection of the refractory in contact with the metal. [4]

Alumina clogging can be reduced by adding calcium to the steel to prevent the formation of solid alumina. As shown in Figure 8, for a typical melt temperature of 1550 °C, liquid is the equilibrium phase for calcia-alumina mixtures containing 40 - 60% alumina. Furthermore, it is believed that under steelmaking conditions, mixtures containing a higher fraction of alumina will be also be liquid. This is based on the observation that when CaO-2Al$_2$O$_3$ inclusions (79% alumina) are found in the final cast product, these inclusions take a spherical form and the nozzle experiences much less clogging. [11]

![Figure 6. Calcia-Alumina Phase Diagram](image)

The reduction in non-metallic inclusions in the steel such as alumina reduces the risk of clogging nozzles during pouring, especially if aluminium-killed steel is being produced. [5]

In aluminum killed steels, calcium is widely used to convert the solid alumina inclusions into liquid calcium aluminate inclusions which form as spherical particles due to surface tension effects. This transformation prevents the nozzle clogging due to the accumulation of solid alumina inclusions.
CaO fragments that pass from dolomite brick to steel provide the Ca-Treatment in steel with less additional Ca.[2]

1.7 High specific Heat

*Improved insulation, increasing energy savings.*

The secondary metallurgy is a high energy-intensive step in steelmaking process as it requires an accurate match of the composition and temperature of the molten metal during the ladle refining, the steel ladle lining plays an important role on the energy consumption of the process, as the refractory thermal properties are strictly related to the ladle ability to keep constant the molten metal temperature. [13] Below you can see some thermal conductivity calculations with different lining types.

Table 1. Thermal calculations for ladle lining

<table>
<thead>
<tr>
<th>Ladle Refractories Thermal Conductivity Values</th>
<th>Magnesia-C (1093°C)</th>
<th>Dolomite-C (1093°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slag Level</td>
<td>8.5 W/mK (12 Carbon)</td>
<td>3.5 W/mK</td>
</tr>
<tr>
<td>Steel Level</td>
<td>6.8 W/mK (10 Carbon)</td>
<td>2.6 W/mK</td>
</tr>
<tr>
<td>Bottom</td>
<td>6.8 W/mK (10 Carbon)</td>
<td>2.6 W/mK</td>
</tr>
</tbody>
</table>

Table 2. Thermal calculations for Dol-C lining

<table>
<thead>
<tr>
<th>Dolomite-C Lining Thermal Calculations</th>
<th>Heat Loss</th>
<th>(W/M/Deg.C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hot Face Temperature</td>
<td>13288,43</td>
<td>Deg.C</td>
</tr>
<tr>
<td>1st Interface Temperature</td>
<td>1680,00</td>
<td>Deg.C</td>
</tr>
<tr>
<td>2nd Interface Temperature</td>
<td>913,41</td>
<td>Deg.C</td>
</tr>
<tr>
<td>Cold Face Temperature</td>
<td>873,14</td>
<td>Deg.C</td>
</tr>
<tr>
<td>Bottom</td>
<td>393,31</td>
<td>Deg.C</td>
</tr>
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</table>

Table 3. Thermal calculations for Mg-C lining

<table>
<thead>
<tr>
<th>Magnesia-C Lining Thermal Calculations</th>
<th>Heat Loss</th>
<th>(W/M/Deg.C)</th>
</tr>
</thead>
<tbody>
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<td>Hot Face Temperature</td>
<td>18992,65</td>
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<tr>
<td>1st Interface Temperature</td>
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</tr>
<tr>
<td>Cold Face Temperature</td>
<td>1205,21</td>
<td>Deg.C</td>
</tr>
</tbody>
</table>

2. Conclusion

Dolomite-C refractories are highly cost effective with long service life with low cost than other other type of ladle linings. Dolomite-C refractories have low oxidation potential and help desulphurization. Also good chemical any physical properties make it favourable in secondary steelmaking metallurgy. This properties also makes it possible to reduce furnace tapping temperatures, and therefore create energy saving.

References

International, Iron and Steel Institute of Japan, June 2002

