HIGH GRADE LADLE LINING CONCEPTS FOR THE PRODUCTION OF ULC STEEL[1]

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Abstract
Refractory linings for the production of ultra low carbon (ULC) steel have to meet numerous requirements. This paper provides an overview of several high grade ladle lining concepts for this application. The different product groups are described, including their advantages, disadvantages, and the optimal application areas. Whilst both carbon-free and carbon-containing refractories are used for the production of ULC steel, in the case of the latter refractory type certain parameters must be taken into account to avoid carbon pick-up. A further decision criteria for the selection of suitable refractory materials is the slag composition. For example, high-alumina refractories are principally used in the case of Al-killed steel grade production and in applications where the slag contains more than 15% Al_2O_3. In addition, monolithic linings are an economic solution for sidewall and bottom linings, whilst magnesia-carbon bricks are the most common and reliable solution for the slag line. Ultimately, in collaboration the steel manufacturer and refractory supplier must make an informed choice from the extensive refractory material options to design a tailor-made refractory solution for steel ladle linings.
Key words: Ultra low carbon steel; Refractory; High-alumina; Magnesia; Monolithic; Chromite

CONCEITOS SOBRE O REVESTIMENTO DE ALTO GRAU DE PANELA DE FUNDIÇÃO PARA A PRODUÇÃO DE AÇO DE ULC

Resumo
Os revestimentos refratários para a produção de aço de baixo teor de carbono (ULC) devem atender a inúmeros requisitos. O presente instrumento apresenta um resumo dos diversos conceitos sobre o revestimento de alto grau de panela de fundição para essa aplicação. Os diferentes grupos de produto são descritos, incluindo suas vantagens, desvantagens e as áreas favoráveis para aplicação. Enquanto tanto os refratários contendo carbono como os sem carbono são utilizados para a produção do aço de ULC, no caso do último tipo de refratário, certos parâmetros devem ser considerados para evitar a absorção de carbono. Um outro critério decisivo para a escolha das substâncias refratárias apropriadas é a composição de escória. Por exemplo, os refratários de alta alumina são utilizados principalmente no caso da produção da classe de aço Al-killed e nas aplicações em que a escória contém mais de 15% de Al_2O_3. Além disso, os revestimentos refratários monolíticos são uma solução econômica para os revestimentos inferiores e laterais, enquanto que os tijolos de magnésia-carbono são a solução mais comum e confiável para a linha de escória. Por fim, juntos, o fabricante de aço e o fornecedor de refratário devem fazer uma escolha entre as diversas opções de substância refratária para produção de uma solução refratária feita sob medida para os revestimentos da panela de fundição de aço.
Palavras-chave: Aço baixo carbono; Refratário; Magnésia; Monolítico; Cromita

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3 *Marketing Steel Production, Ladle Wear Linings for the Production of ULC Steel Grades, RHI Refractories*

1 INTRODUCTION

Over the last few years, the importance of ultra low carbon (ULC) steel grades has steadily increased. When designing a complete ladle lining system, these demands for ULC steel must be taken into account. The following criteria are important for the selection of the optimal ladle wear lining:

- Minimal influence of refractory material on steel quality:
  - Prevention of carbon pick-up
  - Prevention of non-metallic inclusions
  - Prevention of Cr- and Mg- pick-up
- Parameters that affect the refractory material lifetime:
  - Maximum temperature
  - Slag composition (CaO/SiO_2, Al_2O_3, and CaF_2)
  - Heats per day and intermediate stops
  - Oxygen potential and vacuum
  - Hydrodynamics and the influence of purging
- Safety and high reliability:
  - Break out minimization
  - Early failure minimization
- Environmental requirements:
  - Chrome-free
  - Low emissions and non-toxic
- Price/performance:
  - Balanced lining
  - Cost per tonne of steel

A summary of solutions to meet the requirements regarding the prevention of carbon pick-up are detailed in Figure 1.

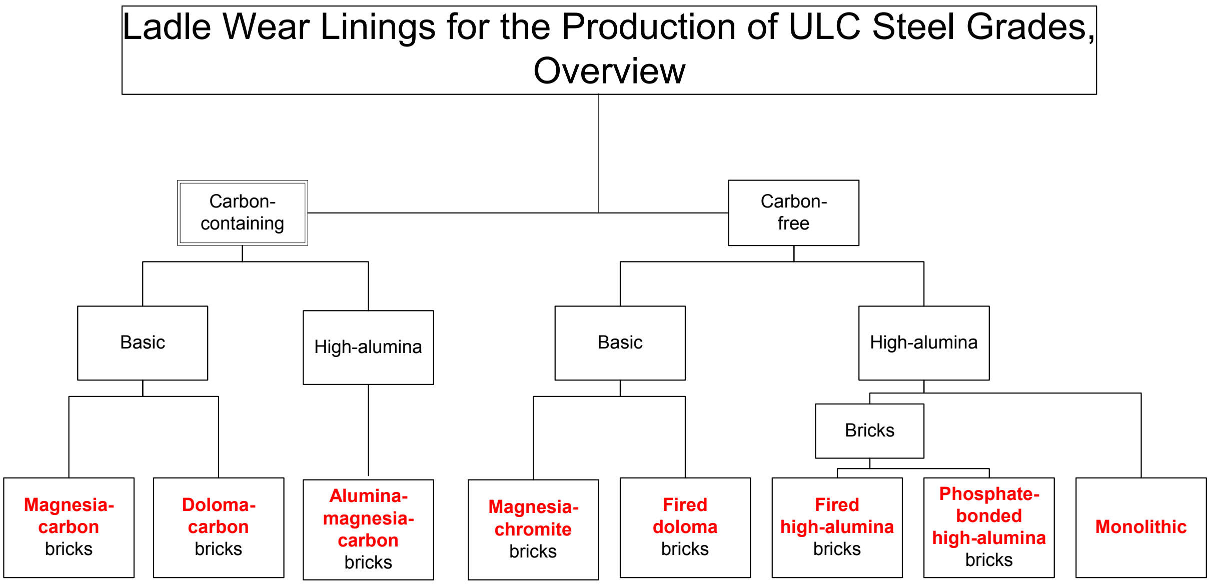


Figure 1. Overview of ladle wear linings for the production of ULC steel grades

2 CARBON-CONTAINING REFRACTORIES

2. . Advantages of Carbon

Pitch and resin are commonly used carbon-binders. In addition to acting as a binding agent, carbon provides the following three important brick characteristics:

- Increased wetting angle of the slag. Typically, whilst slags display a wetting behaviour on refractory oxides, a non-wetting behaviour is demonstrated on carbon. Thereby carbon inhibits slag infiltration on the brick hot-face.
- Carbon reduces slag components including iron oxides and manganese oxides to elemental iron and manganese, which have no deleterious effect on the refractory materials.
- Carbon significantly increases the thermal shock resistance.

However, there are also undesirable effects associated with carbon, including the possibility of carbon pick-up by the steel.

2.2 Carbon Pick-up

Whilst carbon-containing refractories are used for the production of ULC steel grades, there are certain parameters that must be considered to avoid carbon pick-up.

The total recarburization due to carbon-containing refractory materials in a 180 tonne ladle has been estimated at a maximum of 12 ppm carbon for the first melt and approximately 1-2 ppm carbon for the subsequent melts. These figures are based on laboratory tests with carbon-bonded bricks and pure iron. (1)

Carbon can be transferred from the refractory material to the steel bath by two mechanisms: (1) Binder carbon and graphite can dissolve directly into the metal, and (2) contamination can occur due to carbon in a gaseous state. (2)

2.2.1 Influence of dissolved oxygen on carbon pick-up

The equilibrium diagram for the reaction of dissolved carbon and dissolved oxygen in steel to form gaseous carbon monoxide is depicted in Figure 2. According to equation 1, the carbon-solubility is dependent on the partial pressure of carbon monoxide and is inversely related to the dissolved oxygen content:

$(C) + (O) = CO_{(g)}$

$$(\%C) * (\%O) = 2.5 * 10^{-3} * p_{CO} \quad \text{for } T= 1{,}600°C \qquad (1)$$

Accordingly, highly deoxidized steel melts have an increased carbon solubility that results in an increased driving force for carbon pick-up.

The kinetics of carbon pick-up are principally determined by the formation of carbon monoxide according to equation 2 and the formation of a dense MgO-layer at the brick hot face. (3)

$$C_{(graphite)} + (O) = CO_{(g)} \qquad (2)$$

If the oxygen potential is above 10 ppm, a CO-gas pad builds up that separates the graphite and dissolved oxygen reactants and consequently inhibits the carbon pick-up by the melt.(3) In parallel, a high oxygen potential leads to the formation of a dense

MgO-layer, which in addition prevents the metal from making direct contact with the carbon in the refractory.

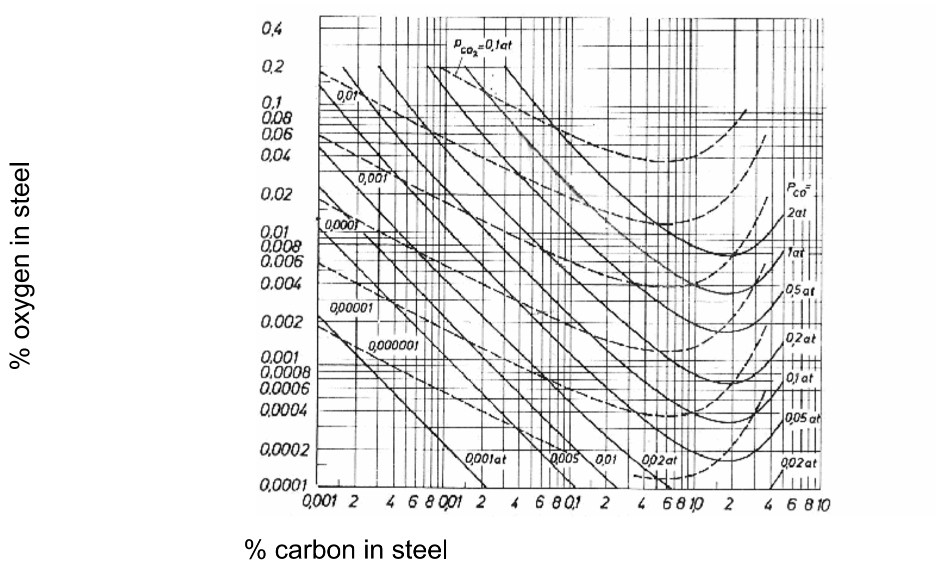


Figure 2. Equilibrium diagram for the reaction of dissolved carbon and dissolved oxygen in steel

2.2.2 Influence of alloying elements on carbon solubility

All alloying elements, that form stable carbides decrease the carbon activity in the steel and result in an increased carbon-solubility and consequently an increased propensity for carbon pick-up. Carbide-forming elements include Ti, Cr, V, W, Mn, Mo, and Nb.
However, there are certain elements that have almost no ability to solubilize carbon (e.g. Ni, Al, and Sn) and by using these as alloying elements in steel, the carbon solubility is decreased resulting in a lower driving force for carbon pick-up.

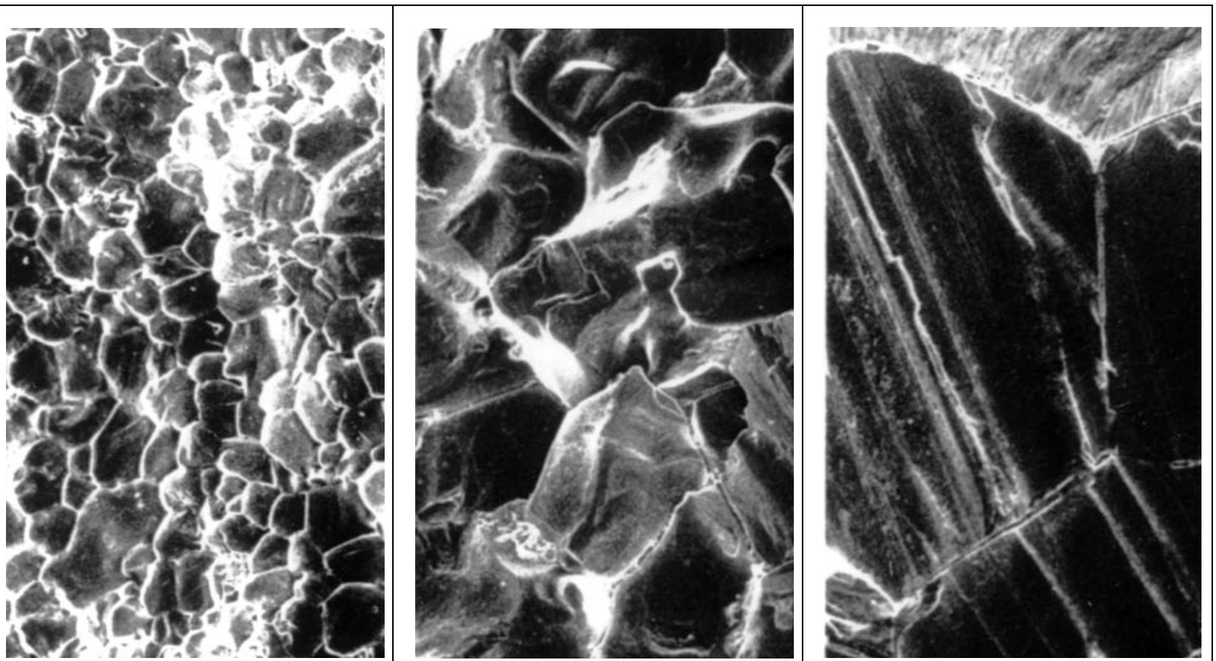
2.2.3 Recarburization in a newly lined ladle

It was determined from laboratory tests, that the carbon pick-up by steel from refractories for the second and subsequent heats is much lower than for the first heat.[1]
During the first heat, the steel and refractory materials have significantly different carbon concentrations, that promote rapid mass transport. As the contact time increases, the concentration difference decreases due to the superficial brick decarburization. Additionally, carbon transmission is obstructed due to the increased slag infiltration into the decarburized zone of the brick. Therefore, carbon pick-up is rather low (i. e., < 2 ppm) during the second and subsequent heats. [1]
Therefore, the use of newly lined ladles should be avoided for the production of ULC steel.

2.3 Magnesia-carbon Bricks

Magnesia-carbon bricks are a long established and reliable solution for steel ladles, especially in slag zones. The main advantages of magnesia are its high refractoriness and excellent resistance to basic slag corrosion.

Corrosion resistance can be further increased by using magnesia with a larger periclase crystals size. The periclase crystal size in various magnesia types ranges from 60-120 µm in standard sinter (Figure 3a) to 130-200 µm in large crystal sinter (Figure 3b), and 500 µm to more than 1000 µm in fused magnesia (Figure 3c), which exhibits the highest corrosion resistance.
For the production of ULC steel grades the carbon content of the magnesia-carbon bricks should not exceed 3% for sidewall and bottom applications (e.g., ANCARBON KC70) and 10% for the slag line.



(a) (b) (c)

Figure 3. Scanning electron micrographs of magnesia raw materials with different periclase crystal size, including (a) standard sinter magnesia, (b) large crystal sinter magnesia, and (c) fused magnesia

2.4 Doloma-carbon Bricks

Carbon-bonded doloma bricks are a cost-efficient alternative for sidewall and bottom lining applications (e.g., PENTABRICK T1). In the case of Si-killed steel grade production, a chemical reaction between the slag and refractory material results in the formation of a protective layer, which consists mainly of dicalcium silicate and tricalcium silicate. However, for Al-killed steel grade productions undesired low-melting calcium aluminates are formed if doloma-carbon bricks are employed.

2.5 Spinel-forming Alumina-magnesia-carbon Bricks

High-alumina bricks are a common solution for ladle linings, with the exception of slag zones. High-alumina refractories are distinguished by their excellent performance for the production of Al-killed steel grades and in cases where the slag has an Al_2O_3-content greater than 15%. However, the lifetime of high-alumina refractories is decreased by contact with highly basic slags.
The concept behind alumina-magnesia-carbon bricks is the in situ formation of magnesia-alumina-spinels that result in irreversible refractory material expansion (Figure 4). The resulting advantages include:[4]

- Decreased apparent porosity during application
- Densification at the hotface
- Joint closing
- Minimization of steel back-infiltration

Following a chemical reaction between the spinel and infiltrating slag, a combination of high and medium melting phases at the brick hot face produces a protective layer that further improves the refractory performance. Furthermore, an outstanding feature of alumina-magnesia-carbon bricks is their resistance to abrasion, which makes them particularly suitable for ladle impact pads.

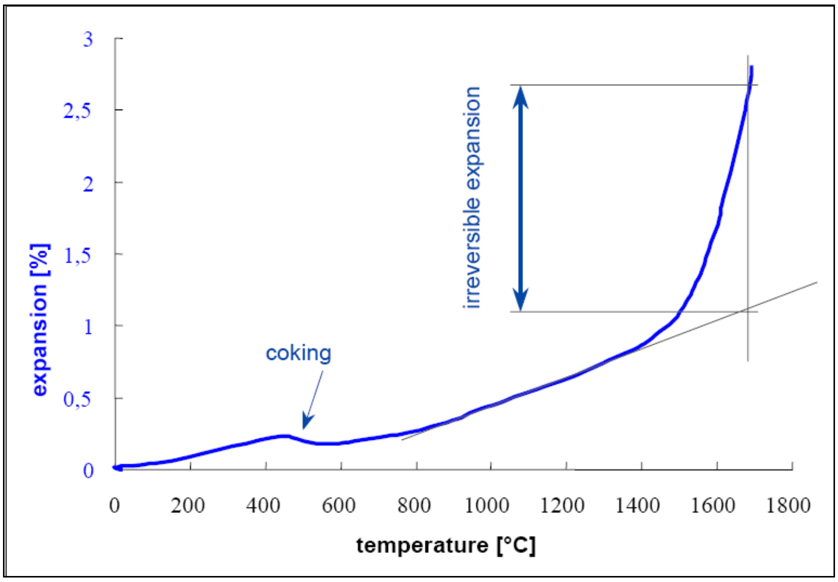


Figure 4. Thermal expansion of a spinel-forming alumina-magnesia-carbon brick

3 CARBON-FREE REFRACTORIES

3.1 Fired Basic Bricks

Fired basic bricks represent one carbon-free refractory option for the production of ULC steel.

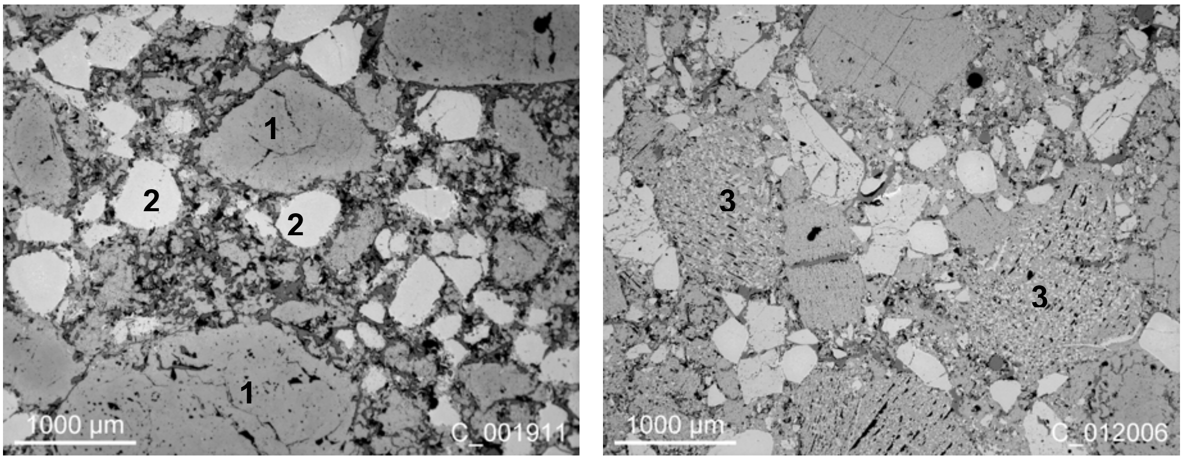
A comparison of the advantages and disadvantages of fired doloma and magnesia-chromite bricks is detailed in Table 1.

Table 1. Advantages (+) and disadvantages (-) of fired basic bricks

	Fired doloma bricks	**Magnesia-chromite bricks**
Hydration resistance	-	+
Corrosion resistance		
- Si-killed steel grades	+	+
- Al-killed steel grades	-	+
Slag infiltration resistance (resulting in spalling)		
- Si-killed steel grades	+	-
- Al-killed steel grades	-	-

3.1.1 Magnesia-chromite bricks

The magnesia-chromite bricks used in steel ladles can be subdivided into the following two groups according to the reaction intensity between the magnesia and chrome ore: (1) direct-bonded (Figure 5a) and (2) re-bonded (Figure 5b) bricks.
The principal raw materials for direct-bonded bricks (e.g., RADEX DB605) are magnesia and chrome ore. The relatively heterogeneous distribution of magnesia and chromite spinels results in an improved thermal shock resistance. Furthermore, to provide sufficient corrosion resistance, this brick type can be fired at the high temperatures of 1,700-1,800 °C. Direct-bonded bricks are mainly used in ladle sidewall and bottom applications.
Fused magnesia-chromite grain is the main raw material used for re-bonded brick manufacture (e.g., RADEX BCF-F11). The fusion process at 2,600 °C in the electric arc furnace produces a raw material with homogeneously distributed chromite spinels that have a large crystal size. This raw material, which is the principal component for re-bonded bricks, is fundamental for the excellent corrosion resistance. In addition, adding micro powder of Cr_2O_3 and MgO results in excellent hot strength and a high resistance to mechanical erosion. Due to these outstanding properties, re-bonded bricks are used in the slag zone.



(a) (b)

Figure 5. Micrograph of the structure of (a) direct-bonded magnesia-chromite and (b) re-bonded magnesia-chromite bricks. Magnesia (1), chromite (2), and fused magnesia-chromite (3) are illustrated

3.2 High-alumina Sidewall and Bottom Bricks

Fired or phosphate bonded bauxite bricks have been state-of-the-art for years in sidewall and bottom lining applications. However, they have serious drawbacks because the high amount of side phases restricts the working temperature and immediate cooling can result in joint opening.
The increasing demand for carbon-free, high performance bricks lead to the development of fired high grade spinel bricks[5] where only the highest purity raw materials are used for their production (e.g., white fused alumina). This new brick grade (e.g., RESISTAL KSP95-1) has shown excellent in service behaviour and in the case of sidewall applications is superior to alumina-magnesia-carbon bricks. A comparison of the composition and properties of specific high-alumina bricks is detailed in Table 2.

Table 2. Chemical composition and physical properties of high-alumina sidewall and bottom bricks. Abbreviations include bulk density (BD), cold crushing strength (CCS), and modulus of rupture (MOR)

	Bauxite		**Alumina-magnesia-carbon** ANKO 90MRC7A	**High grade fired spinel** RESISTAL KSP95-1
Al_2O_3 (wt%)	84		84	95
MgO	0.3		6.5	4.2
SiO_2	**8.8**		**1.5**	**0.2**
TiO_2	**2.5**		**1.0**	**0.1**
Fe_2O_3	**1.7**		**0.2**	**0.1**
P_2O_5, + K_2O + Na_2O	**2.5**		**0.2**	**0.05**
C	**-**		**6.5**	**-**
BD (g/cm^3)	2.90		3.25	3.15
CCS (N/mm^2)	75		75	50
MOR (N/mm^2) (1400 °C)	2.5		4.5	5.0
Bond type	Ceramic	Phosphate	Carbon	Ceramic

3.3 Monolithic Linings

Monolithic ladle linings are an alternative option to meet the requirements of carbon-free top performance. They are based on the principle of using a thixotropic casting mix to produce the lining. The term thixotropic means the casting mix liquefies when subjected to a shear loading caused by vibration. Subsequently, the mix settles when the vibration stops.

The casting process starts with the sidewall using an internal template with an electric vibrator. A frequency converter controls the vibrator's energy. A rotating conveyor belt above the template inserts the castable into the cylindrical-shaped gap (Figure 6). After 4 to 6 hours the template can be removed. The bottom is cast in a second step. Using this method up to 10 tonnes of castable can be processed per hour.

After a given number of heats the lining has to be partially repaired. Only the corroded surface is cleaned. A significant part of the unused refractory material remains in the ladle for further ladle campaigns (Figure 7) and missing or worn sections are replaced. Using this system the ladle can be frequently relined, giving the lining a total lifespan of several hundred heats before the final demolition is necessary.

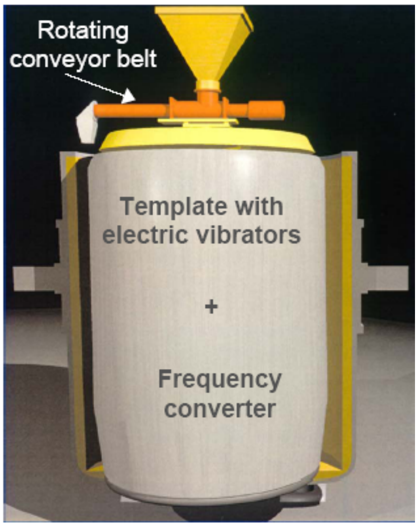


Figure 6. Monolithic lining using a template with electric vibrators.

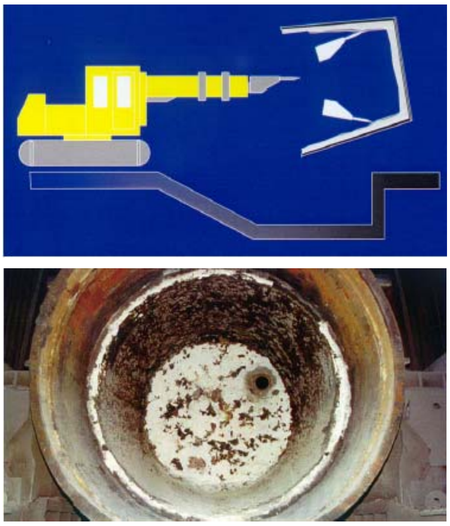


Figure 7. Relining of a monolithic ladle

The advantages of monolithic linings include:

- Faster and easier lining
- Jointless lining
- No well blocks required
- Partial lining possible (lower sidewall and reinforced zone)
- Reduced waste material
- Reduced refractory consumption

In principle, three types of castable, distinguished by their specific raw material content, are suitable for ULC ladle lining applications (Table 3).

The application of spinel forming castables (e.g., ANCOCAST VL93M) is recommended for ladle sidewalls. The expansion of the in situ formed spinel results in favourable fixation of the entire lining. Spinel containing mixes (e.g., ANKOCAST VL92MA) are used for ladle bottoms because they are dense but have a significantly lower expansion than spinel forming castables. The variations in permanent linear change after firing at 1500 °C are illustrated in Table III. The difference is due to the volume expansion as a result of the spinel formation process.

The third type of castable is based on corundum (e.g., ANCOCAST VL98) and is used for both ladle sidewall and bottom applications and has excellent abrasion resistance.

Table 3. Chemical composition and physical properties of ladle lining castables. Abbreviations include bulk density (BD) and cold crushing strength (CCS)

	Spinel forming ANCOCAST VL93M	**Spinel containing** ANKOCAST VL92MA	**Corundum** ANKOCAST VL98
Al_2O_3 (wt%)	92	92	98
MgO	6	5.5	0.1
Fe_2O_3	0.1	0.2	0.1
CaO	0.9	1.5	1.7
SiO_2	0.8	0.2	0.1
Water requirement (%)	5.7	6.0	6.0
BD (g/cm^3)			
After drying (110°C)	3.00	3.00	3.02
CCS (N/mm^2)			
After drying (110°C)	20	40	50
After firing (1500°C)	80	80	70
Linear change (%)			
After firing (1500°C)	1.8	0.05	0.3

4 CONCLUSION

Refractory linings for the production of ULC steel grades have to meet numerous requirements, including metallurgical targets, safety issues, maximal in service lifetimes, and competitive pricing. Therefore, the steel manufacturer and refractory supplier have to make an informed choice from the wide variety of refractory materials in order to design a tailor-made refractory solution.

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