ADVANTAGES OF DENSE CALCIUM HEXALUMINATE AGGREGATE FOR BACK LINING IN STEEL LADLES

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INTRODUCTION
Changes in the secondary metallurgy processes performed in the steel ladle have also required changes in the refractory lining of steel ladles. The residence time of steel in the ladle and the tapping temperature has increased. Thinner refractory linings have been applied to increase the ladle capacity. Therefore it has become necessary to install insulation layers to counterbalance increased heat losses and higher steel shell temperatures [1]. Insulating refractory materials do not provide a safety function when the wear lining is completely worn, so a permanent lining is required as a safety layer to avoid break outs. In addition, the insulating materials need to be protected from too high contact temperatures.

For the selection of back lining materials, it is important to consider not only the thermal conductivity but also the thermo-mechanical stability to ensure a long lining life. Monolithic back linings are often used for one year which accounts for about 800 heats in the steel ladle.

The dense calcium hexaluminate (CA₆) aggregate, Bonite, has a high refactoriness and exhibits a comparably low thermal conductivity combined with high wear resistance. This set of material properties makes it an interesting aggregate for refractories in the permanent lining of steel ladles.

MATERIAL PROPERTIES OF BONITE
The initial objective of the product development was to expand the properties of calcium hexaluminate, which is formed in the matrix of calcium aluminate cement bonded castables, to the whole castable formulation. The CA₆ formation begins at temperatures above 1300 °C, and it is associated with a volume expansion of about 14 %. The newly formed mineral phase bonds strongly to alumina or spinel grains and shows a very high refractoriness, a low wetability by molten metals and slag (ferrous and non-ferrous) and a low solubility in iron-containing slag [2].

The Bonite features the same positive properties as the CA₆ formed as a mineral phase in castables. However, as a pre-reacted aggregate, it shows volume stability over a wide temperature range. Bonite is composed of about 90 % CA₆ with only a minor content of corundum, and traces of calcium di-aluminate (CA₂). It has a bulk density of 3.0 g/cm³, which is about 90 % of the theoretical density of calcium hexaluminate (table 1).

Tab. 1. Typical data of Bonite.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apparent porosity</td>
<td>&lt; 0.02</td>
</tr>
<tr>
<td>Bulk density</td>
<td>3.0</td>
</tr>
<tr>
<td>Apparent porosity</td>
<td></td>
</tr>
<tr>
<td>Chemical Analysis</td>
<td></td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>90</td>
</tr>
<tr>
<td>CaO</td>
<td>8.5</td>
</tr>
<tr>
<td>SiO₂</td>
<td>0.9</td>
</tr>
<tr>
<td>FeMgO</td>
<td></td>
</tr>
<tr>
<td>Bulk density</td>
<td>3.0</td>
</tr>
<tr>
<td>Apparent porosity</td>
<td></td>
</tr>
<tr>
<td>Mineralogical composition</td>
<td></td>
</tr>
<tr>
<td>main phase</td>
<td>CA₆, about 90 %</td>
</tr>
<tr>
<td>minor phase</td>
<td>Corundum</td>
</tr>
<tr>
<td>traces</td>
<td>CA₂</td>
</tr>
</tbody>
</table>

PROPERTIES OF BONITE-BASED CASTABLES
Thermal conductivity
The thermal conductivity of minerals is a directional property with high values for the axis of denser atomic packing and lower values for areas with less dense packing, material defects, and interfaces. The calcium hexaluminate crystals in Bonite appear as platelets and form a structure where the face sides of the crystals are linked to the flat side of another hexagonal crystal thus forming a structure that is similar to a house of cards (figure 1).

Fig. 1. Microstructure of Bonite (polished section). Hexagonal CA₆ platelets and few pores in between.

This microstructure leads to a thermal conductivity of Bonite that is much lower when compared to other minerals with a similar density. Therefore the Bonite-based castable exhibits a much lower thermal conductivity when compared to other high alumina
refractory materials which are often used in a steel ladle permanent lining. It is important that the microstructure of Bonite remains stable even at temperatures above 1500 °C [3], and therefore no change of the thermal conductivity must be anticipated even during the extended life time of a back lining in a steel ladle.

A comparison of the thermal conductivity of a Bonite-based low cement castable and other materials for a steel ladle permanent lining is given in figure 2. In spite of the comparably high density of 2.85 g/cm³, the Bonite-based castable shows a significantly lower thermal conductivity when compared to the bauxite based brick which has a bulk density of 2.7 g/cm³. It is even lower in comparison to the andalusite based castable which has a lower bulk density (2.5 g/cm³). The low thermal conductivity of Bonite is of interest for applications where a combination of wear resistance and insulating behaviour is required, for example in the permanent lining in steel ladles.

Fig. 2. Thermal conductivity of refractory materials used for steel ladle permanent linings [4].

**CO-resistance**

The resistance against carbon monoxide attack from hot metal or carbon bonded refractories is an important feature of refractory materials suitable as permanent and insulation linings in steel applications [5,6]. Carbon monoxide can penetrate the ladle lining up to the last insulation layer and it can form carbon deposits that lead to a destruction of the refractories. The deposition of carbon in the pores of insulating materials increases the thermal conductivity and results in a loss of insulating effect.

The attack on refractories by carbon monoxide is discussed in detail by Bartha and Köhne [7] and was recently investigated as part of an AIF-project at the German refractory institute DIFK in Bonn. Although the details of the wear mechanism under CO attack are still under discussion, it is commonly accepted that a selection of appropriate refractory materials is required to achieve a high CO-resistance. Special attention must be given to low iron content of the materials used.

The CO-resistance of a Bonite castable was tested at DIFK/Bonn according to ASTM C288-87. The test bars were made from a conventional castable with 20 % CA-14 M cement and a water demand of 12 %. The purpose was to achieve a high open porosity of 32 % after firing, because a high porosity intensifies the CO-attack on refractories. Despite the high porosity, the Bonite test piece was rated class A (highest resistance class) after pre-firing at 540 °C, and class B after pre-firing at 1095 °C.

**Slag resistance of Bonite**

Although the permanent lining in steel ladles is not in contact with slag under normal conditions, it must provide a certain slag resistance to act as a safety lining in case of wear lining damage. High alumina refractories based on alumino-silicate or bauxite are often used as back linings in steel ladles. Even spinel castables are sometimes applied where the conditions are more severe (slag line, low minimum thickness of the wear lining). The slag resistance of a Bonite-based LC castable, in comparison to bricks from bauxite, andalusite, and forsterite, was determined (table 2).

![Thermal conductivity of refractory materials](image)

Tab. 2. Data of refractories used for permanent lining in steel applications: commercially available bricks and a Bonite-based low cement (LC) castable.

<table>
<thead>
<tr>
<th>Chemical analysis [%]</th>
<th>BD [g/cm³]</th>
<th>Po [Vol.]</th>
<th>Cp [J/kg K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>SiO₂</td>
<td>CaO</td>
<td>MgO</td>
</tr>
<tr>
<td>Bauxite</td>
<td>80</td>
<td>13</td>
<td>0,29</td>
</tr>
<tr>
<td>Andalusite</td>
<td>59</td>
<td>38</td>
<td>0,37</td>
</tr>
<tr>
<td>Forsterite</td>
<td>0,76</td>
<td>36</td>
<td>0,65</td>
</tr>
<tr>
<td>Bonite</td>
<td>91</td>
<td>0,75</td>
<td>0,2</td>
</tr>
</tbody>
</table>

The test was conducted in an induction furnace at the DIFK/Bonn. The brick samples were cut, whereas the Bonite castable was moulded with 6.5% water, dried at 110°C for 24h and prefired at 1000 °C for 5h before being installed. The samples were mounted side by side forming a crucible. The samples were simultaneously subjected to 15 kg of steel ST52 under an oxidising atmosphere (air).

After reaching the test temperature of 1600 °C, 750 g of a synthetical calcium aluminate slag was added. This slag is typical for aluminium-killed steel and had the following composition:

- 41.5 wt.% CaO
- 38.5 wt.% Al₂O₃
- 5 wt.% SiO₂
- 5 wt.% MgO
- 6 wt.% Fe₂O₃
- 4 wt.% MnO
The slag was replenished after one hour and the test was aborted after two hours due to the high wear of one sample. The test specimens were cut in a longitudinal direction and the wear profile was measured at the slag level. The discolouration of the sample, the slag penetration and the formation of cracks were also investigated.

Figure 3 illustrates the result of the corrosion test on the cut samples. The andalusite brick shows the worst result with almost no remaining material in the slag line. This confirms the inferior behaviour of andalusite as a wear lining in steel ladles when calcium aluminate slags with a ratio of CaO to Al₂O₃ of about 1 are used (calcia content above 30 %) [6].

The wear rate of the andalusite brick in the slag test was 12 mm/h whereas in the case of the bauxite brick it was only 4.6 mm/h. However, the bauxite brick was deeply infiltrated by slag which led to the formation of cracks parallel to the attacked surface. The Bonite-based castable performed best with little slag infiltration, no cracking and the lowest wear rate of 3.2 mm/h.

**THERMAL MODELING OF LINING CONCEPTS**

The thermal modeling of different ladle lining concepts was carried out by the CORUS Ceramics Research Center in IJmuiden. The transient FEM analysis of a generic steel ladle (figure 4) was performed to simulate the performance of Bonite-based refractories in steel ladle permanent linings. The aim of the analysis was to predict the temperature profile in the lining and the cooling rate of the liquid steel during a service cycle.

In order to calculate the heat transfer from the surfaces of the modeled ladle, convection and radiation were included. The ambient air was set at 20 °C. The emissivity for radiation ε was set at 0.85 the figure used for white refractories according to [8]. Free convection was defined with the coefficients below [9]:
- vertical walls \( \alpha = 1.63 \cdot \Delta T^{0.3} \)
- horizontal surface facing up \( \alpha = 2.38 \cdot \Delta T^{0.3} \)
- horizontal surface facing down \( \alpha = 1.21 \cdot \Delta T^{0.3} \)

In general, the heat loss through the ladle surfaces can be split to about 55 % through the slag line, about 35 % through the barrel and about 10 % through the bottom. This means that an efficient lining concept for the sidewall is an important measure for energy savings.

![Bauxite, Forsterite, Andalusite, Bonite](https://example.com/fig3.png)

**Fig. 3.** Samples after slag test; CaO/Al₂O₃-ratio 1.08 (Induction furnace, 1600 °C / 2 h; air)

**Fig. 4.** Transient, two-dimensional, and axis-symmetrical FEM model of a steel ladle.

The following settings were used for the simplified model:
- AluMagCarbon bricks (7 % MgO, 7 % C) as wear lining in the barrel; two cases: 1) “new” wear lining (155 mm) and 2) old/worn lining (50 mm); a comparison of different permanent lining concepts,
- MagCarbon bricks (10 % C) in the slag line (187 mm), permanent lining alumina-spinel-castable (100 mm) plus vermiculite insulation (10 mm),
- Alumina-spinel-castable in the bottom (250 mm), permanent lining high alumina castable (150 mm) and no insulation,
- For simplification, wear has only been considered for the barrel but not for the slag line or the bottom,
- Tapping temperature 1670 °C,
- Tap to tap time 260 minutes (about 5 heats per day): 120 minutes from converter to continuous casting machine, casting time 40 minutes, 100 minutes back to converter; Casting time was split between “filled” time (120 + 20 minutes) and “empty” time (100 + 20 minutes),
- Ten service cycles performed in a row to achieve quasi stationary thermal conditions in the lining,
- Eleventh cycle used for calculations of temperature profile and heat loss.
The results of the following permanent lining concepts will be discussed in detail:

- Bonite low cement castable compared to bauxite brick, with vermiculite as the insulation layer.
- Bonite low cement castable compared to andalusite brick, with vermiculite as the insulation layer.

More concepts were evaluated, including combinations of Bonite with the microporous CA, insulating material, SLA-92, but the results cannot be discussed here in detail.

Figures 5 and 6 show the result of a typical bauxite based permanent lining when compared to the Bonite-based castable. All conditions were kept constant during the comparison, so the differences in results are only due to the use of Bonite. It can be clearly seen that for the “new” lined ladle with Bonite as back lining the temperature of the steel shell is about 20 °C lower. For the worn ladle (50 mm remaining in the wear lining) the difference is even higher at 30 °C.

The difference in the steel cooling rate makes the positive influence of Bonite even clearer. The cooling rate of the bauxite version is around 0.03 °C/min higher (0.71 vs. 0.68 °C/min) when compared to the Bonite version. This amounts to an energy saving with the Bonite version in the range of about 22,000 € per year per ladle (assumption of 800 heats per annum for the permanent lining and according to calculations in [10]). In addition, the Bonite layer reduces the contact temperature at the insulation layer by about 100 °C. This becomes important in case of the worn ladle because it reduces the risk of overheating the insulation layer. Such overheating during the long lining life of the back lining, can lead to a considerable deterioration of the insulation layer. The whole lining stability may be reduced.

The comparison of the Bonite-based permanent lining with the andalusite brick version shows comparable results with regard to the steel shell temperature. Here Bonite provides considerably higher protection against break outs in case of wear lining damage. This is due to the superior slag resistance.
SUMMARY AND OUTLOOK

The dense calcium hexaluminate aggregate Bonite shows clear advantages for applications in the back lining of steel ladles or other industrial furnaces:

- High refractoriness and thermo mechanical stability,
- Resistance against carbon monoxide attack,
- Resistance against calcium aluminate steel ladle slag,
- Low thermal conductivity.

These properties enable refractory concepts for back linings which combine safety with the reduction of heat losses during the process. The Bonite-based low cement castable has displayed superior slag resistance when compared to andalusite bricks and even bauxite bricks which are often used in the back lining of steel ladles. The simulation of different ladle lining concepts has shown the potential of Bonite-based material for the reduction of contact temperature of an insulation layer, steel shell temperature, and heat losses during the process. This also indicates a potential for reduced lining thickness to increase the overall steel ladle capacity.

Bonite can be combined with the microporous insulating calcium hexaluminate SLA-92. This enables the formulation of a wide range of insulating products and lining concepts for other back lining applications in addition to steel ladles.

REFERENCES


