DESIGN OF PRECAST & PREFIRED LADLE NOZZLE IN 
\( \text{Al}_2\text{O}_3 – \text{Al}_2\text{MgO}_4 \) SYSTEM FOR IMPROVED PERFORMANCE

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Abstract
Nowadays, cleanliness of steel is the most important criteria to get defect free and desired quality. The common techniques are to eliminate inclusions by adding Silicon or Aluminium in different forms. In case of alumina inclusions there is a chance of aluminium clogging inside the nozzle which affects the castability of steel. In order to improve the castability, calcium treatment is getting importance day by day which converts the alumina inclusions in liquid calcium aluminate.

Refractories have a major role to keep the inclusion of different oxides in minimum level in molten steel. The inclusions of refractories come in steel due to corrosion and erosion. The control of corrosion and erosion of refractories not only keep the inclusions in minimum level but also enhance the performance. It is very important to design different refractory items like ladle nozzle, collector nozzle, slide plate, seating block, well block etc. in such a way so that its corrosion and erosion behaviour will be minimized to eliminate inclusions of steel like silicon, aluminium or calcium killed steel.

In present paper, precast & prefired ladle nozzle is designed in \( \text{Al}_2\text{O}_3 – \text{MgAl}_2\text{O}_4 \) system for calcium treated steel. This nozzle has excellent thermal spalling resistance and negligible tendency towards slag corrosion against the tundish slag. Two different kinds of spinel are used to design this product. Different physical properties are measured after firing at different temperatures like AP, BD, CCS, MOE, PLC etc. along with the different mineralogical phases formed after firing by XRD. Optical microstructure is carried out to know the penetration of slag and penetration depth after static slag corrosion test.

This developed nozzle has already been tried in an integrated steel plant and given enhanced performance. The rate of corrosion cum erosion was also measured to know its actual potential. The same technology can be followed while designing the collector nozzle, seating block and well blocks. But the optimization of spinel is very important to get best performance.

Introduction
In steel making, the durability and performance of castables depend on various factors like corrosion and erosion resistance against slag/metal, thermal, volume & structural stability, high refractoriness to withstand at application temperature etc. The high-alumina castables showed high refractoriness because of different constituents present having higher melting points. Along with high refractoriness there are other parameters which are very important to get good performance from the castables being used in different purpose in steel making like seating block, well block, porous plug, ladle nozzle, collector nozzle etc. High alumina castables having higher content of \( \text{Al}_2\text{O}_3 \) are not fulfilling all the desired parameters to achieve expected performance. It has been observed that addition of MgO or \( \text{MgAl}_2\text{O}_4 \) spinel in \( \text{Al}_2\text{O}_3 \) based castables enhanced the slag corrosion, erosion and thermal spalling resistance significantly [1].

To get the best performance from \( \text{Al}_2\text{O}_3 - \text{MgAl}_2\text{O}_4 \) spinel castable, addition of spinel is very important. It has been reported [2] that \( \text{Al}_2\text{O}_3 \)-rich \( \text{MgAl}_2\text{O}_4 \) spinels in a quantity ranging from 10 to 30 wt% provide superior properties as compared to \( \text{Al}_2\text{O}_3 \)-spinel castables. In case of \( \text{Al}_2\text{O}_3 - \text{MgAl}_2\text{O}_4 \) spinel castables corrosion and penetration of slag or metal are the performance determining factors and therefore it is very important to design a castables having negligible corrosion and penetration of slag or metal inside it. In \( \text{Al}_2\text{O}_3 \)-spinel castables containing 4 –16 wt% high alumina cement and observed that penetration resistance increased with increased cement content from 4 to 12 wt% and leveled off at 12–16 wt%, while erosion resistance significantly decreased with increased cement content [3]. Structural stability under the temperature fluctuation is another important factor which has to be considered while designing \( \text{Al}_2\text{O}_3 - \text{MgAl}_2\text{O}_4 \) spinel castables. It was observed that a large amount of high alumina cement was required for \( \text{Al}_2\text{O}_3 - \text{MgAl}_2\text{O}_4 \) spinel castables in order to enhance thermal and structural spalling resistance [4]. On the other hand with increasing CaO content apparent porosity and reversible thermal expansion (RTE) increased slightly, while bulk density decreased slightly. The increase in RTE is due to growth of CA\(_6\) crystals which hinders the sintering of the castables. In general, \( \text{Al}_2\text{O}_3 - \text{MgAl}_2\text{O}_4 \) spinel castables designed with high purity raw materials like white tabular or fused alumina along with either addition of MgO for in-situ spinel formation or pre-formed spinel. Since, base raw materials are very pure so in nature there is negligible amount of impurities in...
system. The hot modulus of rupture generally increased with increasing CaO content in the temperature range 1300° to 1500°C, while it remained almost constant in the temperature range 1000°–1300°C. On investigation of microstructure of fired castable it was observed that some CaO crystals have grown out of the spinel grains in the bonding matrix of the castable. The hot strength enhancement of high-\(\text{Al}_2\text{O}_3\) castables with addition of \(\text{Al}_2\text{O}_3\)-rich spinel is due to bond linkage between the \(\text{CA}_6\) and the spinel grain in presence of CaO.

It was reported [5] that thermal expansion of \(\text{Al}_2\text{O}_3\)-\(\text{MgAl}_2\text{O}_4\) spinel castables abruptly increases from \(\sim 1100°C\) and continues to increase with increasing temperature up to 1500°C while designing it with the formation of in-situ spinel. On the other hand thermal expansion of \(\text{Al}_2\text{O}_3\)-\(\text{MgAl}_2\text{O}_4\) spinel castables also noticeably increases from 1100° up to 1300°C and then gently decreases with increasing temperature while adding pre-formed spinel. The thermal expansions of these castables could be effectively suppressed by the addition of very small quantity (<1%) of microsilica. The thermal expansion study [6] of the high-alumina castables showed that the expansion and contraction, was minimum at around 1500°C. This minimum expansion was due to the formation of \(\text{CA}_2\) and then increase in expansion from 1500°C was attributed to the formation and growth of \(\text{CA}_6\). The microscopic observation of \(\text{Al}_2\text{O}_3\)-\(\text{MgAl}_2\text{O}_4\) spinel castables [7] 15 wt% spinel and 1.7 wt% CaO suggests that \(\text{CA}_6\) crystals grows out of the spinel grains in the bonding matrix of castable containing 2.04 wt% CaO and 20 wt% spinel. The probability of bond linkage between the \(\text{CA}_6\) and spinel grains in the bonding matrix of the castable was increased with increase in temperature, CaO and spinel contents, as well as number of spinel grains. The PLC change was caused by the growth of \(\text{CA}_6\) crystals. The growth of \(\text{CA}_6\) crystals in alumina grains leads to complete disintegration of the grains resulting in the increase of apparent porosity. Hot modulus of rupture of \(\text{Al}_2\text{O}_3\)-\(\text{MgAl}_2\text{O}_4\) spinel castables gradually increased with increase in spinel content and temperature from 1000 to 1500°C is due to growth of \(\text{CA}_6\) crystals and bonding with spinel in matrix.

The improvement in flowability for castables is very important from the viewpoint of good workmanship, uniform and homogenous structure, make complicated shapes etc. Many efforts have been focused on particle size distribution to develop high performance self-flow refractory castables based on Andreassen theory. It was observed that the rheological and thermo-mechanical behavior of the high performance castables was very much influenced [8] with change in the particle size distribution.

The particle size distribution of the raw materials particularly of fine is very important to improve the flowability of the castables. In order to improve the physical properties the water demand must be reduced. Dispersants have a vital role to give good flow with reduced amount of water. Therefore, selection of suitable dispersants is very important.

To get the best performance from \(\text{Al}_2\text{O}_3\)-\(\text{MgAl}_2\text{O}_4\) spinel castables it must be designed with very pure raw materials like white tabular alumina, alumina-rich spinel along with selected dispersing agent to get excellent flow and improved physical properties with reduced amount of water.

In this paper, \(\text{Al}_2\text{O}_3\)-\(\text{MgAl}_2\text{O}_4\) spinel castables has been designed for different precast and pre-fired items especially for high performing ladle nozzle. The ladle nozzle has already been tried in one integrated steel plant and gives satisfactory performance.

**Experimental:**

\(\text{Al}_2\text{O}_3\)-\(\text{MgAl}_2\text{O}_4\) self–flow spinel castables has been designed using white tabular alumina, alumina-rich pre-formed spinel (two verities), reactive alumina, high alumina cement and selective dispersing agents (two types). For evaluation of different properties 10 Kg sample was prepared as per specified recipe. While preparing the sample dry mixing was carried out in high intensity Hobart mixer for five minutes followed by addition of water in two steps. 80% of total water was added in the beginning and wet mixing for two minutes followed by addition of rest 20% water and wet mixing was continued for another three minutes to achieve self-flow consistency.

Samples having different sizes were prepared for evaluation of different properties. For measurement of CCS, CMOR, AP, BD and PLC sample size was 160mm X 40mm X 40mm and for measurement of thermal spalling resistance cubes of size 65mm X 65mm X 65mm were made. For measurement of CMOR, CCS, AP, BD & PLC, samples were dried at 110°C for 24 hours followed by firing at 800°C, 1100°C, 1500°C & 1650°C with 3 hours soaking. While measuring PLC the initial length was considered after drying the samples at 110°C for 24 hours. For measurement of HMOR, samples of size 150mm X 25mm X 25mm were prepared. HMOR was measured at 1500°C by pre-firing the sample at 800°C, 1100°C, 1500°C for 3 hours soaking. Thermal spalling test was carried out by water quenching method, from 1300°C to water on the oven dried samples at 110°C for 24 hrs. The samples were directly put inside the muffle furnace at 1300°C. Samples were kept inside the furnace for 15 minutes at 1300°C and then taken out for quenching in water for 3 minutes. After that, samples were dried at 110°C for 15 minutes and in the same manner repeatedly spalling was carried out until there was crack formation and chipping out of sample. Static slag corrosion test (Cup test) was carried out in cube sample.
of size 65mm X 65mm X 65mm using slag collected from an integrated steel plan by making a hole of size 25 mm diameter and 40 mm depth. Before drilling hole of specified size the block was dried 110°C for 24 hrs. After making hole, it was again dried followed by filling the slag inside the hole. The test was done at 1650°C with 3 hours soaking. The test pieces were cut in two pieces to observe the slag corrosion and penetration depth.

Different mineralogical phases were identified after firing the samples at 800°C, 1100°C, 1500°C & 1650°C by XRD study. Microstructure of fired samples was also carried out by doing SEM and EDAX analysis.

**Results & Discussions:**
The formulation of Al₂O₃ - MgAl₂O₄ spinel castables was designed with Andreassen distribution co-efficient of 0.23 and maximum particle size = 6 mm. Water was added 4.6% to achieve sufficient self-flow. The flowability of castable was shown in Fig. 1. The chemical analysis of newly designed castable is given in Table – 1.

![Fig.-1: Self flowability with 4.6% water](image)

**Table 1: Chemical analysis of designed castable**

<table>
<thead>
<tr>
<th>Constituent</th>
<th>% by wt.</th>
</tr>
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<tbody>
<tr>
<td>Al₂O₃</td>
<td>94.1</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.12</td>
</tr>
<tr>
<td>SiO₂</td>
<td>0.14</td>
</tr>
<tr>
<td>CaO</td>
<td>2.43</td>
</tr>
<tr>
<td>MgO</td>
<td>1.59</td>
</tr>
<tr>
<td>Na₂O + K₂O</td>
<td>0.11</td>
</tr>
</tbody>
</table>

Variation of apparent porosity (AP) after drying as well as after firing at different temperatures is shown in Fig.- 2. There is increasing trend of AP while firing at 800°C and 1100°C but it has increased significantly while firing at 1500°C. Beyond 1500°C there is reduction in AP is observed while firing at 1650°C. The reduction in AP is due to sintering of sample followed by densification beyond 1500°C. The changes of bulk density (BD) are reversed i.e. decreasing up to 1500°C followed by increasing at 1650°C (Fig.-3). The sudden decreased in BD at 1500°C is due to volume expansion of the sample while formation of different mineralogical phases.

![Fig.-2: Variation in apparent porosity with temp.](image)

![Fig.-3: Variation in bulk density with temp.](image)

There is no significant change in CCS while firing the samples upto 1100°C. But sudden increase in CCS is found while firing the samples at 1500°C and 1650°C (Fig.-4).

![Fig.-4: Variation in CCS with temp.](image)
Sintering at higher temperature and densification results higher CCS beyond 1500°C. Volume stability at operating temperature can be judged while measuring PLC and RTE. The change in PLC with temperature is shown in Fig.-5.

Fig.-5: Change in PLC with firing temp.

There is no change in PLC upto 1100°C. Significant expansion is observed at 1500°C followed by decreasing at 1650°C. Different phases are formed which result expansion and contraction in the system. The sudden increase in PLC may be due to growth of CA₆ at 1500°C and followed by sintering at 1650°C.

HMOR of samples were measured after at 1500°C with 30 minutes soaking after pre-firing at 800°C, 1100°C and 1550°C to observe the effect of pre-firing temperature. There is no remarkable change in HMOR while pre-firing the samples at 800°C and 1100°C. But significant improvement is observed while pre-firing at 1550°C (Fig.-6). The improvement in HMOR with higher pre-firing temperature is mainly due to sintering, growth of CA₆ crystals and bonding of spinel in matrix.

Thermal spalling resistance test was carried out through water quenching method from 1300°C to water. This is very severe test and it is observed that normal Al₂O₃ - MgAl₂O₄ spinel castable broken into pieces after 7 cycles (Fig.-7) whereas developed castable showing no cracks even after 10 cycles (Fig.-8). It shows newly designed castable having excellent thermal spalling resistance against normal Al₂O₃ - MgAl₂O₄ spinel castable.

Slag corrosion resistance was carried out with BOF slag collected from an integrated steel plant at 1650°C with 3 hours soaking both for existing castable and newly designed Al₂O₃ - MgAl₂O₄ spinel castable. There is remarkable improvement both in slag corrosion
resistance and penetration in newly designed castable (Fig.-9). The cut surfaces are sharp indicates very less slag corrosion and penetration against existing one.

![Fig.-9: Static slag corrosion test at 1650\(^\circ\)C](image)

Different mineralogical phases formed during firing have been identified by XRD and shown in Fig.-10. The major phases are corundum, spinel, CA\(_2\) and CA\(_6\). The peak intensity for CA\(_6\) has increased significantly when fired the samples at 1500\(^\circ\)C & 1650\(^\circ\)C. At higher temperature CA\(_2\) phase transformed into CA\(_6\) phase.

![Fig.-10: XRD of samples after firing at diff. temp.](image)

Microstructure of fired samples was done through SEM followed by EDAX after firing at 800\(^\circ\)C, 1500\(^\circ\)C and 1650\(^\circ\)C. The grain appearance and its orientation after firing at 1500\(^\circ\)C and 1650\(^\circ\)C is shown in Fig.-11 & 12. Mineralogical study using EDAX spectra revealed the presence of CA\(_2\), CA\(_6\), MgAlO\(_2\) and α-Al\(_2\)O\(_3\). Presence of these phases in the structure may be attributed to the higher strength and refractoriness at 1500\(^\circ\)C and 1650\(^\circ\)C. The CCS & CMOR increased significantly at these temperatures may be due to the formation of CA\(_6\).

![Fig.-11: SEM of sample fired at 1500\(^\circ\)C](image)

![Fig.-12: SEM of sample fired at 1650\(^\circ\)C](image)

It is observed that above 1500\(^\circ\)C coarsening of grains takes place which may result to degradation in both physical and mechanical properties. But there is strong bonding of spinel in matrix is observed and finally there is improvement in both physical and mechanical properties while firing the samples at 1650\(^\circ\)C.

With newly developed castable, ladle nozzles were made for trial in an integrated steel plant having ladle capacity ~ 160 MT. The finished nozzles are shown in Fig.-13.

![Fig.-13: Finished ladle nozzle manufactured from developed castable](image)
Total 18 heats were taken from ladle nozzle. After 18 heats bore erosion was increased to 87 mm (Fig.-14). Initial bore diameter was 60 mm and hence erosion rate is only 1.5 mm per heat. The nozzle had still potential to take another 4–5 heats. More significantly there was no abnormal erosion or cracks formation.

**Fig.-14: Bore erosion after 18 heats**

With this developed castable not only the ladle nozzle but also other items like collector nozzle, seating block, well block, porous plug etc. were manufactured and tried at different steel plants. In all cases performance is encouraging.

**Conclusions**

$\text{Al}_2\text{O}_3$ - $\text{MgAl}_2\text{O}_4$ spinel castable can be designed either to introduce MgO to form in-situ spinel or addition of pre-formed spinel. While introduction of MgO there is sudden increase in volume expansion due to formation of spinel. It is very difficult to control the expansion. Even several cracks formed while conversion of MgO into spinel during firing. On the other hand, introduction of alumina-rich pre-formed spinel gives much better properties in terms of volume stability and other thermo-mechanical properties. Addition of pre-formed spinel in different fractions and its distribution not only help to improve thermal spalling resistance but also improve the resistance against slag corrosion and penetration. Good self-flow was achieved with < 5% water due to selection of more than one dispersing agent. The developed castable was initially tried as ladle nozzle. On satisfactory performance the same castable was used to make different other items like seating block, well block, porous plug, collector nozzle etc and tried. The performance of all the items has improved significantly.

**References:**