EFFECT OF CALCIUM ALUMINATE TYPE ON PLACING, MECHANICAL PROPERTIES AND ABRASION RESISTANCE OF LOW CEMENT AND MEDIUM CEMENT CASTABLES FOR DRI APPLICATIONS

G. Bhattacharya*, Ch. Wöhrmeyer, Susan Li and C. Parr

Kerneos Kolkata, India

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ABSTRACT

India leads the DRI production in the world and uses significant amount of low cement castable for this application. In low cement compositions together with reactive fine fillers and additives calcium aluminate cement forms deflocculated binder phase. It influences placing and mechanical properties of castable directly and therefore, castable performance depends significantly on calcium aluminate cement. Also the combination of the calcium aluminate cement, reactive filler and additives can be optimized to provide improved properties vital for a targeted application.

This paper discusses some key properties of DRI application such as flow, exothermic profile, compressive strength from 6h after casting to 3h at 1200ºC, porosity and bulk density up to 1200ºC and abrasion resistance after 5h at 1200ºC in a commonly used low cement and a medium cement composition with different calcium aluminate cements - SECAR® 68V, SECAR® 71 and a reference local cement. SECAR® 68V is designed for low cement castables till mid-temperature range for applications in DRI, tundish furniture, permanent lining, reheating furnaces, boilers, fired heaters, cement pre-heater and cooler sections, whereas SECAR® 71 is a versatile cement designed for applications above 1400ºC. Conclusions are drawn on the observations of the results and specific advantages of each cement.

1 Introduction

Direct Reduction of Iron (DRI) or sponge iron continues to contribute significantly to the steel production around the world. Unprecedented global recession has forced crude steel production in the world down by 13.6% YTD at the end of October, 2009. DRI industry, although faced the same trend, is down by 10% in the same period, from 48.890 million tonnes (January to October 2008) to 43.994 million tonnes (January to October 2009) [1].

India continues to lead DRI production in the world. Its production, despite global slow down and melting price levels continues to grow although at a significantly low rate – 4.13% from 16.670 million tonnes (January to October 2008) to 17.390 million tonnes (January to October 2009). India witnessed a massive DRI growth in the late nineties till 2007. From 1996 to 2006 compound annual growth rate reached 33%. India produced 39.5% of the total DRI production of the world this year till October.

Triggered by the growth in the infrastructure, housing and automobiles, domestic steel demand in India grew strongly (around 7%) from April to September 2009 and exceeded supply growth (around 4%) during the same period [2]. High domestic demand is expected to drive robust growth of the steel industry, which should mean rapid growth of DRI industry. The fundamental reasons for growth of DRI industry such as low investment, scarcity of steel scrap are still prevalent. However, more government control for environment protection may trim the rapid growth of late nineties and the beginning of this decade.

DRI plants in India predominantly have rotary kilns, which are lined with low cement castables. These kilns are coal fired and the maximum temperature reaches 1100º-1200ºC. Although, the kilns do not require very high temperature resistance, they suffer from accretion build up which clogs the feed movement through the kiln and eventually forces the kiln to shut down to remove accretion. Low quality coal with high alkali promotes penetration in the refractory wall causing accretion. Thus smooth and homogeneous lining surface with less porosity should resist accretion formation. High mechanical strength of the castable supports durability of the lining when the accretion is removed from the kiln. The refractory lining also needs high abrasion resistance as they are exposed to abrasion from the feed materials due to the movement of the kiln [3]. Good placing characteristics of the castable for this application, not only include excellent flow, but also rapid strength development. The rotary kiln is cast in segments, each of which should develop enough strength before the kiln is rotated for the next segment to cast.

Although, low cement (LCC) formulations are very common in India, well designed medium cement castables (MCC) are expected to offer better properties such as higher strength, lower porosity and better abrasion resistance, which can be linked to the DRI castable performance. Also, calcium aluminate cements have a major role in improving all of the above properties. In the present study three cements SECAR® 68V, SECAR® 71 and a reference local cement were tested in an approximately 80% alumina low cement and a medium cement castable. These six compositions were tested for placing properties such as flow profile and setting, installed and fired properties (at 800ºC and 1200ºC) such as compressive strengths, bulk density, open porosity and abrasion resistance.

2 Experimental procedure

Flow and flow decay with time was tested by ASTM C230. A flow cone with base diameter 100mm (d_1), 50mm height and 70mm top diameter was used. The cone was filled with castable, lifted and then vibrated for 30sec. with amplitude of 0.5mm. The final diameter (d_2) was measured and the flow % is calculated as:

Flow (%) = $((d_2 – d_1) / d_1) * 100$

All the experiments were carried out at 30ºC. To understand the setting characteristics exothermic profiles of each composition were determined at 30ºC with castable samples placed in an insulated chamber. A thermocouple was imbedded in the cast sample and linked to a data recorder and the temperature was recorded as a function of time [4].

Cold Crushing Strength (CCS) was tested on 40x40x160 mm prisms. Samples were then cured for 24h, dried at 110°C for 24h. The dried samples were then heated for 3h at 800°C and 1200°C. Strength measurements were conducted at room temperature.

To determine the abrasion resistance of the samples abradability index were tested according to British Standard 1902 Part 1A. 25x50x75mm test plates were cast, dried and fired 5h at 1200ºC. The fired test pieces were exposed to the flow of SiC grains. Abradability index was calculated from weight loss of the plates, bulk densities and a correction factor.

Properties of calcium aluminate cements

Properties of three different calcium aluminate cements, which were used in this study, are listed in table 1. Surface area (Blaine) of SECAR® 68V, SECAR® 71 and the reference cement are 4300, 3900 and 3800cm^2/g respectively.

Table 1: Chemical composition of SECAR® 68V, SECAR® 71 and reference cement

Compound	SECAR®68V - wt%	SECAR®71 -wt%	Ref. cement - wt%
Al_2O_3	66.8	69.2	72.9
CaO	31.0	29.9	25.8
SiO_2	1.3	0.4	0.61
Fe_2O_3	0.3	0.17	0.35
MgO	0.2	0.23	0.25

Model formulations

To study the effect of different calcium aluminate cements on low cement and medium cement castables following model formulations (Table 2) were used. The LCC formulation contains around 80% alumina and is commonly used in DRI application. The MCC formulation was arrived by adding 5% extra cement on LCC formulation and reducing fine Chinese bauxite by the same amount. This led to slight decrease of alumina % for MCC compositions compared to the LCC.

Table 2: Model formulations

Ingredients (wt %)	LCC	MCC
Chinese bauxite 3-5 mm	17	17
Chinese bauxite 1-3 mm	27	27
Chinese bauxite 0-1 mm	30	30
Chinese bauxite -200 mesh	16	11
Elkem 951U(China)	5	5
Calcium aluminate cement	5	10
Sodium hexa meta phosphate (Zhifeng, China)	0.1	0.1
Sodium tripoly phosphate (Tianjin Chemical plant)	0.1	0.1
Citric acid	0.02	0.03
Total	100.22	100.23

Three different calcium aluminate cements – SECAR® 68V, SECAR® 71 and a reference local cement were used for each composition leading to six different formulations, which are marked as follows (Table 3).

Table 3: Compositions and respective marks

Compositions	Marks
Low cement castable with SECAR® 68V	LC 68V
Low cement castable with SECAR®71	LC 71
Low cement castable with a reference local cement	LC LC
Medium cement castable with SECAR® 68V	MC 68V
Medium cement castable with SECAR® 71	MC 71
Medium cement castable with a reference local cement	MC LC

3

Properties of the LCC And MCC Compositions Using Different Calcium Aluminate Cement

Placing properties of castables using SECAR®68V

At 30ºC LCC and MCC were tested for vibra flow with time. Water % was found to vary depending on the type of composition (LCC or MCC) and calcium aluminate cement. Water % was adjusted for each composition to achieve similar initial flow (110 to 125%).

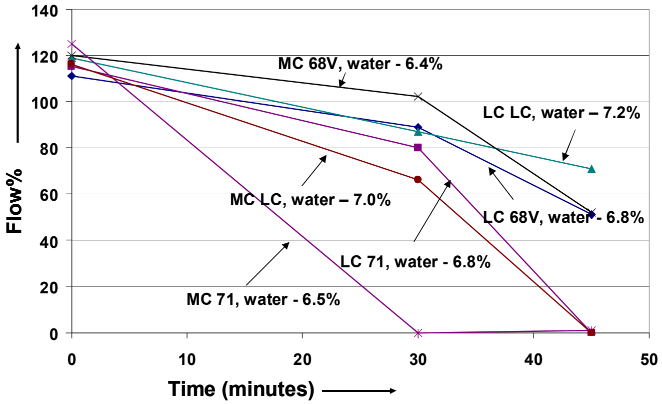

Figure 1: Flow decay with time in LCC and MCC using SECAR® 68V, SECAR® 71 and reference cement

LCC compositions took more water than the MCC for same calcium aluminate cement (Figure 1). SECAR® 68V and SECAR® 71–containing LCC compositions (LC 68V and LC 71) took exactly same water % and the MCC compositions (MC 68V and MC 71) took almost same water %. Reference local cement-containing LCC (LC LC) and MCC compositions (MC LC) took more water than all other LCC and MCC compositions respectively.

Setting retarders such as citric acid have a strong impact on flow retention. MCC compositions have slightly higher citric acid than the LCC (Table 2). However, most of the LCC compositions are found to have less flow decay compared to MCC composition.

Since the water % differs for different cements, flow retention is not appropriate to compare among these cements. However, SECAR® 71-containing castables, since have similar water requirement as SECAR® 68V-containing castables, can be compared and are found to have greater flow decay compared to SECAR® 68V-containing respective castables (Figure 1).

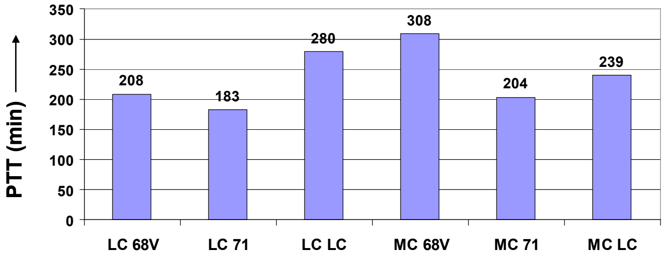

Figure 2: Peak time temperature (PTT) of all castables at 30ºC

Peak time temperature data for LCC and MCC compositions do not show any clear trend on castable setting, which is rather found to be more dependent on cement type (Figure 2). For both LCC and MCC, SECAR® 71-containing compositions are found to set quicker than the other cement-containing compositions.

Installed and fired properties

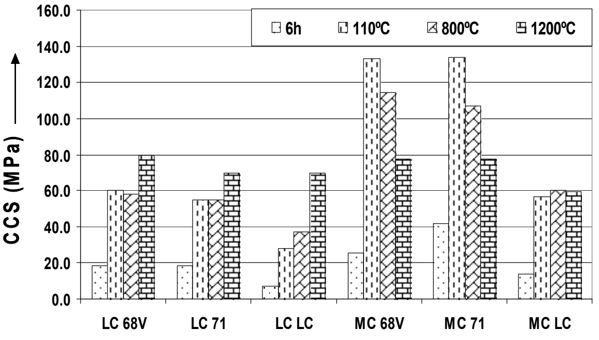

Figure 3: CCS of LCC and MCC compositions using different calcium aluminate cement after 6h at 30ºC, 24h at 110ºC, 3h at 800ºC and 3h at 1200ºC.

LCC compositions show increase in strength with temperature, whereas MCC compositions, particularly MC 68V and MC 71 are found to show very high 110ºC, followed by 800ºC and 1200ºC (Figure 3). MC LC shows similar strength from 110ºC to 1200ºC.

For each temperature MCC compositions showed higher strength than corresponding LCC compositions. This difference is very prominent at lower temperatures.

High 6h strength is very important as it enables quicker installation in the rotary kiln. LCC compositions with SECAR® 68V (LC 68V) and SECAR® 71 (LC 71) show significantly higher strength than that with reference cement (LC LC) after 6h. MCC compositions also follow the same trend. However, MCC composition with SECAR® 71 (MC 71) shows higher strength after 6h than that with SECAR® 68V (MC 68V), which is consistent with faster flow decay, shorter PTT for MC 71 than MC 68V indicating faster hardening or cement hydration for SECAR® 71 in these compositions than SECAR® 68V.

Dried (24h at 110ºC) and fired strength (3h at 800ºC) are significantly higher for MCC compositions than those for the LCC. However, after 3h at 1200ºC the difference in strength is not significant. SECAR® 68V and SECAR® 71-based compositions (both LCC and MCC) show significantly higher strength than the reference cement-based compositions and the difference is less prominent at 1200ºC.

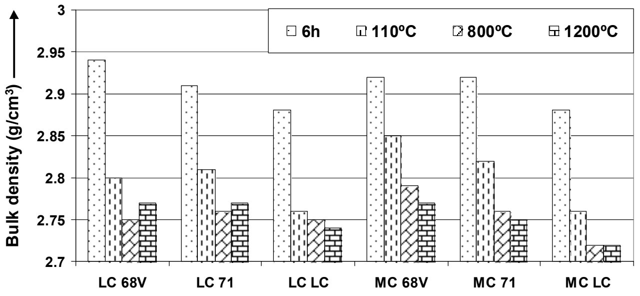

Figure 4: Bulk density of LCC and MCC compositions using different calcium aluminate cements after 6h at 30ºC, 24h at 110ºC, 3h at 800ºC and 3h at 1200ºC.

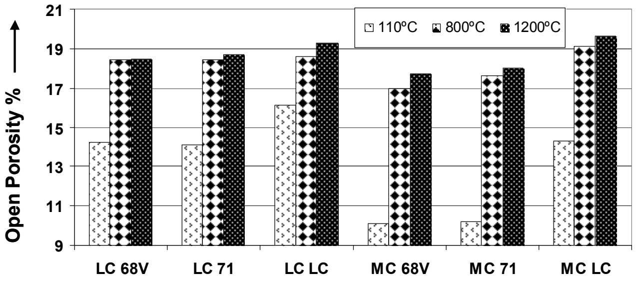

Figure 5: Open porosity of LCC and MCC compositions using different calcium aluminate cements after 24h at 110ºC, 3h at 800ºC and 3h at 1200ºC.

Bulk density after 6h does not vary significantly with respect to the variation of castable type (MCC or LCC) or calcium aluminate cement (Figure 4) due to the presence of water in the pores. However, significant differences could be observed from 110ºC. MCC compositions, after 24h at 110ºC show lower porosity (Figure 5) and higher bulk density than the LCC due to lower water demand in the former. At higher temperatures (1200ºC) the effects are less obvious. SECAR® 68V and SECAR® 71-containing MCC compositions (MC 68V and MC 71) show lower porosity after 3h at 800ºC and

1200ºC than corresponding LCC compositions (LC 68V and LC 71). However, this is not reflected completely by the bulk density values, probably due to the compositional difference between MCC and LCC composition, as 5% calcined bauxite of LCC compositions was replaced by cement in MCC compositions. Calcined bauxite (5%) possibly provides slightly higher density than equal amount of calcium aluminate cement. Increase in bulk density for MCC compositions compared to the LCC at 800ºC and 1200ºC can only be observed for those cements which develop bigger difference in water% between the LCC and MCC compositions. After 3h at 800ºC and 1200ºC MC 68V shows higher bulk density than LC 68V, MC 71 shows similar values with LC 71 and MC LC shows lower values than LC LC. It is consistent with the corresponding difference in water % which are 0.4, 0.3 and 0.2 respectively.

Abrasion resistance

Abradability Index values after 5h at 1200ºC (Figure 6) reveal that MCC composition with SECAR® 68V (MC 68V) and SECAR® 71 (MC 71) have better abrasion resistance than the corresponding LCC compositions (LC 68V and LC 71), whereas MCC with reference cement show lower abrasion resistance than the LCC (Figure 6). SECAR® 68V-containing compositions, i.e. MC 68V and LC 68V have highest abrasion resistance than the corresponding castable types with other cements, whereas the reference cement-containing compositions have lowest abrasion resistance.

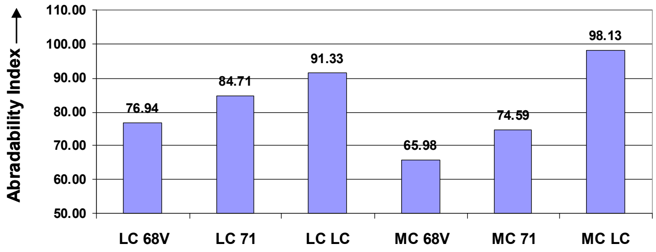

Figure 6: Abradability Index of LCC and MCC compositions using different calcium aluminate cement after 5h at 1200ºC.

4 Effect of Calcium Aluminate and Castable Type

MCC compositions, although contain higher cement% than the LCC, require lesser water (Figure 1) to cast possibly due to the high open porosity of fine bauxite present in higher quantity in LCC compositions. Lower water% for MCC in general produced lower porosity (Figure 5), higher strength (Figure 3) and better abrasion resistance (Figure 6). Unlike high cement castables, LCC show continuous strength improvement with increase in temperature. MCC compositions show decrease of strength at 1200ºC from 110ºC, however their strength levels are higher than LCC compositions for all temperature. Higher cement % in MCC compositions provides better hydraulic strength and same fraction of microsilica (5%) as in the LCC ensures flowability and fills the pores resulting very high strengths at low temperatures. SECAR®68V and SECAR® 71-containing compositions follow the above trend distinctly, whereas the reference cement is found to be significantly different. It absorbs much higher water and develops lower hydraulic strength, possibly due to presence of less reactive hydraulic phases and lower surface area. At higher temperature when the hydraulic bond disappears, the reference cement-containing compositions are found to reduce the gap in the properties with SECAR® cement-containing compositions. However, even at 1200ºC reference cement-containing compositions did not reach the key properties such as porosity, CCS, abrasion resistance of SECAR® cement-containing compositions.

5 Conclusion

Ageing of CAC seems to proceed by two periods, each one leading to weight increase and characterised by increase of LOI, but having opposite impact on reactivity. The first period is a surface pick up of H_2O and CO_2 which leads to a delay of dissolution, working time and demoulding time. At this stage there is generally no visible sign of ageing like lumps. The second period is characterised by a decrease of working time and the precipitation of hydrates.

Other components of the formula also play a role in ageing, either because they bring moisture and increase internal humidity within the bag, or by hydroscopic behaviour of some admixtures.
In order to better understand ageing mechanisms and design rapid ageing test it is necessary to generate insitu internal humidity and temperature within bags during shelf life. Rapid ageing tests can be performed in the laboratory, for example at 90% RH the level of ageing after one day is equivalent to several months in bags.

6 Acknowledgements

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