High Alumina Self-flow Castables with Different Binders

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The effect of binders and their amount on high alumina self-flow castables has been studied. Self-flow castables have been prepared by fixing the distribution coefficient q at 0,21, in the continuous particle size distribution model, as proposed by *Dinger-Funk*. High alumina cement and silica sol were used at 4 and 6 mass-% as binder and water was added during mixing till self-flowing consistency was achieved in the castable mix. The cast castable cubes were dried and heat-treated at 950 °C and 1550 °C. All the dried and heat-treated samples were characterized for bulk density, volume shrinkage, cold crushing strength and phase analysis by XRD.

1 Introduction

The ever-increasing demand and application of unshaped refractories to replace conventionally shaped refractories due to many major advantages [1] have inspired scientists and manufacturers to continuously investigate these materials in depth and to improve their quality and performance. Since the early 1960s, the availability of purer calcium aluminate cements (CACs) with higher alumina content has made the unshaped refractory system cleaner and allowed them to be applicable for various high-temperature applications [2]. Among the various unshaped refractories, castables lead in all the areas of research, development, manufacturing and application. Physical, mechanical, chemical and thermo-mechanical characteristics of various castable systems as well as their processing and bonding mechanisms are the focus of such investigations.

Refractory castables are combinations of refractory aggregates, matrix components, bonding agents, and admixtures. The proportions of each component used vary in each castable composition to achieve the desired properties essentially required for the intended application. Among different bonding agents calcium aluminate cement is the commonly used hydraulic binder in refractory castable compositions, but presence of CaO in the cement results low melting phases with Al_2O_3 and Al_2O_3-SiO_2 refractory systems [1, 2]. Another important concerns for cement containing castables are the curing and dewatering steps, which must be carefully conducted in order to reduce explosive spalling [1]. A significant increase in the life and performance of alumina based castables has been made possible by decreasing the cement-content, thus avoiding/reducing the formation of liquid phase at application temperatures, which in turn improves the corrosion resistance and creep strength. Following this scientific backup, low cement castable (LCC), ultra low cement castable (ULCC), no cement castable (NCC) and self-flow castables (SFC) have already become popular in the refractory industries [3–5].

Further development work resulting in a new bonding system with superfine materials prepared through the sol-gel route, appeared in the industry, which opened a new horizon for refractory technologists. When combined with other solid particles, sol can be linked together in branched chains, in a process known as gelation [6, 7], which can be induced by water removal. During the drying step, the hydroxyl groups (Si–OH) on the surface of the particles generate siloxane bonds (Si–O–Si), which results in a three-dimensional network [7]. So, in a refractory system formation of a three dimensional network gel structure from a sol that surrounds the refractory aggregates results in strength in the system during drying. Sol reduces/removes the cement from the castable composition and on subsequent heating develops strength through the formation of ceramic bonding at low temperature (faster sintering due to finer size) resulting in superior properties [8–10]. Silica and alumina sols have been tried for this purpose to a great extent and successful commercialization has also been achieved mainly by using silica sol.

The present work is designed to compare these two binders, namely high alumina cement and silica sol, at different percentages in a high alumina self-flow castable with a continuous particle size distribution with a distribution coefficient (q-value) of 0,21. Castable compositions were mixed to attain similar self-flowability. The cast was cured, dried and fired. The dried and fired shapes were tested for a comparative study.

2 Experimental

High alumina self-flow castables were prepared using white tabular alumina (WTA) (*Almatis*/IN), white fused alumina (WFA) and brown fused alumina (BFA) (both from *Orient Abrasives*/IN) grains/aggregates, technical alumina fines (*INDAL*/IN), high alumina cement (*Polychem*/IN), silica sol

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Tab. 1 Physico-chemical properties of the starting materials of the castables

Constituent	WTA Grain	BFA Grain	WFA Grain	Alumina Fines	Fume Silica 971 U	Alumina Cement	Silica Sol
SiO_2 [%]	0,04	0,4	0,1	0,2	96,1	0,95	29,6
Al_2O_3 [%]	99,4	95,66	98,92	98,0	0,4	73,30	
Fe_2O_3 [%]	0,04	0,4	0,06	0,06	0,1	0,20	
TiO_2 [%]		0,64	traces	0,11			
CaO [%]		0,01			0,2	24,50	
MgO [%]					0,1	0,45	
$Na_2O + K_2O$ [%]	0,16		0,08	0,34	0,4		
LoI [%]				0,2	0,9	0,35	70,3
Average size [µm]				6–8	<45		~ 0,014
Bulk density [g/cm³]	3,61						
App. Porosity [%]	3,92						
Spec. surface area [m²/g]					~20	0,43	
Phase analysis	corundum			corundum	amorphous	CA_2, CA	

(*Dr. Khan's Laboratory*/IN), silica fume (*Elkem*/IN) and additives like deflocculants and set retarder. Details of the physico-chemical properties of the starting materials are provided in Tab. 1. Continuous particle size distribution model as proposed by *Dinger* and *Funk* was used for the castable system with a distribution coefficient q = 0,21, using the coarsest particle size of 5,6 mm and the finest of 0,001 mm [11–12]. Tab. 2 shows the cummulative percentage finer than (CPFT) of different particles sizes calculated from the formula. Tab. 3 shows the percentages of the different particle size fractions that are used for for making the castable compositions. Four different castable batches were prepared using 4 and 6 mass-% of cement (henceforth the batches are termed as 4C and 6C) and 4 and 6 mass-% of silica sol (henceforth the batches are termed as 4S and 6S). Other than binder silica fume at an amount of 4 mass-%, sodium hexa-metaphosphate at an amount of 0,1 mass-%, citric acid 0,05 mass-% and organic fiber 0,05 mass-% were used for the cement containing compositions. And for the sol containing compositions organic fiber at an amount of 0,05 mass-% was used. All the batches were processed under similar conditions.

First, all the raw materials were dry mixed in a planetary mixer, water was added till the mix attains self flowing consistency. Next the mixed batches were poured into lubricated moulds of a dimension of 50 mm³. The excess mix was scrapped off and smoothened by a trowel. The mixes were allowed to aged for 24 h in inside the mould under humid condition. Next they were de-molded and allowed to be air dried for 24 h followed by oven drying for 24 h. The dried samples were then fired at 950 °C and 1550 °C with 2 h soaking time at peak temperatures.

Dried and fired cubes were characterized for volumetric shrinkage, bulk density (BD) and cold crushing strength (CCS) (all measured as per Bureau of Indian Standard (BIS) specifications, IS 1528–1974, Part XII, Part VIII and Part IV, reaffirmed on 2002). Each data represented here are an average of five individual measurements. Also the 6 mass-% binder containing 1550 °C fired samples were tested for phase analysis by X-ray diffraction method.

Chemical analyses of the starting raw materials were conducted using the acid-dissolution method. Densification studies

Tab. 2 CPFT (cummulative percentage finer than) for various particle sizes

Fraction [mm]	CPFT [%]
5,6	100
2,8	83,81
2,0	76,76
1,0	63,72
0,5	52,45
0,25	42,7
0,15	36,37
0,075	28,8
0,001	0

Tab. 3 Percentage of aggregate for each fraction

Fraction [mm]	Percentage [%]
–5,6 to +2,8	16,19
–2,8 to +2,0	7,05
–2,0 to +1,0	13,04
–1,0 to +0,5	11,27
–0,5 to +0,25	9,75
–0,25 to +0,15	6,33
–0,15 to +0,075	7,57
–0,075 to +0,001	28,8

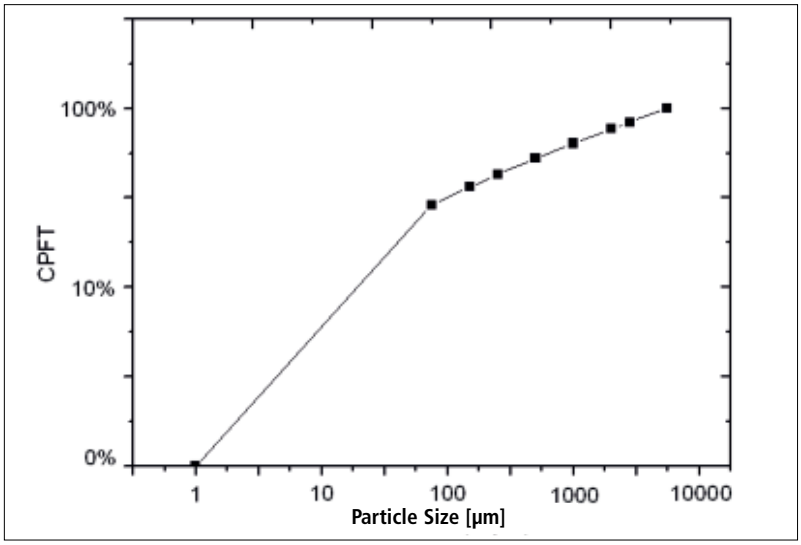

Fig. 1 Plot of CPFT against particle size on log-log scale

Tab. 4 Water consumption in casting

Binder Amount [%]	Water Required for Casting [%]	
	Cement Based Castable	Sol Based Castable
4	6,2	2,8
6	7,2	2,0

were conducted using the conventional liquid-displacement method according to the Archimedes principle. Phase identification was performed in a X-ray diffractometer (PW-1830, *Philips*/NL) using Cu Kα radiation with a scanning speed of 2°/min. Firing schemes were conducted in a programmable electric furnace (*Bysakh & Co.*/N). Cold crushing strength was measured in a compressive testing machine *(AIMIL*/N).

3 Results and discussion

Fig. 1 shows the plot of CPFT against particle size for the distribution coefficient q = 0,21. The highest particle size of 5,6 mm has a CPFT of 100 % and the lowest particle size being 1 µm shows 0 % CPFT. There is an abrupt change in the slope of the plot in the finer size range due to high fine content (28,8 %) in the compositions (low q-value).

Tab. 4 shows the water required for attaining self-flowing consistency of the cement-bonded and sol-bonded castables.

Cement-based castables show higher water consumption than sol-based castables as sol has a solid content of 30 % and the rest is liquid, which supports the flowability. The water requirement to attaining self-flowability in cement-based castables increases with increase in high alumina cement content due to higher water requirement for hydration of higher amount of cement. For sol based castables the water requirement decreases as the percentage of sol increases (4 to 6 mass-%) as the amount of free liquid also increases.

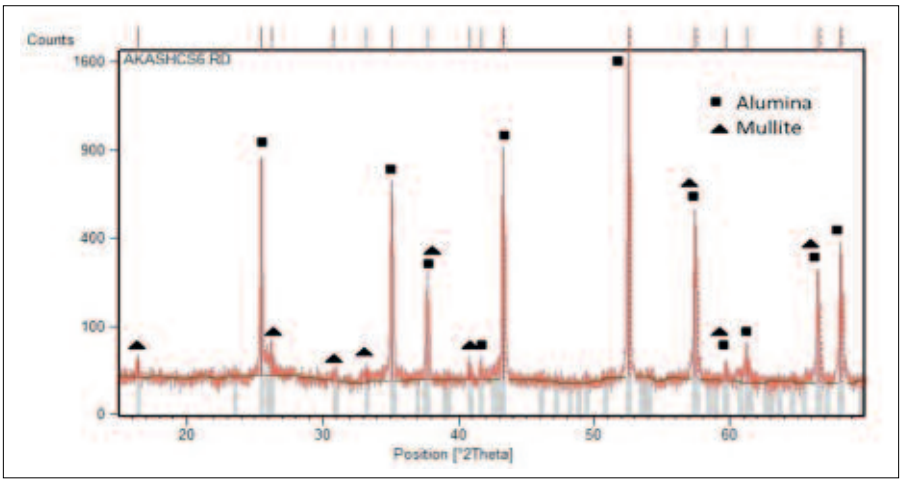

Fig. 2a XRD plot of 6 mass-% silica sol-based castables fired at 1550 °C

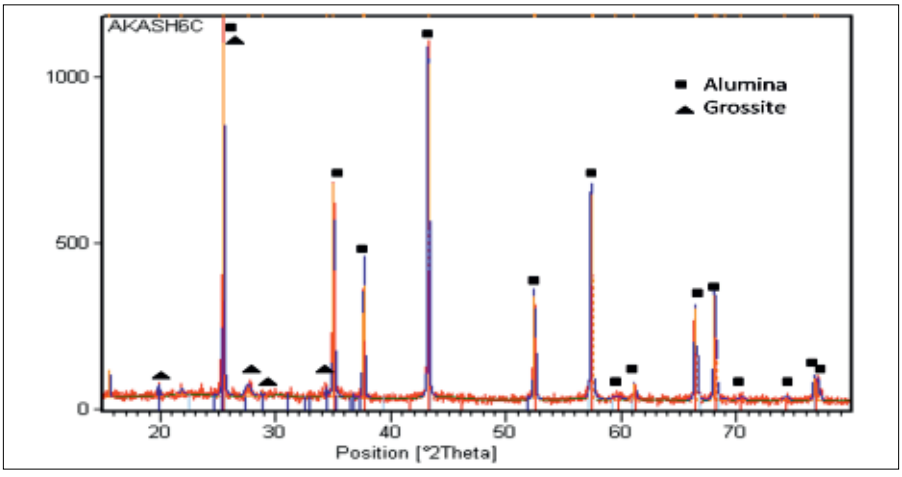

Fig. 2b XRD plot of 6 mass-% high alumina cement-based castables fired at 1550 °C

3.1 Phase analysis of 1550 °C fired castables

Silica sol containing castables show (Fig. 2a) that corundum is present as the major phase and little amount of mullite as minor one. Mullite may be formed due to the reaction at high temperatures between fine alumina particles and SiO_2 particles coming from sol in the matrix phase of the castable.

Again XRD analysis of the cement containing castable shows (Fig. 2b) that the major phase present is corundum and the minor phase is grossite (CA_2). No hibonite phase (CA_6) formation was observed. Again the calcium aluminate (CA) phase was also not found (which was present in cement) may be due to reaction between fine alumina and CA phase at high temperatures in the matrix of the castable.

3.2 Bulk density study

Fig. 3 shows the variation of bulk density of different compositions studied against temperature. For sol containing castables, the 4 mass-% sol containing composition showed lower density values than that of 6 mass-% sol containing ones due to presence of higher amount of moisture required for attainment of self flowing consistency. But the density values of both the sol containing compositions sharply decreased on firing at 1550 °C due to formation of a mullite phase, which has a much lower specific density than a corundum phase.

Also sol-containing castables showed higher values of density than cement-containing ones due to presence of a lower extent of moisture. Again for cement-containing compositions, 6 mass-% cement containing one showed a lower density values than 4 mass-% ones, due to the presence of higher amount of moisture.

3.3 Volume shrinkage study

Fig. 4 shows the variation of the volumetric shrinkage against temperature for different binders at different percentages. The cement-based castables show shrinkage at

both the 950 °C and 1550 °C firings whereas sol-based castables show shrinkage at 950 °C and expansion at 1550 °C.
Expansion is due to the formation of the mullite phase, as observed in the phase analysis. At 1550 °C, as higher amount of mullite is formed in 6 mass-% sol based castable than 4 mass-% sol-based castable. It shows higher expansion.

3.4 Cold crushing strength study

Fig. 5 shows the variation of the cold crushing strength of different castable compositions containing different amount of binders against temperature. At 110 °C, the cement-based castables show higher strength values than the sol containing castables due to presence of hydrated bonding phases, compared to coagulation bonding in sol containing compositions.
6 mass-% cement-based castable gives higher strength than 4 mass-% cement-based castable due to higher amount of the hydraulic bond formation. But the strength values for these cement-containing castables at 110 °C are lower than the conventionally/commercially used castables due to presence of CA_2 phase as the major one in the cement and strength degradation at 950 °C was not observed unlike theoretical estimation, as because the major phase present in the HAC is CA_2, which produces a AH_3-gel on hydration, results in better filling of pores and restricts the strength degradation.
At 1550 °C, the cement-based castables show higher strength values than sol-based castables due to higher densification and also expansion associated with mullite formation in sol-containing castables results in finer cracks thus reducing strength.

4 Conclusion

Effect of binder and its amount on the high alumina self-flow castable, with a distribution coefficient q = 0,21 as per the continuous particle size distribution model proposed by Dinger-Funk, has been studied.
Mullite phase is found in the sol-bonded castable due to the reaction between silica particles from sol and fine alumina present in the matrix at high temperatures and the sol-containing castables showed expansion characteristics with a fall in density values at 1550 °C.

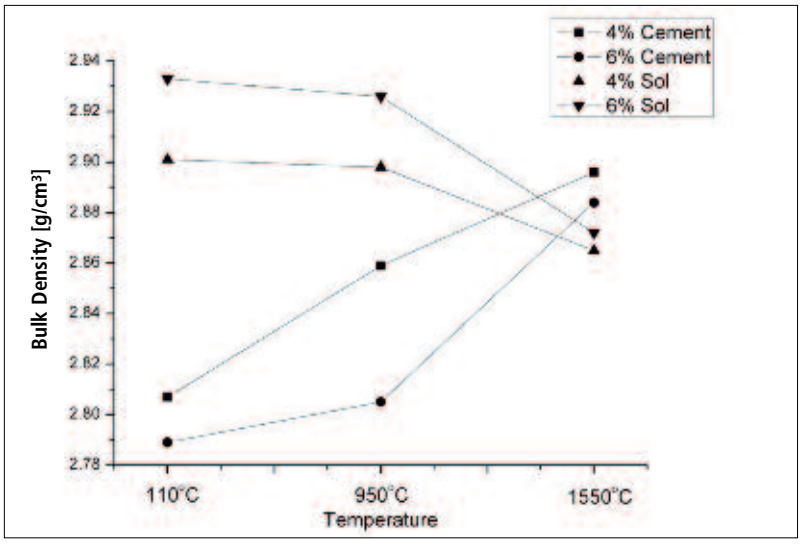

Fig. 3 Variation of bulk density against temperature

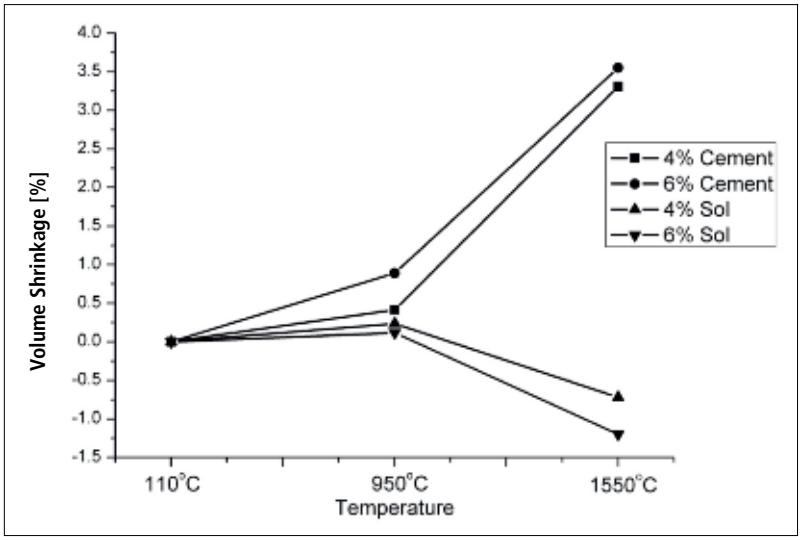

Fig. 4 Variation of volume shrinkage against temperature

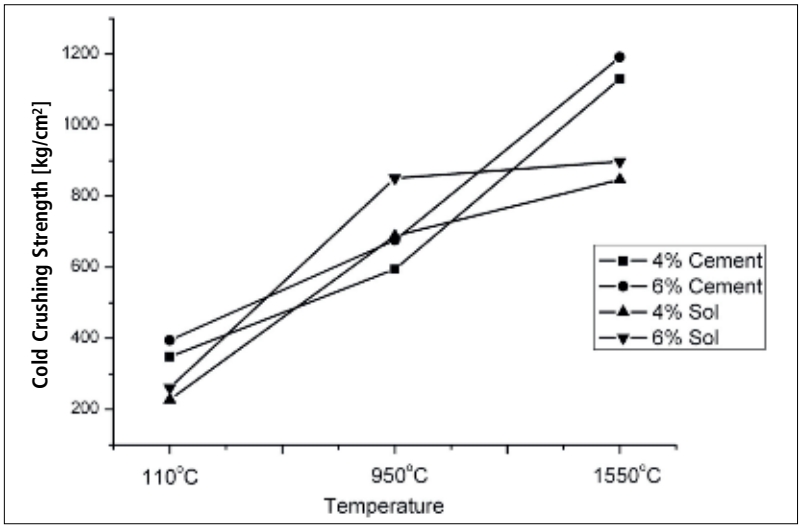

Fig. 5 Variation of cold crushing strength against temperature

Only grossite is found other than corundum phase in XRD of cement-bonded castable may be due to an unreacted grossite phase from high alumina cement or due to formation of grossite phase by reaction between of calcium aluminate and fine alumina present in the matrix at high temperatures.

Initial strength of the sol-bonded castable was found to be lower than that of the cement-bonding one due to the coagulation bond mechanism of sol as compared to that of the chemical hydrate bond formation in cement containing ones.

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