

Effect of Cement and Sol Combined Binders on High-Alumina Refractory Castables

R. Sarkar, J. Srinivas

Combined and individual bonding effects of high-alumina cement and silica sol on high-alumina castable were studied. The castable compositions were prepared as per the Dinger and Funk particle size distribution model with distribution coefficient $q = 0,21$ and $0,29$ respectively. Bonding systems used in the castables had a cement/sol ratio as 00:100, 25:75, 50:50, 75:25, and 100:00. Castables were processed per conventional preparation, cast under vibration, and heat treated at 110, 900 and 1500 °C respectively. The physical, mechanical and thermomechanical properties of the prepared castables were characterized. The dried strength was found to increase with the increase in cement content in the binder system but the hot strength values were found to decrease. Phase analysis study of the matrix phase of fired compositions confirmed the formation of mullite, grossite, hibonite and anorthite phases in the castables.

1 Introduction

The iron and steel industry is undergoing revolutionary changes for adaptation of automation and advanced technologies to improve the quality and production of steel. As a consequence, refractories that are in use need to adapt these changes in process conditions and are to face severe challenges to meet the critical operational parameters at high temperatures with less down time. Unshaped refractories having several advantages over conventional shaped refractories [1] are gradually replacing the shaped ones in most of the critical and stringent application areas and resulting in better performance with increased life and productivity. Since the development and wide commercial availability of purer calcium aluminate cements (CACs) with higher alumina content in 1960s, developmental work on unshaped refractories got the momentum and the refractory researchers and manufacturers are in constant pursuit to improve further their quality and performance for high temperature applications [2]. Unshaped refractories, especially castables, have quickly grown at the expense

of shaped ones because of faster, easier and cheaper installation; ready availability; reduced corrosion due to the absence of lining joints; greater volume stability and better spalling resistance [2, 3]. Castables are the most studied and widely used unshaped refractory which has modified with time from a simple mix of different fractions alumina source and binder to a complex and technical formulations, suitable for various critical applications with very specific and tailored properties. A castables can be defined as a blended mix of different fractions of aggregates with bonding agent and additives, which is transported to the user industry as a dried mass of loose powders and mixed with a liquid (mostly water) and placed (installed) to form the desired shape or structure that becomes rigid due to setting of the binder and then fired to complete the process [4].

Among different bonding agents used for castables, calcium aluminate cement is the commonly used hydraulic binder. But presence of CaO in the cement produces low melting compounds at high temperatures by reacting with Al_2O_3 and $Al_2O_3-SiO_2$ refractory aggregates and affects the high

temperature properties [1, 2]. Also curing and dewatering of the castable require special attention to reduce any crack formation and explosive spalling [1]. To reduce the detrimental effects of lime in the alumina castable system, a reduction in lime content in the cement was tried but that results in reduced hydraulic activity of the cement and degradation of cured properties essentially required for installation purpose. A significant increase in the castable lining life and performance are achieved by decreasing the cement content in the castable adjusting with the addition of certain additives, which reduces the amount of liquid phase formed at application temperatures. This also improves the corrosion resistance and creep strength properties. Also lesser cement content reduces the risk of cracking after drying. Following this scientific backup, low cement castable (LCC), ultra-low cement castable (ULCC), no cement castable (NCC), etc., have developed and already became popular in the industries [3–6].

The benefit of reduction in total lime content in the castable composition was found to be incremental as the presence of lime, even in lesser amounts, produces low melt-

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Tab. 1 Physico-chemical properties of the raw materials

Oxide [mass-%]	WTA	TA Fines	FS	HAC	SS
SiO ₂	0,1	0,03	96,2	0,21	29,8
Al ₂ O ₃	99,1	99,5	0,4	71,64	
Fe ₂ O ₃	0,035	0,03	0,1	0,11	
CaO		0,02	0,2	26,91	
MgO		0,01	0,1	0,32	
Na ₂ O+K ₂ O	0,4	0,1	0,4	0,27	
L.o.I. [%]			0,8		70,1
Average size [µm]					
		6–8	100 % <45		0,02
Bulk density [g/cm³]	3,61				
App. porosity [%]	3,9				
Spec. surface area [m²/g]		2,5	~20	0,4	
Phase analysis	corundum	corundum	amorphous	CA ₂ , CA	

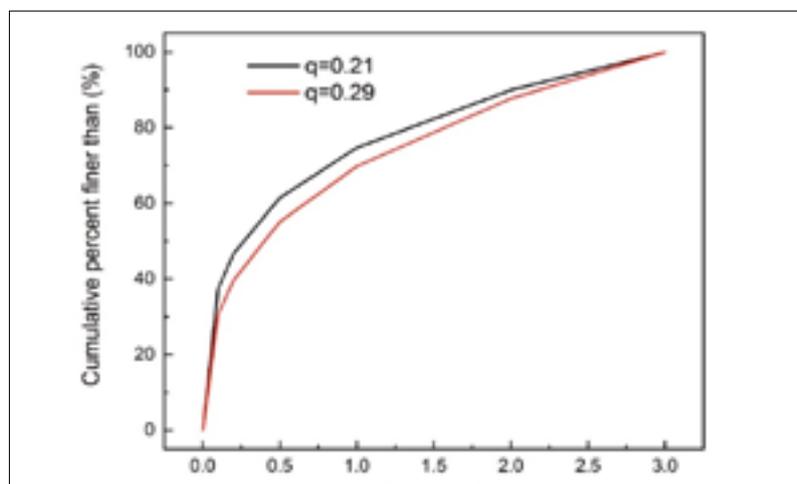


Fig. 1 Particle size distribution plot of castables with $q = 0,21$ and $q = 0,29$

ing phases, may be in lesser extent and the application temperature was increased marginally. Hence the researchers were in search of new bonding system avoiding lime which came as the sol-gel bonding system and opened up a new horizon for refractory technologists. Sol is a metastable condition of very fine colloidal particles, which on variation in time, temperature, pH and water removal, linked together in branched chains to form a three dimensional network of gel structure; and the process is known as gelation [6, 7]. Among ceramic systems, due to greater stability at higher solid content silica sol is commonly used for refractory castables. During the drying step, the hydroxyl groups of silica sol (Si-OH) on the surface of the particles get dehydrated and generate the three dimensional network of siloxane bonds (Si-O-Si) [8]. This network structure

of gel bonding surrounds the refractory aggregates/particles present in the castable system and results in strength development during drying. Further heating of the castable compositions develops ceramic bond due to sintering at low temperature (faster sintering due to finer size) resulting in superior properties [9–11]. Thus the lime free (no cement) castable system is developed.

But as the gel structure from sol is based on weak coagulation bonding compared to strong hydraulic bonding of cement, the castables with sol-gel bonding are weak (low strength) at cured/dried condition [12, 13] and in some cases takes longer time to set and develop strength after installation. Hence, none of the bonding systems is free from any demerits and some compromise is to be accommodated for each bonding system to attain certain desir-

able properties in the composition. Though literature provides plenty information on the use of cement or sol as binder in castable compositions, but hardly there is any information on the use of both binders in combination to study their combined effect on the properties of high-alumina castable. And such a work is planned in the present study. High-alumina castable compositions with distribution coefficients $q = 0,21$ and $0,29$ respectively as per Dinger and Funk particle size distribution (PSD) model were used. Only cement (4 mass-% as LCC) and sol (6 vol.-% to mass-%) bonded compositions were prepared as base compositions to study. Combined binders using cement to sol ratio as 25:75, 50:50 and 75:25 (as compared to the amount used in base composition) were also used in the castable composition. All castables were processed conventionally and characterized for density and cold strength after heat treatment at different temperatures as well as hot strength and phase analysis after firing.

2 Experimental

The starting materials used are white tabular alumina (WTA) of different fractions, technical alumina fines (TA) as the castable main constituent; calcium aluminate cement (HAC) and silica sol (SS) as binder. The details of the raw materials are given in Tab. 1. Castable formulation was prepared using the PSD formula proposed by Dinger and Funk [14], as follows,

$$CPFT = (D^q - D_s^q) / (D_l^q - D_s^q) \times 100$$

where, $CPFT$ = cumulative percent finer than (the size D), D = particle size, D_s = minimum particle size, D_l = maximum/largest particle size, q = distribution coefficient/modulus. In the present work, q value of 0,21 and 0,29 are used and the plot for PSD, used in the study, is shown in Fig. 1.

For the cement containing compositions, fume silica (FS) as flow modifier (equal in amount to the amount of cement used), darvan C as deflocculant (7,5 mass-% to the amount of cement used in the composition) and citric acid as set retarder (2,5 mass-% to the amount of cement used in the composition) were added as additives. Also 0,05 mass-% of polypropylene fiber was used for all the compositions for easy removal of moisture vapour during drying.

All the raw materials were first dry mixed as per the batch composition (Tabs. 2, 3) in a planetary mixer (Hobart/GB, model N50). Next water and or silica sol was added to the dry mixed batches while mixing. Mixing was continued thoroughly till proper consistency was attained. Addition of water was done to attain the proper flow consistency on vibrator. Mixed batches were then cast into 50 mm cube shaped lubricated moulds on a vibratory table with 3200–3600 vibrations/min and an amplitude of $\pm 0,5$ mm. Cast products were then cured in humid condition within the mould for 1 day, next demoulded, air dried for another 1 day and further oven dried at 110 °C for 1 day. Dried products were fired at 900 and 1500 °C with 1 h soaking time. All the firings were conducted in a 1700 °C programmable electric resistance furnace (Okay/IN).

The bulk density (BD) and cold crushing strength (CCS) of the dried, 900 °C and 1500 °C heat treated samples were measured as per Bureau of Indian standard IS 10570 (2011) specification. Cold crushing strength was measured in a compressive testing machine (Aimil/IN). 1500 °C fired samples were also evaluated for the hot strength (MOR) measurement at 1400 °C in an HMOR furnace (Bysakh & Co./IN) with alumina supporting and mullite loading rods. Phase analysis study of the matrix part (grains were avoided to reduce the interference of the corundum grain phase and identify any trace phase formed) of the castables fired at 1500 °C was also done by powder X-ray diffraction technique, using Cu K α radiation through Ni-filter, in an x-ray diffractometer (Rigaku/JP, model Ultima-IV).

3 Results and discussion

Physico-chemical properties of the raw materials show (Tab. 1) that the materials are pure and contain very minimum amount of impurities. Among the two different aluminas used, TA is marginally purer. Cement used is a mixture of both calcium aluminate (CA) and calcium dialuminate (CA $_2$) phases. Silica sol used is also pure with about 30 % solid content. Fig. 1 shows the PSD of the castables with distribution coefficient $q=0,21$ and $0,29$ respectively. It can be seen that increasing q value resulted in decreasing amount of fines and increasing amount of coarse content in the granular compositions. Tab. 2–3 show the batch compositions

Tab. 2 Batch composition, binder content and water used for castables with $q = 0,21$

Material [mass-%]	Batch 0	Batch 25	Batch 50	Batch 75	Batch 100
WTA (3–0,05 mm)	62,72	62,72	62,72	62,72	62,72
TA (0,05–0,01 mm)	37,28	35,28	33,28	31,28	29,28
Cement	0	1	2	3	4
Fume silica	0	1	2	3	4
Darvan C	0	0,075	0,15	0,225	0,3
Citric acid	0	0,025	0,05	0,075	0,1
Silica sol	6	4,5	3	1,5	0
Water	0	1,9	3,8	5,7	7,5

Tab. 3 Batch composition, binder content and water used for castables with $q = 0,29$

Material [mass-%]	Batch 0	Batch 25	Batch 50	Batch 75	Batch 100
WTA (3–0,05 mm)	69,53	69,53	69,53	69,53	69,53
TA (0,05–0,01 mm)	30,47	28,47	26,47	24,47	22,47
Cement	0	1	2	3	4
Fume silica	0	1	2	3	4
Darvan C	0	0,075	0,15	0,225	0,3
Citric acid	0	0,025	0,05	0,075	0,1
Silica sol	6	4,5	3	1,5	0
Water	0	1,8	3,6	5,5	7

of the castables studied. Cement and fume silica is considered as the fine component of the castable and for compositions with these two components, the fines content of the castable is adjusted with a reduction in fine alumina content. Amount of binders to be used was fixed in the batch and addition of water was done to attain proper flow consistency in the mixer for vibration casting. Increasing amount of water is required with increasing amount of cement content (reduction in sol amount). Also a marginal decrease in water requirement was observed for the batches with higher q values, even for similar binder content, due to reducing amount of fines present in the systems resulting in reduced surface area to wet by the liquids. Again total amount of liquid required for similar consistency was found to be minimum for the only silica sol containing compositions, this may be due to the presence of nanometric and spherical silica sol particles present in greater extent which improves the flowability.

3.1 Phase analysis study

Phase analysis study of the matrix phase of 1500 °C sintered samples are shown in Fig. 2. Only sol containing composition (batch 0) showed the presence of

mullite ($3Al_2O_3 \cdot 2SiO_2$) phase other than corundum in the matrix, confirming the reaction between silica of sol particles and alumina of the matrix phase at 1500 °C. No other phases were found in the composition. Whereas, the only cement containing one (batch 100) showed the presence of minor amount of mullite, grossite ($CaO \cdot 2Al_2O_3$), hibonite ($CaO \cdot 6Al_2O_3$) and anorthite ($CaO \cdot Al_2O_3 \cdot 2SiO_2$) phases in the matrix phase indicating reactions between fine alumina particles of the matrix phase with cement and fume silica at 1500 °C. The batch 50, containing the silica sol and cement in 50:50 ratio also showed similar type of matrix phase analysis but with little different intensities of the peaks. This also confirms the reactions among the fine alumina with cement, sol and fume silica particles in the matrix phase at 1500 °C.

3.2 Density study

Bulk density values of the castables treated at different temperatures are shown in Fig. 3. A general trend of higher density values for the castables with higher q value is observed may be due to presence of greater extent of coarser particles in the batch. This trend is observed for all the different binders at all the temperatures. Also a trend of reduced

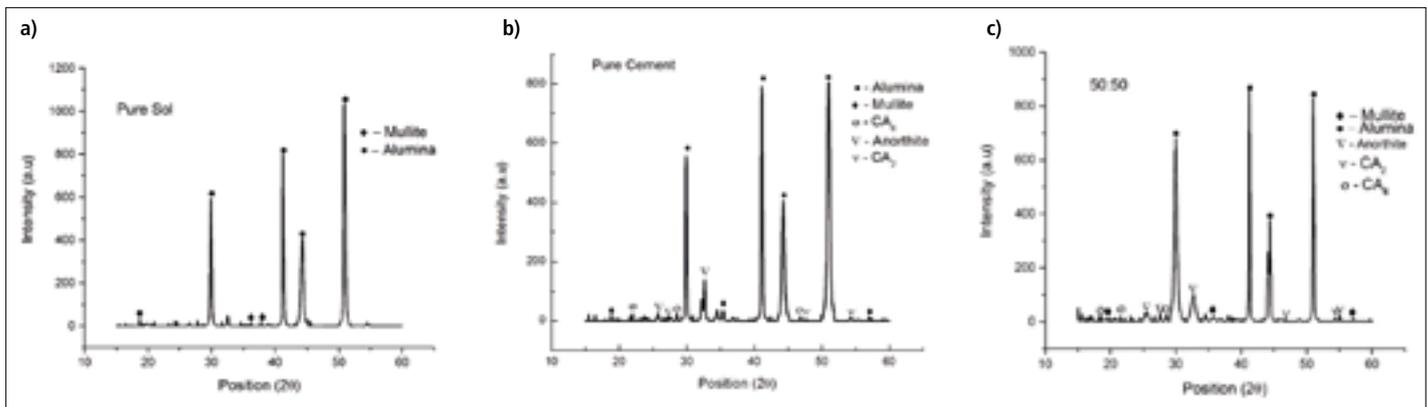


Fig. 2 a–c X-ray diffraction plots of the matrix phase of 1500 °C sintered: a) pure sol, b) pure cement, c) 50:50 sol:cement containing castables

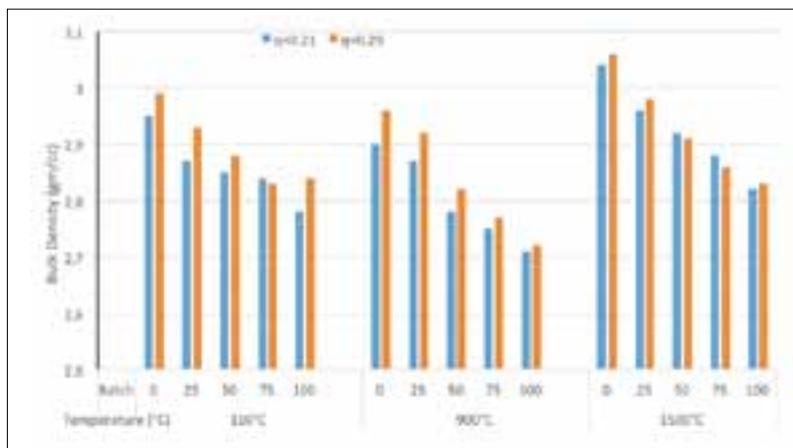


Fig. 3 Bulk density study of the castables heat treated at different temperatures

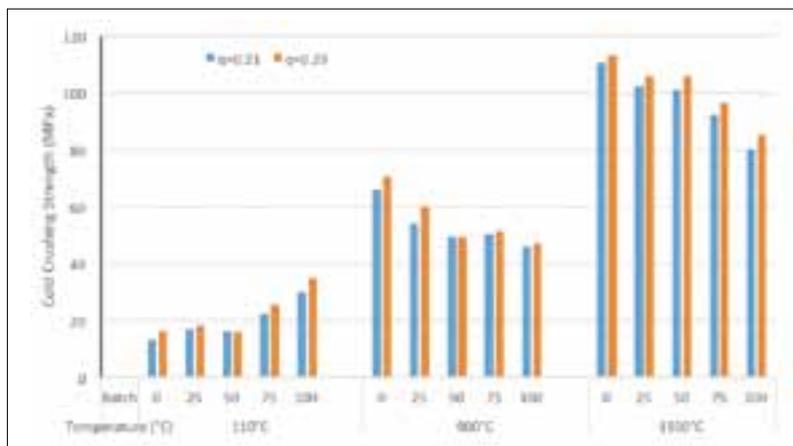


Fig. 4 CCS study of the castables heat treated at different temperatures

density value for 900 °C fired samples and then again increased values for 1500 °C sintered samples are observed for all the compositions having different binders and distribution coefficients. Reduction in density at 900 °C for all the different binder combinations is due to the removal of structural/chemical water associated with the bond causing in weight loss and may be some rup-

turing of the sample during bond breaking. Again increase in density values at higher temperatures is due to sintering in the castable composition. Also a trend of decreasing density values was observed with increasing amount of cement for all the different temperatures. At dried conditions, greater extent of low density hydrated phases present in cement containing compositions and use of

higher amount of water causing a void space in the cast shape are may be the reasons. For intermediate temperature (900 °C), greater extent of removal of moisture (chemical bonded) causing a relative porous structure may be the reason. Again for higher temperature (1500 °C) lesser extent of sintering due to less finer particles present in the system compared to sol bonding may be the reason for attaining lower density in cement containing compositions.

3.3 Strength study

The cold crushing strength (CCS) values of the castables treated at different temperatures are shown in Fig. 4. Here also a general trend of higher strength value for higher distribution coefficient was observed for all the compositions at all the different heat treatment temperatures. The dried strength of the castables increases with the increase in the cement content in the binder composition. This is due to the presence of stronger hydraulic bonding in cement containing compositions compared to coagulation bonding in sol containing ones [15]. But at 900 °C, sol containing compositions are found to have greater CCS values and increasing amount of cement reduces the strength. Disruption of hydraulic bond present in the cement containing compositions resulting in a weak porous structure and non-initiation of sintering at that temperature is the reason for such deterioration. But for sol binder, there is no such disruption of bond and no such fall in strength. Also, presence of very fine (nanometer size) silica particles in sol containing compositions might have started the sintering process in the compositions with the increase in strength at 900 °C. Increasing amount of cement in the binder compos-

ition increases the effect of structural disruption and causes greater deterioration in the strength properties. At high temperature, the CCS values are higher compared to dried and intermediate temperature fired samples, due to sintering. Here, the CCS values of the sol containing composition showed higher strength may be due to greater extent of sintering occurred in presence of finer sol particles and also due to mullite formation in the composition, as observed in the phase analysis study. Mullite provides extra bond in the composition and improves the strength. Reduction in sol content (on increase of cement) reduces the fine particles content and also the mullite formation, causing reduction in strength values.

3.4 Hot strength study

Hot strength (as HMOR) measurement of the 1500 °C sintered samples of the castables are done at 1400 °C and the values are shown in Fig. 5. HMOR values are found to decrease with increasing amount of cement content in the binder composition.

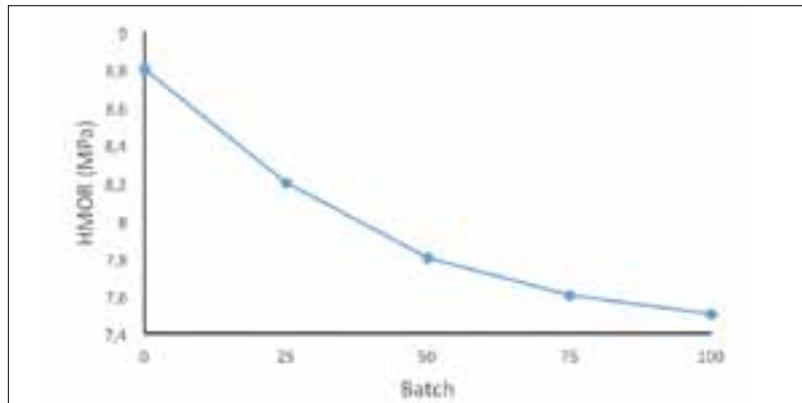


Fig. 5 Hot strength study (at 1400 °C) of the 1500 °C sintered castables

Higher hot strength values are observed in pure silica sol bonded composition due to the presence of greater extent of mullite, as compared to cement containing composition. Mullite, being a high melting compound, provides extra bonding and increases the strength of the composition even at elevated temperatures. But introduction of cement reduces the hot strength due to the formation low melting compounds, espe-

cially anorthite, as observed in phase analysis study. Increasing amount of cement increases the anorthite phase formation and gradually decreases the hot strength values. The minimum hot strength was observed for the only cement bonded composition.

4 Conclusions

- High alumina refractory cement and silica sol are used separately and in three differ-



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ent combinations as bonding material for making high alumina refractory castables with distribution coefficients, $q = 0,21$ and $q = 0,29$.

- The bulk density of the castables decreases with increasing cement content in binder.
- The dried strength values increases with the cement content in the castable composition and highest dried strength was obtained for the only cement bonded composition, due to greater extent of hydraulic bond formation.
- Strength at 900 °C and 1500 °C was found to be higher for higher sol containing compositions.
- Formation of mullite phase in the of sol bonded compositions provides excellent mechanical and thermomechanical properties.
- Presence of anorthite phase in cement containing compositions resulted in reduction in hot strength values and minimum hot strength is observed for only cement containing composition.

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