

Chapter-3

(Synthesis of high alumina cements by gel trapped co-precipitation process and their implementation as castables)

Synthesis of high alumina cements by gel trapped co-precipitation process and their implementation as castables

3.1 Introduction

High alumina cements (HACs) or calcium aluminate cements (CACs) are the only options as refractory cements due to their high refractoriness for high temperature applications (Scrivener and Capmas, 2004). Their hydraulic strength development is due to water bonding reactions of the calcium aluminates to form water-resistant hydrated phases (Taylor, 1999; Nocun-Wczelik et al., 2011). It is a cold hydraulic bonding system. The alumina content in high performance HAC exceeds 70% and the remaining is mainly CaO content. High-performance concretes are possible from CACs and also ultra-high strength concretes have been proposed (Scrivener et al., 1999). The flexural strength of macro-defect-free concrete samples based on HAC show much higher values (Birchall et al., 1981). The difference in refractoriness between HAC and ordinary portland cement (OPC) is due to the presence of C_2S and C_3S as its main constituents in OPC, which have low eutectic points. On the other hand, HAC with high Al_2O_3 (low CaO and SiO_2), possesses a higher melting point and is used as refractory cement. CA ($CaAl_2O_4$), CA_2 ($CaAl_4O_7$), CA_6 ($Ca_{12}O_{19}$) and $C_{12}A_7$ ($Ca_{12}Al_{14}O_{33}$) are the main constituents in HAC (Zawrah and Khalil, 2007). Sometimes, it also contains some minor amount of un-reacted alumina. Very little amounts of C_3A ($Ca_3Al_2O_6$) are observed, only when samples are heated above $1500^\circ C$ (Scrivener and Capmas, 2004). The amount of the Ca-rich phase $C_{12}A_7$ is found to decrease with calcination time as it further reacts with alumina to form CA_2 or CA and the amount of CA_2 formed decreases comparatively slowly with time (Iftekhar et al., 2008).

High alumina cement is used as binding material for monolithic applications and a significant advancement in monolithic technology is the development of refractory concretes or castables. Castables are complex refractory formulations, requiring high-quality precision-sized aggregates, modifying fillers, binders and additives.

The use of reduced cement contents in monolithic, such as low cement castables (LCCs) and ultralow cement castables (ULCCs), has grown significantly over the past 10 years. They may be cast in molds to form specific products (precast shapes) or cast “in place” as when forming a lining for a kiln furnace. The main technical advantages of LCCs and ULCCs are their excellent physical properties, such as high density, low porosity, high cold/hot strengths, high abrasion and corrosion resistance (Ye et al., 2004). The working life of HAC in steelmaking and other ceramic industries is greatly dependent on the material’s ability to withstand high temperatures without undergoing significant deformation and corrosion (Pera and Ambroise, 2004). Therefore, one of the approaches used throughout the later decades is to improve the performance of HAC by reduction of the liquid content formed at elevated temperatures in high-alumina refractory castables (Gaztanaga et al., 1993). Low-melting point eutectic phases are often formed in these castables because of the reaction between Al_2O_3 , SiO_2 and CaO . Outstanding gains in refractoriness have been obtained through the reduction of CaO , SiO_2 and increasing the Al_2O_3 content in HAC (Scrivener and Capmas, 2004).

Conventionally, HACs are obtained by fusing or sintering a mixture of suitable proportions of aluminous and calcareous materials such as CaO or CaCO_3 and alumina (Al_2O_3) at temperatures above 1500°C and subsequent grinding. The resultant product is a fine powder and typically has low specific surface area ($<1 \text{ m}^2/\text{g}$) (Kumar et al., 2009; Abo-El-Enein et al., 2010). The completion of such reactions depends on the particle size, specific surface area and the mixing of the reactant powders. Even after repeated firing and grinding cycles to eliminate all of the un-reacted materials, the product batch frequently contains undesirable CaAl_4O_7 , $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ and un-reacted starting materials. Calcium aluminate powders prepared by chemical processing techniques proved to be X-ray amorphous and of high surface area when calcined at low temperatures (Mukhopadhyay et al., 2003). Parr (2008) prepared CaAl_2O_4 by evaporative decomposition of a solution made from calcium and aluminum nitrate precursors. After heat treatment at 900°C for less than 1 h, crystalline CaAl_2O_4 was obtained. Therefore, one part of present

research work was aimed to prepare calcium aluminate powders through the chemical route. Combined gelation-precipitation process as reported earlier (Oliveira, and Pandolfelli, 2009) was employed to prepare HAC. A modified sol-gel process has been developed to prepare nano structured spinel (MgAl_2O_4), Al_2O_3 , ZrO_2 and their composite materials. This process controls the shape and size of the powders with narrow particle size distribution. High reactivity of powders is obtained with better homogeneity and purity. The conventional process for preparing HAC is carried out at around 1600°C and needs ball milling for a longer duration to reduce the particle size to sub micrometer level (Kopanda and Maczura, 1987; Darweesh, 2004) but the gel powders prepared in this manner were calcined at lower temperatures for various soaking periods. The gel powders as well as the calcined cement powders were characterized for their different physical properties and phases. The results of this work show the formation of desired phases between 1200°C and 1350°C for a maximum soaking period of 180 min. The prime cementing phases observed were mainly CA, CA_2 , CA_6 , C_3A_5 and $\text{C}_4\text{A}_3\text{SO}_4$. The calcium sulfoaluminate phase ($\text{C}_4\text{A}_3\text{SO}_4$) is quick setting phase and gives the initial strength (Kuzel, 1996). This constituent, calcium sulfo-aluminate or $\text{C}_4\text{A}_3\text{SO}_4$, has been known as a cementing phase for many decades. Further, HACs thus prepared by gelation and precipitation method were used to prepare LCCs. For this purpose, refractory grade of high alumina containing bauxite of different grain sizes were selected as aggregates. First, the packing density of samples was optimized by selecting different fractions of aggregates and the best batch of composition was then selected to give maximum packing density. These castable samples were further studied for their thermo-mechanical and structural properties. The bauxite matrix was also partially replaced by micro-fine ZrO_2 and its effect on physical properties of castables was observed. The experimental results were also compared with the standard commercial existing HAC from Almatris (Kolkata, India) (code name CA-14M with 70% Al_2O_3 and CA-25 C with 80% Al_2O_3).

3.2 Experimental procedure

3.2.1 Material characterization

The chemical composition of raw materials as provided by supplier is given in Table 3.1. It may be concluded that the major impurities of the calcium carbonate source under study are SiO₂, K₂O. Chemical composition of aluminum sulphate (~99.462% purity) and calcium carbonate (~98% purity) have high purity.

Table 3.1: Chemical composition of raw materials (in wt %), LOI (loss on ignition).

Raw materials	Al ₂ O ₃ (%)	CaO (%)	SiO ₂ (%)	K ₂ O (%)	Na ₂ O (%)	Fe ₂ O ₃ (%)	MgO (%)	Cl (%)	LOI (%)
Al ₂ (SO ₄) ₃ .18 H ₂ O	99.4	0.02	--	0.2	0.05	--	-	0.0	71.1
CaCO ₃	--	98.0	0.01	0.2	0.05	0.001	1.0	0.2	38.4

3.2.2 High alumina cements powder preparation

Aluminum sulfate lends itself easily to gel formation and is a low cost material. The solution of aluminum sulfate easily reacts with NH₄OH and forms aluminum hydroxide. Proper selection of molarity and simultaneous stirring gives it a gel like structure. It was therefore decided to use it with calcium carbonate as starting raw materials to prepare HAC through a composite gel process. In this system, clear solution of aluminum sulfate of 0.3M was obtained by dissolving the salts in distilled water with simultaneous magnetic stirring and subsequent filtering. For complete dissolution of the salt, the solution was kept on a hot plate at around 60°C with simultaneous stirring. Solutions having concentrations of 0.3M were prepared in this manner. CaCO₃ was mixed in double distilled water to obtain a suspension of

CaCO₃ having 50 wt. % mass. This suspension was then mixed in aluminum sulfate solution to give a final 7:3 and 8:2 Al₂O₃/CaO molar ratio. For the preparation of the gel, ammonia solution was added drop wise into mixed solutions of aluminum sulfate and calcium carbonate with continuous magnetic stirring. A point was reached when the gel became fully viscous and the process of stirring was stopped due to the viscous nature of the gel. The gel obtained in this process was the composite of aluminum hydroxide, aluminum sulfate and calcium carbonate because at this concentration some amount of aluminum sulfate remained unreacted and was trapped within the hydroxide gel network (Nanda, 1994; Ochiai et al. 1994; Mori et al., 1995; Hey et al., 1996; Innocentini et al., 2003). The prepared gel was air dried in an oven at 80°C to complete dryness. The dried gel powders were calcined at varying temperatures ranging from 1200°C to 1350°C. They were kept for a 3h soaking period in the SiC muffle furnace. The heating rate was maintained at 5°C/min.

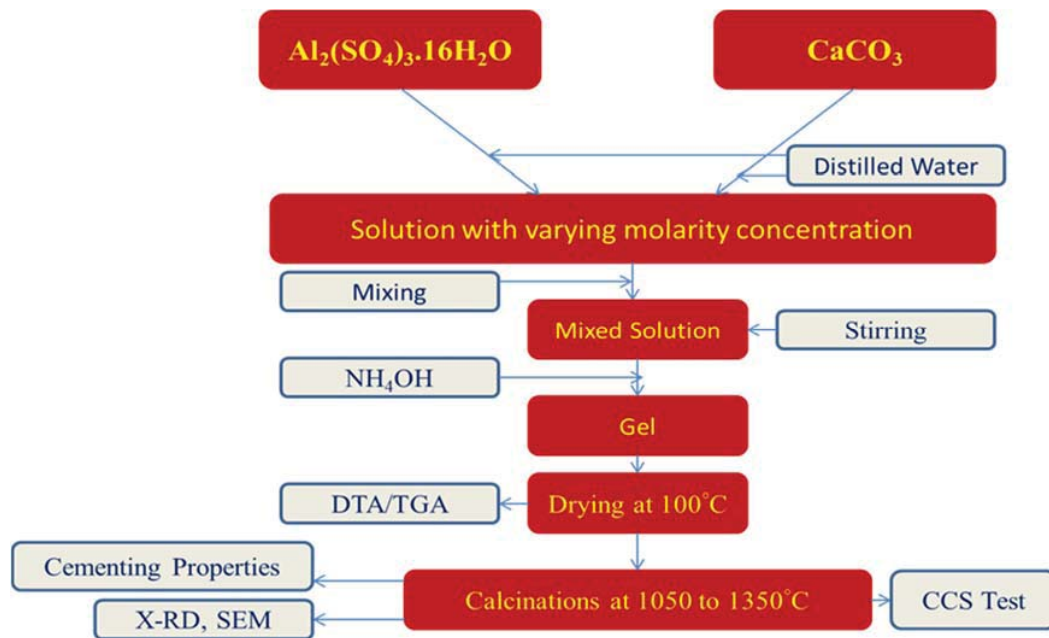


Figure 3.1: Flow chart of high alumina cements powder preparation.

3.2.3 Consistency of cement

Consistency is a measure of plasticity of a cement paste. It refers to the degree of wetness exhibited by a freshly mixed concrete, mortar or neat cement whose workability is considered acceptable for the purpose of handling. It is measured as the amount of water required to a particular wt% of dry cement which permits the Vicat's plunger of 10 mm diameter to penetrate to a point 5-7 mm from the bottom of Vicat's mold with gauging time of 3-5 min. Calcined HAC powder having 70% alumina and 80% alumina content samples were tested for consistency by Vicat's apparatus.

3.2.4 Setting time test

Calcined powders were tested for initial and final setting by Vicat's apparatus according to ASTM C-403.

3.2.4.1 Initial setting time of HAC: The early period in the hydration and strengthening of cement is referred to as the "initial setting" of cement. The initial setting time was measured by taking 50 gm of HAC mixed with the percentage of water required for normal consistency. In Vicat's apparatus, a needle is allowed to penetrate through the cement block prepared. In the initial stage, a thicker needle is allowed to pierce through the test block. This procedure is repeated till the paste starts losing its plasticity and the penetration is limited only to 5-7 mm depth. This duration of setting is counted and is termed as the initial setting time.

3.2.4.2 Final setting time of HAC: The cement is considered as finally set when upon lowering the attachment gently cover the surface of the test block and the thinner needle makes an impression. The duration of this process is considered as the final setting time.

3.2.5 Castable formulation

Refractory castables were prepared using approximately 5 wt% HAC cements as low cement castable in refractory grade of high alumina containing bauxite and other refractory materials (Furuta et al., 1995; Stenly and Lansday; 1997). The calcined bauxite that was used in castable formulation in the present study, contained approximately 70%, 18%, 3%, 4% and 1% by weight Al_2O_3 , SiO_2 , Fe_2O_3 , TiO_2 and alkalis respectively as specified by the supplier. The bauxite matrix (Bauxite Supplier, Kailash Marketing Associates, Mumbai, India) was subsequently replaced by small additions of micro-fine ZrO_2 powder. The effect of ZrO_2 addition on thermo-mechanical and structural properties was also observed. In the first step for cement castable formulation, calcined bauxite was oven dried, crushed and grinded for grading in a planetary ball mill. The jar and grinding media were of titanium-coated steel material. At one time, 200 gm of calcined bauxite material was taken in a jar and grinded in a planetary ball mill for 30 min at 500 rpm. Similarly, it was processed to complete the grinding of 3 kg material. The ground material was then kept in various selected sieves and set up on the motorized vibro-sieving equipment for grading. After separation of different graded bauxite, experiments were performed further. The particle size distribution has an important role in the properties of refractory castable. Incorrect particle size distribution may cause militancy or the excess water requirement by the castables. The particle size distribution of the fine fraction is generally a representation of the flow characteristics. The trials of aggregate proportions were taken in a 1000 cm^3 flask filled up to 250 cm^3 and vibrated for 20 sec. Then packing density calculations were carried out for each trial. Aggregates having highest packing densities were chosen for further analysis.

In the next step, batches were prepared by taking different grades of materials in the proper proportion. The materials were dry mixed in a plastic container for 10 min by spatula and then were taken for sample preparation. Generally, ultra and LCCs require less than 5 wt% of water to achieve the desired rheology; therefore,

water was added in two steps. The casting was done by adding two-thirds proportion of water at a time. Then one-third of water was added slowly to get a homogenous mixing. The wet mixing was performed for 5-6 min to achieve proper flow. Immediately after wet mixing, the castable mix was filled into a cube (30 mm × 30 mm × 30 mm) made of hard steel. The cube was placed on the vibrating table filled with the wet mixed castable and the mixes were vibrated for 5 min, showing better compactness. For each composition, several cube samples were prepared for laboratory testing. The samples were cured in a moisture-saturated environment (95% RH) in a humidity chamber at room temperature for different time periods. For firing the samples, they were first oven dried at 110°C for 24 h. The test samples were fired at 1400°C with a variation of ±5°C in an electric furnace having SiC heating element, with maximum soaking time of 3 h. The cured samples as well as the fired samples were tested for bulk density, apparent porosity, cold modulus of rupture, thermal shock resistance and cold crushing strength (CCS). These samples were also analyzed by XRD for phases present and by SEM for their morphological behavior.

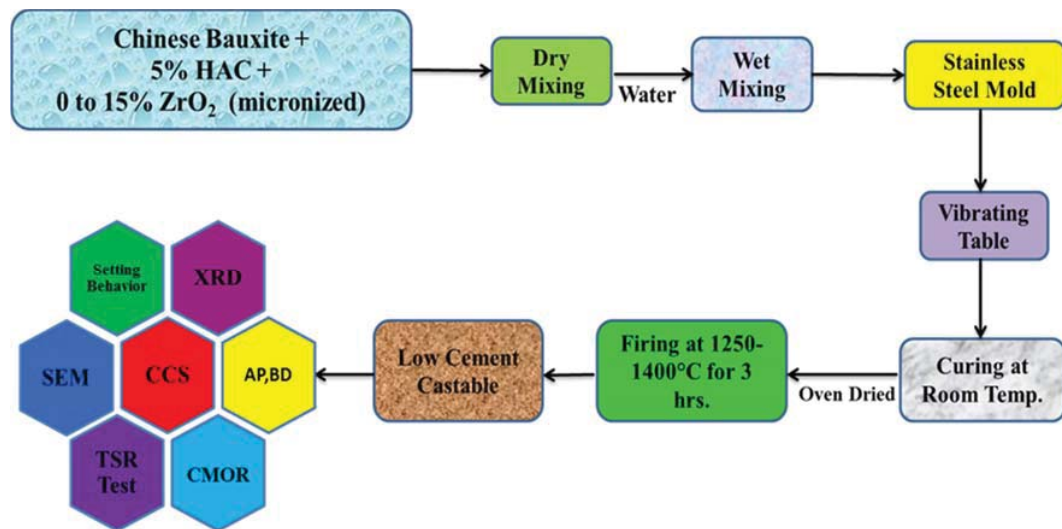


Figure 3.2: Low cement castable preparation.

3.2.6 Cold crushing strength (CCS) of HAC and LCC formulated

The CCS is the capacity of a material to withstand axially directed pushing forces. By definition, the compressive strength of a material is that value of uniaxial compressive strength reached when the material fails completely. CCS of cement was measured as the compressive strength of a 2.5 cm cement cube made of pure HAC (without any aggregates). These samples were tested for compressive strength after 3 h, 1 d and 2d curing respectively, according to (ASTM C-1194). The castables prepared with varying compositions (bauxite aggregates and fine zirconia) were also tested for their CCS and CMOR. For testing of each composition, 12 cubic and bar shape samples were prepared.

3.2.7 X-Ray diffraction spectroscopy (XRD)

The X-ray diffractometer (XRD) is an efficient characterization technique to determine the crystal structure and crystal orientation of bulk materials, powders, thin films and nano-materials. In XRD technique, the sample is irradiated with an X-ray beam of a single wavelength which produces reflection from the sample to form a diffraction pattern. X-ray diffraction involves very high frequency photons (typically, $\lambda = 1.54 \text{ \AA}$) to scan the reciprocal space lattice points corresponding to very short crystal lattice ($< 5 \text{ \AA}$). The constructive interference between the diffracted X-ray waves from the atoms of crystal sample take place only for those waves that follow the Bragg's law given by:

$$2d \sin \theta = n\lambda$$

where, d is the inter-planar distance between the crystal lattice, θ is the refraction angle and λ is the wavelength of the X-ray. The diffraction pattern is obtained only if the X-ray waves are reflected back from planes or atoms with inter-planar or inter-atomic distance of d and only in the direction where the path difference between the diffracted waves is an integer multiple of the X-ray wavelength. In this way, the diffraction pattern informs about the atoms or planes that are arranged in a periodic manner in a particular direction to the crystal plane. X-ray diffraction patterns were

observed using a Rigaku portable XRD machine (Rigaku, Tokyo, Japan). Calcined sample powders were analyzed by X-ray diffraction for phases present in the fired sample. Phase identification analysis was carried out by comparing the respective powder X-ray diffraction patterns with the standard database stated by JCPDF. Detailed analyses of the phase formation and changes over the temperature range and variation in compositions were carried out.

3.2.8 Scanning electron microscopy (SEM)

SEM produces images of nanostructure samples by scanning it with a high-energy focused beam of electrons in a raster scan pattern. Once the electron beam hits the sample, a variety of signals are generated after interacting with electrons in the sample. Out of these signals some specific signals are collected by the detectors and are then sent to a viewing screen that produces a topographical image or an elemental composition of the sample and other properties such as electrical conductivity. The types of signals produced by an SEM include secondary electrons, backscattered electrons (BSE), characteristic X-rays, light (cathode-luminescence), specimen current and transmitted electrons. The SEM gives information on the surface morphology of the sample, which help to check whether the growth is proper.

3.3 Results and discussion

3.3.1 Thermal analysis

The dried gel powders were examined for DTA/TGA. Thermal analysis (DTA/TGA) of the dried gel was carried out in NETZSCH STA 409 (NETZSCH Technologies India Private Limited, Chennai, India) by heating the sample in an alumina crucible at 10°C/min up to 1300°C. Figures 3.3-3.5 are the DTA/TGA curves of alumina gel, calcium carbonate gel, and composite gel for HAC powders, respectively.

Figure 3.3 shows the DTA/TGA curve for alumina sulfate gel. Exactly 22.5 mg of dried gel was taken and heated at the rate of 10°C/min up to 1300°C. Thermal analysis of alumina gel shows the loss of the hydroxyl group and decomposition of remaining aluminum sulfate salts. Decomposition started at 80°C and ended at 800°C. At 100°C, evaporation of free water starts. At 225°C, loss of chemically combined water is completed. At 235°C-360°C, decomposition of ammonium sulfate and this peak is endothermic. Weight loss at 360°C is 22.22%. At 360°C-430°C, decomposition of aluminum hydroxide and this peak is endothermic. Weight loss at 430°C is 35.55%. At 840°C, there is 71.11% weight loss. At 400°C-800°C, decomposition of sulfates occurs. Weight loss at 580°C is 48.0%. Five endothermic peaks occur in the temperature range 300°C-900°C. All the losses occur up to 840°C and there are no remarkable changes above this temperature. Beyond 900°C there is no change in weight.

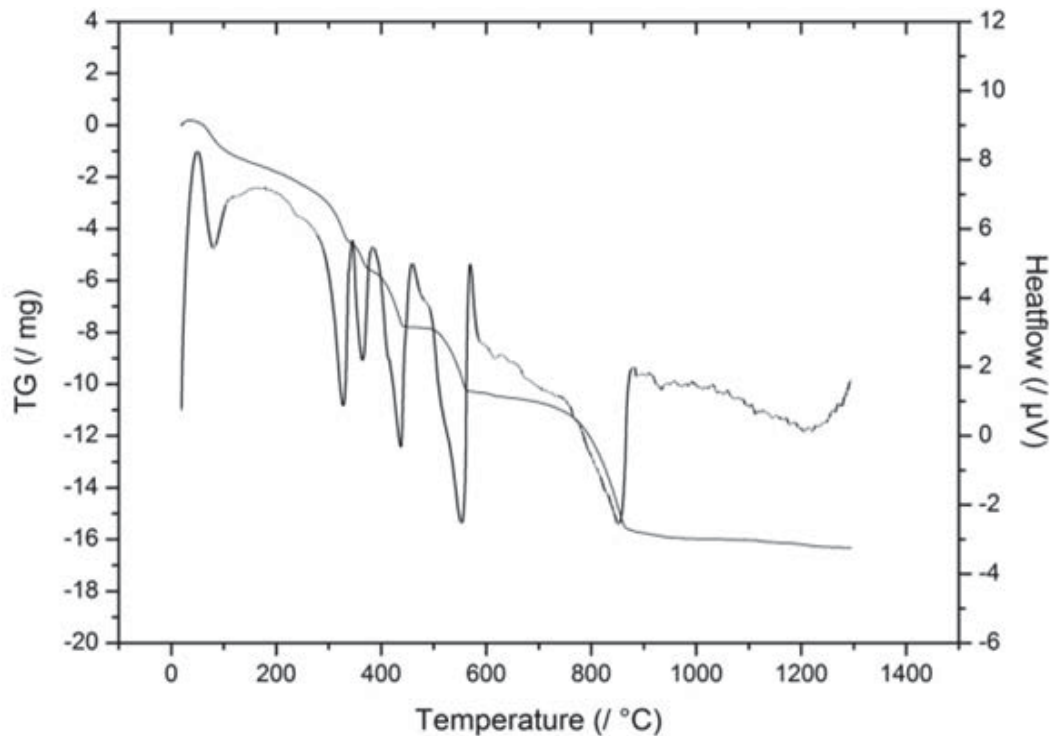


Figure 3.3: DTA-TGA of alumina sulfate gel heated at the rate of 10° C/min up to 1300°C.

From figure 3.4, decomposition of CaCO_3 can be predicted around 800°C showing a great exothermal change.

Figure 3.5 shows the decomposition of composite gel powder, prepared to obtain HAC. 24.7 mg of dried gel was taken and heated at the rate of 10°C/min up to 1300°C. Decomposition occurs in the temperature range 80°C-1300°C. Many exothermic peaks were observed in the temperature range 1000°C-1300°C showing the formation of different phases. At 100°C, there is 8.09% weight loss. At 530°C, there is 23.48% weight loss. At 840°C, there is 36.45% weight loss.

A comparison of the three figures shows that there is less loss and low thermal effect in the composite gel powder. Results showing the exothermal peaks above 1000°C just indicate the formation of different phases in these composite gel powders.

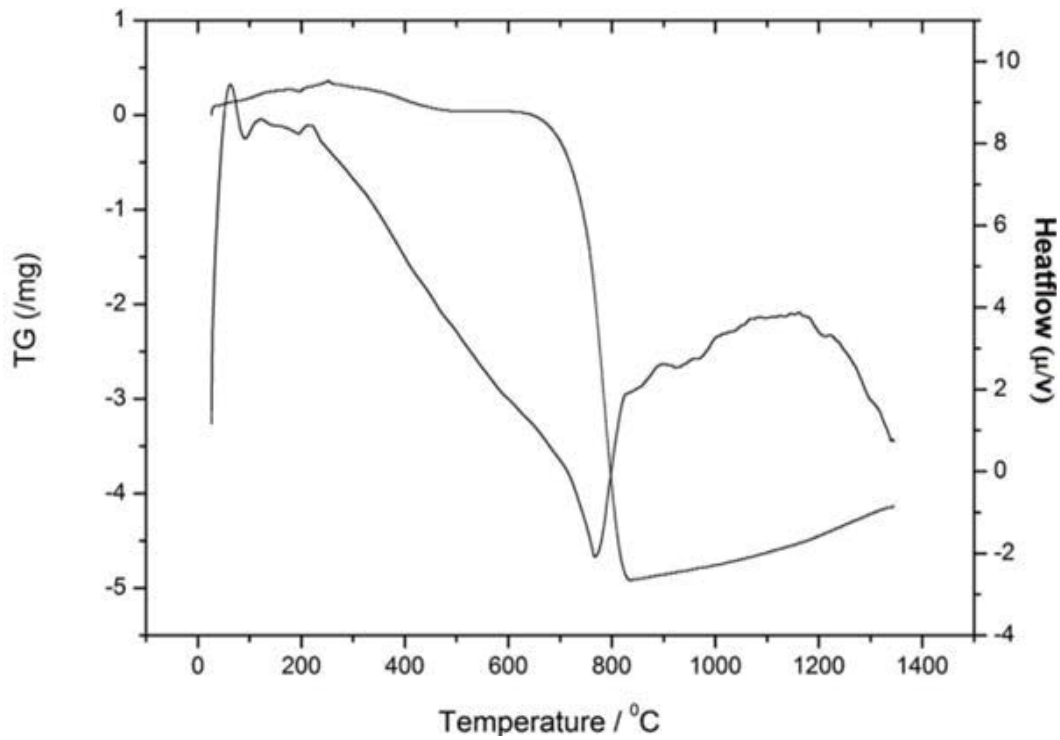


Figure 3.4: DTA-TGA of CaCO₃ heated at the rate of 10°C/min up to 1300°C.

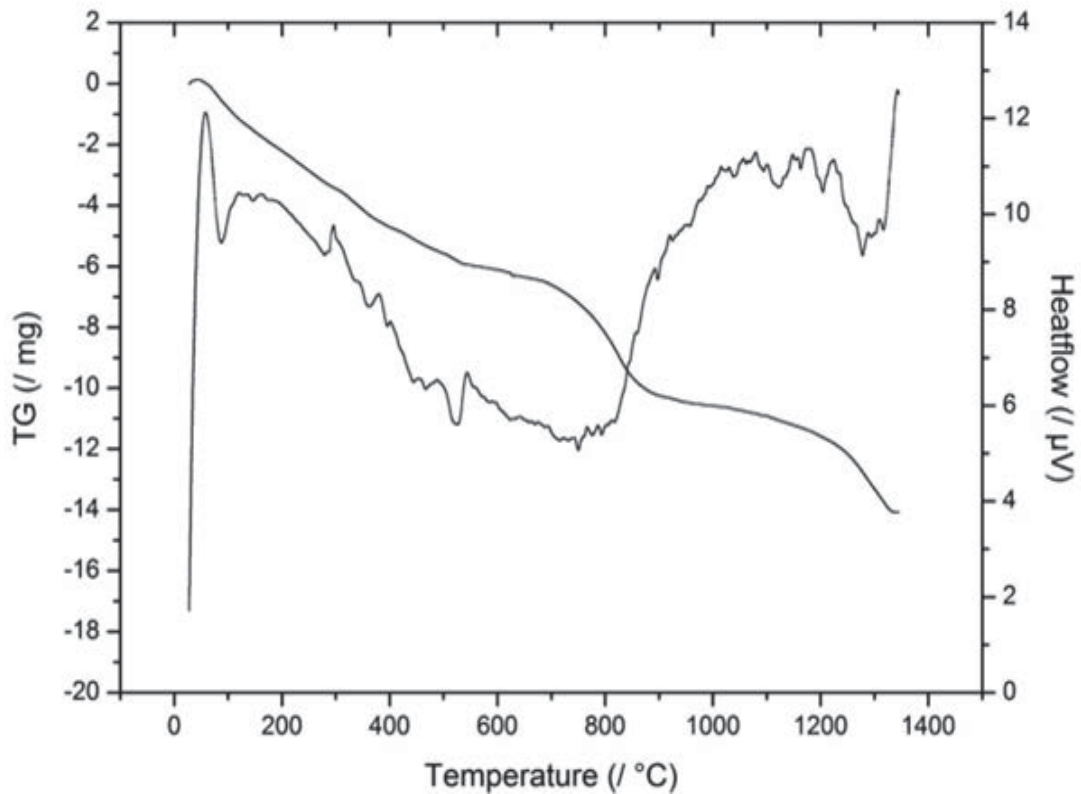


Figure 3.5: DTA-TGA of composite heated at the rate of 10°C/min up to 1300°C.

3.3.2 Evolution of phases by X-Ray diffraction

X-ray diffraction patterns were observed using a Rigaku portable XRD machine (Rigaku, Tokyo, Japan). Calcined sample powders were analyzed by X-ray diffraction for phases present in the fired sample. Phase identification analysis was carried out by comparing the respective powder X-ray diffraction patterns with the standard database stated by JCPDF (Richard et al., 1995). Detailed analysis of the phase formation and changes over the temperature range and variation in compositions were carried out.

Figures 3.6 and 3.7 are the XRD patterns of samples fired at 1350°C with 70% and 80% alumina, respectively. CA₆ begins to form in the temperature range starting

from 1250°C in both compositions, one having 70% alumina and the other having 80% alumina. The major phase in both compositions is found to be CSA. The formation of this phase is concluded due to the presence of sulfates which remained unreacted with ammonium hydroxide. Evolution of sulfates at high temperature yields the formation of CSA. Figure 3.6 shows that the sample is composed mainly of mono-calcium aluminate CaAl_2O_4 (CA), di-calcium aluminate CaAl_4O_7 (CA_2), calcium sulfo-aluminate $\text{C}_4\text{A}_3\text{SO}_4$, dodeca-calcium hepta-aluminate $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ (C_{12}A_7), and calcium hexa-aluminate $\text{CaAl}_{12}\text{O}_{19}$ (CA_6) peaks.

Figure 3.7 shows peaks, characterizing as CSA, CA, CA_2 , and CA_6 with few amount of C_{12}A_7 . The readily formed and thermodynamically stable phases in the CaO- Al_2O_3 binary system with increasing refractoriness in the above order could be predicted due to excess alumina content (Kubaschewski, 1970; Nurse et al., 1975). In the conventional preparation route by high temperature solid-state synthesis, the batch usually contains CaO rich phases and un-reacted Al_2O_3 before the appearance of the desired product phase (Singh and Ali, 1980; Singh et al., 1990).

A single-phase mono calcium aluminate was produced only after a prolonged reaction time at high temperatures in a batch that was proportioned for CA (Midgley, 1990; Fentiman et al., 2008). The formation sequence of phases in these mixtures was always from calcia-rich phases to the proportioned phase. For example, when the starting mix was prepared for CA_2 ($\text{CaO}:\text{Al}_2\text{O}_3 = 1:2$), initially Ca formed in large amounts, which with time and temperature, converted to CA (Singh and Mandal, 1982). Singh et al. explained this behavior by a higher reactivity of CaO with respect to Al_2O_3 . Contrary to this observation, CA and CA_2 were both observed in the early stages of crystallization in chemically prepared mono calcium aluminate powders (Singh et al., 1990).

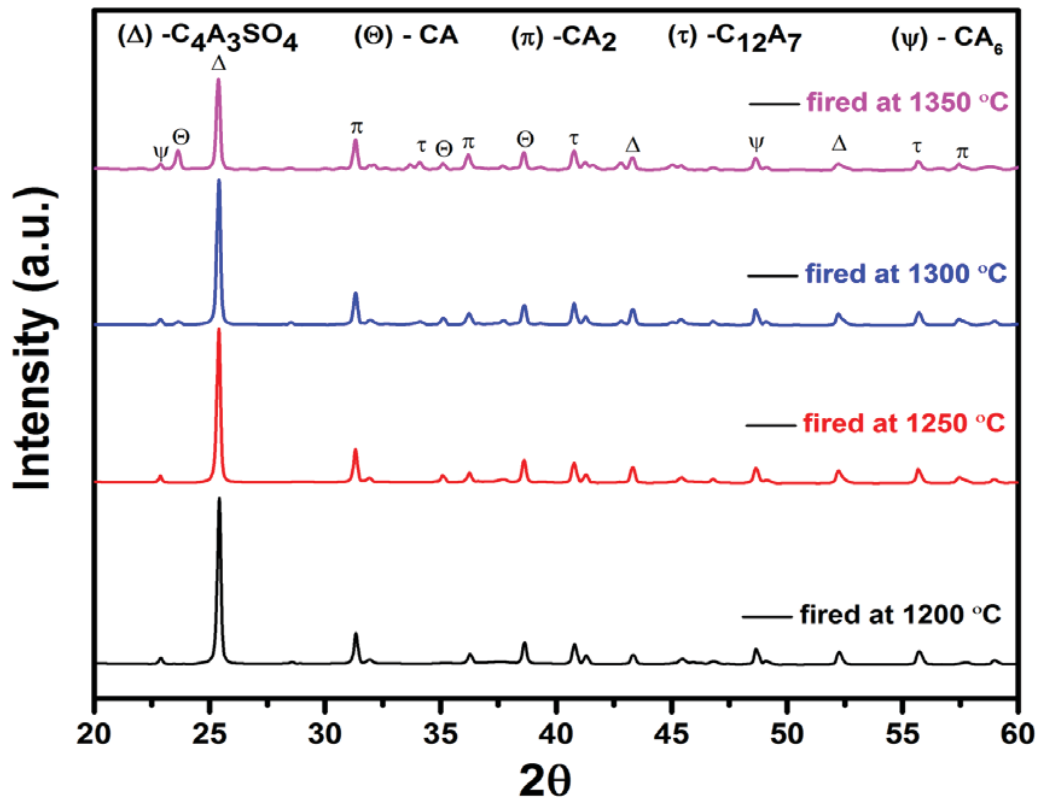


Figure 3.6: XRD of HAC containing 70% Al₂O₃ fired with varying range of temperature.

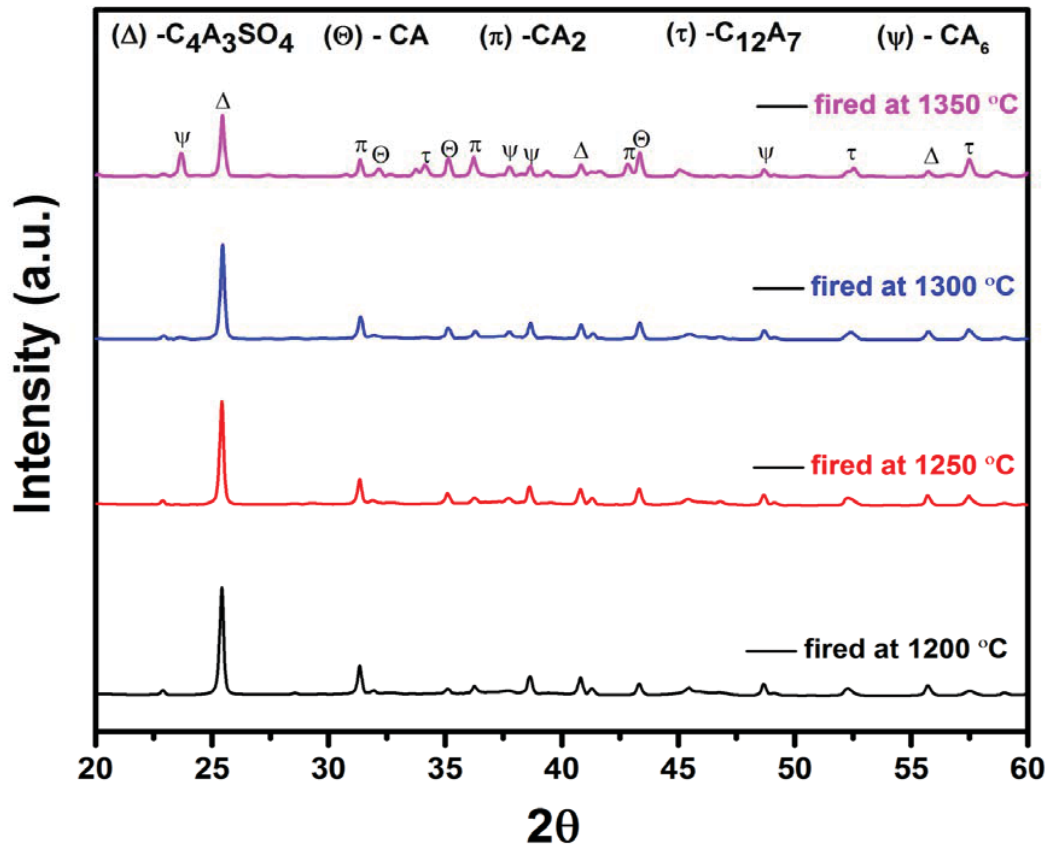


Figure 3.7: XRD of HAC containing 80% Al_2O_3 fired with varying range of temperature.

3.3.3 Setting behavior of HAC

Figure 3.8 shows the setting behavior of HAC. The prepared HAC powders were mixed with water (0.85 P). At room temperature, 70% alumina containing cement gave an initial setting time of 13 min and final setting occurred in 38 min. Another composition of HAC having 80% alumina had an initial setting time of 15 min and a final setting time of 62 min. With the increasing alumina content in HAC, the setting time showed an increasing trend.

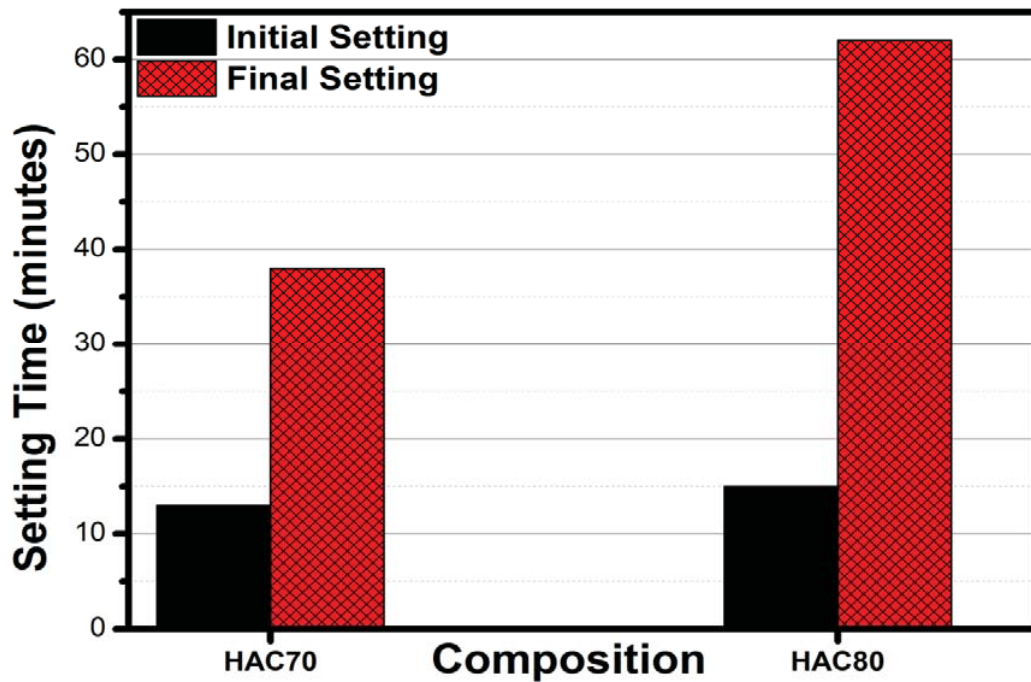


Figure 3.8: Setting behavior of HAC.

3.3.4 CCS of HAC fired at 1350°C

The pure (without any aggregates) HAC attained good structural strength as per the results obtained in experimental work and shown in figure 3.9. Samples were tested after curing for 3h, 24h and 48h respectively. The strength increased rapidly with curing time in all the compositions. Initially, in 3 h, the CCS value obtained for HAC sample having 70% alumina is 6.3 MPa and for 80% alumina, it is 10.2 MPa. After 48 h, it is 60.75 and 67.3 MPa for 70% and 80% alumina cement, respectively. The obtained value is better than the commercially available CA-14M-55MPa and CA-25C-50MPa (Almatis). It gets the maximum strength within 48 h and after this period, there is a very slight variation. It can be predicted that HAC samples having 80% alumina have more compressive strength than the 70% alumina sample. The higher strength of 80% alumina is ascribed to the presence of CA_2 and $C_{12}A_7$ as a major component, as it reacts rapidly with water. It is well known that CA_2 and $C_{12}A_7$ react significantly in the early ages of hydration, and the hydration of $C_{12}A_7$ is

very exothermic, so the formation of stable hydrates generally occurs sooner. Although CA_2 is known to react slowly with water in the early stages of hydration, its presence along with CA results in an overall faster hydration rate as the heat of hydration resulting from the hydration of CA activates CA_2 and makes it react relatively faster with water than it would do alone but not than $C_{12}A_7$ (Singh and Mandal, 1982; Zawrah and Khalil, 2002). CCS data of the sintered ceramics bodies exhibit high strength of both samples after firing. This is due to the formation of the ceramic bond. The higher strength of 80% alumina-containing cement sintered at 1350°C is due to the presence of $C_{12}A_7$ and CA_6 , which has low melting eutectic point as shown in the phase diagram of $\text{CaO-Al}_2\text{O}_3$ (Scrivener and Capmas, 2004). This low melting phase led to a decrease in porosity and an increase in mechanical properties (Matusinovic et al., 2003).

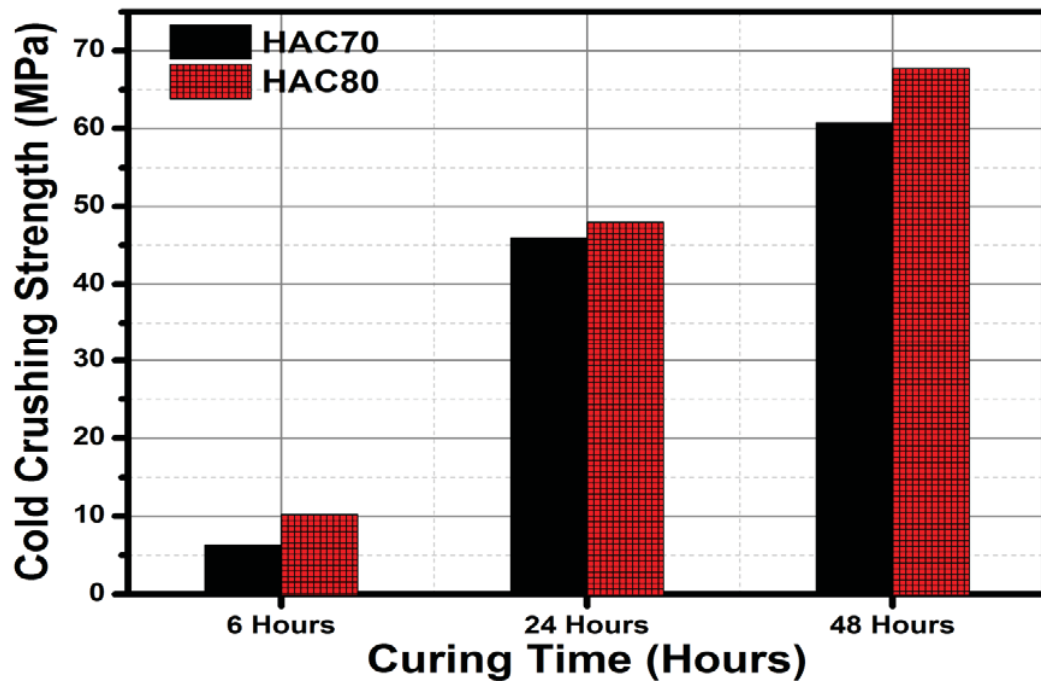


Figure 3.9: Effect of curing period on CCS of HAC fired at 1350°C .

3.3.5 Soundness of HAC Fired at 1350°C

The HAC samples were tested for soundness by the Le Chatelier method to find out the expansion. The expansion was 1.3% in an HAC sample having 70% alumina and 1.0% in an HAC sample having 80% alumina content.

3.3.6 Scanning electron microscopy (SEM) of formulated high alumina cement and castables

Broken pieces of formulated castable were examined using a FEI Inspect S-50 (FEI ASIA PACIFIC, Shanghai, China) scanning electron microscope. The samples were made conducting by gold sputtering for better image definition. Figure 3.10 shows SEM micrographs of a hydrated HAC sample containing 80 wt% Al_2O_3 (numbers 1–4 in the figure show their magnification). Networks of well-crystallized interlocking hexagonal plates of CAH_{10} and C_2AH_8 can be observed in Figure 3.10. The phases known to be the main hydration products of CA, CA_2 and C_{12}A_7 play a bonding role in such materials. The higher C/A ratio of C_{12}A_7 favors the formation of C_2AH_8 and very little to CAH_{10} . Figure 3.11 shows SEM micrographs of a castable at different locations and magnifications. The microstructure of the castable in figure 3.11 shows a highly homogenous formation of corundum and mullite after firing the castables prepared at 1400°C. This firing leads to dense body formation. Coarse particles of corundum are observed to be embedded in the bed of finer needle-shaped particles of mullite. This shows the uniform packing of bauxite matrix due to proper grain bonding. The same could be observed with different magnification levels (numbered a–d) with more clear aspects.

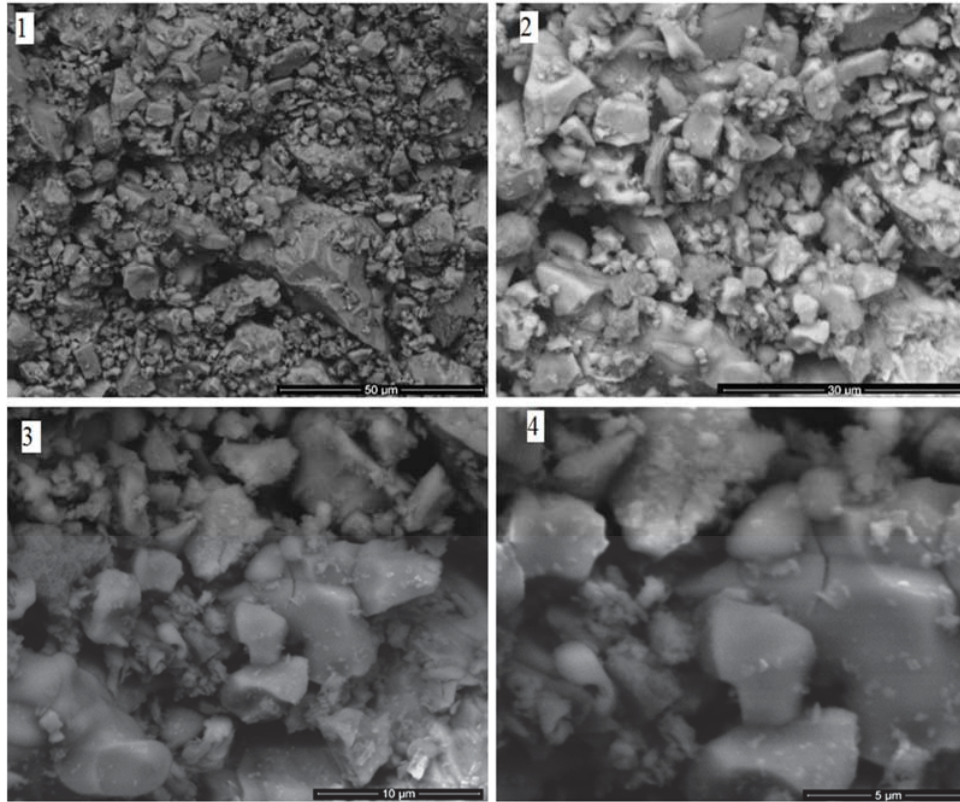


Figure 3.10: SEM of hydrated HAC containing 80% Al₂O₃ with different magnifications. Figures with numbers 1, 2, 3 and 4 represent their magnifications, viz., 2500, 5000, 10000 and 20000×, respectively.

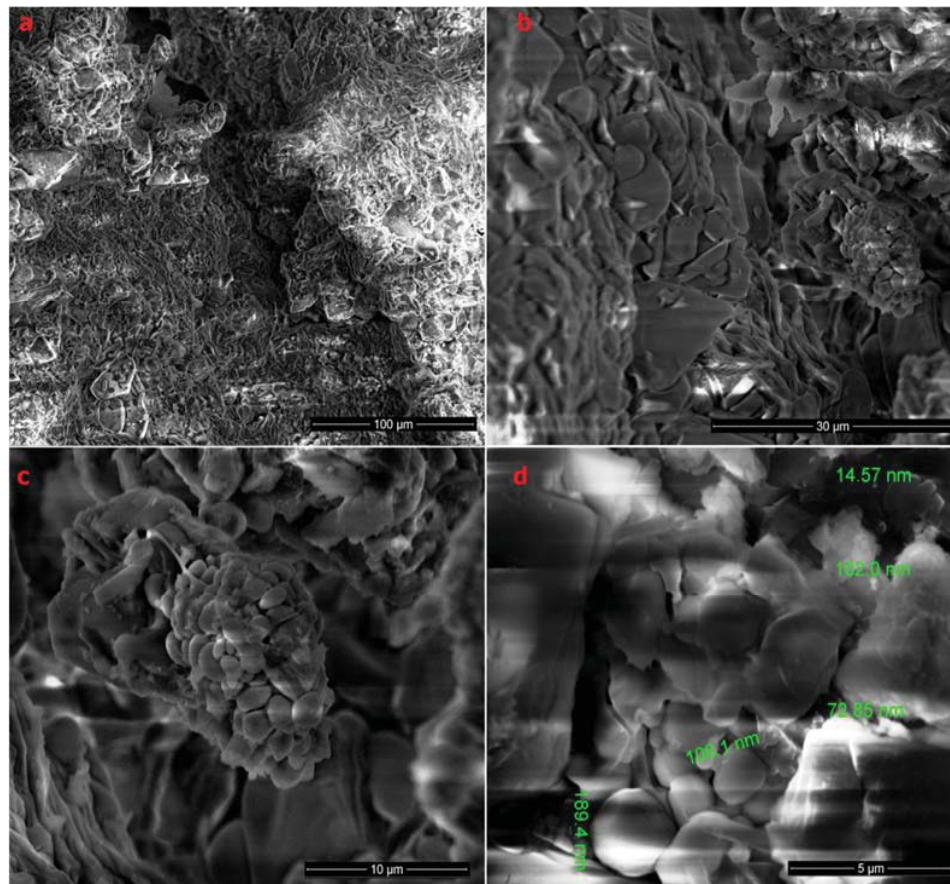


Figure 3.11: SEM of the LCC prepared by HAC containing 80% Al₂O₃ with different magnifications. Figures with numbers a, b, c and d represent their magnifications, viz., 1000, 5000, 10000 and 20000×, respectively.

3.3.7 XRD patterns of castables fired at 1400°C for 3 h

Figure 3.12 shows the XRD pattern of LCC prepared with 70% Al₂O₃ containing HAC and figure 3.13 shows the XRD pattern of LCC prepared with 80% Al₂O₃ containing HAC. Here, Y0, Y5 and Y10 indicate the content of 0%, 5% and 10% zirconia, respectively, introduced in the bauxite matrix with a constant 5% weight of 70% alumina containing HAC. Similarly, Z0, Z5 and Z10 are the one with 80% alumina containing HAC. The corundum phase appeared due to the transformation of bauxite minerals to corundum. The presence of different impurities in bauxite versus alumina helps the formation of the mullite phase that appeared as a result of the reaction between silica impurities and alumina in the castable samples sintered at 1400°C for 3 h.

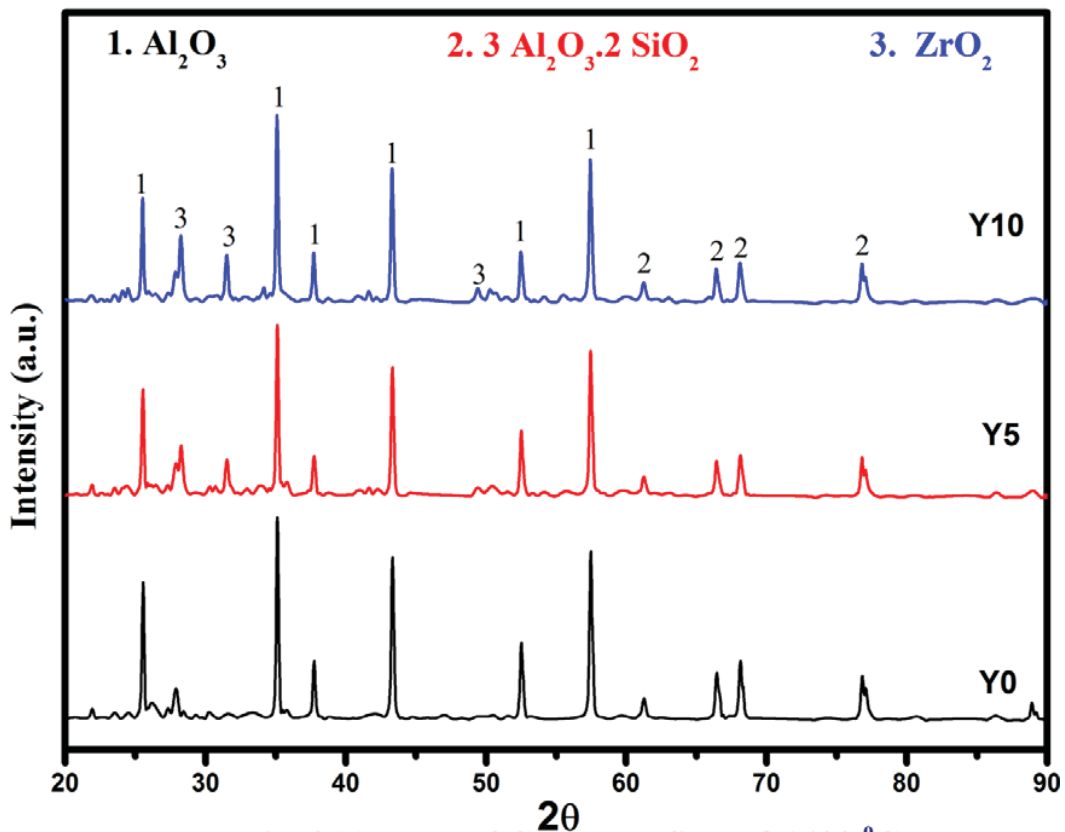


Figure 3.12: XRD of castables prepared by HAC containing 70% Al₂O₃.

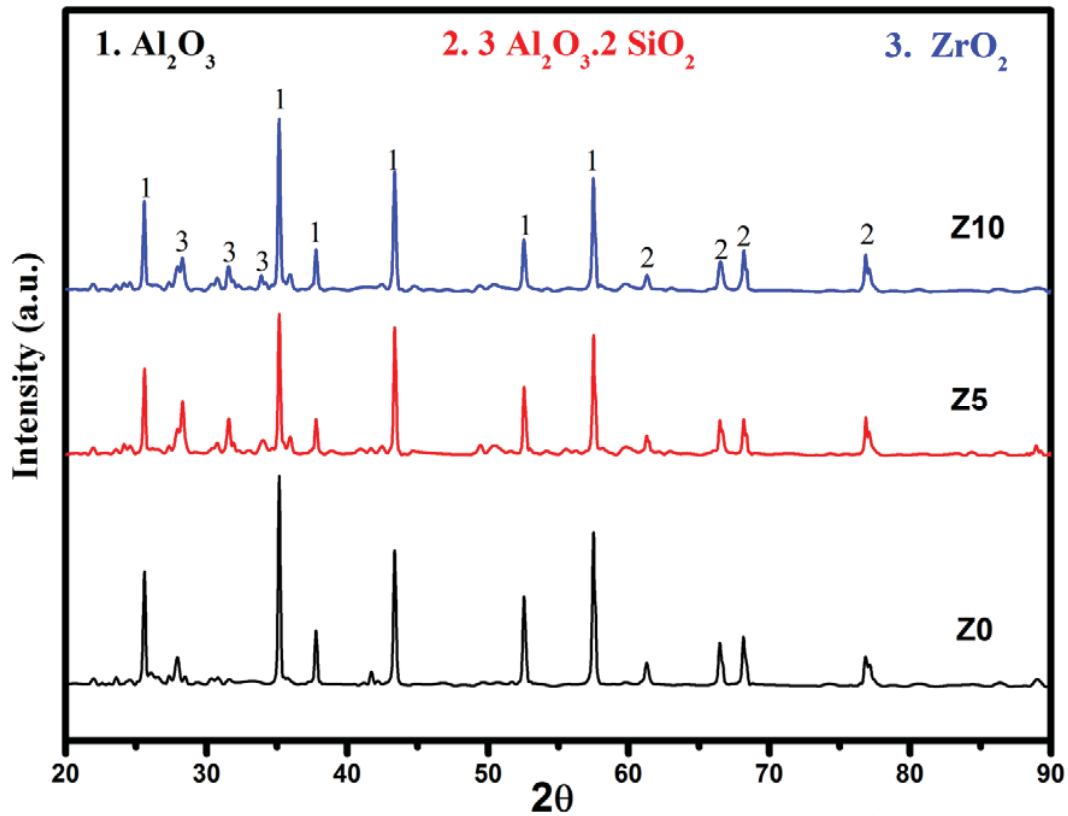


Figure 3.13: XRD of castables prepared by HAC containing 80% Al_2O_3 .

3.3.8 Bulk density and apparent porosity

In the castables prepared, highest average bulk density is achieved at around 2.82 g/cm^3 for the compositions having 10wt% zirconia. This can be attributed to the use of higher percentages of alumina and micro-fine zirconia in the aggregate. Apparent porosity was measured to be around 9% in the castables prepared with 10 wt% of zirconia. All these tests were performed on LCC prepared with 80% Al_2O_3 containing HAC.

3.3.9 CCS of different castable compositions fired at 1400°C for 3 h

Prepared HAC was used as cement for LCC. It consisted of 80-100 wt% calcined bauxite aggregate and 5 additional wt% HAC. Zirconia was substituted for bauxite by 0, 5, 10 and 15 wt%. Y and Z have same notations and compositions as described in section 3.3.7. CCS of the castables fired at 1400°C is shown in figure 3.14. Seventy percent alumina containing HAC castables Y0, Y5, Y10 and Y15 samples shows high values of CCS: 225, 235, 280 and 260 MPa, respectively. The highest values of CCS of castables are certainly related to the formation of mullite, which strengthens the structure at high temperature. When the percentage of fine particles (zirconia) increases in the castables, the CCS increased. Similarly, 80% alumina containing HAC castable Z0, Z5, Z10 and Z15 had CCS values of 250, 275, 325 and 290 MPa, respectively. The CCS of the HAC prepared is higher in comparison with the CCS of Secar:71-160MPa and Secar:80-200MPa with conventional bauxite containing LCC. The CCS of the samples of zirconia and bauxite castables is determined and shown in figure 3.14. The maximum average strength is attained in castables with 10 wt% of zirconia.

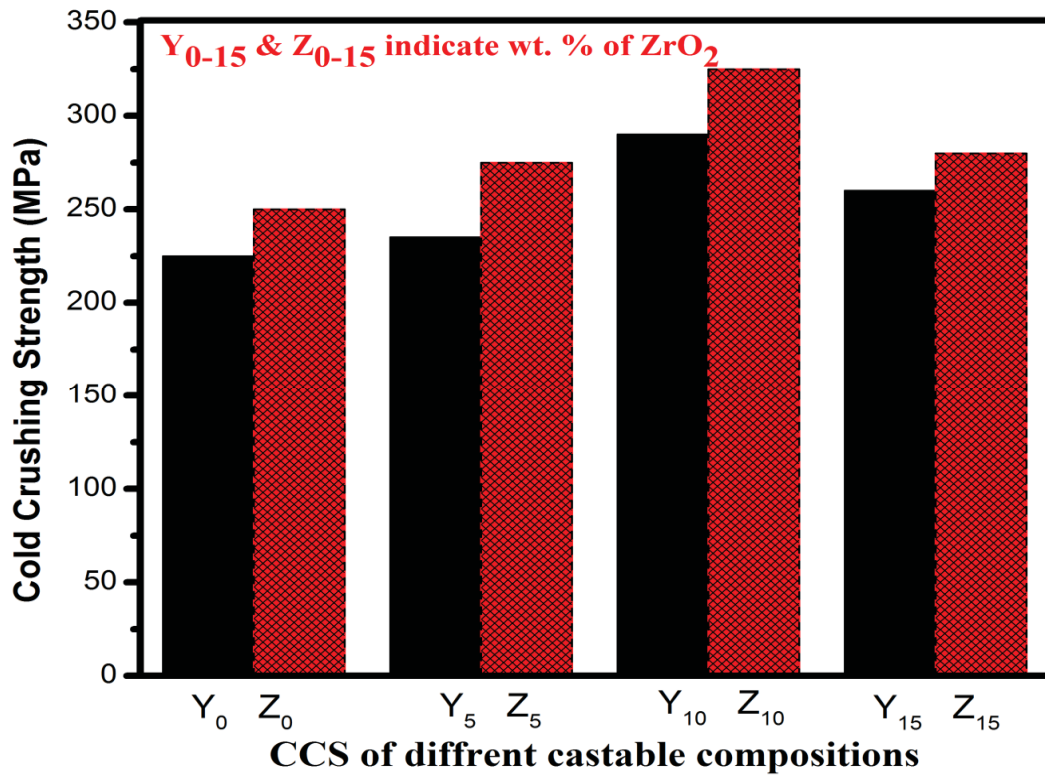


Figure 3.14: CCS of different castable compositions fired at 1400°C for 3 h.

3.3.10 CMOR and TSR of different castable compositions fired at 1400°C for 3 h

Cold modulus of rupture (CMOR) measurements were carried out under three-point bending tests (ASTM C133) using 152mm × 25mm × 25mm samples. CMOR tests were conducted at room temperature using Universal Materials Test Equipment (Model 810, MTS System, Eden Prairie, MN, USA) for samples pre-fired at, 1400°C for 3h. Seventy percent alumina containing HAC castables Y0, Y5, Y10 and Y15 samples shows high values of CMOR: 65, 67, 72 and 69 MPa, respectively. The highest values of CMOR of castables are certainly related to the formation of mullite, which strengthens the structure at high temperature. When the percentage of fine particles (zirconia) increases in the castables, the CMOR increased. Similarly, 80% alumina containing HAC castable Z0, Z5, Z10 and Z15 had CMOR values of 68, 71, 76 and 70 MPa, respectively. The CMOR of the HAC prepared is higher in comparison with the CMOR of Secar:71-60MPa and Secar:80-66 MPa with conventional bauxite containing LCC.

Thermal-shock resistance tests were run to analyze the influence of the mullite content and the characteristics on the castables thermal-mechanical properties. The tests consisted of 10 heating/cooling cycles (DT = 1200°C). Samples pre-fired at 1400°C completed one thermal cycle after a holding time of 20 min inside the furnace followed by another 20 min of cooling in air at room temperature. All the Y and Z series samples exhibited high thermal shock and spalling resistance completing 11 cycles while Y10 and Z10 attained 15 and 17 cycles, respectively.

3.4 Conclusions

The gel-trapped precipitation process used in my research work to prepare HACs yields fine and thermally reactive powders. Desired cementing phases like CA, CA₂, C₁₂A₇, CA₆ and C₄A₃SO₄ began to form in the temperature range of 1200°C-1350°C. This may be the possible and suggestive method for the commercial production of HAC at lower temperatures. Cement selection was made on the basis of optimization of physical and thermal properties. HAC formed at 1350°C was found to be superior in these properties among all HACs that formed at varying temperature ranges. One advantage of this process is that we can exclude silicate phases in cements, which provide low eutectic temperatures in such cements. These silicate phases decrease the refractoriness and the cement cannot be used at higher temperatures. Castable samples prepared by HAC having 80% alumina have better physical and cementing properties than the HAC having 70% alumina. Although these samples have longer initial and final setting time, better CCS values at different curing times were obtained. Moreover, the HAC samples attain maximum strength within 48 h. The XRD patterns of the bauxite based castables indicate the formation of the corundum phase along with mullite phase in all samples. Castable containing 10 wt% zirconia substituted for bauxite improves physico-mechanical and refractory properties at most. Mullite formed at high temperature, acts as a bonding phase and is accounted for the high CCS and CMOR values. These excellent properties of such castables enable their uses in various refractory applications, such as fabrication of steel, aluminum, copper, glass, cement, chemicals and ceramics.