

3.1 Introduction

It was discussed in the previous chapter-2 that the major constituents present as silica and alumina in the both types of bottom ash could be utilized as a potential material for the manufacturing of useable products. The present chapter will discuss about the possibilities for manufacturing construction/building bricks using both types of bottom ash by geopolymerization methods. However, it is well established method for the fly ash. Geopolymer is an inorganic polymer having three-dimensional structure, obtained by reaction of an aluminosilicate material with a strong alkaline solution (Djobo et al., 2016).

The production of geopolymers is very simple in technology, therefore its handling, storing as well as monitoring are very simple. This is also known as an environment-friendly technology. It is estimated that for the production of one-ton geopolymer cement from kaolin emits ~ 0.180 ton of CO₂, but production of one ton of portland cement emits one ton of CO₂. Thus, the production of geopolymer emits approximately six times less CO₂ than the Portland cement (Davidovits, 2002; McLellan et al., 2011). If the manufacturing of geopolymer is considered by the coal ashes (i.e. fly ash/ bottom ash), the emission of CO₂ would be negligible as the geopolymerization process does not require heat treatment.

Regarding the durability of using the portland cement, some studies reported that the new cement is strongly affected when exposed to aggressive climatic conditions, and its life duration is estimated to be approximately 50 years. The early deterioration in built structures using the modern portland cement was reported by several researchers (Chen et al., 2010; Huntzinger and Eatmon, 2009; Torgal and Jalali, 2010). However, mortars like those found in Rome are still unchanged which were built more than 2000 years ago, when modern portland cement was not even discovered. The conventional portland cement depends on the

use of lime and can be dissolved by acidic solutions, reaching 30-60% mass loss (Davidovits, 2002). Among the enthusiasts, investigators now search for possible substitutes to produce the new cement which could be matched with the durability of antique cement or mortar.

The geopolymerization techniques are gaining popularity day by day due to their diversity of raw materials used which favour the possibility of industrial production since the geopolymers do not require very high purity raw materials. Geopolymers also do not show stoichiometric composition and comprise of amorphous to semi-crystalline structures, and their empirical formula can be described as: $M_n[-(\text{SiO}_2)_z-\text{AlO}_2]_n \cdot w\text{H}_2\text{O}$, where z is 1, 2 or 3, M is the cation of alkali metal, and n is the degree of polycondensation. From the findings of geopolymers, the mechanisms involving in these materials were sorted out by developing the new formulations (Davidovits, 2011; Davidovits and Davidovics, 1991; Habert et al., 2011; Turgut, 2012)

Geopolymer is an alkali-activated aluminosilicate which can react to produce a Si–O–Al framework at low temperatures. Different steps involved for making geopolymers product are described in Figure 3.1. Strong alkali solution attacks the aluminium silicate and dissolves the Al and Si species to form oligomers. These oligomers form Si–O–Si and Si–O–Al like bonds by polymerization reactions. These oligomers are reoriented to form the three-dimensional structures of aluminosilicate. These three dimensional structures increase the polymeric chain and bond with the remaining solid filler particles to the aluminosilicate network for additional enhancement in the strength and stability (Izquierdo et al., 2009; Thakur and Ghosh, 2009). The above process is facilitated by molecular thermal agitation which could successfully occur by heating in the temperature range 60–80°C under the humid atmospheric condition for 24–48 hours curing time to complete the reaction. Although

the strength could be increased with time as the reaction reaches towards the completion (Bakharev, 2006).

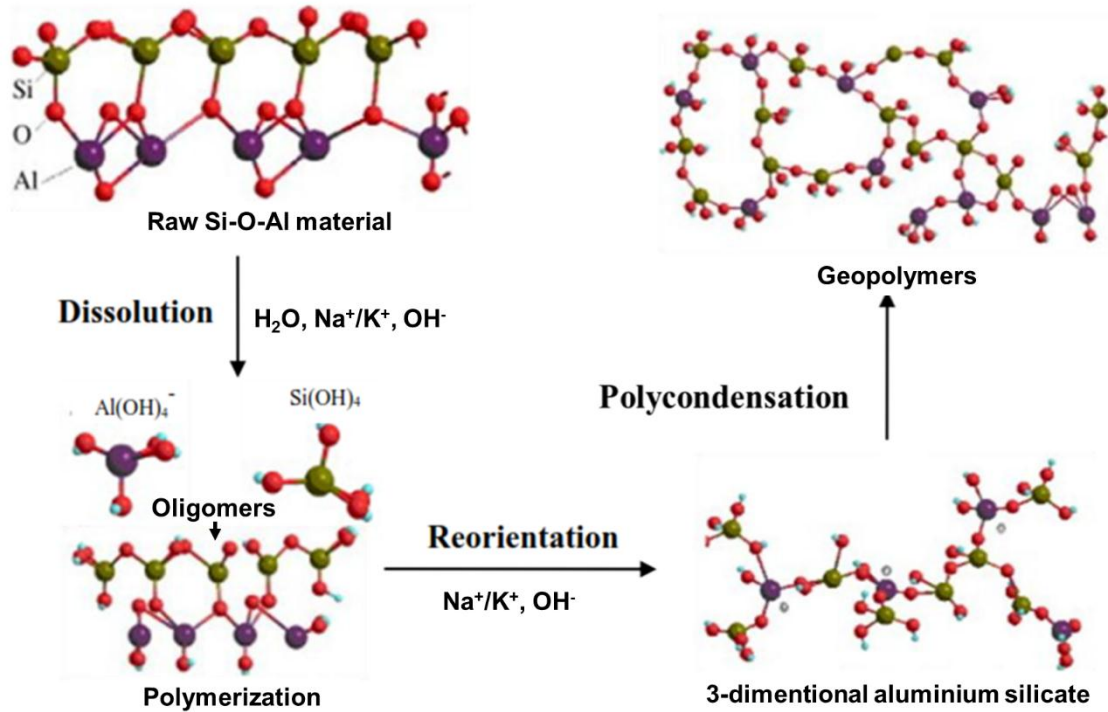


Figure 3. 1 Steps of geopolymerization reactions

The sources of geopolymers are aluminosilicate (i.e. fly ash, bottom ash, clay), the sodium silicate in aqueous solution (water glass), sodium hydroxide and water. The concentration of sodium hydroxide was found to be the best around 14M in water (Sarker, 2009; Temuujin et al., 2010). Although bottom ash and fly ash have similar chemical compositions but bottom ash was found to be the less reactive due to its coarseness. That's why, the bottom ash has little or almost no use in the manufacturing of geopolymers (Chindaprasirt et al., 2009).

Temuujin et al., and Sarker et al. have reported the excellent properties of geopolymer mortar having 73% fly ash, 18% water glass, 7% 14M sodium hydroxide

solution and 2% water (Sarker, 2009; Temuujin et al., 2010). Barbosa et al. reported from his work the optimum ratio of the sodium silicate/NaOH of 1.0, liquid/ash ratio of 0.6 and ash/sand ratio of 2.75 for making the geopolymer. It was reported that the calculated optimum oxide ratio are: $\text{SiO}_2/\text{Al}_2\text{O}_3 = 3.0$, $\text{Na}_2\text{O}/\text{SiO}_2 = 0.3$ (Barbosa et al., 2000). The curing temperature was maintained in the range 40-80°C as reported by different researchers. (Boonserm et al., 2012; Chen et al., 2012; Chindaprasirt et al., 2009; Topçu et al., 2014; UI Haq et al., 2014).

The objective of the present study is to prepare geopolymer samples separately from PCC and FBC bottom ash having same fineness and to examine their qualities for the end use.

3.2 Experimental

Due to the laboratory limitation and quantity availability of raw materials, test samples (as cylindrical specimen) were prepared for the present study instead of making standard size bricks.

3.2.1 Materials for test sample preparation

For the preparation of test samples, FBC as well as PCC bottom ash of similar fineness were used. The bottom ash samples were ground to 0.075 mm size which is being used for making geopolymer samples. Water glass (sodium silicate solution with 9%Na₂O, 30%SiO₂ and 61% H₂O with specific gravity of 1.35g/cm³) and 5M, 10M and 15M sodium hydroxide solution (prepared by dissolving sodium hydroxide pellets ~ 98% pure in distilled water) were used. The details of mix proportion and their final calculated oxide ratio are shown in Table 3.1 and 3.2 respectively. The different oxide ratio was maintained in such a way that it remained between the range of optimum ratio as mentioned by *Barbosa et al.*, (Barbosa et al., 2000).

Different mix proportion was used to make the geopolymer as shown in Table 3.1, to get the optimum oxide ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3=3$ as calculated in Table 3.2.

Table 3. 1 Mix proportion of raw materials used for making brick samples

Raw materials	Unit	Quantity
Bottom ash	gram	100
Sodium silicate	gram	20
NaOH (5M/10M/15M)	milliliter	5
Water	milliliter	10

Table 3. 2 Calculated optimum oxide ratio in different mix

Raw materials	5(M) NaOH			10(M) NaOH			15(M) NaOH		
	$\text{SiO}_2/\text{Al}_2\text{O}_3$	$\text{Na}_2\text{O}/\text{SiO}_2$	$\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$	$\text{SiO}_2/\text{Al}_2\text{O}_3$	$\text{Na}_2\text{O}/\text{SiO}_2$	$\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$	$\text{SiO}_2/\text{Al}_2\text{O}_3$	$\text{Na}_2\text{O}/\text{SiO}_2$	$\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$
FBC bottom ash	3.00	0.23	0.70	3.00	0.33	1.00	3.00	0.43	1.30
PCC bottom ash	3.62	0.22	0.81	3.62	0.32	1.16	3.62	0.42	1.52

3.2.2 Procedure for test sample preparation

3.2.2.1 Sample preparation and curing

The mixtures were prepared by mixing ash (bottom ash), water glass, sodium hydroxide and water all together in a ceramic jar for 10 min to get homogenized mixture as per composition mentioned in the Table 3.1. Excess water enhances the plasticity and castability of the mixture but it is detrimental for the properties of geopolymer. Thus, the water content in the mixture should be kept less than the optimum moisture content (OMC) in order to make samples by pressing. Required fixed quantity of mixture was put into 15 mm ϕ cylindrical mould, followed by applying 20 MPa pressure through a hydraulic press (Figure 3.2). Green sample (approximately 15mm height) was made and then removed from the mould and transferred immediately in to an air tight container to prevent moisture evaporation. Samples

were cured at different temperatures (40, 65 and 80°C) for a wide range of curing time (upto 84 hrs). Cured samples were taken out at different intervals of time i.e. 12, 24, 36, 48, 60, 72 and 84 hrs. The flow chart for the preparation and characterization of the test samples is shown in Figure 3.3.

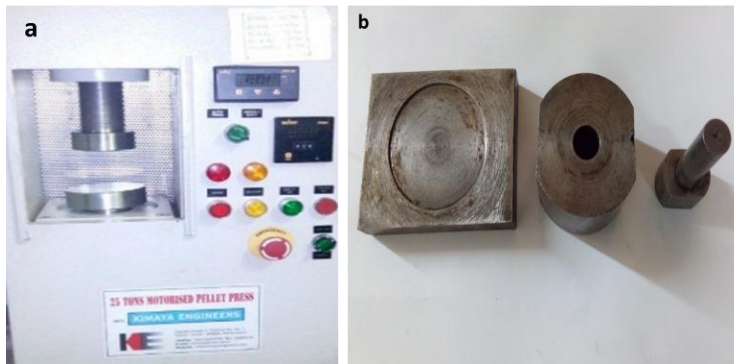


Figure 3. 2(a) Hydraulic press and (b) Mould for sample preparation

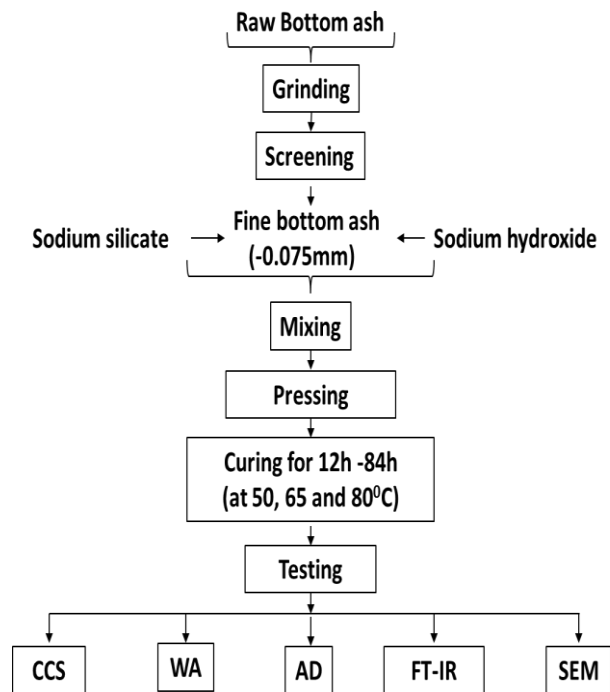


Figure 3. 3 Flow chart for production and evaluation of geopolymer samples

3.2.3 Testing of samples

Cold crushing strength test was performed to measure compressive strength of cured samples produced at different conditions using low range Universal Testing Machine (UTM) at a constant loading rate of 0.1 mm/min (Make: SHIMADZU; Type: SBL-5Kn, P/N: 340-43120 - 01; Capacity: 5kN / 500 kg f Cell code: 8). In the present study, the effect of bottom ash type, curing temperature, curing time were investigated. The Apparent porosity, Bulk density and water absorption properties of cured samples were determined by using boiling water method as per ASTM C-20. (ASTM C20, 2010). X-ray diffraction (XRD) analysis was performed using Rigaku diffractometer, with $\text{CuK}\alpha$ radiations generated at 40kV and 20 mA. Fourier transformation infrared (FT-IR) spectroscopy was performed using Thermo Nicolet 5700 spectrometer with diamond crystal as a probe for determination of nature and relative content of the bond present in the samples.

3.3 Results and Discussions

The samples of different composition for both types of bottom ash, cured at 65 °C for 24 hours are shown in Figure 3.4.

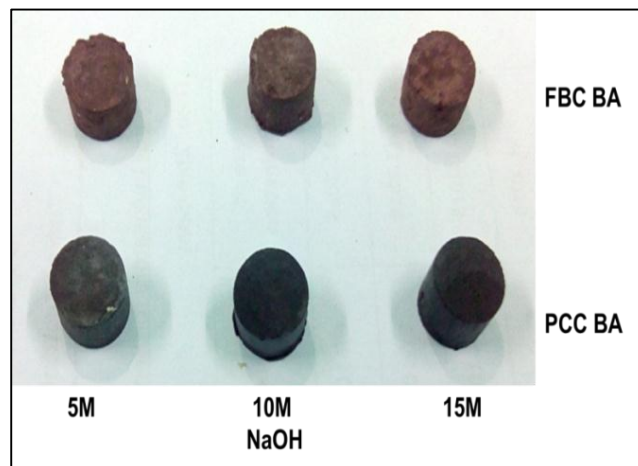


Figure 3. 4 Cured samples of different composition for both bottom ash

ASTM C62 standard describes the classification of building bricks based on the weathering condition where it could be used (ASTM C62, 2013). There are three categories based on the suitability of the weathering condition could be classified as NW, MW and SW which means negligible, medium as well as severe weathering condition (as shown in Table B.4 of Appendix-B). Based on the properties achieved in the different brick samples in the present studies were categories as per ASTM C62 specification which are mentioned in the following sections.

3.3.1 Cold crushing strength

Cold crushing strength is a vital property of the bricks depending upon their service condition. In case of building bricks, the strength requirement is more stringent in comparison to insulation bricks. In case of FBC bottom ash samples, cured at a 50°C temperature, with increasing molar concentration of alkaline solution, the cold crushing strength (CCS) of all cured samples showed increases trends with increasing curing time. But after 48 hours of curing, the CCS values gradually decreased as shown in Figure 3.5a. With increasing curing temperature (i.e. 65° C) of samples, the strength of the samples started decreasing after 36 hours of curing time, simultaneously with increasing molar concentration beyond 10M solution, strength also started decreasing as shown in Figure 3.5b. Similar phenomena was also observed for curing temperature 80°C, where strength decrement was started at 24 hours only as shown in Figure 3.5c. In case of PCC bottom ash samples, from the obtained results as shown in Figure 3.5d-f, it was found to be the similar trends of strength increment as found in the case of FBC bottom ash, but the level of the strength is more in all the cases except few samples when cured at 50 °C. The early stage of strength formation (i.e. 12 hours curing time), FBC bottom ash sample developed more strength

compared to PCC bottom ash samples when cured at 50°C. Increasing molar concentration, upto 15M, no decrement in strength values were observed in case of samples produced by PCC bottom ash (Figure 3.5d-f).

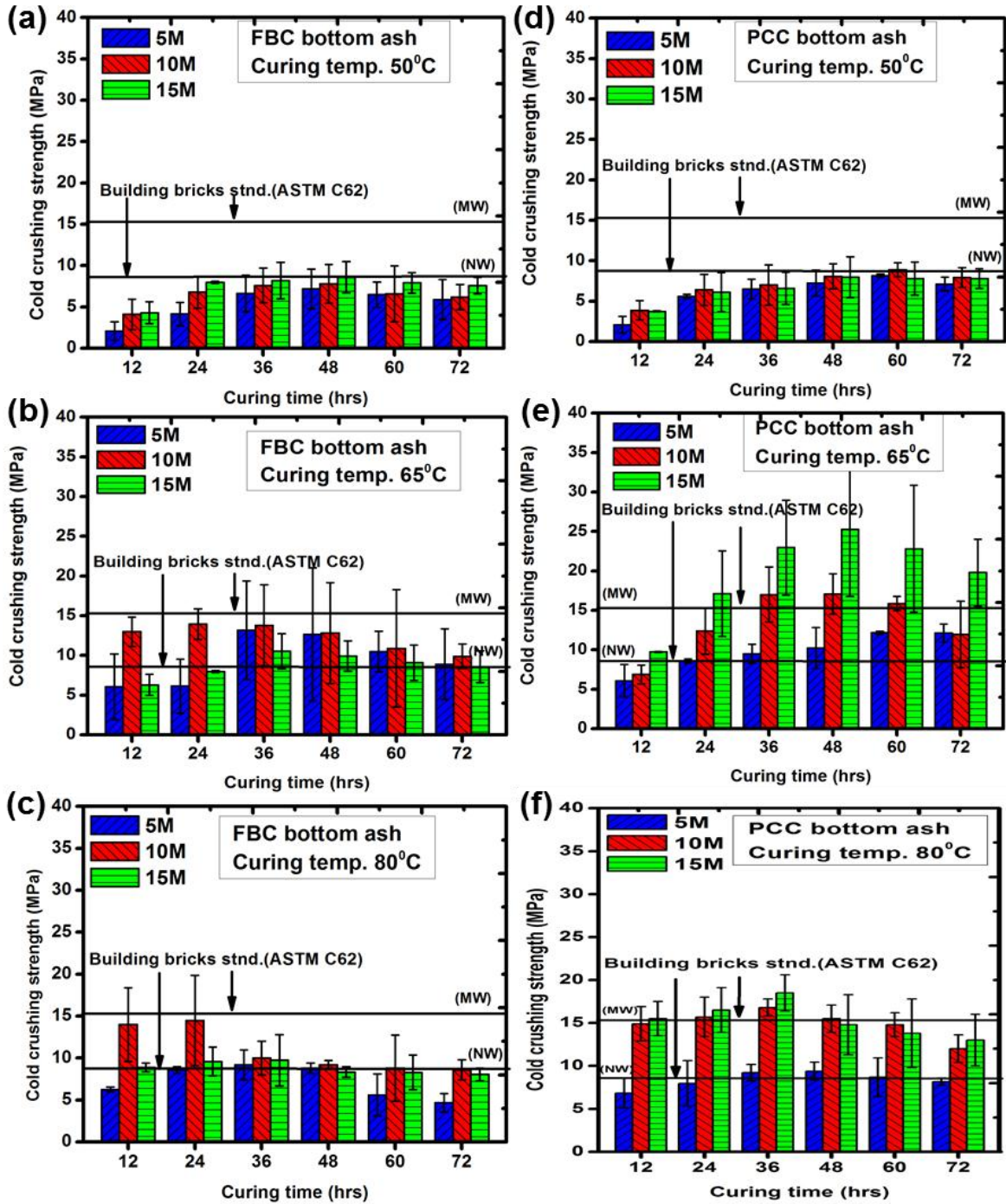


Figure 3. 5 Effect of various parameters on Cold Crushing Strength

All the batches of 50°C cured FBC as well as PCC bottom ash samples did not fulfill the strength requirement of building bricks of either NW or MW category of ASTM C62 (ASTM C62, 2013). Samples of FBC bottom ash having the curing temperature of 65°C and 80°C, fulfilled the strength requirement of building bricks of NW category (Figure 3.5b,c). Except few batches, all the samples of PCC bottom ash cured at 65°C and 80°C fulfilled the criteria of crushing strength requirement of building bricks for NW as well as MW category as per ASTM standard (ASTM C62, 2013).

3.3.2 Water absorption

Water absorption is the property of bricks which deals with the absorption of water by the bricks when it is exposed in suitable humid condition. It is generally used for the determination of building bricks. In the present study, water absorption by the brick sample was observed within the limit of standard bricks in all the batches where higher crushing strength was reported in the previous section. It may be due to the increasing geopolymerization reaction where increased amount of gel formation was occurred. The polycondensation process covered the outer layer of the unreacted particles as well as inter particle spaces, resulting less water absorption values. The overall water absorption values were observed more in PCC bottom ash samples (Figure 3.6 d-f) as compared to FBC bottom ash samples (Figure 3.6 a-c) due to porous structures of PCC bottom ash. As per NW category for building bricks, there is no such requirement for water absorption. Hence, all the batches were fulfilled the NW category for building bricks as per ASTM standard . It was also observed that except PCC bottom ash samples cured at 50°C (Figure 3.6d), all the remaining samples were fulfilled the water absorption criteria for building bricks for MW category as per ASTM standard (ASTM C62, 2013).

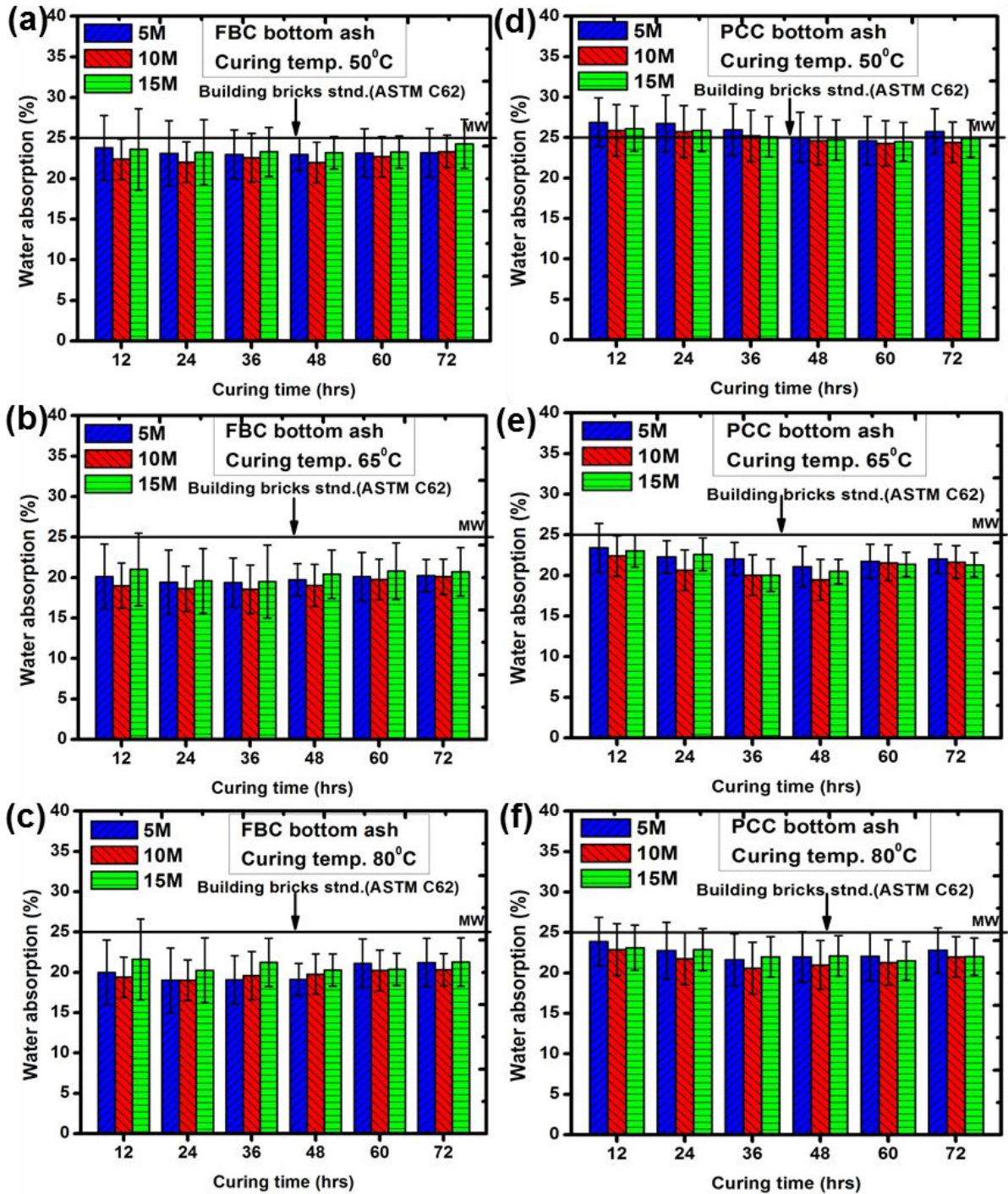


Figure 3. 6 Effect of various parameters on water absorption

3.3.3 Apparent Density

As mention in the section 3.3.2, due to increased geopolymerization which formed denser structure, resulting higher apparent density as shown in Figure 3.7. For the same reason, apparent density is slightly more in case of all the sample cured at 65°C. It was also observed relatively more apparent density values in case of FBC bottom ash due to non porous structure (Figure 3.7a-c). There is no such strict requirement of apparent density for building bricks, but it should be as low as possible. For that reason, PCC bottom ash samples were found to be more preferable with respect to density requirements (Figure 3.7d-f).

3.3.4 Phase analysis

The phase analysis of geopolymer samples were carried out by XRD to understand the different phases produced after geopolymerization and their effects on the strength in the samples. The X-Ray diffraction patterns was shown in Figure 3.8 for the produced geopolymer samples which made from both ashes using different alkali concentration and curing times. The major crystalline phase of quartz in FBC bottom ash geopolymers, decreased with increasing curing time and temperature to form sodium aluminium silicate, resulting enhanced strength in the sample as shown in Figure 3.8a,c. In case of PCC bottom ash samples, initially the free quartz phase took part in geopolymerization reaction, resulting decrease in quartz phases which was observed upto 24 hours of curing time. After that it was observed the dissolution of mullite phases to form oligomers. Therefore, after 24 hours of cured samples showed the decreasing trends in peak height of mullite (Figure 3.8d).

Sodium silicate addition was made for making of geopolymer which was also detected in XRD. Excess sodium hydroxide solution reacted with CO₂ to form sodium bi

carbonate phase. Therefore, presence of sodium bi carbonate phase indicated the incomplete geopolymerization or addition of excess alkali solution in the samples (Figure 3.8b).

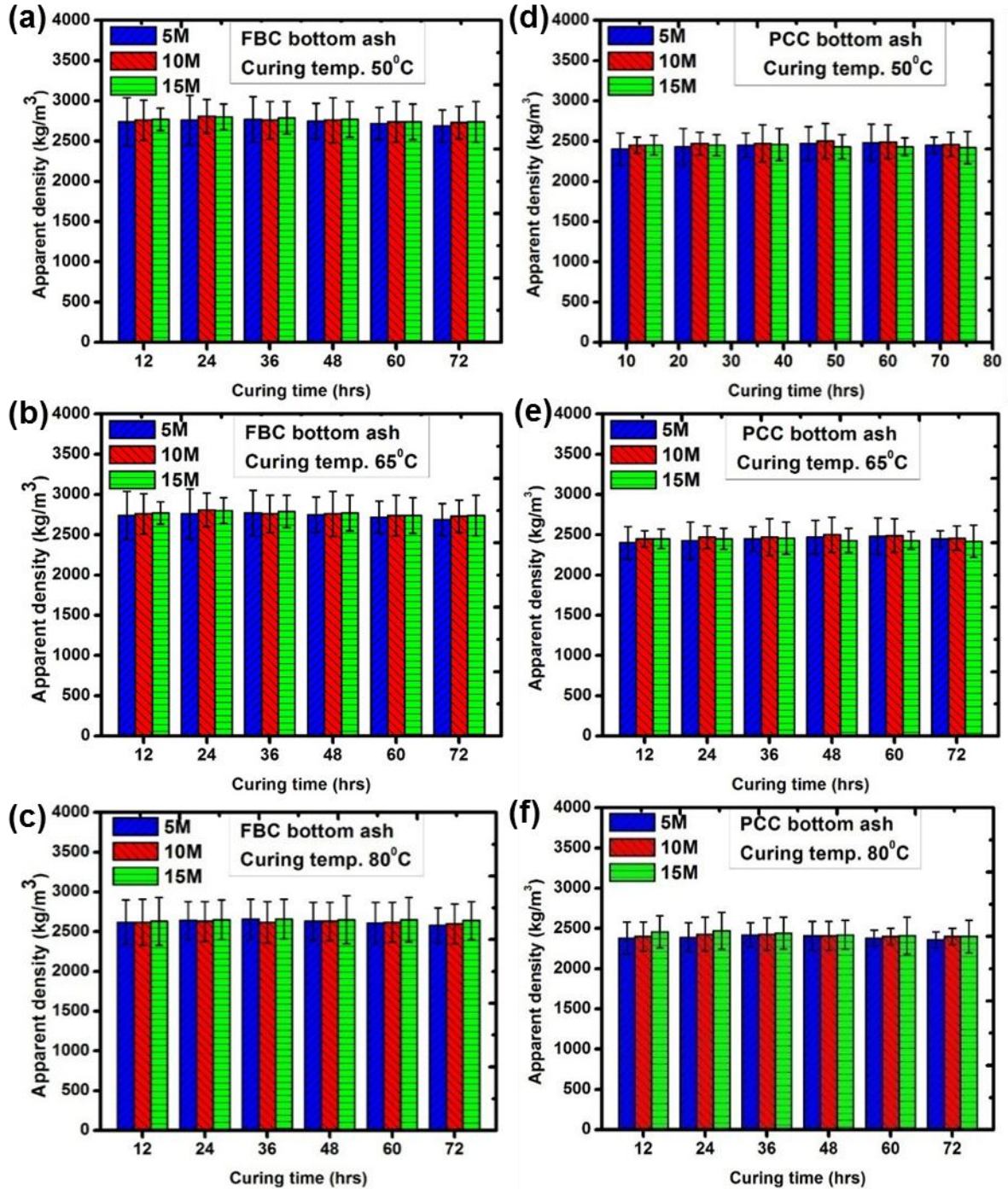


Figure 3. 7 Effect of various parameters on apparent density

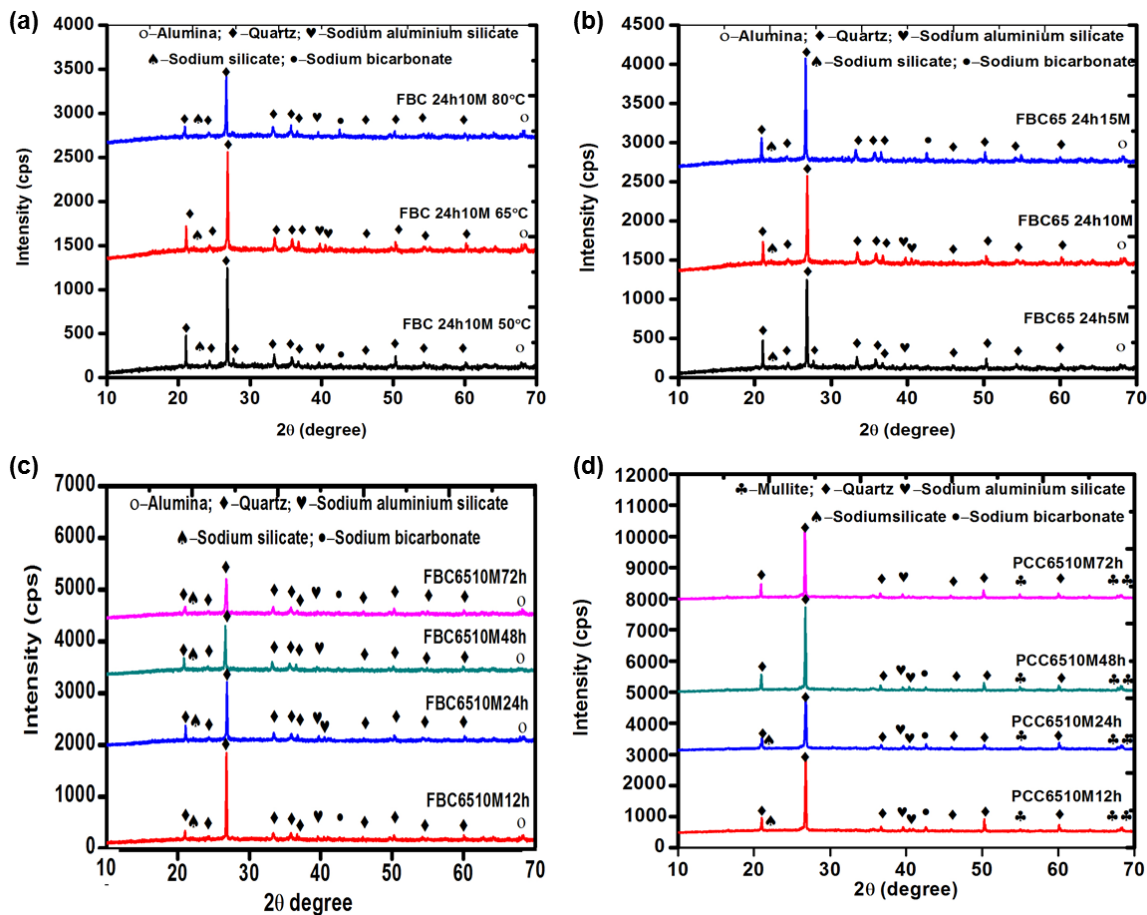


Figure 3. 8 XRD analysis of different samples

These phase were present in the samples when cured for 12 hours and 72 hours as well as in case of higher molarity of alkaline solution (i.e. 15M). The lower strength inside the brick sample was observed due to incomplete geopolymerization. That’s why lower as well as higher curing time and temperature showed decreasing trends of strength inside the brick samples.

3.3.5 FT-IR analysis

FT-IR study was performed to notice the effect of geopolymerization on the samples of both type of ashes quantitatively as well as qualitatively. A band corresponding to Si–O–Al

vibrations generally present in the range of 550-650 cm^{-1} in geopolymers (Krivenko and Kovalchuk, 2002; Kumar and Kumar, 2013).

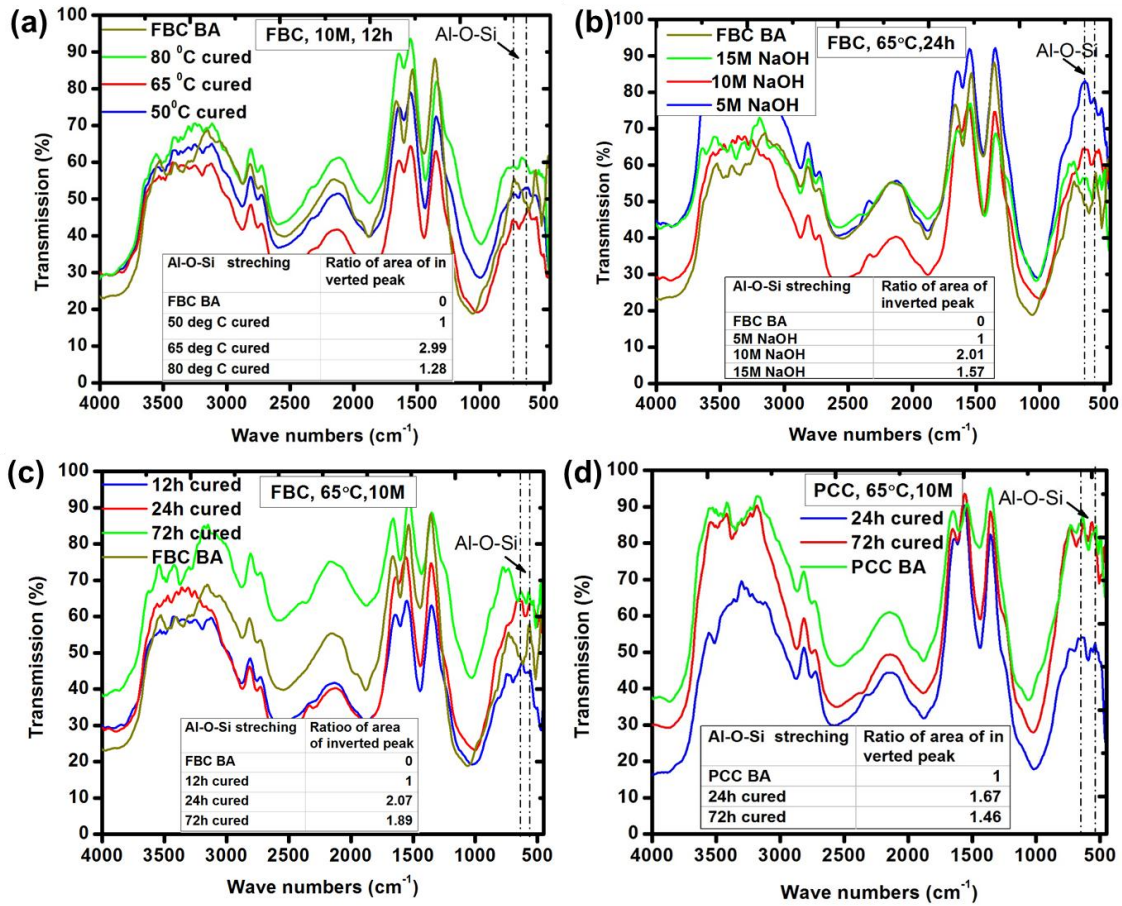


Figure 3. 9 FT-IR analysis of geopolymer samples

The degree of geopolymerization indicates quantitatively in terms of height ratios and area ratios of the present Si–O–Al stretching peaks in the FT-IR spectra of geopolymers to their corresponding ashes peaks (Chindaprasirt et al., 2009). The ratio of area is often used to determine the degree of geopolymerization which was calculated and values are tabulated in the Figure 3.9. The ratio of these peak indicates the maximum geopolymerization occurred for 65°C FBC cured samples for 12 hours as compared to 50°C as well as 80°C (Figure 3.9a). Simultaneously, in case of 10M alkaline solution and 24 hours cured samples showed maximum values as compared to 5M and 15M (Figure 3.9b) as well as for 12 to 72 hours

(Figure 3.9c) cured samples. In comparison to FBC, a slight decreased amount of geopolymerisation was observed in case of PCC bottom ash samples (Figure 3.9d). But in the case of strength increment, it was observed that PCC bottom ash samples showed more strength as compared to FBC bottom ash samples. It may be due to the presence of hard, wear resistant mullite phase inside the PCC bottom ash which enhanced the crushing strength in the samples.

3.3.6 SEM analysis

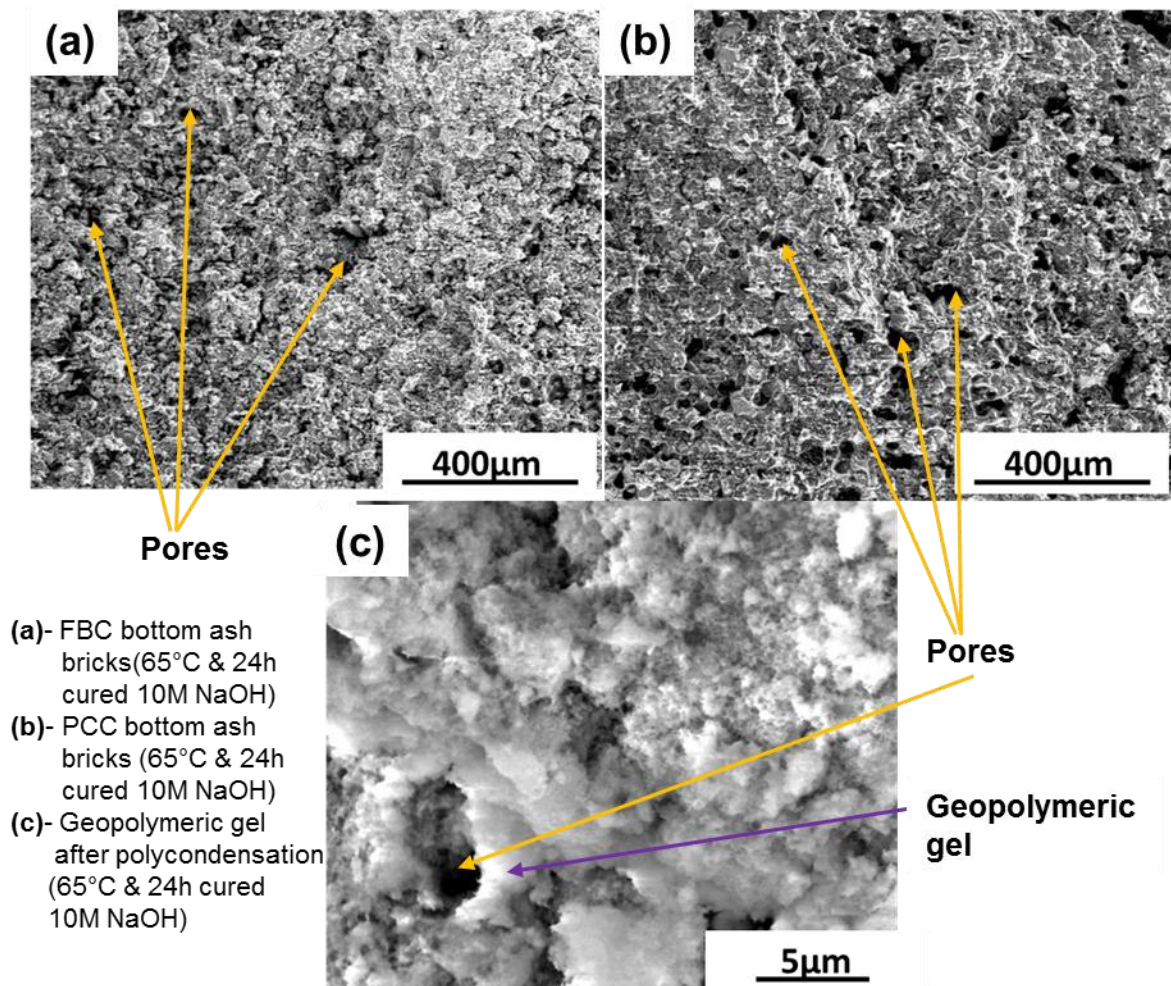


Figure 3. 10 SEM micrograph of bricks samples

SEM micrographs were evaluated to investigate microstructural features developed in geopolymers samples as shown in Figure 3.10. SEM micrographs revealed the presence of

more porosity in case of PCC bottom ash samples as compared to FBC bottom ash samples due to porous structure although similar fineness was used (Figure 3.10a,b). Due to high porosity, the increased water absorption as well as lower apparent density were reported in the previous section for PCC bottom ash samples (Figure 3.6 and 3.7). Figure 3.10c showed the magnified pictures of geopolymeric gel after polycondensation (65°C & 24h cured 10M NaOH) of FBC bottom ash sample which confirms the formation of gel around the surface of particles.

3.3.7 Tentative bonding mechanism

Based on the results obtained from the different experiments were performed as mentioned in previous section 3.3.1-3.3.6, a tentative mechanism could be predicted for the strength development inside the geopolymer samples as shown in the Figure 3.11.

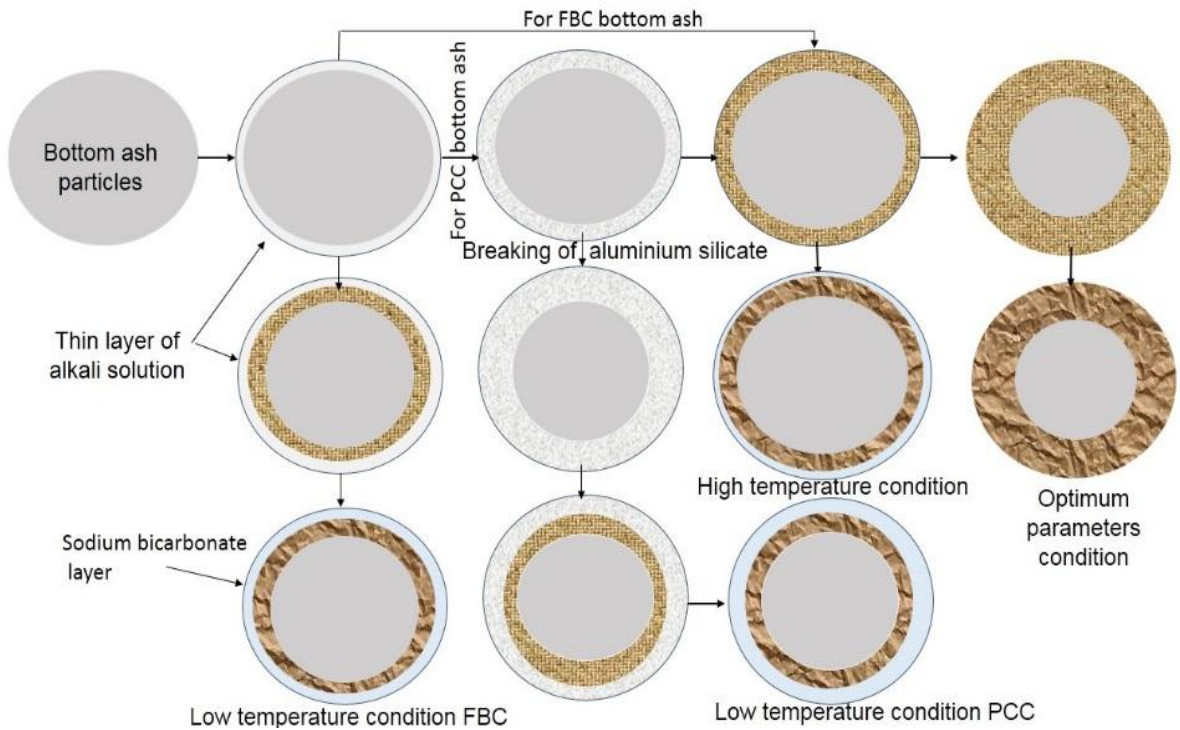


Figure 3. 11 Tentative mechanism of geopolymerization in different types of bottom ash

In the case of FBC bottom ash samples, when the particles of the bottom ash come into contact with alkaline solution, where silica and alumina present as an uncombined state, started reaction to form geopolymeric gel. But in the case of PCC bottom ash samples, first dissolution of aluminium silicate phases started to form oligomers of silica and alumina. This geopolymeric gel formation continued till the start of polycondensation where hard structure started to form. At optimum curing time, molarity of alkali solution as well as curing temperature (i.e. 24-48 hrs, 10M and 65°C), dissolution and geopolymeric gel formation may be happened simultaneously until the alkali solution exhausted, before initiation of polycondensation. Hence maximum strength formation may be occurred at the optimum condition. In the case of higher temperature of curing (i.e. 80°C), the rate of polycondensation became fast compared to dissolution, resulting the formation of high strength impervious structure with the help of available alumina and silica (Davidovits, 2002). This structure restricts the further dissolution of silica alumina species with the alkali solution, resulting the less strength development inside the samples. The unconsumed alkali solution reacted with CO₂ to forms sodium bi carbonate phase. Therefore, the presence of sodium bicarbonate phase in the sample was observed by XRD in case of high temperature cured samples (i.e. 80°C). Increasing the molar concentration of alkaline solution (beyond 10M), it becomes more viscous which also restricts the dissolution of the silica alumina species and forms a layer over the particles, resulting less strength formation in case of high molar concentration. At lower temperature of curing (i.e. 50°C), the dissolution of silica alumina species occur but the required energy to form geopolymeric gel followed by polycondensation is very less. Therefore the presence of sodium bicarbonate phase was also

observed in XRD analysis, resulting lower strength inside the samples and it was also reported by other researchers (Chen et al., 2011; Hardjito et al., 2004; Xu et al., 2010).

3.4 Conclusions

1. Geopolymerization technique of brick making using bottom ash may be feasible by using sodium silicate and sodium hydroxide.
2. The rate of geopolymerization appears faster initially in case of FBC bottom ash as compared to PCC bottom ash. The breaking of aluminium silicate bond may not be required in FBC samples because silica alumina presence in free state.
3. Geopolymerization may be slightly more in case of FBC, yet PCC bottom ash appears more suitable for strength development due to the presence of hard aluminium silicate phase.
4. Geopolymerization reaction increases up to 65°C, and then decreases with further rise in temperature may be because of higher rate of polycondensation that restricts further dissolution of ash particles.
5. Increasing NaOH concentration, ensures more geopolymerization up to 10M but further addition causes formation of possible highly viscous NaOH layer covering the surface which may restrict further geopolymerization.
6. The brick sample produced by geopolymerization using both types bottom ash having at least 10M NaOH, with 24 hours curing at 65°C temperature fulfilled the criteria of light weight building bricks of NW category as per ASTM C-62. However in case of

sample produces by PCC bottom ash, fulfilled the criteria of building bricks standard of MW category.