CHAPTER VI

CONCLUSION
1. Titabor clay is a conglomerate of many substances of varied nature. It can be fractionated into several fractions by gravity separation method. The heavy fraction contains coarser particles and is rich in silica. The light fraction is made up of fine particles, which are mainly amorphous, and is rich in alumina. The total $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ content of the clay or any of its fractions is more than 81.5% and well within the requirements for being recommended as a pozzolana.

2. XRD analysis has revealed that mineralogical compositions of different fractions and the parent clay are comparable. The materials are composed of large proportions of amorphous substances together with some crystalline phases. $\alpha$-quartz is the major crystalline phase with a number of clay mineral and non-clay mineral. Kaolinite is the most prominent of the clay minerals present in the clay.

3. IR spectras of the clay also indicate presence of small quantity of kaolinite and quartz in the clay.
4. Thermal analysis of the clay indicates that the clay is a complex mixture containing very fine crystals of quartz, amorphous materials and several clay and non-clay minerals. Kaolin, dickite, nacrite, montmorillonite, halloysite, chlorite, talc, muscovite, pyrophyllite, glauconite etc. are the clay minerals likely to be present in the clay. The amorphous material may be mixed silica-alumina-gels, called clay-gels, like allophanes, hisingerite etc.

5. The clay undergoes dehydroxylation at different temperature regions from near 500°C to around 800°C.

6. Particle size distribution of the clay have shown that the diameters of the particles vary from around 56.6 μm to 1.6 μm. 50% of the particles in the clay have diameters less than 9.4 μm whereas for the heavy, middle and light fractions the diameters of 50% of the particles are 11.9, 7.2, 6.0 μm respectively.

7. The cation exchange capacities (CEC) of the light fraction of the clay is the highest among all fractions as this fraction contains the most of the exchangeable cations. The CEC of this fraction is higher than even parent clay. Probably this property has relation with the amorphous components of the clay.
8. The clay undergoes many changes during calcination depending upon the temperature used. XRD and IR analyses show that during calcination, water present in the material in various forms such as, adsorbed, combined or interlayer, goes off and structural change of the clay minerals sets in at the temperature region of 500-800°C. The mixed silica-alumina-gel present in the clay undergo dehydration during calcination leading to collapse of pores in the amorphous material. Scanning Electron Microscopic studies (SEM) of the parent and calcined clay support this view.

9. Heating of the clay beyond 800°C results in formation of many new phases like α-cristobalite, spinels, γ-alumina, mullite, enstatite, olivine etc. Surface area of the calcined material diminishes rapidly due to melt formation leading to agglomeration of fine particles and sintering.

10. Rice husk ashes prepared at 500, 600, 700, 800, 900 and 1000°C contain a maximum of 89.22% silica and stack burnt ash contains 91.60% of it. In addition, the ashes contain Al₂O₃, Fe₂O₃, CaO, MgO, MnO, Na₂O, K₂O, P₂O₅, SO₃, etc. in small quantities. The ashes prepared at temperatures below 800°C contain some unburnt carbon. The amount of silica increases with increase in ashing temperature. The loss on ignition (LOI) is high for the ash prepared at a lower temperature and it decreases with increase in ashing temperature. The
LOI of the stack burnt ash is 0.49 which falls between those of the ashes prepared at 800 and 900°C. Carbon free ashes white to pinkish-white in colour. Unburnt carbon imparts a grey to black colour to the ash depending upon the ashing temperature and the amount of unburnt carbon present.

11. Different rice husk ashes exhibit different moisture absorption capacities. It decreases with increasing ashing temperature. Silica in rice husk ash is mostly silica-gel which has high internal surface due to presence of fine pores which can retain water. At high ashing temperature, the pores collapse resulting in decrease of moisture absorption capacity.

12. XRD of rice husk ash prepared at different temperatures upto 800°C are almost identical. These ashes contain amorphous silica together with some α-quartz. Ashes prepared at 900 and 1000°C contain α-cristobalite in addition to α-quartz.

13. α-cristobalite is not thermodynamically stable. The formation of α-Cristobalite at a temperature less than the stability temperature is attributed to the catalytic effect of alkali and alkaline elements present in rice husk.

14. IR spectra of the ashes show that the materials prepared at 500-800°C contain -OH group which is gradually removed when the ashing temperature is
increased. Dehydroxylation is complete above 900°C. The bands in the region of 1400-1000 cm$^{-1}$, assigned to Si-O, become sharper with increasing ashing temperature which indicate attainment of crystallinity. Crystallization of silica to α-Cristobalite at 900°C and above is preceded by dehydroxylation of silica.

15. The IR spectra of rice husk ash prepared at temperatures 500-1000°C do not show any absorption band corresponding to any organic functional group indicating that all organic matters present in the rice husk has undergone decomposition below 500°C.

16. The differential thermal analysis curves of the ashes prepared at different temperatures are nearly identical. These curves indicate presence of water in surfaces or pores of various energy levels which suggest amorphous gel-like nature of the silica in the ash. The DTA curves show exothermic trend between 550 and 900°C which are ascribed to collapse of pore structure. Above 900°C structural transformation takes place forming crystalline silica. The processes of pore collapse in silica and its structural transformation, occurring during thermal treatment of the ash, are vary sluggish in nature.

17. The particle size distribution of the ashes ground under similar conditions show that the low temperature ash contains more of the smaller particles than a
high temperature ash. 50% of the particles in the ashes prepared at 800 and 1000°C have diameters less than 11.2 and 23.3 μm respectively. This shows that the grindability of the 800°C burnt ash is more than that of 1000°C burnt ash. Surface area of rice husk ash also decrease with increase in ashing temperature. The 1000°C burnt ash has only 55.5% surface area of the 800°C burnt ash. The decrease in surface area is attributed to collapse of pore structure of silica in the ash and their crystallization.

18. Stack burnt rice husk ash is comparable in composition and physical properties to the ash prepared at 800°C. It is low in α-cristobalite and contains amorphous silica as found from XRD and IR analyses. Its MAC is more than that of the 900°C burnt ash. Surface area, particle size distribution and LOI of this ash are comparable to the 800°C burnt ash. It has a pinkish-white colour which indicate complete removal of unburnt carbon possibly due to the vary long exposure to heating conditions.

19. Pozzolanic reactivity of calcined clay and rice husk are determined by lime reactivity method. The raw clay exhibits some lime reactivity. It does not increase much with increase in reaction time. Calcined clay shows improve lime reactivity in comparison to raw clay. Lime reactivities of calcined clay varies with calcination temperature and reaction time. The clay calcined at 600°C has the highest lime reactivity up to 120 hours of reaction time and the
ash prepared at 800°C shows the highest lime reactivity at longer reaction times.

20. Amorphous and reactive components, SiO₂·Al₂O₃ present in the pozzolanic material combine with lime during lime reactivity measurements. Silica as well as alumina has low solubilities in neutral media. In high pH conditions, such as in saturated lime solution, solubilities of silica and alumina increase. As a result phases like C-S-H, C-A-H or C-A-S-H are produced and precipitated out as they have very low solubility products. These products are similar to those produced during hydration of Portland cement.

21. Calcination of clay between 600 and 800°C cause dehydroxylation of clay minerals resulting in formation of more amorphous materials which are reactive towards limes. 800°C was found to be the optimum temperature for complete dehydroxylation of the clay minerals.

22. Clay calcined at 900°C and above undergo crystallization as well as agglomeration due to melt formation. These processes reduce lime reactivity. Such materials show reasonably high lime reactivities at longer durations, after 120 hours. This is attributed to the slow release of sodium and potassium etc. from the calcined clay matrix as a result of which the pH of the solution
increases Silica and alumina then dissolve out from the clay matrix to form C-S-H, C-A-S-H etc. phases.

23. Lime reactivities of rice husk ash varies with ashing temperature and reaction time. Ash sample prepared at 500°C shows high lime reactivity at low reaction time and its reactivities at longer reaction times are comparable to those of other ashes prepared at higher temperatures upto 800°C. At long reaction time the ash prepared at 800°C shows the highest lime reactivity.

24. The reactivities of the ashes prepared at 900°C and above are lower due to crystallization of silica.

25. XRD and IR analyses of the lime reaction products shows formation of C-S-H phases. These are the products of reaction between reactive silica and lime formed in a way similar as in calcined clays.

26. XRD and IR results show presence of calcite in the lime reaction products of clay and rice husk ash which have possibly formed from Ca(OH)$_2$ by carbonation due to CO$_2$ in the atmosphere.

27. The specific gravities of blended cements containing calcined clay and rice husk ash are less than the neat cement.
28. Blended cement prepared using both rice husk ash and calcined clay require more water than the neat cement for obtaining paste of standard consistency. The water requirement increases with the amount of addition of pozzolana. The water requirements of the blended cements containing rice husk ash are more than those containing calcined clay. The higher water requirements of the blended cements are attributed to high surface areas of the materials.

29. Both rice husk ash and calcined clay delay initial and final setting times of cements. The delay in setting time is related to increase in water demand of the cement. Carbon present in rice husk ash contributes to delay in setting times of the cement containing rice husk ash.

30. The three day compressive strength of the mortar cubes prepared using blended cements containing either rice husk ash or calcined clay is less than that of the neat cement but at 7 days it is comparable and at 28 days it is higher than that of the neat cement. Gain in strength of the blended cement at later period is attributed to the formation of additional C-S-H phase formed by reaction of silica with Ca(OH)$_2$ formed in hydration of the cement.

31. The compressive strengths of the blended cement prepared by mixing both calcined clay and rice husk ash at all ages are higher than cements containing
any one of the pozzolanic material or the neat cements. It is attributed to synergic effect.

32. The amount of non-evaporable water in the 1 day hydrated pastes of the blended cements containing rice husk ash and/or calcined clay is in general higher than that of the neat cement paste. The pozzolanas accelerate the early hydration of cement. This is attributed to fine particle size of pozzolanic materials which acts as nuclei for precipitation of Ca(OH)$_2$.

33. The amount of non-evaporable water in the hydration products of the pastes of the blended cements at 28 and 90 days in general are less than that of the neat cement. This is attributed to consumption Ca(OH)$_2$ and formation of C-S-H phase due to pozzolanic activity of the material.

34. The study reveals that rice husk ash produced at 800$^\circ$C is highly reactive. The stack burnt rice husk ash is comparable to 800$^\circ$C burnt ash in long time reactivity with Ca(OH)$_2$ solutions.

35. Stack burnt rice husk ash laying unutilized may be used in manufacturing of blended cement for their pozzolanic reactivity.

36. Titabor clay calcined at 800$^\circ$C s is a highly reactive pozzolana. Mixture of burnt clay and rice husk ash exhibits very high reactivity. The strength
characteristics of blended cements containing mixtures of calcined clay and rice husk ash is very high. This suggests that highly reactive pozzolana may be obtained by co-calcination of rice husk and Titabor clay at 800°C.

37. More research, particularly to investigate the durability of blended cement containing stack burnt ash, calcined Titabor clay and their mixtures, are required for utilizing these materials as mineral admixtures to cement.