ABSTRACT

Water-mineral interactions are the backbone of civil engineering infrastructural applications; with examples being the hydration of cement and the swelling of clay. From the perspective of chemistry, the cause and effect of hydrogen bonds play a key role in the water-mineral interaction process. The primary objective of this study is to develop a fundamental theoretical understanding of the role of hydrogen bonds in these civil engineering processes.

Hydrogen bonds (HB) are formed between hydrogen and other electronegative atoms (oxygen, nitrogen, fluorine, etc). The classification of HB relies on the energetic and geometric criteria in Molecular dynamics (MD) which have been employed to explain the physics of experimentally observed shock induced phase transition of bulk liquid water to ice VII like crystal structure. However, the onset of hydration of cement or swelling of clay involves complex charge transfer. These have been studied using density functional theory (DFT) along with Natural Bond orbital (NBO) based population analysis. Characterization of different types of bonds formed in the process based on the calculation of electronic charge density and its Laplacian are made using the Quantum theory of Atoms in Molecules (QTAIM) approach.

A fundamental step in cement hydration at the cluster level involves silicate oligomerization realized through condensation, fluxionality, and Si-OH rupture. The role of HB between water and silicate minerals in the process has been elucidated in this study. Crystal level studies investigating surface chemical reactivity (chemical hardness, electrophilicity, Fukui indices) and absorption of water molecules on different surfaces of minerals to initiate the hydration reaction have also been explored in the study. Another application investigated in the thesis involves the swelling of smectite clay minerals - montmorillonite. The competing role played by metal-ligand bonding and HB in the process of absorption of water at the interlayer spacing of the mineral with different metallic cations has been elucidated in this thesis.