Theoretical and experimental study of structures and properties of cement paste: The nanostructural aspects of C–S–H

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ABSTRACT

Ordinary Portland cement (OPC) paste with water to cement ratio 0.5 has been studied by FTIR spectroscopy and TEM/SAED techniques. The progressive shift in frequencies and change in intensity of characteristic peaks in the FTIR spectra of cement powder indicate polymerization of silicates due to hydration reaction. The appearance of new peaks around 975–985 and 3640–3650 cm^{-1} in FTIR spectra of cement paste has been attributed to the formation of two principal hydration products (C–S–H) and Ca(OH)$_2$, respectively. There is a strong resemblance of peak shape at 980 cm^{-1} of cement paste with that of synthesized 1.1 nm Tobermorite. TEM/SAED techniques reveal the presence of three distinct types of C–S–H nanostructures viz. spherical particles, fibres and bundle of fibres, and nano tubes in cement paste. Theoretical study of two C–S–H clusters by MNDO and Density Functional Techniques shows excellent agreement between computed structural data and reported experimental results of Tobermorite and Jennite. The computed interplanar Ca–Ca distance (11.162 Å) of C–S–H cluster (Ca/Si=1.125) indicates greater structural similarity of this cluster to 11 Å Tobermorite. There is a strong similarity of IR profile of C–S–H cluster (Ca/Si=1.125) with 1.1 nm Tobermorite. Above study indicates that this cluster is probably the most likely basic unit of C–S–H phases formed during the early stage of OPC cement hydration.

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1. Introduction

Ordinary Portland cement is a complex material consisting of several crystalline components with four major phases viz. alite (C$_3$S-Ca$_3$SiO$_5$), belite (βC$_2$S-Ca$_2$SiO$_4$), aluminate (C$_3$A-Ca$_3$Al$_2$O$_6$), aluminoferrite (C$_4$AF-Ca$_2$FeAlO$_5$) and gypsum (CaSO$_4 \cdot$2H$_2$O). When cement powder reacts with water, it slowly transforms itself into a rigid, complex porous structure called cement paste. The cement paste is a multi-phase material, which continuously evolves with time with consequent change of structure, composition and morphology and may be viewed as a composite material in which calcium hydroxide crystal, aluminates and unreacted cement particles are all embedded into a matrix of amorphous nanostructured hydration product called C–S–H gel [1–34]. This gel is the most important hydration product because it is the primary binding phase of Portland cement based system. It constitutes about 60–70% of the fully hydrated cement paste. One of the primary objectives of contemporary research in cement chemistry is to develop a basic understanding of the structure, composition and mechanism of the formation of different C–S–H nanostructures from OPC and PPC cements during the early stage of cement hydration reaction. Several analytical techniques are normally used to characterize the structure and composition of cement and cement paste. Since the C–S–H gel phase in cement paste is amorphous, it cannot be identified by XRD technique but its presence in the hydration product and the important characteristic features of the gel can be detected by a combination of other techniques like FTIR [11–17], Solid State ^{29}Si NMR [18–26], TEM/SAED [27–31], SEM/EDX [32–34], etc. The C–S–H gel phase is normally characterized by Ca/Si ratio, which varies in the range of ~1.2–~2.3 with a mean of ~1.75 in neat OPC cement paste [27]. The sizes of nanoparticles observed in OPC cement paste are in the range of 2–6 nm but may vary depending upon composition, cement/water ratio and temperature of curing, etc. [27,28]. Much of the existing knowledge on the nanostructure of C–S–H gel has been gained from structural comparison with other crystalline calcium silicate hydrates. In fact, several models have been proposed so far that are based on the similarity of C–S–H gel structure with two important crystalline calcium silicate hydrates viz. Tobermorite (T) [Ca$_5$Si$_6$O$_{16}$(OH)$_2 \cdot$4H$_2$O] and Jennite (J) [Ca$_8$(Si$_3$O$_9$H)$_2$(OH)$_8$Ca$\cdot$6H$_2$O]. Both Tobermorite and Jennite crystals contain their SiO$_4$ tetrahedra condensed into linear chains that are kinked so that they repeat at intervals of three tetrahedral units. This kind of structural arrangement is called "dreierkette" and has an empirical formula of Si$_3$O$_9$. Comparing with the structural features of Tobermorite (T) and Jennite (J), C–S–H gel can be approximately viewed as a layered structure in which calcium oxide sheets are ribbed on either side of silicate chains and free calcium ions and water molecules are present in the interlayer space. This viewpoint based on layered crystal-like

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structures, which resemble clay morphologies [2], may be used as the starting point for computational work to develop a suitable structural model for C–S–H gel. However, experimental evidence [4,5] shows that if the structure of gel contains segments of Tobermorite and Jennite crystals, then these will have multiple defects and imperfections and the long range order observed for pure T and J crystals will be partly lost [4]. Structural analysis by Solid State ^{29}Si NMR spectroscopy has revealed that only dimeric silicate chains (Q^1, Q^2) are present in early and mature hydration products of both alite and OPC cement paste [19,23]. In a silicate chain, Q^1 denotes chain end group tetrahedron and Q^2 denotes the middle groups or a bridging tetrahedron that is positioned between two pairs of 'paired' tetrahedrons to form a continuous SiO_4 chain. Taylor [6,7] reported that C–S–H with a Ca/Si ratio < 1.5 [called C–S–H(I)] has a structure similar to Tobermorite and C–S–H with Ca/Si ratio > 1.5 [called C–S–H(II)] has a structure similar to Jennite. Viehland et al. [29,30] have shown by TEM observation that C–S–H in modern ordinary Portland cement (OPC) paste contains both Tobermorite and Jennite structural elements along with amorphous volumes. In fact, it is believed that the C–S–H gel present at the early stage could be a mixture of both Tobermorite-type and Jennite-type of dimeric structures (T2 and J2), whereas that formed at later stage approaches more to longer Jennite-type crystal morphologies [4–7]. However, it is still not clear how compositional variations of C–S–H are accommodated structurally, whether there is more than one type of C–S–H phase and what is the role of specific structural component such as Si–OH linkages in the formation of gel structures.

It is quite obvious from the above discussion that a more comprehensive understanding of the process that favours the formation of different types of C–S–H nanostructures in cement paste is required to design and control the desired C–S–H phase in a reaction product. A fundamental approach based on the bottom-up method of nanostructure formation from a set of ions of Ca^{++}, SiO_4^{-4}, H^+ and OH^- that are normally present in cement paste, will be very useful in this context. A recent theoretical study by Manzano et al. [35], based on *ab-initio* quantum chemical calculations (Hartee–Fock level), has shed new light on the mechanisms of formation of C–S–H nanoparticles starting with a suitable precursor (P), which resembles both Tobermorite-like and Jennite-like dimeric structures and consists of two silicate chains with a single calcium oxide layer sandwiched between the two silicate chains.

The objective of the present investigation is to explore in details the structure, morphology, composition, mechanism of formation and properties of C–S–H nanostructures that are formed during the initial stage of cement hydration process by a comprehensive theoretical and experimental approach. In this paper, we present the results of a comprehensive theoretical work by both *ab-initio* Density Functional Technique (DFT) and semi-empirical (MNDO) method on the optimum structure, mechanism of formation and other characteristic properties of two models of C–S–H nanoparticles with Ca/Si ratios 1.0 and 1.125 and compare the computed properties of these models with the experimental results obtained from an OPC cement paste. On the experimental front, we have used several techniques to characterize the micro and nanostructure of cement and cement hydration products and the results obtained from FTIR, TEM and SAED studies of the samples of cement paste are reported here.

2. Theoretical

The computational work reported here was primarily carried out by *ab-initio* Density Functional Technique (DFT) [36–42], which has been widely used in literature for optimizing the chemical structure of molecules [43–47], as well as semi-empirical

MNDO technique [48]. In DFT technique, we have used both Local Density Approximation (LDA) with Perdew and Wang functional (PWC) [49] and Generalized Gradient Approximation (GGA) with BLYP functional [50,51] to determine the optimum structure, total energy, atomic charge, dipole moment, infrared (IR) frequencies and intensities. The computed results were then used to interpret and analyse the FTIR spectra and features of nanostructure of OPC cement paste recorded as a function of different hydration time up to a week. We have also compared the computed theoretical IR data with published experimental FTIR results of synthesized calcium silicate hydrates (C–S–H) with different Ca/Si ratios, 1.1 nm Tobermorite, 1.4 nm Tobermorite and Jennite [11]. The computed structural data was also compared with experimental XRD results of 1.1 nm Tobermorite, 1.4 nm Tobermorite and Jennite crystals [8–10].

The specific computer code of DFT techniques used in this work is known as DMol3 (Version 4.1.0.0) [52,53], which is a part of Materials Studio software developed by Accelrys Software Inc. In Dmol3, the atomic basis sets are defined numerically by a set of points (typically 300) from the origin to an outer distance of 5.3 Å (10 μB), each one described by a function of cubic spline coefficients, piecewise analytic to generate first and second order energy derivatives. We have used DNP standard basis sets along with polarization in this work. DMol3 generates a molecular grid in a spherical pattern around each atomic centre, out to 5.3 Å, with a number of radial points typically given by $14(Z+2)^{1/3}$ [54], where Z is the atomic number. These radial shells are logarithmically spaced to treat the rapid oscillations of the molecular orbitals near the nuclei. The angular points for each r-shell increase with the quantum number l and are selected by schemes designed to yield exact angular integration using quadrature methods and a product-Gauss rule in $\cos\theta$ and Ø [54]. The total number of points per atom in the grid is approximately 1000. After generating the molecular grid, the programme interpolates all the atomic quantities to this new set of mesh points. To accelerate convergence far from the nucleus and to avoid integrating over the nucleus, a partition function is used [52,55,56]. In Dmol calculations we have used an SCF tolerance of 10^{-6} a.u. for electronic density, a gradient convergence of 0.002 a.u. for each coordinate, and a fine grid. We have used spin-unrestricted calculations and symmetry constraints were applied. To save the computer time, initial optimization of all the structures was carried out in a computer module called "Forcite", which is based on Molecular Mechanics. All computational data reported in this work was carried out in a Pentium-4 PC.

3. Experimental

3.1. Methods and materials

An OPC grade commercial cement sample was used in this work under as received condition from the supplier without any pretreatment to prepare two sets of cement paste samples (Set I and Set II) with water to cement ratio 0.5. The hydration reaction monitored in Set I is for the time periods 12, 24, 48, 72 h and 1 week and in Set II reaction is monitored for 6, 12, 18, 24, 48, 72 and 96 h.

To prepare the cement paste, 10 g of cement powder and 5 g of distilled water were weighed and mixed together in a plastic beaker. The reaction mixture was stirred for approximately 1 min using a glass rod. The beaker was then covered with a watch glass and kept undisturbed for the desired time period at normal room temperature for hydration to take place. After the reaction time was over, the cement block was first dipped in acetone for half an hour and then dipped in diethyl ether for half an hour to terminate the hydration reaction. The cement block was then