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FTIR study of the effect of temperature and nanosilica on the nanostructure of C–S–H gel formed by hydrating tricalcium silicate

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HIGHLIGHTS

- The effect of temperature and nanosilica on C_3S hydration was studied by FTIR and TEM.
- Temperature favours the jennite-like structure of C–S–H formed by hydrating C_3S.
- An increase in the Ca/Si ratio of the C–S–H gel at high temperature.
- Nanosilica amorphous accelerates the C_3S hydration.
- Nanosilica induces the tobermorite structure of C–S–H gel with lower Ca/Si ratio.

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ABSTRACT

Fourier transform infrared spectroscopy (FTIR) was used to explore the effect of temperature (25°, 40° and 65 °C) and the presence of amorphous nanosilica (nSA) on the nanostructure of the C–S–H gel generated during tricalcium silicate (C_3S) hydration.

Rising temperatures were shown to modify the nanostructure of C–S–H gel. The bands at around 1076 cm^{-1}, 909 cm^{-1} and 540 cm^{-1} that appeared on the FTIR spectrum for C_3S paste with rising temperatures were attributed to the formation a jennite-like structure. Moreover, irrespective of temperature, as the reaction progressed, the initial tobermorite-like C–S–H gel changed to a jennite-like structure. With the addition of nSA, the band generated at 960–970 cm^{-1} appeared from the first day of hydration, an indication that nanosilica accelerates C_3S hydration. The presence of nSA induced no narrowing of the bands at 1076 cm^{-1} or 909 cm^{-1} at any curing time, a sign that these gels had a smaller proportion of jennite-like species than the gels in the nSA-free pastes. Finally, compositional date of C–S–H was provides.

1. Introduction

Alite, a tricalcium silicate (C_3S in cement chemistry notation), is the majority phase (approximately 50–70%) in clinker. This phase is not pure, however, but found in solid solution, i.e. with impurities such as MgO, Al_2O_3, and Fe_2O_3 in its structure, and has a number of polymorphs [1]. Given the impurities present in ordinary portland cement, the monoclinic polymorph (M_I and M_{III}) usually prevails [2]. Pure tricalcium silicate (C_3S), in turn, is also polymorphic, with seven temperature-dependent forms: the three appearing at 620–980 °C are triclinic (T_I, T_{II} and T_{III}) and the three at 980–1060 °C, monoclinic (M_I, M_{II} and M_{III}); a single rhombohedral polymorph appears at temperatures of over 1070 °C (R) [1]. C_3S synthesised in the laboratory at 1450 °C from calcium oxide (calcined calcium carbonate) and silica gel only, followed by rapid cooling to ambient temperature, adopts a crystalline triclinic (T_1) structure. While the position of the Ca^{2+} and O^{2-} ions and the silicon atoms is similar in all these polymorphs, the orientation of the SiO_4^{4-} tetrahedra differs substantially. The main structural differences between polymorphs have to do with the coordination of the Ca^{2+} ions and the position of the oxygen atoms in the SiO_4^{4-} tetrahedra [2].

The main reaction products in C_3S hydration are crystalline portlandite (CH) and an amorphous or poorly crystalline calcium silicate hydrate known as C–S–H gel. This gel is the major hydration product both because it determines cement paste strength and durability and because it accounts for approximately 70–80% of the total.

C–S–H gel is known to have a disordered nanostructure arranged in layers that resemble the pattern found in crystalline calcium silicate hydrates such as 1.4 tobermorite and jennite.

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Counting its main layer and its interlayer, 1.4 tobermorite [3,4] is 1.4 thick. The main layer is a sandwich, whose centre, a sheet of CaO_2, is flanked on both sides by parallel chains of SiO_4 tetrahedra arranged in groups of three. Two of these tetrahedral units, which are linked to one another and usually called paired tetrahedra, share oxygen atoms with the central Ca–O sheet [3–5]. The third acts as a bridge between the two paired units and so is termed the bridging tetrahedron [5]. This arrangement is known as a "dreierkette". The interlayer space, occupied by water molecules and additional calcium ions, is the region between successive main layers, which are not chemically bonded. This same layered nanostructure is found in jennite, whose central Ca–O sheet is flanked on both sides by rows of tetrahedra arranged into dreierkette. As in tobermorite, this structure is separated from other similar layers by interlayers [6]. In jennite, only half of the oxygen atoms in the central sheet are shared with the SiO_4 chains, while the rest form part of OH groups [3]. Consequently, jennite has a much higher Ca/Si ratio than tobermorite [3].

Abbreviated symbols are normally used to describe the SiO_4 units [7] in the silicate chains present in the gel structure. In that system, each unit of SiO_4 is symbolised as Q^n, where "n" represents tetrahedral connectivity, i.e. the number of oxygen atoms shared with the adjacent Si, and ranges in value from 0 to 4. Q^0 represents isolated tetrahedra, Q^1 end tetrahedra or dimers, Q^2 intermediate tetrahedra, Q^3 branching site tetrahedra and Q^4 cross-linked tetrahedral [7].

Experimental (TMS/GPC and ^{29}Si MAS NMR) evidence [8–10] shows that the C–S–H nanostructure in C_3S or portland cement pastes is flawed: bridging SiO_4 tetrahedra are often missing, giving rise to finite silicate chains with 2, 5, 8,..., $(3n - 1)$ units [5]. The mean silicate chain length (MCL) can be calculated with Richardson's equation [11] from ^{29}Si MAS NMR data.

Any theoretical model developed to explain the nanostructure of C–S–H gel must be consistent with laboratory findings [12]. The literature describes two main models, based on tobermorite and jennite, to explain C–S–H gel nanostructure [5,12]. The first, proposed by Taylor [3,4], likens C–S–H gel structure to either 1.4 tobermorite or jennite in which some of the bridging tetrahedra are missing. It assumes, moreover, that bridging tetrahedra carry only one H atom, so that when a tetrahedron is missing only one of the broken ends of the chain has a hydrogen terminus. Since the net charge therefore remains unchanged, the amount of interlayer Ca need not vary to compensate for the shortage of tetrahedra [12]. The theoretical Ca/Si ratio may be readily calculated for jennite and tobermorite of whatsoever chain length based on Taylor's description of their structure. For jennite, the extreme values of Ca/Si ratio are 1.5 for infinite chains and 2.25 for dimers. For 1.4 tobermorite, the respective values are 0.83 and 1.25 [3]. Nonetheless, no experimental data have yet been forthcoming to prove the existence of the aforementioned charge balance, even though the C–S–H gel nanostructure and composition suggested by the model are reasonable and consistent with a broad corpus of experimental data [12]. The Ca/Si ratio of the C–S–H gel formed during the hydration of the C_3S present in portland cement ranges from 1.2 to 2.3 [11].

In the second model, proposed by Richardson and Groves (1992–1993) [13–14], the tobermorite–jennite or T/J model, tobermorite-like structural elements would be intermixed with jennite-like constituents. This model is wholly flexible with respect to the possible degree of protonation of the silicate chains, and assumes that Al^{3+} ions replace Si^{4+} ions at bridging sites only [5,12]. The greater flexibility of this model leads to a wider range in the Ca/Si ratio of the gels [12]. For jennite dimers, the highest ratios are 2.5, 2.25 and 2.0, for 0, 1 and 2 degrees of silicate chain protonation, respectively, while for 1.4 tobermorite, the values are 1.5, 1.25 and 1.0 [5,13]. Consequently, the Taylor model may be assumed to be a specific case of the Richardson and Groves model [12].

Two of the factors that affect nanostructural changes in C–S–H gel are the addition of pozzolanic materials and temperature, the two objects of the present study. Today's portland cement may contain additions to improve not only strength and durability, but to make cement manufacture more sustainable. Such additions modify the nanostructure, composition, morphology and porosity of the C–S–H gels formed in the various types of portland cement pastes. They have a substantial but poorly understood impact on the properties developed by these gels and consequently on the properties of the pastes themselves. As a rule, amorphous nanosilica (nSA), a pozzolan, reduces the amount of portlandite forming during cement powder hydration by reacting with the mineral: this is known as the pozzolanic reaction. The resulting decline in the amount of portlandite is beneficial, because this phase makes no contribution to cement paste mechanical strength or durability. Moreover, the additional C–S–H released as a product of the pozzolanic reaction enhances those properties. This new gel can be distinguished from the C–S–H gel obtained by hydrating C_3S alone on the grounds of the differences in their nanostructure, morphology and composition [5,15–17].

Another factor that modifies C–S–H gel nanostructure is temperature. This has practical consequences, inasmuch as precast concrete structures, in whose manufacture hydrothermal curing is applied, are being more and more commonly used in construction. ^{29}Si MAS NMR studies have shown that temperature accelerates C_3S hydration [18,19], although a number of questions about temperature-induced variations in C–S–H gel nanostructure remain unanswered. For one, the effect of temperature on the Ca/Si ratio of C–S–H gel is uncertain and, as Scrivener and Weiker [20] point out in their review, the data at hand are contradictory. A number of authors have reported an increase in the Ca/Si molar ratio at high curing temperatures [21], while others, such as Escalante-García and Sharp [22], observed the opposite: a decline in the Ca/Si ratio in the C–S–H gel formed during ordinary portland cement hydration when the temperature was raised from 10 to 60 °C. These changes in the Ca/Si ratio should affect the scantly studied C–S–H gel nanostructure. Moreover, whereas ^{29}Si MAS NMR and TG studies show that temperature lowers the tobermorite/jennite ratio in the C–S–H gels obtained during C_3S hydration [23], the variation in the infrared bands generated by the gels has yet to be explored as an avenue for determining the ratio between these phases.

Since C–S–H gel is amorphous or only barely crystalline, it cannot be analysed by X-ray diffraction. It can, however, be characterised by FTIR and other techniques such as ^{29}Si magic angle spinning nuclear magnetic resonance (^{29}Si MAS NMR). FTIR is apt for studying both crystalline and amorphous compounds, because functional groups absorb different wavelengths depending on their constituent atoms, geometry and chemical environs.

In most C–S–H studies, the gels are synthesised from silica and portlandite to pre-determined Ca/Si ratios. The resulting nanostructure, closer to tobermorite than jennite, generates what are known as C–S–H_I gels [1], while the C–S–H gel formed from C_3S hydration in the presence of excess water, C–S–H_{II}, exhibits a jennite-like nanostructure [24]. Although the variation in the FTIR bands on the spectra for C–S–H_I gels with different Ca/Si ratios has been studied [25], it has not been related to changes in the nanostructure of the C–S–H gel formed during the hydration of tricalcium silicate in the presence of amorphous nanosilica at high temperatures. The present study therefore aimed to use infrared spectroscopy to monitor the effect of temperature and the addition of amorphous nanosilica on the nanostructure of the C–S–H gel obtained in C_3S hydration. Although jennite and tobermorite have similar structures, jennite has both Ca–OH and Ca–O bonds in