



Confocal Raman microscopy as a non-destructive tool to study microstructure of hydrating cementitious materials

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ABSTRACT

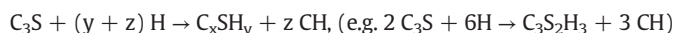
Non-destructive investigation of hydrated cement microstructure is still a big challenge. In this study, we present non-destructive image and structural analysis of hydrated monoclinic C₃S clinker by means of confocal Raman microscopy (CRM), which to the best of our knowledge is used for studying hydrating cementitious systems for the first time. In detail, CRM enabled structural and spatial characterization of calcium-silicate-hydrate phases (C-S-H), portlandite (CH) and reactants on the micrometer scale without the need for extensive sample preparation. Two complementary data analysis tools (cluster analysis and graph basis analysis) revealed that m-C₃S can be fully or partly hydrated to C-S-H as the ubiquitous phase. Furthermore, CH could be identified as macroscopic flakes of different size as well as intimately mixed with the C-S-H phase on a sub-micrometer scale. In addition, good quality Raman spectra of non-synthetic C-S-H, containing rarely reported lattice vibrations at ~130 cm⁻¹ and other characteristic Raman bands, are reported over a broad spectral range from around 100 up to 3700 cm⁻¹. Hence, this study introduces CRM as a promising novel technique for microstructural characterization of hydrating cementitious pastes.

Cement chemistry notation: C: CaO, S: SiO₂, H: H₂O

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1. Introduction

Cement hydration is a complex process involving several interdependent reactions. C₃S is the principal component of ordinary Portland cement (OPC) and its main hydration product, C-S-H, is chiefly responsible for cement hardening. C₃S exists in three modifications (triclinic, monoclinic and rhombohedral), from which the monoclinic C₃S (m-C₃S or alite) is the dominant modification found in technical clinker. The reaction of m-C₃S with water leads to two main hydration products, the already mentioned C-S-H and CH. C-S-H can vary in composition, which is the reason for typically using hyphens between C, S and H. Yet, a general reaction of m-C₃S with water can be written as follows [1]:



Nonetheless, the overall reaction involves several important interdependent sub-reactions with different kinetics and the reaction rarely goes to completion. Based on isothermal calorimetry heat flow measurements five main hydration periods have been defined [2]; the initial wetting/dissolution (I), induction (II), acceleration (III), deceleration (IV) and continuous (V) period, where the last two periods are

sometimes combined into one. In addition, several supplementary methods including in situ quantitative X-ray diffraction (XRD) [3–7], nuclear magnetic resonance spectroscopy (NMR) [8–15], quasi-elastic neutron scattering (QENS) [16–20] as well as small angle neutron and X-ray scattering (SANS/SAXS) [21–28] or alternative methods [29] have been used to describe hydration kinetics and have consequently shed light on fundamental chemical, induction or diffusion-controlled reactions. The chemical reactions occurring during these periods are still under some debate and the current state-of-the-art is discussed in depth in a recent review by Bullard et al. [30]. The absolute extensions in time of these partly overlapping periods depend on several parameters like clinker composition and thermal history, particle fineness, temperature, water content and the presence of accelerator/retarder additives, but for m-C₃S with a typical w/c-ratio of 0.5 (the system studied here), the continuous period is typically reached at the latest 1 d after hydration.

Mathematical modeling of clinker hydration has also gained a lot of attraction during the last decades and the complexity has increased with increasing computational power. Fig. 1 illustrates an intentionally simple impression of a hydration simulation for C₃S hydration, inspired by recent hydration simulation [31–33] and electron microscopy studies [34–37]. For simplicity, the C₃S particles are illustrated as spherical, which is also a basic assumption in most if not all simulation approaches. Of main importance for the current study is the distribution of C-S-H and CH with respect to partly converted C₃S particles. While

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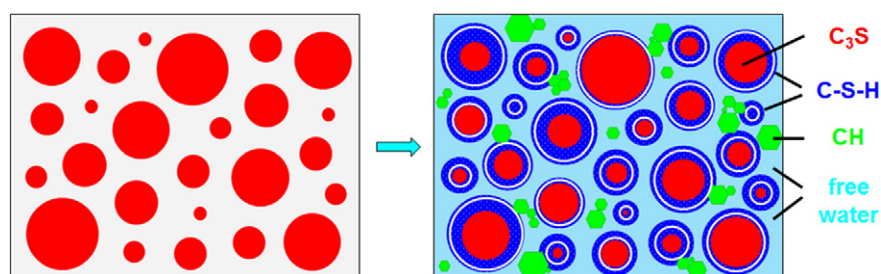


Fig. 1. Schematic image of C_3S hydration: before (left) and after hydration (right). Original grain boundaries are displayed in white.

C-S-H is surrounding partly hydrated C_3S particles, the CH is rather randomly distributed in the pore space between the particles or adjacent to particle surfaces. The hydration layer thickness is not constant, but varies between the particles and does not depend on particle size [37]. Furthermore, hydration can take place both outside and inside of the original grain boundaries, resulting in the formation of C-S-H (inner product) and C-S-H (outer product) [35].

Despite being in relatively good agreement with what has been observed experimentally, no mathematical simulation approach presented to date captures all features observed experimentally even when applied to bulk data, which was typically obtained by isothermal calorimetry. This is due to the fact that the system under study is heterogeneous both in terms of physical or chemical properties and the values of important reaction constants are often not known. In addition, microstructural investigations based on electron microscopy analyses require extensive and destructive sample preparation steps and the experiments are normally performed under vacuum, both of which can lead to artefacts. Here, we present data obtained by means of confocal Raman microscopy (CRM) on a 7 d hydrated m- C_3S paste, i.e. on a sample that has reached the continuous period. No polishing or other sample preparation was performed. The results confirm some of the already proposed microstructural characteristics of hydrated C_3S pastes, but also reveal new aspects that will contribute to a better understanding of the microstructure of hydrating cements, thus introducing CRM as a promising experimental technique for such analyses.

2. Background: Raman spectroscopy and imaging of cementitious materials

The use of conventional Raman spectroscopy for studying less crystalline cementitious materials was established by Bensted in the 70s [38]. Yet, spectral quality was limited due to scattering effects and especially due to fluorescence of some components in the cement, which put a limit to the applicability of this technique. However, detailed Raman spectroscopic studies using novel laser systems, spectrometers with faster acquisition times and higher detector efficiencies allowing the use lower laser power have led to a resurgence of Raman spectroscopic investigations of cementitious materials, as summarized in a highly informative treatise by Black from 2009 [39]. Many of these studies focused on anhydrous constituents of OPC and their hydration and degradation products. Nevertheless, it was the inability to obtain good quality Raman spectra from OPC and other contemporary cement blends, which hindered the widespread application of Raman spectroscopy in this field.

The strongly overlapping Raman bands in real cementitious systems, scattering effects, fluorescence and the lack of relevant reference spectra naturally limits the extension of Raman spectroscopy on bulk systems to spatially resolved Raman spectroscopy, i.e. Raman imaging. However, recent technical developments allow spectroscopic data of high quality to be obtained at low laser intensities and at the optical resolution limit. In a confocal set-up the excitation and the detection focus lie on top of each other, allowing the detection of Raman scattered light only from the focused layer, which makes a confocal microscope an ideal

instrument for heterogeneous materials that show local fluorescence. Furthermore, a small pixel size reduces the influence of inter-particle scattering, which also minimizes the need for sample preparation. The importance of measuring with high confocality is demonstrated in the supporting information, where Raman spectra of a hydrated m- C_3S paste have been measured with less and more confocality, respectively, using two different objectives (see supporting information, Fig. S1). The merits and limitations of CRM as a combination of conventional Raman spectroscopy and confocal microscopy have been thoroughly discussed by Dieing et al. [40]. Among the merits of CRM with respect to cement research is the non-destructive nature of the method, it can easily be applied to aqueous systems and both amorphous as well as crystalline components can be studied.

The first Raman spectrum on hydrating triclinic C_3S pastes was published by Tarrida et al. as late as 1995 [41]. While CH could be clearly identified, C-S-H could not. Besides, Deng et al., Martinez-Ramirez et al. and Ibanez et al. tried to document the characteristic features attributed to C-S-H [42–44]. Unfortunately, the obtained spectral quality did not allow for an unequivocal assignment of Raman signals characteristic for C-S-H. Finally, Black and Garbev et al. could obtain good quality Raman spectra from synthetic, crystalline C-S-H standards lacking the clinker phases present in cementitious materials [45,46]. These results obtained for synthetic C-S-H were in agreement with Richardson's conclusion based on NMR measurements performed on fresh pastes that C-S-H formed in hydrated C_3S pastes has most likely a tobermorite-like structure [47]. However, good quality Raman spectroscopic data with complete structural information over a broad spectral range is yet to be demonstrated for real hydrating multi-phase systems due to the above discussed reasons.

The first successful and to date only Raman imaging study on cementitious materials was very recently published by Schmid et al. in 2013 [48]. Here, polished cross sections were used with the aim of identifying binder remnants and aggregates in historic cement stone. This study revealed the chemical heterogeneity of distinct clinker remnants, consisting of various crystalline, polymorphic and amorphous phases and visualized different crystal orientations. Hydration products like CH or C-S-H have not been described and Raman spectra were recorded in the range from 200 cm^{-1} up to 1100 cm^{-1} . However, for C-S-H, it would be beneficial to study relevant lattice vibrations (LV) at lower wavenumbers in parallel with vibrations corresponding to bound water or OH, appearing at higher wavenumbers. Hence, there is still no Raman imaging study reported on fresh hydrating cementitious pastes. The current investigation is aimed at filling this gap.

3. Materials and methods

3.1. Synthesis of m- C_3S

The monoclinic (M3) modification of C_3S was synthesized from the raw materials CaCO_3 (Merck), SiO_2 (Alfa Aesar), Al_2O_3 (Alfa Aesar) and MgO (Merck) to achieve a composition of CaO (71.7 wt.%), SiO_2 (25.9 wt.%), Al_2O_3 (0.6 wt.%) and MgO (1.8 wt.%) [7]. Al_2O_3 and MgO were added to stabilize the monoclinic modification of C_3S . All

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