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Tracing the status of silica fume in cementitious materials with Raman microscope

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HIGHLIGHTS

- Raman microscope can trace the status of silica fume (SF) in cementitious materials.
- The agglomerates exist both in the raw SF slurry and the hydrated SF-PC pastes.

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ABSTRACT

Silica fume (SF) is an essential material for formulating high performance concrete (HPC). However, its small particle size could cause safety-hazards. Although replacing SF powder with slurry can somehow avoid the potential bio-toxicity, its long-term stability within cementitious materials is unknown. In this study, Raman microscope which combines Raman spectroscopy with light-optical microscope was successfully applied to characterise the composition and morphology of SF in original slurry and hydrated SF-Portland cement (PC) pastes. The unhydrated SF-agglomerates were clearly detected in the original SF slurry and the 22-hour and 6-month hydrated SF-PC pastes.

1. Introduction

Silica fume (SF) is a super-fine material consisting mainly of amorphous silica spheres (85%–95%) with an average particle diameter of 150 nm [1,2]. It is a supplementary cementitious material (SCM) widely used in construction industry for manufacturing high performance concrete (HPC) with promising properties such as supreme long-term durability and high strength [2–4]. These positive actions of SF can be mainly attributed to the following two mechanisms: (i) *excellent pozzolanic reactivity*. As SF mainly consists of highly reactive amorphous silica, it can react with calcium hydroxide (CH) (usually arising from the hydration of Portland cement) to form calcium silicate hydrate (CSH) – the most important binding and strength giving hydration product in cementitious materials; (ii) *physical filling effect*. Because of its very small particle size, SF can fill in the various pores in the hardened cement matrix and hence enhance the density and the strength of the hardened paste [5,6]. Both mechanisms can lead to improved durability and strength. However, whilst SF has numerous advantages, it also has the common failing of nano-scale materials, i.e. potential safety hazards to living systems [7]. This is induced by the ultrafine particles of SF and thus could be easily absorbed through the skin, lungs or digestive tract, causing health risks to the living systems [8,9]. Therefore, nowadays it is preferred to use SF slurry (i.e. SF in aqueous dispersions) with a typical solid content of 50 wt% in practical operations. Although this can somehow avoid the safety hazards incurred to the operators to a certain extent and decrease the difficulty encountered from handling dry bulk powders, the potential safety hazards of the SF used in the slurry form still exist as the long-term stability and activity of unhydrated/hydrated SF in concretes is largely unknown.

In more detail, the following two aspects need to be clearly understood before SF slurry can be confidently used in civil engineering applications:

(i) *The status of SF particles in original SF slurry*. It is now well established that dry densified SF exists almost in the form of SF agglomerates, i.e. nano-spheres linked together into

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chains or clusters, rather than isolated spheres [10–12]. However, there is rare knowledge about the status of SF particles in the slurried SF and, if there are any SF agglomerates in the SF slurry, their status is also largely unknown. Hence, it is of great importance to identify the status of the SF particles in the SF slurry. Furthermore, as the breakdown of the agglomerates during mixing processes is highly relevant to the effectiveness of the crushing and shearing actions applied by the mixer, the information obtained could also be invaluable for guiding the *on-site* mixing operations.

(ii) *The status of SF within cementitious materials over different hydration time.* Theoretically speaking, the amorphous silica in the SF is considered to react with calcium hydroxide (CH) and thus transform into calcium silicate hydrate (CSH), making contribution to the strength improvement of the cement materials. However, unhydrated SF agglomerates were observed in the long-term hydrated cementitious materials fabricated by the dry densified SF, which could be attributed to the fact that the SF agglomerates may break down only partially in normal concrete mixing processes [10,11]. The status and the stability of these unreacted agglomerates would cause another potential concern to the safety of the living systems exposed directly or indirectly to the concrete structures.

Currently, many techniques are employed to identify the morphology and the composition of SF and SF-containing cement products, such as Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDX) [10,11]. SEM can provide clear figures of the morphology of SF agglomerates in the original dry densified powder and also the SF-containing hydrated cement pastes. However, it cannot illustrate the chemical composition of the SF and hence another quantitatively analysis facility needs to be applied simultaneously. At the same time, liquid sample cannot be analysed with high precision under the SEM. Whilst EDX could indicate the composition of SF, it can only give information on the elemental composition of SF such as Si and O, but not the chemical composition with intrinsic atomic-ratio (i.e. SiO_2). Raman spectroscopy, a vibrational spectroscopy, can provide 'fingerprint' information of molecular structures for solids, liquids and gases. It works on inelastic scattering that the Raman scattered light occurs at wavelength (frequency) being shifted up or down from the incident laser light. As this wavelength shift is specific to the chemical bonds and the symmetry of molecules, Raman scattered signal can thus be used to identify substances [13,14]. Over routine characterisation tools, Raman spectroscopy showcases unique advantages in characterising chemical composition not only for crystalline but also amorphous phases – which explores a much wide analysing area in cement and concrete such as the identification of amorphous silica (SiO_2) in SF. Furthermore, the application of Raman microscope which combines Raman spectroscopy with light-optical microscopy offers a promising analysis tool for identifying both the chemical composition and physical morphology of the SF-containing cementitious materials.

In the current study, attempts were made to establish a protocol of using Raman spectroscopy to firstly identify the status of SF in the original SF slurry and then to trace the status of SF within cementitious materials at the nano-scale over different time scales, namely early (about 22 h) and long-term (six months) hydration periods. Light-optical microscope was simultaneously used to characterise the morphology of various samples.

2. Experimental

2.1. SF slurry and diluted SF slurry

The as-received SF slurry, a dark-grey slurry with water content of 50%, was used as the raw material in this study. Its chemical composition is given in Table 1. To characterise the individual SF particles with Raman spectroscopy, diluted SF slurry was also prepared at a slurry-to-water ratio of 1:5 by hand mixing in order to achieve a better dispersion of the SF particles before the Raman characterisation.

2.2. SF blended paste

The Portland cement (PC) used in this study was CEM I (in accordance with BS EN 197-1:2011 [15]) and its chemical composition is also shown in Table 1. The SF-bearing PC paste was pre-

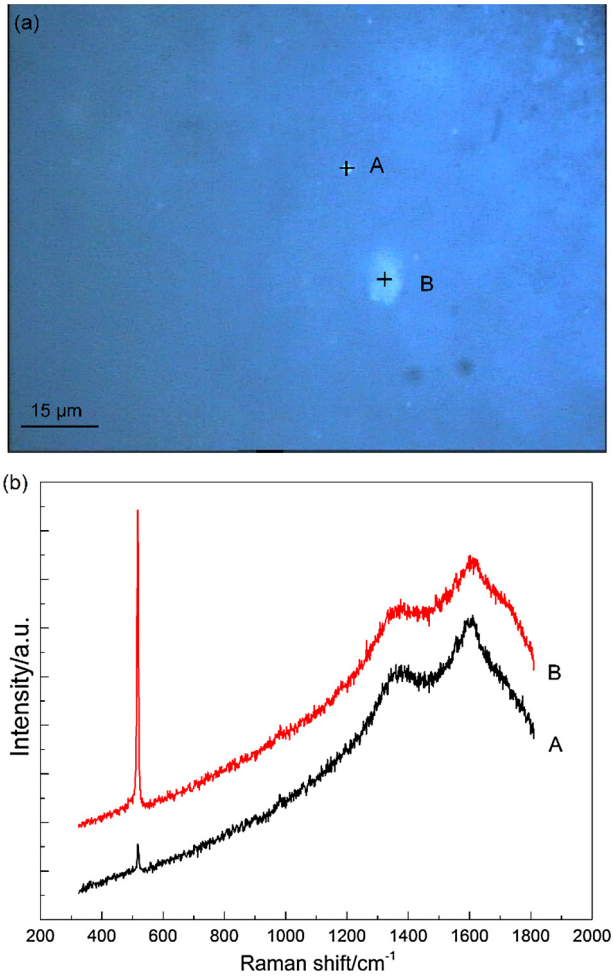

Fig. 1. (a) Light-optical micrograph of original SF slurry (100×). (b) Raman spectra of sampling points A and B as shown in (a).

Table 1
Chemical composition of Portland cement and silica fume.

Oxides/%	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3
SF	93.00	0.70	1.20	0.30	1.20	1.80	1.50	0.30
PC	23.00	6.15	2.95	61.30	1.80	0.68	0.22	2.50