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Rheological characterization of cement pastes with functional filler particles

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ABSTRACT

Cement pastes were studied using conventional rheological methods. The effect of different types of functional fillers on the rheological properties and hydration rate of the pastes was analysed. The fillers were found to have varying chemistry and therefore surface properties. Porous titania particles raised the cohesive energy of the paste significantly already at low additions. Limestone particles raised the cohesive energy somewhat, but clearly less than titania. The zeta potential of the particles was found to somewhat affect the rheology. Reaction rates of the pastes were measured using oscillatory rheological measurement with constant amplitude and frequency. Titania particles were found to accelerate the hydration rate more than limestone particles. Of the limestone particles pure calcite increased the reaction rate more than dolomitic limestone. When the limestone particles were modified to provide C–S–H nucleation sites the cohesive energy was raised and the reaction rate was further increased.

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1. Introduction

Cement hydration is a complex set of chemical reactions and the complete chain of intermixed chemical events is not yet fully understood [1,2]. According to contemporary knowledge cement hydration consists of a pre-induction phase, a dormant phase, an acceleration phase and a deceleration phase [1–4]. Because of the complex nature of the system and the chemical reactions involved the exact mechanisms and reasons for the structuring of the different phases remain partly unknown [2]. The properties of cement in the pre-induction phase are critical for achieving the desired properties of the final, solid concrete. If e.g. particle or aggregate segregation takes place in the initial stages the results can be detrimental and the concrete structure may fail [1]. It is therefore important to be able to measure changes in the properties of cement as a function of time, not only from a technological but also from a scientific point of view [5,6]. New understanding of the processes involving cement setting can thereby be gained which enables improvements to the performance of cement during processing.

It is well established that concrete properties can be modified by adding different types of filler particles to the system [7]. Important factors when selecting filler materials are cost and any effects they may have on cement hydration and concrete properties. Limestone is used as an additive because it is relatively cheap and due to its effects on the rate of cement hydration and hydration products [1,8,7,9–11]. Furthermore some environmental benefits can be gained by lowering the cement content in the concrete [8]. According to contemporary theories limestone favours the formation of monocarbonate over monosulfate, resulting in a higher content of ettringite [12]. The source of limestone is an important issue, since limestone can contain both calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$), where some of the calcium ions have been replaced with magnesium ions. Dolomite is known to undergo dedolomitization reactions, which may be problematic in the long run [13–15]. Titanium dioxide is being studied for the possibility of making self-cleaning surfaces using UV light [5,16]. Titania particles have been found to raise the viscosity of cement and to accelerate the hydration [17–19]. Agents accelerating cement hydration have also been studied, of which synthetic C–S–H particles in solution have shown promise. These particles enhance the formation of C–S–H in concrete, and some commercial products are available [20,21]. A more recent application is to coat the particles with C–S–H [22]. The chemical properties of filler particles are known to affect the flow properties of concrete, for example Plank et al. stated that the zeta potential of filler particles affected the adsorption of superplasticisers [23]. Certain compounds and elements are known to be problematic in concrete manufacture, for example magnesium, sugar and sulfate. Sugar retards hydration, while sulfate can lead to secondary ettringite formation. Magnesium can lead to the formation of brucite phases. Both brucite and secondary ettringite are expansive phases and are detrimental to long term concrete strength [13,24–27].

Rheological methods can be seen as powerful tools for characterising flow properties of liquid matter such as suspensions [28,29]. Reactive

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systems can also be analysed in order to understand the colloidal interfacial interactions, which have an important role during the restructuring chemistry during sol and initial gel transformation stages [6,30,31]. Rheological tools provide flow characteristics as related to particle structural, dimensional and interactive properties as well as quantitative information on specific particle–particle and particle–medium interactions [32]. The liquid cement paste state is traditionally characterised by its workability properties and the hydration phases by their kinetics, as evaluated by e.g. calorimetric, gravimetric or rheological means [33–36]. The properties of interest are particle interactions, packing, arrangement and agglomeration tendency which will govern the behaviour of cement paste, and thus influence the properties of concrete made with it. It has been proposed that the property governing the rheology of fresh cement paste and concrete is reversible flocculation of the components, which are governed by the surface properties of the particles [30]. The rheological method developed by Ramsay et al. [37] and Tadros [38] was applied here to calculate the internal cohesive energy U_c [Pa] of the wet cement paste according to:

$$U_c = \int_0^{\hat{\gamma}_c} \sigma d\gamma = \int_0^{\hat{\gamma}_c} \gamma_0 G' d\gamma = \frac{1}{2}\hat{\gamma}_c^2 G' \tag{1}$$

where G' is the elastic modulus, $\hat{\gamma}_c$ is the critical amplitude where the linear viscoelastic region (LRV) measured using an amplitude sweep ends, and σ is the measured shear stress of the sample. This method allows for quantification of the flocculating particles in a suspension. A benefit of this model is that it takes into account both the elastic modulus and the critical amplitude where flow commences. A drawback with this method is the low amplitude used in the shear, which means that only the static state of the cement paste is analysed, thereby providing only limited information on the paste flow properties. However, the applied dynamic oscillation amplitude sweep method allows for a clear identification and validation of the shear region where the strength of the structures (attractions between particles leading to particle networks and flocs) within the sample is overcome by the applied shear forces. The method is well-recognised and commonly applied within dispersion research for detecting the linear region of viscoelasticity [28,37,38].

2. Experimental

The investigated materials consisted of Aalborg white cement (OPC) because of its low alumina and limestone content. The chemical composition of this cement, as seen in Table 1, is known to be very constant. The particles consisted of two different ground limestone powders (FC 2.5 and Sipi 10, occasionally abbreviated S10, both received from Nordkalk OY, Finland) and an anatase titanium dioxide powder (Hombikat N100, received from Sachtleben). The manufacturer of N100 has reported a mean particle size of 2 μm (by laser diffraction), a mean crystal size of 20 nm (TEM) and a surface area of 100 m^2/g (BET, ISO 4562). A sample of Sipi 10 was also modified with synthetic C–S–H (calcium silicate hydrate) to provide nucleation sites for C–S–H. The modified Sipi 10 sample was received as a 38 wt.% slurry. The aim of this was to achieve C–S–H nucleation and growth on the particle surfaces and a better incorporation into the cement matrix. The modification process was performed by Vehmas et al. and SEM pictures confirmed the presence of a C–S–H coating [22].

Gas adsorption was measured using an ASAP 2010 nitrogen sorptometer (Micromeritics, Norcross, GA, USA) and a Hydrosorb 1000 water vapour sorptometer (Quantachrome, FL, USA). Water vapour sorption gives some idea about the interaction with a polar substance, while nitrogen sorption is the standard method for surface area measurement. Sedimentation measurements were performed with a Microscan X-ray sedimentator (Quantachrome, FL, USA) with custom software using Stokes law to calculate the particle size. A polycarboxylate ether dispersant (superplasticiser) was used during the sedimentation measurements to prevent the particles from flocculating.

Zeta potential and particle size measurements with ESA (electrokinetic sonic amplitude) were performed using an Acoustosizer 2 (Colloidal Dynamics, FL, USA, software v3.27) using 1 M NaOH and 1 M HCl to perform titrations. We used the Smoluchowski value calculated by the software.

X-ray diffraction (XRD) was performed with a Bruker D8 Discovery (Bruker-AXS, Karlsruhe, Germany) using CuKα radiation (λ = 1.54184 nm), a 0.5-mm collimator, a Göbel mirror and a 2D HI-STAR© detector. The samples were attached onto a single-crystal SiO_2 sample holder. The XRD spectra were collected in the 2θ range of 5.7°–100.1° using a 2D Hi-Star detector measuring three frames using 300 s/frame, with each frame covering approximately 30° 2θ. The X-ray tube was operated at 40 kV and 40 mA. For phase identification a PDF-2 database (2010) was used. The size of the crystals was calculated with the Topas 4.2 software (Bruker-AXS).

XPS measurements were performed at Top Analytica (Turku, Finland) using a Physical Electronics Quantum 2000 scanning spectrometer with a monochromatic Al Kα X-ray source (1486.6 eV) (Physical electronics, Chanhassen, USA).

Rheological experiments were performed using a Bohlin VOR rheometer (Malvern Instruments, Malvern, UK) using 20 mm serrated plate–plate geometry to minimise wall slip. The OPC was mixed with the filler in dry powder form when possible. For the amplitude sweeps deionised water was added to the paste in a 0.6 water/powder ratio by volume and was mixed manually in an ultrasonic bath (Finnsonic Oy, Lahti, Finland) for 2 min at ambient temperature. This method of mixing was energetic, and was therefore not necessarily comparable to traditional ways of mechanical mixing. However, since our experimental aim was to study chemistry this was deemed appropriate. A sample of the wet cement paste was placed in the measuring system and the rheological measurement was started exactly 6 min after water addition. Amplitude sweeps were performed at 1 Hz oscillation from 0.01 to 20 mrad on the 40 vol.% OPC sample. When used, the filler particles replaced the OPC by volume. Since one of the aims with the C–S–H coating was to replace cement we used significantly higher quantities than recommended in earlier experiments [8]. The pore volume of N100 from the water vapour sorption measurement was considered when calculating the water addition. Since we measured 7 different added fractions of filler particles we considered the measurements close to parallel, and chose not to repeat the measurements.

Kinetic experiments were performed as a time sweep at 1 Hz and 0.2 mrad at 0.6 Water/OPC ratio by volume. The apparatus had an

Table 1
Chemical composition of Aalborg white cement.

Component	Amount (%)
CaO	69
SiO_2	24
Al_2O_3	2.1
Fe_2O_3	0.3
MgO	0.7
C_3A	<5

Table 2
Characterizations and measurements performed on the raw materials, x denotes a performed measurement and numbers denote the fraction of particles used in the measurement.

	Strain sweep	Time sweep	Adsorption	XPS	XRD	Zeta potential
Sipi 10	5–50%	15%	N_2/H_2O	x	x	x
MSipi 10	5–40%	15%	N_2/H_2O	x	x	x
FC 2.5	5–50%	15%	N_2/H_2O		x	x
N100	5–10%	15%	N_2/H_2O		x	x
OPC	x	x	N_2		x	

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