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# Rheology of hydrating cement paste: Crossover between two aging processes



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## ABSTRACT

The roles of applied strain and temperature on the hydration dynamics of cement paste are uncovered in the present study. We find that the system hardens over time through two different aging processes. The first process dominates the initial period of hydration and is characterized by the shear stress  $\sigma$  varying sub-linearly with the strain-rate  $\dot{\gamma}$ ; during this process the system is in a relatively low-density state and the inter-particle interactions are dominated by hydrodynamic lubrication. At a later stage of hydration the system evolves to a high-density state where the interactions become frictional, and  $\sigma$  varies super-linearly with  $\dot{\gamma}$ ; this is identified as the second process. An instability, indicated by a drop in  $\sigma$ , that is non-monotonic with  $\dot{\gamma}$  and can be tuned by temperature, separates the two processes. Both from rheology and microscopy studies we establish that the observed instability is related to fracture mechanics of space-filling structure.

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## 1. Introduction

Hardening process of cement in the presence of water has been a subject of research besides its industrial importance [1]. Cement paste, usually a dense suspension of non-Brownian particles, exhibits complex rheological properties that depend on several factors including particles' shape and size, cement composition, cement/water ratio, measurement methods etc.[2–4]. In the presence of water, ordinary portland cement (OPC) – a commonly used binding agent – forms gel-like structure that arises predominantly from the chemical reactions producing calcium-silicate-hydrates (C-S-H) [5–7]. Besides C-S-H, aluminates – a fast reacting phase present in OPC – form space filling needle-like structures called Ettringites. This is accompanied with the growth of a cohesive system-spanning network of C-S-H which bridges the hydrating cement grains. As a result stress-bearing submicron structures form in the system which offer resistance in response to applied shear. The Ettringites, however, contribute to the solidification of cement only during its initial stage of hydration [1].

As the hydration reaction proceeds over time, the morphology of the C-S-H network grows in a manner that gives rise to an overall decrease of pore density and relatively a compact structure evolves [4,8]. With the availability of water running out the inter-particle interactions in this stage of hydration are mainly frictional in nature [5,9]. Hardening of the system at long times is analogous to the ubiquitous phenomena of aging observed in frictional systems [10]. It relates to the reconstruction of the interfacial contact zones [10,11] and flow induced reconfigurations of its constituents, such that, a low density cluster of particles which has fewer contacts with its neighbors evolves into a denser structure that shares more contacts with its neighbors [12–14].

Aggregation and network formation are out-of-equilibrium phenomena that are commonly influenced by mechanical perturbations, e.g., shear flow [3,15,16]. Such perturbations would lead to mechanical failure [17] at multiple length scales., e.g., at the scale of the contact region between the particles it is related predominantly to the breaking of the calcium-silicate-hydrate bonds while at larger scale it relates to the shear-induced transformation of particle configurations [15]. However, most studies that address the issues related to the emergence of mechanical strength in cement paste have been performed in the presence of small external stresses that perturb the system about a local minima of its potential energy landscape [1,16,18,19].

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Temperature plays multiple roles; it enhances the rate of hydration [9], determines the filling of the interstitial space between the grains and allows thermally activated processes to release the internal stresses via creep [20,21]. Arguments in similar lines are usually proposed to understand the variation of the mechanical properties of cement on its curing temperature [20,22]. Cement cured at low temperatures develops a more compact structure with improved mechanical stability through a slow and controlled process of filling up the interstitial space between the cement grains. In contrast, curing at high temperature produces non-uniform structure with low compressive strengths [22,23].

In this paper we study the hardening process of cement paste as a function of temperature and in the presence of large-scale mechanical perturbations (large oscillatory shear) where the imposed shear disrupts the energy landscape by constantly restructuring the interwoven matrix of hydrate needles. We observe that the cement paste gains shear rigidity via two distinct aging processes; the first aging process is associated with the *setting* process that generates space-filling structures (e.g., Ettringite needles) and provides the system its initial rigidity. This system has flow curves that show shear-thinning behavior. In contrast, the second process is associated with the *hardening* phenomena that arises from the formation of C-S-H networks and the material manifests shear-thickening behavior. In addition, the crossover from the first to the second aging process occurs through a global weakening in the system, indicated by a drop in the measured shear stress. We also show that with lowering temperature the drop occurs later in time and its magnitude decreases. Both these phenomena are related to the reaction kinetics of the hydrates formation. Finally, we establish that the weakening is related to the fracture mechanics of the space-filling structure formed during the initial phase of cement hydration.

## 2. Experiment

In experiments, we use a cement paste prepared by mixing OPC (c) with deionized water (w) in a ratio  $w/c = 0.5$  for about a minute and then immediately transferred to the rheometer for measurements [24]. This water to OPC ratio allows us to access the hydrodynamic lubrication regime between the cement grains during its initial phase of hydration. We also perform the rheological measurements on Alite paste, prepared in the same water to cement ratio, and

compare the data with that of OPC. Alite ( $C_3S$ ; tricalcium silicate) - a major phase present in the cement - is believed to contribute primarily to the mechanical strength of hydrating cement paste through formation of C-S-H; it does not produce Ettringites [7,25,26].

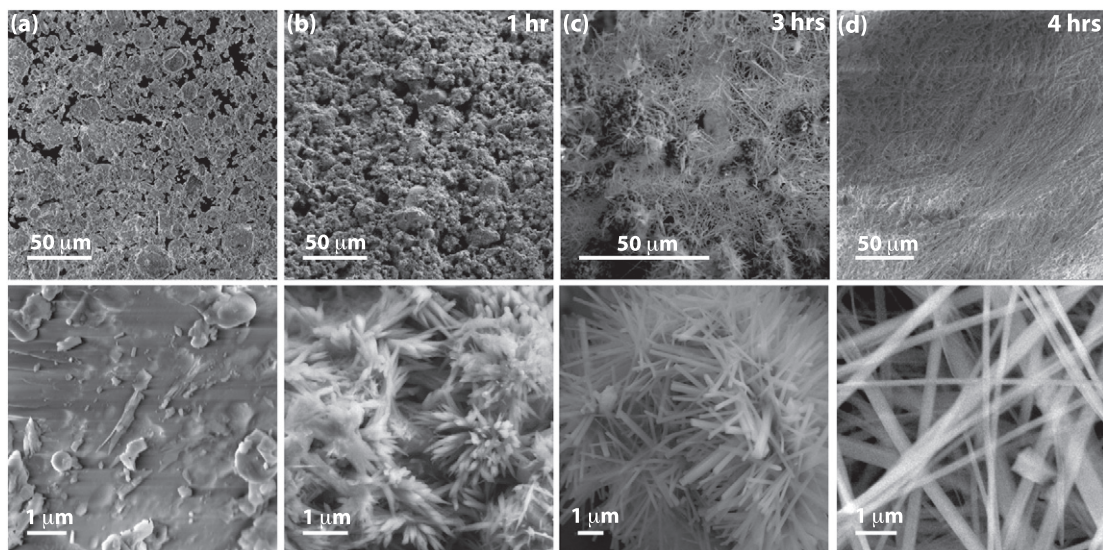
### 2.1. Microscopy

The scanning electron micrographs in Fig. 1 capture the evolution in the morphology of the cement particles during the process of hydration at temperature  $T = 30^\circ\text{C}$ . In the early stage of hydration, Ettringite (calcium sulfoaluminate hydrate) forms, which is a faster growing compound and can be seen as needle-shaped structures in Fig. 1 (b–d), and primarily occupies more volume in the system.

### 2.2. Oscillatory rheology

A conventional strain-controlled rheometer (MCR301; Anton Paar) is used to perform oscillatory rheological measurements of the cement paste as a function of time  $t$  and at various temperatures  $T$ . The cement paste is subjected to a sinusoidal shear strain of amplitude  $\gamma$  at a fixed oscillation frequency  $\omega$  and correspondingly waveform of torque is being recorded by the rheometer. Typically the time varying angular displacement of the measuring device and the measured torque are converted to strain and shear stress, respectively by multiplying them with suitable 'form factors' which are specific to a given measuring system. However, the conversion from angular displacement to strain is obtained by assuming a linear velocity profile in the measurement gap region and no-slip conditions at the walls. For some applications this assumption may not strictly hold, e.g., avalanche motion in sand piles is a surface phenomenon where the particulate matter screens the stress such that only a shallow region close to the moving surface is sheared [27]. For these systems both shear stress and strain are underestimated by the rheometer [28].

The measurements are done in two methods: (1) a parallel-plate geometry is used (see schematic in Fig. 2 (a)) and oscillatory strain of amplitude  $\gamma = 1\%$  at  $\omega = 6.28$  rad/s is applied to the cement paste. The process of hardening of the cement paste is monitored by measuring the amplitude  $\sigma$  of the waveform associated to the shear stress as a function of hydration time ( $t$ ). The measurement is repeated on fresh cement paste for different gap height  $h$  between



**Fig. 1.** (a) Scanning electron micrographs of dry cement powder grains. (b–d) Low (top panel) and high (bottom panel) magnification micrographs of hydrated cement at  $30^\circ\text{C}$  with  $t = 1$  h, 3 h and 4 h, respectively. The interweaved needle structure and its growth with time are evident in the high magnification images.

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