Effect of surfactants on the yield stress of cement paste

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Blandine Feneuil, Olivier Pitois, Nicolas Roussel[*]

Laboratoire Navier, UMR 8205, École des Ponts ParisTech, IFSTTAR, CNRS, UPE, Champs-sur-Marne, France

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ABSTRACT

Although many surfactant molecules are available to produce stable aqueous foams, these molecules can strongly interact with cement grains. We focus therefore here on the interactions between various surfactants and cement grains in order to identify some selection criteria for surfactants dedicated to foam cement production. First, we check the surfactant ability to produce aqueous foam in synthetic cement pore solution. Then, we observe that most surfactants do adsorb on cement grains, inducing concentration-dependent effects on the yield stress of cement paste. Our results suggest that, for some of these surfactants, the yield stress increases significantly as inter-particle hydrophobic attractive forces develop at the surface of the grains. However, above a concentration threshold, those attractive forces sharply drop because of the formation of surface micelles acting as steric barriers between particles, which results in a strong decrease in yield stress

1. Introduction

Cement foams are promising materials. Indeed, addition of air into cement paste may offer, besides substantial material savings, improved thermal properties. This is why, since several years, the study of aerated cementitious materials has become an active field of research. In order to control cement foam morphology, the destabilization mechanisms of fresh cement foams, until cement hardening, must be stopped or slowed. Stabilization can be achieved by monitoring rheological properties of the fresh cement paste, especially its yield stress [1–3].

Most formulations of cement foams include chemicals known as surfactants. Surfactants can either enhance air entrainment into cement paste (air entraining agents) during fast stirring of the cement slurry, or they can be used to create a pre-formed aqueous foam which is later incorporated into the cement slurry. In both processes, surfactants remain in the cement paste and may thus affect the rheological and early age properties of the cement matrix.

Besides cement foams, surfactants can be used as air entraining agents in frost-resistant concrete and as shrinkage reducing admixtures [4].

In this study, we consider the interaction of surfactants with a cement paste. We first investigate the effect of a synthetic pore solution on the foaming ability of these surfactants. Then, we measure the effect of surfactant addition on the yield stress of the cement paste. Our results show the major role played by the amounts of surfactant adsorbed at the surface of the cement grains both on fresh cement paste yield stress and on the hydrophobization of the cement grains.

2. Background

2.1. Surfactant molecules in cement paste

Surfactant molecules are composed of a hydrophilic head and a hydrophobic hydrocarbon tail. In aqueous solution, some surfactant molecules adsorb at the air-water interface, with their hydrophobic tails towards air, which reduces the liquid-air surface tension γ [5,6]. Above the Critical Micelle Concentration (CMC), the air-water interface becomes saturated with surfactant molecules while residual surfactant molecules in bulk solution gather into elements called micelles. As a consequence, above CMC, liquid-air surface tension does not decrease any more with increasing surfactant concentration as shown in Fig. 1.

The hydrophilic head can either be charged (ionic surfactants) or polar (non-ionic surfactants). Ionic surfactants are said cationic if their charge is positive, anionic if their charge is negative and amphoteric when their head include both types of charge [5,6]. Surfactants enhance foam creation and foam stability through several mechanisms. First, lowering surface tension means that less energy is needed to create air-water interface. Then, layers of surfactant on both sides of the water film separating two bubbles repel each other due to some steric interactions and, in the case of ionic surfactants, some electrostatic interaction. In addition, it was shown that micelles or other structures inside the film may contribute to its stabilization [5]. It is worth noting that dynamics of surfactant adsorption at air-water interface is also an important aspect for foam generation and stability: to stabilize newly formed interfaces, surfactant adsorption must indeed be faster than

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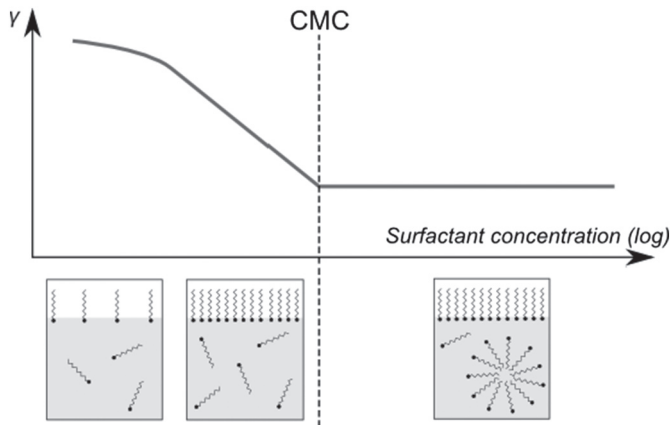
Fig. 1. Surfactant distribution and surface tension.

Fig. 2. Destabilization mechanisms in a foam.

surface formation [5]. Length of stretched hydrocarbon chain in nm is related to the number of carbon atoms n_C by [7]

$$l = 0.1275(n_c - 1) + 0.19 + 0.23 \tag{1}$$

Stretched length of a 10 carbon chain is therefore 1.57 nm, which gives an idea of the size of these molecules compared to other organic compounds used as additives in the cement and concrete industry, namely around 5 nm for water reducing agents such as PCE comb copolymer coils [8–10] and around 50 nm for the coiled macromolecules used as viscosity agents [11].

Most organic additives for cement adsorb on the cement grain surfaces [12,13]. In the case of large molecules, such as poly-carboxylic ethers, adsorption of polymer coils leads to steric repulsion between grains and to a decrease in the yield stress of the suspension [14,15].

Adsorption of surfactant molecules on cement grains has been reported by [16,17,6]. Due to their specific molecular structure, surfactant molecules may adsorb in various configurations. Indeed, single molecules adsorption is reported to find its origin in either the hydrophilic head or the hydrophobic tail depending on the surface properties [12,13]. While in 1992, Uchikawa et al. [16] made the hypothesis that hydrophilic heads were oriented towards the bulk solution, the hypothesis of electrostatic adsorption of the head was latter most common for ionic surfactants [17,6,13]. Zhang et al. [17] measured adsorption on cement of three surfactants - cationic, anionic and non-ionic - and compared adsorption isotherms with contact angle on compacted cement powder pastilles (see details of a similar protocol in Section 3.2.5). They observed no adsorption with the non-ionic surfactant, whereas partial adsorption of both tested ionic surfactants was measured no matter their initial concentrations. For ionic surfactants, adsorption of ionic heads on the cement particle surface is reported to lead to an hydrophobization of the grain surface and thus to an increase of the contact angle of water on the resulting hardened material, up to a maximum value reached when the grain surface is saturated. At higher concentrations, hydrophobicity of the cement grains surface was noted to decrease in the case of anionic surfactant. This effect was explained by the formation of surfactant agglomerates at the surface of the grains. Recently, Petit et al. [18] also measured the above hydrophobicity maximum at intermediate concentrations for one anionic surfactant. The experimental procedure was the imbibition of cement powder by the surfactant solution. They observed no effect of cationic surfactant on cement surface properties.

2.2. Foam stability

Before cement setting and hardening, the initial pores structure obtained after mixing can get destabilized through three distinct mechanisms (Fig. 2): (1) the gravity driven flow of the paste through the rising bu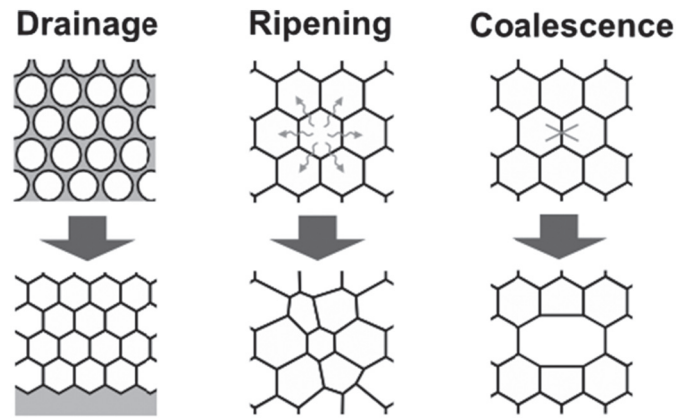bbles leads to an heterogeneous distribution of air within the sample, (2) difference in capillary pressure between bubbles of different sizes leads to gas exchange (ripening); it leads to bubble rearrangements and a global increase of the average bubble size R_b as a function of time, and (3) foam films breakage induces the coarsening of the bubble assembly through coalescence events. It is to note that the magnitude of the two latter mechanisms increases as the gas fraction increases, which is precisely a consequence of gravity drainage.

Bubble coalescence is generally counteracted by a significant disjoining pressure arising in thin liquid films due to the presence of surfactants at concentrations above the CMC. However, in cement pastes and more specifically in the high ionic strength interstitial fluid, the ability of common surfactants to ensure the stability of thin water films is not obvious and deserves specific investigation [6].

A relevant strategy to control the destabilizing mechanisms of a foam is to take advantage of yield stress (τ_y) properties of pastes [1–3]: basically, drainage stops as $\tau_y \sim \rho g r$, where ρ is the density of the paste and r is the typical size of interstices between the bubbles. Moreover, the ripening process is strongly dampened as $\tau_y \sim \gamma/R_b$, where γ is the surface tension of the liquid/air interface. An alternative foam stabilization strategy involves particles adsorption at the bubbles surface thanks to the in-situ hydrophobization of the particles contained in the paste to be foamed [19,18]. No matter the strategy chosen to stabilize the foamed material, adsorption properties of surfactants at the surface of cement grains appear in all literature available as a crucial parameter.

2.3. Yield stress of solid suspensions

Cement paste is a suspension a solid cement grains in aqueous phase. The yield stress τ_y depends on the interaction of each solid particle with its closest neighbors. A relation between macroscopic yield stress and particle interaction has been proposed in the so-called Yodel [20]. In this model, the inter-particle force parameter $G(h)$ is defined as

$$G(h) = \frac{F_{VdW} + F_{ES} + F_{Ster}}{\tilde{a}} \tag{2}$$

where F_{VdW} is Van der Waals attractive force between particles, F_{ES} is the electrostatic interaction, F_{Ster} is the steric interaction and ã refers to the radius of curvature of the particle surface. G depends on the distance h between solid grains. Flatt and Bowen [20] showed that the yield stress of a suspension is proportional to the maximum value of G, obtained at the minimal inter-particle distance.

Hence, to understand the change of yield stress with surfactant addition, analysis of the interactions between cement grains must be carried out. First, attraction due to the Van der Waals force is inversely proportional to the square of the interparticle distance: $F_{V dW} \propto 1/h^2$. Thus, increasing distance between the cement grains reduces the Van der Waals interaction. Secondly, for a charged surface in an electrolyte