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Generation and stability of bubbles in a cement based slurry

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ABSTRACT

In this article, the fabrication of a single stable cement bubble is investigated. To achieve this goal, the stability of model particle covered bubbles is firstly experimentally studied, by bubbling in a pool filled with micrometric silica particles. Bubble stability is shown to be governed mainly by particle covering rate, which is maximized when particle wetting angle prior to liquid approaches π/2. This angle can be adjusted in situ by electrostatic adsorption of cationic surfactant on silica if proper amount of surfactant is added in the silica suspension. The covering rate is also shown to be governed by the time spent by the bubble in the pool, allowing us to define a timescale for particle adsorption at the liquid/gas interface. In the end, this method is shown to be successful with other types of foamed granular materials such as cement, and the fabrication of a stable and fully covered solid cement bubble is for the first time demonstrated.

1. Introduction

Buildings currently account for 40% of the global primary energy consumption, mainly through its daily use during its life time [1], and in particular through thermal regulation. In this context, designing a material with large insulation properties keeping a good mechanical resistance remains a crucial challenge. Solid foams, and particularly foamed concrete, gather these characteristics [2], which explains the renewed interest for this material. These particular foamed materials also possess a light weight with densities between 1600 and 400 kg/m^3 [2] thus reducing primary material consumption and consequently decreasing the greenhouse-gas emissions due to the manufacture of Portland cement, which today represents 5% of all human generated emissions [3].

Solid foams are constituted of air voids captured in a solid matrix, with a gas fraction which can reach up to 97% [4,5]. Foam is a multiscale material, whose macroscopic properties, like mechanical strength [6], are strongly related to the microstructure of the foam. For example, thermal and acoustical insulations are governed by the structure of closed or interconnected bubbles [6,7], an open porosity being in some situation a drawback for a good insulation. Moreover, material durability is strongly affected by this porosity because of fluid and ion transport [8] within the foam matrix. Consequently, to achieve a performant material, foam porosity must be controlled to obtain disconnected air bubbles within the matrix [5,9,10]. Many factors such as drainage, coarsening or rupture affect the interconnection between bubbles, mainly during foam generation and solidification. The first step to achieve such a material is the possibility to create one single, closed and solidified, bubble. Then, a prerequisite is the formation of a longstanding stable concrete bubble that will in a second step solidify via concrete hydration reaction. The conditions required for these two processes to be achieved, the stable bubble formation and its subsequent solidification, are discussed in the following.

Indeed, a bubble, which consists of a thin liquid film separating two gas regions, is intrinsically an out-of-equilibrium system that will eventually collapse. To stabilize a bubble, amphiphile molecules such as surfactants, which adsorb on the interface and allow spontaneous cicatrization of some holes created by external perturbations, are added in the liquid solution. These molecules allow to stabilize foams or bubbles for times ranging from a few minutes to a few hours. Another type of surface active stabilizers are nano or micro particles, which are more protective as they remain attached on the interface. Indeed, the desorption energy of a particle attached to a liquid/gas interface depends on the wetting property of the solid with respect to the liquid and the gas and reads $W = \pi R_p^2 \gamma_{lg} (1 - cos\theta)^2$, with R_p the radius of the particle, γ_{lg} the surface tension of the liquid/gas interface, and $\theta < 90°$ the contact angle [11–13]. This desorption energy is maximal around 90° and of thousands of kT for microparticles. Thus, foam stabilized only by solid particles can last for months as the particle layer at the interface inhibits film collapse and then bubble coalescence and/or coarsening [14]. The main challenge of this method is to adsorb the particles on the interface, which can be achieved by tuning in situ the relative solid/liquid wetting properties. Martinez et al. [14] changed the liquid properties by adding a small amount of volatile ethanol in the initial mixture that will

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eventually evaporate, and then reduce the particle affinity with the liquid. Another common method is to modify the wetting properties of particles by electrostatic adsorption of oppositely-charged short-chain surfactants on the solid surface [15–21]. We investigate in the following the possibility of this processes on particle and cement stabilized bubbles.

The second prerequisite is to keep a stabilized bubble during solidification. Indeed, a solid thin film and then a closed bubble are obtained only if the hydration reaction occurs within the thin film covering the bubble: the film needs to be filled with particles but also requires a sufficient quantity of water for the hydration reaction to occur. Moreover, the reaction adds new destabilization factors to the foam, because of water movement, modification of particle properties, cement reactivity and shrinkage.

To investigate these two steps, we first study the fabrication of stable long standing bubble in a model suspension that is constituted of silica beads whose wettability is changed in situ by surfactant adsorption. The effect of suspension wettability, concentration and bubble rising time are investigated. The methodology employed is then applied to bubbles created in a cement paste where the solidification process is tested. The article is organized as follows: after a first part dedicated to the material and method employed, the fabrication of bubbles fully covered with solid spherical silica beads is considered as a model system. Then, the conditions for obtaining a bubble stabilized with cementitious particles and its subsequent solidification are successfully experimentally investigated.

2. Materials and methods

2.1. Materials

In order to study bubble formation in a model paste, silica beads (*Tecosphere*) with a mean diameter of 36 μm and a standard deviation of 37 μm are suspended in an aqueous solution of surfactants at different concentrations between 5×10^{-4} and 2 times the critical micellar concentration (CMC) of the system. Sodium dodecyl sulfate (SDS) is used as a model anionic surfactant (Sigma, 98.5%, No. L4509, CMC = 8×10^{-3} mol L^{-1} [22]), and tetradecyltriammonium bromide (TTAB) is used as a model cationic surfactant (Sigma, 99%, No. T4762, CMC = 3.5×10^{-3} mol L^{-1}). Glycerol is added to vary the bulk viscosity η of the suspending phase between 1 and 10.7 mPa s [23]. The solid volume fraction ϕ in the suspension is varied between 26% and 52%. The reference compositions are given in Table 1. TTAB and SDS are not used simultaneously and the different parameters of the system are varied independently. The viscosity of the suspending fluid is measured with a capillary viscosimeter (Ubbelohde) with a precision of 15% because of temperature variations and the surface tension is measured by the Wilhelmy plate method (Nima) with a precision of 5%.

In our real cement paste, Portland cement CEM I 52.5 R is mixed with a limestone filler (*Betocarp HP Orgon de Omya*) and the water/powder mass ratio is 0.25. Solutions of two different admixtures are made in deionized water: polycarboxylate polymers (PCP) containing grafted PEO chains as superplasticizer, and surfactants (either SDS or TTAB). Small quantities of paste are used, so the powder is gently stirred by hand during 1 min in the aqueous solution. Tables 1 and 2 summarize respectively the different reference compositions and solid phase physical properties used in our experiments.

Table 2
Physical properties of the particles, with d the density, Σ the specific surface and R_p the particle radius.

Material	Silica	Cement	Limestone
d (kg m^{-3})	2500	3110	2750
Σ (m^2 g^{-1})	–	0.42	1
R_p (μm)	5–40	1–50	1–50

2.2. Methods

Air bubbles are injected through an aperture at the bottom of a cylindrical tank of diameter 26 mm initially filled with the paste. After detaching, bubbles rise by gravity in tubes of height $h = 3.1$ cm. A syringe pump allows to inject a controlled air volume (30 μL) at a given injection rate (0.1 mL s^{-1}), in order to obtain single bubbles. When the bubble reaches the interface, a liquid film is formed, which is fully covered with particles. The movement of the particles on the bubble thin film is then observed through a stereomicroscope, as depicted in Fig. 1. When the bubble reaches the interface, a liquid film is formed, which is fully covered with particles. The movement of the particles on the bubble thin film is then observed through a stereomicroscope, as depicted in Fig. 1.

The particles rearrange in two zones, a covered one and a bare one as reported in Fig. 2. Obtained with reflected light, the stereomicroscope images allow to distinguish the area covered by particles from the bare area, as soon as the bubble reaches the surface. Then, the evolution of the covering rate of particles on the bubble is determined as a function of time. The covering rate is at equilibrium generally 15 s after the bubble reaches the surface, and a mean value of the covering rate is measured at equilibrium for 5 to 10 different bubbles.

As wettability of our suspending solution versus particles is a crucial point on our experiments, two types of wettability measurements are performed, depending on the case considered. The contact angles of the different solutions on silica surface are determined by drop deposition on a clean plane silica slide, and side view image analysis as shown in Fig. 3-top. Each value is a mean of six measurements. Wettability of cement particles is measured by imbibition [24,25] of the liquid through the powder. A cylindrical column of 6 cm of height and 1.5 cm of diameter is filled with 13 g of packed cement powder. The bottom of this column is put in contact with a solution of PCP and SDS, as shown in Fig. 3-bottom. An estimation of powder wettability is deduced from the impregnation dynamics through Washburn law, with h_w the height of column filled by liquid, d_p the pore diameter, and t the time:

$$h_w(t) \simeq \sqrt{\frac{d_p t \gamma_{lg} cos\theta}{2\eta}} \qquad (1)$$

Table 1
Reference composition of the suspensions in the different experiments: concentration of TTAB, SDS (mol L^{-1}) and PCP (g L^{-1}), glycerol content (wt.%), solid volume fraction ϕ (%), mass of silica beads, cement and filler in the solid phase (%).

System	a	b	c	d	e	f
TTAB	$[10^{-5};10^{-2}]$	–	5×10^{-4}	–	5×10^{-4}	–
SDS	–	8×10^{-4}	–	$[10^{-6};10^{-2}]$	–	$[10^{-6};10^{-2}]$
PCP	–	–	4.8	4.8	–	–
Glycerol	[10;60]	10	–	–	–	–
ϕ	52	52	58	58	35	35
Silica	100	100	–	–	–	–
Cement	–	–	33.7	33.7	33.7	33.7
Filler	–	–	66.3	66.3	66.3	66.3