Cement & Concrete Composites 62 (2015) 44–51

Contents lists available at ScienceDirect

Cement & Concrete Composites

journal homepage: www.elsevier.com/locate/cemconcomp

Pozzolanic hardened three-phase-foams

Christina Krämer*, Torsten L. Kowald, Reinhard H.F. Trettin

Universität Siegen, Institut für Bau- und Werkstoffchemie, Paul-Bonatz-Str. 9-11, Siegen, Germany

ARTICLE INFO

Article history:
Received 21 August 2014
Received in revised form 9 May 2015
Accepted 3 June 2015
Available online 14 June 2015

Keywords:
Nanoparticles
Inorganic foams
Foam stability
Three-phase-foams
Pozzolanic reaction
Pozzolan

ABSTRACT

The field of lightweight materials is becoming more and more important due to the desire for material and cost savings with a simultaneous combination of thermal insulation and sustainability. It is of specific interest to obtain materials in a low density range of 60–150 kg/m^3 with high stability comparable to heavier weight materials currently in use, whilst under the constraint of reducing the content of inorganic binders. A new approach is the chemical treatment of foams based on three phases. The third phase consists of pozzolanic active nanomaterials, which can be varied and surface treated. Aided by chemical treatment of the three-phase-foams, a hardening of the foams has been achieved. Results based on studies of the microstructure and phase formation will be illustrated and discussed.

1. Introduction

Foams offer various and differing applications. In the foodstuffs, cosmetic, and construction industries, and in many other areas of material production, foams are utilized [1]. Also in nature, various applications of stable construction based on solid and gas content are found. There are many examples of lightweight materials, such as bamboo and bone structures, which, for example, have been adapted by material scientists. Here the aim is to design modern building materials by following the examples of nature, so that the advantages of weight and material savings are exploited. To achieve this goal, air is introduced into the materials in the form of foams. In this way, the performance of materials can significantly be increased [2]. One approach is to use wet foams for the production of lightweight materials. Wet foams can be produced and stabilized using proteins and surfactants. These two-phase-foams show destabilizing effects over time, for example drainage, coalescence and Ostwald ripening [3–5]. To enhance stability, particles are introduced in the liquid–gas interface to reduce this destabilization by lowering the high interfacial energy and thereby the free energy of the system [6–12]. In this way, caused by the energy of attachment of the particles, an irreversible adsorption at the interface can occur [6]. Gonzenbach et al. were the first researchers who reported a simple method for the preparation of high-volume, particle-stabilized foams with low densities [12–15]. These three-phase-foams show fewer destabilizing effects compared to two-phase-foams, where only surfactants are present in the water–air-interface.

Within three-phase-foams, metalloid or metal based nanoparticles are used as the solid phase. Integration of nanoparticles in the gas–liquid (disperse-continuous) interface is induced by electrostatic forces between the particles and surfactants. This interaction leads to a sorption of surface-active agents to the particle, resulting in partial hydrophobation. The hydrophobized particles can dip into the gas (disperse) phase and lead to high stability, along with a low density, after foaming, even after complete water diffusion or drying of the foams [12–14].

The main objective of our work is the improvement of foam stability and the production of stable inorganic foams with low densities of 110–150 kg/m^3. The improvement is based on a chemical treatment of an additional third solid phase of pozzolanic active nanoparticles inside three-phase-foams. The treatment leads to pozzolanic hardened and stable inorganic foams. This enables one to reduce the content of inorganic binders in the resulting low-density material, and thus provides a method for the production of lightweight materials which are low cost and energy saving. The lightweight materials produced can be exploited in a number of areas, for example as thermal insulation or in gas and fluid filtration.

Abbreviations: NS B, 35% w/w A90 dispersion and 60 mmol/L betaine; NS H, 35% w/w A 90 dispersion and 75 mmol/L n-hexylamine; MO B, 30% w/w MOX 80 dispersion and 10 mmol/L betaine.

* Corresponding author. Tel.: +49 271 740 4655; fax: +49 271 740 2938.
E-mail address: kraemer@chemie.uni-siegen.de (C. Krämer).

http://dx.doi.org/10.1016/j.cemconcomp.2015.06.002
0958-9465/

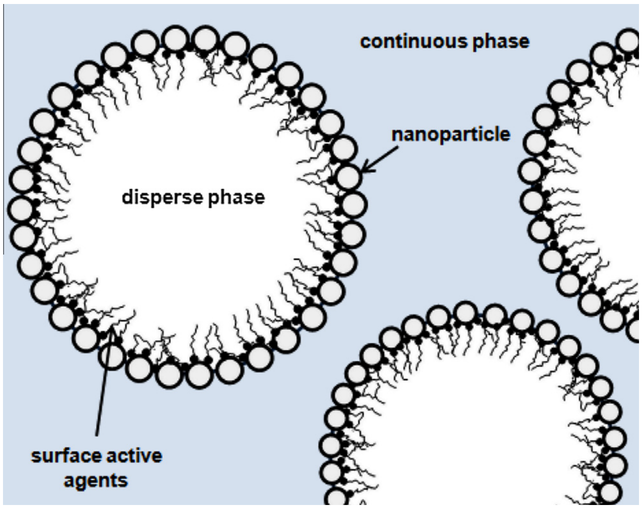
2. Preparation of pozzolanic hardened three-phase-foams

In the first step, high concentration water-based dispersions of the nanoparticles have to be prepared. Here, it is crucial to adapt the nanoparticles to the surface active agents. To achieve this, the particles are characterized by pH dependent zeta potential measurement, which is maximized to avoid agglomeration. These measurements are of further importance to determine the charges of functional groups with respect to the degree of protonation or deprotonation at different pH values. Increasing the pH leads to an increased density of deprotonated groups on the particle surface ($M{-}O^-$), and, by decreasing the pH, protonated groups dominate ($M{-}OH_2^+$). The charge-to-size ratio of the solid oxide used influences the reactivity and also the observed surface groups at the particular pH. At the isoelectric point (IEP), the ratio between deprotonated and protonated groups is one [12]. The surface active agents are selected such that the functional groups are protonated or deprotonated to permit sorption on the surface of the particle with respect to the present pH (Scheme 1). The sorption takes place after mixing the protonated or deprotonated agent and particle dispersion. To adapt both of the components, the chain length, functionalities and constitution of the surface active agents and the degree of hydrophobation of the particles can be varied.

The air entrainment is carried out by a mechanical foaming process, using a continuous dynamic stirrer which disperses gas in the fluid. Here, gas is entrained by shear forces and large bubbles are cut into smaller ones with a homogeneous distribution. The quality of the foam strongly depends on the gas content and attaining a homogeneous bubble distribution. To select the appropriate foaming method, the viscosity of the fluid, flow conditions and the conveying direction of the stirrer have to be adjusted. The pore diameter is dependent on the selected surface active agent and its adsorption. A faster adsorption will lead to smaller pore diameters. The occupation and stabilization of the disperse–continuous interface depend on the degree of adsorption. The higher the degree of adsorption, the faster occupation and stabilization take place, which inhibits destabilizing influences [16–19]. A schematic representation of the three-phase-foams after foaming is shown in Scheme 2.

In a further step, the three-phase-foams were modified/stabilized by chemical reaction in solution. As solid phase, SiO_2 nanoparticles were chosen. These can react with a $Ca(OH)_2$ solution which leads to calcium silicate hydrates (C–S–H) as a reaction product:

$$2SiO_2 + 3Ca(OH)_2 + mH_2O \rightarrow 3CaO \cdot 2SiO_2 \cdot (m+3)H_2O$$

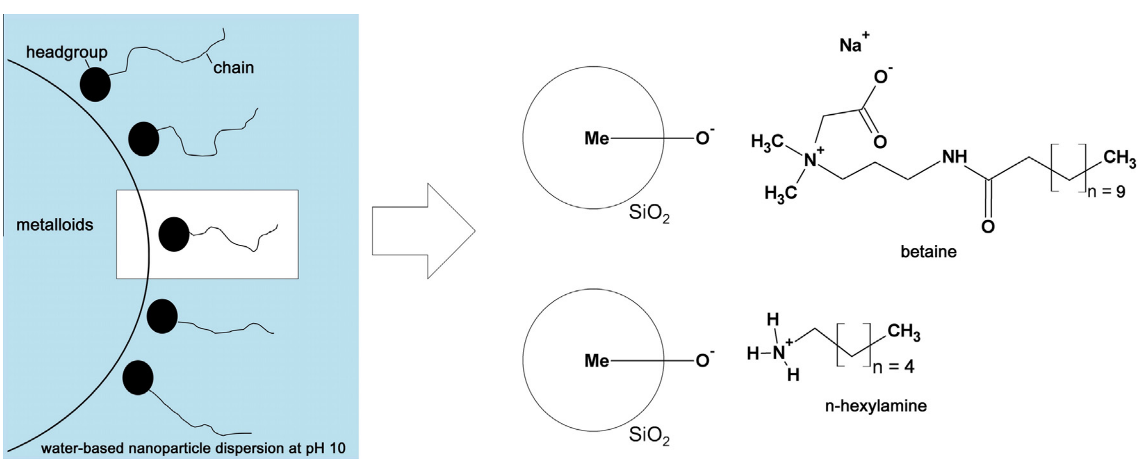


Scheme 2. Schematic representation of three-phase-foams after foaming.

This reaction is termed a pozzolanic reaction. The nanosilica used has an average particle size of 20 nm, which leads to a high specific surface area and a good pozzolanic reactivity compared to other coarser SiO_2-based materials [20]. Because of the very small size, these particles are suitable for preparing three-phase-foams and, additionally, the surface increases exponentially and the pozzolanic reaction is strongly accelerated. C–S–H phases are mostly X-ray amorphous calcium silicate hydrates with the general formula $(CaO)_x{\cdot}SiO_2{\cdot}(H_2O)_y$ [21]. A comparison of the reaction of quartz flour, microsilica and nanosilica in the presence of $Ca(OH)_2$ to C–S–H phases makes the increased reactivity clear. While the quartz flour in rough shape without additional heat input shows no chemical reaction, the microsilica react in the presence of $Ca(OH)_2$ after a few days or weeks, and nanosilica after only 24 h, to C–S–H phases. The latter shows a high amount of C–S–H phases after a few hours, which allows it to be considered as an independent material [20,22].

Preliminary experiments show a successful hardening and increased foam stability by pozzolanic hardening of three-phase-foams (Fig. 1).

After drying and hardening of the foams, no destabilizing effects occur. A further advantage is not only the higher stability compared to the foams without particles, but also the formation of strength improving reaction products.



Scheme 1. Scheme of electrostatic interaction between surface active agent and particle surface.