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Adsorption and heterocoagulation of nonionic surfactants and latex particles on cement hydrates

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Abstract

The adsorption of nonionic surfactants of the alkyl–phenol–poly(ethylene oxide) family and of acrylic latex particles on several anhydrous (but hydrating) or fully hydrated mineral phases of Portland cement was studied. No or negligible adsorption of the surfactant was observed. This was assigned to the ionized character of the surface silanol groups in calcium–silicate–hydrates and to the strongly ionic character of the OH groups in calcium hydroxide and in the calcium–sulfoaluminate–hydrates, which prevents the formation of surface–ethoxy hydrogen bonds. In contrast, provided they are properly stabilized by the surfactant, the latex particles form a loose monolayer on the surface of hydrating tricalcium silicate particles. The attractive interaction between the positive mineral surface and the negative latex surface appears to be the driving force for adsorption. In line with this, adsorption is reduced by sulfate anions, which adsorb specifically onto the silicate surface. Compared to tricalcium silicate, portlandite and gypsum interact only marginally with the latex particles. Our results show that the stability of the nonionic surfactant/latex/cement systems is essentially controlled by the latex colloidal stability and the latex–cement interactions, the surfactant having little direct interaction, if any, with the mineral surfaces.

Keywords: Cement; Latex; Nonionic surfactants; Adsorption; Heterocoagulation; Hydrates

1. Introduction

Composite mineral–organic materials and particularly cement–organic materials are increasingly used in civil engineering, petroleum engineering, and construction applications. Most of the time, the polymer is introduced into the mineral slurry or paste in the form of a latex suspension, stabilized by surfactants. The ternary character of these mixtures (in fact, quaternary, taking water into account) and the composition fluctuations which they experience in practice—primarily due to the variable cement composition but also to the variable water/cement ratio caused by dilution, evaporation, or water loss to porous supports or rock formations—makes it difficult to maintain their colloidal stability in all circumstances.

The present study is devoted to nonionic surfactant/acrylic latex/cement interactions in aqueous medium. The surfactant belongs to a well-known family of alkyl–phenol–poly(ethylene oxide) compounds and the latex is a classical commercial alkyl acrylate-based formulation, with a soft polymer core and surface carboxylic groups, stabilized by the surfactant. The major source of complexity in this system comes from the multiphase character of cement particles and the poorly known surface properties of the hydrates (see Section 2). As an example of the type of problems that may arise, Fig. 1 illustrates the evolution of a calcium silicate paste to which an increasing volume of latex suspension stabilized by a nonionic surfactant was added, while the total water/silicate ratio was kept constant. With small additions of the latex suspension, the system is clearly unstable,

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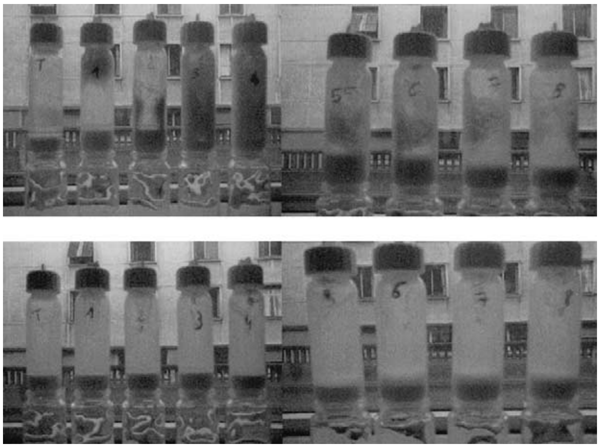

Fig. 1. Top sequence: a series of calcium silicate pastes to which an increasing (from left to right) volume of acrylic latex suspension stabilized by TX405 was added, while keeping the total water/silicate ratio constant. Notice the coagulated mixture sticking on the tube wall at small latex concentration (i.e., under conditions where the added volume of latex suspension was highly diluted in the total liquid volume). Bottom sequence: the same, but with an excess constant concentration of surfactant. No coagulation is observed.

with the (hetero)coagulated latex/cement mixtures sticking to the vessel walls. In contrast, if an excess of surfactant is added, coagulation is avoided (this does not prevent sedimentation, which is unavoidable, considering the high density ($3.2\ \mathrm{g\,cm^{-3}}$) and the particle size (5 µm) of the silicate).

To provide a basis for understanding this type of behavior, we measured the adsorption isotherms of widely used nonionic surfactants of the Triton family and a standard acrylate latex on the mineral phases involved. Rather than measuring the adsorption isotherms on cement particles, which are highly heterogeneous, we performed separate measurements on the different phases that are formed by reaction of Portland cement with water (the so-called hydrates) and on pure tricalcium silicate, the major component of Portland cement. When possible, the measurements were performed in solutions in ionic equilibrium with the mineral phase. As will be shown, the stability of the cement–latex–surfactant system is essentially controlled by the latex stability, the surfactant having little interaction, if any, with the mineral surfaces.

2. Cement hydrates and their surface properties

Portland cement is the ground form of clinker, the artificial rock obtained from the nonequilibrium cooling of a sintered mass in the system $CaO–SiO_2–Al_2O_3$, with magnesium and iron impurities, starting from a mixture of clay and lime as raw material [1]. It is a mixture of several mineral phases, the most abundant being impure tricalcium silicate, Ca_3SiO_5 (alite, C_3S, for short) and bicalcium silicate, Ca_2SiO_4 (belite, C_2S, for short). The other phases, which are liquid during the synthesis at 1450 °C, are a tricalcium aluminate, $Ca_3Al_2O_6$ (C_3A, for short), and a calcium aluminoferrite, $Ca_4Al_2Fe_2O_{14}$ (celite, C_4AF, for short). Gypsum, $CaSO_4{\cdot}2H_2O$, is added to ground clinker to regulate the reactivity of the aluminate phases. When cement is mixed with water, it undergoes a dissolution reaction generating, among others, calcium, silicate, and aluminate anions in the interstitial solution. Though present in minor amounts in the anhydrous phases, potassium, sodium, and sulfate ions contribute greatly to the ionic strength because of their high solubility. Very soon, new products of low solubility precipitate, the most important being calcium–silicate–hydrate (C–S–H) and calcium hydroxide (portlandite). The aluminate ions react with the calcium and sulfate ions to form first calcium–trisulfoaluminate–hydrate (ettringite) and later, after all the gypsum has been consumed, calcium–monosulfoaluminate–hydrate, by reaction of ettringite with residual tricalcium aluminate.

C–S–H is basically a nonstoichiometric compound [2,3]. The average Ca/Si ratio in ordinary hardened cement paste is around 1.7 but it may decrease locally to much lower values. Local values, measured by analytical electron transmission microscopy, fluctuate between 0.6 and 2 or more [2,3]. Though generally poorly organized (hence the widespread use of the words “C–S–H gel”), C–S–H is widely recognized to have a layered crystal structure, akin to that of the mineral tobermorite or to that of jennite, with a layer thickness in the nanometer range [1,4–8]. High-resolution ^{29}Si, ^{1}H, and ^{17}O NMR, X-ray absorption spectroscopy, and IR and Raman spectroscopy [9–14] have brought considerable information on the structure of the layers. It is now generally admitted that their two-dimensional backbone is a double plane of Ca^{2+} ions 6-coordinated by central O^{2-} ions, to which disordered silica chains are grafted on each side. These composite layers stack along the 001 direction, being separated by Ca^{2+} ions and water molecules. In the reference mineral tobermorite, with $Ca/Si = 0.66$, the chains are infinite and run parallel to the b axis [15]. The repeating units along the chains are so-called dreierketten, with two pairing tetrahedra linked to the CaO polyhedra by sharing edges with them, and one bridging tetrahedron pointing away from the CaO polyhedra layer. In perfect tobermorite, all the oxygen atoms involved in the dangling bonds of the silicate chain are protonated as hydroxyl groups, so that the structure is neutral.

Up to $Ca/Si = 1.5$, C–S–H may be considered as a defect tobermorite structure. A crucial point is that the solution in equilibrium with C–S–H is always at very high pH. For $Ca/Si = 1$, it is already beyond 12. In the low Ca/Si, regime, the structural evolution appears to be the progressive replacement of the protons of the initially doubly protonated bridging tetrahedra by Ca^{2+} ions, which go into the hydrated interlayer space. At $Ca/Si = 1$, a first phase transition seems to occur and a new type of C–S–H with a lower degree of polymerization of the chains appears. The main defects are missing bridging tetrahedra. The higher the Ca/Si ratio, the larger the number of missing bridging tetrahedra and the shorter the average chain length. This length goes from average pentameric units at $Ca/Si = 1$ to dimeric units