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Surface phenomena related to applications regarding optimum dosages of casein superplasticizer in self-leveling underlayment cements

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Abstract: We experimentally investigated the optimum dosage of casein superplasticizer (SP) in self-leveling underlayments (SLUs). The undersaturated adsorption state of casein in cement pore solution was characterized by zeta potential measurements. Different amounts of casein were dosed in SLU pastes and their dispersion performance was investigated by a mini slump test. Flow values of the SLU pastes were found to increase with casein dosage, but an obvious segregation of the pastes was observed at high dose levels of SP. At an SP dosage of 0.12 wt.% bwob (by weight of binder), a homogeneous SLU paste with a spread flow of >15 cm over a time span of 30 min was obtained, which was identified as the optimum casein dosage for SLUs. Casein was found to adsorb significantly onto the surface of cement, thus producing strong dispersive power at low dose levels.

Keywords: admixture; casein; dosage; mortar.

1 Introduction

Self-leveling underlayments (SLUs) are commonly used to level floors and to cover cracks prior to the application of a flooring finish [1–4]. They are marked by good flow characteristics as well as self-leveling and fast setting/drying properties. Compared to other “normal” grouts, SLU materials help save working time and labor at construction sites [5].

The composition of SLUs is rather complicated, as they may contain inorganic binders, fillers, accelerators, retarders, defoamers, redispersible powders, superplasticizers (SPs), etc. Among them, SPs play a significant role since they provide excellent dispersing effectiveness in SLU grouts. The mechanism is known to be based on the adsorption of SP molecules at cement particles, thereby breaking their agglomeration by repulsion of same charges/steric hindrance and releasing entrapped water. Based on this concept, an underdose of SP reduces the charges/hindrance on the surface of cement particles, which results in poor cement paste dispersion. By contrast, an overdose of SP will release excessive free water, resulting in segregation and retardation of setting with cement. Therefore, proper dosing of SP is of great importance for the performance of SLUs.

In this work, we studied the influence of SP dosage on the properties of cement-based SLUs. Casein, a natural milk protein, has been used as SP in the formulations for many years. Casein is one of the most widely used dispersants in SLUs [6–11]. It stands out above other SPs because it not only provides excellent dispersing effectiveness but also shows a self-healing effect on the surface of the SLU grout. Our earlier study revealed that in the pores of SLU casein dissociates into negatively charged submicelles, which get adsorbed on the positively charged cement surface, thus providing a densely packed polymer layer [12]. Through this mechanism, strong electrostatic repulsion between the cement particles is created and high flowability of the SLU paste is achieved. However, it has been noticed that the performance of SLUs is sensitive to the casein dosage, especially for the homogeneity of the paste. Bleeding or segregation of cement paste was observed in less well formulated SLUs. Therefore, it is of great importance to explore the influence of casein dosage on the performance of SLUs and to determine its optimum value in the formulation.

2 Materials and methods

Commercial casein, provided by Ardex GmbH, Witten, Germany, was used directly without any treatment or purification.

The flowability of SLU pastes was measured versus time according to EN 12706. A slump cone of internal diameter of 30 mm and height 50 mm was used for the slump tests. The zeta potentials were measured using a DT 1200 electroacoustic spectrometer (Dispersion Technology, Inc.,
Bedford Hills, NY, USA). The amount of casein adsorbed on the binder surface was measured using total organic carbon (TOC) analyses and ion chromatography (IC).

3 Results and discussion

3.1 Interaction of casein with cement

In this work, the influence of casein on the zeta potential of binder particles was measured on ordinary Portland cement only, since premature setting of the SLU system does not allow zeta potential measurements. A water/cement ratio of 0.5 was used in the measurement. First, the ionic background of the cement filtrate was determined, which was automatically subtracted from the zeta potential values in the experiment. An aqueous casein solution (c_{casein} = 5.0 wt.%, pH 12) was titrated stepwise into the cement slurry. Thereby, the zeta potential of cement particles was obtained as a function of the casein dosage (Fig. 1). It is seen that the zeta potential of the cement was −5 mV in the absence of casein. With increasing dosage of SP, the zeta potential gradually increased to more negative values until a maximum value of −10.4 mV was reached at 0.24 wt.% of casein. After that, the increase in casein dosage did not lead to any further increase in the zeta potential, and the curve leveled off.

The increase in the zeta potential with increasing casein dosage can be attributed to the adsorption of SP on the cement particles. The adsorption of negatively charged casein changes the charge on the electrical double layer of the cement particle surface, resulting in an increase in the absolute value of the zeta potential. This effect promotes stronger electrostatic repulsion between the cement particles. As a consequence, the stability of the dispersion is improved. The electrical double layer at the binder particle surface in the native state and after saturation is depicted in Fig. 2.

3.2 Dispersing effectiveness of casein

The dispersing effectiveness of the SP casein in SLUs is mainly determined by the electrostatic repulsive forces it introduces into the binder surfaces, which can be typically characterized by zeta potential measurement. But it is to be noted that the above zeta potential measurement was carried out in pure Portland cement at a w/c ratio of 0.5. However, a typical SLU formulation consists of a Portland-cement-dominated ternary binder system. Therefore, 0.24 wt.% of casein may not be the optimum dosage at which a maximum flow of the SLU paste can be achieved. For further determination of the influence, the dispersing effectiveness of casein was characterized by measuring the spread flow of the SLU paste. An SLU model formulation based on a ternary binder system was used in this measurement (Table 1), where 0.24 wt.% of casein was added to follow up the dispersing effectiveness. The flow of the paste as a function of time was recorded, and the result is shown in Fig. 3. Over a time span of 60 min, the flow remained >17 cm, before it dropped as a result of accelerating cement hydration, suggesting the excellent plasticizing effect exerted by casein. However, during the measurement, strong segregation and bleeding occurred in the SLU paste, as shown in Fig. 4. The spread flow of the paste greatly fluctuated, which is unacceptable in actual application.

To eliminate the bleeding problem of the cement grout, the dosage of casein SP was adjusted to 0.20, 0.15, 0.12, and 0.10 wt.%. The flowability of these SLU pastes and the bleeding phenomena were characterized, and the results are shown in Figs. 3 and 4, respectively. According to the data, decreasing the dosage of casein effectively reduced the bleeding of the mortar. At a casein dosage of 0.12 wt.%, a coherent and homogenous SLU paste was achieved, suggesting that the segregation problem has been solved. At this dosage, a spread flow of >15 cm over a time span of 30 min was obtained, which indicates sufficient dispersing performance of casein under these conditions. Based on our results, we can conclude that the optimum dosage of casein SP in this SLU formulation is 0.12 wt.% bwob (by weight of binder).
3.3 Adsorption of casein

Furthermore, the amount of casein adsorption on the binder surface was measured using total organic carbon (TOC) analyses and ion chromatography (IC). First, the total amounts of retarder and of the casein superplasticizer left unadsorbed in the SLU pore solution were measured by TOC analysis. Next, the retarder amount was quantified using IC measurement. As a result, the casein concentration remaining in the pore solution could be obtained by subtraction. Based on the above method, the adsorption of casein on the binder was found to be 90.7%. This indicates that casein SP has a strong tendency to be adsorbed on the surface of cement particles. The negatively charged casein changes the charges on the electrical double layer.
of the cement surface, which in the native state promotes electrostatic repulsion between the cement particles. As a consequence, a good dispersing effectiveness can be achieved at a rather low dose level of casein.

4 Conclusion

In this study, we investigated the optimum addition ratio of casein in SLU formulations. The saturated adsorption state of casein on the cement particles and its corresponding dosage were characterized by zeta potential measurements. The flowability of SLU pastes with different proportions of casein was monitored by slump tests. The optimum dosage of casein SP was found to be 0.12 wt.% bwob, which resulted in a homogeneously dispersed SLU paste with a large spread flow. Further, a rather high adsorption of casein on the binder was revealed by TOC and IC experiments, indicating the strong tendency of SPs to interact with cement, and accordingly explains the significant dispersing performance of casein even at a low dose level.

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References


