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Communication

Microstructural development in an ultrafine cement — Part II

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Abstract

Improvements in setting characteristics and strength development were achieved in an ultrafine cement with a specific surface area >7000 cm^2/g by adding small dosages of a solid retarder and a solid HRWRA. Incorporation of 20% superfine fly ash resulted in lower heat generation and better flowability. The microstructural development of these mixes was studied using SEM/EDXA. Calcium hydroxide formation as a function of hydration age was quantified by XRD and TGA. Their paste porosity at 28 days was also measured.

Keywords: Microstructure; Hydration; C–S–H; $Ca(OH)_2$; SEM/EDXA

1. Introduction

The most common application of ultrafine cement is in the grouting of fine fissures [1]. However, ultrafine cement produced simply by grinding finer a portland cement can result in unusually short setting times, and strength retrogression can occur after hardening. These characteristic problems are attributed to the fine particle size of these cements. The authors have demonstrated [2] that the heat evolution of ultrafine cement within the first 24 h can be exceptionally high compared to that of an ASTM Type III cement. This results in rapid consumption of the available water, which in turn leads to limited hydration at later ages. As a consequence, strength gain of ultrafine cement can be low. High heat is also likely to generate microcracks.

Experiments were carried out to improve the properties of an ultrafine cement with a Blaine specific area greater than 7000 cm^2/g by adding small dosages of a solid retarder and a solid HRWRA [2]. Replacing 20% ultrafine cement with a superfine fly ash resulted in still lower heat generation and improved flowability, but the strength tends to be lower than corresponding mixes without any fly ash.

The microstructural development of these ultrafine cement mixes was studied using SEM/EDXA. X-ray diffraction (XRD) analysis and TGA were carried out to quantify the amount of $Ca(OH)_2$ generated as a function of hydration age.

2. Results

2.1. X-ray diffraction analysis

It is well known that the amount of $Ca(OH)_2$ increases as a function of water–cement ratio, etc. [3]. As a matter of fact, this is often used empirically to measure the hydration kinetics of cement. Out of the several mixes that were tested, the two candidate mixes that were selected for microstructural study were (i) 100% ultrafine cement + 1% HRWRA + 1% retarder and (ii) 80% ultrafine cement + 20% superfine fly ash + 1% HRWRA + 1% retarder. The amplitude of the $Ca(OH)_2$ peak at around 18°2θ was measured for these cement pastes at different hydration ages. A Type III cement was used for comparison. The results are presented in Table 1.

It is evident that in both the ultrafine cement mixes, no $Ca(OH)_2$ crystallization occurs at Day 1, implying marginal hydration at this age. This is attributed to the retarder introduced in these mixtures. However, $Ca(OH)_2$ crystallization in the corresponding Type III cement paste is significant from the very beginning, and continues to increase as a function of time. Calcium hydroxide in the

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Table 1
Amplitude of $Ca(OH)_2$ peak (total counts) at 18°2θ

Hydration age	Type III cement	Ultrafine cement + 1% HRWRA + 1% retarder	80% Ultrafine cement + 20% fly ash + 1% HRWRA + 1% retarder
1 day	20400	N/M	N/M
7 days	28478	13997	6701
28 days	42137	9343	1336

N/M = not measurable.

ultrafine cement mixes appears only at 7 days, but the amount is distinctly lower than that of the counterpart Type III cement. No further $Ca(OH)_2$ forms at 28 days in any of these ultrafine cement two pastes. Incorporation of 20% fly ash by mass of cement can be considered to act as a diluent. Its pozzolanic effect most likely begins to become operative at 28 days, when a further reduction in $Ca(OH)_2$ is seen to occur [4]. In the mix without any fly ash in it, $Ca(OH)_2$ reduces at 28 days, implying a reduction in the rate of hydration.

The low amount of $Ca(OH)_2$ in these mixtures is fortuitous because $Ca(OH)_2$ is the most readily soluble hydration phase; in fact, it is the first mineral to dissolve out, making the rest of the cement matrix vulnerable to chemical attack [5].

From examination of the XRD patterns of the three cement pastes the amount of alite was noted to be significantly higher in the ultrafine mixtures than in the Type III cement at Day 1. Calcium hydroxide generation, however, was lower compared to that of Type III cement, confirming that effective hydration was yet to commence. The XRD patterns displayed a considerable amount of alite consumption at 7 days in these mixes when $Ca(OH)_2$ also forms.

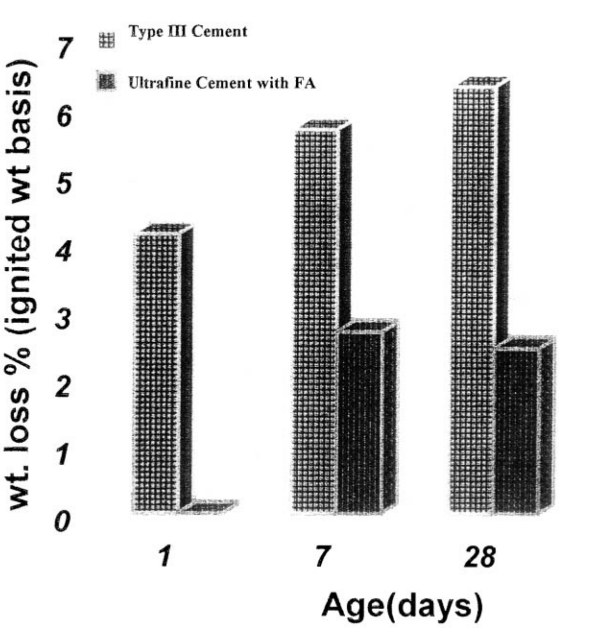

Fig. 1. Weight loss as a function of hydration age.

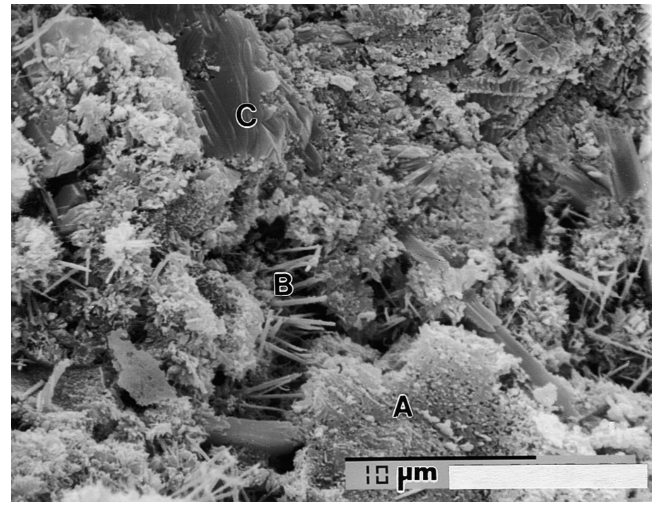

Fig. 2. S.E.M. image of porous paste of Type III cement at 28 days A = C–S–H, B = ettringite, C = $Ca(OH)_2$.

2.2. Thermogravimetric analysis (TGA)

TGA was carried out on the mixture containing 80% ultrafine cement + 20% superfine fly ash + 1% retarder + 1% HRWRA and Type III cement hydrated for 1, 7, and 28 days, respectively. The histogram (Fig. 1) of the measured weight loss shows exactly the same trend as observed in XRD analysis, except that the reduction in the amount of $Ca(OH)_2$ at 28 days is not as much from TGA as from XRD analysis.

2.3. Porosity

The porosity of the two ultrafine cement pastes was measured at 28 days using mercury porosimetry. Although both the pastes have the same pore diameter range from 0.01

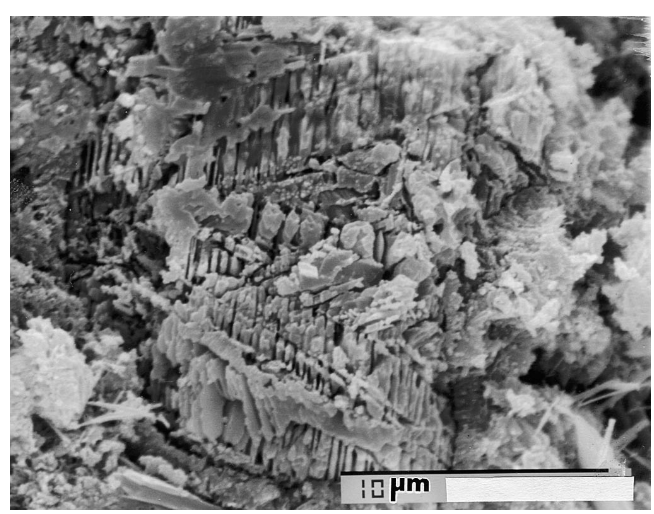

Fig. 3. S.E.M. image of a partly hydrated cement grain. The relict lamellar structure suggests that it is a belite grain.

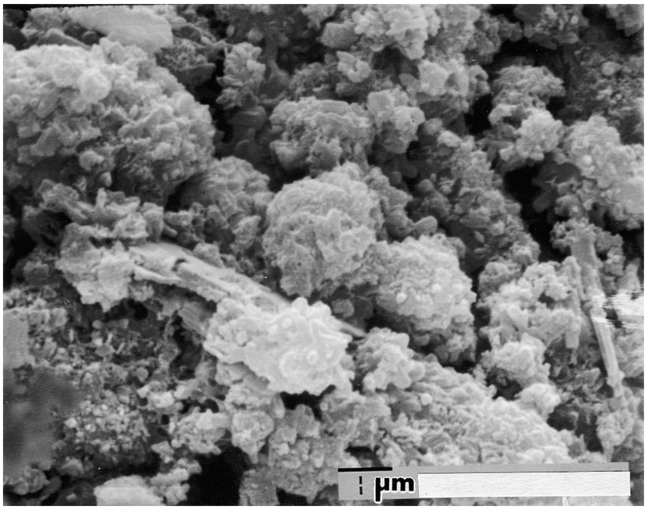

Fig. 4. S.E.M. image of highly porous paste of mix containing 100% ultrafine cement + 1% retarder + 1% HRWRA at Day 1.

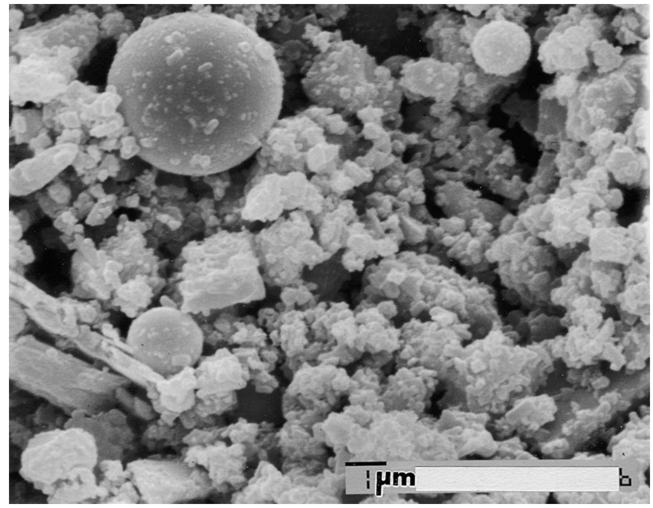

Fig. 6. S.E.M. image of 80% ultrafine cement + 20% fly ash + 1% retarder + 1% HRWRA at 1 day.

to 1.0 μm, the ultrafine cement paste containing only retarder and HRWRA was characterized by three sizes of pores, the coarsest pore diameter being 0.75 μm. The most frequently occurring diameter was 0.1 μm, and a small number of much finer pores, with a diameter of 0.02 μm, was present. In contrast, the paste of the mixture containing fly ash consists of a coarse pore size of diameter of 0.8 μm, and a finer one with a diameter of 0.1 μm. A comparison of dv/dv values indicated that the amount of mercury intrusion in mix containing fly ash is somewhat lower than that of the counterpart mix.

2.4. Scanning electron/energy dispersive X-ray analysis

Paste samples were prepared at a constant water–cementitious ratio (W/C) of 0.50. These were then kept sealed in bottles until the examination age, that is, 1, 7, and 28 days, when the samples were removed from the bottles, immersed in acetone for 15 min, and then dried to constant weight in oven at 60°C.

2.4.1. Type III cement paste at 28 days

Only the 28 day sample was examined. The paste is characterized by a porous microstructure and a multitude of voids (Fig. 2). The C–S–H consists of an irregular core with characteristic peripheral fibrillar outgrowth [6]. Some of the needle-like structure in the paste is possibly ettringite, although the amount is low and beyond the detection level of XRD. Abundant massive and tabular $Ca(OH)_2$ forms in the paste, and partially hydrated cement grains (Fig. 3) and hollow shell hydration features are very common. EDX analysis of paste C–S–H yielded the characteristic Ca/Si ratio of 1.25 to 1.30, with Al and K as the foreign ions in the lattice.

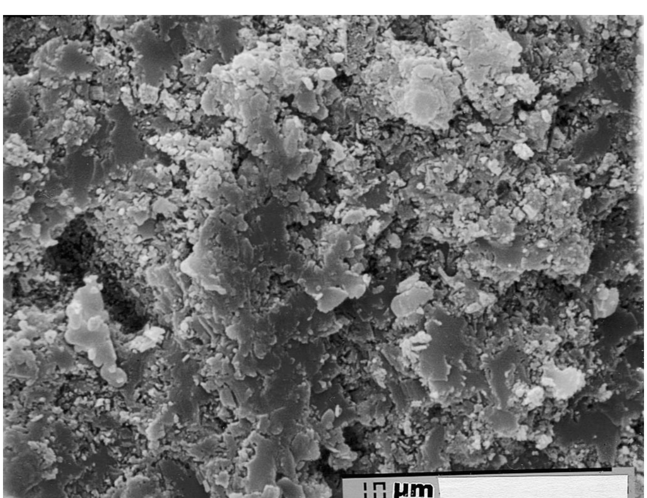

Fig. 5. S.E.M. image of the same paste has acquired denseness at 28 days.

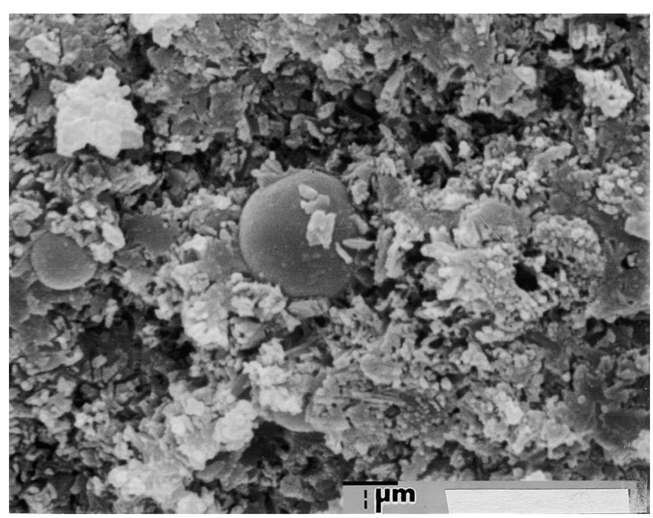

Fig. 7. S.E.M. image of platy microstructure of the paste at 7 days.

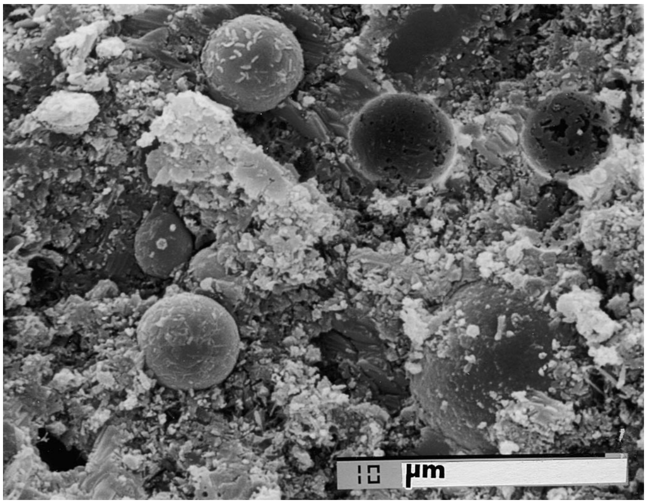

Fig. 8. S.E.M. image of dense paste at 28 days.

2.4.2. 100% Ultrafine cement + 1% retarder + 1% HRWRA

At Day 1 the paste is highly porous and consists of near spherical cement particles that are extremely fine in size (2 μm) as shown in Fig. 4. The cement particles exhibit nominal hydration, and $Ca(OH)_2$ is extremely rare in the paste, which confirms the XRD results. By 7 days the paste acquires some denseness. Cement particles begin to hydrate and $Ca(OH)_2$ appears in the paste. At 28 days the paste acquires extreme denseness, and the paste porosity decreases. Most of the cement grains appear to have hydrated (Fig. 5). Neither significant increase nor decrease in $Ca(OH)_2$ was discernable.

2.4.3. 80% Ultrafine cement + 20% fly ash + 1% retarder + 1% HRWRA

As in the counterpart mix, initially the paste is highly porous (Fig. 6). The cement grains display nominal hydration as do the ultra fine fly ash particles in this mixture. Compared to the microstructure at 1 day the paste densifies by 7 days. Some of the ash particles begin to hydrate. Platy $Ca(OH)_2$ crystals also appear in the paste. The dissolution of Al from the fly ash becomes more pronounced. The composition of the new additional binder was identified as C–A–S–H. It is amorphous like C–S–H, but somewhat platy in appearance. SEM micrograph (Fig. 7) clearly shows this morphological feature. By 28 days, the paste becomes sufficiently dense, as illustrated in Fig. 8. Some ill-crystallized $Ca(OH)_2$ crystals form around ash grains, but the composition of C–A–S–H remains unchanged.

3. Conclusions

TGA at ages 1, 7, and 28 days corroborates with the XRD data on hydration kinetics. Only nominal amount of $Ca(OH)_2$ is generated at 1 day in the 80% ultrafine cement + 20% fly ash mix. The maximum amount of $Ca(OH)_2$ produced at 7 days is still significantly lower than that of Type III cement, with gradual reduction occurring at 28 days. The Type III cement, on the other hand, continues to produce $Ca(OH)_2$ at an increased rate up to 28 days. This mix is also characterized by two sets of pores, while the counterpart mixture has three sets. The volume of pores worth a diameter of 0.1 μm is lower in mixture No. 6. This is attributable to the presence of fly ash in the mixture.

SEM/EDXA reveals that in the ultrafine mixes with or without fly ash the paste at Day 1 is quite porous and consists of near spherical, extremely fine unhydrated and nominally hydrated cement particles, with $Ca(OH)_2$ being extremely rare in the paste. By 7 days the paste acquires some degree of denseness, cement particles begin to hydrate, and $Ca(OH)_2$ appears in the paste. At 28 days the paste becomes extremely dense, and the paste porosity decreases. Most of the cement grains appear to have hydrated. Neither appreciable increase nor decrease in $Ca(OH)_2$ was discernible.

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