Pergamon

CEMENT AND CONCRETE RESEARCH

Cement and Concrete Research 31 (2001) 119–123

Communication

# Important properties of an ultrafine cement — Part I

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Received 11 January 2000; accepted 8 August 2000

**Abstract**

Experiments were carried out to eliminate strength retrogression and unusually fast setting characteristics of an ultrafine cement with a Blaine surface area > 7000 $cm^2/g$. A solid retarder, a solid HRWRA, and a superfine fly ash were incorporated in the ultrafine cement to improve its properties. The changes in the important physical, chemical, and other associated properties that result from such additions are reported. 

*Keywords:* Heat of hydration; Setting times; Superfine fly ash; HRWRA; Retarder

## 1. Introduction

Cement producers over the years have developed several new types of binders which either have extended the area of usage of cement or have demonstrated technical and ecological advantages [1]. Grouting technology is one such area of application that has gained considerable significance. The common types of grouts that are available are lime-based, ultrafine cement-based, micro cement-based, or polymeric [2]. The efficiency of different groups varies, depending on the dynamic viscosity and setting characteristics, minimum injectable dimension of voids, and mechanical strength. Grouting as a repair and strengthening technique is constantly used for remediating highly radioactive waste trenches, stabilization of tall buildings, mine subsidence, dam joints, and restoration of masonry structures [3].

In the recent past, an ultrafine cement was used to improve oil production in nearly 200 wells in the Provost area of eastern Alberta, Canada. A water shutoff system was developed using a silicate-based polymer slurry, followed by an ultrafine cement [4]. Mac Eachern and Young [5] succeeded in sealing a slow leak in a casing collar in a single operation in a high-temperature well in Mobile Bay, AL by squeezing in an ultrafine cement. Harris and Johnson [6] and Clarke and McNally [7] have outlined the increasing use of ultrafine cement in oilwell cementing. Clarke et al. [8] reported the use of ultrafine slag cement and ultrafine Portland cement for tertiary grouting of a control shaft in the Warm Springs Dam in Sacramento, CA. Nearly 5700 $ft^3$ of grout was placed in the water-filled voids and cracks in this operation.

However, an ultrafine cement cannot be produced simply by grinding finer any Portland cement. The main problems that occur are (i) very short setting times and (ii) strength retrogression a few days after hardening. Both these abnormalities are attributed to fine particle size. Faster

Table 1
Chemical composition of ultrafine and Type III cement (mass %)

| Oxide | Ultrafine cement | Type III cement |
|---|---|---|
| $SiO_2$ | 19.36 | 19.66 |
| $Al_2O_3$ | 4.89 | 5.76 |
| $Fe_2O_3$ | 1.70 | 1.92 |
| CaO | 63.98 | 64.74 |
| MgO | 1.07 | 1.28 |
| $SO_3$ | 4.32 | 4.14 |
| $Na_2O$ | 0.12 | 0.14 |
| $K_2O$ | 0.70 | 0.65 |
| $TiO_2$ | 0.24 | 0 |
| $P_2O_5$ | 0.22 | ND |
| $Mn_2O_3$ | 0.03 | ND |
| SrO | 0.09 | ND |
| LOI | 2.59 | 1.71 |
| $Na_2O$ equiv | 0.59 | 0.57 |

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0008-8846/01/$ – see front matter 
PII: S0008-8846(00)00393-8

Table 2
Soluble alkalies (mg/kg)

| Cement | Ca | Na | K |
|---|---|---|---|
| Ultrafine | 13,010 | 487 | 4072 |
| Type III | 13,890 | 422 | 3003 |

Table 3
Setting times of cements

| Cement type | Initial setting time (min) | Final setting time (min) |
|---|---|---|
| Ultrafine | 23 | 81 |
| Type III | 176 | 251 |
| Type I | 180 | 278 |

release of alkalies from the finer cement particles may also be a contributory factor. Geymayer et al [9] who investigated a series of cements with different levels of fineness concluded that the cohesion and structural viscosity vary with fineness.

## 2. Experimental

A series of experiments were carried out in order to develop an ultrafine cement which would be free of these problems. The chemical composition of the fine ground Portland cement with 98% particles finer than 10 μm, which was the starting material, is compared with that of a Type III cement from the same cement plant in Table 1. Minor variations in composition of the two cements that are evident are common between different batches of cement. The soluble Na and K ions were measured according to EPA 200.7 method to determine if there is any additional release of alkalies in solution from the ultrafine cement. The values presented in Table 2 indicate a marginal increase in alkalies, which confirms the nominally higher $Na_2O$ equiv. of the ultrafine cement (Table 1).

The heat evolution of the ultrafine cement (Fig. 1) is nearly 2.5 times than that of the Type III cement within the first 15 min. The amplitude of the second peak is equally high. The heat of hydration experiment was carried out at a high W/C of 1.0, so that the excess water allowed the

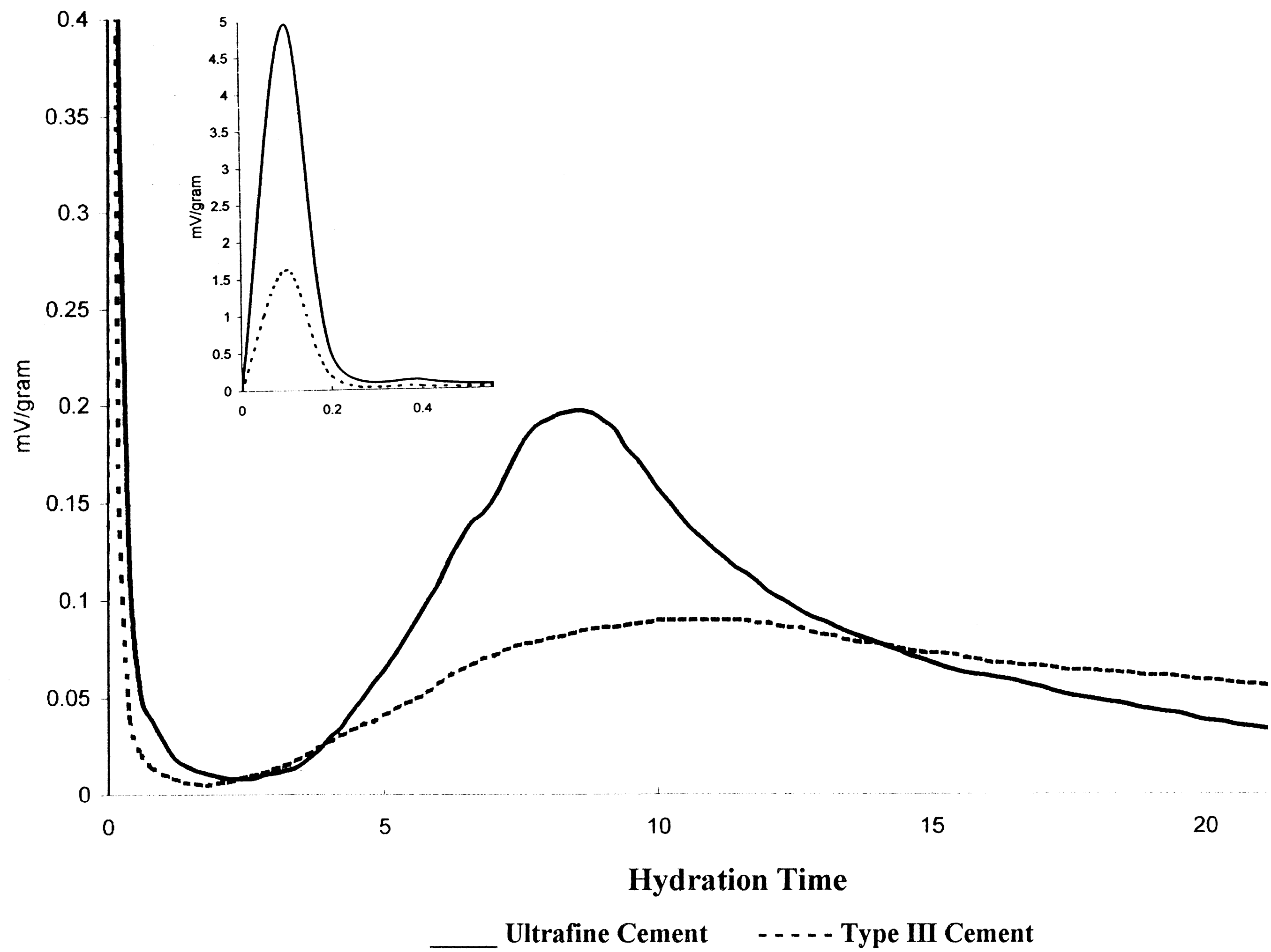


Fig. 1. Heat of hydration curves for ultrafine and Type III cements.

Table 4
Phase mineralogy of ultrafine and Type III cement from XRD analysis

| Phase | As-received cement |
|---|---|
| Alite | Type III >> ultrafine. |
| | Monoclinic II in Type III Rhombohedral in ultrafine |
| Belite | Type III > ultrafine |
| $C_3A$ | SAM-treated cement |
| | Type III >> ultrafine. Predominantly cubic in both |
| $C_4AF$ | Type III > ultrafine |
| Gypsum | Ultrafine > Type III |
| Hemihydrate | Ultrafine > Type III |
| Anhydrite | Type III > ultrafine |
| Free Lime | Type III > ultrafine |
| Periclase | Trace amount in Type III. Not detected in ultrafine |
| Thenardite | Trace amount in Type III. Not detected in ultrafine |
| Syngenite | Trace amount in Type III. Not detected in ultrafine |

reactions to be completed. The abnormally high heat generation is due to the high specific surface are of the ultrafine cement, which results in very rapid consumption of the available water. This leads to restricted hydration at later ages, as a result of which strength gain is low. Such a high heat is also likely to generate microcracks in the hardened cement paste/mortar.

In order to perceive the fast setting times of the ultrafine cement, the Vicat needle method (ASTM C 191–92) was used to test a series of cements. The results are presented in Table 3. Consistency of the paste of the ultrafine cement was obtained at W/C = 0.485, whereas it was at W/C = 0.30 and 0.35 for Type I and Type III cements, respectively.

Phase mineralogy is also considered to be a contributory factor for setting time abnormalities. X-ray diffraction (XRD) was used to identify the phases [10] and compare their relative proportions. Salicylic acid + methanol (SAM) treatment was applied [11] for a better delineation of the interstitial matrix phases and minor compounds. The results are summarized in Table 4. Though minor differences in the amount of identifiable phases do exist, it is apparent that the exceptionally fast setting characteristics of the ultrafine cement are not related to the phase mineralogy. As a matter of fact, its $C_3A$ content is lower than that of Type III cement, and the alkali sulfate compounds are also lower in amount.

## 3. Results

The objective was to extend the setting times of the ultrafine cement to values that are comparable to those of Type III cement. It was surmised that once normal setting times can be achieved, the problem of strength retrogression can be eliminated.

Table 5
Mix compositions

| Mix no. | Composition (mass percent) | Mortar flow (mm)[a] |
|---|---|---|
| 1 | Cement + 1.2% retarder | 41 |
| 2 | Cement + 1.0% retarder + 0.5% HRWRA | 60 |
| 3 | Cement + 1.0% retarder + 1.0% HRWRA | 103 |
| 4 | 80% Cement + 20% superfine FA + 1.0% retarder + 1.1% HRWRA | 116 |

[a] Tested according to ASTM C 230.

Table 6
Compressive strength of mortar

| Mix no. | Composition (mass percent) | Compressive Strength, MPa (psi) | | |
|---|---|---|---|---|
| | | 3 days | 7 days | 28 days |
| 1 | Cement + 1.2% retarder | 63.3 (9190) | 68.6 (9940) | 71.2 (10,330) |
| 2 | Cement + 1.0% retarder + 0.5% HRWRA | 57.5 (8430) | 68.2 (9890) | 71.4 (10,360) |
| 3 | Cement + 1.0% retarder + 1.0% HRWRA | 48.4 (7020) | 58.7 (8510) | 68.2 (9110) |
| 4 | 80% Cement + 20% superfine FA + 1.0% retarder + 1.1% HRWRA | 31.6 (4580) | 44.6 (6470) | 47.3 (6860) |

### 3.1. Mix compositions and flow characteristics

Three admixtures, namely a potent retarder (sodium salt of amine trimethylene phosphonic acid) available in a powder form, a sodium naphthalene polysulfonate high-range water-reducing admixture (HRWRA), also in a powder form, and an air-classified superfine Class F fly ash whose mean particle size was 3 μm, were considered for regulating the setting times of the ultrafine cement. After several trials at mixing different amounts of these admixtures singly and in combination, the mixes that proved to be promising are listed in Table 5.

Since ASTM C 109 specification requires a flowability of 110 ± 5mm, the two mix compositions which meet this criteria are mix nos. 3 and 4. It is evident that the flowability improved over 10% by replacing 20% of ultrafine cement with a corresponding amount of the superfine fly ash.

### 3.2. Compressive strength of mortar cubes

The compressive strength of mortar cubes (average of three), measured according to ASTM C 109 are presented in Table 6. These results demonstrate that incorporating a HRWRA causes a slight reduction in the early strength in comparison to the mix containing only the retarder, but its

Table 7
Setting times of ultrafine cement mixes

| Cement/mix composition | W/C | Initial set (min) | Final set (min) |
|---|---|---|---|
| Type I cement | 0.30 | 181 | 278 |
| Type III cement | 0.35 | 176 | 251 |
| Ultrafine cement + 1.0% retarder + 1.0% HRWRA | 0.485 | 161 | 222 |
| 80% Ultrafine cement + 20% superfine fly ash + 1.0% + 1.1% HRWRA | 0.485 | 183 | 248 |

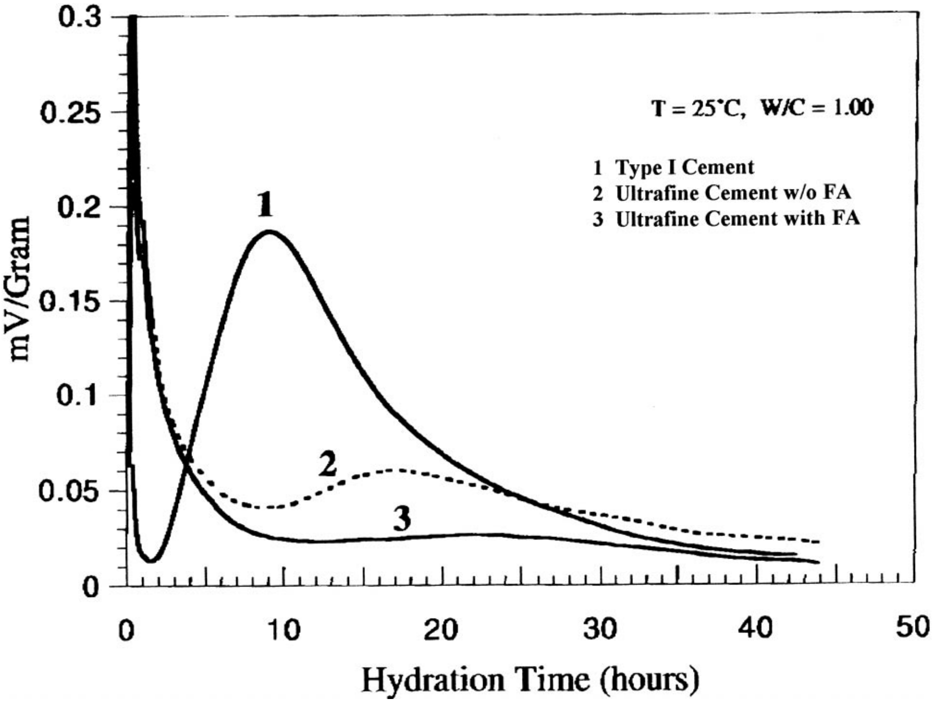


Fig. 2. Heat of hydration curves for the mix containing 100% ultrafine cement + 1.0% retarder + 1.0% HRWRA and the 80% ultrafine cement + 20% superfine fly ash + 1.0% + 1.1% HRWRA mix are compared with that of a Type I cement.

28-day strength exceeds that of the counterpart mix. The early strength decreases still further when the HRWRA dosage is doubled from 0.5% to 1.0% by mass of cement. Replacement of the cement with 20% superfine fly ash reduces the early strength.

### 3.3. Setting times

The superior flow characteristics of the mixes containing higher dosages of HRWRA (Table 5) led the authors to select these for further tests. Their setting times are compared with those of Type I and Type III cements in Table 7.

The setting times of the product containing 80% ultrafine cement + 20% superfine fly ash + 1.0% + 1.1% HRWRA are very similar to those of Type I and Type III cements.

### 3.4. Heat of hydration

The heat of hydration curves for the mix containing 100% ultrafine cement + 1.0% retarder + 1.0% HRWRA and the 80% ultrafine cement + 20% superfine fly ash + 1.0% + 1.1% HRWRA mix are compared with that of a Type I cement in Fig. 2. A slight hump is visible at the second peak position for the ultrafine cement + 1.0% retarder + 1.0% HRWRA mix, but the virtual absence of this hump in the other mix is attributed to the presence of superfine fly ash. Since this mix achieves a reasonably high strength at 3 days, effective hydration in this mix possibly begins after 40 h (limit of the experiment).

### 3.5. Particle size distribution

The particle size distribution pattern was studied using a laser particle size analyzer. The results are presented in Table 8. Each sample was tested twice, one as-received and the other after sonication for 1 min. These results indicate that the effect of 20% superfine fly ash addition on the particle size distribution characteristics of the mix is marginal. The mean diameter increases nominally when the superfine fly ash is added. No change in the distribution

Table 8
Particle size distribution characteristics measured by laser diffraction

| Mix no. | Surface area mean diameter (μm) | 10% Below (μm) | 50% Below (μm) | 90% Below (μm) |
|---|---|---|---|---|
| Ultrafine cement (as-received) | 0.85 | 0.28 | 2.83 | 7.32 |
| Ultrafine cement (sonicated) | 0.87 | 0.31 | 2.18 | 4.78 |
| Mix no. 3 (as-received) | 0.88 | 0.29 | 2.76 | 6.90 |
| Mix no. 3 (sonicated) | 0.81 | 0.29 | 1.91 | 4.33 |
| Mix no. 4 (as-received) | 0.94 | 0.32 | 2.78 | 7.55 |
| Mix no. 4 (sonicated) | 1.09 | 0.39 | 2.52 | 5.93 |

Table 9
Specific surface area

| Mix composition | Specific surface area ($cm^2/g$) |
|---|---|
| Ultrafine cement (as-received) | 7250 |
| Ultrafine cement + 1.0% retarder + 1.0% HRWRA | 8500 |
| 80% Ultrafine cement + 20% superfine fly ash + 1.0% + 1.1% HRWRA | 6600 |

pattern occurs when retarder and HRWRA are mixed in a powder form. There are definite indications that sonication for a brief period of time helps to dissociate particle agglomeration, if any.

### *3.6. Specific surface area*

Since ultrafineness is the principal characteristic of this cement, the specific surface areas were measured in accordance with ASTM C 204 (Table 9). The incorporation of superfine fly ash results in a slight decrease in specific surface area. The augmentation in specific surface area seen in the mix containing powder HRWRA and retarder is attributed to experimental error, because only 2.0% fine powders added to the ultrafine cement is unlikely to cause such a significant increase.

## 4. Conclusions

Increasing the specific surface area of a cement by a substantial amount, that is, grinding it much finer, can result in two major shortcomings, namely, strength retrogression at later ages and faster setting times. Both these abnormalities are attributed to finer particle size.

In order to eliminate these deficiencies in an ultrafine cement whose specific surface area was measured to be in excess of 7000 $cm^2/g$, experiments were carried out in the laboratory to incorporate different dosages of a retarder and a HRWRA, both in the powder form. Initial testing showed that very small amounts of these admixtures are required to modify the properties. The changes in some of the important physical and chemical properties that arise from the addition of these admixtures as well as a superfine fly ash are reported. Results indicate that up to 1.0% retarder and 1.0% HRWRA by mass of cement can be added to the benefit of the ultrafine cement. Replacement of cement with 20% superfine fly ash no doubt results in a still lower amount of heat generation, and improves the flowability, but the strength decreases in comparison to the other mixes.

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