Pergamon

Cement and Concrete Research 29 (1999) 713–717

CEMENT AND CONCRETE RESEARCH

Influence of high temperature on gypsum-free Portland cement materials

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Manuscript received 21 August 1997; accepted manuscript 29 January 1999

Abstract

Materials based on gypsum-free (GF) Portland cement cements resists better the effects of temperature over the range of 20–1200°C. Refractoriness of GF cement modified by addition of 12% silica fume closely approaches that of materials based on alumina cements. The content of $Ca(OH)_2$, which is lower in hardened GF cement, also is important from the standpoint of refractoriness. GF cement provides the possibility of preparing special materials without the need to change the chemical and phase compositions of the Portland clinker.

Keywords: Compressive strength; Durability; Alkali-activated cement; Portland cement; Refractory cement

Research of gypsum-free (GF) Portland cements is stimulated by Lukjanova et al. [1], who substituted gypsum with calcium ligninsulfonate + K_2CO_3. Their work was followed by Brunauer et al. [2] and Brunauer [3].

GF Portland cements, or alkali-activated cements, may be described as a system of ground Portland cement clinker (specific surface 300–700 m^2/kg) + anion-active surface active agent with hydroxyl groups (ligninsulfonate, sulfonated lignin, sulfonated polyphenolate) + a hydrolyzable alkali metal salt (carbonate, bicarbonate, silicate). The difference between GF and common Portland cement lies in the grinding (absence of gypsum and/or greater grinding fineness, grinding admixture) and in the set regulator. The basic property of GF cements is the possibility of preparing pastes, mortars, and concretes with very low water-to-cement ratio [2–6]. This characteristic is responsible for attainment of high early and long-term strengths, for the ability to set and harden at low and even subzero temperatures, and for high resistance to the effects of aggressive environments [7–11]. Our results (plus technological investigations) resulted in the design of GF Portland cements. GF cement was produced [12,13] on the industrial level (CEVA Prachovice Inc., Cement Banská Bystrica Inc.) and has been used for special projects in the building industry since 1989.

Hydrated inorganic materials of low porosity and high strength based on GF Portland cement (hereafter GF cement) have been subject to long-term research at the Department of Glass and Ceramics of the Institute of Chemical Technology in Prague [6–11]. The present communication is concerned with the behavior of GF cement mortars over the temperature range of 20–1200°C [14].

1. Experimental

The pastes and mortars were prepared with GF cement of 470 m^2/kg specific surface area from commercial production by CEVA Prachovice Cement Works Inc. (Czech Republic). The clinker had the following chemical composition: 66.5% CaO, 21.8% SiO_2, 4.49% Al_2O_3, 2.76% Fe_2O_3, CaO_{free} 1.2%, and 1.05% SO_3. Standard Portland cement of class 42.5 with specific surface 320 m^2/kg, made in the same cement works, was used as reference material. Silica fume containing 98% SiO_2 was used in some of the experiments, as well as alumina cement Lafarge Fondu containing 39% Al_2O_3, 37% CaO, 4.3% SiO_2, and 15.6% Fe_2O_3 + FeO.

The cements used (GF, Portland, and alumina cement) have very different rheological properties at given water-to-cement (w/c) ratios. For example, GF cement mortar with w/c ratio = 0.50 is settling, whereas Portland cement mortar with the same w/c ratio has a plastic consistency. The GF and alumina cment mortars were made with different w/c ratios, but with almost identical rheological properties corresponding to Portland cement mortar with w/c ratio = 0.50. The rheological properties (workability) of mortars was measured by a method described in European standard ENV 459 (spreading on the flow table). The mortars (cement:sand = 1:3) were prepared from quartz sand of continuous granulometry (standard cement-testing sand) or from corundum grain size fractions 0–1 mm and 1–2.5 mm. The w/c ratios ranged from

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PII: S0008-8846(99)00026-5

0.27 to 0.32, depending on the aggregate. In some instances, 5 to 12 wt% of the GF cement was substituted with silica fume [w/c = w/(cement+silica fume]. In place of gypsum as regulating additive, Na_2CO_3 and commercial-grade sodium lignosulfonate (virtually free of monosaccharides) were used. The regulating substances were added in amounts ranging from 3 to 4 wt% of GF cement. Standard mortars with w/c ratio = 0.50 were prepared from the PC 42.5. The test specimens 4 × 4 × 16 cm were kept in a medium of saturated water vapor for 24 h and then in water at 20°C until day 28.

The specimens for determining the effects of temperature over the range from 20–1200°C were prepared in the same way. In reference experiments, mortars were prepared from alumina cement using w/c ratio = 0.43. All of the mortar specimens were subject to elevated temperature exposure after 7 days of hydration and subsequent drying at 105°C. The heating rate was 5°C/min and the time of exposure at the respective temperature was 2 h. The strength was tested after cooling the specimens down. Strength at high-temperature deformation to ISO 1893 (hollow specimens) was determined. Before determination, the specimens were heated to the classification temperature (that at which the linear deformation due to elevated temperature exposure did not exceed 1.5%).

The products of hydration at high-temperature exposure were studied by the standard methods of thermal analysis, scanning electron microscopy including energy-dispersive spectrometer, and X-ray diffraction spectroscopy.

2. Results and discussion

The effects of temperatures over the range of 20–1200°C on hardened mortars of Portland cement and GF cement are shown in Figs. 1 and 2.

For comparison, the diagrams include plots of strengths attained with specimens prepared from Lafarge alumina cement (containing Al_2O_3 and CaO) and the same aggregate, and having the same workability as those of GF cement. The course of strength in cooled-down condition (after 2-h elevated temperature exposure) for Portland cement exhibits a virtually monotonous loss in strength in terms of increasing temperature. Drying at 105°C causes an increase in strength of 20–30%. In the 800–1000°C region, the residual strengths of the Portland cement specimens are very low, on the order a few MPa. Melting takes place at temperatures above 1000°C and the cold strength rises correspondingly.

In the case of GF cement mortars, drying at 105°C causes a marked increase in strength of 40–55% (cf. Figs. 1 and 2). The strength then remains practically unchanged roughly up to 400–500°C. Over the range above 500–550° the strength falls dramatically by more than 50%, which is more than with the Portland cement mortars. The loss in strength then proceeds similarly to that of Portland cement specimens. However, the residual strengths within the 800–1000°C temperature range are higher.

A significant increase in the strength of GF cement mortars after exposure to high temperatures was achieved by additions of silica fume (Fig. 3). The GF-silica fume cement mortar specimens showed considerably higher strengths up to 500°C, and the fall in strength was shifted up to about 800°C. Over the temperature range of 700–800°C, the mortars still exhibited strengths exceeding 70 MPa, which is substantially higher than those based on alumina cement. Exposure at 800–1000°C again causes a loss in strength, but the residual strength of the GF-silica fume mortar was substantially higher than that of GF cement mortar alone, and it was comparable to that of alumina cement mortar.

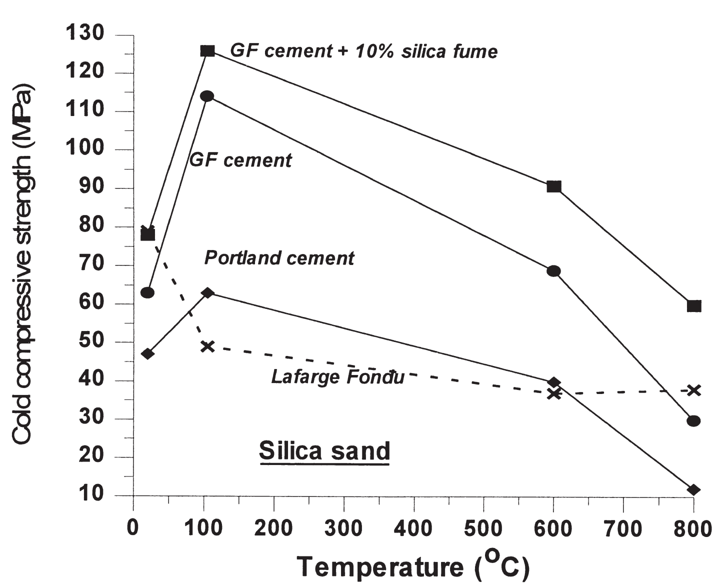

Fig. 1. Cold compressive strength vs. temperature of firing (2 h), GF mortars w/c = 0.30, Portland cement mortar w/c = 0.50, alumina cement mortar w/c = 0.43, and silica sand.

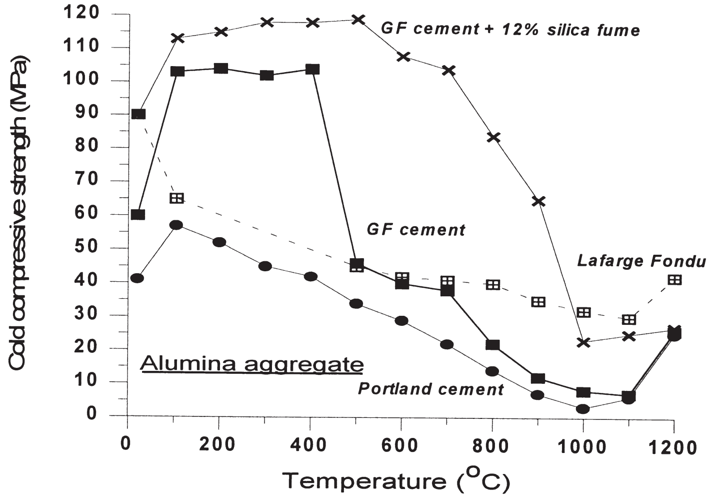

Fig. 2. Cold compressive strength vs. temperature of firing (2 h), GF mortars w/c = 0.30, Portland cement mortar w/c = 0.50, alumina cement mortar w/c = 0.43, and alumina aggregate 0–2.5 mm.

Fig. 4 shows the results of resistance to high-temperature deformation according to ISO 1893. The measurements show that the difference between the $t_{0.5}$ temperatures of the Lafarge alumina cement and the GF-silica fume cement amounts to only 5°C, even though different types of clinker are involved. The high resistance of GF cement-based materials to aggressive solutions of salts is due mostly to the low porosity of the materials. The reduced porosity is a result of the superior workability of GF mixes, which allows mortars and concretes to be prepared with w/c ratios of 0.27–0.32 and even lower. Hardened GF cement has a microstructure different from that of hardened Portland cement. The GF cement microstructure does not contain the characteristic formations of portlandite [$Ca(OH)_2$]. The microstructure of hardened $Ca(OH)_2$ (portlandite) is characterized by its high compactness and dispersivity of the hydration products. These factors play a role in the superior high-temperature properties (refractoriness) of GF cements as compared to those of Portland cement.

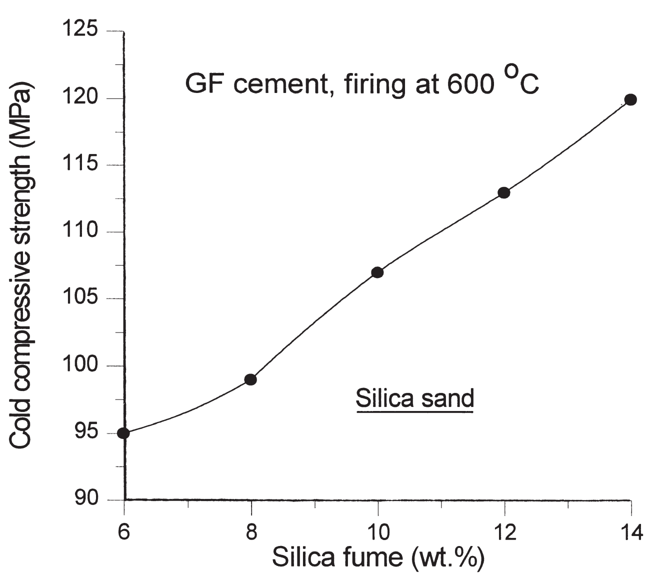

Fig. 3. Cold compressive strength vs. silica fume contents in GF cement, mortar w/cement+silica fume = 0.27, fired at 600 °C for 2 h, silica sand 0–2 mm.

The content of X-ray detectable $Ca(OH)_2$, which is lower in hardened GF cement (Fig. 5), is important from the standpoint of refractoriness. Study of the composition of the hydration products by X-ray diffraction and thermogravimetric analysis in hardened GF cement showed that a part of the $Ca(OH)_2$ (at least 40–50%) is in an amorphous form. During hydration of GF cement, the ultrafine (up to amorphous) form develops as a result of the steric conditions ensuing from the low w/c ratio. This ultrafine form of $Ca(OH)_2$ plays its distinct role during high-temperature exposure of hardened GF cements (in the 550°C region) in contrast to the coarser form of $Ca(OH)_2$ (massive microcrystals) in the microstructure of hardened Portland cement. This is probably why the strength of GF cements decreases relatively more during high-temperature exposure than that of Portland cement. The addition of silica fume eliminated completely the loss in strength of GF cement due to heating in the 500°C region as a result of its bonds to $Ca(OH)_2$ or CaO. The compressive strength of the GF-silica fume cement mortar after exposure at this temperature was roughly three times higher than that of the mortar bonded by GF cement alone. The higher residual strengths of GF cement compared to Portland cement can be explained primarily by the higher initial strengths of the former. These higher strengths result from compaction at a lower w/c ratio and from the larger specific surface area of GF cement. The high-temperature properties of GF cement are favorably affected by the absence of gypsum, which (in the form of sulfate anions) influences negatively the refractoriness. The

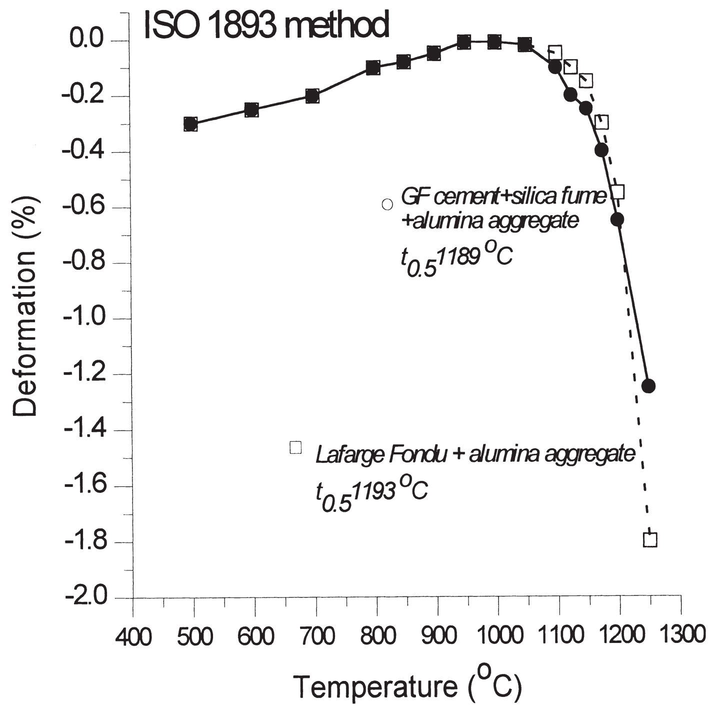

Fig. 4. Deformation vs. temperature, ISO 1893 method, GF cement+silica fume mortar w/c = 0.30, alumina cement w/c = 0.43, and alumina aggregate 0–2.5 mm.

sulfate anions (from gypsum and ettringite in the case of Portland cement) affect strongly the properties of the clinker melt, reducing considerably its viscosity and surface tension [15]. The melt of hardened GF cement arising in the 1100°C temperature region has almost similar properties of melt of alumina cement with a lower content of Al_2O_3, as shown in the course of deformation vs. temperature (ISO 1893 method) (Fig. 5).

The results obtained indicate that the durability of hardened GF cements is distinctly superior to that of standard Portland cement. They also give evidence for the possibility of using GF cement in the preparation of refractory concrete

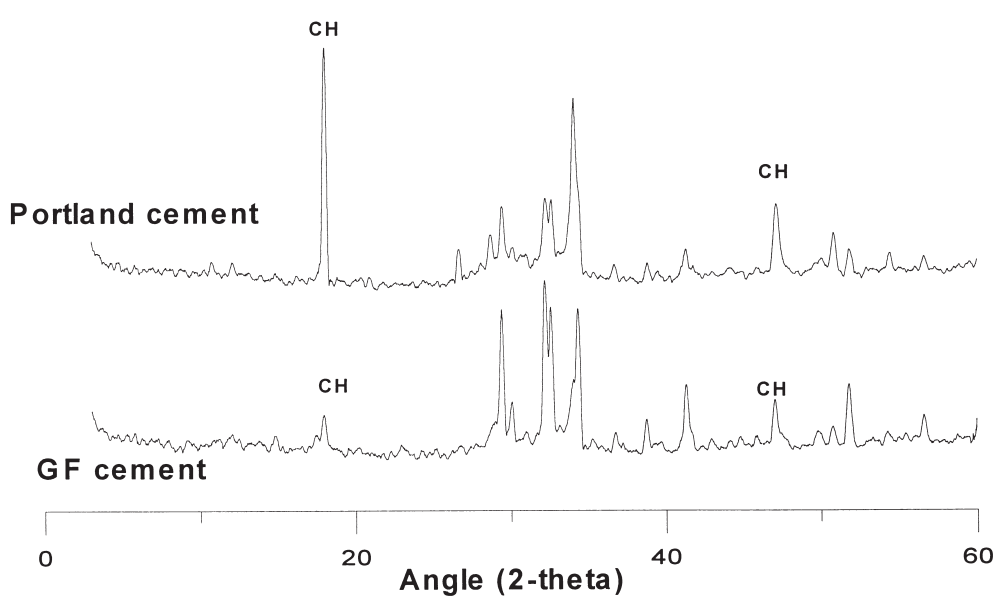

Fig. 5. Hydrated cement pastes of GF and Portland cement at 28 days, 20°C, drying at 105°C.

for application temperatures of 1100–1200°C. The high-temperature properties of materials based on GF cements (with silica fume) come close to those of alumina cements with a lower Al_2O_3 content.

3. Conclusions

Materials based on GF cements resist better the effects of temperature over the range of 20–1200°C and their refractoriness closely approaches that of materials based on alumina cements. Incorporation of silica fume is important to reduce strength loss at temperatures above 400–450 °C. The microstructure of hardened GF cement differs from that of hardened Portland cement. The differences are due to the low porosity and high dispersity of hydration products in hardened GF cements. The structure of hardened GF cements does not contain the formations characteristic of hardened Portland cement, such as ettringite and massive microcrystals of $Ca(OH)_2$. In hardened GF cement, $Ca(OH)_2$ is present in partially amorphous form. GF cement provides the possibility of preparing special materials without the need to change the chemical and phase compositions of the clinker.

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