HIGH-TEMPERATURE PROPERTIES OF A BINDER BASED ON GYPSUM-FREE PORTLAND CEMENT OVER THE TEMPERATURE RANGE OF 20 TO 1200 °C

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Hydration products of GF cement differ from those of Portland cement in morphology of Ca(OH)$_2$ which in hydrated GF cement is in an extremely fine, and for the most part X-ray amorphous form. The morphologically different Ca(OH)$_2$ in hardened GF cement is very disadvantageous with respect to the development of strength at temperatures at which Ca(OH)$_2$ is decomposed. This fact is responsible for a rapid decrease in strength of hydrated GF cement at about 500 °C. Over the entire temperature range of 20 to 1200 °C hydrated GF cement exhibits a higher post-firing strength than Portland cement made of clinker of the same composition. Mortar of GF cement with corundum aggregate and stabilized with 15% silica fume attained $t_{0.5}$ = 1189 °C after firing at 1200 °C (measured to ČSN ISO 1893), which is a performance property comparable to that of alumina cement with a lower Al$_2$O$_3$ content.

Keywords: Gypsum-free, Portland cement, Refractory, High-temperature properties

INTRODUCTION

Hydrated inorganic materials of low porosity and high strength, based on gypsum-free Portland cement (hereinafter GF cement) have been a subject of long-term research at the Department of Glass and Ceramics of the Institute of Chemical Technology in Prague. GF cement is based on ground clinker of Portland cement (hereinafter PC) with a specific surface area of 450 to 600 m^{2}kg^{-1} whose setting is controlled by a synergically acting mixture of a sulphonated electrolyte (sulpho-nated lignine, sulphonated polyphenolate) with an alkali metal salt (Na$_2$CO$_3$, K$_2$CO$_3$) [1 - 7]. The possibility of working materials of GF cement (pastes, mortars and concretes) at very low water-cement ratios (of down to 0.20 with pastes) while retaining acceptable workability is their main outstanding property. The properties of GF pastes, mortars and concretes, among others their ability to achieve high early strengths and their setting and hardening at low and subzero temperatures, have been described by a number of published studies [2 - 7].

The present paper deals with the effects of temperature over the range of 20 to 1200 °C on the properties of hardened GF cements [8, 9].

EXPERIMENTAL

In the experiments use was made of gypsum-free cement produced commercially by CEVA Prachovice, a.s. under the designation GF cement 52.5 R HI-Q [7], with a surface area (Blaine) of 480 m^2 kg^{-1}. Gypsum as setting regulator was replaced by a combination of sodium lignosulphonate Eucobet 300 (manufactured by Holderchem, Switzerland) with Na$_2$CO$_3$. Portland cement was used as reference to allow comparison with the behaviour of gypsum-free Portland cement, and for this purpose clinker made by the same manufacturer was employed (CEVA Prachovice, a.s.). The Portland cement was CEM I 42.5R (the highest strength grade manufactured by the cement works). Both cements were made of the same clinker having the following composition (wt.%): CaO 63.2, SiO$_2$ 20.8, Al$_2$O$_3$ 5.8, Fe$_2$O$_3$ 3.3, MgO 3.6, K$_2$O + Na$_2$O 2.1, free CaO 0.88; the content of gypsum in the PC was 2.85 wt.% (as SO$_3$). The specific surface area of PC was 320 m^2 kg^{-1} (Blaine). Alumina cement served for comparison with the high-temperature properties of the hydrated modified GF cement. The classical low-alumina Lafarge Fondu cement with 40 wt.% Al$_2$O$_3$ was selected for this purpose.

The mortars were prepared with white crushed co-rundum as aggregate, using the fractions F1 = 0.125 mm and F2 = 0.2 mm in ratio 2.5 : 1. The corundum aggregate was chosen because of its satisfactory inertness with respect to the cement matrix. Use of the corundum aggregate allows the properties of the binders proper to be studied without having to deal with any interfering reactions between cement and the aggregate in the

course of firing. Silica fume (manufactured by Elkem, Norway), containing approx. 98 wt.% SiO_2, was employed as another admixture.

Cement pastes of gypsum-free Portland cement were prepared with $w = 0.25$, and 0.85 wt.% sodium lignosulphonate and 1.70 wt.% Na_2CO_3 (both of the weight of cement) were used as setting modifiers in place of gypsum. The PC pastes were prepared with $w = 0.32$ and at that water-cement ratio had identical rheological properties as the GF pastes. All the samples were cured in a medium of 100 % relative humidity for 7 days at about 22 °C. In the case of specimens for X-ray and thermal analyses, and for studying the morphology under the electron microscope, the hydration was stopped by saturating with acetone and drying in vacuo. The compressive strengths were measured after 7 days of hydration on mortars of gypsum-free cement free from admixtures, on those with silica flue admixture, and on mortars of Portland cement and those of alumina cement. White ground corundum was employed as aggregate in the mortars. The water-cement ratios of the mortars were determined on the basis of identical rheological properties (workability). For the systems PC + corundum, GF cement + corundum + silica flume (0 - 15 wt.%), GF cement + corundum + silica fume (more than 15 wt.%), and for the system alumina cement + corundum the water-cement ratios were 0.45, 0.32, 0.33 and 0.42, respectively.

The test specimens for compressive strength determination were prisms 20 × 20 × 100 mm in size, and the same specimens were employed for determining the additional linear changes. The dimensions of the other test specimens conformed to the respective standard specifications. All the test specimens were cured in an environment of 100 % relative humidity for 7 days at about 22 ºC.

The following standard tests were employed in the determination of refractory properties of the mortars:

a) Resistance to deformation under load at high temperatures (ČSN ISO 1893)
b) Refractoriness (ČSN ISO 528 and ČSN ISO 1146)
c) Additional linear dimensional changes (to standard test modified for use of specimens 10 × 20 × × 100 mm in size).

The composition of hydration products was studied on samples of hardened cement specimens (after destructive tests) by X-ray diffraction (Seifert, FRG), GTA and DTA (Mettler, USA). The morphology of the samples was examined by means of the JEOL Superprobe scanning electron microscope fitted with the ED spectrometer (Japan).

RESULTS AND DISCUSSION

The composition of hydrated GF cement differs little from that of hardened PC. GF cement is characterized by absence of diffraction lines of
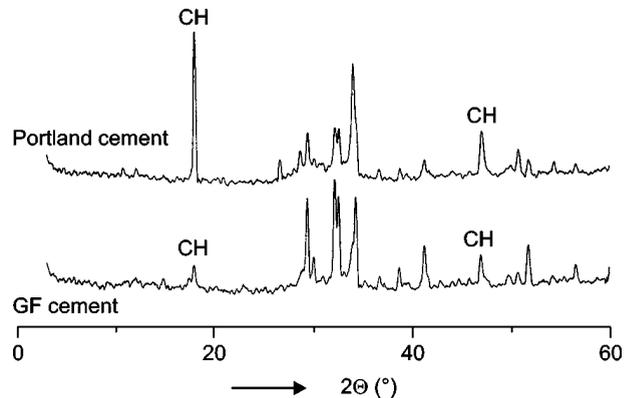

Figure 1. X-ray diffraction pattern of hydrated pastes of GF cement and Portland cement (28 days, 20 °C, dried at 105 °C).

monosulphate (C_4AH_{12}) and ettringite ($C_6A_3H_{32}$) as a logical consequence of the replacement of gypsum in the cement (figure 1). The intensities of diffraction lines of $Ca(OH)_2$ (abbreviation CH in figure 1) in hydrated GF cement are substantially lower than those in conventional Portland cement (figure 2). The results of GTA show that after 7 days of curing, hydrated Portland cement contained 11 wt.% $Ca(OH)_2$ whereas hydrated GF cement only 9 wt.%. The results are in apparent contradiction and indicate that in hydrated GF cement the $Ca(OH)_2$ is found mostly in X-ray amorphous form. The presence of X-ray amorphous form of $Ca(OH)_2$ is also indicated by the fact that unlike the intensity of $Ca(OH)_2$ lines, the intensities of CaO lines in the fired samples of both cements were comparable.

In the case of fired hardened GF cement, X-ray diffraction analysis revealed decomposition of alite (C_3S) yielding secondary belite (C_2S) and free CaO already at temperatures from 800 ºC upwards. A detail
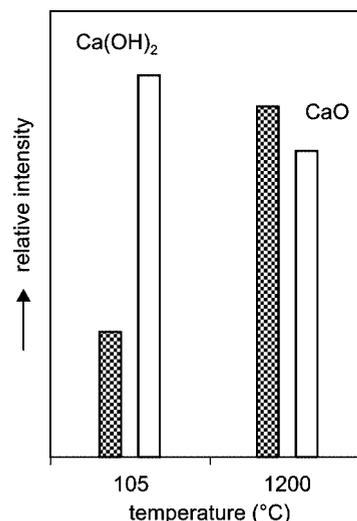

Figure 2. Relative intensities of $Ca(OH)_2$ and CaO diffractions in GF cement and Portland cement after drying at 105 °C and after firing at 1200 °C. ■ - GF cement, □ - Portland cement
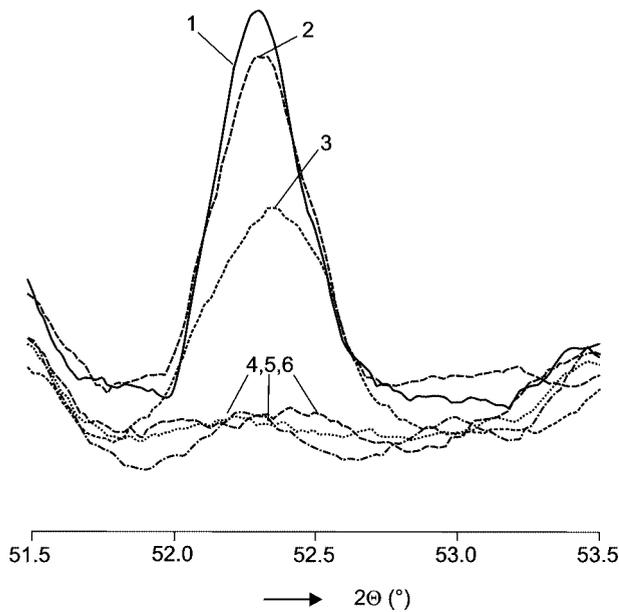
Figure 3. Detail of X-ray diffraction pattern - diffraction of C_3S (0.1764 nm) in hydrated GF cement fired at temperatures of 105 to 1200 °C. 1 - 105 °C, 2 - 300 °C, 3 - 800 °C, 4 - 1000 °C, 5 - 1100 °C, 6 - 1200 °C
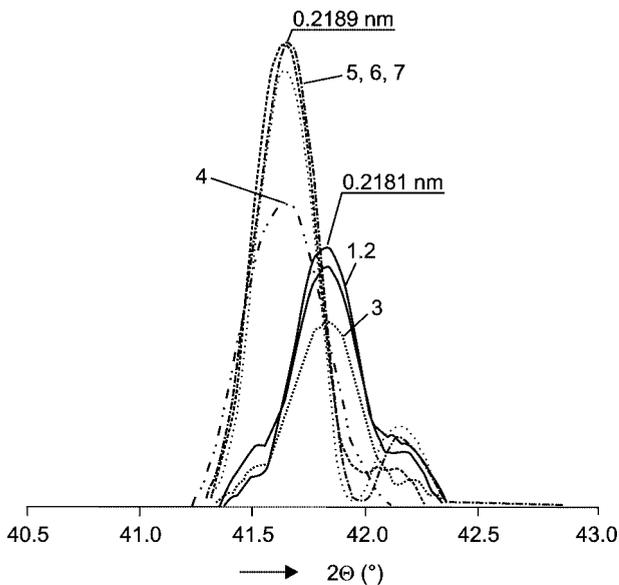

Figure 4. Detail of X-ray diffraction pattern - diffraction of C_3S (0.2181 nm) and C2S (0.2189 nm) in hydrated GF cement fired at temperatures of 105 to 1200 °C. 1 - 105 °C, 2 - 300 °C, 3 - 500 °C, 4 - 800 °C, 5 - 1000 °C, 6 - 1100 °C, 7 - 1200 °C

of X-ray pattern in figure 3 in the region of the 0.1764 nm line shows that the intensity of the C_3S diffraction line decreases sharply after firing at 800 °C and disappears completely after firing at 1000 °C. The decomposition of C_3S is further demonstrated by the section of the X-ray diffraction pattern with diffractions

of C_3S (0.2181 nm) and C_2S (0.2189 nm). The diffractions of C_3S and C_2S, which for the most part overlap, are illustrated in figure 4. The figure shows that the intensity of C_2S diffraction increases sharply after firing at 800 °C and at 1000 °C becomes stabilized up to the final temperature of 1200 °C. At the same time, intensity of C_3S diffraction decreases. The subsequent increase in CaO diffraction intensity (figure 5) over the range of 800 to 1000 °C, which is in agreement with the results mentioned above, testifies to the fact that at this temperature C_3S has already decomposed to C_2S while yielding free CaO. It is also interesting that up to the temperature of 550 °C the relative intensity of CaO diffraction (figure 5) is zero while according to the decomposition temperature all of the $Ca(OH)_2$ must already have decomposed. This finding is indicative of transient existence of amorphous CaO which converts to its crystalline form at the higher temperatures.

Compressive strength measurements of hardened GF and PC after firing over the 20 to 1200 °C temperature range were carried out for the purpose of comparing the high-temperature behaviour of the two cements. The results are plotted in figure 6.

The courses of post-firing strengths are indicative of the following deviations in the behaviour of the two cements:

1. *Higher residual post-firing strengths of GF cement*. The results showed that over the entire temperature range (20 - 1200 °C) GF cement
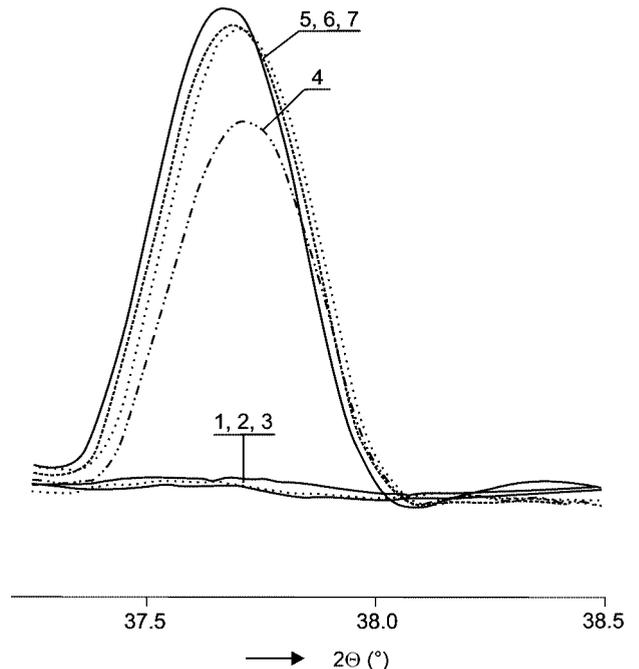

Figure 5. Detail of X-ray diffraction pattern - diffraction of CaO (0.2054 nm) in hydrated GF cement fired at temperatures of 105 to 1200 °C. 1 - 105 °C, 2 - 300 °C, 3 - 550 °C, 4 - 800 °C, 5 - 1000 °C, 6 - 1100 °C, 7 - 1200 °C

attains higher residual strengths than PC. The post-firing strengths of GF cement established are obviously closely related to its higher "starting" strengths, resulting from a faster course of hydration and lower porosity compared to PC. In the case of GF cement, at higher temperatures a significant role is played by the absence of gypsum which has a negative effect on high-temperature properties of Portland cement by promoting formation of melt.

2. *Rapid decrease of strength of GF cement after firing at about 500 °C*, related to decomposition of $Ca(OH)_2$. The results of GTA show that this rapid loss in strength during decomposition of $Ca(OH)_2$ takes place in spite of the lower content of $Ca(OH)_2$ content in GF cement than that in PC cement. The difference in the behaviour of GF cement and PC is therefore not due to more difference in $Ca(OH)_2$ content in the two cements. $Ca(OH)_2$ is also contained in the hydration products of PC but there occurs no rapid decrease in strength at the temperature of $Ca(OH)_2$ decomposition.

3. The cause of this different behaviour of the two cements at about 500 °C was studied by means of SEM. Figure 7 (hydrated PC) shows a typical crystal of $Ca(OH)_2$ in the form of hexagonal portlandite embedded in a virtually amorphous C-S-H phase. The C/S ratio in the C-S-H phase, determined by ED spectrometer analysis, amounted on the average to 2.1. No morphologically distinguishable form of $Ca(OH)_2$ was found in hydrated GF cement (not even under the maximum available magnification of 20,000 ×). The C/S ratio in the C-S-H phase, determined by

ED spectrometer analysis, was higher in hydrated GF cement than in PC, and amounted on the average to 2.65.

Study of the morphology of fracture surfaces revealed a significant difference in $Ca(OH)_2$ morphology between the hydration products of GF cement and PC. It may therefore be assumed that the presence of a morphologically different form of $Ca(OH)_2$ in GF cement in place of crystalline portlandite is responsible for the abrupt loss in strength at temperatures of about 500 °C. The presence of a dissimilar form of $Ca(OH)_2$ in GF cement results in an apparent discrepancy between the results of GTA and X-ray analyses. According to GTA, the content of $Ca(OH)_2$ in hydrated GF cement is lower by only about 3% compared to conventional Portland cement, whereas the intensity of the strongest $Ca(OH)_2$ diffraction line (0.490 nm) in hydrated GF cement attains only 1/7 of intensity of the corresponding $Ca(OH)_2$ line in hydrated PC.

3. *Minimum strength of Portland cement after firing at 1000 °C and steady decrease of strength of GF cement up to 1200 °C*. The minimum strength at about 1000 °C (figure 6) is probably due to the presence of gypsum in PC, which has a fluxing effect. On the other hand, the steady decrease in strength of GF cement in terms of temperature up to 1200 °C indicates that no undesirable formation of melt takes place. The decrease of strength at about 500 °C, due to decomposition of $Ca(OH)_2$, eliminates to a certain degree the advantage of higher "starting" strength of GF cement compared to conventional PC.

On the basis of the results obtained it may be assumed that in the case of GF cement it would be more advantageous to combine the $Ca(OH)_2$ directly during hydration of the cement instead of binding the free CaO only after the $Ca(OH)_2$ has decomposed, as is the case of classical refractory concretes based on Portland cement [10]. In this way it would be possible to avoid the great loss in strength due to decomposition of $Ca(OH)_2$ in GF cement, and also to eliminate the risk of rehydration of free CaO (formed by decomposition of $Ca(OH)_2$).

Further experiments were aimed at verifying the possibility of improving the high-temperature properties of GF cement by binding the $Ca(OH)_2$ by means of active additives in the course of cement hydration. Silica fume and finely ground $Al(OH)_3$ (use of the latter has not yet been described) were selected for binding $Ca(OH)_2$ in GF cement [8,9]. The results obtained with additions of $Al(OH)_3$ to GF cement [9] will be published later on.

The results of GT analyses prove that the efficiency of binding $Ca(OH)_2$ in hydrated GF cement with an admixture of silica fume is substantially higher (by about 100%) than in the case of conventional PC. The difference in the efficiency of binding $Ca(OH)_2$ in
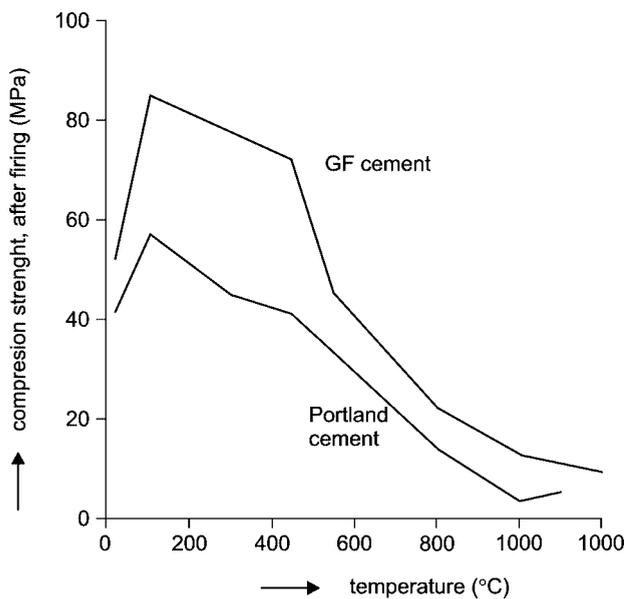

Figure 6. Strength of corundum mortars after firing, GF and Portland cement, 7 days of hydration.
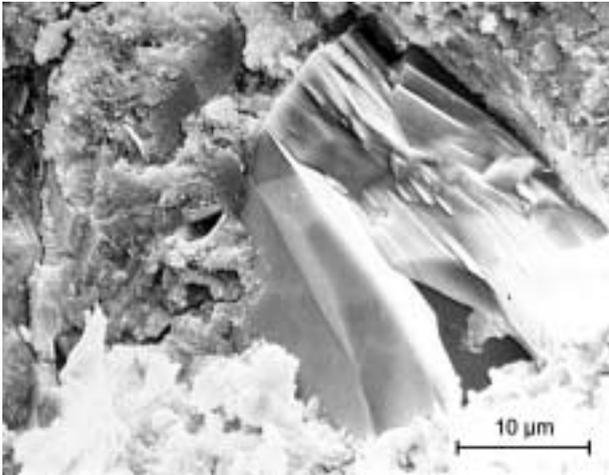
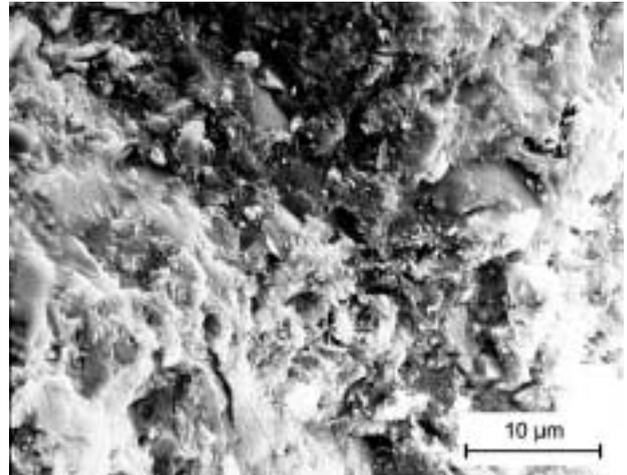Figure 7. Fracture surface of hardened Portland cement paste, 7 days of hydration.

Figure 8. Fracture surface of hardened GF cement paste, 7 days of hydration.

GF cement compared to conventional PC has not yet been fully explained. However, it may be assumed that the higher efficiency of silica fume addition to GF cement is due to the established higher fineness of X-ray amorphous $Ca(OH)_2$ in GF cement, and possibly also due to the alkaline activation of the reaction between SiO_2 of silica fume and $Ca(OH)_2$ in hydrating GF cement (as Na_2CO_3 is a part of its setting regulator). An addition of 10 to 15 wt.% of silica fume is sufficient for virtually complete elimination of $Ca(OH)_2$ liberated during hydration of GF cement (figure 9).

X-ray diffraction analyses of hydrated GF cement after firing at 1200 °C indicate that the phase compositions of fired hydrated GF cement with an addition of 10 and 20 wt.% silica fume show qualitative differences. It was found that the higher admixture of silica fume (20 wt.%) brings about formation of gehlenite (C_2AS), which is not produced by the lower addition (10 wt.%). Formation of gehlenite in terms of the amount of added silica fume can be well demonstrated by its strongest line (0.2863 nm), c.f. figure 10. Gehlenite can be found in hydrated GF cement after firing at 1200 °C only when the amount of silica fume added was in excess with respect to $Ca(OH)_2$. The diffraction patterns of GF cement containing 20 wt.% silica fume exhibit absence of diffraction 0.727 nm, which probably belongs to C_4AF. In the case of the other lines of C_4AF occurrence (2.77, 2.68 and 2.62 nm) one can also observe a decrease in intensity by 50, 100 and 30 % respectively. Participation of C_4AF in the formation of gehlenite is therefore probable. Lower relative intensities in the diffraction pattern of sample with 20 wt.% silica fume were also exhibited by diffractions of C_2S and C_3S. The diffractions of C_2S and C_3S. are usually superimposed but one can assume that at 1200 °C the C_3S was already decomposed. The lower relative intensities in the region of occurrence of C_2S and C_3S may thus indicate that also C_2S takes part in the formation of gehlenite.

The results of determining the post-firing strengths (figure 11) confirm that stabilization of GF cement with silica fume additions results in superior compressive strength of hydrated GF cement all over the firing temperature range of 105 to 1200 °C. Figure 11 also shows that a relatively small addition of silica fume (5 wt.% of cement weight) has a relatively small effect on post-firing strength, while an addition of 10 to 15 wt.% improves significantly the post-firing strength of hydrated GF cement. Namely, an addition of 10 to 15 wt.% silica fume increases the strength of GF cement after firing at 550 and 800 °C roughly by 100% compared to GF cement free of silica fume addition.
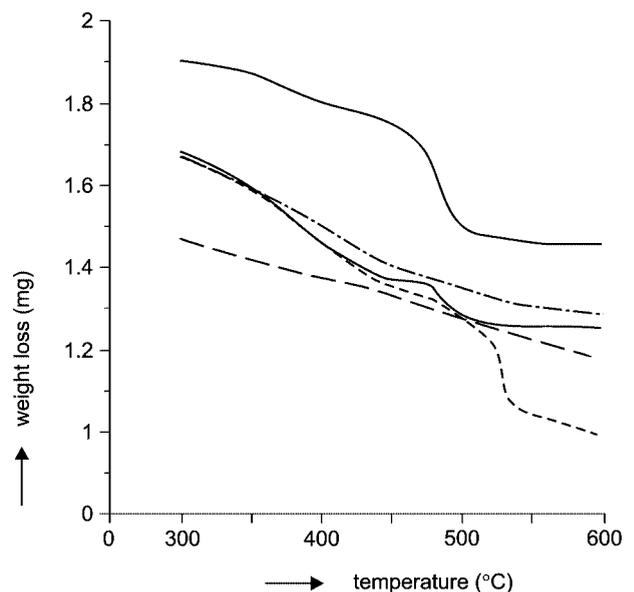

Figure 9. Detail of GTA curves for GF cement with ad addition of silica flue, 7 days of hydration.
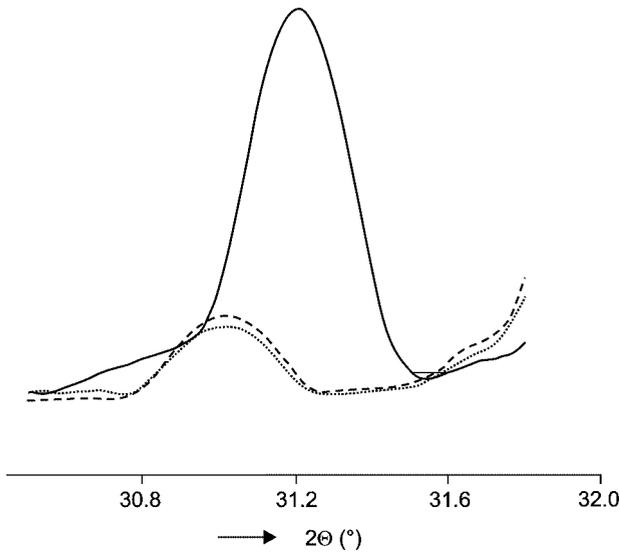—— 0, - - - - 5, —— 10, - · - · - 15, – – – 20 wt.% silica fume

Figure 10. Detail of X-ray diffraction pattern, diffraction of gehlenite C2AS (0.2863), in GF cement with silica fume addition, after 7 days of hydration and subsequent firing at 1200 °C. · · · · · - 0, ——— - 10, - - - - - 20 wt.% silica fume
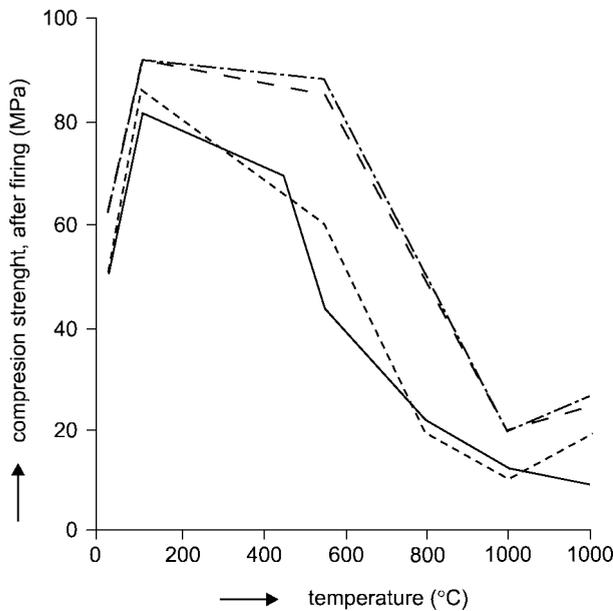

Figure 11. Strength of corundum mortars after firing, GF cement with silica fume admixture, 7 days of hydration.
——— - 0, - - - - - 5, – – – – - 10, – · – · – 15 wt.% silica fume

The strengths of GF cement modified in this way do not decrease below 20 MPa even after firing at 1000 and 1200 °C. The morphology of a fracture surface of GF cement containing silica fume addition after firing at 1200 °C is shown in figure 12.

The refractory properties such as resistance to deformation at high temperature under load were determined on mortars of GF cement with 12 wt.%
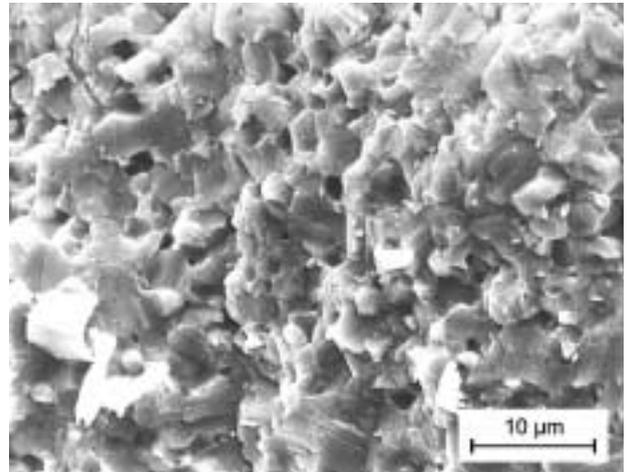

Figure 12. Fracture surface of hardened GF paste with silica fume admixture, after 7 days of hydration and subsequent firing at 1200 °C.

silica fume, and compared with those of low-alumina cement Lafarge Fondu. The composition of the mortars was derived from optimum rheological properties and strengths achieved before firing. The record of measuring the high-temperature resistance to deformation under load of GF cement-corundum mortar stabilized with 12 wt.% silica fume provided $t_{0.5}$ = 1189 °C (figure 13). The maximum elongation during the measurement did not exceed 0.752 %. The value of
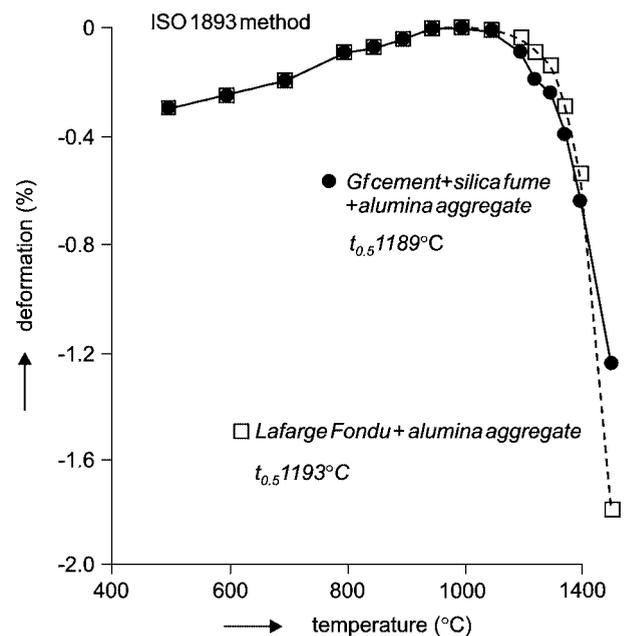

Figure 13. Resistance to deformation under load at high temperature of cement-corundum mortar of GF cement with an admixture of 12 wt.% silica fume, and that of low-alumina Lafarge Fondu cement, measured on test specimens after firing at 1200 °C.

$t_{0.5}$ = 1193 °C, established for the fired test specimen of Lafarge Fondu alumina cement, corresponded roughly to the company´s specification for highdensity refractory concrete with corundum aggregate, i.e. $t_{0.5}$ = 1200 °C. On a non-fired specimen after drying, the $t_{0.5}$ value amounted to 909 °C. The maximum elongation established on an unfired specimen was 0.147 %, and that on a pre-fired one was 0.704 %.

With respect to practical utilization of refractory concretes, additional linear changes, from which their classification temperature is derived, represent a significant factor. Determination of classification temperature of individual refractory cement-corundum mortars can be partially replaced by measuring the additional linear changes after firing at 1200 °C. This was effected on 20 × 20 × 100 mm test specimens before measuring their post-firing compressive strength. The linear additional changes of both pure and stabilized GF cement after firing at 1200 °C did not exceed 1 %.

CONCLUSIONS

The hydration products of GF cement differ from the products of hydration of PC essentially in the morphology of $Ca(OH)_2$; in the case of GF cement, the $Ca(OH)_2$ occurs in very fine, mainly part X-ray diffraction amorphous form.

Over the entire temperature range of 20 to 1200 °C, GF cement exhibits higher post-firing compressive strength than Portland cement made of the same grade of clinker. For possible use of GF cement in refractory concrete, decomposition of the non-hydrated portion of alite represents one of the possible sources of undesirable free CaO.

In hydrating GF cement, reactivity of silica fume with respect to $Ca(OH)_2$ is substantially higher than that of PC. $Ca(OH)_2$ formed during hydration of GF cement can be effectively eliminated by an addition of about 10 - 15 wt.% silica fume.

The refractory properties of GF cement stabilized with an admixture of silica fume are comparable to those of alumina cement with a lower Al_2O_3 content.

Acknowledgement

References

1. Lukyanova O.I., Segalova E.E., Rebinder P.A.: Koll. Zhurnal *19,* 82 (1957).
2. Brunauer S.: US Patent 3689294 (1972).
3. Shpinova L.G., Ostrovskii O.L.: *Concretes for Use under Winter Conditions*, Kiev 1985 (in Russian).
4. Škvára F.: *Gypsum-free cement*, Second Doctorate Thesis, ICT Prague 1991 (in Czech).
5. Škvára F.: Mat.Res.Soc.Symp.Proc.Vol. *370,* 153 (1995).
6. Škvára F.: Stavivo *7,* 8 (1984).
7. Škvára F., Ševčík V.: Cem.Concr.Res. *29,* 713 (1999).
8. *Prachovice Cement and Lime Works*, Catalogue of Special Products 1995 (in Czech).
9. Ševčík V.: *High-temperature behaviour of GF cements*, PhD Thesis, ICT Prague 1999.
10. Ševčík V., Škvára F.: CZ Patent 283 459 (1998), SK Patent 280 385 (2000).
11. Nekrasov K.D., Tarasova A.P.: *Refractory concrete based on Portland cement*, Moscow 1969 (in Russian).

VYSOKOTEPLOTNÍ VLASTNOSTI POJIVA Z BEZSÁDROVCOVÉHO PORTLANDSKÉHO CEMENTU V ROZMEZÍ TEPLOT 20 – 1200 °C

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Hydratační produkty GF cementu se od produktů hydratace PC zásadně liší morfologií $Ca(OH)_2$, přičemž v GF cementu se $Ca(OH)_2$ nachází ve velmi jemné a z velké části RTG amorfní formě. Morfologicky odlišný $Ca(OH)_2$ v zatvrdlém GF cementu je velmi nevýhodný z hlediska vývoje pevností v okolí teploty rozkladu $Ca(OH)_2$. Tato skutečnost se projevuje prudkým poklesem pevnosti hydratovaného GF cementu při cca 500 °C. GF cement dosahuje v celém rozsahu teplot 20 - 1200 °C vyšších pevností v tlaku po výpalu než portlandský cement ze slínku stejného složení. Malta z GF cementu stabilizovaného 15 hmotn.% úletu SiO_2 s korundovou výplní dosáhla po předchozím výpalu na 1200 °C $t_{0,5}$=1189 °C (měřeno podle ČSN ISO 1893), což jsou vlastnosti srovnatelné s vlastnostmi hlinitanového cementu s nižším obsahem Al_2O_3.