STABILIZING THE HIGH-TEMPERATURE PROPERTIES OF GYPSUM-FREE PORTLAND CEMENT BY Al_2O_3 ADDITIONS

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The study deals with high-temperature properties of gypsum-free Portland cement (GF cement) based on ground clinker of Portland cement and processed with additions of Na_2CO_3 and lignine sulphonate. An admixture of $Al(OH)_3$ is sufficient for eliminating $Ca(OH)_2$ from hydrating GF cement. The admixture of Al(OH)3 in hydrating GF cement results in formation of a hydrogarnet having the composition $Ca_3Al_2(SiO_4).(OH)_8$. According to the results of the standard test "Determination of Resistance to Deformation under Load at High Temperatures" (ČSN ISO 1893), the behaviour of the modified GF cement is comparable to the properties of alumina cement with a lower content of Al_2O_3.

INTRODUCTION

Free CaO in refractory concrete based on Portland cement can be eliminated by means of fine-grained fillers [1] or reactive additives that remove CaO indirectly by combining with $Ca(OH)_2$ in the course of hydration of the cement. A classical active additive to PC is represented by silica fume [2-5], a by-product of the metallurgical industry. The ability of silica fume to react with $Ca(OH)_2$ under normal conditions is on the whole limited. Effective combining of free CaO with silica fume can be achieved by hydrothermal treatment. The respective materials are usually designated CBC - Chemically Bonded Ceramics, and are recommended for high-temperature applications of up to at least 800°C when their residual strength amounts to 40% of their maximum one. Free $Ca(OH)_2$ can also be eliminated by substances of pozzolanic nature which react with CaO producing hydrated calcium silicates. Pozzolanic cements can also be used as binders for refractory structures on the condition that the respective concrete is first allowed to cure for several months in a moist environment or in humid atmosphere in order to let the pozzolanic reactions proceed fully before exposing the concrete to high temperatures. The effect of silica fume on high-temperature properties of gypsum-free Portland cements (hereinafter GF cements) was described in a previous study [6].

In the paper by Mathieu [7] the possibility of using finely ground $Al(OH)_3$ for the stabilization of refractory properties of cements was indicated.The present study is concerned with the effect of $Al(OH)_3$ on hydration and high-temperature properties of GF cements [8].

EXPERIMENTAL

In the experiments, use was made of GF Portland cement produced commercially by CEVA Prachovice under the designation BS cement 52,5R HI-Q, with a specific surface area (Blaine) of 480 $m^2\ kg^{-1}$. Gypsum was substituted by a combination of sodium lignosulphonate Eucobet 300 (manufactured by Holderchem, Switzerland) with Na_2CO_3. Portland cement was used as reference to the behaviour of gypsum free Portland cement, and for this purpose it was made from the same clinker (manufactured by CEVA Prachovice, a.s.) under the designation of CEM I 42.5R. Both cements were made from the same clinker having the following composition (wt.%): CaO 63.2, SiO_2 20.8, Al_2O_3 5.8, Fe_2O_3 3.3, MgO 3.6, $K_2O + Na_2O$ 2.1, SO_3 0.8, free CaO 0.88. The gypsum content amounted to 2.85 wt.% (as SO_3). The specific surface area was 320 $m^2\ kg^{-1}$. Alumina cement was employed as reference for assessing the refractory properties of mortars from the chemically modified GF cement. The classical low-alumina

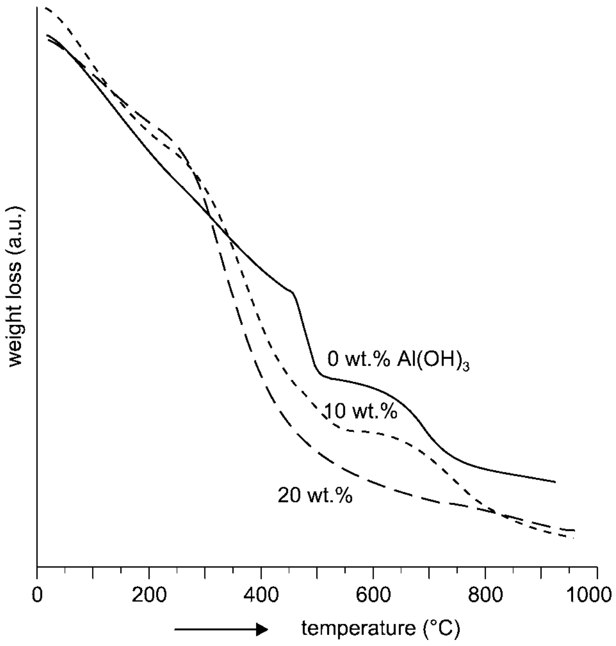

Figure 1. GTA of GF cement stabilized with various amounts of $Al(OH)_3$ (7 days of moist curing at 20°C).

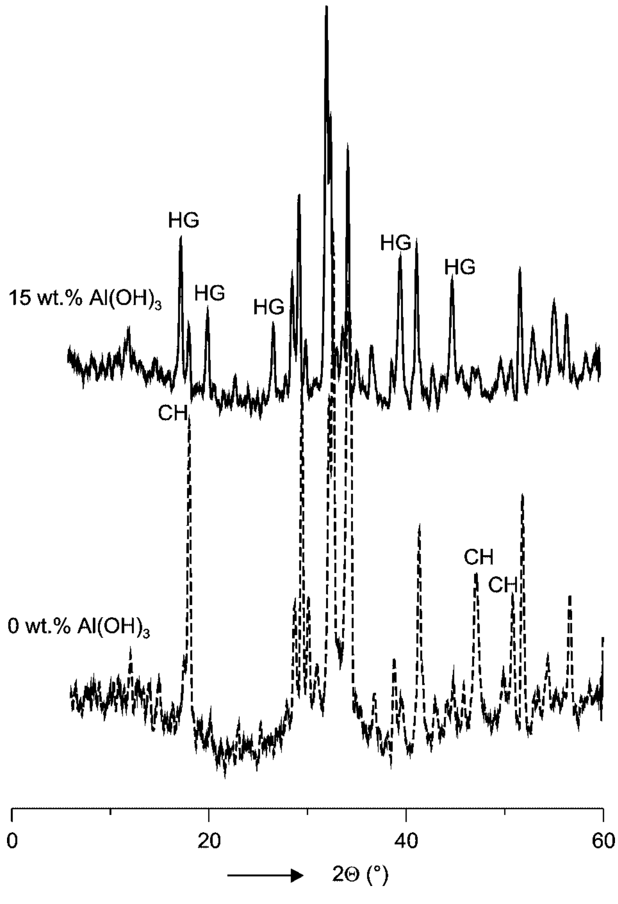

Figure 2. X-ray diffraction patterns of GF cement pastes with an addition of 0 and 15 wt.% $Al(OH)_3$ (7 days of moist curing at 20°C).

Lafarge Fondu cement containing 40 wt.% Al_2O_3 was selected for this purpose.

The procedure described [6] was used for the preparation of corundum mortars. $Al(OH)_3$ (made by Fluka GmbH, Germany) with a mean particle size of 100 µm (determined by sedimentation analysis) and further ground on a vibration mill to mean particle sizes of 30, 15, 10, 7 and 4.5 mm, was employed as the alumina additive in the experiments.

Preparation of the GF and PV cement pastes was also described in [6]. The compressive strength was determined after 7 days of hydration on mortars of GF cement both with and without additives, as well as on mortars of the PC and alumina cements. The water-cement ratios were adjusted on the basis of comparable rheological properties, i.e. the pastes and mortars were prepared so as to have virtually identical workability. In the case of the PC + corundum system, of the GFC + corundum + $Al(OH)_3$ system, of the GFC + corundum + $Al(OH)_3$ (0-15 wt.%) system, of the GFC + corundum + $Al(OH)_3$ (above 15 wt.%) system, the w/c values were 0.45, 0.32, 0.33 and 0.42 respectively. The specimens for compressive tests were 2×2×10 cm in size, and the same specimens were used for determining additional linear changes. The sizes of the other specimens corresponded to the respective standards. All the test specimens were cured in 100 % R.H. for 7 days at approx. 22°C.

The following standard tests were used for determining the refractory properties of the mortars:

a) Resistance to high-temperature deformation under load (ČSN ISO 1893)
b) Refractoriness (ČSN ISO 528 and ČSN ISO 1146)
c) Additional linear changes (modified standard test using prisms 2×2×10 cm).

The composition of the hydration products was studied on samples of hardened cement pastes (after destructive tests) by X-ray diffraction, GTA and DTA. In the case of samples for X-ray and thermal analyses and for determination of morphology by the electron microscope, the hydration was terminated by saturating with acetone and drying in vacuum. The morphology of the samples was studied by the JEOL Superprobe scanning electron microscope with ED spectrometer.

RESULTS AND DISCUSSION

The distinct difference in the high-temperature behaviour of hydrated GF cement compared to that of ordinary PC is based on an abrupt decrease in strength which takes place within a narrow temperature interval at about 500°C. This loss in strength is due to a different morphology of decomposing $Ca(OH)_2$ which in the case of GF cement is present in an extremely fine-grained form. For this reason in the instance of GF

Figure 3. Fracture surface of hardened GF cement paste containing an addition of 15 wt.% $Al(OH)_3$ after 7 days of curing. 1 - C-S-H phase, 2 and 3 - C-S-H phase + hydrogarnet, 4 - particles of unreacted $Al(OH)_3$, 5 - hydrogarnet.

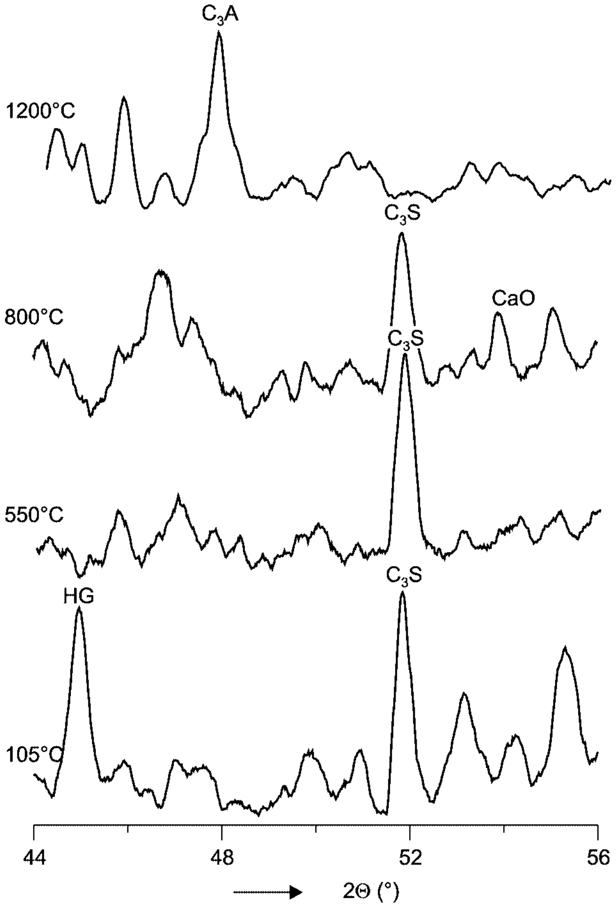

Figure 4. Detail of X-ray diffraction pattern of hydrated GF cement with an addition of 15 wt.% $Al(OH)_3$ after firing from 105 to 1200°C.

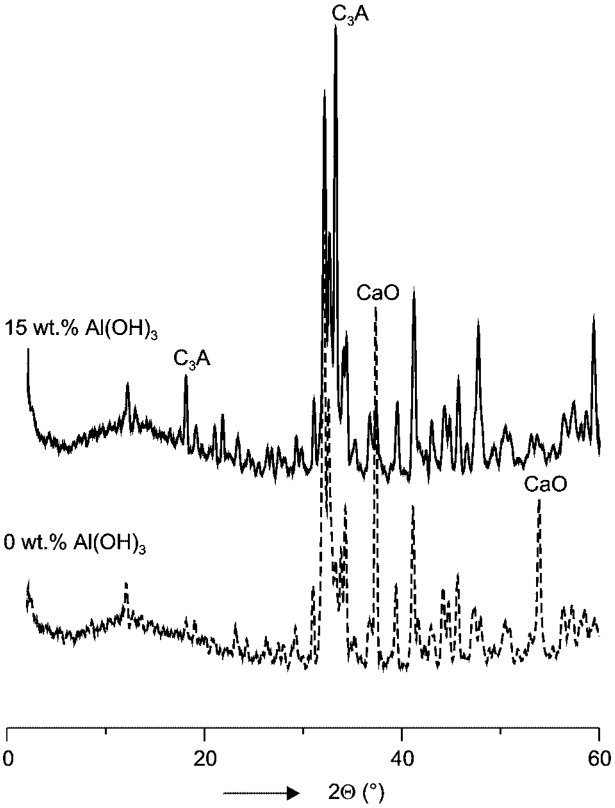

Figure 5. X-ray diffraction pattern of GF cement with additions of 0 and 15 wt.% of $Al(OH)_3$, respectively, after 7 days of moist curing at 20°C.

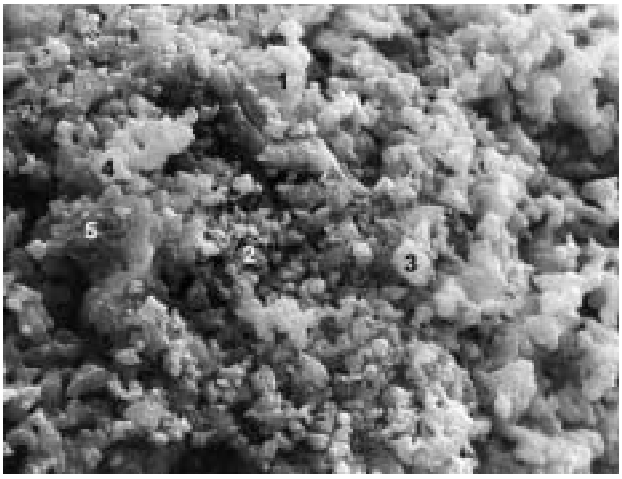

Figure 6. Fracture surface of hardened GF cement paste stabilized with 15 wt.% $Al(OH)_3$ after firing at 1200°C. 1,2 and 4… C_2S + C_3A, 3… C_3S + C_3A.

cement it would be more advantageous to combine the free $Ca(OH)_2$ directly in the course of hydration of the cement instead of reacting the free CaO following the decomposition of $Ca(OH)_2$ as is the case of classical refractory concrete based on ordinary Portland cement. This principle brought satis-factory results with the use of silica fume as additive to GF cements, as demonstrated by [1].

Our additional experiments were therefore aimed at verifying the possibility of improving the high-temperature properties of hydrated GF cements by combining the $Ca(OH)_2$ by means of an active additive of finely ground $Al(OH)_3$.

The efficiency of $Al(OH)_3$ additions strongly depends on their fineness, as the ability to bind $Ca(OH)_2$ has only been proved with grain sizes of less than 10-30 μm. The results of GTA analyses of hydrated GF cement, shown in figure 1, were achieved with $Al(OH)_3$ having a mean particle size of 4.5 μm. The GTA was carried out on samples after 7 days of curing and subsequent drying at 105°C (for 24 hours). The results show that the efficiency of combining $Ca(OH)_2$ by adding $Al(OH)_3$ to hydrating GF cement is comparable to than the corresponding efficiency of silica fume additions (cf. [6,8]). The addition of 10 to 15 wt.% of finely ground $Al(OH)_3$ (mean particle size 4.5 μm) is sufficient for virtually complete elimination of $Ca(OH)_2$ liberated during hydration of GF cement.

The X-ray diffraction pattern of hydrated GF cement with 15 wt.% $Al(OH)_3$ (after drying at 105°C) revealed the presence of a hydro-garnet having the composition $Ca_3Al_2(SiO_4).(OH)_8$ (figure 2). Fracture surfaces of hydrated GF cement with an addition of $Al(OH)_3$ show a prevailing presence of the C-S-H phase and also formations corresponding to the possible composition of hydrogarnet (by ED spectrometer analysis), apart from unreacted coarse fractions of $Al(OH)_3$.

The changes in the structure of hydrated GF cement with an addition of $Al(OH)_3$ after firing are well demonstrated by the detail of the X-ray diffraction patterns in figures 4,5 where there appear distinct lines of C_3A (1.9293 nm), C_3S (1.7944 nm) and CaO (1.7659). The phase composition of hydrated GF cement stabilized by fine-grained $Al(OH)_3$ (mean particle size 4.5 μm) following firing at 1200°C indicates that GF cement with an addition of 15 wt.% $Al(OH)_3$ after firing at 1200°C does not contain any free CaO, in contrary to hydrated fired GF cement alone. It was also found that the addition of $Al(OH)_3$ to GF cement results in a steep increase in the intensity of C_3A lines in diffraction patterns. In contrast to figure 5, there is also a part of the diffraction pattern of GF cement with an addition of 15 wt.% $Al(OH)_3$ after firing at 800°C. The details of diffraction patterns in figure 5 illustrate comprehensively the fact that following the firing at 1200°C of hydrated GF cement containing 15 wt.% $Al(OH)_3$, C_3A is formed and formation of CaO is completely suppressed. On firing at 800°C, when C_3A has not yet formed, the C_3S is decomposed, yielding secondary CaO. After firing at 1200°C, no free CaO is already present, as it has obviously been combined by firing at 1200°C. The absence of the CaO peak in the case of fired hydrated GF cement is obviously due to combination of $Ca(OH)_2$ which has taken place during hydration.

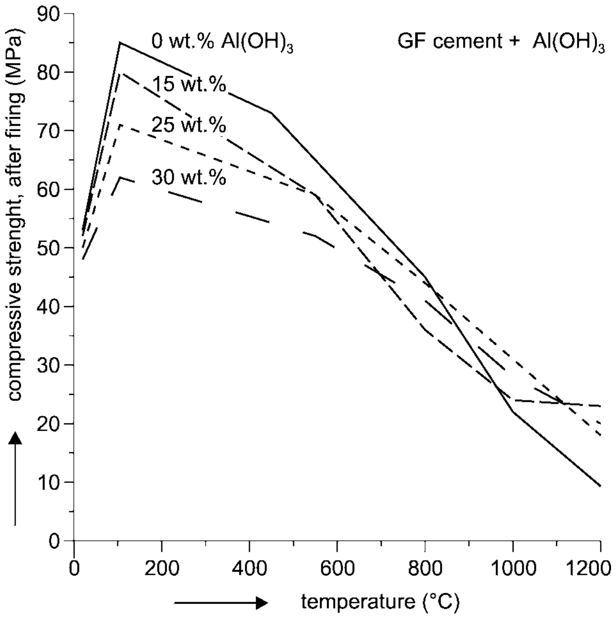

Figure 7. Post-firing strength of hydrated GF cement stabilized with 0-30 wt.% $Al(OH)_3$ vs. firing temperature.

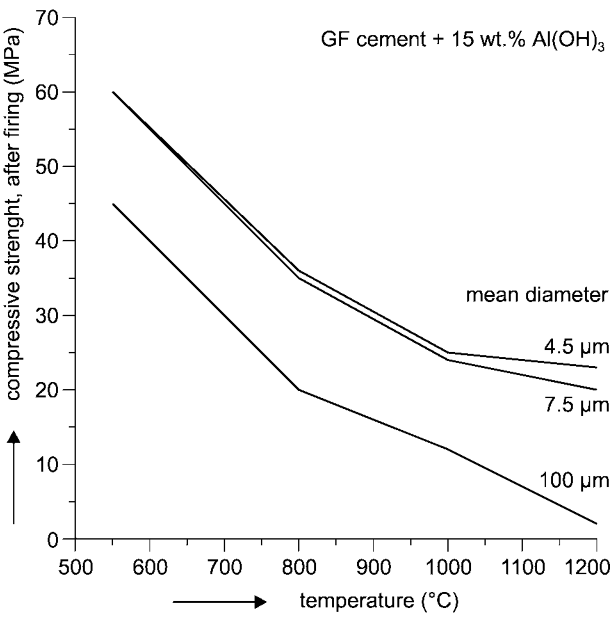

Figure 8. Post-firing strength of hydrated GF cement stabilized with 15 wt.% $Al(OH)_3$ of various particle sizes vs. firing temperature.

Figure 6 shows the fracture surface of hydrated GF cement with an addition of finely ground $Al(OH)_3$ after firing at 1200°C. The appearance of the fracture surface resembles a ceramic material. However, in the case of the $Al(OH)_3$ admixture the individual grains exhibit less mutual bonding than in the case of the silica fume admixture where the grains were mutually joined over most of their surface (figure 3). SEM micrographs indicate that in the case of GF stabilization with $Al(OH)_3$, firing at 1200°C brings about lesser or slower sintering than with the silica fume addition (figure 6). The composition of the products (ED spectrometric analysis) corresponds essentially to C_2S or to C_3S with C_3A.

The results of compressive strength tests after firing in terms of firing temperature are plotted in figures 7 and 8. The addition of finely ground $Al(OH)_3$ resulted in increased post-firing compressive strength of hydrated GF cement. The courses of the curves show that the dry strength of hydrated GF cement decreases with increasing amount of the $Al(OH)_3$ admixture and with its increasing particle size, whereas with firing temperatures above 500°C begins to have its positive effect on post-firing strength, and that on firing at temperatures of 800°C, 1000°C and 1200°C the strength was increased.

The resistance to deformation under load at high temperature of hydrated GF cement stabilized with finely ground $Al(OH)_3$ was examined with an addition of 15 wt.% $Al(OH)_3$ which was found sufficient for eliminating the CaO formation during firing. Records of the measurements are given in figures 9 and 10. The $t_{0.5}$ attained was 1283°C and the maximum linear expansion did not exceed 0.752 %. The $t_{0.5}$ value of 1193°C established for a fired specimen of Lafarge Fondu alumina cement corresponds roughly to the manufacturer's specifications for high-density refractory concrete with corundum aggregates. The maximum elongation of an unfired test specimen amounted to 0.147 %, and that of a pre-fired specimen to 0.704 %.

The additional linear changes, from which the classification temperature is derived, are significant with respect to the practical utilization of refractory concrete. A partial substitution of classification temperature determination for individual cement-corundum mortars is provided by measuring the additional linear changes after firing at 1200°C. This was carried out on 20×20×100 mm test specimens prior to testing their compressive strength after firing. The linear additional changes of both pure and stabilized hydrated GF cement after firing at 1200°C did not exceed 1 %.

According to the results of the standard test "Resistance to Deformation under Load at High Temperature (ČSN ISO 1893), the high-temperature behaviour of the modified GF cement is comparable to the properties of the Lafarge Fondu alumina cement (cf. [9]).

CONCLUSIONS

1. $Ca(OH)_2$ originating in hydrating GF cement can be effectively combined with finely ground $Al(OH)_3$. An addition of approx. 15 wt.% of $Al(OH)_3$ with a mean particle size of 4.5 μm is sufficient for virtually complete elimination of $Ca(OH)_2$ from hydrating GF cement by 7-day curing.
2. The $Al(OH)_3$ in hydrating GF cement combines to form a hydrogarnet having the composition $Ca_3Al_2(SiO_4).(OH)_8$.
3. The admixture of $Al(OH)_3$ in hydrated GF cement results after firing at 1200°C in the formation of C_3A.
4. Measurement of post-firing strength showed that the combination of $Ca(OH)_2$ in GF cement results, apart from reducing formation of free CaO on firing, also in a reduction of the loss in strength at temperatures of about 500°C. Increasing additions of $Al(OH)_3$ lead to lowering strength of hydrated GF cement after drying.

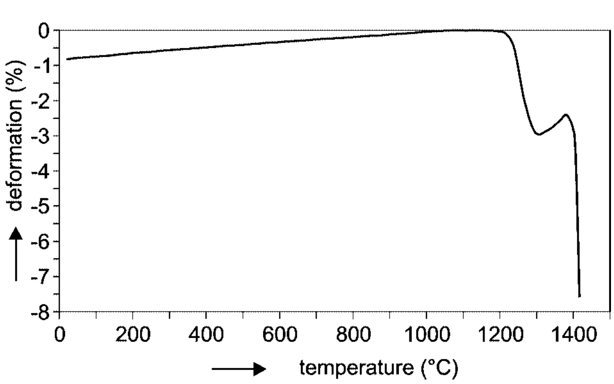

Figure 9. Resistance to high-temperature deformation under load of GF cement with 15 wt.% $Al(OH)_3$ - corundum mortar, measured on test specimens after firing at 1200°C, $t_{0.5}$ = = 1238°C, t_1 = 1228°C, maximum elongation 0.752 % at 1136°C.

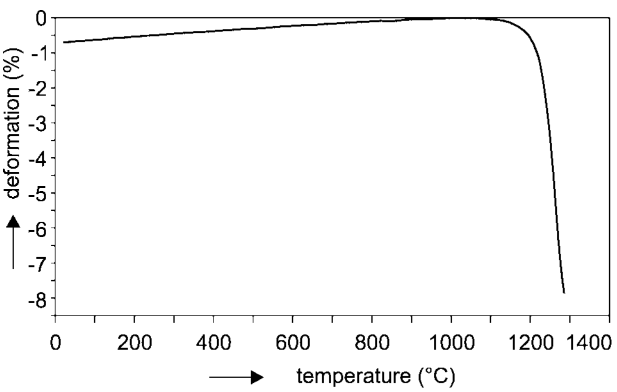

Figure 10. Resistance to high-temperature deformation under load of low-alumina Lafarge Fondu cement - corundum mortar, measured on fired specimens (1200°C, 2 hours), $t_{0.5}$ = 1193°C, t_1 = 1214°C, maximum elongation 0.704 % at 1008°C.

5. Additions of 15 to 30 wt.% $Al(OH)_3$ to GF cement result in decreasing strength of hydrated GF cement after drying. However, on firing at above 500°C the additions of $Al(OH)_3$ bring about increasing post-fired strength, and firing temperatures of 800°C, 1000°C and 1200°C cause the strengths to increase.
6. After firing at 1200°C, mortar of GF cement stabilized with 15 wt.% $Al(OH)_3$, containing corundum aggregate, attains $t_{0.5}$ = 1238°C (measured to ČSN ISO 1893).
7. Shrinkage due to firing at 1200°C of test specimens (cement-corundum mortar with 15 wt.% $Al(OH)_3$, specimens 20×20×100 mm) did not exceed 1 %.
8. According to the results of the standard test "Determination of Resistance to Deformation under Load at High Temperatures (ČSN ISO 1893), the behaviour of the modified GF cement is comparable to the properties of alumina cement with a lower content of Al_2O_3.

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STABILIZACE VYSOKOTEPLOTNÍCH VLASTNOSTÍ BEZSÁDROVCOVÉHO PORTLANDSKÉHO CEMENTU PŘÍSADOU Al_2O_3

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V práci byla věnována pozornost vysokoteplotním vlastnostem bezsádrovcového portlandského cementu (GF cement), který je založen na mletém slínku portlandského cementu a je zpracováván za přísady Na_2CO_3 a ligninsulfonanu. Zásadním rozdílem GF cementu vůči portlandskému cementu je možnost zpracování při nízkém vodním součiniteli. $Ca(OH)_2$ v hydratujícím GF cementu lze efektivně vázat jemně mletým $Al(OH)_3$. Pro odstranění $Ca(OH)_2$ z hydratujícího GF cementu po 7-denní hydrataci stačí přídavek cca 15% hmot. $Al(OH)_3$ o střední velikosti částic 4.5 μm. Reaktivita $Al(OH)_3$ v hydratujícím GF cementu se projevuje vznikem hydrogranátu o složení $Ca_3Al_2(SiO_4).(OH)_8$. Přídavek $Al(OH)_3$ se v hydratovaném GF cementu po výpalu na 1200°C projevuje vznikem C_3A. V případě přídavku 15-30 hmot.% $Al(OH)_3$ do GF cementu dochází s rostoucím množstvím $Al(OH)_3$ ke snížení pevnosti GF cementu po vysušení, avšak při teplotě výpalu nad 500°C se přídavek $Al(OH)_3$ začíná výrazněji projevovat zlepšením pevností v tlaku po výpalu a při teplotách výpalu 800°C, 1000°C a 1200°C dochází ke zlepšení pevností cca o 70-100 %. Malta z GF cementu stabilizovaného 15 hmot.% $Al(OH)_3$ s korundovou výplní dosahuje po předchozím výpalu na 1200°C $t_{0,5}$ = 1238°C (měřeno podle ČSN ISO 1893). Smrštění experimentálních těles (cementokorundová malta s 15 hmot.% $Al(OH)_3$) o rozměrech 20×20×100mm po výpalu na 1200°C nepřesáhlo 1 %. Měření povýpalových pevností potvrdilo, že vázání $Ca(OH)_2$ v GF cementu vede kromě omezení vzniku volného CaO při výpalu i ke zmírnění propadu jeho pevností v okolí teploty 500°C. V případě přídavku $Al(OH)_3$ dochází s rostoucím množstvím $Al(OH)_3$ ke snížení pevnosti GF cementu po vysušení, avšak při teplotě výpalu nad 500°C se přídavek $Al(OH)_3$ začíná výrazněji projevovat zlepšením povýpalových pevností a při teplotách výpalu 800°C, 1000°C a 1200°C dochází ke zlepšení pevností cca o 100%. Podle výsledků normové zkoušky „Stanovení únosnosti v žáru“ (ČSN ISO 1893) je chování modifikovaného BS cementu srovnatelné s vlastnostmi hlinitanového cementu s nižším obsahem Al_2O_3.