

# GYP SUM-FREE PORTLAND CEMENT BASED ON WHITE CEMENT CLINKER

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Submitted February 7, 2003; accepted April 3, 2003

**Keywords:** Gypsum free cement, White cement clinker, Low porosity, High strength.

*The article presents the results of study of the properties of GF cements prepared from standard white cement clinker. The properties of GF cements based on white cement clinker are fully analogous to those of GF cements based on conventional ("grey") Portland cement clinker. The effect of reduced content of  $Fe_2O_3$  and of the significantly lowered content of the  $C_6A, F_y$  phase in white GF cement has no discernible influence on the properties. White GF cement has equal or better refractory properties compared to those of alumina cement (with a low content of  $Al_2O_3$ ).*

## INTRODUCTION

The gypsum-free Portland cement is a binding agent based on ground Portland cement clinker in which the regulating effect of gypsum has been replaced by the synergically acting mixture of a sulphonated electrolyte (lignine sulphonate, sulphonated polyphenolate) and a hydrolysable alkali metal salt ( $Na_2CO_3$ ,  $K_2CO_3$ ) [1-3]. Binders based on GF cement (pastes, mortars, concrete) have the outstanding property of allowing well workable mixes to be prepared at very low water-to-cement ratios (of down to 0.20 in the case of pastes). The other properties of GF pastes, mortars and concrete, such as in particular attainment of high early and long-term strengths, the ability to set and harden at low and even subzero temperatures, their resistance to aggressive environments and to high temperatures, have been described in a number of published papers [2-7]. The properties of GF cement are significantly influenced by the mineralogical composition of the clinker, especially its content of alite and free CaO [8]. The resistance to very high temperatures of up to 1100°C is also an important property of GF cements based on silicate clinker. The refractory properties of GF cement-based materials have been further improved by using a stabilizing addition of  $Al(OH)_3$ , as described in [7]. Use of white cement clinker with a low content of  $Fe_2O_3$  in the manufacture of GF cement is an interesting prospective

way of still improving the refractoriness of GF-based materials. The properties of GF cement based on white cement clinker have not yet been described in the literature, as the available data are concerned with standard white cement containing gypsum as regulating agent.

## EXPERIMENTAL

The GF cements were prepared from two clinkers (designated #D and #H respectively, taken from standard production of white cement. The chemical and mineralogical compositions of the clinker samples and white cement are given in tables 1 and 2.

The #H and #D white cement clinkers were ground in a ball mill to a specific surface area of 470 m<sup>2</sup>/kg (#H) and 420 m<sup>2</sup>/kg (#D) using the ALSON TEA grinding aid in amounts of 0.05 % of the clinker weight. White Portland cement with a specific surface area of 335 m<sup>2</sup>/kg was used as reference material. The cements thus obtained (designated GFC#D and GFC#H respectively) were used for preparing cement pastes and mortars with a water-to-cement ratio (w) ranging from 0.21 to 0.40. In the preparation of GF cement pastes and mortars, use was made of plastifier additions mixed with the alkali carbonate. On the basis of optimising tests, GFC#D was mixed with 2 wt.% Ultrazine Na (sodium lignosulphonate + 1.5%  $Na_2CO_3$ ), and GFC#H with 1.5 wt.%

Ultrazine Na + 1.5 wt.% Na<sub>2</sub>CO<sub>3</sub>, to prepare pastes with  $w = 0.22$ . Test specimens  $2 \times 2 \times 2$  cm in size were prepared from the cement pastes. All the specimens were cured in the environment of saturated water vapour for a period of 24 hours /measured from the time of mixing the components together). After removing from the moulds the specimens were placed in water for a period of 28 days. In the course of curing, the 2, 4 and 24-hour and 7- and 28-day strengths were determined. The remaining specimens were placed in air for 360-day strength determination.

Following the compression strength testing, further hydration of the broken up specimens was stopped by heating at 105°C for 24 hours, and for SEM by immersing in acetone for 2 hours and subsequent drying in vacuum for 2 hours. The specimens treated in this way were kept in a desiccator over a moisture absorbent and subjected to further testing.

The refractory properties were tested on mortar specimens  $2 \times 2 \times 10$  cm in size prepared from mortar whose composition was described in [6] (corundum mortars,  $w = 0.29$ ). The resistance to loading at high temperature was determined to ČSN ISO 1893.

Table 1. Chemical composition of the clinkers and of the white PC (wt.%).

Components determined	White PC	Clinker #D	Clinker #H
SiO <sub>2</sub>	21.60	24.54	23.36
Al <sub>2</sub> O <sub>3</sub>	4.09	4.38	4.52
Fe <sub>2</sub> O <sub>3</sub>	0.25	0.73	0.61
MgO	1.29	0.55	2.50
CaO	67.15	67.43	67.36
Na <sub>2</sub> O	0.07	0.06	0.05
K <sub>2</sub> O	0.32	0.65	0.29
Ignition loss	2.6	1.04	1.22
Total SO <sub>3</sub>	2.51	0.51	0.03

Table 2. Mineralogical composition of the clinkers (microscopically) (wt.%).

Content of the phase	Clinker #D	Clinker #H
C <sub>3</sub> S	62.0	81.3
C <sub>2</sub> S	26.0	1.7
C <sub>3</sub> A	11.4	14.2
C <sub>4</sub> AF	0.1	0.1
C <sub>vol</sub>	0.5	2.8

Table 3. Weight losses after 28 days of hydration, as determined by TGA (%)

Decomposition reaction		White PC 28 days	GFC#D 28 days	GFC#H 28 days
approx. 450°C	moisture, C-S-H, C-A-H	13.3	9.3	10.5
approx. 550°C	Ca(OH) <sub>2</sub>	2.8	1.0	1.5
approx. 800°C	CaCO <sub>3</sub>	4.8	4.2	3.3

## RESULTS AND DISCUSSION

The admixture of Na<sub>2</sub>CO<sub>3</sub> and lignine sulphonate in suspensions of GF cement (in the absence of gypsum) results in an extensive plastifying synergic effect which allows freely flowing pastes of GF cement to be prepared with a water-to-cement ratio as low as  $w = 0.21$ . This synergic effect (described elsewhere for GF cements based on standard Portland cement clinkers) is effective even when the clinker composition has been changes. Pastes of white Portland cement (containing gypsum) exhibited analogous rheological properties at substantially higher  $w$  of 0.32-0.40. The synergic effect of the additions in suspensions of GF cement causes the initial set to be retarded, thus replacing the effect of gypsum.

The strength development of white GF#D and GF#H is shown in figure 1. Similarly to the case of the previously studied types of GF cements (based on standard Portland cement clinkers), high early and long-term strengths have been attained.

Hydration of white GF cement differs from the hydration of Portland cement in that in the former case there does not arise any gradual loss of workability. Following the period of acceptable workability there occurs rapid hardening and thus attainment of measurable early (2-hr) strength. There is also a difference in the compositions of hydrated GF cement and that of P cement in that the former does not contain ettringite (C<sub>6</sub>AS<sub>3</sub>H<sub>32</sub>), logically a result of the absence of gypsum in GF cement (figures 2 and 3). DTA curves of hydrated GF cement (peaks at 96-165°C) indicate the presence of hexagonal C<sub>4</sub>AH<sub>n</sub> phases, which have been stabilized and do not convert to the C<sub>3</sub>AH<sub>6</sub> cubic forms, not even after 1 year of hydration. Disputed is the presence of C<sub>3</sub>AC<sub>3</sub>H<sub>11</sub> which could have formed in place of ettringite by reaction of C<sub>3</sub>A with Na<sub>2</sub>CO<sub>3</sub>. Both DTA and TGA curves clearly show the presence of phases Ca(OH)<sub>2</sub> and CaCO<sub>3</sub> in white gypsum cement as well as in white GF cement. The contents of Ca(OH)<sub>2</sub> and CaCO<sub>3</sub> in hydrated GF cement and in hydrated PC differ. According to table 3, the amount of Ca(OH)<sub>2</sub> in percent in GFC#D is lower by more than 60 %, and in the case of GFC#H by more than 45 % compared to white hydrated PC. A lower CaCO<sub>3</sub> content has likewise been observed in GF cement, but this decrease corresponded only to 12-30 %.

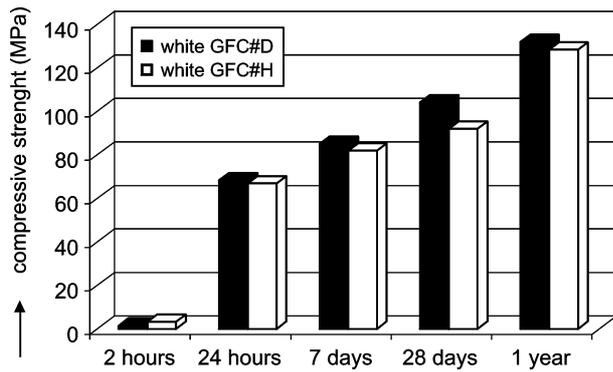


Figure 1. Time development of strength,  $w = 0.21$ , white GF cement #H and #D.

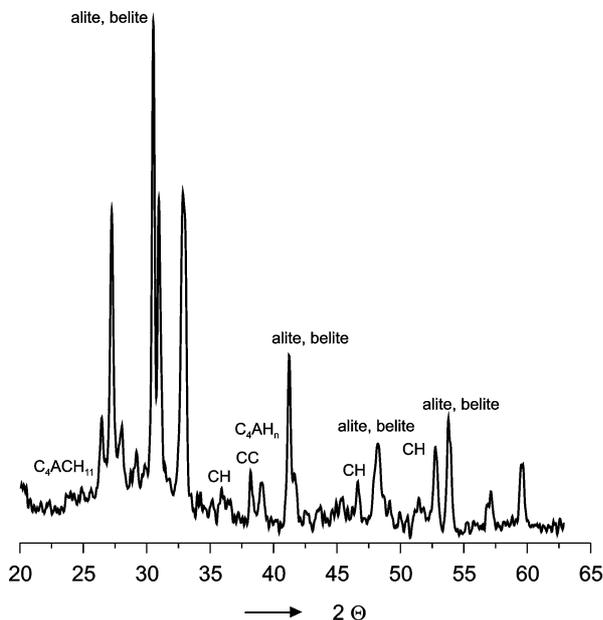


Figure 2. X-ray diffraction pattern of hydrated GF cement after 7 days (part). CC -  $\text{CaCO}_3$ , CH -  $\text{Ca(OH)}_2$ .

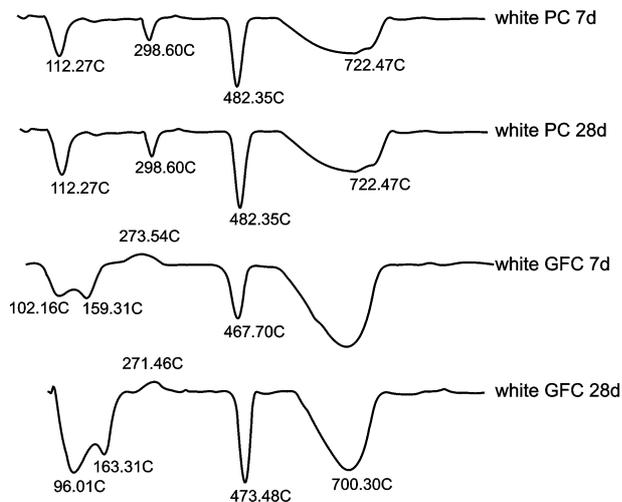


Figure 3. DTA thermograms of hydrated GF cement and of Portland cement after 7 and 28 days.

However, the content of  $\text{Ca(OH)}_2$  corresponding to the intensities of diffraction lines of  $\text{Ca(OH)}_2$  in hydrated white GF cement is significantly lower than that in Portland cement. These results are in apparent disagreement with the results of TA and indicate that  $\text{Ca(OH)}_2$  in hydrated GF cement (at low  $w$ ) occurs for the most part in X-ray amorphous form, as already described in [8,9].

The morphology of fracture surfaces of hydrated white GF cements differ distinctly from those of white Portland cement, as demonstrated by figures 4-6. The mass of hydrated GF cement is composed of amorphous gel of the C-S-H phase (Type III) in which the other hydration products are dispersed. This structure does not contain the characteristic portlandite crystals typical of hydrated Portland cement (figures 5,6) found in GF cements based on Portland clinker [3,10].

The following significant differences have been found in the study of the refractory properties of GF cements and white Portland cement:

- higher residual strengths of GF cements after firing,
- a rapid decrease of strength after firing the GF cement in the  $500^\circ\text{C}$  temperature range,
- the minimum strength of Portland cement after firing at  $1000^\circ\text{C}$  as compared to the steady decrease of strength when firing the GF cement up to  $1200^\circ\text{C}$ .

Over the whole temperature range studied ( $20\text{--}1200^\circ\text{C}$ ), the white GF cement exhibited higher residual strengths than the white PC. The residual strengths of GF cement after firing are closely associated with its higher initial strengths due to a faster course of hydration and a lower porosity compared to that of PC.

The decrease in strength of GF cement at around  $500^\circ\text{C}$  is associated with the decomposition of  $\text{Ca(OH)}_2$ , see figure 7. The results of TGA therefore indicate that the sharp decrease of strength of GF cement takes place in spite of the fact that GF cement contains lower amount of  $\text{Ca(OH)}_2$  than PC.  $\text{Ca(OH)}_2$  is likewise contained in hydration products of PC, which however, does not exhibit the sharp loss of strength at the temperature of  $\text{Ca(OH)}_2$  decomposition. The study of morphology of fracture surfaces of the hydrated cements shows that the greatest difference between the hydration products of GF cement and PC lies in the morphology of  $\text{Ca(OH)}_2$ . It may therefore be assumed that it is just the presence of a morphologically different form of  $\text{Ca(OH)}_2$  in GF cement in place of crystalline portlandite which is responsible for the sharp decrease of strength at about  $500^\circ\text{C}$ . The increase in the content of CaO and belite (X-ray diffraction), resulting from the decomposition of  $\text{Ca(OH)}_2$ ,  $\text{CaCO}_3$  and alite, is illustrated by figure 8.

The minimum residual strength after heating the specimens of PC at about  $1000^\circ\text{C}$  is obviously due to the presence of gypsum in PC, which is responsible for the onset of melting. On the other hand, the steady

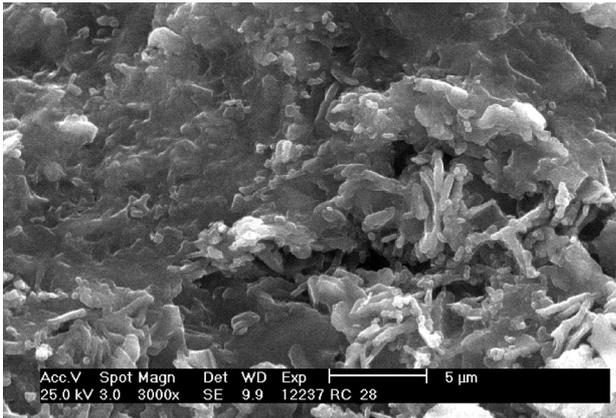


Figure 4. Fracture surface of hydrated GF cement after 28 days (paste  $w = 0.21$ ).

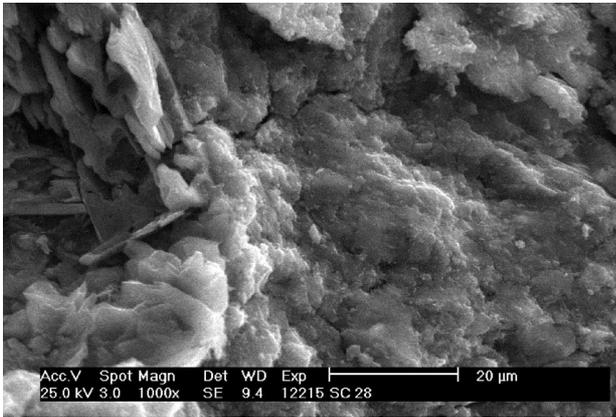


Figure 5. Fracture surface of hydrated white Portland cement after 28 days ( $w = 0.32$ ).

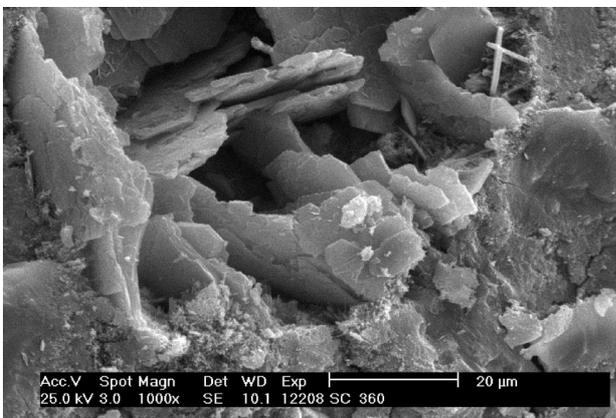


Figure 6. Fracture surface of hydrated white Portland cement after 28 days ( $w = 0.32$ ), detail.

increase in strength of GF cement after firing to at least 1100°C shows that no undesirable formation of melt takes place at temperatures of at least 1100°C. The morphologies of fracture surfaces of specimens fired at 600-1200°C are shown in figures 9-11. Decomposition of the C-S-H phase is indicated at temperatures above 600°C, and sintering resulting from the formation of flux at temperatures above 1100°C.

Measurement of refractory properties (resistance to deformation at high temperatures under load) was carried out on mortars of GF cement, using low-alumina Lafarge Fondu cement as reference material. The  $t_{0.5}$  values for the individual cements were as follows: white GFC#D 1196°C, white GFC#H 1231°C, Lafarge Fondu 1193°C. These results show that white GF cement has at least comparable if not superior refractory properties compared to the low-alumina refractory cement.

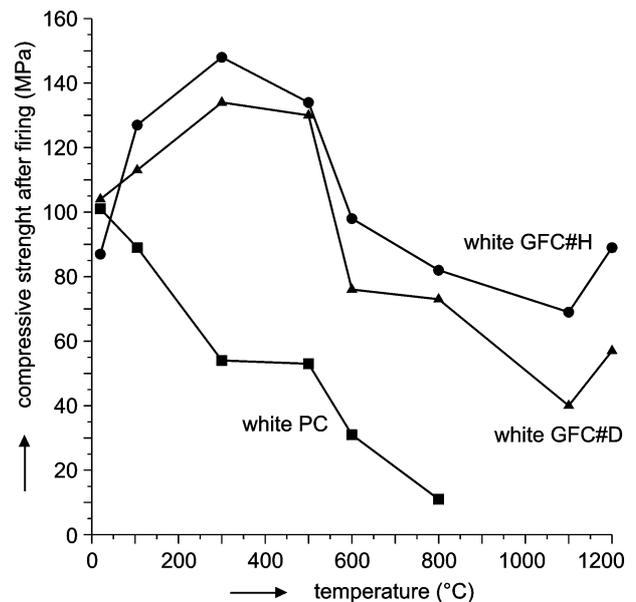


Figure 7. Strength of mortars of GF cement and white Portland cement after firing (2 hours).

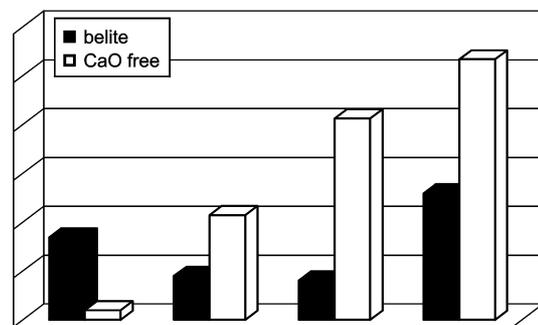


Figure 8. Intensities of X-ray diffractions in fired GF cement.

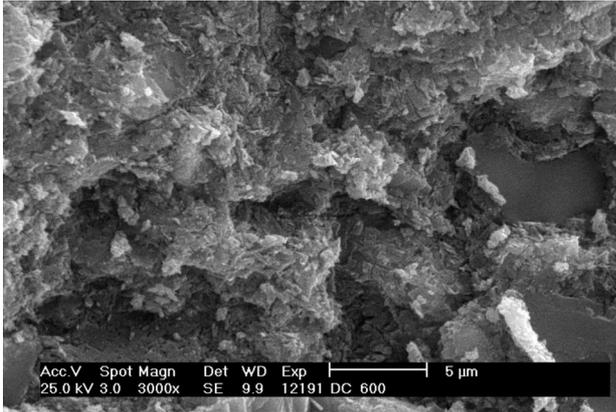


Figure 9. Fracture surface of GF cement mortar fired at 600°C.

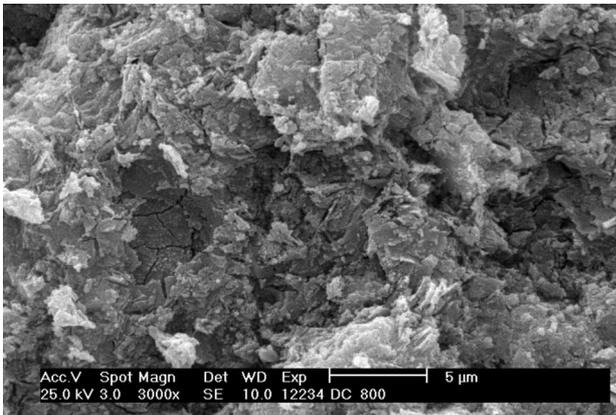


Figure 10. Fracture surface of GF cement mortar fired at 800°C.

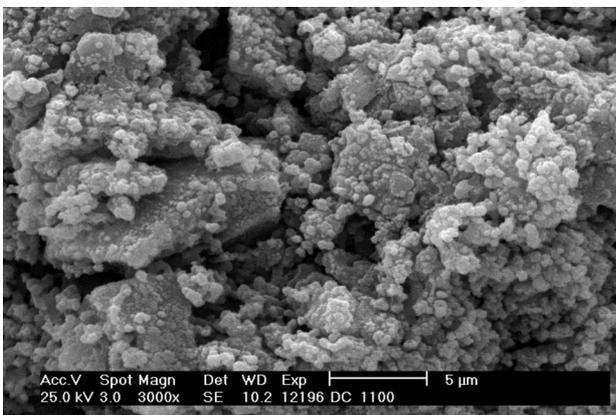


Figure 11. Fracture surface of GF cement mortar fired at 1100°C.

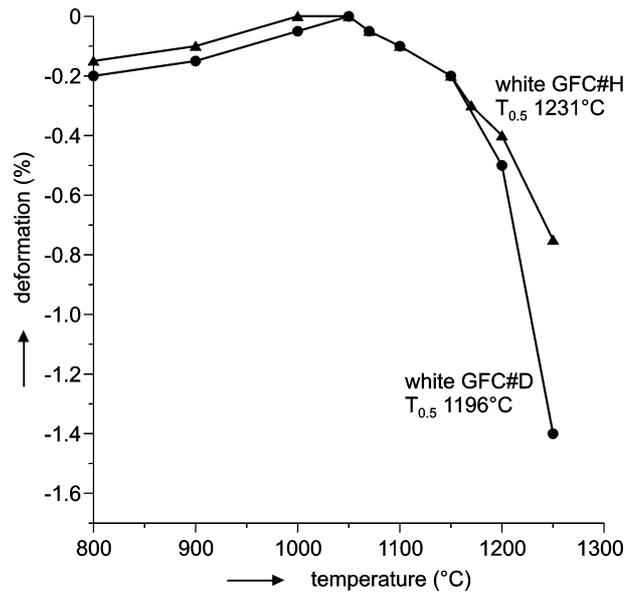


Figure 12. Stress-strain dependence vs. temperature, mortars of GF cements.

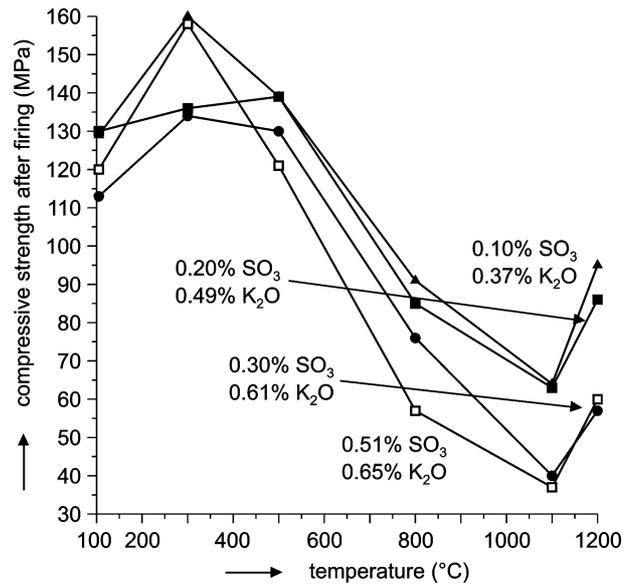


Figure 13. Strength of GF cement mortars after firing in terms of K<sub>2</sub>O and SO<sub>3</sub> content.

In the course of studying the refractory properties of GF cements, differences have been found between GFC#H and GFC#D in terms of residual strength after firing and in that of strength under load at high temperatures (figures 7 and 11). These differences can be obviously explained by the different content of alkali metal oxides and SO<sub>3</sub> in the clinkers of white cement #H and #D. When the composition of white GF cement from clinker #H (with a low content of K<sub>2</sub>O and SO<sub>3</sub>) was

adjusted by an addition of  $K_2SO_4$ , this resulted in considerable differences in the strength after firing. At a content of  $K_2O$  and  $SO_3$  corresponding to the composition of GFC#D (with a higher content of  $K_2O$  and  $SO_3$ ), the same refractory properties were achieved with GFC#H. The alkali metal oxides and  $SO_3$  affect the properties of the clinker flux (lower temperature of melting, lower viscosity, surface tension [11]). These results indicate that for the purpose of achieving high refractoriness of white GF cement it would be necessary to monitor the content of alkali metal oxides and  $SO_3$  in the clinker to be used in the manufacture of the GF cement.

On the basis of the results obtained it may be concluded that the study of hydrated GF cements based on white cement clinker yielded results analogous to those obtained with GF cements based on conventional (grey) cement clinker [3,4,8]). The effect of reduced content of  $Fe_2O_3$  and the markedly reduced content of the  $C_6A_xF_y$  in white GF cement had no noticeable influence on the properties except for the refractory ones. It may therefore be generalized that the effect of the synergically acting system of anion-active tenside (e.g. lignine sulphonate) and a hydrolysable salt of an alkali metal (such as carbonate) is virtually identical for GF cements based on a silicate clinker regardless of even considerable differences in the chemical and mineralogical composition of the clinker.

## CONCLUSION

The properties of GF cements based on white cement clinker are quite analogous to those of GF cements based on clinkers of conventional (grey) Portland cement.

The hydration of white GF cement differs from that of Portland cement.  $Ca(OH)_2$  in hydrated GF cement is prevailingly in X-ray amorphous form.

The reduced content of  $Fe_2O_3$  and the markedly reduced content of the  $C_6A_xF_y$  in white GF cement has no noticeable effect on its properties.

It may therefore be generalized that the effect of the synergically acting system of an anion-active tenside (e.g. lignine sulphonate) and a hydrolysable salt of an alkali metal (such as carbonate) is virtually identical for GF cements based on a silicate clinker regardless of even considerable differences in the chemical and mineralogical composition of the clinker.

White GF cement has refractory properties that are equal to or superior to those of alumina cement (with a low content of  $Al_2O_3$ ).

If the white GF cement is to attain a high resistance to temperatures in the  $1200^\circ C$  region, it is necessary to ensure a low content of alkali metal oxide and  $SO_3$  in the clinker to be used in the manufacture of the white GF cement.

## Acknowledgement

*This study was part of the research project CEZ:MSM 223100002: Preparation and properties of modern materials - modelling, characterisation, technology.*

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## BEZSÁDROVCOVÝ PORTLANDSKÝ CEMENT NA BÁZI SLÍNKU BÍLÉHO CEMENTU

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Vlastností GF cementů na bázi slínku bílého cementu jsou zcela analogické jako u GF cementů založených na slíncích běžného („šedivého“) portlandského cementu. Vliv sníženého obsahu  $Fe_2O_3$  a výrazně snížený obsah fáze  $C_6A_xF_y$  v bílém GF cementu nemá znatelný vliv na jeho vlastnosti. Vliv synergicky působícího systému anionaktivního tenzidu (např. ligninsulfonanu) a hydrolyzovatelné soli alkalického kovu (např. uhličitanu) je pro GF cementy založené na křemičitanovém slínku prakticky stejný i při značných rozdílech v chemickém i mineralogickém složení slínku. Hydratace bílého GF cementu se liší od hydratace portlandského cementu. Přísady nahrazující působení sádrovce oddalují počátek tuhnutí a umožňují svým synergickým účinkem přípravu kaši a malt s velmi nízkým vodním součinitelem.  $Ca(OH)_2$  v hydratovaném GF cementu je převážně v RTG amorfni formě. V hydratovaném GF cementu není přítomen  $C_6A_3H_5$  a jsou stabilizovány hexagonální formy hydrátů  $C_4AH_n$ . Bílý GF cement má stejně nebo lepší žárové vlastnosti než hlinitanový cement (s nízkým obsahem  $Al_2O_3$ ). Pro dosažení vysoké odolnosti bílého GF cementu vůči teplotám v oblasti  $1200^\circ C$  je nutný nízký obsah alkalií a  $SO_3$  ve slínku bílého cementu, který byl použit pro výrobu GF cementu.