

## THE EFFECT OF THE MINERALOGICAL COMPOSITION OF CLINKER ON THE PROPERTIES OF GYPSUM-FREE PORTLAND CEMENTS

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*The present paper summarizes the results obtained in the study of the effect of the composition of clinkers from various Czech cement works on the properties of gypsum-free (hereafter GF) cements. The study has demonstrated a significant effect of free CaO and a small effect of alite ( $C_3A$ ) in clinker on the properties of GF cement. To attain high early strength in GF cements, the clinkers should not be highly alitic and should not have a low content of free CaO.*

## INTRODUCTION

Gypsum-free Portland cement [1, 2] (hereafter GF cement) is a hydraulic inorganic binder based on ground Portland cement clinker (usually ground with a grinding aid), in which the regulating effect of gypsum is replaced by a synergically acting mixture of a sulphonated polyelectrolyte (e.g. lignin sulphonate or polyphenol sulphonate) with an alkali metal compound (such as carbonate). This cement exhibits a number of properties differing from those of the conventional Portland cement, in particular the possibility of using a very low water-to-cement ratio, and achieving high early and final strengths. The properties of this cement, resulting from a low porosity of a hardened material (high resistance to aggressive environments, resistance to high temperatures), as well as the course of its hydration and the microstructure of the hydration products, have been described in earlier papers [3, 4, 5]. The GF cement has been produced on an industrial scale by CEVA Prachovice a.s. since 1989.

Similarly to the standard Portland cements, the properties of GF cements are also strongly influenced by the chemical and mineralogical composition of the clinker. The present communication is devoted to a study of the effect of the chemical composition of clinker on the properties of GF cements.

## EXPERIMENTAL

For the purposes of the present study, clinker samples about 50 kg in weight were taken at intervals of days to months from Czech cement works Lochkov, Čížkovice, Maloměřice, Mokrá, Štramberk and Prachovice. In addition to this, clinker samples with certain extreme values in their chemical and mineralogical compositions were selected. The clinker samples were subjected to chemical and mineralogical phase analyses (determination of minerals on polished sections).

The clinkers were ground into GF cements under laboratory conditions, using as grinding aids either

0.1% ethylene glycol, or 0.05% alkanol amide of dodecylbenzenesulphonic acid. The grinding was controlled to achieve a specific surface area of 460–530  $m^2/kg$  (Blaine), and in some instances also one of up to 600  $m^2/kg$ .

Cement pastes with  $w = 0.24$  (free-flowing consistency) were prepared from the GF cements obtained. The pastes contained the same combination of additives which replaces gypsum, namely 0.4% Kortan FM (a polyphenol sulphonate of Czech manufacture) and 1%  $Na_2CO_3$ . Substances with strongly retarding effects were also used in some cases. The amounts of the additives were related to the weight of the GF cement and the additives were always dissolved in the mix water. For 24 hours after preparation, the pastes were placed in a medium of saturated water vapour at 20 °C, then from the 1st to the 28th day in water at 20°C, and after the 29th day in air at 20 – 25°C. The initial set (Vicat) and the time course of strength development were determined. The strengths were measured at time intervals of 2 or 6 hours, after 24 hours, after 3, 7, 28 and 180 days. In addition to these determinations, the constancy of volume of the cements was tested (Rosa-Kallauner method, cake test by boiling). The morphology of fracture surfaces on the hardened specimens was studied by the scanning electron microscope, and selected formations were analyzed by the EDAX method, using the procedure described in [1].

## THE RESULTS AND THEIR DISCUSSION

The data reported in the present paper summarize the results of studying the effects of clinker composition on the properties of GF cements between 1982 and 1990, and have been made use of in the launching of their industrial production in the Czech Republic.

The results, demonstrated in a comprehensive form in Figs. 1 through 7, indicate that the properties of GF cements are affected by both the chemical and the mineralogical composition of the clinker. However, the chemical composition of clinker influences the properties of GF cements in a way different from that of Portland cements.

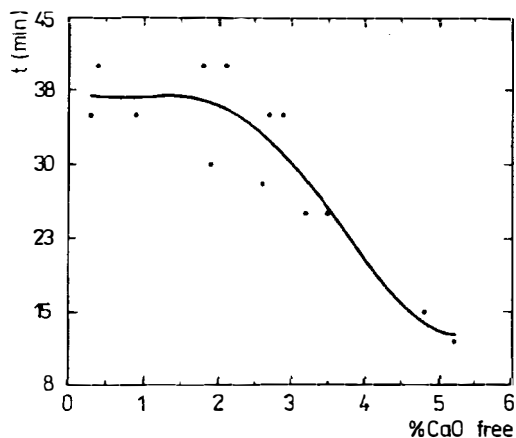


Fig. 1. Early set of paste ( $w = 0.24$ ) of GF cement from Lochkov clinker vs. free CaO content in clinker. Additives: 1%  $\text{Na}_2\text{CO}_3$  + 0.4% Kortan FM.

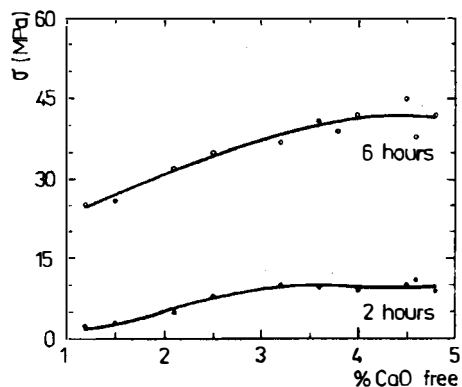


Fig. 2. Compressive strength of paste ( $w = 0.24$ ) of GF cement from Lochkov clinker after 2 and 6 hours vs. free CaO content in clinker. Additives: 1%  $\text{Na}_2\text{CO}_3$  + 0.4% Kortan FM.

The content of free CaO (Fig. 1) was proved to be a factor affecting in a significant way the early set of GF cements. Once a certain content of free CaO has been exceeded (approx. 3%), virtually no retarding agent suitable for GF cements is capable of retarding the early set.

The content of free CaO also influences the course of early strength development (particularly after 2 to 6 hours). At a free CaO content of approx. 3.5%, strengths of up to 45 MPa were achieved (paste with  $w = 0.24$ ). A low content of free CaO in clinker is responsible for a relatively low early strength (especially that after 2 hours) (cf. Fig. 2). There is a noticeable increase in early strength in terms of increasing free CaO content (figs. 2 and 3). In the case of long-term strength (more than 3 days), the increasing content of free CaO brings about a relative decrease of strength.

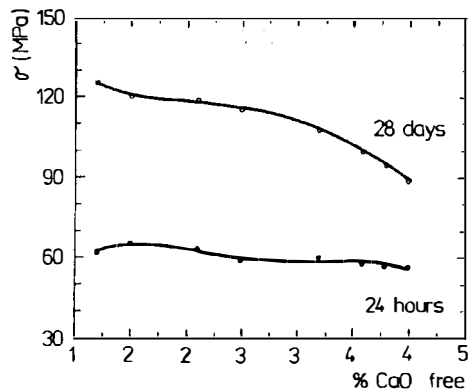


Fig. 3. Compressive strength of paste ( $w = 0.24$ ) of GF cement from Lochkov clinker after 1 and 28 days vs. free CaO content in clinker. Additives: 1%  $\text{Na}_2\text{CO}_3$  + 0.4% Kortan FM.

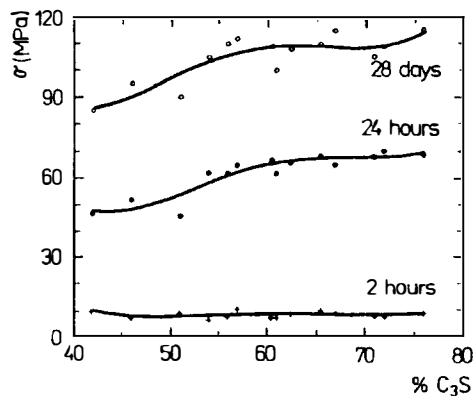


Fig. 4. Compressive strength of paste ( $w = 0.24$ ) of GF cement from Štramberk clinker after 2 hours, 1 and 28 days respectively vs.  $\text{C}_3\text{S}$  content in clinker. Additives: 1%  $\text{Na}_2\text{CO}_3$  + 0.4% Kortan FM.

In all of the instances, the 180-day strengths exceeded those after 28 days, even in cases of high contents of free CaO. It was found that GF cements prepared from clinkers with a high free CaO content (even exceeding 2%, in particular with clinker from Lochkov and other cement works) are fully capable of achieving high long-term strengths.

Tests of the long-term constancy of volume (soundness) of GF cements with various contents of free CaO show that the cements are stable at a free CaO content of up to about 2–3%. Expansion and cracking occurred at higher free CaO contents (above 2–3.5%). As proved by microscopic analysis (SEM + EDAX) of the fracture surfaces of hardened pastes, the expanding formations contain virtually solely  $\text{Ca}(\text{OH})_2$ , similarly to the case of standard Portland cement. The results obtained demonstrate the effects of the other components of Portland clinker on the proper-

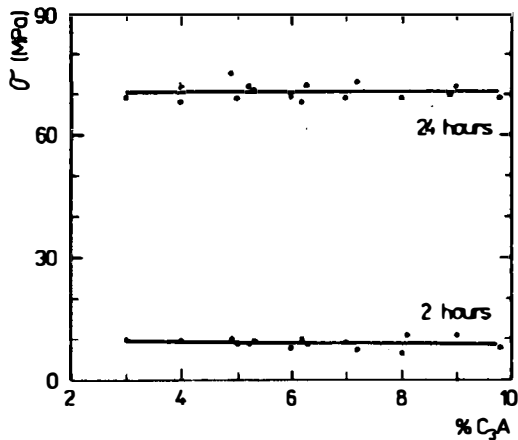


Fig. 5. Compressive strength of GF cement paste ( $w = 0.24$ ) after 2 hours, 1 and 28 days respectively of GF cement from Štramberk clinker vs.  $C_3A$  content in clinker. Additives: 1%  $Na_2CO_3$  + 0.4% Kortan FM.

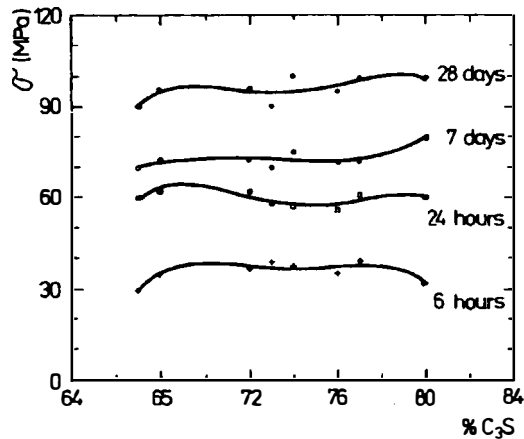


Fig. 6. Compressive strength of GF cement paste ( $w = 0.24$ ) after 2 hours, 1 and 28 days respectively of GF cement from Maloméřice, Prachovice, Čížkovice and Mokrá clinkers respectively, vs.  $C_3S$  content in clinker. Additives: 1%  $Na_2CO_3$  + 0.4% Kortan FM.

ties of GF cements. As illustrated by Figs. 4 and 6, the content of alite does not influence the strength of GF cement as significantly as it does with Portland cements. The small influence of alite on initial strengths is particularly surprising. There was some effect of alite on the long-term strengths, but only a slight one (Figs. 4 and 6).

These results indicate that GF cements can also be made from clinkers belitic in character. Experiments showed that even belitic-type clinkers can be made into GF cements with high early strengths, as proved by Szatura et al. [6].

$C_3A$  has a very small effect on initial strength of GF cements, as indicated by Fig. 5.

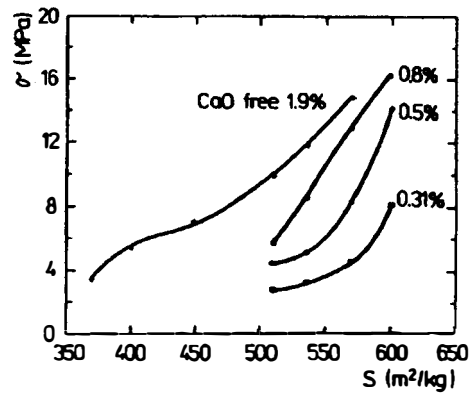


Fig. 7. Compressive strength of GF cement paste ( $w = 0.24$ ) after 7 hours vs. the specific surface area of GF cements from clinkers with various free CaO contents. The clinkers had the mineralogical composition of 56 - 75% alite, 6 - 22% belite, 0.6 - 13%  $C_3A$ , 0.3 - 2.5% free CaO.

The results obtained show that the content of free CaO in clinker is the dominant factor affecting the properties of GF cements. High early strength of GF cements (which is frequently the main requirement for their use) made from clinkers with a low CaO content can only be achieved at the cost of a high fineness. Fig. 7 summarizes the results of a series of clinkers with relatively different compositions, that is 73 - 75% alite, 6 - 9% belite and 10 - 13%  $C_3A$ , and 56 - 59% alite, 22 - 26% belite and 0.6 - 3%  $C_3A$ , and a free CaO content of 0.3 - 2%. Fig. 7 shows the relationship between strength (after 3 hours) and the specific surface area of the cement, where the effect of free CaO in the clinker is distinct (in spite of the differences in the content of the other minerals), Fig. 7 indicates that GF cement with a free CaO content over the 1.5 - 1.9% range attains the same early strength (3 hours) at a specific surface area of 450  $m^2/kg$  as GF cement with a free CaO content of about 0.5%, but with a much larger specific surface area (550 - 600  $m^2/kg$ ).

These results indicate that to attain a high early strength of GF cements, no extra-fine grinding is necessary, as a surface area of 450 - 550  $m^2/kg$  is quite sufficient at the optimum free CaO content of 0.8 - 1.5%. In contrast to Portland cements, GF cements do not need a high alite content to achieve high early strengths.

In Portland cement, the effect of free CaO is mostly associated with its effect on cement soundness after hardening (constancy of volume). As shown by Uchikawa's studies [7, 8], free CaO in clinker has also some influence on the properties of Portland cement. With increasing free CaO content, the time of early set of Portland cement is shortened and the 3- and 28-

day strengths are mildly reduced. In contrast to BF cements, no increase in early strength due to a higher content of free CaO was established with Portland cements.

The C-S-H phase is the main component responsible for early strength in GF cements, while in Portland cements this part is played by the C-A-H phases, e.g. by ettringite. This is why the explanation of the effect of free CaO in clinker on the properties of GF cements should obviously be sought in the change at the beginning of the hydration of alite (as well as belite). As found by Uchikawa [7, 8], the hydration of alite is strongly accelerated in the presence of Na<sup>+</sup> (K<sup>+</sup>) ions, particularly when free CaO is also present. Moreover, in the strongly alkaline medium (formed by the additives replacing gypsum) the concentration of Ca(OH)<sub>2</sub> is strongly suppressed, as found by Locher [9], so that the hydration of alite is accelerated. It may further be assumed that during hydration of GF cements, the effect of free CaO in clinker, apart from changing the concentration of Ca(OH)<sub>2</sub>, can also modify the conditions for nucleation of the C-S-H phase.

The phenomena mentioned above then bring about a shortening of the time of initial set and a rapid development of early strength of GF cements (due to acceleration of C-S-H phase formation) made from clinker with an elevated content of free CaO.

### CONCLUSION

1. The chemical and mineralogical compositions of clinker affect the properties of GF cements. However, these effects differ from those in the case of Portland cement.
2. The effect of free CaO is very marked at the initial set and in the development of early strength. The final strengths are negatively affected by high free CaO contents (on exceeding the value of approx. 3%).
3. Alite content in clinker affects the strength of GF cements less distinctly compared to standard Portland cements.
4. There is virtually no effect of C<sub>3</sub>A content in clinker on the early strength of GF cements.
5. Highly alitic clinkers with a low content of free CaO are not suitable for GF cements. To achieve high early strength, GF cements from such clinkers have to be ground to a significantly higher fineness (at least 550 – 600 m<sup>2</sup>/kg).
6. At a free CaO content of 0.8 – 1.5%, high early strengths of GF cements can already be achieved in the surface area region of about 450 m<sup>2</sup>/kg.

The issue of the effect of mineralogical and chemical composition of clinker (in particular the effect of free CaO and other minority components such as alkalis or sulphur, or the effect of the structure of alite) on the properties of GF cements should be given

systematic attention, especially with respect to possible fluctuations of the properties of GF cement from large-scale production.

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### VLIV MINERALOGICKÉHO SLOŽENÍ SLÍNKU NA VLASTNOSTI BEZSÁDROVCOVÝCH PORTLANDSKÝCH CEMENTŮ

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Chemické a mineralogické složení slínku má vliv na vlastnosti bezsádrovcových portlandských (dále jen BS) cementů, kde je regulační účinek sádrovce nahrazen synergicky působící směsí sulfonovaného polyelektrolytu (ligninsulfonan, sulfonovaný polyfenolát) a alkalické sloučeniny (uhlíčitán). Tento vliv se však projevuje jiným způsobem než u portlandského cementu. Obsah volného CaO se významně projevuje na počátku tuhnutí BS cementů a na vývoji počátečních pevností. Rostoucí obsah volného CaO negativně ovlivňuje (při překročení hodnoty cca 3%) hodnoty dlouhodobých pevností. Obsah alitu ve slínku ovlivňuje pevnosti BS cementů méně výrazným způsobem než je tomu u standardních portlandských cementů. Vliv obsahu C<sub>3</sub>A ve slínku se prakticky neprojevuje na počátečních pevnostech BS cementů. Pro BS cementy nejsou vhodné vysoce alitické slínky s nízkým obsahem volného CaO. Pro dosažení vysokých počátečních pevností BS cementů z těchto slínek je nutná výrazně vyšší jemnost mletí (v oblasti nejméně 550–600 m<sup>2</sup>/kg). Při obsahu volného CaO 0,8–1,5% lze dosáhnout vysokých počátečních pevností BS cementů již v oblasti měrných povrchů cca 450 m<sup>2</sup>/kg.

*Obr. 1. Závislost počátku tuhnutí kaše (w = 0.24) BS cementu ze slínek cementárny Lochkov na obsahu volného CaO ve slínku. Přísady: 1% Na<sub>2</sub>CO<sub>3</sub> + 0.4% Kor-tan FM.*

- Obr. 2. Závislost pevnosti v tlaku po 2 a 6 hodinách kaše ( $w = 0.24$ ) BS cementu ze slínek cementárny Lochkov na obsahu volného CaO ve slínku. Přísady: 1%  $\text{Na}_2\text{CO}_3$  + 0.4% Kortan FM.
- Obr. 3. Závislost pevnosti v tlaku po 1 a 28 dnech kaše ( $w = 0.24$ ) BS cementu ze slínek cementárny Lochkov na obsahu volného CaO ve slínku. Přísady: 1%  $\text{Na}_2\text{CO}_3$  + 0.4% Kortan FM.
- Obr. 4. Závislost pevnosti v tlaku po 2 hodinách, resp. 1 a 28 dnech kaše ( $w = 0.24$ ) BS cementu ze slínek cementárny Štrambersk na obsahu  $\text{C}_3\text{S}$  ve slínku. Přísady: 1%  $\text{Na}_2\text{CO}_3$  + 0.4% Kortan FM.
- Obr. 5. Závislost pevnosti v tlaku po 2 hodinách, resp. 1 a 28 dnech kaše ( $w = 0.24$ ) BS cementu ze slínek cementárny Štrambersk na obsahu  $\text{C}_3\text{A}$  ve slínku. Přísady: 1%  $\text{Na}_2\text{CO}_3$  + 0.4% Kortan FM.
- Obr. 6. Závislost pevnosti v tlaku po 2 hodinách, resp. 1 a 28 dnech kaše ( $w = 0.24$ ) BS cementu ze slínek cementárny Maloměřice, Prachovice, Čížkovice a Mokrá na obsahu  $\text{C}_3\text{S}$  ve slínku. Přísady: 1%  $\text{Na}_2\text{CO}_3$  + 0.4% Kortan FM.
- Obr. 7. Závislost pevnosti v tlaku po 3 hodinách kaše ( $w = 0.24$ ) na měrném povrchu BS cementu ze slínek s různým obsahem volného CaO. Slínky měly mineralogické složení 56–75% alitu, 6–22% belitu, 0.6–13%  $\text{C}_3\text{A}$ , 0.3–25% volný CaO.

## Book Reviews

OPTICAL PROPERTIES OF GLASS Eds.: D. R. Uhlmann, N. J. Kreidl. The American Ceramic Society, USA, 1991, 266 pages, 137 figures.

Utilization of glass as the basic material for optical instruments has been known for several centuries. In spite of this, many new significant findings on the optical properties of glasses have appeared during the last decades. New optical devices and non-traditional technologies have been devised, such as photochromic glasses, glasses with photochromic layers, transparent conductive layers, optical conductors with low attenuation, optical memories, materials with non-linear optical properties, new lasers with glass fibres. The authors of the publication are firmly convinced of the promising prospects of new optical materials and emphasize the significance of studying and describing the relationships between the preparation of new materials, their structure and their optical properties. The authors have chosen several highly interesting subjects dealing with both the classical and the newest types of optical glasses. Each of the subjects has been dealt with by the foremost world expert(s) in the respective field. The subjects are divided into the following seven chapters:

- Optical Properties of Oxide Glasses – W. Vogel
- Optical Properties of Halogenide Glasses – J. Lucas and J. L. Adam
- Non-Linear Optical Properties of Glasses – N. F. Borrelli and D. W. Hall
- Photochromic Glasses – R. J. Araujo and N. F. Borrelli
- Optical Basicity – J. A. Duffy and M. D. Ingram
- Optical Fibres – M. A. Newhouse
- Effects of Radiation – E. J. Friebele.

The first chapter gives a survey of classical oxide

glasses. Abbé's  $n_e$ - $v_e$  diagram is used to plot the classical as well as the most recent optical materials, and tables list the chemical compositions and optical properties of the selected types. The effect of chemical composition on the dispersion behaviour of glasses is discussed. The effect of temperature on the optical properties and the dependence of thermo-optical data on chemical composition are also explained in detail. The author gives an account of absorption in the UV region for colourless glasses and deals with the formation of colours in glasses coloured with ions or colloidal metal particles, as well as with colours in striking glasses and dispersion filters.

The second chapter acquaints the reader with the known glass-forming halogenide systems. The authors deal in more detail with the more stable fluoride glasses containing  $\text{ZrF}_4$  (e.g. ZBLA and ZBLAN), multicomponent glasses free of Zr and containing heavy metals (e.g.  $\text{Ba}_{16}\text{Th}_{28}\text{Yb}_{28}\text{Zn}_{28}$  and  $\text{Ba}_{30}\text{In}_{30}\text{Zn}_{20}\text{Y}_{10}\text{Th}_{10}$ ). Examples are further given of glasses with heavy halogenides (Cl, Br, I), exhibiting higher transmittance in the IR region. The purpose of the account was to explain the relationships between the chemical composition of halogenide glasses, which determines the structure and the character of bonds, and their optical properties.

In the introduction to the third chapter, its authors define the basic terms in the field of non-linear optics. The second part of the chapter deals with the properties of non-linear susceptibility characterizing the non-resonance non-linearity of glass. The anharmonical oscillator is discussed as a possible model of optical non-linearity. This section also presents a brief description of phenomena observed in glasses (e.g. the non-linear refraction index) and is concerned with the principles of techniques employed in measuring the non-linearity. Likewise described are the relations between the microscopic origin of non-linearity