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THE GYPSUM-FREE PORTLAND CEMENT HYDRATION AND THERMAL PROPERTIES

Frant. Škvára, Joint Laboratory for Silicate Chemistry
Prague 6, Czechoslovakia
Lad. Pekárek, Boh. Velička, Ferrous Metallurgy Institute
Dobrá u Frýdku-Místku, Czechoslovakia

ABSTRACT

The ground clinker (without gypsum) + ligninsulfonate (sulfonated polyphenolate) + alkali metal salts (carbonate, bicarbonate, silicate) represents a new type of binding agent (gypsum-free portland cement, GF cement) that differs from the conventional portland cement in its short- and long-term strength and resistance to high temperatures (to 1450°C). The GF cement processed at low water/cement ratios shows a different progress of hydration (RTG, TA, SEM study) and different development of microstructure than the portland cement (absence of portlandite crystals). The GF cements had been used with success as refractory materials in the steel industry.

INTRODUCTION

In our earlier papers (1-3) we described the properties of the inorganic binding agent which is based on ground clinker in the absence of gypsum. Such a gypsum-free portland cement (GF cement) may be characterized as a system of : ground clinker (specific surface up to 700 m^2/kg) + surface-active substance (ligninsulfonate, sulfonated polyphenolate) + hydrolyzable salt of alkali metal (carbonate, bicarbonate, silicate). The GF cements differ from the common portland cements (PC) primarily in the possibility of being processed at a low water/cement ratio and in their high resistance to corrosive environment. Another difference is in clinker grinding in the absence of gypsum and in a different setting regulator. This paper deals with the results obtained in the study of GF cements hydration and resistance to the action of high temperatures.

MATERIALS AND METHODS

In our experiments we used the GF cement that was made by grinding the ordinary cement clinker to attain its specific surface of 700 m^2/kg in the presence of 0.5% of pure natrium ligninsulfonate. The clinker composition was as follows: CaO 66.3%, SiO_2 21.7%, Al_2O_3 6.1%, Fe_2O_3 2.6%, MgO 1.0%, SO_3 0.29%, Na_2O+K_2O 0.79%, CaO free 1.1%. GF cement pastes were prepared (w = 0.23 to 0.25) and

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mixtures of GF cement and quartz sand (1:3 by weight), and those of GF cement plus corundum, magnesite, and chrommagnesite (1:6 to 1:9). When processing the GF cements, the following supplements were used: natrium ligninsulfonate, sulfonated polyphenolate, Na_2CO_3, NaOH in the total amount equal to 1.5 to 3% of the GF cement weight. In the materials obtained this way, we studied the composition of the hydration products (DTA + DTG, SEM, RTG, EDAX) and the development of strength at 20°C. (Details of the methods used were described earlier (3). The mixtures of GF cements and aggregates were tested for the compression strength following their firing at 500 to 1000°C. These were also examined for their resistance to deformation in heat at a 0.2 MPa load (in line with the Czechoslovak Standard No.726015).

RESULTS AND DISCUSSION

The results of the study of the chemical and phase composition of hardened GF cement pastes (w = 0.23 to 0.25) obtained by way of the DTA (Fig. 1), RTG, SEM, and EDAX analyses show that it is close to the composition of hardened PC pastes. The binding products of GF cement hardened pastes after 1 to 3 hours of hydration (compression strength 1 to 9 MPa) consist of crystal and amorphous products the CaO/SiO_2 ratio is 1 to 5, and that of CaO/Al_2O_3 some 10 to 50. Within 12 to 24 hours, a compact microstructure would develop (of the 50 to 80 MPa strength) the morphological character of which would remain unchanged (Fig. 2) but the strength would continue to increase. In the compact structure no crystal parts typical of hardened PC pastes were found (portlandite, ettringite). The $Ca(OH)_2$ production was markedly slower than in the PC pastes, and the content of portlandite in hardened GF cement pastes was by 30 to 50% lower than in hardened PC pastes. No sulphoaluminate hydrates (ettringite, monosulfoaluminate) were identified in the course of GF cement paste hydration. The existence of carboaluminate complexes (analogues of sulphoaluminate hydrates) was not clearly proven. At the C-S-H stage of hardened GF cement pastes the CaO/SiO_2 ratio was found to be 2.7 ± 0.1 by using the EDAX analysis. Apart from cubic hydroaluminate we found the hexagonal hydroaluminates C_4AH_4 as well as C_2AH_8 too. The major component of hardened GF cement pastes is the high-calcium hydrosilicates impregnated with very fine $Ca(OH)_2$ and highly dispersed hydroaluminates. Also non-hydrated clinker particles (micron-sized) were found in hardened pastes. The absence of crystal aggregates(typical of hardened PC pastes) in GF cement

pastes and the high level of compactness and dispersion of the hydration products are, apart from a lower water/cement ratio effect, responsible for higher strengths attained in the GF cements. The microstructure and composition of hydrated GF cements result not only in a higher strength after hardening and greater resistance to aggressive environment but also in a different response to higher temperature.

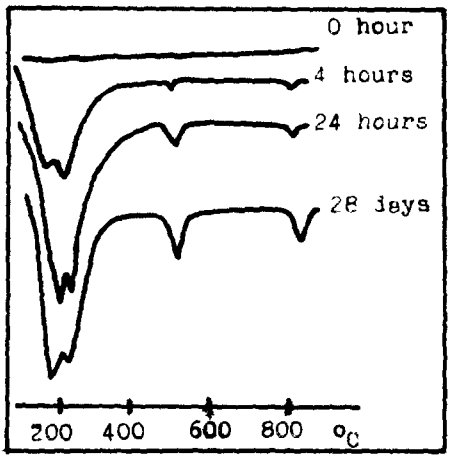

Fig. 1 DTA of hydrating paste (w = 0.23)

Hardened GF cements show - in contrast to PC - a strength decline at temperatures of 800-900°C, and a distinct strength drop only beyond the 1000°C limit. Their products by burning at 500-900°C did not contain any pseudomorphoses originated from disintegrated typical portlandite crystals (which is the case of PC). A subsequent temperature increase leads to a fast clinkering involving the melt due to a great level of hydration products dispersion. The resultant GF cement melt exhibits - because of the absence of sulphate anions (of gypsum origin) - a distinctly higher surface tension and viscosity than the PC cement melt. This is why the GF cements showed a high resistance to heat deformation (Tab. 1).

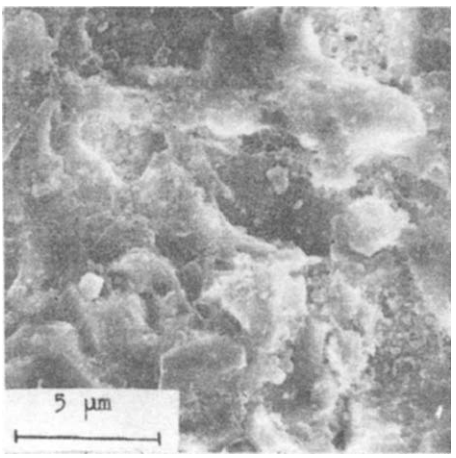

Fig. 2 SEM of GF cement paste, 28 days.

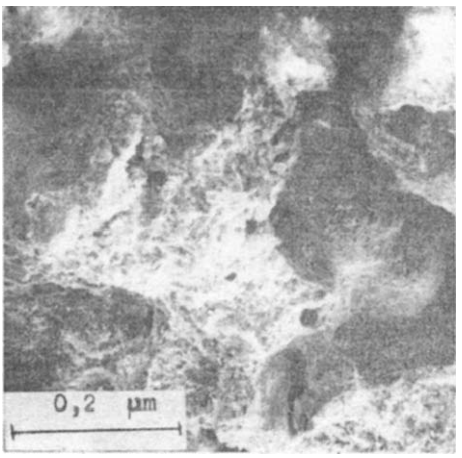

Fig. 3 SEM of porous refractory material (GF + chrommagnesite) after 8 meltings.

Table 1

MIXTURE	RESISTANCE TO HEAT DEFORMATION	COMPRESSION STRENGTH AFTER 3 DAYS (MPa)
13.4% GF cement + 86.6% corundum	1450°C	40
30.0% GF cement + 70.0% chrommagnesite	1380°C	25

APPLICATION OF GF CEMENTS

The GF cements (mostly of 500 to 700 m^2/kg specific surface) were used with success in Czechoslovakia in a number of experimental cases (repairs, grouting, etc.), and apart from this heat-resistant materials based on GF cements were employed in quick improvements and rapairs of metallurgical and hot-wind furnaces (linings). Porous refractory stones (Fig. 3) on the basis of GF cements were developed too, and these are suitable for argon and nitrogen blasting into liquid steel or cast iron at off-furnace processing (4).

CONCLUSIONS

1. The GF cements represent a new type of organic binding agent based on current cement clinker. This binding agent is suitable primarily for special purposes.
2. The GF cements attain higher strength levels than PC ones and are resistant to higher temperatures.
3. The hydration products of GF cements are similar to those of PC ones. Their resistance to high temperature is due to a lower content of $Ca(OH)_2$, the sulphoaluminate products and great compactness of hardened GF cement pastes.

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