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Changes of thermal events of macrodefect-free (MDF) cements due to the deterioration in the moist atmosphere☆

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Abstract

Sulfoaluminate ferrite belite (SAFB) clinker premixed with Portland cement in mass ratio 85:15 was combined with hydroxypropylmethyl cellulose (HPMC) or sodium poly-phosphate (poly-P) for the macrodefect-free (MDF) process and subsequent moisture treatment. Mass changes as the measure of the moisture resistance and thermoanalytical traces of MDF cements gave useful information. The mass change depends more on the humidity than on the composition (polymer and inorganic constituents) of the MDF cement or duration of the original MDF cement synthesis. The values of mass changes at 100% relative humidity (RH) and at ambient conditions are affected by the nature of the polymer, poly-P being highly advantageous. Attack by environmental water and carbon dioxide increases the contents of $C_4(A,F)\bar{S}H_{12}(AFm)$ and $CaCO_3$, represented by thermogravimetry (TG) effects at 250°C and differential thermal analysis (DTA) peaks at 600–700°, respectively. In contrast, the quantity of cross-linking, where the decomposition of Al(Fe)–O–C(P) bonds typically produces TG–DTA effects at 250–550°C, remains intact during the moisture attack.

Keywords: Humidity; Thermal analysis; Al(Fe)–O–C(P) cross-links; Blended cement; Polymers

1. Introduction

Since the introduction of macrodefect-free (MDF) cements in 1981 there has been much interest in these unique materials. Various clinker/polymer combinations have been said to have potential as regards formation of MDF cements [1]. It is proposed that MDF cements composed of calcium aluminate cement and polyvinyl alcohol/acetate (PVA) have microstructures with close-packed unreacted cement particles acting as a filler within the binding matrix [2,3]. The matrix consists of two interpenetrating phases: a cross-linked clinker with polymer and a nanocomposite interphase region around the cement particles. Portland cement-based MDF cements do not have this microstructure [3]. Sensitivity to moisture, a technologically critical parameter [3–5], is caused through adsorption of water by the polymer phase and diffusion to the reactive cement filler which then hydrates. The microstructure is thus degraded to a hydrate-bonded matrix. The substitution of PVA by a hydrophobic phenol-formaldehyde thermosetting resin may produce a highly water-resistant product [3,6].

We have formerly reported on the processability of individual constituents of potential sulfoaluminate ferrite belite (SAFB) clinker, and of SAFB clinker itself, in combination with hydroxypropylmethyl cellulose (HPMC) or sodium poly-phosphate (poly-P) [5,7–9]. Our studies demonstrate the potential of low-energy SAFB clinker and cements for the MDF cement process. The results have pointed to (a) the involvement of Al, Fe, P, C and O atoms in cross-links within amorphous *AFm*-like reaction product or intergranular gel, and (b) the influence of cross-link chemistry on porosity, electrical impedance, microstructure and moisture resistance. HPMC or poly-P in reaction mixtures improves processability and moisture resistance.

Blends of SAFB clinker (85 mass%) with Portland cement (15 mass%) exhibit generally better properties than SAFB clinker alone, i.e. setting times and other technological properties [10]. There are no data on MDF cements

☆ The use of cement chemistry notation is as follows: C=CaO, A=Al_2O_3, F=Fe_2O_3, S=SiO_2, $\bar{S}$=SO_3, H=H_2O, c=CO_2, w/s=water/solids mass ratio.

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synthesized from similar blends. The present work is therefore focused on MDF systems using SAFB clinker with Portland cement and HPMC or poly-P. The aim of our study was to follow the effect of Portland cement in the raw mix on processing and subsequent moisture resistance. The information was collected from (i) the values of mass changes as a measure of the moisture resistance and (ii) thermogravimetry (TG)–differential thermal analysis (DTA) traces of hydraulic phases. Cross-linking and phases arising from moisture attack on MDF cements are reported and discussed.

2. Experimental

Complex SAFB clinker (in which the individual clinker phases were present along with C_2S, belite, 25% by mass) was synthesized at 1250°C. Low-energy SAFB plant clinker was produced at 1240–1270°C in a standard medium-sized rotary kiln (Cimus, Romania). Sintering conditions (raw materials, potential phase composition, sintering temperature and duration) have been optimized previously [5,9,11–13]. Powder X-ray diffraction revealed the presence of C_2S, $C_4A_3\bar{S}$ and C_4AF in lab-scale as well as in plant clinker. SAFB clinker blended with Portland cement (CEM I 42.5) in mass ratio 85:15 was used for the MDF cement process and subsequent moisture treatment; both procedures are described below.

Processing was carried out as follows, cf. [5,7–9,13]: (a) Initial dry premixing of the cement blends with HPMC (5% of total mass) was followed by either (b) addition of water to give w/s = 0.2 or (c) addition of an aqueous solution of sodium polyphosphate (poly-P) to incorporate 5% (by mass) of poly-P and give w/s = 0.2 ("s" includes clinker and mass equivalent of the dissolved poly-P). (d) Twin-rolling was employed until the mixture reached the consistency of dense dough (up to 5 min), (e) static 5 MPa pressure in a pellet die (diameter 10 mm) was applied for intervals ranging from 30 min to 5 h and (f) chemical reactions were kinetically frozen by air drying at 50°C. HPMC (Aldrich) used corresponds to the viscosity of a 2% aqueous solution 80–120 cP. The sodium polyphosphates (Aldrich) were of formulae $(NaPO_3)_n$ and $Na_5P_3O_{10}$. The use of $Na_5P_3O_{10}$ (exhibiting low solubility) required a modification of the MDF process in that the cement mixture was premixed dry with the $Na_5P_3O_{10}$ (5% of total mass) and the process continued through Steps (b), (d), (e) and (f).

The moisture resistance of model MDF cement samples was investigated at two different relative humidities. Cylindrical samples were kept in desiccators at controlled relative humidity (RH) values, namely (a) above saturated $NaHSO_4$(aq) (52% RH) and (b) above deionized water (100% RH). Mass changes were recorded by periodic weighing until constant mass (incremental change $\Delta m < 0.01\%$) defined equilibrium at the given RH. Further measurements of the (decreasing) masses of test pieces previously equilibrated at extreme humidity, 100% RH, were similarly carried out during reequilibration under ambient laboratory conditions; these measurements led to an estimation of irreversible portion of mass changes due to the moisture attack at 100% RH. More methodological details can be found in Refs. [5,13].

Both cross-linking and phases associated with the irreversible component of the mass increase were investigated thermoanalytically. Simultaneous TG and DTA were conducted from 20°C to 1000°C using a T.A.I. SDT 2960 instrument (sample mass 10–20 mg, heating rate 10°C/min, in flowing air). Thermoanalytical studies were made on powders of two series of MDF cement samples (as synthesized and after the completion of given sequence of the moist treatment).

3. Results and discussion

3.1. Mass changes as a measure of the moisture resistance of MDF cements

The mass changes as the function of duration of exposure to environments of given RH are given in Fig. 1; equilibrium mass values are attained within 8 to 13 days for either of the humidities. The present series is considered and discussed as follows: the effect of 52% RH or 100% RH, in the latter case subdivided into irreversible change (the residual mass after decrease at ambient conditions) and reversible change (difference between the mass at 100% RH and the residual mass). The results show nearly negligible mass changes at 52% RH for the MDF cement samples studied. The equilibrium mass increase after the treatment at

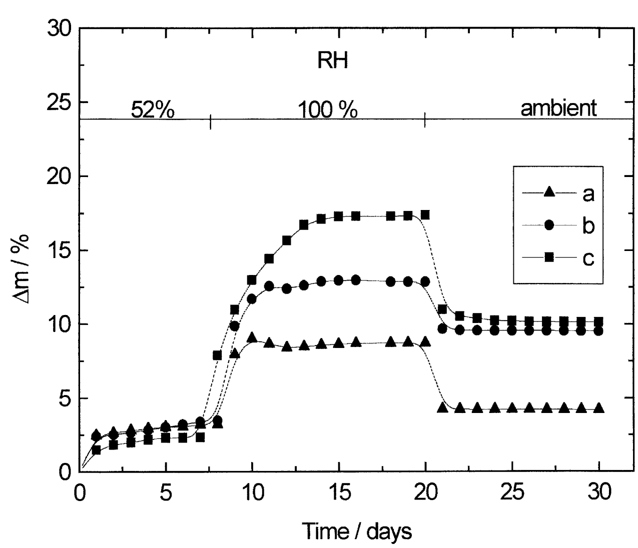

Fig. 1. Mass change Δm as a function of time for MDF cement test pieces fabricated from blends of SAFB clinker and Portland cement with (a) dissolved poly-P–$(NaPO_3)_n$, (b) powdered poly-P–$Na_5P_3O_{10}$ and (c) HPMC, and treated at 52% RH (for 8 days), at 100% RH (from Days 9 to 21) and under the ambient conditions (from Days 22 to 30).

100% RH strongly depends on the nature of polymer, Δm(HPMC) > Δm(poly-P), the lowest values being found with samples containing soluble poly-P. Irreversible values after reequilibration range from 3 mass% (samples with dissolved poly-P) through 7 mass% (samples with dry premixed poly-P) to 10 mass% (samples with HPMC). The results show a step-wise influence of the moist atmosphere. The association of low mass change with higher moisture resistance is consistent with the barrier or impregnation effect of cross-links comprising polyphosphate ions, proposed earlier [5,8,13].

The effect of individual humidity upon the evolution of mass is larger than the influence of composition (polymer and inorganic constituents) of MDF cements or duration of the original MDF cement synthesis. However, values at 100% RH and after the reequilibration at ambient conditions are strongly affected by the nature of the polymer in MDF cement based on SAFB clinker [5,9,13] or on blends of SAFB clinker and Portland cement (Fig. 1). The moisture resistance dropped by 1–2% for identical conditions of treatment when Portland cement was added. Dissolved poly-P remained the most favorable polymer; this supports the validity of the key role of atomic level interactions of polyphosphate ions for the moisture resistance of SAFB clinker and Portland cement-blended MDF cement compositions.

3.2. Thermoanalytical identification of the deterioration in the moist atmosphere

Table 1 gives TG and DTA data. Figs. 2–4 are given as examples. The dependence of the TG traces of moisture attacked samples on the type of polymer (Fig. 2) are similar to those discussed earlier [9]. Individual sequences, as well as total mass changes for poly-P or HPMC-containing MDF cements attacked by extreme moisture (17.4% for poly-P vs. 23.2% for HPMC) support the hypothesis about the impregnation or barrier effect of poly-P, quoted earlier. Figs. 3 and 4 (before and after moisture attack, respectively) illustrate individual TG and DTA curves for MDF cements made from SAFB clinker, Portland cement and powdered poly-P. The TG and DTA data confirm the differences between attacked and nonattacked MDF cement samples. There is a significant difference in the case of nonattacked MDF cements with or without Portland cement. The TG curves of nonattacked MDF cements in the systems containing SAFB clinker and HPMC or poly-P exhibit two temperature ranges [9,13], while the TG curves of MDF cements in the systems containing the blends of SAFB clinker and Portland cement and HPMC or poly-P exhibit three temperature ranges (Table 1, Fig. 3). The temperature ranges of the thermal events (TG curves) of moisture-attacked MDF cements are similar to those reported for MDF cements in the systems containing SAFB clinker and HPMC or poly-P [9,13]. However, mass losses differ in the respective temperature ranges.

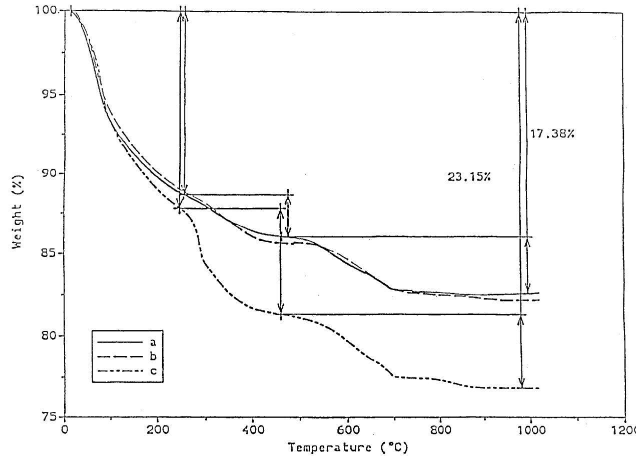

Fig. 2. TG curves for MDF cements made with different polymers and irreversibly attacked at 100% RH. (a) Dissolved poly-P–$(NaPO_3)_n$, (b) powdered poly-P–$Na_5P_3O_{10}$ and (c) HPMC.

Table 1
Summary of TG intervals (°C) and DTA peak temperatures (°C) of MDF cement samples based on blends of SAFB clinker and Portland cement

	MDF samples			
	As synthesized		After irreversible attack of 100% RH	
Polymer additives	TG	DTA	TG	DTA
HPMC	20–250	190	20–250	92, 180
	250–500*	282*	250–500*	295*
	500–600 (CH)		500–700 (CH) (Cc)	680 (Cc)
poly-P	20–250	181	20–250	76, 180
	250–500*	308*	250–500*	315*
	500–600* (CH)		500–720* (CH) (Cc)	667 (Cc)

Thermal events are assigned as follows: * = decomposition of cross-linked section of MDF cements; CH = decomposition of $Ca(OH)_2$; Cc = decomposition of $CaCO_3$. Values in the presence of poly-P are similar if $(NaPO_3)_n$ or $Na_5P_3O_{10}$ is used in the syntheses.

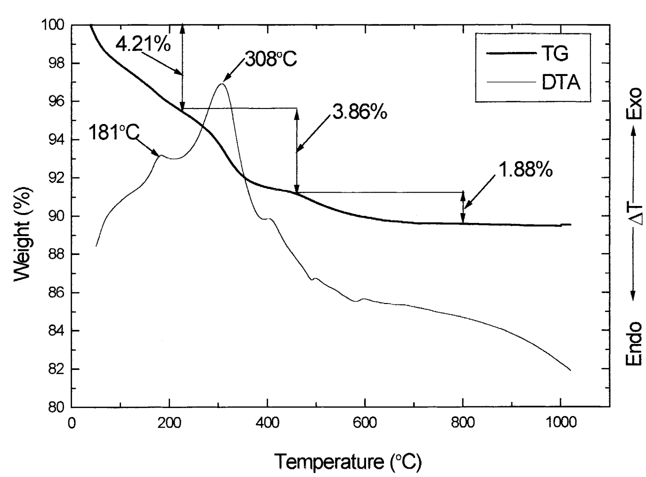

Fig. 3. TG and DTA curves for a sample made using SAFB clinker, Portland cement and powdered poly-P ($Na_5P_3O_{10}$).

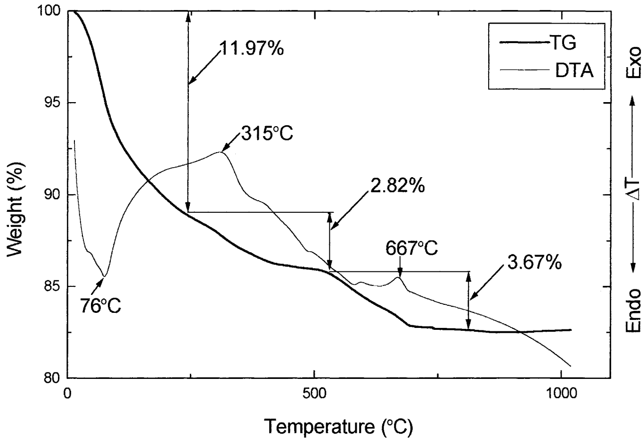

Fig. 4. TG and DTA curves for a sample made using SAFB clinker, Portland cement and powdered poly-P ($Na_5P_3O_{10}$), irreversibly attacked at an extreme level of moisture (100% RH, for 13 days and subsequently ambient conditions for an additional 8 days).

Three distinctive temperature regions in the thermoanalytical traces for both series of MDF cements (both as synthesized and reequilibrated after moisture attack) are useful for investigation of the phase changes due to the deterioration in a moist atmosphere. The ratio in the blends of SAFB clinker/Portland cement (85:15) suggests that *AFm* and *AFt* are the key hydrates. Decomposition of these is more important than the decomposition of other hydrates when discussing the thermal events of the studied MDF cements.

(i) Up to 250°C — main temperature region of decomposition of the hydration products formed from Portland cement and SAFB clinkers [14,15]. Specimens attacked by moisture show an increase of 4–7% in the loss in this region. The mass losses are associated with DTA effects at 76–190°C (Figs. 3 and 4 and Table 1), the temperature region typical for the decomposition of $C_4(A,F)\bar{S}H_{12}$ and related *AFm* compositions [14]. These arise due to the moisture attack on clinker grains only partly hydrated in the original MDF cements.

(ii) 250–500°C — temperature region of decomposition of the cross-links and $Ca(OH)_2$ [5,9,13,14]. The closely similar TG and DTA characteristics in both series (Figs. 3 and 4) indicate that the clusters of Al(Fe)–O–C(P) cross-links are unaffected by moisture under the test condition used. Thus, Portland cement, if properly mixed with SAFB clinker, does not affect the moisture resistance of the *AFm*-like cross-linked section of the MDF cements and the impregnation effect [5,9] of Al(Fe)–O–C(P) cross-links is conserved.

(iii) Above 600°C — temperature region of carbonate decomposition [14–16], seen in the moisture attacked samples as an additional mass loss of 1.5–4%, with a DTA peak typically 667–680°C (Fig. 4 and Table 1). The TG and DTA effects in this temperature region provide evidence that the other crucial phase change of MDF cement samples in moist environments is carbonation. CO_2 like water is transported to the reactive cement filler as described in Refs. [3,4].

The results indicate that, in the MDF cements studied, the Al(Fe)–O–C(P) cross-linkages resist attack by moisture but that the secondary reaction of unhydrated clinker phases occurs through inward diffusion of moisture and carbon dioxide.

4. Conclusions

(1) The extent of moisture attack on MDF cements synthesized from the blends of SAFB clinker, Portland cement and HPMC or poly-P has been quantified using mass changes as a measure of moisture resistance, which is strongly affected by the nature of the polymer. The method proved to be a powerful tool for studying moisture attack on various MDF cement compositions. The addition of Portland cement in the raw mix improves the moisture resistance of MDF cements.

(2) Thermal analysis shows that an irreversible mass gain of 3–10% arises from carbonation and secondary hydration of cement grains. The Al(Fe)–O–C(P) cross-links in the *AFm*-like region remain intact in the moist environment at either ambient or extreme levels of humidity.

(3) Studies of mass changes and thermal analysis provide useful information on the moisture sensitivity of MDF cements. The present results support our previous hypothesis about the impregnation or barrier effect of poly-P on the MDF cement systems and enlarge the validity of this hypothesis to the blends of SAFB clinker, Portland cement and HPMC or poly-P. The advantage of poly-P for the MDF cements has been outlined.

Acknowledgments

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