ATTACK BY MOISTURE ON ADVANCED CEMENT*-BASED MACROSCOPIC DEFECT-FREE MATERIALS
A thermoanalytical study

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Abstract

When exposed to attack by moisture, macroscopic defect-free materials (MDFs) undergo mass and phase changes. The nature of such changes was studied thermoanalytically. Attacked samples differ from non-attacked samples in the degradation of classical cement hydrates (TG, below 200°C) and calcium carbonate (TG, DTA, 550–650°C). Quantitative assessment favours the hypothesis of the impregnation/barrier effect due to the incorporation of polyphosphate glass into the structure of the MDFs. The identity of the thermal decomposition of attacked and non-attacked samples in the range 250–400°C demonstrates the resistance of cross-linked sections of polymer and clinker constituents to the effects of moisture.

Keywords: attack by moisture, macroscopic defect-free materials, thermal stability

Introduction

The increasing knowledge relating to macroscopic defect-free materials (MDFs), together with the definition of chemically bonded ceramics as a class, has led to the gradual acceptance of a chemical hypothesis of the origin of their properties. It is considered that the chemical cross-links and changes in bulk properties (relative to those in polymer-free cements) are the result of reactions occurring during the formation of MDFs. Birchall *et al* [1] outlined the use of aluminous cements, portland cements and sulfate clinkers, and a wide range of water-soluble carbonaceous polymers. Several models involving atomic-level cross-linkages have been postulated to explain the chemical origin of the exceptional properties of MDFs produced from aluminous cements and polyvinylalcohol-acetate [1–6]; these models are complementary and evidently provide a realistic chemical view of the reactions occurring.

We earlier reported [7, 8] on the involvement of Al, Fe, P and C atoms in cross-links within the amorphous AFm-like reaction product/intergranular gel during the

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* The cement chemistry notation used is as follows: C=CaO, A=Al₂O₃, F=Fe₂O₃, S=SiO₂, S̄=SO₃, H=H₂O, c=CO₂, w/s=water:solidus mass ratio

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MDF development process of sulfobelitic (SAFB) clinkers with other examples of water-soluble polymers: hydroxypropylmethyl cellulose (hpmc) and polyphosphate glass (poly-P). The design of Al(Fe)–O–C(P) cross-links resulted from magnetic resonance studies. The thermoanalytical curves display characteristic effects (TG, DTA, 250–350°C) due to the presence of polymers in the reaction products and to the thermal decomposition of linkages of Al(Fe)–O–C(P) in the material in the given temperature range. Thus, the heat evolution dynamics of the reactions and the decomposition temperatures of the reaction products higher than those of classical hydrates [16] support the presence of solidified polymers in cross-links within AFm-like intergranular regions.

Control of the resistance of MDFs to moisture is an exceptionally important task for both scientists and technologists. The incompleteness of conversion of clinkers is obvious at the given ratios *w/s* (typically, *w/s* ranges from 0.1 to 0.2), and this incompleteness exerts a negative effect: low (or undefined) moisture resistance. Studies on the resistance of MDFs to moisture are not uniform as concerns their results. Igarashi and Takarashi [9] differentiate the effects of moisture below and above a relative humidity (*RH*) of 65%; the lower *RH*s did not deteriorate the MDFs, whereas the higher *RH*s did. Their study was performed on portland cement-based MDFs. Results have also been presented for aluminous MDFs [10, 11]; the resistance of these to moisture was believed to be high. Percolative principles controlling the kinetics of degradation of moisture have been discussed in general by Chu and Robertson [12], but the effects are not satisfactorily defined for MDFs. Our earlier studies on the control of the resistance of MDFs based on sulfobelitic clinker to moisture [13, 14] showed that the presence of clusters with cross-links decreases the percolation if the *RH* is less than or equal to 52%. A substantial mass increase occurs in an environment with 100% *RH*, with reversible and irreversible mass changes depending on the nature of the polymer. This has led to the postulation of a hypothesis of the impregnation/barrier effect of poly-P in the structure of MDFs.

The present work focused on the thermoanalytical recognition of the irreversible phase changes that occur when MDFs based on sulfobelitic clinker, hpmc and/or poly-P are exposed to extreme humidity (*RH*=100%). The regions and phases resistant or not resistant to attack by moisture have been distinguished and correlated with the localization of the cross-linked sections in the original MDF.

Experimental

Laboratory clinker phases (C_4AF, $C_4A_3\overline{S}$) and physical mixtures of them were prepared [7] by reactions of chemical grade compounds at 1250°C. More complex SAFB clinkers (in which the individual clinker phases were present together with C_2S, belite, 25% by mass) were synthesized at 1250°C [13]. Low-energy SAFB plant clinkers were produced at 1240–1270°C in standard medium-sized rotary kilns (Cimus Ltd, Romania). Sintering conditions and phase analysis data are given in Table 1.

Processing to obtain model MDF materials was carried out as follows: (i) Dry premixing of clinker phases or cement with hpmc (5% of total mass). (ii) Addition

Table 1 Clinker fabrication conditions and the presence of clinker minerals

No.	Ignition conditions	Phases present (powder X ray)	Notes
1a	laboratory furnace 1250°C	C_4AF	1a+1b in mass proportions 1:1, 1:2 or 2:1 gave the mixtures of $C_4AF+C_4A_3\bar{S}$ for MDF-processing
1b	laboratory furnace 1250°C	$C_4A_3\bar{S}$	
2	laboratory furnace 1250°C	$C_4AF+C_4A_3\bar{S}+C_2S$	ground, dry-stored and MDF-processed
3	laboratory furnace 1250°C, quenched	$C_4AF+C_4A_3\bar{S}+C_2S$	ground, dry-stored and MDF-processed
4	plant rotary kiln 1240–1270°C	$C_4AF+C_4A_3\bar{S}+C_2S$	ground, dry-stored and MDF-processed

of water to give w/s=0.2, or addition of an aqueous solution of sodium polyphosphate to incorporate 5% (by mass) of poly-P and give w/s=0.2 (s includes clinker and the mass equivalent of the dissolved poly-P). (iii) Twin-rolling until the mixture attains a consistency of dense dough (up to 5 min). (iv) Static 5 MPa pressure in a pellet die (diameter 10 mm), applied for periods of 30 min to 6 h. (v) Chemical reactions kinetically frozen by air-drying at 50°C. Hydroxypropylmethyl cellulose (Aldrich) was of p.a. purity (viscosity of 2% aqueous solution: 80–120 centipoise). Sodium polyphosphate glass (Budit 9, approximate stoichiometry of a tetraphosphate) was supplied by Chemische Fabrik R.A. Oetker (Budenheim, Germany).

The resistance of model MDF samples to moisture was investigated at two different RHs. Cylindrical samples were kept in desiccators in an environment with constant RH: (i) saturated $NaHSO_4$ aq (RH=52%) or (ii) deionized water (RH=100%). Mass changes were recorded by periodic weighing up to equilibrium mass increases defined by the incremental change $\Delta m<0.01\%$ at RH=52 and 100%. Further measurements of the mass (its decrease) of test samples (after equilibration at RH=100%) were carried out during equilibration under ambient laboratory conditions (again until $\Delta m<0.01\%$). The resulting values are further considered and discussed as irreversible mass changes due to attack by moisture. With the above sequence, four series of mass changes were determined and discussed earlier [14]:

- the effect of RH=52%;
- the effect of RH=100%, subdivided into
– irreversible change (the residue after mass decrease under ambient conditions),
– reversible change (the difference between the total and the residue).

The reactions and phase changes associated with the irreversible component of the mass changes were of interest. Accordingly, the residues after treatment at RH=100% and subsequent storage under ambient conditions were powdered and investigated thermoanalytically. Simultaneous TG and DTA were conducted from am-

bient temperature to 1000°C, using a T.A.I. SDT 2960 instrument (10–20 mg sample mass, 10°C min⁻¹ in flowing air), on two series of MDF samples (as-synthesized and after attack by moisture). Additional runs incorporating 'equilibration' segments at selected temperatures (according to the analysis of the original data) were taken for representative samples of both series. Equilibration at a given temperature is an optional segment of the SDT 2960 control mode. the other measuring conditions were identical with those in the original runs.

Results and discussion

Data relating to the whole range of studied compositions during thermal treatment are presented in Table 2.

Table 2 Indicative TG intervals (°C) and DTA peaks temperatures (°C) of sulfobelite clinker based MDF samples

Polymer additives	MDF samples			
	as-synthesized		after irreversible attack by 100%*RH*	
	TG	DTA	TG	DTA
hpmc	100–200	100	100–250	100
	250–400*	300*	250–350*	300*
			500–700 (Cc)	570 (Cc)
poly-P	100–200	100	100–400	100
	250–350*		200–350*	350*
	500–700*		450–750* (Cc)	570 (Cc)
hpmc + poly-P	100–200	100	100–250	100
	200–400*	300*	250–400*	300*
	500–700*		400–700 (Cc)	570 (Cc)

Indicative thermal events: * – decomposition of cross-linked section of MDFs, (Cc) – decomposition of $CaCO_3$

Thermal treatment generally demonstrated differences between attacked and non-attacked MDF samples in the first (100–250°C) and third (450–750°C) temperature intervals. Figures 1 and 2 illustrate the sequences of thermal decomposition of attacked and non-attacked MDF samples. Evaluation of the mass losses and relation of these to the effects in the DTA curves confirmed three distinct temperature intervals and particular changes within these intervals after attack by moisture, as follows:

- 100–250°C – increased mass loss from samples after attack by moisture,
- 250–450°C – no change in DTA or TG curves of samples after the attack,
- 450–750°C – additional mass loss from samples after attack by moisture.
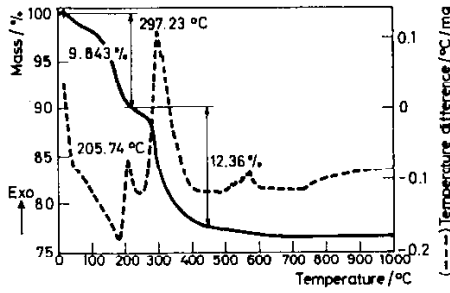
Fig. 1 Thermoanalytical curves of the model MDF material. The sample was synthesized from the laboratory model of sulfobelitic clinker (No. 2 in Table 1) with hpmc
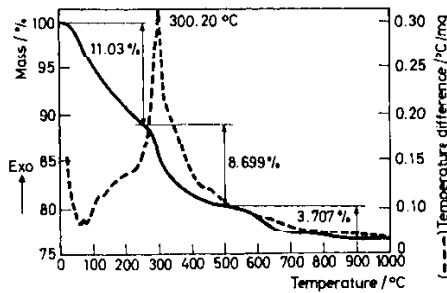

Fig. 2 Thermoanalytical curves of the model MDF material. The sample was synthesized from sulfobelitic clinker (No. 4 in Table 1) with hpmc; it was then irreversibly attacked for 20 days in an environment with 100% *RH* and for 5 days under ambient conditions (up to mass equilibration)
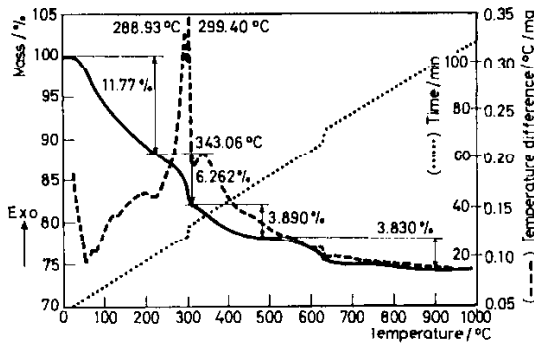

Fig. 3 Thermoanalytical curves of the model MDF material. The sample was synthesized from sulfobelitic clinker (No. 4 in Table 1) with hpmc; it was then irreversibly attacked for 20 days in an environment with 100% *RH* and for 5 days under ambient conditions. Equilibration segments during thermal decomposition were included at 300 and 650°C

Further, we measured a quasi-isothermal segment of the process of decomposition of the examined samples. As mentioned in the experimental section, this SDT 2960 control mode allows equilibration at given temperatures. We estimated these temperatures in accordance with the analysis of the original data. This series of results shows (Fig. 3) that quasi-isothermal equilibrium segmentation is a powerful tool in studies of the thermoanalytical details of MDF materials. The thermal events in the first and second temperature intervals were established for both moisture-attacked and non-attacked samples. The first step of mass loss is fully completed by 250°C; the attacked samples exhibit a mass loss higher by 2–4% in this step. For the attacked samples, the second interval was subdivided into two steps, with characteristic effects in the DTA curve (300 and 340°C), the former being the typical feature of the decomposition of the Al(Fe)–O–C(P) linkages [8, 13]. Within experimental error, the mass loss was the same for individual non-attacked samples.
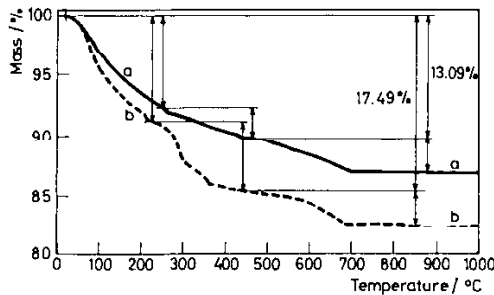

Fig. 4 Effect of polymer identity on TG steps during heating of the model MDF materials irreversibly attacked in an environment with 100% *RH*: a – sulfobelitic clinker with poly-P; b – sulfobelitic clinker with hpmc

The above results highlight from the aspect of phase changes the irreversible portion of the mass increase of MDFs during moisture uptake. The irreversible mass increase varies from 2% (MDFs with poly-P) to 10% (MDFs with hpmc) [14]. The attacked probes exhibit:

• a higher proportion of classical cementitious C–(A,F)–$\overline{S}$ hydraulic phases, decomposing by 250°C (Figs 2 and 3, Table 2);
• an equal amount of AFm-like cross-linked section, with typical thermoanalytical traces in the temperature region 250–400°C [8, 13];
• newly-formed $CaCO_3$ (2–4%), decomposing at 550–650°C [15].

As regards the details of the local structure of the MDFs [4–7, 10, 11], there are two unequivalent regions in MDFs as concerns the resistance to moisture. The TG and DTA traces of the studied SAFB-based MDFs show that the region with a cross-linked section of Al(Fe)–O–C(P) is resistant. Thermal events attributed to unresistant material occur in temperature regions typical for cementitious hydraulic phases [16] and $CaCO_3$ [15].

The effect of the polymer used in the original synthesis upon the resistance to moisture was discussed earlier [13, 14]. Materials containing poly-P exhibit 1/2 to

2/3 of the mass loss of the corresponding hpmc-containing materials, both in the individual steps and overall. The present results permitted a quantitative assessment of the effects of hpmc and poly-P on the mass loss during the thermal decomposition of MDF samples attacked by moisture at 100% *RH* (Fig. 4). Both the individual sequences and also the total mass changes for poly-P or hpmc-containing MDFs attacked by extreme levels of moisture (10–13% if poly-P is present *vs.* 16–19% if hpmc is present, *cf.* Fig. 4) support the hypothesis concerning the impregnation/barrier effect of poly-P. The presence of poly-P minimizes the range of irreversible mass and the phase changes due to moisture uptake in the environment of 100% *RH*. Additional straightforward study (of microstructures and conductivities) is needed before a full comparison may be made of the effects of hpmc and poly-P upon the properties of MDF materials.

Conclusions

1. Attack by extreme levels of moisture ($RH=100\%$) results in a substantial mass increase. Its irreversible part is obviously connected with changes in phase composition that furnish distinct thermoanalytical traces.

2. In MDF samples exposed to attack by moisture, thermoanalytical methods revealed the formation of secondary C–(A,F)–$\overline{S}$ hydrates and $CaCO_3$ only. The amounts of these are substantially suppressed when the original material contains poly-P.

3. Thermoanalytical studies allow a clear distinction of the regions and phases within MDF samples that are resistant (cross-linked sections of clinker hydrates with polymers) or unresistant (regions free of polymers) to the uptake of moisture.

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References

1 J. D. Birchall, A. J. Howard, K. Kendal and J. H. Raistrick, European Pat. Spec., (1988) No. 0055035, B1.
2 S. A. Rodger, S. A. Brooks, W. Sinclair, G. W. Groves and D. D. Double, J. Mater. Sci., 20 (1985) 2853.
3 R. N. Edmonds and A. J. Majumdar, J. Mater. Sci., 24 (1989) 3813.
4 P. G. Desai, J. F. Young and R. P. Wool, Proc. Mat. Res. Soc. Symp., 245 (1992) 179.
5 D. M. Roy, M. R. Silsbee and D. Wolfe, Proc. Mat. Res. Soc. Symp., 245 (1992) 309.
6 W. P. Ma and P. W. Brown, J. Mater. Res., 9 (1994) 1291.
7 M. Drabik, L. Galikova, F. Hanic and R. C. T. Slade, Proc. of 10th Internat. Congress on the Chemistry of Cement, Gothenburg (1997, Ed.: H. Justnes) paper 3iii011.
8 M. Drabik, L. Galikova, Z. Sadlekova and M. Kubranova, J. Thermal Anal., 46 (1996) 479.
9 H. Igarashi and T. Takarashi, Proc. Mat. Res. Soc. Symp., 245 (1992) 173.
10 J. A. Lewis, M. Boyer and D. P. Bentz, J. Amer. Ceram. Soc., 77 (1994) 711.
11 J. A. Lewis and P. G. Desai, Proc. of MAETA Workshop on High Flexural Polymer-Cement Composite (Sakata 1996) 49.

12 T. J. Chu and R. E. Robertson, J. Mater. Sci., 29 (1994) 2683.
13 M. Drabik, L. Galikova, F. Hanic and J. H. Sharp, Chem. Papers, 51 (1997) 363.
14 M. Drabik, P. Zimmermann and R. C. T. Slade, Advances in Cement Research, 10 (1998) 129.
15 C. A. Strydom and J. H. Potgieter, Proc. of 10th Internat. Congress on the Chemistry of Cement (Gothenburg, 1997, Ed.: H. Justnes) paper 2ii049.
16 P. C. Hewlett, Lea's Chemistry of Cement and Concrete, 4th Edition, Arnold Publ. 1998, pp. 264–265, 270–271 (Chapter 'Hydration, setting and hardening of Portland cement', by I. Odler), pp. 447–453 (Chapter 'The production of low-energy cements'. by C. D. Lawrence).