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SYNTHESIS, MOISTURE RESISTANCE, THERMAL, CHEMICAL AND SEM ANALYSIS OF MACRO-DEFECT-FREE (MDF) CEMENTS

S. C. Mojumdar[1*], *B. Chowdhury*[2], *K. G. Varshney*[3] *and K. Mazanec*[4]

[1]Institute for Research in Construction, National Reseach Council of Canada, M-20, 1200 Montreal Road, Ottawa, ON, K1A 0R6, Canada
[2]Matech Associates, 407 WLE, Lake Ariel, PA 18436, USA
[3]Department of Applied Chemistry, Aligarh M. University, Aligarh-202002, India
[4]Institute of Materials Chemistry, Faculty of Chemistry, Brno Technical University, Brno, CR

Abstract

The results, presented here discusses the Macro-Defect-Free (MDF) cements prepared from the blends of sulfoaluminate ferrite belite (SAFB) clinkers, ordinary Portland cement (OPC), Al_2O_3 and poly(butyl acrylate) (PBA), styrene/acrylonitrile co-polymer (SACP) or sodium polyphosphate (poly-P). Though MDF cements have several attractive properties, their utilization has been limited due to the insufficient moisture resistance. It is a very challenging task for scientists and technologist to improve the moisture resistance of MDF cements. Therefore, the new MDF cements were subjected to various moist atmospheres to investigate their moisture resistance. The most significance of this work is the improvement of moisture resistance of the studied MDF cements. The aim of this work was to understand the effects of polymers, Al_2O_3, OPC and SAFB clinkers in the raw mix and delayed drying on MDF cements and also on their subsequent moisture resistance and thermal stability as well as to discover the new properties of these materials. Their chemical, thermal and scanning electron microscopic (SEM) analysis was also carried out before and after exposure to moisture. PBA was found to be the most suitable polymer for MDF cement synthesis, since the samples containing PBA showed the highest resistance to moisture. There are three main temperature regions on TG curves of both series of MDF cement samples. The significant differences in SEM of MDF cements before and after moisture attack and with different polymers were observed.

Keywords: chemical, MDF cements, moisture resistance, polymers, SEM, TG-DTA analysis

Introduction

In general, MDF cements are prepared by using OPC, alumina cements or sulfate clinkers with water-soluble polymers, and by applying mechanochemical processing techniques at very low water-cement ratios (0.08–0.20). MDF cements are known to show instability in water, with swelling and reduction in strength [1, 2]. The term 'Macro-Defect-Free (MDF)' refers to the absence of relatively large voids or defects

* Author for correspondence: E-mail: scmojumdar@hotmail.com

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Akadémiai Kiadó, Budapest
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that are normally present in conventional cement pastes because of entrapped air and/or inadequate mixing [3]. MDF cements display unique properties relative to traditional cement pastes. For example, their flexural strength is approximately 200 MPa as compared to 5–10 MPa for hardened OPC pastes [3, 4]. MDF cements also have several other attractive features such as low fabrication temperature (<100°C), high toughness and good dielectric properties [4]. It is not surprising therefore that many authors have investigated MDF cements and also examined their properties and applications [5–32]. Present work is focused on MDF cements synthesized from the blends of SAFB (SAFB1 or SAFB2) clinkers and OPC with Al_2O_3 and poly(butyl acrylate) (PBA), styrene/acrylonitrile co-polymer (SACP) or sodium polyphosphate (poly-P) dried at 50°C immediately or 24 h after the finishing of pressure application (delayed dried). The blends of SAFB clinkers and OPC exhibit improved properties compare with SAFB clinkers alone [33–36].

Experimental

Processing of MDF cements was similar to that described elsewhere [37, 38]. The only differences are the addition of Al_2O_3 (10%) and the type of polymers used. The moisture resistance of the model MDF cements was investigated at room temperature above saturated $NaHSO_4(aq)$ (52% relative humidity (RH)) and above deionized water (100% RH). Simultaneous TG-DTA was carried out from ambient temperature to 1000°C by using a TA instruments SDT 2960 instrument (sample mass 10–20 mg, heating rate 10°C min^{-1}, in flowing air, rate 90 cm^3 min^{-1}). Scanning electron microscopic (SEM) measurement was carried out by Jeol 6300F equipped with a Kevex Quantum EDS at an accelerating voltage of 25 kV. The chemical composition of the samples was determined by wet chemical methods. The oxide content in the soluble portion related to the cement binder in wt.% was calculated. The MDF cement samples were heated to 100°C at first. This humidity loss corresponds with water exclusion from cement hydrates like ettringite and gypsum. Then the samples were calcined at 1000°C temperature. The mass losses were recorded. Residue after ignition was dissolved in concentrated HCl and the insoluble solid residue was also weighted. Soluble portions were investigated by qualitative and quantitative analytical methods and oxides contents were then obtained.

Results and discussion

Chemical analysis

Chemical and mineralogical composition and free CaO content, calculated from the composition of MDF cements synthesized from SAFB clinker and various polymers are given in Table 1. In case of poly-P, total oxide content in soluble portion was only 97.51%. The most probable explanation is that the used method for chemical analysis cannot determine PO_4^{3-} ions in polyphosphate system and the rest to hundred percent may be content of phosphates. Presence of cca 3 percent of negative trivalent

Table 1 Chemical composition of the studied MDF cements from different polymers

Composition	Content/wt.%		
Humidity loss to 100°C	PBA	ST/AN	poly-P
Ignition loss to 1000°C	2.38	3.26	7.03
Soluble portion	12.92	15.75	8.56
Insoluble residue	76.19	72.88	76.52
Humidity loss to 100°C	8.51	8.11	7.89
	Oxide content in soluble portion/wt.%		
SiO_2	18.31	18.95	14.50
MgO	1.61	2.02	0.95
CaO	52.36	51.99	46.59
Al_2O_3	17.00	16.49	26.25
Fe_2O_3	3.28	3.35	2.34
SO_3	7.09	7.07	6.12
PO_4^{3-}	–	–	3.25
Total	99.65	99.87	100.00

phosphates slightly reduces content of SiO_2. Higher contents of Al_2O_3 and SO_3 and simultaneously lower content of CaO argue the samples were prepared from SAFB low-energy clinkers with Al_2O_3 addition. Table 2 shows the mineralogical composition of SAFB1 and SAFB2 clinkers and OPC.

Table 2 Mineralogical composition of SAFB1 and SAFB2 clinkers and OPC

Type of cement	Component						
	C_3S	C_2S	C_3A	C_4AF	$C_4A_3\bar{S}$	$C\bar{S}$	free CaO
SAFB1	–	56.3	–	7.9	27.5	4.4	–
SAFB2	–	51.5	–	15.0	10.0	16.1	0.2
OPC	44.5	25.8	8.5	13.4	–	4.7	0.1

SEM analysis

Surface images of MDF cements are studied by SEM. SEM micrographs of OPC and MDF cement containing PBA are presented in Fig. 1. Two SEM micrographs before and after exposed to high RH of model MDF cements with styrene/acrylonitrile co-polymer are presented in Fig. 2 as an example. No macropores are observed in the SEM of MDF cement samples (the presence of macropores is typical in cement without polymer, Fig 1. top). Significant differences in SEM of MDF cements with different polymers as well as before and after moisture attack were observed (Figs 1 and 2). Interfaces do not exhibit radial boundaries. A further consequence of the presence of polymers is the partial elimination of pores. The remaining pores appeared isolated

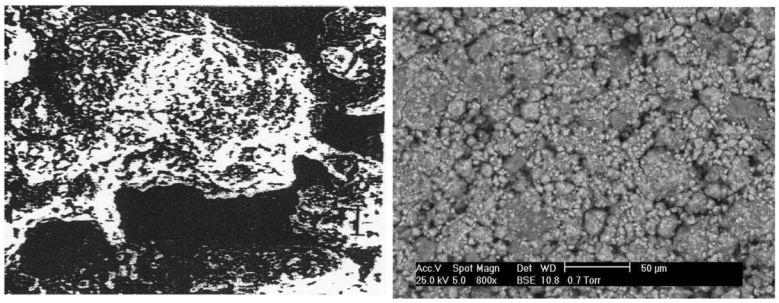

Fig. 1 The SEM micrographs of model OPC (left) and MDF cement (right), synthesized from blend of SAFB1 clinker with Al_2O_3 and PBA, 5 MPa pressure was applied for 4 h (magnification is 800)

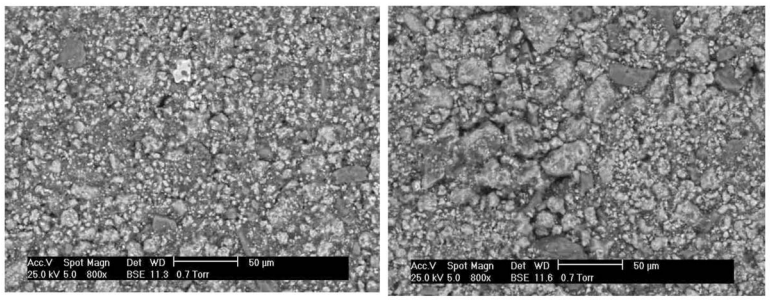

Fig. 2 The SEM micrographs of MDF cement sample (synthesized from blend of SAFB1 clinker with Al_2O_3 and styrene/acrylonitrile copolymer, 5 MPa pressure was applied for 4 h) before (left) and after (right) exposed to high relative humidity, magnification is 800

and spherical. Randomly broken grains of clinker phases are common in model MDF cements. This is due to the more rigid intergrowths for a polymer-intergranular mass-clinker phase in MDF cements than for a clinker phase-hydrate in samples without polymer.

Thermal properties of MDF cements

TG and DTA curves of MDF cements with SACP, PBA and poly-P are given in Figs 3–5. Unlike the moisture resistance, the duration of pressure application does not have significant influence on the thermoanalytical properties of MDF cements. Data relating to the whole range of studied compositions during thermal treatment are presented in Table 3. The effects of polymer used in the original synthesis upon the TG curves of moist attacked probes remain the same as discussed elsewhere [10–14, 33]. The presence of PBA and delayed drying minimise the scope of mass (reversible (difference of the mass at 100% RH and the residual mass) and irreversible (the residual mass after the decreasing at ambient conditions)) as well as phase changes due to the moisture uptake by MDF cements from SAFB clinkers, OPC,

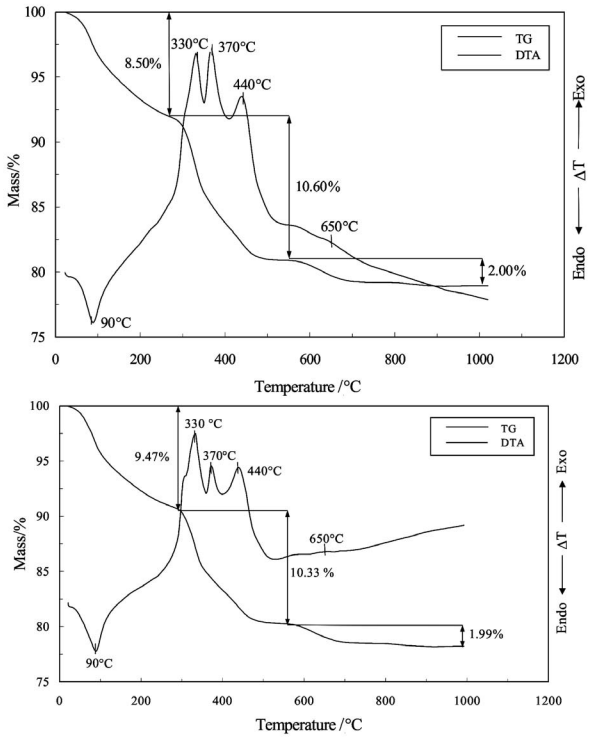

Fig. 3 Thermoanalytical curves of moisture attacked MDF cement synthesized from blend of SAFB1 clinker and Al_2O_3 with styrene/acrylonitrile copolymer, 5 MPa pressure was applied for 5 (top) and 3 (bottom) h

Al_2O_3 and PBA at 100% RH. Thermoanalytical treatment supports the differences of attacked and non-attacked MDF cements probes (Table 3). The temperature intervals of thermal events (TG and DTA curves) are similar to that reported for MDF cements in system of SAFB clinkers and HPMC or poly-P [37–40].

Table 3 Mass changes of non-attacked and attacked MDF cements obtained from TG curves

Polymer additives	Mass losses in separate thermal intervals[%] non-attacked/moisture attacked MDF cement					
	Up to 250°C	Δ	250–550°C	Δ	above 550°C	Δ
poly-P	9.40/10.47	+1.07	5.06/5.15	+0.09	2.26/3.00	+0.74
styrene/ acrylonitrile	8.50/9.47	+0.97	10.60/10.73	+0.13	2.00/2.28	+0.28
PBA	7.09/7.91	+0.82	7.61/7.66	+0.05	1.62/1.80	+0.18

Three distinct temperature regions were observed in the thermoanalytical traces of both series of MDF cements (as synthesised and re-equilibrated after the moisture attack):

- Up to 250°C – temperature region of typical cement hydrates decomposition [40–45], where TG curves exhibit 0.07–0.93% higher mass loss (depending on polymer) in moisture attack probes. It clearly displays an increase of the content of typical cement hydrates. These arise due to the moisture attack of clinker grains only partly converted in original MDF cements samples [37–44]. Figure 3 shows the above region from 50 to 250°C.
- 250–550°C – temperature region of $Ca(OH)_2$ and polymer-cement cross-linking decomposition [37–46] with DTA peaks at 330–450°C.
- Above 550°C – temperature region of $CaCO_3$ decomposition [37–47] with maximum of typical DTA effect at 670–680°C. TG and DTA characteristics in this temperature region provide the evidence that the other crucial phase change of MDF cements in the moist environment is the carbonation (reactions 1 and 2). The moisture attack causes the formation of additional $CaCO_3$ according to the reactions 1 and 2.

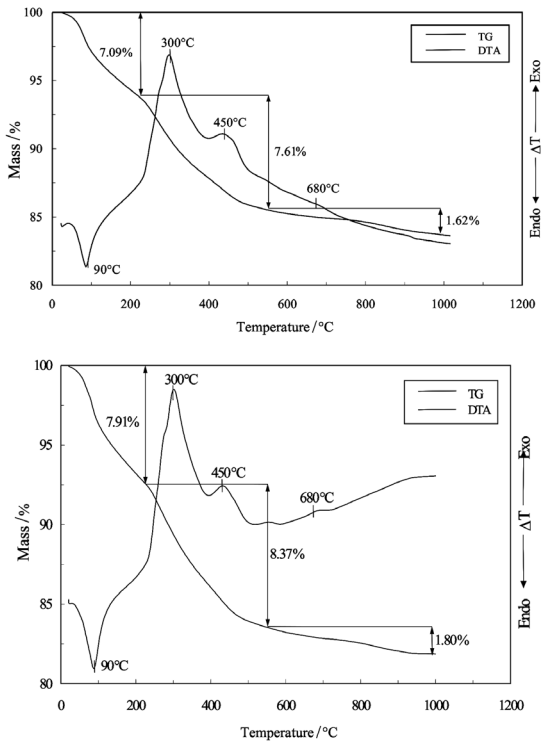

Fig. 4 Thermoanalytical curves of moisture attacked MDF cement synthesized from blend of SAFB1 clinker, Al_2O_3 and PBA, 5 MPa pressure was applied for 5 (top) and 3 (bottom) h

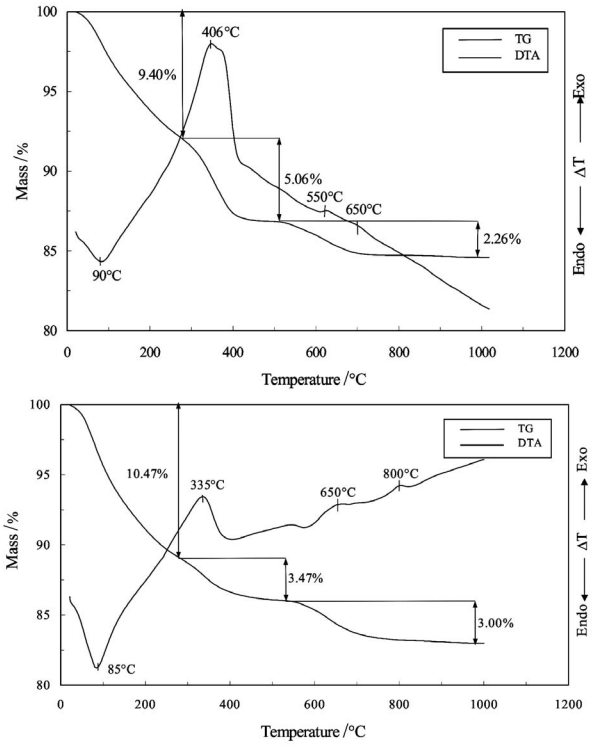

Fig. 5 Thermoanalytical curves of moisture attacked MDF cement synthesized from blend of SAFB1 clinker and Al_2O_3 with poly-P, 5 MPa pressure was applied for 5 (top) and 3 (bottom) h

$$CaO(s) + H_2O(l) = Ca(OH)_2(s) \quad (1)$$

$$Ca(OH)_2(s) + CO_2(g) = CaCO_3(s) + H_2O(l) \quad (2)$$

Generally, MDF cements are synthesized at very low water-cement ratios (0.08–0.20). Therefore, the partly converted clinker grains suffer frequently for this type of phase change at high RH.

Moisture resistance of MDF cements

The mass changes of delayed dried MDF cements with PBA, SACP and poly-P as functions of duration of the exposure in the environments with given RH are displayed in Figs 6–8. The effect of individual humidity upon the evolution of mass is more pronounced than the effects of composition of MDF cement or duration of the original MDF cement synthesis. However, mass increases at 100% RH and re-equilibrated at ambient conditions are strongly affected by the nature of the polymer (Table 4 and Figs 6–8), in both in SAFB clinkers-based MDF cements and in MDF cement based on blends of SAFB clinkers and OPC. The most important improvement of

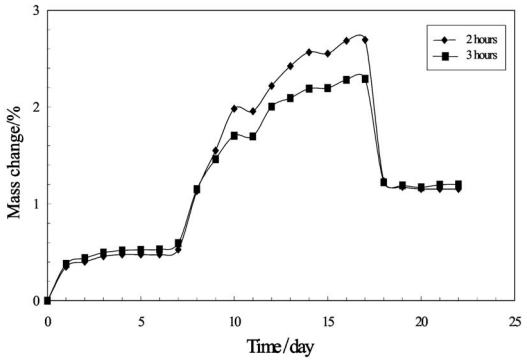

Fig. 6 Mass change as a function of time at room temperature for MDF cement test pieces fabricated from blend of SAFB1 clinker and Al_2O_3 and PBA, 5 MPa pressure was applied for 2 or 3 h

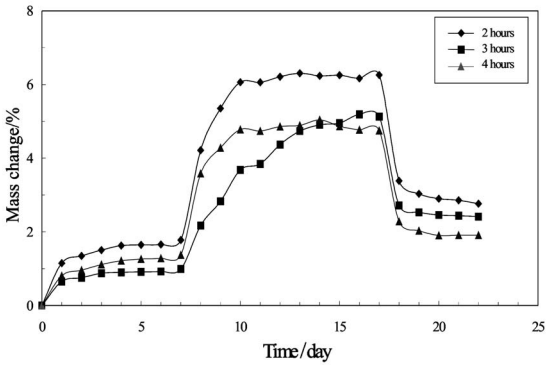

Fig. 7 Mass change as a function of time for MDF cement test pieces fabricated from blend of SAFB1 clinker and Al_2O_3 and styrene/acrylonitrile copolymer, 5 MPa pressure was applied for 2, 3 or 4 h

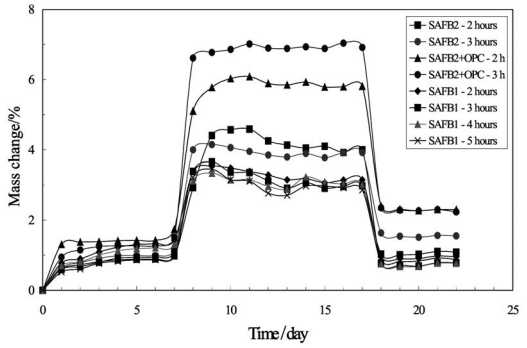

Fig. 8 Mass change as a function of time for MDF cement test pieces fabricated from blend of SAFB2, SAFB2+OPC (85%+15%) or SAFB1 clinker and Al_2O_3 and poly-P, 5 MPa pressure was applied for 2 or 3 h, in case of SAFB1 2, 3, 4 or 5 h

moisture resistance of MDF cements is achieved in materials containing PBA, delayed dried and 5 MPa pressure applied for 3 h (Fig. 6). The lower mass change being the evidence of higher moisture resistance [37–44].

Conclusions

The findings of this investigation support our previous hypothesis on the impregnation/barrier effect of polymers incorporated in the structure of MDF cements. Materials are evolving faster now than at any previous time in history; concurrently incredible industrial needs are also increasing faster than in the past. Industries are very enthusiastic about searching for new materials; on the other hand, they are still not fully satisfied. Hence, this is the time to find places that can replace cement with better performing products. Our studies display the advantage and prospectus of PBA for the MDF cements synthesized from SAFB1 clinker with PBA and blends of these with OPC. The recent development of moisture resistance of MDF cements (only about 2% mass increase at 100% RH) is a significant breakthrough of the improvement of the moisture resistance of this type of materials.

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