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MACRO-DEFECT-FREE (MDF) CEMENTS
Synthesis, thermal, chemical, SEM and magnetometric study and moisture resistance

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MDF cements using the blends of sulfoaluminate ferrite belite (SAFB) clinkers and ordinary Portland cement (OPC) in mass ratio 85:15 with Al_2O_3, and starch, polyphosphate (poly-P) or butylacrylate/acrylonitrile were subjected to moist atmospheres (ambient, 52 and 100% relative humidity (RH)) to investigate their moisture resistance. Their chemical, thermal, electron microscopic and magnetic properties were also studied before and after moisture attack. Butylacrylate/acrylonitrile (BA/AN) copolymer was found to be the most suitable for MDF cement synthesis since the sample containing BA/AN showed the best moisture resistant. There are significant differences in scanning electron microscopy (SEM) of MDF cements before and after moisture attack and with different polymers. New data on the paramagnetic nonhysteresis magnetization curves for all the samples are observed. The MDF cements synthesized from SAFB clinker with dissolved poly-P give the best signal/noise (*S*/*N*) ratio. Three main temperature regions on TG curves of both series of MDF cements are observed. In the inter-phase section of MDF cements, the content of classical cement hydrates decomposing by 250°C is increased. Combustion of organic material took place by 550°C. In the temperature range 550–800°C, the decomposition of $CaCO_3$ occurs.

Keywords: *magnetic activity, MDF cements, moisture resistance, SEM, TG-DTA*

Introduction

Study of mass equilibration and thermal analysis give an effective knowledge of the moisture sensitivity phenomenon of MDF cements. The results favour our previous hypothesis on the impregnation/barrier effect of polymers incorporated in the structure of MDF cements. The discovery of the magnetic activity of MDF cements, enlarge the application and importance of this kind of materials. 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 prospects of butylacrylate/acrylonitrile (BA/AN) for the MDF cements synthesis. The recent development of moisture resistance of MDF cements (only about 2% mass increase at 100% RH) proved that the old saying 'where there's a will there's a way' is very true with MDF cements and their future developments.

The term 'macro-defect-free (MDF) cement' refers to the absence of relatively large voids or defects that are normally present in conventional cement pastes because of entrapped air or inadequate mixing. MDF cements display unique properties relative to traditional cement pastes. For example, their flexural strength is roughly 200 MPa as compared to 5–10 MPa for hardened OPC pastes. MDF cements indicate also several other attractive features such as low fabrication temperature (<100°C), high toughness and good dielectric properties [1–4]. It is well known that the addition of polymers to cementitious systems significantly improve the materials' properties. Therefore, it is not surprising that many authors have investigated polymer-cementitious materials and also examined their properties and applications [4–32]. The aim of this study was to understand the effects of polymers, Al_2O_3, OPC in the raw mix and of delayed drying on MDF cements synthesis and also on subsequent moisture resistance and thermal stability of newly synthesized MDF cements. This work is a continuation of the previous studies on MDF cements [33–39]. Present work is focused on MDF cements from the blends of SAFB clinkers and OPC with the addition of Al_2O_3, and starch, poly-P or BA/AN and drying at 50°C immediately or 24 h after the finishing of pressure application (delayed drying). Blends of SAFB clinkers and OPC exhibit better properties as compared to SAFB clinkers alone [40–42].

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Experimental

Synthesis of MDF cements

Processing of MDF cements was as follows: (a) Initial dry mixing of the cement mixtures (SAFB and OPC) and Al_2O_3 with starch, or butylacrylate/acrylonitrile (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 dye (diameter 10 mm) was applied for 0.5, 1, 2, 3 and 5 h and (f) chemical reactions were completed by air drying at 50°C.

Measurements

Chemical composition of the samples was determined by wet chemical methods. The moisture resistance of model MDF cements was investigated above saturated $NaHSO_4$ (aq) (52% relative humidity (RH)) and above deionised water (100% RH). Simultaneous TG-DTA was conducted from ambient temperature to 1000°C on a T.A.I. SDT 2960 instrument by using platinum crucible (sample mass 10–20 mg, heating rate 10°C min^{-1}, in flowing air). SEM was carried out by JEOL 6300F equipped with a Kevex Quantum EDS at an accelerating voltage of 25 kV. The magnetic properties of MDF cements were investigated by a SQUID magnetometer [43].

Results and discussion

Chemical analysis

The results of chemical analysis are presented in Table 1. Humidity loss to 100°C corresponds with the loss of water from cement hydrates. A relatively high loss on ignition to 1000°C in all samples reflects the presence of an organic phase with maximum burning temperature of approximately 350°C. Residue was dissolved in concentrated HCl and insoluble solids were weighed, calculating the soluble part from the difference in mass. Soluble portion is the rest to hundred. Soluble portions were investigated by qualitative and quantitative analytical methods, estimating oxide contents. Since the samples were prepared from SAFB low-energy clinkers with Al_2O_3 addition, they have relatively high content of Al_2O_3 and SO_3 and correspondingly low CaO content.

SEM analysis

Surface images of model MDF cements with butylacrylate/acrylonitrile are presented in Fig. 1 as an example. No macro-pore is observed in SEM of MDF cement samples, which is typical for cement without polymer. Significant differences in SEM of MDF cements with different polymers as well as before and after moisture attack were observed (SEM images have not been shown). Interfaces do not exhibit radial boundaries. A further consequence of the presence of polymers is the partial elimination of pores. Randomly broken grains are common in model MDF cements.

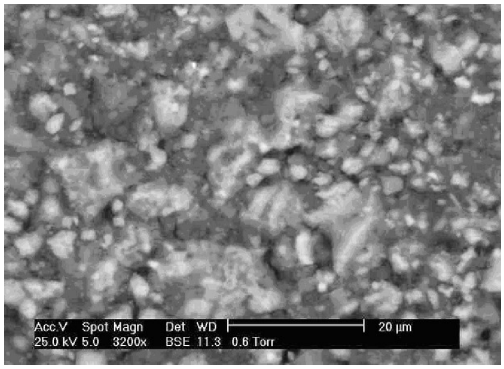

Fig. 1 The SEM micrographs of the moisture attacked MDF cement synthesized from blend of SAFB clinker and OPC with Al_2O_3 and butylacrylate/acrylonitrile copolymer, 5 MPa pressure was applied for 2 h

Magnetic properties of MDF cements

The AC volume magnetization characteristics of the MDF cement sample synthesized from SAFB clinker with dissolved poly-P was measured at liquid nitrogen temperature after the zero-field cooling by the compensation method using second order SQUID gradiometer. The best *S*/*N* ratio was obtained for the MDF cement sample synthesized from SAFB clinker with dissolved poly-P. The paramagnetic non-hysteresis magnetization curves were identified for all samples. An example is given in Fig. 2.

Thermal analysis of MDF cements

Data relating to the whole range of studied compositions during thermal treatment are presented in Table 1. Presence of butylacrylate/acrylonitrile and delayed drying reduce the possibility of mass (reversible and irreversible) as well as phase changes, such as $CaO \rightarrow Ca(OH)_2 \rightarrow CaCO_3$ due to the moisture uptake by MDF cements, synthesized from SAFB clinkers, OPC and starch, poly-P or butylacrylate/acrylonitrile at 100% RH. Thermoanalytical treatment supports the differences of attacked and non-attacked MDF cements probes (Table 2).

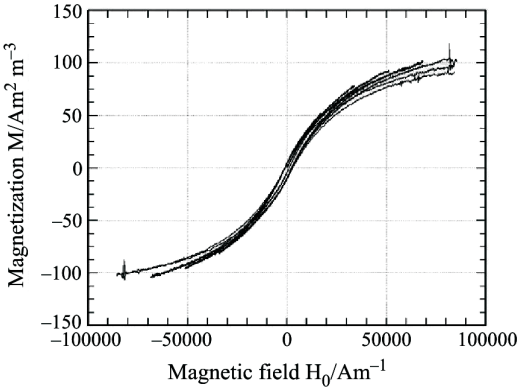

Fig. 2 The AC volume magnetization characteristics of the MDF cement sample synthesized from SAFB clinker, OPC and dissolved poly-P

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

- Up to 250°C occurs the decomposition of 'typical' cement hydrates. The TG curves exhibit 0.07–0.83% higher mass loss (depending on polymer) in moisture attacked samples. 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 [44–46]. Figure 3 shows the above relation exactly from 50 to 250°C.
- 250–550°C-temperature region of $Ca(OH)_2$ and of combustion of polymer materials [44–47].
- Above 550°C occurs the $CaCO_3$ decomposition [45] with maximum of typical DTA effect at 670–680°C. TG and DTA characteristics in this temperature range provide an evidence of that the carbonization is the other crucial phase change of MDF cements in the moist environment. The moisture attack causes the formation of additional $CaCO_3$ according to the reactions (1) and (2).

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

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

Moisture resistance of MDF cements

Moisture resistance could be defined as the ability of a material to resist swelling, blistering or other damage caused by moisture. Mass changes (increases) were used as the measure of the moisture resistance of MDF cements. The lowest mass increase (lowest environmental deterioration) corresponds to the highest moisture resistance. The mass changes of delayed dried MDF cements with butylacrylate/acrylonitrile as the function of dura-

Table 1 Chemical composition of the MDF cements synthesized from SAFB1 clinker and polymers

Composition	Content/mass%		
	Starch	Poly-P	BA/AN
Humidity loss to 100°C	3.87	7.03	3.47
Ignition loss to 1000°C	10.92	8.56	9.47
Soluble portion	76.92	76.52	78.14
Insoluble resiude	8.29	7.89	8.92
	Oxide content in soluble portion/mass%		
SiO_2	18.68	14.50	19.50
MgO	0.35	0.95	1.14
CaO	54.04	46.95	52.41
Al_2O_3	15.24	26.25	15.36
Fe_2O_3	4.38	2.34	3.49
SO_3	7.31	6.12	7.26
PO_4^{3-}	–	3.25	–
Total	100.00	100.00	99.16

Table 2 Mass changes of non-attacked and moisture 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
Starch	7.79/8.42	+0.63	6.53/6.62	+0.09	2.39/2.91	+0.52
Poly-P	9.40/10.47	+1.07	5.06/5.15	+0.09	2.26/3.00	+0.74
Butylacrylate/acrylonitrile	9.50/9.74	+0.24	5.60/5.61	+0.01	0.57/0.88	+0.31

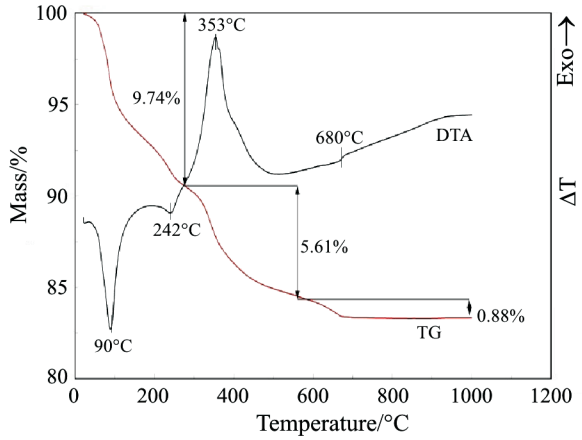

Fig. 3 TG and DTA curves of moisture attacked MDF cement synthesized from blends of SAFB clinker, OPC and Al_2O_3 with butylacrylate/acrylonitrile

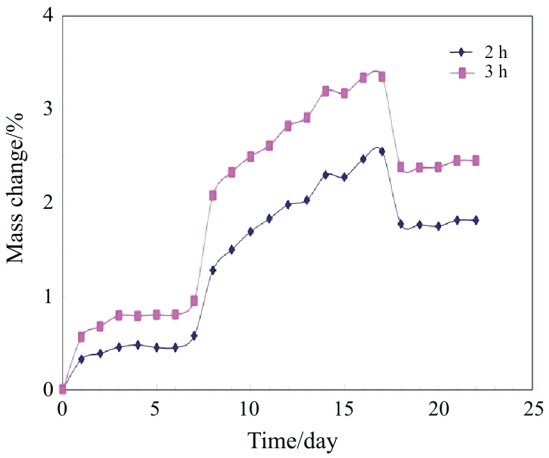

Fig. 4 Mass change as a function of time for MDF cement test pieces fabricated from blend of SAFB clinker, OPC, Al_2O_3 and butylacrylate/acrylonitrile

tion of the exposure in the environments with given RH are displayed in Fig. 4 as an example. Relative humidity describes the amount of water in the air compared with how much the air can hold at the current temperature. Example: 50% relative humidity means the air holds half the water vapor that it is capable of holding; 100% relative humidity means the air holds all the water vapor it can. At 100% RH, no more evaporation can occur until the temperature rises, or until the water vapor leaves the air through condensation. The effect of individual relative humidity, such as 100% RH upon the increase of mass is more pronounced than the effects of composition of MDF cement or duration of the pressure application during the MDF cement synthesis. However, the mass increase at 100% RH and at re-equilibration at ambient conditions are strongly affected by the nature of the polymer, in both in SAFB clinker-based MDF cement (without OPC) and in MDF cement based on blends of SAFB clinkers and OPC. The most important improvement of moisture resistance of MDF cements is achieved in materials containing butylacrylate/acrylonitrile, delayed drying and 5 MPa pressure applied for 2 h (Fig. 4), the lower mass change being the evidence of higher moisture resistance [33–39, 47].

Conclusions

The following conclusions can be made from this study.

- The possibility of moisture attack on MDF cements, synthesised from the blends of SAFB clinkers, OPC, Al_2O_3 and starch, poly-P or butylacrylate/acrylonitrile co-polymer has been quantified using the values of mass increases as the measure of the moisture resistance. The method has been proved as a powerful tool for an effective test of moisture attack on various MDF cements.
- The effect of individual humidity on the moisture resistance of MDF cements is more intensive than the effect of composition of MDF cements or duration of the pressure application on MDF cements synthesis. However, detailed values of mass increase at 100% RH are strongly affected by the nature of polymer. The highest moisture resistance has been observed for delayed drying MDF cements with butylacrylate/acrylonitrile co-polymer and with 5 MPa pressure for 2 h.
- The irreversible mass increase is strongly connected to both the carbonization and secondary hydration of cement grains in the inter-phase region of the structure of MDF cements as determined by methods of thermal analysis. Minimisation of the above phase changes together with minimal direct mass changes in moist environment of delayed drying MDF cements indicates a possibility to improve the moisture resistance (environmental deterioration) of MDF cements.
- The thermoanalytical data showed that Al(Fe)–O–C(P) cross-links, formed between polymers and cement grains remain intact in the moist environment of either ambient or extreme levels of humidity.
- Study of mass equilibration and thermal analysis gives important information and control of the moisture sensitivity phenomenon of MDF cements. The results on MDF cements system in SAFB, OPC, Al_2O_3 and starch, poly-P or butylacrylate/acrylonitrile co-polymer favour our previous hypothesis on the impregnation/barrier effect of polymers incorporated in the structure of MDF cements.

References

1 K. Kendal, Philos. Trans. R. Soc. London, A310 (1983) 139.
2 J. A. Lewis and P. G. Desai, MAETA Workshop on High Flexural Polymer-Cement Composite, 3–4 October 1996, Sakata, Japan 1996, pp. 49–58.
3 J. D. Birchall, A. J. Howard, K. Kendal and J. H. Raistrick, European Pat. Specification, 6, 0055035, B1, 1998.
4 M. Delucchi and G. Cerisola, Constr. Build. Mater., 15 (2001) 351.
5 G. K. D. Pushpalal, J. Mater. Sci., 35 (2000) 981.
6 S. C. Mojumdar and L. Raki, J. Therm. Anal. Cal., 82 (2005) 89.
7 C. Y. Rha, J. W. Seong, C. E. Kim, S. K. Lee and W. K. Kim, J. Mater. Sci., 34 (1999) 4653.
8 S. C. Mojumdar and L. Raki, Res. J. Chem. Environ., submitted.
9 C. K. Park, J. Cer. Soc. Jap., 106 (1998) 268.
10 J. A. Lewis and M. A. Boyer, Adv. Cem. Bas. Mater., 2 (1995) 2.
11 M. Tan, J. Lu and K. Wu, Cem. Concr. Res., 24 (1994) 1185.
12 P. G. Desai, J. A. Lewis and D. P. Bentz, J. Mater. Sci., 29 (1994) 711.
13 I. A. A. Ibrahim, H. H. ElSersy and M. F. Abadir, J. Therm. Anal. Cal., 76 (2004) 713.
14 M. Drábik, L. Gáliková, K. G. Varshney and M. A. Quraishi, J. Therm. Anal. Cal., 76 (2004) 91.
15 J. Dweck, P. F. Ferreira da Silva, R. Silva Aderne, P. M. Büchler and F. K. Cartledge, J. Therm. Anal. Cal., 71 (2003) 821.
16 S. C. Mojumdar and L. Raki, J. Therm. Anal. Cal., submitted.
17 W. Roszczynialski and W. Nocuń-Wczelik, J. Therm. Anal. Cal., 77 (2004) 151.
18 J. Podìbradská, R. Černý, J. Drchalová, P. Rovnaníková and J. Šesták, J. Therm. Anal. Cal., 77 (2004) 85.
19 D. S. Klimesch, M. Gutovic and A. Ray, J. Therm. Anal. Cal., 75 (2004) 197.
20 Z. Pytel, J. Therm. Anal. Cal., 77 (2004) 159.
21 T. Stepkowska Ewa, J. L. Pérez-Rodríguez, M. J. Sayagués and J. M. Martínez-Blanes, J. Therm. Anal. Cal., 73 (2003) 247.
22 T. Grounds, D. V. Nowell and F. W. Wilburn, J. Therm. Anal. Cal., 72 (2003) 181.
23 J. Sawków and Wiesława Nocuń-Wczelik, J. Therm. Anal. Cal., 74 (2003) 451.
24 B. Pacewska, I. Wilińska, M. Bukowska, G. Blonkowski and W. Nocuń-Wczelik, J. Therm. Anal. Cal., 77 (2004) 133.
25 S. C. Mojumdar, L. Raki and D. Wang, Polym. Eng. Sci., submitted.
26 M. Bukowska, B. Pacewska and I. Wilińska, J. Therm. Anal. Cal., 74 (2003) 931.
27 C. Evju, J. Therm. Anal. Cal., 71 (2003) 829.
28 K. Rajczyk, E. Giergiczny and M. A. Glinicki, J. Therm. Anal. Cal., 77 (2004) 165.
29 P. Y. Yan, F. Zheng and Z. Q. Xu, J. Therm. Anal. Cal., 74 (2003) 201.
30 M. Palou and J. Majling, J. Therm. Anal. Cal., 71 (2003) 367.
31 P. Myśliński, W. Precht, L. Kukiełka, P. Kamasa, K. Pietruszka and P. Małek, J. Therm. Anal. Cal., 77 (2004) 253.
32 J. Strnad, J. Protivínský, D. Mazur, K. Veltruská, Z. Strnad, A. Helebrant and J. Šesták, J. Therm. Anal. Cal., 76 (2004) 17.
33 S. C. Mojumdar, J. Therm. Anal. Cal., 64 (2001) 1133.
34 M. Drabik, L. Galikova and S. C. Mojumdar, Key Eng. Mater., 206 (2002) 1867.
35 S. C. Mojumdar, in: Proceedings of the 29th NATAS Annual Conference on Thermal Analysis and Applications, St. Louis, Missouri, USA, September 24–26, 2001, Omnipress, Madison 2001.
36 M. Drábik, S. C. Mojumdar and R.C. T. Slade, Ceramics – Silikaty, 46 (2002) 68.
37 S. C. Mojumdar, Challenges for Coord. Chemistry in the new century, 5 (2001) 453.
38 S. C. Mojumdar, A. Ray, M. Drábik, A. Cigan, F. Hanic and P. Capek, Sol. Stat. Phenom., 90 (2003) 365.
39 S. C. Mojumdar, in: Proceedings of 21st Cement and Concrete Science, August 30–31, 2001, University of Aberdeen Press, Scotland 2001.
40 I. Janotka and L'. Krajči, Adv. Cem. Res., 11 (1999) 35.
41 S. C. Mojumdar and I. Janotka, Acta Physica Slovaca, 52 (2002) 435.
42 I. Janotka and L'. Krajči, Bul. Mater. Sci., 23 (2000) 521.
43 V. Zrubec, A. Cigan and J. Manka, Physica, C 223 (1994) 90.
44 S. C. Mojumdar and M. Drabik, in: Proceedings of Science of cement and concrete-Kurdowski symposium, June 20–21, 2001, Cracow, Poland, Akapit Scientific Publisher, Cracow 2001.
45 S. C. Mojumdar, B. Chowdhury, K. G. Varshney and K. Mazanec, J. Therm. Anal. Cal., 78 (2004) 135.
46 H. F. W. Taylor, Cement Chemistry, London, 2nd Edition, 1998, Vol. 1, Chap. 7.
47 M. Drabik, S. C. Mojumdar and L. Galikova, Cem. Concr. Res., 31 (2000) 751.

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