

MACRO DEFECT FREE MATERIALS; MECHANOCHEMICAL ACTIVATION OF RAW MIXES AS THE INTENSIFYING TOOL OF THE ENTIRE MDF SYNTHESIS

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A challenge in the field of MDF materials, which has not been followed or indicated by now, are the options of improvement of cross-linking through intensified mixing of dry MDF raw mixes of cement and polymer. The potential of mechanochemical treatment to intensify the atomic level of cross-linking already in the raw mixes and, thus, the activation of raw mixes has been critically verified earlier. Processes of the mutual MDF syntheses of both standard and activated raw mixes are presented and discussed in this paper. The scope of cross-linking as a key item of the successful MDF synthesis has been studied by two independent experimental methods – thermal analysis and IR spectroscopy. The knowledge has been achieved about (i) phenomenon of internal pressure during MDF synthesis from mechanochemically activated raw mixtures and (ii) increase of the content of cross-links by one third in MDF materials synthesized from mechanochemically activated raw mixtures in comparison with these synthesized from standard raw mixtures. Mechanochemical activation of raw mixtures undoubtedly leads to the intensification of cross-linking in MDF materials; if applied (prior to water addition and pressure application) it increases the rate of cross-links formation in the system through the effect of internal pressure. The reported approach and results represent besides the contribution to the knowledge about MDF materials themselves also the challenge for the development of a variety of new and innovative materials strategies.

INTRODUCTION

Among the recent advancements in cement chemistry and technology the most noteworthy is the development of superplasticized concrete mixtures which give very high fluidity at relatively low water contents [1, 2]. The low porosity, high strength and high durability are the challenging potentials of resulting materials. Chemically bonded ceramics (CBC), and within these especially macro-defect-free (MDF) materials, are examples of alternative technological approaches to obtain low-porosity high-strength products. CBC are mortars with little or no coarse aggregate, a very high cement content, and a very low w/c ratio. They are densified under high pressure and then thermally cured to obtain very high strength. The MDF materials are made with a cement paste containing up to 7 percent by mass of a water soluble plasticizing agent, such as hydrolyzed polyvinyl acetate, hydroxypropyl-methyl cellulose, polyacrylamide or sodium polyphosphate. Glycerol is often added as an additional plasticiser. The paste is subjected to high shear mixing, and the products are moulded under medium pressure levels and finally heat cured at temperatures up to 80°C (176 F) [1, 3].

MDF materials represent a potentially attractive range of materials whose properties lie between those of conventional cements and ceramics. It is expected that these materials would not have an impact on the concrete industry as a whole, but their challenge for special technologies is anticipated to grow in the future [1, 3, 4]. Concerns about their durability in humidity have limited research activity in recent years, but there appear to be established routes by which these may be overcome [4]. It is anticipated that the revolutionary breakthrough in the issue of poor durability of MDF materials in the moist environment would bring already chemistry based studies directed as to the materials themselves, so to both subsystems and procedures with specific affinities towards cross-linking and/or stabilizing the polymers [2, 4, 5]. The data on the effects of cement and polymer composition, including a variety of organic or organometallic coatings, on strength and water sensitivity of CAC-PVA MDF materials appeared in [2, 6, 7–14]. Authors reported effectiveness of an organic barrier in improving the water stability, optimum alumina content in cement and hydrolysis degree in PVA, and also the potential of a group of organotitanate compounds. All those are the issues which, in addition

to Al based cross-links, imply impregnation effects and the increase of moisture resistance. However, the available data do not allow to control the influence of the rate of water permeation on the weakening processes if the additional phases increase the complexity of the system.

The studies on the reactivity of inorganic-polymeric networks in this class of cement-based materials and the focus toward nano- and atomic levels of grafting of polymers on interfaces represent some of the success stories of materials chemistry [3, 12, 15-18, 31]. Studies have shown a key role of atomic level cross-linked and functionalized interface of cement and polymer during the formation process. However, external moisture exerts an adverse effect on the mechanical properties of MDF cement products through the uptake of humidity and carbon dioxide by cement phases and hydrates free of cross-links. The schematic model interrelates the specific data on the atomic level of functional interfaces in MDF materials [16, 17] and generally accepted microlevel concept of functional grafting on the surface of grains [31], as shown in Figure 1. It gives a quick navigation through the state-of-art of the knowledge on MDF materials summarizing both the current approaches to syntheses and atomic-level interpretations of formed functional interfaces (part I) and the microlevel of functional grafting of polymer on the surface of grain (part II).

Most MDF production has used a twin roll mill to produce high shear mixing of cement, polymer and water, and this allows a satisfactory homogenous mix to form in the appropriate reaction time. The intimate mixing of the polymer phase and the inorganic cement phases is vital to produce a truly composite material, exhibiting much of the strength of the material with high fracture toughness [8–10, 18]. MDF formation reactions mutually occur in the heterogeneous system of cement (*s*) – polymer (*s* or *l*) and water (*l*), under medium pressure and with the application of high shear twin-rolling, which is in its essence a type of mechanochemical processing. The

conditions induce cross-link formation interactions at the interfaces involving both atoms of a cement-based component and appropriate group of atoms of polymer [8–10, 12, 16–21].

A challenge, which has been of restricted interest by now, is the intensification of mixing a cement with polymer prior to the addition of water. Here one of the procedures which may exert the specific affinities towards cross-linking is the mechanochemical treatment of solid raw mixes before the water is added and pressure through twin rolling applied. The mechanochemical conditions facilitate especially the changes of the atomic level of solid interfaces, while the varieties of positive effects have been reported for the reactivity of various systems [22]. Both, the topical knowledge on MDF materials and a choice of principles and methodologies of mechanochemical activations suggest that the appropriate method of mechanochemical treatment of raw mixes is a challenge which would increase the potential of raw mixes to form MDF materials more effectively.

Our recent study [23] has shown that due to the mechanochemical treatment the activation of appropriate part of the system of raw mixtures occurs. This activation consists in the initiation and measurable formation of Al(Fe)-O-P cross-links already in the treated raw mixes. The mechanochemical activation of raw mixes in the high energy planetary mill for the duration of 5 minutes has been proposed as the specific mixing and activation/ /pre-reaction step preceding the entire MDF synthesis procedure. During the proposed step the formation of cross-links is facilitated already in raw mixes to a substantial measure. Potential of the mechanochemical treatment of dry raw mixes to initiate the atomic level cross-linking and, thus, to activate the raw mixes for syntheses of MDF materials was proved in the system of Portland cement and sodium polyphosphate. Anyway, the scope and/or restrictions of applicability and effects of given methodology should be thoroughly tested and analyzed in the entire MDF syntheses processes of mechanochemically treated raw mixes.

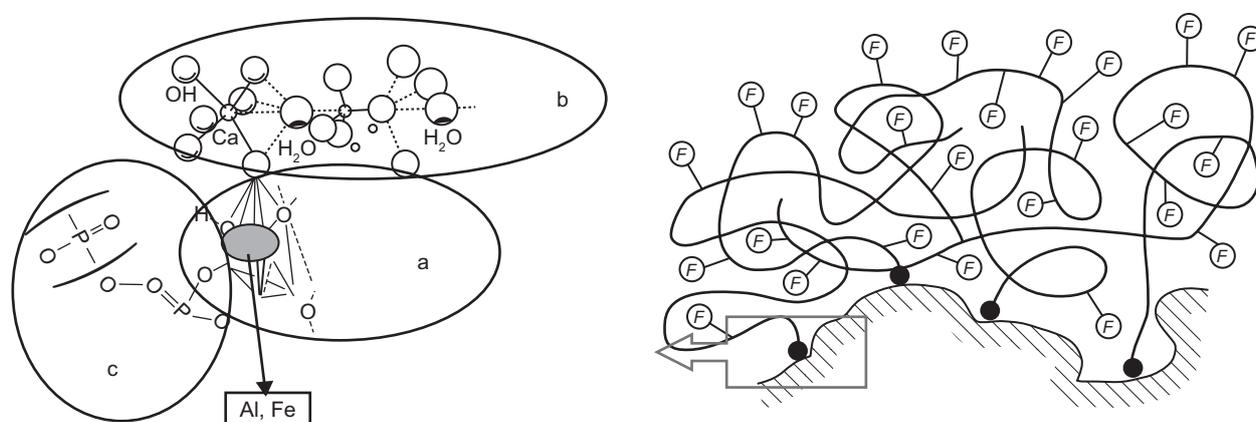


Figure 1. Formed cross-links (region a in part I, left) in the atomic level of functional interfaces (entire part I, left) [16, 17] due to the MDF synthesis procedure and the microlevel of functional grafting of polymer on the surface of grain (part II, right) [31].

The goal of present paper has been to evaluate the influence of mechanochemical activation of a choice of raw mixtures upon the intensification of MDF syntheses. Experimental tests have been carried out in the broad scope, the results are analysed and discussed predominantly from point of view of an appearance of cross-linking due to both mechanochemical activation and entire MDF syntheses. The knowledge gained would contribute also to the development of new and innovative materials; among others selected items of the machinery of pump wheels where one of the tested materials strategies involves also MDF materials and relevant raw meal compositions and production procedures.

EXPERIMENTAL

The choice of raw materials comprised the Portland cement of CEM III type, poly-P of formula $(\text{NaPO}_3)_n$, and $\text{Na}_5\text{P}_3\text{O}_{10}$. The dry mixing of components has been carried out by standard mechanical procedure and, subsequently, a mechanochemical treatment/activation [23] has been applied on dry mixes. Each raw mix composition has been treated by the generally accepted and referred sequence of steps of MDF synthesis [3, 16, 24, 25]. The details on the composition and treatment modes of both dry mixing (incl. the mechanochemical activation) and procedure of MDF synthesis itself cf. in Table 1. The range of raw mixes compositions resulted in MDF probes which have been tested with the aim to define the effect of mechanochemical mixing/activation of raw mixes on a potential improvement of the entire MDF syntheses. MDF probes synthesized from standard mechanical mixes have been included for purposes of comparison.

Thermoanalytical data were collected on the sdt 2960 device of T. A. Instruments, and TGA/DSC 1 device of Mettler Toledo. Both under the following experimental conditions: from laboratory temperature to 1000°C, heating rates $10^\circ\text{C min}^{-1}$, air atmospheres. The data were collected and evaluated using the Thermal Analyst 3100 (sdt 2960) and STAR^e (TGA/DSC 1) software. The sensitivity of thermal events (TG, DTG,

DTA) in the region of 200 - 330°C upon the presence (and thermal decomposition) of Al(Fe)-O-P cross-links [16, 17, 23, 26] is for the studied probes illustrated in Figure 2. It has been used as the indication of key changes in synthesized MDF probes due to the combined effect of mechanochemical and MDF treatments. The data based on mass losses (from TG curves) are reported and discussed as the semiquantitative measure of Al(Fe)-O-P cross-links formation giving the assessment of the scope of cross-links formed in the probes of the entire interest of this study.

For the FT-IR analyses the mechanochemically activated mixture of cement and poly-P was mixed with water and glycerine. Samples were taken after 3, 5, 10, 15, 30, 45 and 60 minutes whereas the chemical reactions were stopped by acetone. The dried samples were powdered, mixed with KBr and the pressed KBr-tablets were measured with a spectrometer of Nicolet, Avatar 320 in the range of 4000 - 400 cm^{-1} with 32 scans and evaluated with the Omnic software.

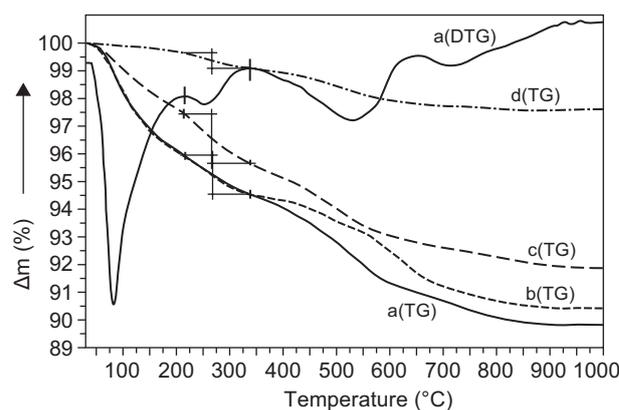


Figure 2. TG and DTG curves of typical MDF probes exemplifying the evaluation of cross-links decomposition – cf. the area of temperature interval 200 - 330°C on curve a(DTG), and the entire TG mass losses - Δm (%), in that temperature region – curves a(TG) and b(TG) for MDF probes synthesized from the mixture which was mechanically premixed only, c(TG) for MDF probe synthesized from the mixture which was mechanically and also mechanochemically premixed, d(TG) for mechanochemically activated raw mixes. The complete data acquired on Δm (%) cf. in Table 2.

Table 1. Ranges of composition and sequences of the MDF treatment of studied mixes.

Composition	Mechanical dry mixing	Mechano-chemical dry mixing	Entire MDF procedure conforming [3, 16, 24, 25]
CEM III + Poly-P (5 mass %)	√	–	MDF syntheses of each dry mixture consisted of steps: a) addition of water to yield w:s = 0.20, b) twin-rolling until the consistency of a dense dough (up to 5 min), c) application of 5 MPa on a probe for 30 min to 1 h, and d) “freezing of chemical reactions”, air drying at 50°C
	√	√, 1 min.	
	√	√, 5 min.	
CEM III + POLY-P (10 mass %)	√	–	Steps as above for each combination of dry mixtures
	√	√, 1 min.	
	√	√, 5 min.	

RESULTS AND DISCUSSION

Synthesized and studied have been and discussed are as MDF probes from standard raw mixtures (in Table 1 cf. “mechanical dry mixing”) so MDF probes from the raw mixtures activated mechanochemically (in Table 1 cf. “mechanochemical dry mixing”). The data on MDF probes from standard raw mixtures confirm the results which we have reported earlier [16, 17, 27, 28]. During the procedure of MDF syntheses with mechanochemically activated raw mixes has been observed that the originally loaded pressure of 5 MPa is increasing upto 120 % of its value (5,80 - 6,10 MPa) in course of synthesis itself. Further, the pressure increases not only in the usual period of synthesis duration (30 min – 1 hour), but these particular reaction systems need additional approx. 4 hours to stabilize the reported value of 5,80 - 6,10 MPa. It is likely that part of pressure is originated from inside of the MDF reaction system of mechanochemically premixed mixes. In the text, it will be referred to as “the phenomena/effect of internal pressure“ [29, 30]. Mechanochemical activation of dry raw mixes induces the internal pressure during the subsequent MDF interaction itself, and it should be seen as the sign of minimization of a reaction barrier on part of interface of solid reagents [5, 23, 29]. The appearance of cross links and the scope of its formation under individually differing conditions of MDF synthesis have been of prior interest when analysing the collected experimental data of each synthesized probe. With the aim to highlight “the phenomena / effect of internal pressure“, included and discussed are also the data of probes which have been kept under the MDF synthesis conditions until the internal pressure has equilibrated.

The results of both, thermogravimetry and differential thermal analysis (Figure 2, Table 2), display the thermoanalytical events in the region of 200 - 330°C, the nature of which is due to the presence (and thermal

decomposition) of Al(Fe)–O–P cross-links [16, 17, 26]. The insight on the scope of cross-links formation during the MDF procedures of mechanochemically treated raw mixtures has resulted from the evaluation of mass losses connected with the thermal events in the region of 200 - 330°C.

Signs + in the column DTG, DTA of Table 2 denote the occurrence of the indicative [16, 26] thermoanalytical events (DTG and DTA) of cross-links. Values of mass losses (%) of individual MDF probes are those directly estimated from TG curves in the temperature interval 200 – 330°C (cf. Figure 2). Full meanings of notations in the column “composition of the analysed probe” are as follows: A. M. 5 min. (mean) – mechanochemically activated raw mixes, the mean value of Δm , reported in [23]; F. P. – final MDF probes, where postfixes “mech.”, “mech-chem.” and “■“ indicate the key distinguishing items of the whole MDF synthesis procedure. In particular: „mech.“ denotes MDF probes synthesized (5 MPa loaded for the duration of 1 hour) from the mixture which was mechanically premixed only, postfix „mech-chem.“ denotes MDF probes synthesized (5 MPa loaded for the duration of 1 hour) from the mixture which was mechanically and also mechanochemically premixed, postfix „■“ denotes the later probes kept under the MDF synthesis conditions until the internal pressure equilibrates (probes treated for additional 4 – 5 hours under the pressure load).

The mean values of TG mass losses, which are due to the decomposition of cross links in the mechanochemically activated mixes and in the final products, as reported in Table 2, increase in a specific order. Namely; Δm (mean) of mechanochemically activated raw mixes < Δm (mean) of final MDF probes from the mechanical mixture < Δm (mean) of final MDF probes from the mixture mechanically and also mechanochemically premixed ~ Δm (mean) of the later MDF probes additionally kept under the MDF synthesis conditions until the internal pressure equilibrates. More on the values of Δm (mean) of mechanochemically activated raw mixes cf. also in [23]. The value of Δm (mean) of final MDF probes from the mixture premixed by both mechanical and also mechanochemical mode is by 0.37 % higher than that of MDF probes premixed by mechanical mode only. This difference represents the relative increase of 31 % due to the inclusion of mechanochemical premixing. The last three lines of data in Table 2 show that prolonged pressure load, until the internal pressure in the system equilibrates, does not result in the formation of additional amount of cross-links.

MDF probes synthesized from the mixture which was mechanically and also mechanochemically premixed generally achieve the content of cross-links higher by one third relative to MDF probes synthesized from the mixture which was mechanically premixed only (compare above and in Table 2). These data together

Table 2. Data sets extracted from DTG, DTA and TG curves in the temperature region 200-330°C to give insight (TG mass loss / %) on the scope of cross-links formation due to the mechanochemical activation – A.M., 5 min (mean) [23], and in the final MDF probes – presented as the series of F.P.-s [this work].

DTG, DTA	TG, mass loss Δm / %	Composition of the analysed probe
+, +	0,54	A.M. 5 min (mean)
+, +	1,20	F.P. , mech.
+, +	1,22	F.P. , mech.
+, +	1,21	F.P. mech. (mean)
+, +	1,40	F.P., mech-chem.
+, +	1,60	F.P., mech-chem.
+, +	1,73	F.P., mech-chem.
+, +	1,58	F.P. mech-chem. (mean)
+, +	1,45	F.P., mech-chem., ■
+, +	1,70	F.P., mech-chem., ■
+, +	1,58	F.P. mech-chem. ■ (mean)

with the reported internal pressure show that the effect of internal pressure consists in the initial improvement of the rate and effectiveness of cross-links formation during MDF syntheses of mechanochemically activated raw mixes. The mechanochemical procedure of dry mixes of cement and polymer keep the composition of raw mix system unchanged – no further additives are used. This approach proposes and defines the mode of inclusion of the specific mixing step within the MDF procedure. The effectiveness of such step should be seen in the initiation and formation of measurable quantity of Al(Fe)-O-P cross-links already in the raw mixes composed of Portland cement and polyphosphate [23]. The knowledge represents an experimental evidence of the increased number of points where grafting [31] of atoms originated from poly-P on grains of cement has been suggested [17, 31]. Modification of intimacy of contacts among components is frequently discussed [4–15] as the vital goal in the MDF reaction systems. The data on MDF probes synthesized from the mechanochemically pre-treated raw mixes (including the phenomena/effect of internal pressure) suggest that already the mechanochemical modification, with the features reported and discussed in [23] and here, may represent one successful example which leads to immediate increase of the content of cross links. These aspects may exert also the technological advantage, more straightforward tests of this phenomenon continue.

The representative IR spectra of probes relevant in this system are reported in Figure 3. Features of IR spectra indicating the presence of clinker minerals, like alite and belite, basically bands at 930 and 520 cm^{-1} of Si–O and Al–O vibrations, remain unchanged if compared the spectra of both raw materials and MDF probes. This knowledge confirms that the cementitious components of raw mixture reacted only partially, the

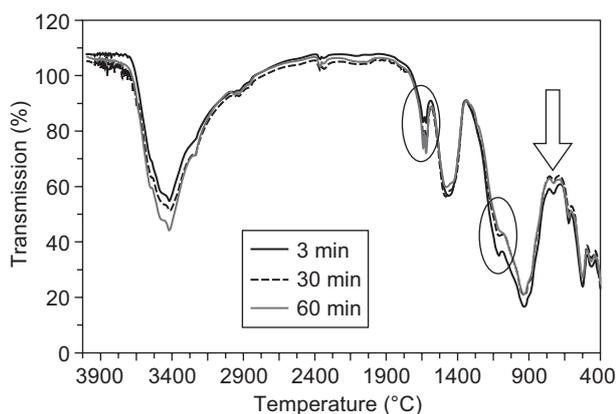


Figure 3. The representative IR spectra of MDF probes relevant in the studied system, the period of spectra acquisition (interaction duration) is quoted directly in the Figure. The vibrations of crystalline water ($\approx 1600 \text{ cm}^{-1}$) and Si–O groups ($1100 - 1200 \text{ cm}^{-1}$) are those in encircled areas, a band at $720 - 730 \text{ cm}^{-1}$ (discussed as the effect of phosphorus atom from the position in P–O–Al upon Al–O vibration) is marked by the arrow.

phenomenon commonly typical of MDF materials [3, 4 and a choice of papers cited therein]. Areas of IR spectra of MDF materials where these differ from IR spectra of raw materials comprise the bands at wavelengths characteristic for vibrations of crystalline water ($\approx 1600 \text{ cm}^{-1}$) and S–O groups at around 1620 cm^{-1} , carbonates ($\approx 1500 \text{ cm}^{-1}$), vibrations of Si–O groups ($1100 - 1200 \text{ cm}^{-1}$) and a band at $720 - 730 \text{ cm}^{-1}$. The shift of the later band by $16 - 26 \text{ cm}^{-1}$ from a value of specific vibrations of Al–O groups (746 cm^{-1} , [32]) should be seen as the effect of phosphorus atom from its position in P–O–Al cross-links upon Al–O vibration. Similar shifts and sensitivity of IR bands and vibrations, also due to Si–O–Al linkages, have been reported [33] in a choice of minerals. The analysis of acquired IR spectra gives another and independent experimental evidence of both partial conversion of clinker phases and formation of cross-links during the process of MDF syntheses in the particular system of Portland cement and polyphosphate.

The scope of cross-linking accepted as the key set of phenomena of a successful MDF procedure, can be besides methods employed in this study experimentally followed independently by various techniques including MAS NMR spectroscopy; cf. in [16, 17, 26], but also in [4, 6, 12, 15]. The data on which relies present study clearly show that the mechanochemical treatment of raw mix indeed leads to the increased content of cross links in the MDF probes. Occurrence and quantity of Al(Fe)-O-P cross-links in the MDF probes formed from raw mixes which have been mechanochemically treated/activated are in accord with the suggested atomic-level interpretation of functional grafting of polymers [31]; namely the phosphorus atoms originally from poly-P are through oxygen atoms bonded with aluminium or iron atoms of the grains of cementitious components. Thus, the uniform atomic-level interpretation of cross-linked functional interfaces in both activated raw mixes and successfully synthesized MDF probes is fully consistent with our earlier model [17], cf. also Figure 1. Achieved and discussed knowledge is a challenge; it adds to key features of MDF formation reactions - water addition and pressure application, also the option and effect of mechanochemical activation and internal pressure.

CONCLUSIONS

1. The scope of cross-linking in MDF materials synthesized from mechanochemically activated raw materials has been studied by two independent experimental methods (thermal analysis and IR spectroscopy). Thermal effects have been evaluated using our earlier original methodologies. The data of IR spectroscopy showed that also this method is sensitive upon the presence of Al–O–P cross links, especially in the region of specific Al–O vibrations.

- The mechanochemical activation represents a new challenge; already during the treatment of raw mixtures the initiation of cross-linking is achieved and it is further intensified in course of MDF syntheses themselves, where the effect of internal pressure causes the improvement of the rate and effectiveness of cross-links formation. Semiquantitative comparison of thermoanalytical data showed that the content of cross-links in MDF materials synthesized from mechanochemically activated raw mixtures is by one third higher than that in MDF materials synthesized from standard raw mixtures.
- The reported approach and results represent as the contribution to the knowledge about MDF materials themselves so the challenge for the development of a variety of new and innovative materials strategies. It is suggested to include among the key features of MDF formation reactions besides (and prior to) water addition and pressure application also the option of mechanochemical activation of raw mixtures; this option increases the rate of cross-links formation in the system through the effect of internal pressure.

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REFERENCES

- Mehta P. K.: *Concrete International* 21, 69 (1999).
- Delluci M., Cerisola G.: *Construction and Building Materials* 15, 351 (2001).
- Odler I. in: *Special Inorganic Cements*, E & F N Spon, London, New York 2000.
- Donatello S., Tyrer M., Cheeseman, C.R.: *Construction and Building Materials* 23, 1761 (2009).
- Soukal F., Brandstetr J., Havlica J., Odler I.: *Silika 1-2*, 45 (2007).
- Comotti A., Simonutti R., Sozzani P.: *J. Mater. Sci.* 32, 4237 (1997).
- Titchell I.: *J. Mater. Sci.* 26, 1199 (1991).
- Lewis J. A., Boyer M.: *Adv. Cem. Based Mater.* 2, 2 (1995).
- Pushpalal C. K. D., et. al.: *Cem. Concr. Res.* 29, 121 (1999).
- Ekincioglu O., Ozkul M. H., Struble L. J., Patachia S.: *Cement and Concrete Composites* 34, 556 (2012).
- Ekincioglu O.: *Investigations of water sensitivity in macro defect free cements*, PhD thesis. Istanbul, Istanbul Technical University, 2009.
- Desai P. G., Young J. F., Wool R. P.: *Mater. Res. Soc. Symp. Proceedings* 245, 179 (1992).
- Masilko J., Soukal F., Buzek L., Koplik J. in: *Proc. of 12th Intl. Inorganic Bonded Fiber Composites Conference*, p. 321–325, Aalborg Univ. Denmark, 2010.
- Masilko J., Buzek L., Koplik J., Soukal F., Repka M. in: *Proc. of 14th Intl. Conference Ecology and New Building Materials and Products*, p. 311–314, VUSH, Telc, Czech republic, 2010.
- Popoola O. O., Kriven V. V. M., Young J. F.: *J. Am. Ceram. Soc.* 26, 1928 (1991).
- Drabik M., Slade R. C. T.: *Interface Sci.* 12, 375 (2004).
- Drabik M.: *Pure & Appl. Chem.* 81, 1413 (2009).
- Birchall J. D.: *Phil. Trans. Roy. Soc. London* A310, 31 (1983).
- Atkins K. M., Edmonds R. N., Majumdar A. J.: *J. Am. Ceram. Soc.* 26, 2372 (1991).
- Edmonds R. N., Majumdar A. J.: *J. Am. Ceram. Soc.* 24, 3813 (1989).
- Popoola O. O., Kriven V. V. M., Young J. F.: *J. Am. Ceram. Soc.* 26, 1928 (1991).
- Billik P., Čaplovičová M. in: *Advances in Nanotechnology*, p. 111–164, Eds. Bartul Z., Trenor J., Vol. 8, Nova Publ., New York, 2012.
- Drabik M., Billik P., Galikova L.: *Ceramics – Silikáty* 56, 396 (2012).
- Birchall J. D., Howard A. J., Kendall K., Raistrick J. H.: *Eur. Pat. Specification*, B1, No. 0055035, p. 1 – 17, 1988.
- Young J. F. in: *MAETA Workshop on High Flexural Polymer-Cement Composite*, p. 1 – 12, Ed. Maeda N., MAETA Ltd., Sakata, Japan, 1996.
- Mojumdar S. C., Mazanec K., Drabik M.: *J. Therm. Anal. Calorim.* 83, 135 (2006).
- Drabik M., Mojumdar S. C., Slade R. C. T.: *Ceramics – Silikaty* 46, 683 (2001).
- Drabik M., Mojumdar S. C., Galikova L.: *Cem. Concr. Res.* 31, 743 (2001).
- Drabik M., Galikova L., Billik P. in: *New Trends in Coordination, Bioinorganic and Applied Inorganic Chemistry*, Eds. Melník M., Segľa P., Tatarko M., Press of Slovak University of Technology, Bratislava 2011.
- Drabik M., Billik P., Galikova L. in: *Proc. 10th Intl. Conference Solid State Chemistry*, p. 62, University of Pardubice, 2012.
- Wegner G.: *Acta Materialia* 48, 253 (2000).
- Trezza M.A., Lavat A.E.: *Cem. Concr. Res.* 31, 869 (2001).
- Ritz M., Vaculíková L., Plevová E.: *Acta Geodyn. Geomater.* 8, 47 (2011).