MACRO DEFECT FREE MATERIALS; THE CHALLENGE OF MECHANOCHEMICAL ACTIVATION

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Macro-defect-free (MDF) materials belong, according to Odler's categorisation, to the type of materials where polymers may be successfully combined with cements and water to produce also the parameters of technological novelty and interests. A challenge, which has not been followed or indicated by now, is the option to intensify mixing of dry cement and polymer. The mechanochemical pre-reactions of dry MDF raw mixes consisting of Portland cement and polyphosphate, together with the model of atomic-level interpretations of the formed functional interfaces are proposed, experimentally tested and discussed in the present paper. The results ultimately show the activation of studied system due to the mechanochemical treatment, which 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 is proposed as the specific mixing and activation / pre-reaction step within the entire MDF synthesis procedure.

INTRODUCTION

Among the recent advancements of 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. Concerns about their durability in water have limited research activity in recent years, but there appear to be established routes by which these may be overcome [4]. The crucial conclusions on the ratings the advancement of various materials in concrete technology has been given by Mehta in his review [1]. As refers MDF materials, CBC, and also reactive powder mortars in concrete technology, the ratings are outlined in Table 1. It is expected that these materials would not have an impact on the concrete industry as a whole, but their challenge for specialty technologies is anticipated to grow in the future.

According to Odler's [3] categorisation, MDF materials belong to one of the materials where polymers may be successfully combined with cements to produce also the parameters of technological novelty and interests. The newest review of the research completed on MDF materials, and particularly the polyvinyl-alcohol/calcium aluminate cement (PVA/CAC) system has been published by Donatello & co-w. [4], and the advantages, limitations and potential applications of MDF materials are outlined. Referring procedure and chemistry of MDF materials, great degree of mixing produces strong polymer cross linking during cement hydration, a truly composite material is formed in which the technological parameters are imparted also by the polymer. In the high pH environment that exists at the surface of hydrating cement grains, Ca^{2+} ions will be present as $Ca(OH)_2$ and Al^{3+} ions present as $[Al(OH)_4]^-$. The series of interactions of the polymer phase with aluminium ions via an ester group and/or acetate ions have been postulated [5, 6]; Ca ions can form a hemihydrate calcium acetate following interaction with the polymer, and Al ions rather than Ca ions are thought to have a role in forming the cross-linking interphase [5-8].

The options to initiate and induce formation of cross-links are a challenge of chemistry in this field [9]. The effects of different cement phases have been investigated. For example, using sulphoaluminate–ferrite–belite (SAFB) and Portland cement (PC) blends instead of CAC produced MDF materials that achieve irreversible moisture absorption as low as 0.5-10 % of initial weight [8, 10-14]. Changing the polymer phase has also been investigated; PVA with different degrees of hydrolysis and average molecular weights have been used, as well as sodium polyphosphate (poly-P), hydroxypropylmethyl cellulose (HPMC) and butylacrylate/acrylonitrile (BA/AN) [8, 10-15, 17]. The key occurrence of cross-links, impacts and interrelations similar to those in CAC based MDF materials has been confirmed by a variety of experimental methodologies and methods, i. e. MAS NMR spectroscopy, IR spectroscopy, thermal analysis, microscopies, electrochemical impedance spectroscopy [cf. in a choice of papers cited above].

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 [16]. 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, 17, 19-26]. 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 in the systems where additional phases increase the complexity.

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, 7-9, 18, 24]. 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 oxide by cement phases and hydrates free cross-links. The schematic model, which we have published earlier [9] is shown in Figure 1. It gives a quick navigation through the state-of-art of the knowledge on

Table 1. Suggested ratings for recent advancements in concrete technology, adapted from [1] for a choice of MDF materials, CBC and reactive powder mortars.

Identification of the technology	Complexity of the technology	Initial cost of materials and construction	Life-cycle cost	Environmental friendliness of the product	Future impact on the concrete industry
MDF cement pastes and mortars	High	High	High	Poor	Negligible
Chemically-bonded ceramics	High	High	Unknown	Poor	Negligible
Reactive powder mortars	High	High	Unknown	Poor	Negligible

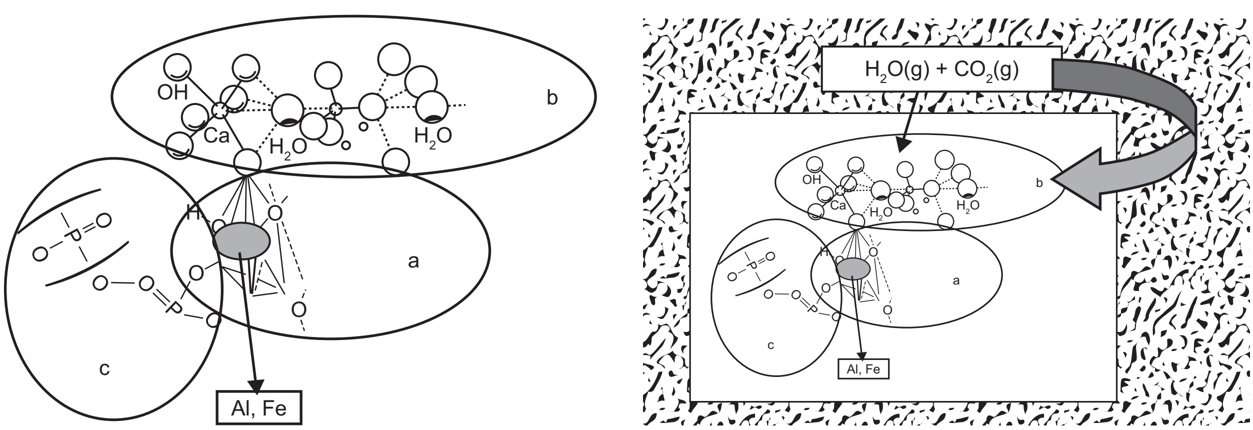


Figure 1. Formed cross-links (region a in part I, left) in the functional interfaces (entire part I, left) and the adverse influence of moisture (part II, right)

MDF materials summarizing current approaches as to the syntheses, so to the atomic-level interpretations of both formed functional interfaces (part I) and adverse influence of the moisture (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 [18, 20, 21]. 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 (a type of mechanochemical processing conditions). The cross-linking interactions are introduced to involve atoms at the interfaces of a cement-based component with an appropriate polymer [5-7, 9, 18, 20, 21, 24].

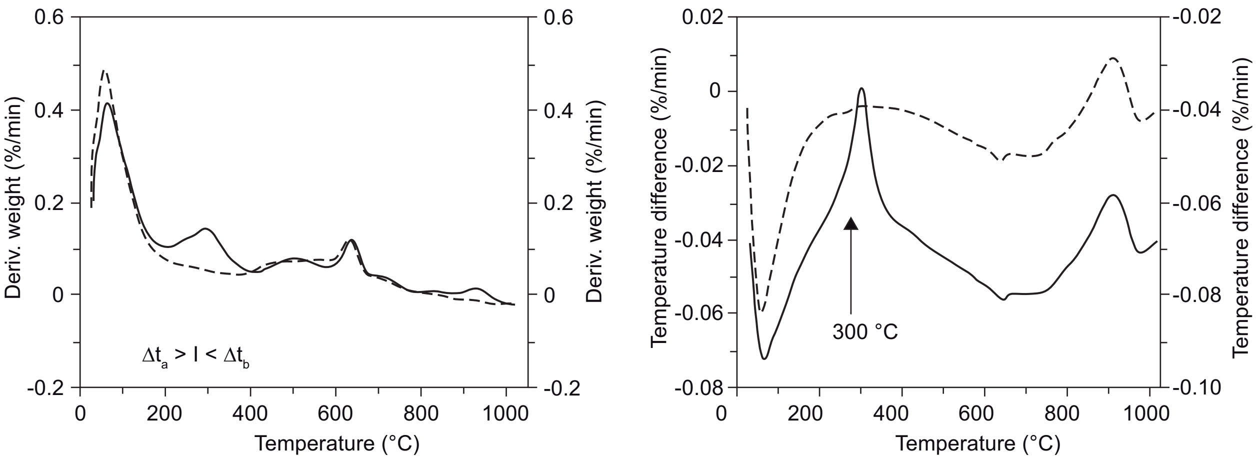
A challenge, which has not been followed or indicated by now, is the intensification of mixing of cement and polymer prior to the addition of water. Here one of the procedures which may exert the specific affinities towards cross-linking is the mechanochemical treatment of solid raw mixes before the 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 [27]. 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. Anyway, the scope and/or restrictions of applicability and effects of given methodologies should be thoroughly tested and analyzed.

The aim of this study has been to combine the critical analysis of applicability of mechanochemical treatment and the experimental tests of mechanochemical activation / pre-reactions of raw mixes of MDF materials. 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 have been followed in the system of Portland cement and sodium polyphosphate.

EXPERIMENTAL

The applicability of mechanochemical treatment has been tested on typical raw mixes composed of Portland cement and sodium polyphosphate (poly-P). Portland cements form an effective alternative of high alumina cements for successful MDF syntheses, if combined with hpmc or poly-P [3, 9, 10]. The choice of raw mixes comprised the Portland cement of CEM III type, poly-P of formula $(NaPO_3)_n$, and $Na_5P_3O_{10}$. The effect and potential of mechanochemical treatment / activation have been studied on the former compositions subsequently after the mechanical mixing. Mechanochemical treatment has been performed in TB-2 high energy planetary mill [27] achieving the effective velocity of 890 RPM. The further parameters comprised milling times 1 & 5 min, steel balls of diameter 10 mm used as milling media, ball : powder mass ratio (MR) 10 : 1.The details on both, composition and treatment cf. in Table 2.

The effects of mechanochemical treatment upon the parameters of composition and properties of raw mixes have been tested by methods of X-ray phase analysis and thermal analysis. The entire system of individual mechanochemically treated probes comprised crystalline phases exclusively in the form of reagent components (clinker phases, poly-P), as indicated from the powder



a) b)

Figure 2. Typical DTG (a) and DTA (b) curves of MDF probes [8, 9, 11]; full lines with the events in the region from 200 to 300°C – Δt_b (DTG) and exoeffect at 300°C (DTA), denoting the occurrence of Al(Fe)–O–P cross-links (synthesis successful), dashed lines – no events in the region from 200 to 300°C due to the absence cross-links (synthesis not successful).

X-ray data. Thermoanalytical measurements were conducted 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°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 200-300°C upon the presence (and thermal decomposition) of Al(Fe)–O–P cross-links (Figure 2) [8, 9, 11], has been used as the indication of key change in raw mixes due to the mechanochemical treatment. 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 raw mixes during the individual mechanochemical treatments.

Table 2. Ranges of composition and sequences of the treatment of studied mixes.

Portland cement	Polymer	Mechanical mixing	Mechanochemical treatment
CEM III	Poly-P (5 mass %)	√	–
		√	√, 1 min
		√	√, 5 min
CEM III	Poly-P (10 mass %)	√	–
		√	√, 1 min
		√	√, 5 min

RESULTS AND DISCUSSION

Effects of mechanochemical treatment/activation are visible from both data of X-ray phase analysis and thermal analysis in a complete set of ball milled intermediates. The diffraction profiles of treated raw mixes showed no phase changes in the crystalline portion of mixes, the individual mechanochemically treated probes comprised crystalline phases exclusively in the form of reagent's components - clinker phases, poly-P. The decrease of intensities of X-ray diffractions and increase of the widths of these in probes which have been mechanochemically activated for the duration of 5 and 10 minutes were followed, these should be attributed to a slight lowering of grain size and partial amorphisation of mixes under the tested conditions of mechanochemical treatment. The choice of methods of thermal analysis, and data of these (Figures 3 and 4) enabled to indicate if the mechanochemistry (milling & reactions initiation) exerts any positive effect upon the MDF procedure (cross-links formation). Moreover, an additional challenge has been the option to extract from the thermogravimetric data the information on the scope of effects which are due to the mechanochemical treatment/activation (Figure 4, Table 3).

The thermoanalytical data represent the crucial, and original, knowledge on the presence of Al(Fe)–O–P cross-links in raw mixes which have been mechanochemically treated/activated for the duration of 5 minutes (Figure 3, right part, Figure 4, left part, Table 3), or longer duration (not presented). DTG and DTA effects of treated/activated probes in the temperature region 200-300°C confirm qualitatively the presence (and decomposition on heating) of cross-links with the Δt_b (DTG) and exoeffect at 300°C (DTA) reported already in this temperature region (cf. Figure 2 and in our earlier studies [8, 9, 11]). TG mass losses of probes in this region give the additional information through the proposed parameter R_{act}. This is defined as the ratio of means of estimated TG mass losses of activated mixes – A. M. (mean) and those of final products – F. P. (mean) in the temperature region 200 – 300°C:

$$R_{act} = A.M.(mean) / F.P.(mean) \qquad (1)$$

For the columns DTG, DTA: + or - denote the occurrence or absence of the indicative thermoanalytical event (DTG and/or DTA) of cross-links. For the column Note: A. M. – mechanochemically activated mixes, F. P. – final products.

The parameter R_{act} topical in the studied system has been calculated using equation (1) and the thermogravimetric data of activated mixes and final products – mean values of the TG mass losses of both (activated mixes and final products) in the temperature region 200-300°C cf. in Table 3.

$$R_{act} = 0,54 / 1,68 = 0,32 \qquad (2)$$

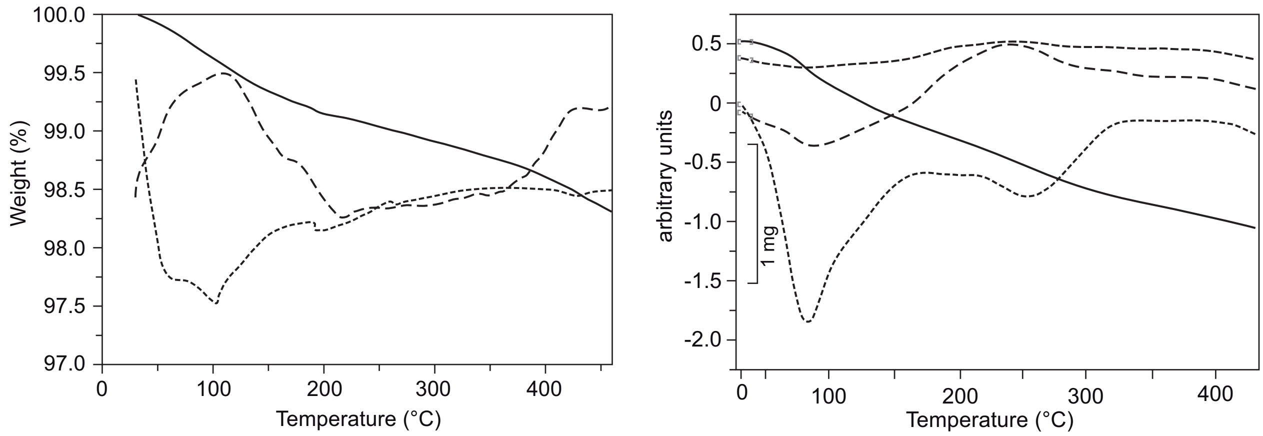
The scope of cross-linking accepted as the key set of phenomena of a successful MDF procedure, can be experimentally followed independently by various techniques including MAS NMR spectroscopy and thermal analysis; cf. in [8, 9, 11], but also in [4, 7, 17, 24]. The entire cross-links functionalize the interfaces and have been reported amorphous, not detectable by X-ray phase analysis [3, 5-10, 24]. The present study relies

Table 3. Data sets extracted from DTG, DTA and TG curves in the temperature region 200-300°C to give semiquantitative insight on the scope of cross-links formation due to the mechanochemical activation.

DTG, DTA	TG mass loss (%)	Note
– , –	-	A. M., 1 min
– , –	-	A. M., 1 min
+ , +	0,47	A. M., 5 min
+ , +	0,56	A. M., 5 min
+ , +	0,58	A. M., 5 min
+ , +	0,54	A.M. (mean)
+ , +	1,60	F. P.
+ , +	1,70	F. P.
+ , +	1,73	F. P.
+ , +	1,68	F.P. (mean)

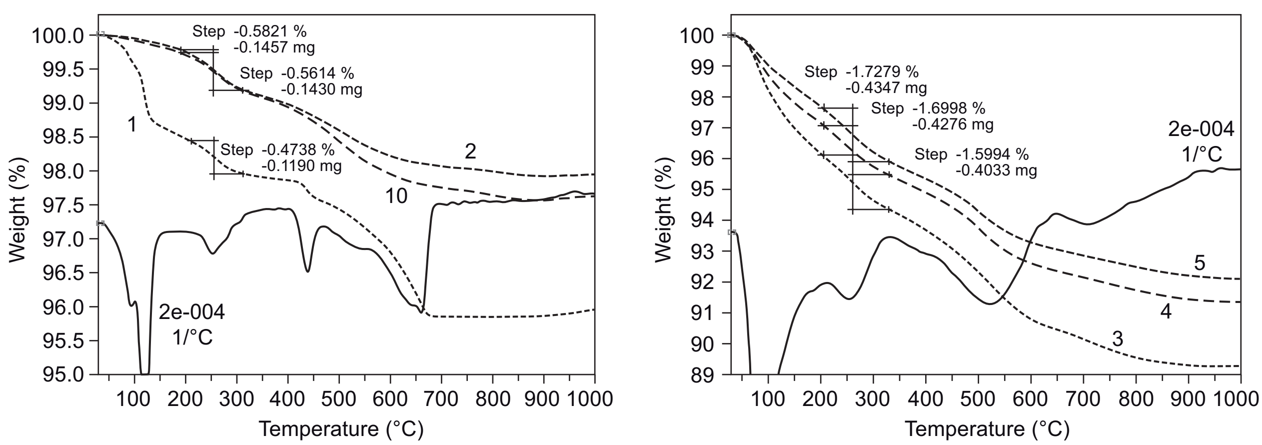
on data and methodologies of two methods of thermal analysis, in particular thermogravimetry and differential thermal analysis, where the sensitivity of the region of 200-300°C upon the presence of Al(Fe)–O–P cross-links was reported [8, 9, 11]. The insight on the scope of cross-links formation during the mechanochemical treatment has resulted from the evaluation of thermal events and mass losses in the region of 200-300°C and from the consideration of the topical value of the parameter R_{act}. Accepting that F. P. (mean) is the maximum achievable value of TG mass loss due to the decomposition of present cross links, than the value of R_{act} = 0,32 (cf. above) shows that given mechanochemical conditions activate the raw mixes facilitating the formation of "seeds" of atomic level cross-links in amounts around 30 % - ages of the entire content of cross-links in the MDF material.

The results, as presented in Figures 3 and 4, and in Table 3, confirm the duration of 5 minutes of the mechanochemical interactions to be optimal; at this duration the cross-links are formed to a substantial measure and independently of the other tested variables (MR or content of poly-P). These findings represent a challenge of this mode of activation which will potentially intensify the cross-linking and development of typical MDF parameters during the mutual process of MDF synthesis. The atomic-level interpretation of functional interfaces consisting of cross-links in activated raw mixes is fully consistent with our earlier model [9], cf. also Figure 1. This consistency makes possible to propose the mechanochemical activation of raw mixes in the high energy planetary mill for the duration of 5 minutes as the specific mixing and activation/pre-reaction step within the entire MDF synthesis procedure.



a) b)

Figure 3. The representative TG, DTG and DTA curves of mechanochemically treated raw mixes for the duration of 1 minute (a) and 5 minutes (b).



a) b)

Figure 4. The evaluation of mass losses on TG curves in the temperature region 200-300°C which is sensitive on the presence (and thermal decomposition) of Al(Fe)–O–P cross-links; a) raw mixes mechanochemically treated for the duration of 5 minutes (in Table 3 referred as A. M., 5 min), b) final MDF probes [8, 9, 11] (in Table 3 referred as F. P.).

The vital goal of any mode of intimate mixing of the polymer phase with the inorganic cement phases is to achieve and produce, through great degree of mixing, stronger polymer cross linking, both, leading to and imparting the strength of hydrated materials with high fracture toughness [4, 7, 17, 19 – 21, 24].The concerns of poor durability of MDF materials in the moist environment led to a decline of research interests on the topics of MDF materials [2, 12, 19]. Anyway, it is anticipated that the revolutionary breakthrough would bring already chemistry based studies [3, 4, 9, 16, 25], which should be directed as to the materials themselves so to modifying additives and procedures, both with specific affinities towards stabilizing the polymers especially by cross-links formation in the system. Approaches reported earlier rely in common on the additions or modifications of phases in the composition of raw mixes, i. e. additions of organotitanate compounds [2, 20, 24, 26], or use of PVA with various hydrolysis degree [15, 19, 22, 23]. The increased complexity of system brought some improvements of intimacy of mixing and cross linking, anyway, it is difficult to control the phenomena quantitatively, cf. [2, 22, 23, 25]. The approach and results presented in this study keep the composition of raw mix system unchanged – no further additives are used, but propose and define the mode of inclusion of the specific mixing step within the MDF procedure. The topical results ultimately show the activation of studied system due to the mechanochemical treatment / pre-reactions; it consists in the initiation and formation of measurable quantity of Al(Fe)-O-P cross-links in the raw mixes composed of Portland cement and polyphosphate.

Occurrence and presence of Al(Fe)-O-P cross-links in the raw mixes which have been mechanochemically treated/activated, together with the suggested atomic-level interpretation [9] are challenge which may affect MDF formation reactions under the subsequent water addition and pressure application. Thus, we propose to incorporate the methodology of the mechanochemical activation as the specific mixing step of the entire synthesis procedure of MDF materials. The anticipated increase of the rate and effectiveness of syntheses will exert also the technological advantage, more straight-forward tests of this phenomenon continue.

CONCLUSIONS

1. 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 topical system of Portland cement and sodium polyphosphate.
2. The mechanochemical procedure contributes to the functionalization of interfaces of cement and polymer; cross-links formed during the optimized treatment achieve the amount close to 30 % - ages of the entire content of cross-links in the MDF material.
3. The results enable to propose the incorporation of the methodology of the mechanochemical activation in the high energy planetary mill for the duration of 5 minutes as the specific step of the synthesis procedure of MDF materials.

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