Macro-defect-free Materials; Potential of Portland cements

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1.   Abstract

Macro-defect-free (MDF) materials and technologies have been originally studied in systems of high alumina cements with polyvinylalcohol/acetate or in systems of Portland cement with polyacrylamide. The high alumina system being reported the promising one, but exerting an economical disadvantage. Our continuous effort is to look for a useful MDF related compositions based on Portland cement (PC) and a variety of polymeric additives, of which specially focused are polyphosphate glasses. The topic is discussed from aspects of chemistry of the system, where both NNN interactions (as reported of MAS NMR spectroscopy) and thermoanalytical data on the stability of cross-linked interface provide us with the nanolevel aspects governing the mechanism and scope of the grafting of polymeric chains on the surface of cement grains. Technologically relevant moisture resistance of studied MDF material is evaluated of the analysis of pore structure, gravimetric and thermogravimetric results; the values are shown to mutually coincide with the scope of the cross-linking and grafting in PC - based MDF compositions.

2.   Introduction

The international scientific community considers several "hot topics" in the field of cement-based materials and composites. The goals to be dealt with cover aspects of cement materials science (esp. chemistry) and also technology. A synergy of the above aspects enables a progress leading to the exploitation of added value of the new and novel materials. Materials chemistry; a combination of noun and adjective that had not previously formed part of chemists' vocabulary (as quoted in preambula of the IUPAC project "Towards defining materials chemistry" [1]), has grown to a distinct discipline during the last 10 – 15 years.

MDF materials are chemically bonded ceramic materials free of the macrodefects typical for hydraulic cement-based materials. The materials are formed through a series of specific procedure steps [2 – 5] applied on the appropriate mixes composed basically of cement, water soluble

polymer and water. Here, in addition to the hydraulic reactions of cement with water, polymers modify the interface through functional bonding/grafting of polymer chains onto the surfaces of cement grains [3]. Both the cross-linked atomic structure and the modified interface coincide well with the model of functional polymers [6] and represent a new type of atomic-level structure in polymer-modified cements. The interpretations are based on the data of magnetic resonance and thermal analysis/decomposition.

High alumina cement with poly(vinyl alcohol)/acetate [2, 4] or sulfate-aluminate-ferrite belitic (SAFB) clinkers and/or Portland cements with three types of water-soluble polymer - polyacrylamide, hydroxypropyl-methyl cellulose (HPMC), polyphosphate glass (poly-P) [2, 3, 7] are the alternative raw mixtures. The high alumina system has been reported as promising but exerts an economical disadvantage. Thus, there are continuous efforts to look for useful MDF related systems based on Portland cement. Mixes of Portland cement with low energy SAFB clinkers, HPMC and, especially, poly-P comprise promising cross-linked compositions [2, 3] additional to the better known MDF materials formed from high alumina cement with poly(vinyl alcohol)/acetate. The principles of co-ordination of P and C atoms (of the polymer) with Al and Fe atoms (originating from the cement) have been highlighted from spectroscopic information on Next-Nearest-Neighbour interactions, along with the effects of second co-ordination spheres [8, 9]. Increased interfacial interactions in novel MDF compositions may reduce an unfavourable uptake of moisture. Carbonation is also the topic of continuing studies in this field.

This paper presents the latest results of our continuous effort in the area. The topical aim has been to check the appropriateness of selected types of Portland cement for the formation of MDF materials and, based on achieved results (nano level changes vs. durability), to critically estimate the potential of Portland cements for the preparation of this material in real conditions.

3.   Experimental

The numerous tests of MDF workability have been made on the mixtures of industrial Portland cements (CEM I - CEM III types), or so called "microcement" (the material specifically elaborated and tested for modified use), and two modes of sodium polyphosphates (solid commercial compound - poly-P (s), and its aqueous solution - poly-P (l)). The effects of twin-roll procedure, duration, mode and extent of pressure application have been also studied.

The synthesis procedure complies with that accepted in Odler's review [2] and the details were as follows: the cement is blended by *either* a)

additions of 1, 5 or 10 mass %-ages of poly-P (s) and water to give the required ratio w/s = 0.15 – 0.20; *or* b) addition of poly-P (l) to incorporate the required amount of poly-P and w/s ratio; the next steps comprise c) twin-rolling until the mixture reaches the consistency of a dense dough (up to 5 min), d) application of static pressure (between 3 to 10 MPa) in a pellet die of 10 mm diameter for 30 min to 5 h, and e) "freezing of chemical reactions" by air drying *either* immediately after the finalizing the pressure application *or* delayed 24 h after the finalizing the pressure application. The full set of tested raw mixtures and synthesis conditions is presented in Table 1.

Table 1. Tests of MDF Synthesis Procedure of Mixes at the w/s = 0.2 and p = 5 MPa .

Raw mixture composition	t/h 0.5 (i.d.)	0.5 (d.d.)	1 (i.d.)	1 (d.d.)	3 (i.d.)	3 (d.d.)
CEMI + 1%poly- (s)	√	√	√	√	√	√
CEMI + 5%poly-P(s)	√+	√+	√+	√+	√+	√+
CEMI + 10%poly-P(s)	√+	√+	√+	√+	√+	√+
CEMI + 1%poly-P(l)	√	√	√	√	√	√
CEMI + 5%poly-P(l)	√+	√+	√+	√+	√+	√+
CEMI + 10%poly-P(l)	√+	√+	√+	√+	√+	√+
CEMIII +1%poly-P(s)	√	√	√	√	√	√
CEMIII +5%poly-P(s)	√**+**	√**+**	√**+**	√**+**	√**+**	√**+**
CEMIII +10%poly-P(s)	√+	√+	√+	√+	√+	√+
CEMIII +1%poly-P(l)	√	√	√	√	√	√
CEMIII +5%poly-P(l)	√**+**	√**+**	√**+**	√**+**	√**+**	√**+**
CEMII +10%poly-P(l)	√+	√+	√+	√+	√+	√+

Footnotes:
- *t/h* - duration of the pressure application, i.d. and d.d. - periods of air drying after synthesis: i.d. - immediately, d.d. - delayed 24 h,   √ - procedure checked, √+ - synthesis successful,   √ **+** - synthesis successful, optimal composition.
- The tests were performed to identical extensions also for variables: "microcement", CEM II, w / s = 0.15, *p* = 3 MPa and 10 MPa.

For each MDF composition a minimum of 2 separate MDF tablet (disk) samples were fabricated and investigated. The moisture resistance was tested on cylindrical tablets as synthesized. The tests focused on the relation of mass changes and field atmospheric environmental conditions for a period of 1 year. Relative humidity during the year of tests have been monitored by an RH-T sensor (HOBO, Amet Ltd.), it varied as follows: 40 – 60 % RH upto the day 180 (dry period of spring and summer), 65 – 85 %

RH between days 181 and 355 (wet period of autumn and winter), and finally around 50 % RH between days 356 and 370 (begining of the second dry period). The relative mass changes ($\Delta m_{ac}/\%$) were monitored throughout these periods and two observed different patterns of mass development need to be considered and discussed (Fig. 1).
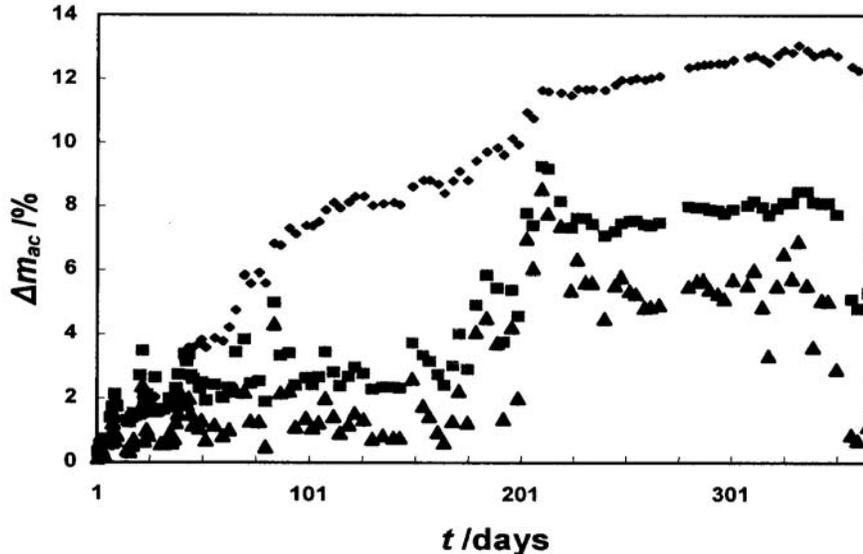
Fig. 1. Mass changes - $\Delta m_{ac}/\%$ as monitored during the year-long period of tests and weighting. Three typical MDF samples [♦ - with 1 % of poly-P, ■ – with 5 % of poly-P (s) and ▲ - with 5 % of poly-P(l)] from among the MDF probes synthesized in the system Portland cement + polyphosphate glass are illustrated.

The pore structure of selected specimens was studied through the use of mercury intrusion porosimetry (MIP) using the high-pressure porosimeter model 2000, and macro-porosimeter model 120 (both Carlo Erba, Milan). The devices enable the determination of micropores with the radius in range of 3.7 - 7500 nm and of larger pores with the radius up to 0,06 mm. From the measured data (volume of micropores up to 7 500 nm, mean micropore radius and mean pore radius, total porosity, and pore size distribution) permeability coefficients of tested pastes were also calculated. The permeability coefficient K (ms^{-1}) as a measure of the mortar/paste structure quality was calculated with the use of equation, which was derived and fully described in [10]. Small pieces of the samples with diameter less than 10 mm were used for the tests. The samples were dried at 105°C to the constant weight before testing.

Simultaneous TG/DTG/DTA was conducted on a T.A.I. SDT 2960 instrument (from ambient to 1000 °C, 10 – 20 mg sample, heated at a rate

of 10 °C min^{-1} in air), the results provided the data on the phase composition of MDF probes and these after the moisture attack. Grinding of samples was accomplished before thermal (TG/DTG/DTA) analysis. The thermoanalytical test of the success of individual MDF synthesis - detection of cross-links, has been used throughout the whole scope of examined compositions, it is illustrated in Fig. 2. The test is based on the data reported earlier [3, 11, 12]; the decomposition of cross-linked functional interface in the MDF probes occurs at the temperature interval by approx. 150 °C higher than that of "classical" cementitious hydrates (cf. Δt_b vs. Δt_a), and proceeds with the typical exoeffect at 300 °C (cf. DTA curve). This difference, as the key nanostructural feature of MDF material, will be discussed also in the paper.
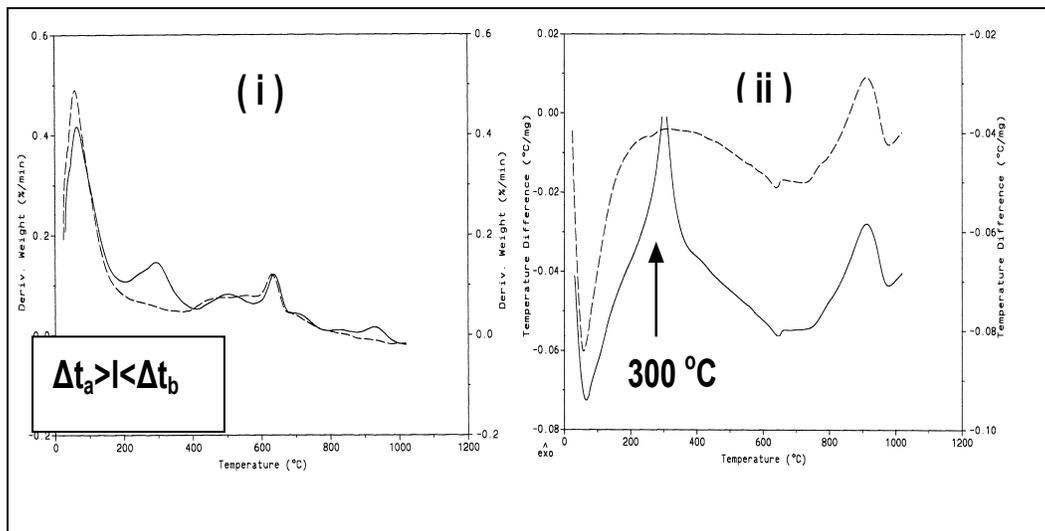
Fig. 2.   Typical DTG **(i)** and DTA **(ii)** curves of MDF test probes; full lines – successful synthesis, dashed lines – synthesis not successful.

4.   Results & discussion

The raw mixture and the manufacturing procedure were optimized: The influence of twin-rolling and applied pressure upon the success of MDF synthesis dominates. Present study shows a. o. that the scope of local cross-linking of cement with polymeric phase is directly related with the amorphous microstructural domains in MDF test pieces; cf. Fig. 6, in Appendix, and discussed also in [12]. Manufacture employing any composition of Portland cement with at least 5 %-ages of poly-P has been successful. Anyway, the most proper mixtures for MDF pieces manufacture are that of CEM III and poly-P (s, l). Clinker phases are in CEM III diluted by blast furnace slag (around 50 % in the tested industrial probes of CEM III), which denotes the advantage for the course of potential reactions - cross-linking is promoted versus hydration in systems

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with low w/s ratio. The effect of clinker phases' dilution similarly relates to the moisture resistance values, shown elsewhere in the paper. The trials to use „microcement" for the attempts to manufacture the MDF pieces were less successful. Phase analysis displayed comparable rates of cross links formation of "microcement" with polymeric phases and the rates of hydraulic reactions of the grains of „microcement". The above finding explains why the key cross-linking is only partial in such a probes at any pressures tested.

Mass changes (as the inverse measure of moisture resistance) within the year-long period of storage and weighing follow one of two patterns of development (Fig. 1). Pattern i): Continuous mass increase during the storage and weighting of probes (series ♦ in Fig. 1) mirrors the insufficient compactness and moisture resistance of the material with 1 % of poly-P added. Pattern ii): The values of increase of the mass of the other probes are limited by atmospheric conditions; $0.5 \leq \Delta m_{ac}/\% \leq 3.5$ at RH $\approx$ 50 %, but $4.5 \leq \Delta m_{ac}/\% \leq 8.5$ at RH $\geq$ 75 % (Fig. 1, series ■ and ▲). Moreover, at least 80 % of mass gained in wet period are reversibly lost from probes when the period changes to dry - cf. the values of Δm_{ac} of series ■ and ▲ in final two (dry) weeks in Fig. 1. This pattern of mass changes is interrelated to the changes of environmental moisture (dry *vs.* wet atmospheric periods). Results mark the compositions (5 % of poly-P added) with Al(Fe)-O-P cross-links compact and dense enough to develop Portland cement-based MDF material of potential commercial use. Only these compositions have been subjected to porosimetric analysis, nanoscale level analysis and localization of phase changes.

Table 2. Typical pore size distribution (PSD) and selected pore structure (PS) parameters (V_{MP} - volume of micropores, V_{TP} - volume of total open pores, M_{MP} - micropore radius median, M_{TP} - pore radius median and BD - bulk density) of tested MDF probes

P S D / %	< 10 nm	10 - 10^2 nm	10^2 - 10^3 nm	10^3 - 10^4 nm	> 10 µm
MDF as synthesized	2	10	70	12	6
MDF moist tested	33	13	43	9	2
P S parameters	V_{MP} mm^3/g	V_{TP} mm^3/g	M_{MP} nm	M_{TP} nm	BD kg/m^3
MDF as synthesized	164,33	180,39	337,48	382,25	1 900
MDF moist tested	94,52	104,05	105,97	141,09	2 310

Porosity data provide technologically relevant characteristics of hydraulic materials. The data on pore structure are thus a proof of the success of

MDF synthesis from point of view of the reduced content of macropores, the data relevant for studied system are given in Table 2 and Fig. 3. Estimated values of porosity and features of pore structure confirm that the MDF syntheses are in reported mixtures successful – typical pore medians fall within the 100 – 500 nm interval, the largest dimensions of pores do not pass over 5 μm. Both these parameters are closely in line with the data published for the other MDF materials [2, 5, 13, 14]. It should be also noted the validity of Griffith's rule, as for the MDF materials so for any concrete: the strength is primarily affected by the dimensions of the largest pores, not by the total porosity. The values of achieved strength and microhardness [14] of a choice of studied probes are in support of this rule. Based on this, there is no doubt that synthesized MDF materials are the example of the increased level of the exploitation of the potential of Portland cement.
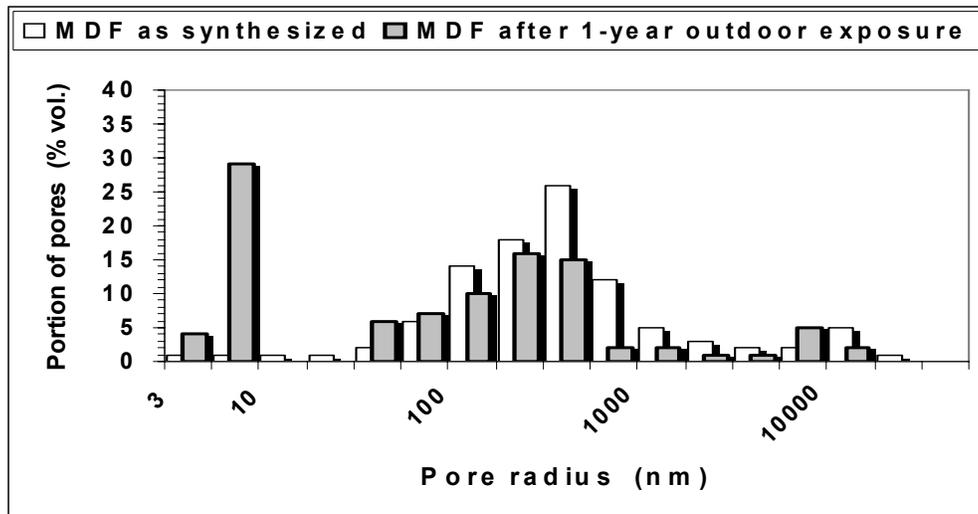
Fig. 3.   Graphical views of PSD in MDF probes and that after 1-year exposure in the atmospheric environment.

Data on porosity and pore structure of samples exposed to 1-year cycle of tests of the effects of atmospheric moisture and CO_2 provide additional correlations. The most remarkable are the decrease of the total pore volume, increased values of bulk density and pore medians oscillating around the value of 150 nm (cf. Table 2 and Fig. 3). The followed tendencies mark the densification of pore structure – pores are filled in by reaction products that arise due to the effect of atmospheric H_2O and CO_2 gases. The knowledge point to the occurrence of secondary hydration and carbonation of MDF samples in the atmosphere, and also to the fact that these changes are localised on the interfaces and in pores independently of the original dimensions of pores. The above is mutually connected with partial changes of microstructural habitus, these changes are localised in domains free of cross-links, cf. and compare in Appendix; Fig. 6 (virgin MDF sample) and Fig. 7 (MDF sample after the moisture attack).
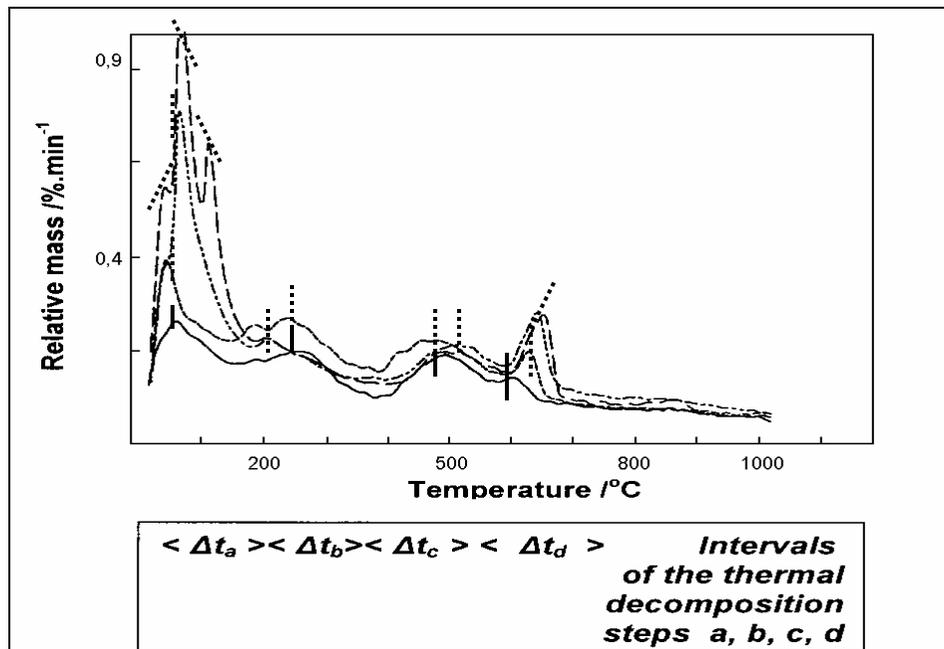
Fig. 4. DTG curves of the typical MDF probe and these probes after the moisture uptake. The distinction and generalization of four basic decomposition steps [12] of phases present : I - decomposition peaks in MDF probe, ⋮ - decomposition peaks in probes after the moisture uptake.

The moisture attack is, according to the results of thermal analysis about the changes of phase composition, mutually connected with the increased content of "classical" hydrates and calcite (Δt_a and Δt_d intervals in Fig. 4), whilst the contents of cross-linked functional interfaces (Δt_b interval in Fig. 4) and portlandite (Δt_c interval in Fig. 4) remain nearly constant. Both these results and that on porosity data favour the occurrence of secondary reactions of cement grain's phases with H_2O and CO_2 from the moist environment in pores of MDF material. MDF structure is additionally filled in, but the concentration of cross-linked functional interfaces does not increase, thus the technological consequences are improper.

The cross-linking of atoms originated as from cement grains (Al, Fe) so from polymer (P) functionalizes the interface between cement grains and polymer molecules during the process of MDF synthesis [3], the results conform the model of functional polymers [6]. According to the current thermoanalytical data (cf. Fig. 2 also), besides cross-linked functional interfaces are in the MDF probes present also AFm and C-S-H to certain extend. The comparison $\Delta t_b > \Delta t_a$, where Δt_b stands for the temperature interval of decomposition of cross-linked functional interface and Δt_a stands for the temperature interval of decomposition of AFm and C-S-H, is a further evidence of the key nanostructural feature of MDF material - stabilizing effect of cross-linking upon the formed material.

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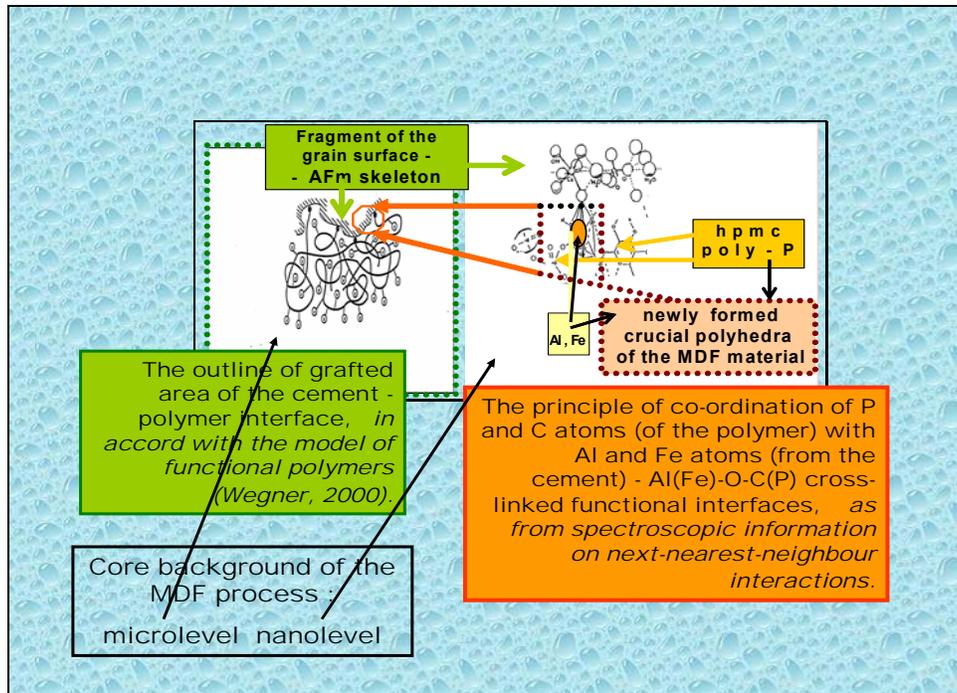
Fig. 5. Cross-linked functional interface in the MDF probes; right - the nano level representation of interactions according to our results, left - the micro level model of grafting derived from general Wegner's model [6].

Specific functionalisation of interface and surface occurring at both the micro- and nano- levels, as graphically outlined in Fig. 5, represents the key features of MDF materials and processes [2, 3] necessary to formation of such material. The nanolevel of the scheme has been constructed of our data on Next-Nearest-Neighbouhr (NNN) interactions [8, 9, 12] and the thermal stability of cross-linked interfaces (cf. here above). It displays that MDF materials, being cement-based composites, are the example where chemical knowledge is crucial as to i) Procedure design (Al-O-P cross-linking is the key nanoscale aspect of the formation process) so to ii) Exploitation (the interfaces comprise compact and stable regions in which Al-O-P cross-links crucially contribute to the control of moisture resistance of the material). The data on MDF materials are incorporated also in the latest discussion on relations of new chemistries and performance of cementitious binders [15]. The relative tendencies of strength development in the reported system are only available now – MDF probes achieve in average 150 to 170 %-ages of the values given by the type of cement used, but exert around 20 to 40 % decreased strength level in the moist treatment. It is well in line with the data on cross-linking during the formation of MDF material *vs.* secondary hydration under the moisture attack.

5.   Conclusions

The results, being of both academe and industry interests, outline an example of the "success story" of materials chemistry approach in cement-based materials. In particular: display the role of inorganic-polymer networks and cross-links in MDF materials, and define these specific nano and atomic levels of interaction within the frame of generally accepted model - grafting of functional polymers on the grain surfaces. The attack by environmental moisture is mutually connected with secondary hydration and partial changes of the microstructure of domains free of cross-links.

6.   References

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7. Appendix
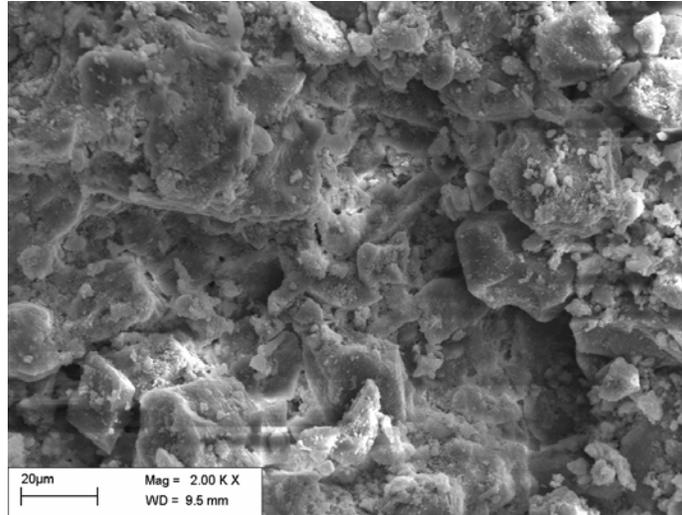
Fig. 6. SEM microphotograph of representative MDF probe directly after synthesis (cross-linked virgin MDF material); typical are amorphous and shape-uniform microstructural domains.
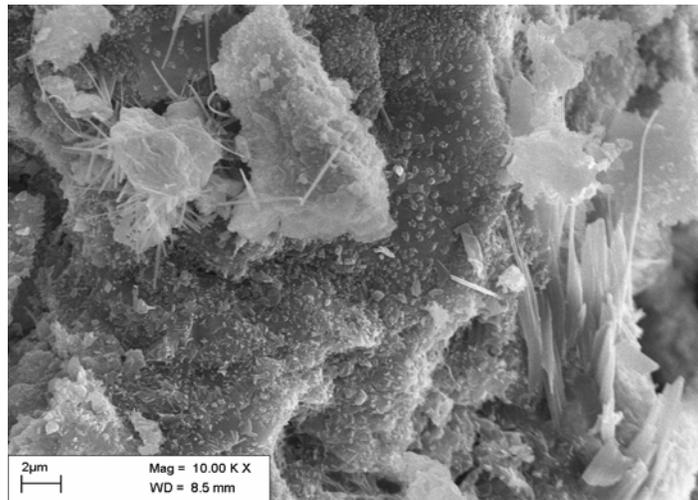
Fig. 7. SEM microphotograph of moisture attacked MDF probe; the crystalline secondary hydration products of cement grains occur at the interfaces of cross-linked domains, but fill the pores preferentially and to the larger extent.