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CROSS-LINKING OF ATOMS AND THERMAL STABILITY OF NEW MDF COMPOSITIONS

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Abstract

We have summarized Al, Fe, C and P atoms incorporations within cross-linking interaction and location of those after MDF procedure of sulphobelitic clinker – hydroxypropylmethyl cellulose (*hpmc*) – sodium salt of polyphosphates (*poly-P*) compositions. Design of Al/Fe–O–C/P cross links is given and discussed. Thermoanalytical patterns (i) give the evidence of the presence of polymers in the reaction products and (ii) confirm the linkages of solidified polymers through X=C or P of Al/Fe–O–X cross links in interphase regions with decomposition temperature interval higher than this in classical hydraulic materials. Designed local structure of interphase regions gives atomic level explanation of the densification of a bulk, its microstructure and exceptional technological properties. Similar phenomenon has been reported for the high aluminium – polyvinylalcohol/acetate MDF compositions. Moreover, variant clinker as well as polymers employed in syntheses represent one of the proposals aimed to the increase of the moisture resistence; our results are in the power of the above alternative for phases of sulphobelitic clinker.

Keywords: Al/Fe–O–C/P cross-links, Macro-Defect-Free materials, thermal stability

Introduction

Macro-Defect-Free (MDF) materials represent one of the promising types of disperse systems that attract interest of researchers. These materials belong to a group of 'chemically bonded ceramics-CBC', where predominantly chemical bonds control technologically important properties [1–3]. Materials of CBC possess properties comparable to those of ceramics despite relatively soft methods of synthesis. Hydration reactions complete, in case MDF's, gelation and so-

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The use of cement chemistry notation is as follows: C=CaO, $A=Al_2O_3$, $F=Fe_2O_3$, $S=SO_3$, $H=H_2O$, w/s=water:solidums mass ratio.

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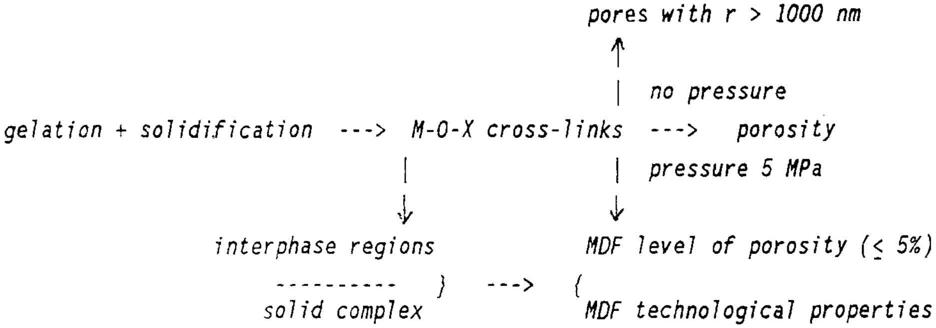
lidification at room temperature and pressure appr. 5 MPa after twin-roll pretreatment of proper proportions and types of clinker and water-soluble polymer(s) in water. MDF's based on Al-cement and pva/ac are superior ones, however, still ever far from industrial production. Chemical hypothesis of genesis of MDF's [3–7] involves reactions, local changes and changes of bulk of the gelated and solidified reaction mixture, as shown in the diagram below:



Interactions and depth of chemical reaction of inorganic matrix with solidified polymer are thus accepted as one of the important sources of MDF properties. Experimental evidence of cross-links is obvious in Al MDF's by IR and HREM studies [3–5]. We have observed MDF processability of unusual compositions; sulphobelitic clinker phases with *hpmc* and *poly-P* [7–9]. Moreover, special positions of portions of Al, Fe, C and P atoms have been deduced of resonance spectroscopies [8, 10, 11]. These phenomena call for (i) complex assessment of cross-linking sites and capacities of Al, Fe, C and P atoms within local structure of these model MDF's and (ii) analysis of thermal stability in the MDF-related structures – interphase regions or solid complex in the diagram. To report on both is the aim of present work.

Experimental

Individual clinker phases (C_4AF, $C_4A_3\bar{S}$) and the mixtures (1:1, 1:2) of these were prepared by reactions of chemical grade compounds at the clinkering temperatures 1200–1250°C, as reported elsewhere [8, 9]. The identities of the clinker phases and conversion of reagents were confirmed by powder XRD (Phillips PW 1050).

Processing to obtain model MDF materials was carried out at room temperature according to the following sequence: (i) Dry pre-mixing of clinker phases or mixtures of those with 5% (by mass) of *hpmc*. Hydroxypropylmethyl cellulose of p.a. purity, Aldrich (of 80–120 cP viscosity) was used. (ii) Addition of water giving $w/s=0.2$, or addition of the solution of sodium polyphosphate introducing 5% (by mass) of the *poly-P* and ratio $w/s=0.2$ into the system. Sodium polyphosphate glasses (Budit 4H, Budit 9) were kindly supplied by the

Chemische Fabrik R.A. Oetker, Budenheim. F.R.G. (iii) Twin-rolling until the mixture reaches consistency of dense dough (upto 5 minutes). (iv) Static 5 MPa pressure in a pellet die (diameter 20 mm) applied for intervals ranging from 30 minutes to 6 h.

The heat characteristics were measured in situ in each system using the method of differential calorimetric analysis (DCA) [16] on DC-J3/JN and DC-N3 ZIAC calorimeters. Differential calorimetry gave $Q=f(t)$, Q_{tot} and dQ/dt, the latter characterizing the periods with different reaction rates. TG, DTG and DTA curves of the reaction products were collected on a Derivatograph D1500Q (MOM, Hungary). Typical conditions were as follows: sample mass 350–400 mg; heating rate 10 K min^{-1}; static air; α-Al_2O_3 standard; mass loss range 0–200 mg; temperature range 20–1000°C.

Changes of individual atomic environments and microstructure we reported in [7–11]; the MDF procedure has altered the local structure sections of both, polymers and hydrated clinkers. Distinct C atoms participate in Al–O–C cross-links, as revealed by ^{13}C MAS NMR spectroscopy. Accordingly, ^{27}Al spectra exert signals (i) with chemical shift closely assignable to those atomic compositions and (ii) with chemical shift typical of Al–O–H [8, 10]. ^{31}P MAS NMR spectrum clearly displays a new signal (–5.5 ppm), with relative intensity close to 70%, it is in the interval of values of P(4)–O–Al(6) linkages or terminating P of polyphosphate anions [11–13]. The most relevant values of isomer shifts δ_{iso} in ^{57}Fe Mössbauer spectra of Fe^{III} (6) are presented in [14, 15]: direct Fe–Fe (0.30 mm s^{-1}), Fe–O in nearly ionic compounds (>0.40 mm s^{-1}) and Fe–O_{br} (>0.42 mm s^{-1}). Values δ_{iso} of Fe in MDF related products fall in the last region, whilst the values in hydrates with nearly ionic Fe–O would lie close to 0.40 mm s^{-1}. If environment of paramagnetic Fe includes, due to synthesis conditions, atoms originally from water and polymers (*hpmc, poly-P*), cross-links formed through covalent bonds of O_{br} with C or P opposite to Fe and distortion of octahedra will decrease the electron density (including 4s electrons) around Fe atoms and the increase of δ_{iso} occurs [11].

Results and discussion

^{13}C, ^{31}P, ^{27}Al and ^{57}Fe resonance spectra proved the interaction: mutual coincidence of the portion of these atoms from the Next–Nearest–Neighbor (NNN) positions leading to the cross-links in samples treated by MDF procedure. As well as generally frequent Al↔Fe substitutions would be in favour of Al/Fe–O–C/P atomic composition of the amorphous *AFm*-like interphase regions. The following design accounts for *hpmc* (Fig. 1) and combined *hpmc–poly-P* (Fig. 2) incorporation within local structure of formed interphase regions.

Cross-links, according to this design, represent bridging regions of originally cationic and anionic layers of *AFm* phase and include new elements in an-

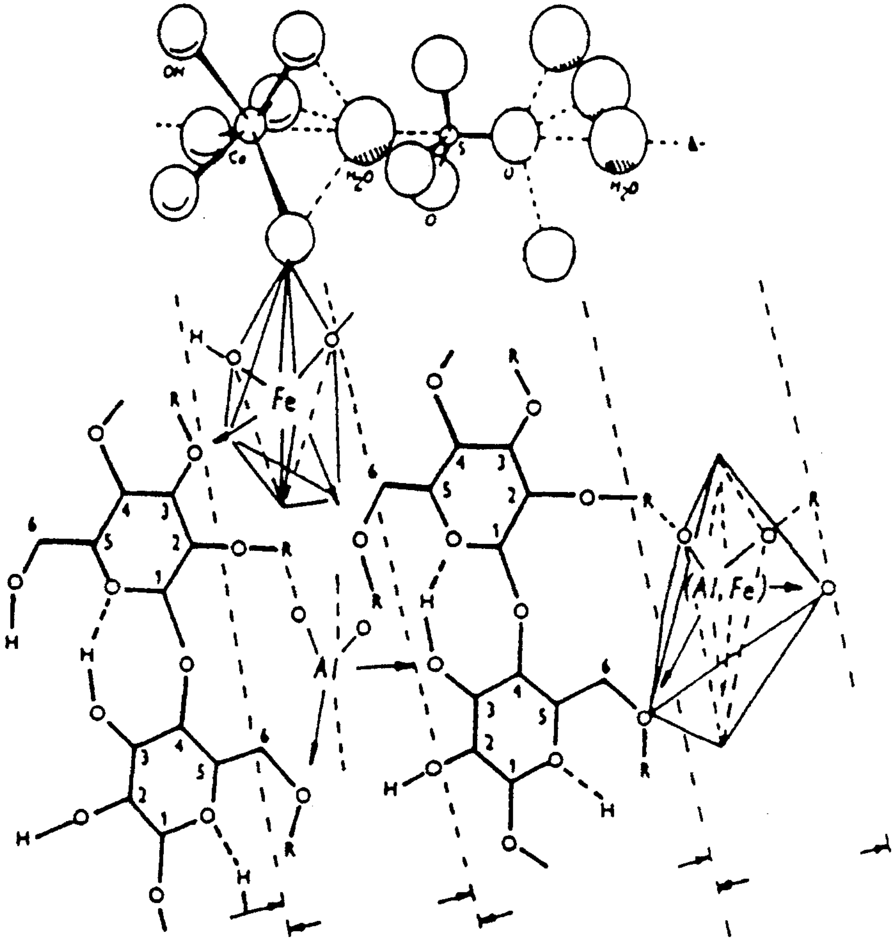


Fig. 1 Design of the local structure of interphase region incorporating solidified *hpmc*

ionic layers of the local structure within interphase region. Local interactions and the scope of these are connected as with affinities and complex formation abilities of atoms contained in reagents [6, 11, 12, 17], so with reaction conditions (composition, pressure) and kinetics of the interphase regions formation (see subsequent discussion of differential calorimetry). Moreover, the bulk and its microstructure are effectively densified through the reported and discussed atomic level changes. Solidification of the former assemblies in originally free space is the phenomenon with crucial impact upon the values of open porosity (5% and less [1, 3, 6, 9]), stability of materials (see further) as well as exceptionality of another technologically relevant properties.

An overall assessment of the reactions leading to the interphase regions formation was deduced from differential calorimetry. Results (Fig. 3) are comparable to

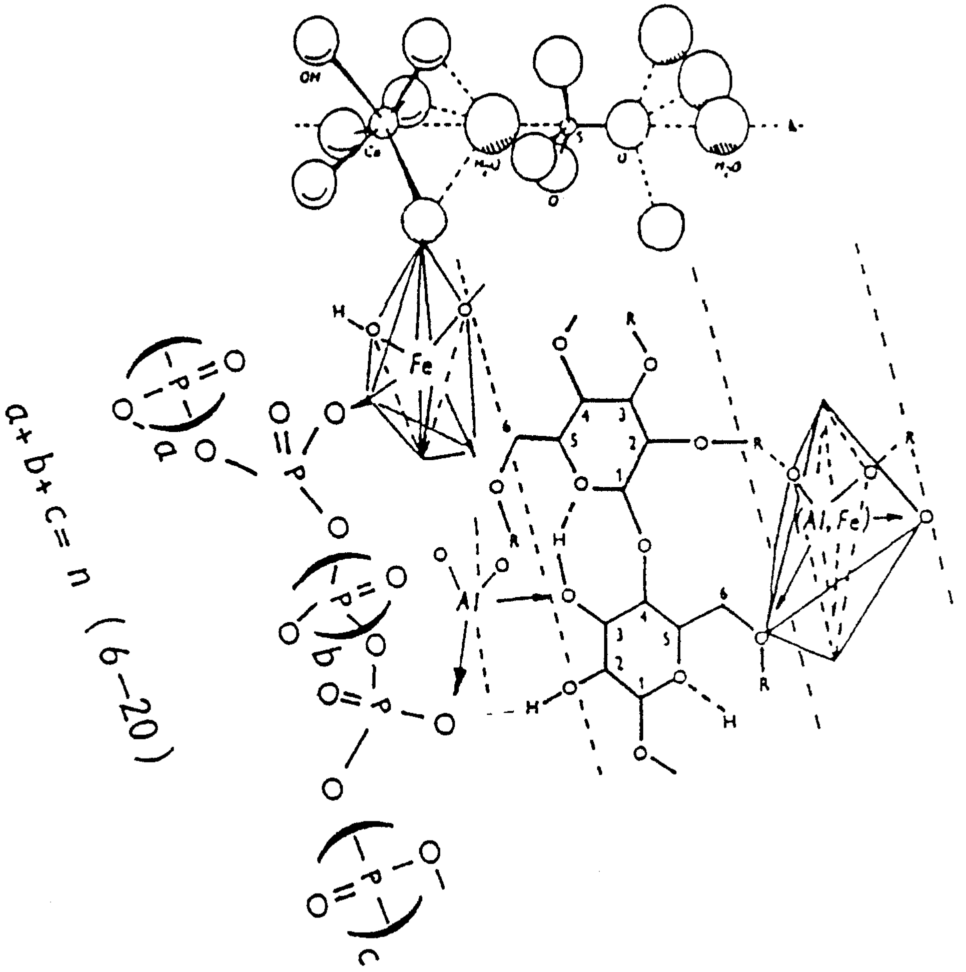


Fig. 2 Design of the local structure of interphase region if both, *hpmc* and *poly-P*, are incorporated

isothermal calorimetry [4–6, 18] on Secar-*pva/ac* and Secar-*pva/ac–poly-P* systems. In particular here: i) Lower amount of total evolved heat is the consequence of low *w/s* in MDF synthesis and it is in relation to the degree of conversion. We have quantified it formerly [8, 19]. ii) The heat evolution exhibiting maximum of its rate between 6 and 10 h of the reaction denotes, that the cross-linking shifts and spreads the interval of dominant reactions – NNN coincidence of atoms, formation and solidification of the interphase regions.

Similar findings in [4–6, 18] are discussed in terms of modifying effects of polymers and the composition of interphase regions is postulated. In our opinion, not only the existence of interphase regions, but also local structure changes in these regions, overlapping with the heat evolution, if realized in re-

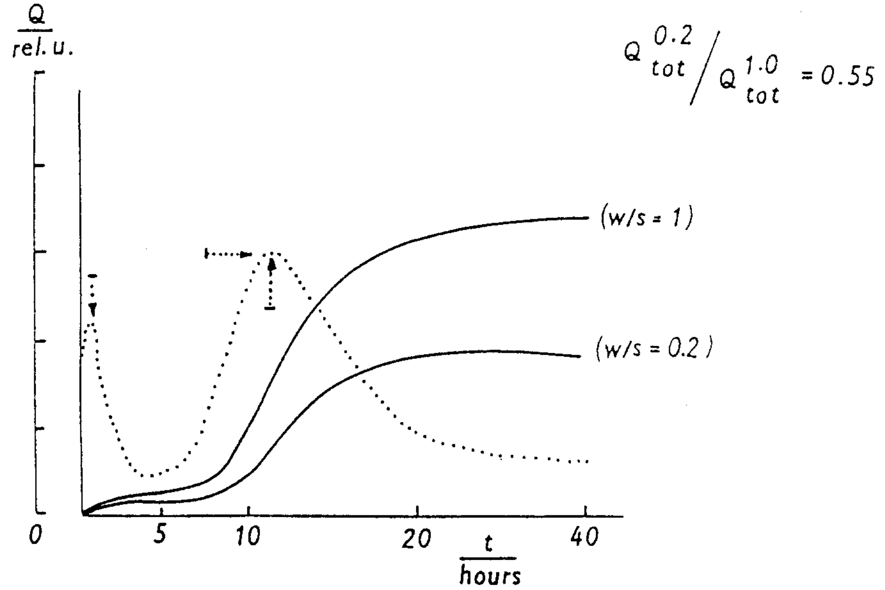


Fig. 3 Total evolved heat (—) and the rate of the heat evolution (.....), as modified by *w/s* ratio and by polymers interaction in the studied MDF related system

alistic period of reactions, are tightly connected with the microstructure, stability and technological properties of MDFs.

Environmentally induced changes of MDF materials are frequently reported [1–3, 6–8, 18–20], however, until now does not exist a joint view upon two extremes: the moisture resistance and the extent of the changes under thermal treatment. In both, due to the atomic level cross-linking, the estimation of thermal stability is getting highly topical. We have conducted the treatment of extensive amount of samples, series has started from mixtures of individual clinker phases with *hpmc* and *poly-P* [8, 19] and through mixtures of sulphobelitic clinker with *hpmc* (Fig. 4) has continued to mixtures of sulphobelitic clinker with *hpmc* and *poly-P* (Fig. 5).

Crucial influence upon the thermal characteristics is derived from the presence of carbonaceous polymer and *poly-P* in reaction mixture and in hydrated samples. Carbonaceous polymer causes stepwise mass loss (50–200°C and 250–350°C) in comparison to monotonous course of dehydration (up to 250°C) of common hydraulic materials [21]. Interval 250–350°C and mas loss within it denote thermostabilizing effect of *hpmc* incorporation into structure of MDF related reaction product. Steps are registered independently of starting clinker composition. Further thermostabilizing effect is included by *poly-P*: 10–20% of total mass loss takes place in temperature interval 400–600°C, again independently of starting clinker composition. DTA exoeffects (320–360°C) mark

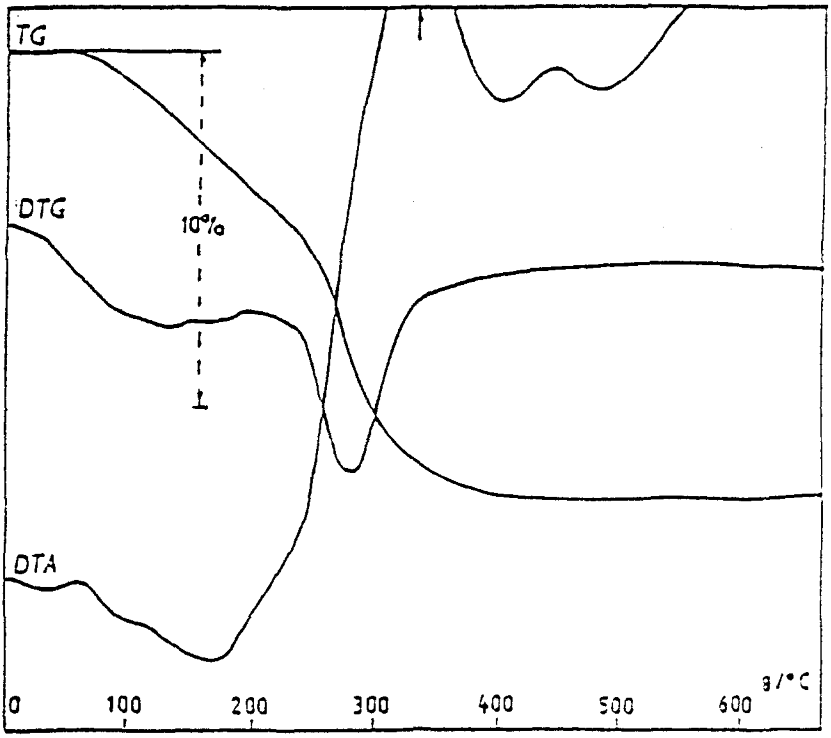


Fig. 4 Thermoanalytical curves of MDF related reaction product of sulphobelitic clinker with *hpmc*

the structural changes: the dehydration and dehydroxylation are completed by the breakdown of the NNN coincidence and bonds within cross-links.

Close temperature intervals of individual mass losses and DTA effects, as detected within whole series, conform to the uniform design of cross-links Al/Fe–O–C/P due to the present polymers. Prehydration composition of clinkers exhibits minor effects upon the thermal characteristics. The discovery of weighty relations among synthesis conditions, interphase regions existence, cross-links and stability (thermal, control of moisture resistance) of MDF related sulphoclinker–*hpmc–poly-P* system is of our continuous interest.

Conclusions

1. Design of cross-links Al/Fe–O–C/P in C_4AF–$C_4A_3\overline{S}$–*hpmc–poly-P* system has resulted from resonance spectroscopies. It is well in line with similar one found for Al MDFs. Nevertheless, a control of the bulk densification through atomic composition of interphase regions and solidification under pressure need to be accounted for, if considering technologically relevant characteristics.

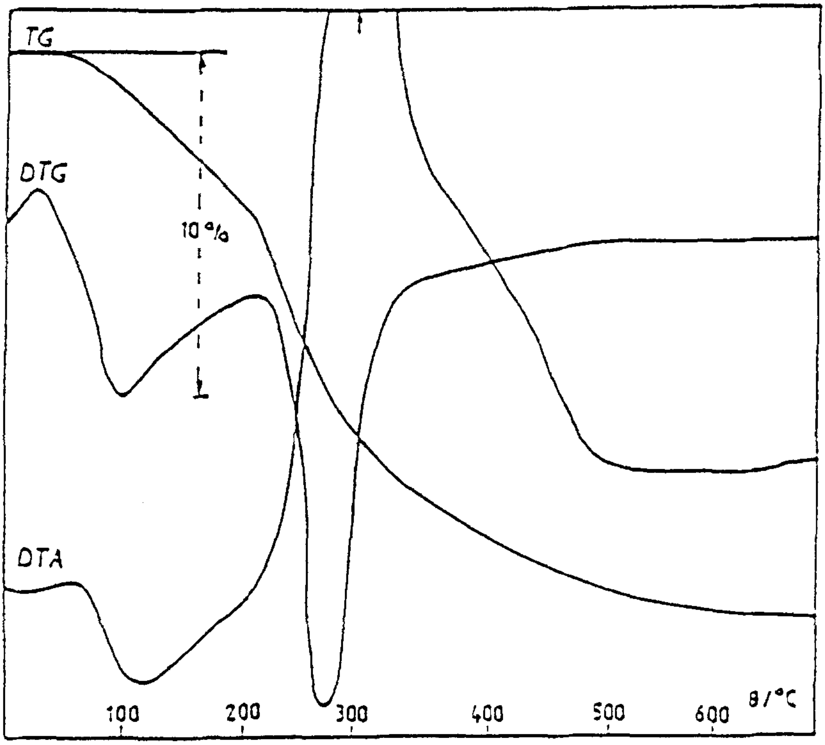


Fig. 5 Thermoanalytical curves of MDF related reaction product of sulphobelitic clinker with *hpmc* and *poly-P*

2. Heat evolution dynamics of the reaction and the increased intervals of decomposition temperatures of the reaction product have supported the presence of solidified polymers in cross-links within *AFm*-like interphase regions. Methods of thermal stability identification together with resonance spectroscopies seem to be very suitable for the extended study of MDF related systems. Moreover, these methods represent a powerful tool of the analysis of sulphobelitic clinker-based systems, especially in moisture environment.

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