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MODEL MDFs RELATED TO SULFOBELITIC SYSTEMS: STUDIES BY ^{57}Fe MÖSSBAUER AND ELECTRICAL IMPEDANCE TECHNIQUES

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ABSTRACT

New studies of the MDF-processibility of particular components of potential sulfobelitic clinkers in combination with hydroxypropylmethyl cellulose (hpmc) and/or polyphosphates (poly-P) are presented. The involvement of Al/Fe, P and C atoms in chemical cross-links within amorphous *AFm* -like reaction products in several subsystems of a complex sulfobelitic clinker/polymer system is examined by (i) ^{57}Fe Mössbauer spectroscopy (to investigate Fe-atom local environments) and (ii) electrochemical impedance measurements (to characterize conductivity variations). Fe^{III} atoms are octahedrally coordinated by oxygens in their first coordination sphere, with some replacement of H atoms by C or P atoms in the second coordination sphere, forming cross-links of the type Al/Fe - O - C/P in hydrated products. Impedance spectra were typical of electronically- insulating materials functioning as solid electrolytes, with conductivity values depending on polymer/gel composition as well as on temperature.

Introduction

Increasing knowledge in the area of macroscopic defect free materials (MDFs) in the late 1980s, together with definition of chemically bonded ceramics as a class, led to the gradual acceptance of a chemical hypothesis of the origin of their properties. According to that hypothesis, chemical cross-links and changes in bulk properties (relative to those in polymer-free cements) are the result of reactions occurring in the fabrication of MDFs. Several models involving atomic-level cross-linkages have been postulated as explanations of the chemical origin of the exceptional properties of MDFs fabricated from aluminous cements and polyvinylalcohol-acetate (pva/ac) (1-3); these models are complementary and evidently provide a realistic chemical view of the reactions occuring. Direct experimental evidence for formation of cross-links, which lie in the interphase regions linking the clinker and polymer, has been reported (1-4).

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A range of different clinker/polymer combinations have been said to have potential as regards formation of MDF materials. In an early patent in this field Birchall et al.(4) outlined the use of aluminous, Portland (PC) and sulfate clinkers, and a wide range of water-soluble carbonaceous polymers. Principles governing the chemistry and its transfer to bulk properties of PC-based MDFs have resulted from the studies of Roy et al. (5), who performed MDF-related studies of Portland cement and polyacrylamide systems. More recently, Ma and Brown (6,7) reported the use of polyphosphates (poly-P) in MDFs. However, little direct experimental evidence concerning cross-links and their link with bulk properties has been reported for non-aluminous systems. We have reported MDF-processibility of particular components/phases arising in potential sulfobelitic clinkers in combination with hydroxypropylmethyl cellulose (hpmc) (8,9) and polyphosphates (poly-P) (10). The results have pointed to (i) the involvement of Al, P and C atoms in cross-links within amorphous *AFm* -like reaction products/intergranular gel, and (ii) the influence of that chemistry on porosity and microstructure.

^{57}Fe Mössbauer spectroscopy has been used in investigation of Fe-atom local environments in clinker phases/hydrates such as brownmillerite and hydrogarnets [*e.g.* (11,12,13)]. Investigations of cementitious systems by electrochemical impedance methods [*e.g.* Beaudoin et al. (14,15)] have shown that the impedance behaviour depends on the ionic concentrations in the pore solution and gel, and on the porosity and the microstructure. In this paper we present the results of ^{57}Fe Mössbauer spectroscopy and impedance investigations in several subsystems of a complex sulfobelitic clinker/polymer system.

Experimental

Fabrication of Model MDFs. Individual clinker phases (C_4AF, $C_4A_3\bar{S}$) and physical mixtures of these (1:1, 1:2, 2:1) were prepared by reactions of chemical grade compounds at 1250°C, as reported elsewhere (8,16). A more complex sulfobelitic clinker (in which the individual clinker phases were present along with C_2S , belite, 25% by mass) was also fabricated at 1250°C. The identities of the phases and of clinkers (and phases therein) were confirmed by powder X-ray diffraction. Hydroxypropylmethyl cellulose was p.a. purity with viscosity of 2% aqueous solution 80–120 centiPoise (Aldrich). Sodium polyphosphate glass (Budit 9, approximately a tetraphosphate) samples were supplied by Chemische Fabrik R.A. Oetker (Budenheim, Germany).

Processing to obtain model MDF materials was as follows :

i) Dry pre-mixing of clinker phases or mixtures of clinker phases with hpmc (5% of total mass).
ii) Addition of water to give w/s = 0.2, or addition of an aqueous solution of a poly-P to incorporate 5% (by mass) of poly-P and give w/s = 0.2 (s includes poly-P and clinker).
iii) Twin-rolling until the mixture reaches the consistency of dense dough (up to 5 min).
iv) Static 5 MPa pressure in a pellet die (diameter 20 mm) applied for reaction times ranging from 30 min to 6 h.
v) Chemical reactions were then kinetically frozen by drying at 50°C in air.

Experimental Investigation of Model MDFs

For each model MDF composition two separate MDF disk samples were investigated. For Mössbauer spectroscopy a sample was ground and dispersed in Perspex powder prior to loading in a Perspex sample container. In impedance studies the faces of an MDF disk were coated with conductive silver paint (Acheson Electrodag 915) and copper disks were then attached using the silver paint as adhesive. Conductivities of hydrous gels are well-known to be affected by relative humidity variations. Pellets were therefore equilibrated in a desiccator over saturated $NaHSO_4$(aq) (relative humidity RH = 52% at ambient temperature).

Mössbauer Spectra. ^{57}Fe Mössbauer spectra were recorded at −196°C (N_2(l)) using a standard constant acceleration spectrometer and cryostat. The velocity scale was calibrated via the spectrum of α-Fe foil, for which the isomer shift ($\delta_{iso} = 0$ by convention) and splitting in the 6-line field are well known. Computer programmes employing iterative multivariate least squares methods were used in the modelling and fitting of the details of shape and multiplet positions *etc.* of the experimental data. Individual lines were taken to be Lorentzian, as is conventional.

Impedance Studies. Samples were mounted in a brass cell holding six samples simultaneously. Temperature (25, 50, 75°C) was controlled by immersion of the cell in controlled temperature bath, allowing at least 30 minutes for equilibrium to be achieved at each temperature (this period was found by experience to be in excess of the minimum necessary to give temporal stability of impedance spectra). Relative humidity (RH) in the cell was controlled by placing saturated $NaHSO_4$(aq) in the bottom of the cell. Impedance spectra were collected in the range 5 Hz–1 MHz (oscillation voltage of 100 mV) using a Hewlett-Packard 4192A LF impedance analyser controlled by an IBM-compatible computer using a program embedding the EQUIVCRT program [fitting impedance spectra to a user-defined equivalent circuit (17)].

Results

^{57}Fe Mössbauer Investigations. The spectrum of brownmillerite (*C4AF*) is shown in Fig. 1(a). The form and empirical Mössbauer parameters of the spectrum are in agreement with published results (11-13). Two superimposed sextets arise from (i) tetrahedral Fe(4) and (ii) octahedral Fe(6) in the brownmillerite structure. The relative intensities Fe(4):Fe(6) = 1:3 are close to the corresponding site occupancies in the crystal structure of brownmillerite (12), indicating similar recoil-free fractions for Fe(4) and Fe(6). Fig 1(b) shows the spectrum of the product of polymer-free hydration of brownmillerite (unpelletised, excess H_2O), for which the spectrum at ambient temperature was reported by Tamas and Vertes (13). The spectrum is a simple quadrupole-split doublet, arising from the presence of Fe^{III}(6)-OH linkages in the *AFm* solid solution (18,19,21).

In samples resulting from MDF procedures, the superimposed sextets (i + ii, see above) of brownmillerite are again seen in Mössbauer spectra (and arise from residual unreacted clinker phase), but there is also an additional quadrupole-split doublet (Fig. 2) for which the relative intensity increases with increasing reatin time. The Mössbauer parameters of the latter doublet, in particular the isomer shift δ_{iso} and linewidth (FWHM), differ from those for polymer-free hydrate (Table 1). The values of the isomer shift δ_{iso} for Fe in the hydrated product in MDF materials are fully consistent with octahedrally coordinated Fe^{III} with an exclusively oxygen-containing first coordination sphere (11), C /P atoms being in the second coordination sphere (next-nearest neighbours to Fe atoms). The increased FWHM in model

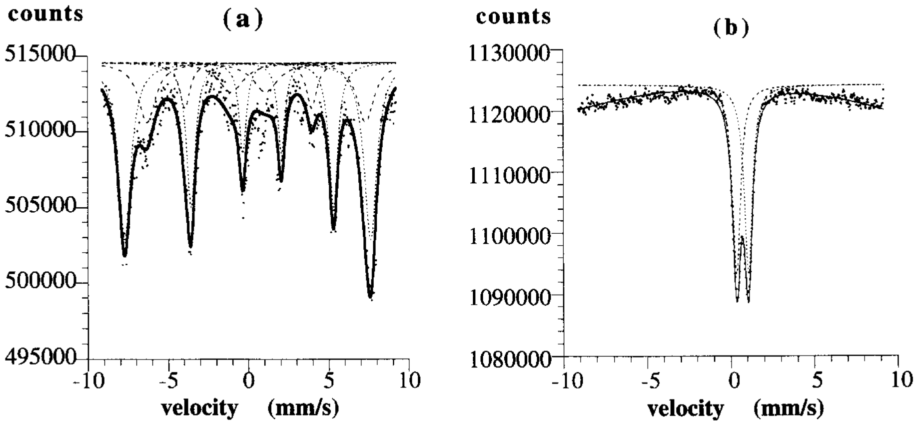

FIG. 1.
Mössbauer spectrum of (a) brownmillerite (*C_4AF*) and (b) the product of its full hydration with excess water alone. Solid lines correspond to the computed fits to the experimental spectra. Dashed lines represent components of fitted model spectra.

MDFs we assign to the presence of iron atoms in both hydrolytic and cross-linking interactions (involving atoms of the polymers).

Impedance Studies. Impedance spectra were typical of electronically-insulating materials functioning as solid electrolytes, with electrodes blocking to the conducting species (20). Example impedance spectra are presented in Fig. 3. Sample resistances (from which conductivities are evaluated) were determined as the intercept of the linear (low frequency) portion with the high frequency arc. Conductivities varied only slightly with reaction time.

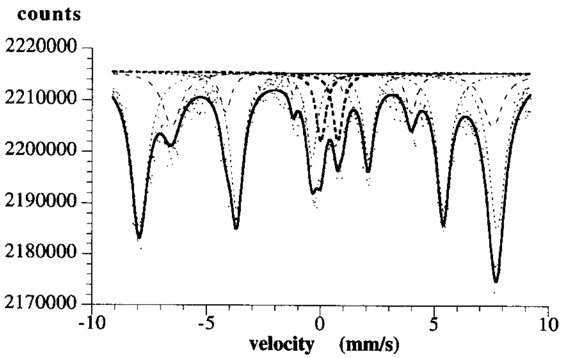

FIG. 2.
Mössbauer spectrum of C_4AF + C_4A_3S + hpmc + poly-P + *H* (reaction time = 1 h). Solid lines correspond to the computed fit to the experimental spectrum. Dashed lines represent components of fitted model spectrum.

TABLE 1

Parameters of Quadrupole Split Doublets (Fits shown in Figs. 1 and 2)

δ_{iso} / mm.s^{-1}	FWHM / mm.s^{-1}	Note
0.50 ± 0.05	1.30 ± 0.05	Fe(6)-OH , in polymer-free hydrate
0.70 ± 0.05	1.50 ± 0.30	Fe(6)-OX , in MDF cross-linked hydrate; superposition of X's = C, P or H

For the model MDFs conductivities $\sigma(T)$ (T = temperature) were in the following ranges : (a) samples containing hpmc as the sole polymer σ(ambient) ~10^{-8} - 10^{-7} S cm^{-1} and σ(50 and 75°C) ~10^{-6} - 10^{-5} S cm^{-1}, (b) MDFs made with hpmc + poly-P σ(ambient) ~10^{-7} - 10^{-4} S cm^{-1} and σ(50 and 75°C) ~10^{-6} - 10^{-5} S cm^{-1}, (c) samples made with poly-P as sole polymer σ(ambient) ~10^{-5} - 10^{-4} and σ(75°C) ~10^{-4} S cm^{-1}. The highest conductivities are observed in systems with poly-P as sole polymer.

Conductitivities ($\sigma(T)$) are more strongly temperature-dependent for systems made with hpmc as sole polymer (increasing by a factor of 10^2 on raising from ambient temperature to 75°C) than for analogous systems made with poly-p (increase $\leq$ a factor of 10), but conductivity values are always higher in the latter case.

Comparison of the results for clinker phases and the complex sulfobelitic clinker gave the following results :

1) MDFs fabricated from clinker phases + poly-P are more conductive than analogous MDFs made from sulfobelitic clinker.
2) In cases with hpmc as sole polymer, MDFs from sulfobelitic clinker have the higher conductivities.

Discussion

Cross-link Formation. In previous studies we have reported the detailed reaction chemistry, thermal events, and development of atomic level (Al, C and P environments) and pore structures in model MDFs of types similar to those in this study (8-10). Tests of shear strength on such materials give values three-times higher than for related polymer-free materials (16). There is clear evidence for formation of Al-O-C/P cross-links and similarity of reaction products to members of the *AFm* solid solution with various substitutions (8,10,18,19). A frequently occurring substitution is Fe^{III} for Al^{III} , and chemical similarities in those two species suggest that Fe-O-C/P links can form.

Substitutions of the type Al <—> Fe and the replacement of hydroxyls by various anions or radicals in sulfated cement hydrates (18,19,21) permit facile interpretation of the current results and those we have reported previously (8,10). Cross-links of the types Al/Fe-O-X are generated; X = C or P to replace some of the hydrogen in the amorphous *AFm* -like interphase regions (the concentration of polymer is insufficient for total replacement). A similar situation has been reported in aluminous MDFs (1-3,6,7,22,23), in which the link between atomic level changes (mechanistic information) and bulk properties (such as percolation and moisture resistance) has been reported (22,23). A possible local structure accounting for the

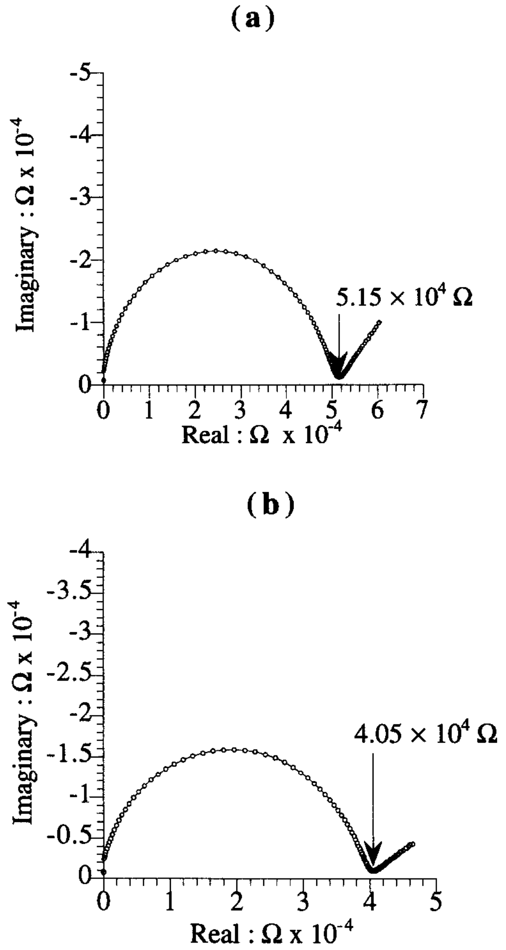

FIG. 3.

Impedance spectra of (a) *sulfobelitic clinker* + poly-P and, shown for the purpose of comparison, (b) *Secar* aluminous cement + poly-P (reaction times = 5 h).

atomic level incorporation of both hpmc and/or poly-P within an *AFm* -like skeleton is given in Fig. 4.

Cross-links of the type Al/Fe-O-C/P seem fundamental in controlling technologically important properties of this class of chemically bonded ceramics. We have previously reported examples of this type of control in model MDFs in this system (9,16), and it is also evident in the conductivity results.

Conductivity. The results of this study can be considered in a similar manner to impedance studies of cementitious systems reported by Beaudoin *et al.* (14,15). Conductivity is affected by microstructure, porosity, and local atomic-level structure in the pore-filling *AFm*-like

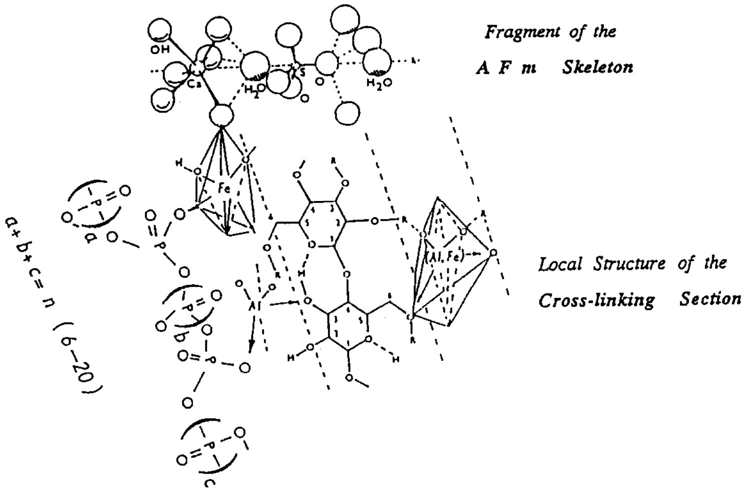

FIG. 4.

Diagrammatic representation of the formation of Al/Fe-O-C/P cross-links. Such a model accounts for next-nearest-neighbour interactions and is derived from the structure of pure *AFm* (18,19) and the reactive centres in hpmc (24,25) and poly-P (6,7,26).

intergranular gel. Microstructure and porosity will differ only slightly in the systems studied (9,16), and conductivity variations will therefore be linked to the gel.

The structure of the gel can be expected to exhibit aspects of the *AFm* structure and also aspects of the structures of gels of pure hpmc (24,25) and/or sodium poly-phosphate glasses (26). In model MDFs formed with hpmc as the sole polymer, the polymer is molecular and conducting ions are likely to arise only from the ionic hydration products of the clinker phases / sulfobelitic clinker, with hpmc being involved in cross-link formation. In the case of MDFs formed with poly-P, an additional contribution will be present from mobile solvated Na^+ ions, phosphate reacting to introduce cross-links (10). That contribution is maximised when poly-P is the only polymer used in fabrication.

When molecular polymer (hpmc) is used, the presence of belite (C_2S) in the sulfobelitic clinker adds to the conductivity relative to MDFs formed from physically mixed clinker phases (in which no belite is present). Hydration of belite (to *CSH*) is known to be slow (18), but will certainly affect the ionic composition within the gel and hence affect the conductivity observed. When poly-P is used, the presence of belite has the effect of lowering the conductivity of the intergranular gel, possibly a consequence of reaction of traces of *CSH* with alkali (a known reaction) to immobilise Na^+.

Conclusions

(1) The Mössbauer spectroscopic data (values of the isomer shift δ_{iso}) for Fe in the hydrated product in the model MDF materials are fully consistent with octahedrally co-ordinated Fe^{III} atoms with an exclusively oxygen-containing first coordination sphere (11,13), C /P atoms being in the second coordination sphere (next-nearest neighbours to Fe).

(2) Substitutions of the type Al <—> Fe and the replacement of hydroxyls by various anions or radicals in sulfated cement hydrates (18,19,21) permit facile interpretation of the current results and those we have reported previously (8,10). Cross-links of the types Al/Fe-O-X are generated: X = C or P to replace some of the hydrogen in the amorphous *AFm* -like interphase regions (the concentration of polymer is insufficient for total replacement).

(3) Impedance spectra were typical of electronically-insulating materials functioning as solid electrolytes, with conductivity values depending on polymer component as well as temperature. Conductivity differences between the various model MDFs arise from the atomic level details of the pore-filling by *AFm* -like intergranular gel, different polymers giving chemically different gels.

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