Microstructure-Property Relationships in Macro-Defect-Free Cement

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Introduction

The term "macro-defect-free" refers to the absence of relatively large voids (or defects) that are normally present in conventional cement pastes due to entrapped air or inadequate mixing. A decade ago, Birchall and co-workers developed a novel processing method that avoids the formation of these strength-limiting defects.[1,2] This method, outlined schematically in Figure 1, consists of mixing hydraulic cement powder, a water-soluble polymer, and a minimal amount of water under high shear to produce a macro-defect-free (MDF) cement composite. Several cement/polymer systems can be processed by this flexible technique, although the calcium aluminate cement/polyvinyl alcohol-acetate (PVA) copolymer system is most common.[3–6] MDF cements display unique properties relative to conventional cement pastes. For example, the flexural strength of MDF cement is more than 200 MPa as compared to values on the order of 10 MPa for conventional pastes.[2] One can view MDF cements as a type of "inorganic plastic." As is the case with plastic processing, fillers such as alumina, silicon carbide, or metal powders can be added to MDF cement to modify its performance properties (e.g., abrasion resistance, thermal or electrical conductivity, and hardness).[7] The combined attractiveness of inexpensive raw materials and flexible, low-temperature processing has generated great interest in this new class of advanced cement-based materials.

Unlike conventional cements, MDF cements incorporate a polymeric constituent and a rather small amount of water. The polymeric phase serves many functions: (1) it acts as a rheological aid facilitating particle packing, (2) it fills the pore space between cement particles, and (3) it reacts chemically with cement hydration products to form an integral microstructural element.[4,7,10] During the high-shear mixing step (refer to Figure 1), the water plasticizes the polymer, giving the paste a workable viscosity. The temperature must be controlled during mixing to prevent the paste from stiffening due to premature setting (or hydration) reactions. On complete mixing, the volume fraction of cement particles in the paste approaches 0.70. This high-volume loading is obtainable due to the broad particle size distribution (e.g., 0.3–70 μm) of the cement powder. In subsequent pressure curing and dry curing steps, water reacts with the cement particles to form hydration products.[3,10] The chemical composition and morphology of these products will be discussed in detail in the next section.

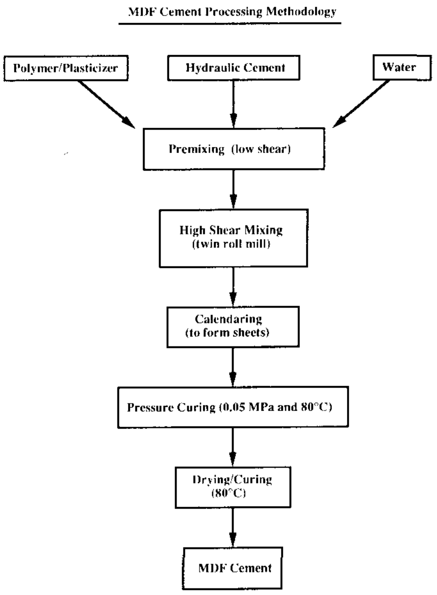

Figure 1. Process flow diagram for MDF cement fabrication.

MDF cement-based composites have many potential applications (e.g., substrates for electronic packaging, structural, or acoustic-damping materials), since they may be filled with secondary phases, metallized, coated, or even stacked and laminated to incorporate fiber-reinforcing layers or other materials between MDF sheets.[7] However, their use is currently limited to low-humidity environments. The hydrophilic nature of the polymeric constituent in MDF cement causes these materials to be highly moisture sensitive. Moisture absorption has a negative impact on most of their performance properties (e.g., flexural strength, dielectric constant, dimensional stability).[11–15] However, with a thorough understanding of microstructure-property relationships in MDF cement, one can envision both an emergence of commercial applications as well as the development of a generic class of MDF materials based on alternative inorganic/polymer systems.

In this article, we present an overview of our current understanding of microstructure-property relationships in the calcium aluminate/PVA system. We begin by highlighting recent microstructural studies that include both the microstructural analysis and microhydration behavior of MDF cement composites. We then discuss the organic phase composition and its percolative nature within the microstructure. Finally, we relate these microstructural observations to their influence on the bulk properties of MDF cement, and discuss their implications for the further development of MDF materials systems.

Microstructural Analysis and Microhydration Behavior

The significant improvement in strength and toughness of MDF cements relative to conventional cement pastes is attributed not only to their low porosity, but also to the chemical reactions that occur between the PVA polymer and the inorganic ions produced when calcium aluminates dissolve in water. A detailed study of the microstructure, microchemistry, and microhydration behavior of MDF and of a layered $CaAl_2O_4$ and PVA model system has been carried out by Kriven and co-workers[8,9,16–20] using a variety of advanced techniques: scanning electron microscopy (SEM), transmission electron microscopy (TEM), high-resolution electron microscopy (HREM), energy dispersive spectroscopy (EDS), parallel electron energy loss spectroscopy (PEELS),[8,16–18] and x-ray photoelectron spectroscopy (XPS).[9,18,19] The TEM samples were prepared by ultramicrotomy to precisely determine the microchemistry of different regions within the MDF cement microstructure.

The general microstructure of MDF cement consists of crystalline agglomerates of calcium mono-aluminate ($CaAl_2O_4$) and calcium di-aluminate ($CaAl_4O_7$) grains ranging from 3 μm to 7 μm in size, randomly dispersed in the PVA polymer matrix (Figure 2). Between the inorganic grains and the organic polymer, an interfacial interphase region of varied thickness (e.g., 100–500 nm) was observed. HREM[8,16–18] showed that the interphase regions consisted of an amorphous polymer matrix containing a fine dispersion of crystallites (5–8 nm in size) that were often twinned (refer to Figure 3). Laser optical diffractometry identified the crystallites as the metastable, pseudo-hexagonal, hydration product $Ca_2Al_2O_5 \cdot 8H_2O$. The expected hydration product (if any) after processing at 80°C would have been $Ca_3Al_2O_6 \cdot 6H_2O$.[17] A typical TEM/EDS[8,16–18] spectrum taken from the interphase region in an Al-coated specimen revealed the presence of Ca, Al, and O. A corresponding PEELS spectrum from the same region confirmed, unambiguously, the presence of carbon, since C-K and Ca-L lines (which overlap in EDS) were differentiable in PEELS. So it was inferred that in the interfacial region, water reacted with the cement ($CaAl_2O_4$) in the presence of polymer, forming the metastable calcium mono-aluminate octahydrate.

The chemical nature of the bulk polymer matrix and of the polymer within the interphase region was probed by XPS analysis of the model PVA/$CaAl_2O_4$ samples, which were prepared by spin-coating a PVA solution onto a dense, sintered $CaAl_2O_4$ substrate. The results of the analysis are presented in Figure 4. Essentially, the dif-

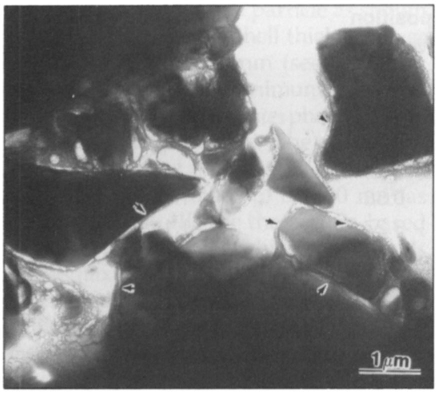

Figure 2. TEM micrograph (bright field) of the general microstructure of MDF cement. Calcium mono- and di-aluminate grains (3–7 μm in size) are dispersed in a PVA matrix (containing dissolved Ca and Al). An interfacial interphase (≈100 nm thick and containing 5–8 nm crystallites) is shared by the organic polymer and inorganic aluminate grains.

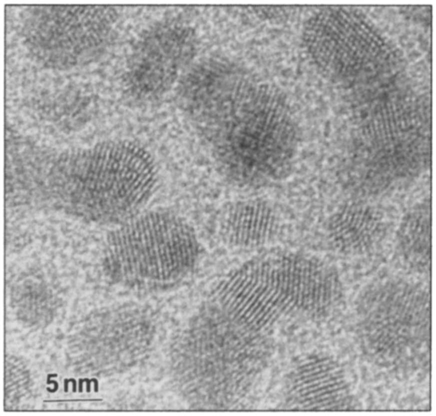

Figure 3. HREM micrograph of the interfacial interphase showing the lattice image of dispersed metastable $CaAl_2O_5 \cdot 8H_2O$ hydration products in the form of fine crystallites, 5–8 nm in size, which were sometimes twinned.

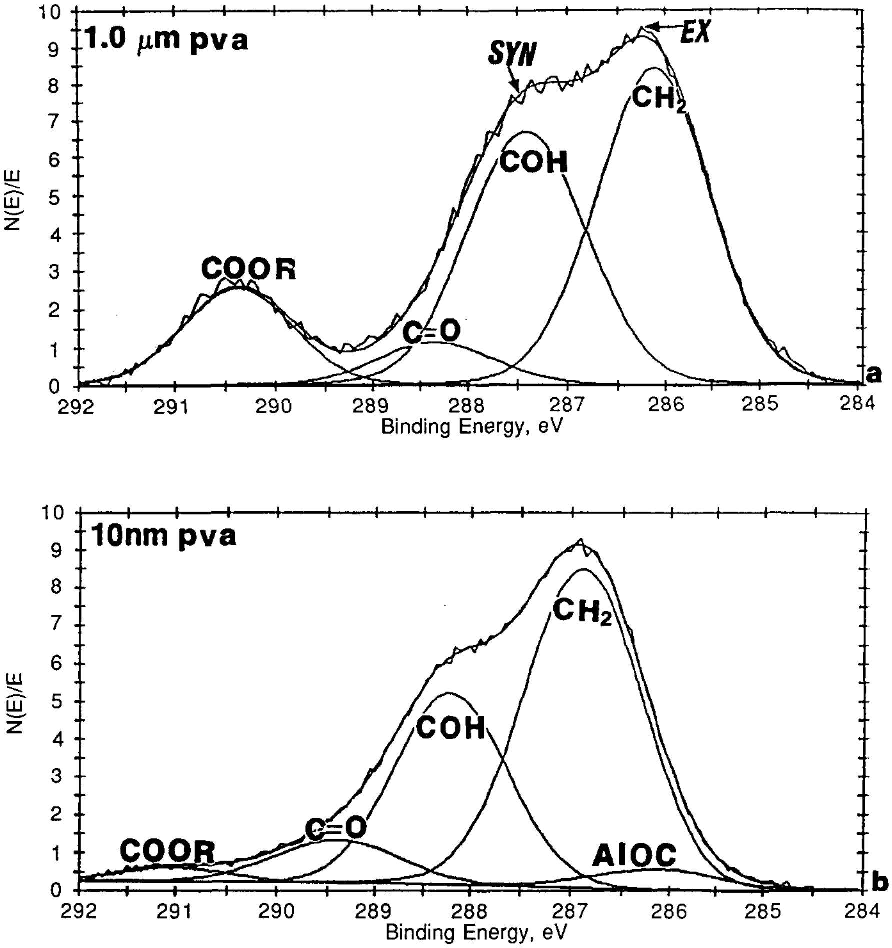

Figure 4. High-resolution experimental (EX) and synthesized (SYN) XPS C(1s) spectra from (a) 1-μm-thick polyvinyl alcohol film on Cu foil or on $CaAl_2O_4$ pellet and (b) 10-nm-thick polyvinyl alcohol film on a dense $CaAl_2O_4$ pellet heat treated for 24 h at 80°C.

ference between the thick PVA coating on Cu (representative of the unreacted matrix polymer) and the thin coating on the $CaAl_2O_4$ pellet (representative of the chemically reacted, interfacial polymer) was the presence of an AlOC complex. This implied that Al ions could be chemically incorporated into the polymeric chains, likely serving as a crosslinking agent. A possible reaction sequence would be first, dissolution of the $CaAl_2O_4$ into H_2O according to the equation:

$$2CaAl_2O_4 + 8H_2O \leftrightarrow 2Ca^{2+}_{(aq)} + 4Al(OH)^{-}_{4(aq)}, \quad (1)$$

followed by the crosslinking of the polymer by Al in a polycondensation reaction of the type:

$$4(CH_2\text{-}CHOH)_n + n[Al(OH)_4]^{-}_{(aq)} \rightarrow n\{(CH_2\text{-}CHO)_4Al\}^{-} + 4nH_2O. \quad (2)$$

The water released in this type of reaction would then be available to form the metastable $Ca_2Al_2O_5 \cdot 8H_2O$ hydration product:

$$CaAl_2O_4 + 5.5\,H_2O \rightarrow 0.5\,Ca_2Al_2O_5 \cdot 8H_2O + Al(OH)_3. \quad (3)$$

In order to understand the mechanism of water/MDF interactions at the microstructural level, an *in-situ* environmental cell TEM study was undertaken.[17] Microstructural changes were monitored continuously for 10 h, as a moist hydrogen atmosphere was passed into the cell containing a 3-nm-thin TEM foil of MDF cement. As the hydration proceeded, the bulk polymer matrix swelled noticeably. After 8 h, the microstructure consisted of swollen globules of polymer into which the interfacial interphase had progressively been dissolved. These observations suggest that moisture attacks both of these key microstructural features, which can be collectively described as the binder phase.

Binder Phase Composition and Percolative Nature

The binder phase acts to "bind" unreacted cement grains together within the MDF cement microstructure, and thus should greatly influence the performance properties of MDF cements, as demonstrated by several investigators.[5,9,11-15] To understand the influence of the binder phase on bulk properties, we must first discuss the binder composition and its distribution (or percolative nature) within the MDF cement microstructure. As discussed above, the binder phase consists of regions that contain the bulk PVA matrix, and the interphase regions that contain both PVA and hydration products in the form of a nanocomposite.

Representative initial and as-cured compositions of MDF cement materials are shown in Table I. The as-cured composition was determined by assuming that hydration occurred according to Equation 3.

The interphase regions comprise about 63 vol% of the total binder phase; only 20% of the total PVA content, however, is contained within these regions.[21] The distribution of binder within the MDF cement microstructure can be directly observed by microscopy or investigated by computer modeling. While an understanding of the two-dimensional MDF cement microstructure provided by microscopy studies is important, it is the three-dimensional microstructure that must be linked to the properties of MDF cements. Computer

Table I: Representative Initial and As-Cured Compositions of MDF Cement.

	Initial Composition	
Component	**Weight %**	**Volume %**
HAC Cement (Secar 71)	84.25	65.21
PVA (Gohsenol KH-17s)	5.90	12.30
Glycerol	0.58	1.35
Deionized Water	9.27	21.14
	As-Cured Composition	
Component	**Weight %**	**Volume %**
Unreacted cement ($CaAl_2O_4$, $CaAl_4O_7$)	78.7	66.6
$Ca_2Al_2O_5 \cdot 8H_2O$	10.1	13.2
$Al(OH)_3$	4.4	4.6
Plasticized-PVA	6.8	15.6
Nonvolatiles	87.7	70.4
Volatiles		
Plasticized-PVA	6.8	15.6
H_2O	5.5	14.0

Table II: Simulation Results on Interphase Region Properties in MDF Cement.

Interphase Region Thickness (nm)	Volume Fraction of Interphase Region	Connected Fraction of Interphase Region	% of Binder in Interphase Region
100	0.0675	0.899	20.2
200	0.1390	0.990	41.6
300	0.2067	0.9995	61.9
400	0.2615	0.999996	78.2
500	0.2987	1.0	89.4

Table III: Simulation Results on Connectivity of PVA Matrix in MDF Cement.

Grid Size	Resolution (nm)	Volume Fraction of PVA Matrix in MDF Cement	Fraction of PVA Matrix Connected to Top	Fraction of PVA Matrix Percolated
150	1000	0.1274	0.0299	0
200	750	0.1273	0.7130	0.6954
300	500	0.1274	0.9568	0.9561

modeling provides a route for bridging the gap between observable two-dimensional microstructure and performance properties.

Lewis and Bentz[21] investigated the percolative nature of the binder phase in MDF cement using a hard core/soft shell continuum percolation model. Both the bulk PVA matrix and the interphase regions were found to form percolative pathways through the model system. This system consisted of a three-dimensional cube, 150 μm on a side, into which 3.005×10^5 spherical particles (hard cores) were placed at random locations, producing a volume fraction of unreacted cement equal to 0.666 (refer to Table I). A soft shell (or interphase region) surrounded each particle as shown in Figure 5. The "best" shell thickness was determined to be 300 nm (see Table II); however, even at the minimum thickness evaluated (100 nm), the interphase regions were found to percolate. The resolution required to detect percolation of the bulk PVA regions was found to be 500 nm (as shown in Table III) for the system based on the "best" thickness, which corresponds to the maximum pore diameter observed experimentally in MDF cements.[15] The combination of direct microstructural observations and computer modeling is a powerful approach to understanding the distribution and percolative nature of the binder regions in MDF cement. We will now examine the influence of these regions on the bulk properties of these composite materials.

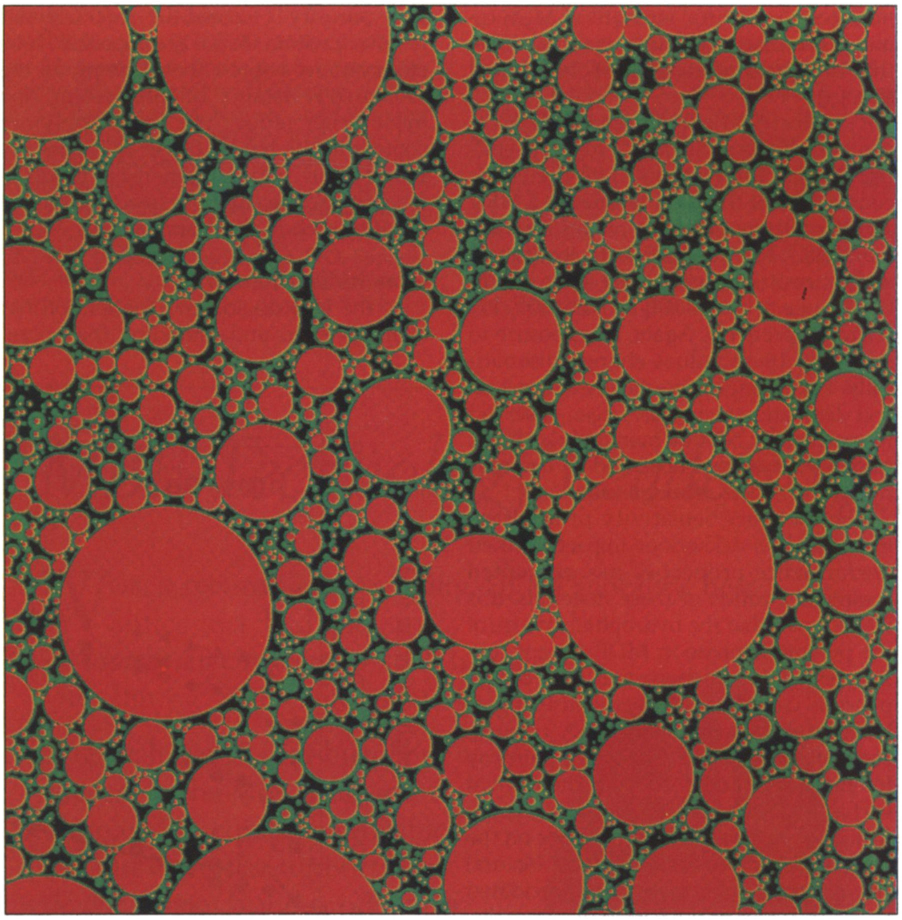

Figure 5. Two-dimensional view of the model MDF cement system, where the unreacted cement grains are shown in red, the interphase regions are shown in green, and the bulk PVA matrix is shown in black.

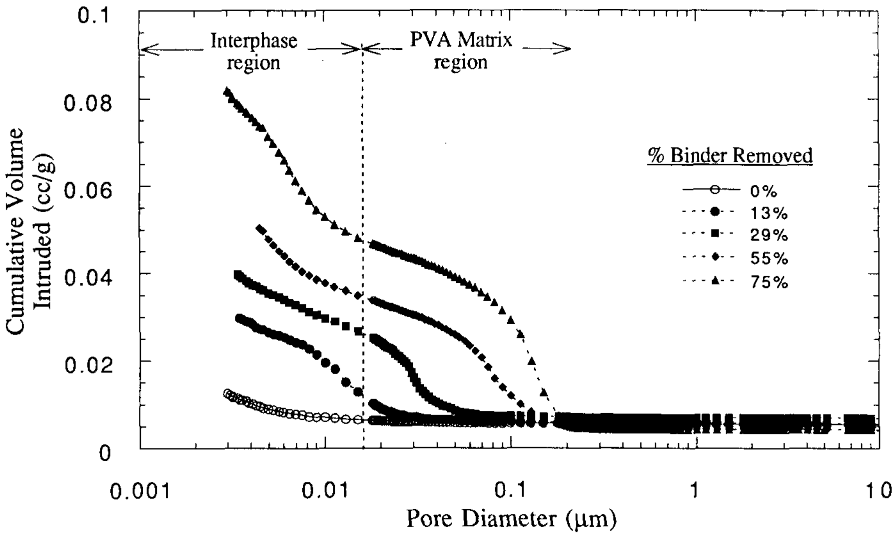

Figure 6. Pore development of heat-treated MDF cements as a function of binder removed.

Influence of Microstructure on Bulk Properties

The bulk properties of MDF cements differ dramatically from those of conventional cement pastes due to their unique microstructure. The bulk polymer matrix, interphase regions, and absence of large pores are among these unique microstructural features, each of which plays an important role in determining the performance properties of MDF cements. In this section, we will discuss the influence of microstructure on the mechanical and electrical properties, as well as on the moisture sensitivity of MDF cements.

The flexural strengths of MDF cements lie in the range 150–250 MPa.[5,12,13] These values represent a tenfold increase relative to the strength of conventional cement pastes. Initially, these high strengths were attributed solely to the absence of large voids (or defects) in the MDF microstructure resulting from the filling of pores by the polymeric constituent.[2] However, it is now known that the percolative interphase network also contributes to these high strengths.[8,9,15] On exposure to high relative humidities (>60%) or immersion in water, the flexural strength of MDF cements decreases with time to a final value that is approximately 50% of their initial strength.

The electrical properties of MDF cements make them attractive for "low-end" packaging applications. The dielectric constant (ε) of these composites at 1 MHz and 0% relative humidity ranges between 8 and 10.[14] The dissipation factor (tan δ) and dc resistivity under the same conditions range between 0.01–0.05 and 10^{12}–10^{13} Ω-cm, respectively. Again, on exposure to moisture, these values change dramatically. For example, the dielectric constant and dissipation factor have been observed to increase by 50% or more, while the dc resistivity has been observed to decrease by several orders of magnitude.

The moisture sensitivity of MDF cements and its deleterious impact on their performance properties has prevented commercialization of these materials. It is well known that the hydrophilic nature of the polymeric phase in MDF cement contributes to this phenomenon. The binder phase is complex, however, consisting of both interphase and bulk PVA regions, each of which could provide a pathway for moisture transport from the cement surface to its interior. In recent work, the influence of these different regions on the moisture absorption kinetics and flexural strength of MDF cement was elucidated by selectively varying their respective distributions within the microstructure.[15]

The binder distribution in MDF cement was varied by heating samples to temperatures between 125°C and 400°C. Chemically bonded water is removed from the system at 125°C, while PVA and water are removed simultaneously at higher temperatures. A bimodal pore-size distribution develops as increasing amounts of binder are removed from the composite, as shown in Figure 6. The fine-scale porosity (pore diameter <15 nm) corresponds to pores developed in the interphase regions, while large-scale porosity (pore diameter >30 nm) corresponds to pores developed in the bulk PVA regions. Exposing these heat-treated MDF cement samples to 100% moisture showed that only the development of large-scale pores led to significant differences in moisture absorption behavior relative to standard MDF cement (refer to Figure 7). This indicates that the interphase regions are highly resistant to moisture transport, and that the predominant transport pathway is through the bulk PVA matrix. Additionally, Figure 8 depicts the flexural strength of these samples as a function of the extent of binder removed. The strength does not decrease significantly until a percolative network of large-scale porosity is formed (i.e., ≈30% binder removed) within the MDF composite. These observations suggest that to improve the moisture resistance of this system, one must either reduce the "bulk" polymer content in the binder phase or chemically modify this region to increase its resistance.[13,15] We are currently investigating the merit of each of these approaches.

Concluding Remarks

In the past decade, much attention has been given to understanding the microstructure and microchemistry of MDF cements and their relation to the unique properties of this materials system. As we have discussed in this article, the MDF cement microstructure is a complex one, differing significantly from conventional cement pastes. The key microstructural features are the bulk polymer matrix, the interphase regions, and the absence of large pores, which contribute to the superior mechanical properties of these composites. However, the hydrophilic nature of the polymeric constituent currently limits

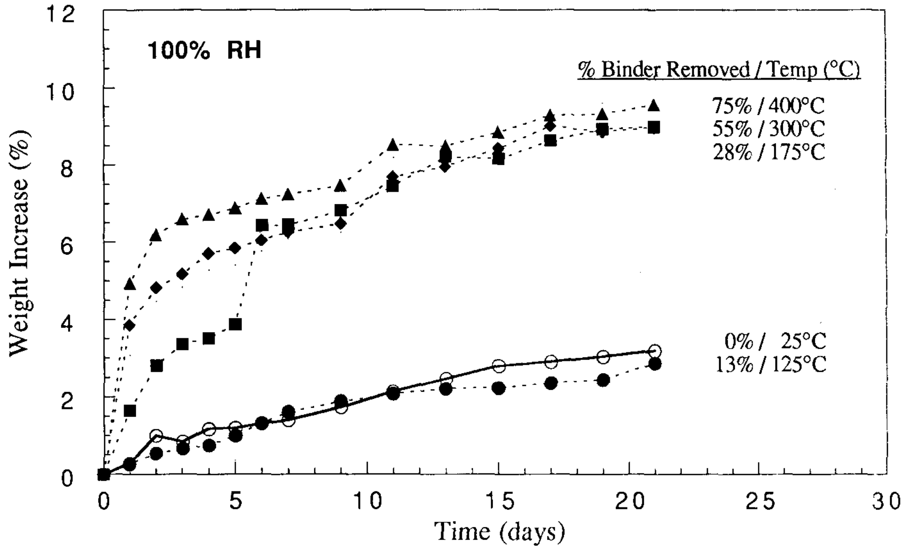

Figure 7. Moisture absorption behavior of heat-treated MDF cements as a function of binder removed.

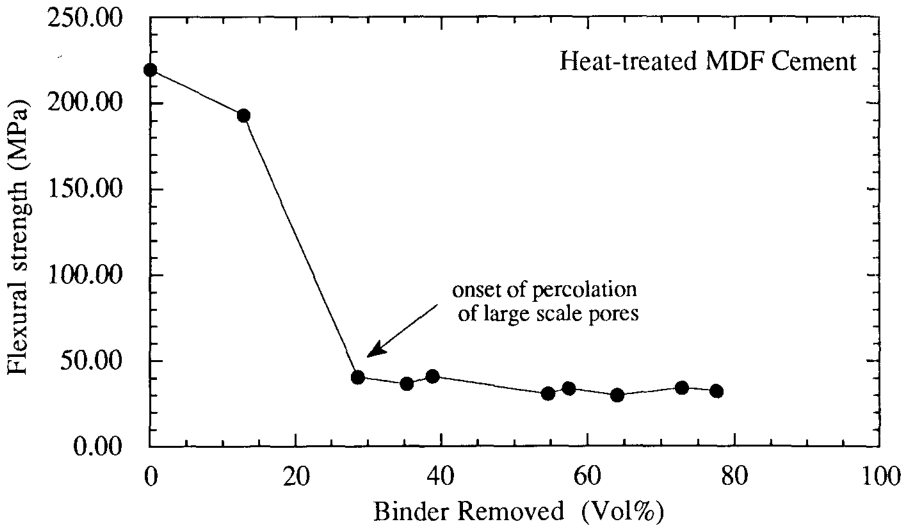

Figure 8. Flexural strength of heat-treated MDF cements as a function of binder removed.

the use of MDF cements in commercial applications. The low processing costs and inherent flexibility has sustained industrial interest in MDF cements. Current research efforts focus on exploiting the flexible processing route to produce noncement-based materials, e.g., ceramics, and on improving the moisture resistance of cement-based MDF composites.

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