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CEMENT PASTE MATRIX COMPOSITE MATERIALS CENTER

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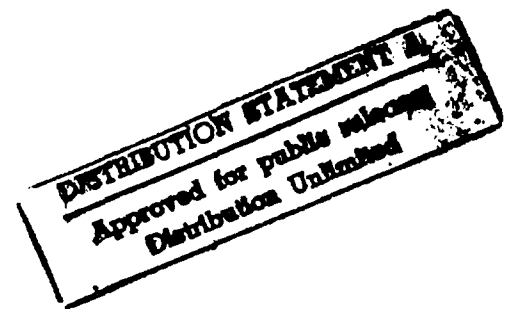(April 1, 1992 - September 30, 1993)

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Investigations of the development of the microstructure of MDF (Macro-defect-free) cement during processing, showed progressive changes in the properties of the poly(vinyl alcohol) matrix. Excessive processing times lead to the introduction of macro-defects, caused by failure of either interphase or polymer matrix. Macro-defects are proceeded by the formation of small tears or voids which coalesce and enlarge.

Further studies on the interdiffusion of polymer interfaces has provided the first experimental evidence of the polymer reptation theory. Interfaces develop fractal character and will influence the fracture of polymer welds and confined polymer fluids.

NMR spectroscopy studies on hydration of cementitious compounds have been extended to calcium silicates, using ^{17}O for the first time. Calcium x-ray adsorption spectroscopy has also been used in an exploratory study. The formation of an reaction intermediate with five coordinated silicon was observed.

The conditions of synthesis of intercalated PVA "organoceramic" complex have been explored. The results suggest that this complex cannot form in MDF cements. An organotitanium complex that improves the water resistance of MDF cement has been shown to form a 3-dimensional PVA gel which is dehydrated to form a water impervious film. The role of PVA cross-linking in controlling processing and properties is discussed.

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1. Introduction

This final report describes scientific progress made over the 3 years of the grant, including a six month no-cost extension. The research program has concentrated on scientific issues underlying the microstructure and performance of a new cement-polymer composite known as Macro-Defect-Free (MDF) cement. This unusual composite is potentially representative of a new type of organic-inorganic composite materials. The cement-polymer combination that is most easily processed and provides optimum properties is calcium aluminate cement with polyvinyl alcohol/acetate co-polymer. Our research has centered on this system.

After high shear mixing on a two-roll mil of the solid components with an appropriate amount of water, the resulting viscoelastic dough is pressed at 80°C/1 MPa for 10 min. and then dried overnight at 80°C. Water is an integral part of the system since it both reacts with the cement and dissolves the polymer phase.

The research program has been divided into five general categories:

1. Interfaces between cement grains and polymer
   (Kriven and Young)
2. Interfaces between polymers
   (Wool)
3. Cross-linking reactions in the polymer matrix
   (Young, Kriven and Wool)
4. Cement hydration reactions
   (Kirkpatrick)
5. Intercalation of polymers in hydrated compounds
   (Stupp)

2. Research Highlights

During the course of the research, not only has an improved understanding of the new MDF cement composites been obtained, but we have also made advances to related fields of science. Important aspects of our work are listed below.

- Documentation of how the MDF cement microstructure develops during processing.

- Clarification of the cement-polymer interactions in MDF cements and how these affects the processing characteristics and the properties of the composite.
- First chemical synthesis of high purity $CaAl_2O_4$ powders.
- First detailed study of the hydration of calcium aluminates using ^{27}Al MAS NMR spectroscopy and the detection of a reaction intermediate, having four-coordinated aluminum atoms.
- First study of hydration by ^{17}O MAS NMR spectroscopy.
- Evidence for the existence of a five coordinated silicon intermediate in the hydration of dicalcium silicate.
- First experimental evidence for the reptation theory of polymer diffusion.
- Demonstration of the formation of fractal interfaces due to interdiffusion of adjacent polymers by reptation.
- Application of interfacial structure to the fracture characteristics of polymer-polymer welds and constrained polymeric liquids.
- Formation of a novel PVA-calcium aluminate hydrate complex (organoceramic). First example of a macromolecule intercalated between the layers of a double hydroxide layered structure.

3. Research Program

3.1 Cement-Polymer Interfaces

Research efforts have taken two main directions: (1) characterizing the actual microstructure of MDF cements, and (2) studying model systems to elucidate particular aspects of the composite structure.

Our early TEM work, completed prior to this project showed the presence of an interphase region linking a modified polymer matrix with embedded unreacted cement grains.[1,2] The interphase region was shown to have a nanocomposite structure with nano-sized crystals of $Ca_2Al_2O_5 \bullet 8H_2O$ embedded in an amorphous matrix. Those details cannot be seen at the lower magnification of SM studies and can only be resolved using TEM and high resolution electron microscopy.

Quantitative microanalysis using EDS and PEELS[2] showed that the amorphous matrix in the interphase region contains carbon, indicating the presence of polyvinyl alcohol (PVA), as well as aluminum. The polymer matrix

itself is aluminum and small amounts of calcium. The proposed cement reaction is therefore:

$$2CaAl_2O_4 + 11\ H_2O \longrightarrow Ca_2Al_2O_5 \bullet 8H_2O + 2Al(OH)_3$$
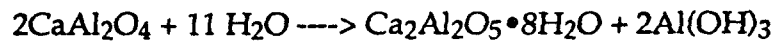
This reaction is unusual in that the expected reaction product under the processing conditions is $Ca_3Al_2O_6 \bullet 6H_2O$. The compound $Ca_2Al_2O_5 \bullet 8H_2O$ is metastable with regard to $Ca_3Al_2O_6 \bullet 6H_2O$ and possible reasons for this are discussed later.

3.1.1. Microstructure Development. Working in conjunction with Professor A. J. McHugh who is supported by the NSF Center for Advanced Cement-Based Materials we have attempted to document the development of the microstructure of MDF cement during processing. This has proved possible due to techniques developed by Professor McHugh[3], which allow the roll-milling process to be duplicated under controlled conditions and over extended processing times.

The results that have been obtained help to explain the observed processing characteristics and properties of the composite. Coupled SEM and TEM analysis indicate that after 2 min of processing in the internal mixer, the composite microstructure shown in Figure 1 already resembles the microstructure of a conventional MDF processed in a twin roll mill. Figure 2 shows that some reactions in the composite have taken place, however, most of the polymer matrix is still unreacted. The mechanical deformation lines on the polymer indicate that the matrix is still soft and deformable. The EDS analysis of this sample showed that the interphase region between the polymer matrix and the ceramic grain contains considerable amounts of calcium and aluminum, whereas the amount of calcium and aluminum in the polymer matrix is less than that of silicon, which is only a common impurity in the commercial polymers. Thus it is suggested that after two minutes of processing most of the polymer is still unreacted and flows easily under shear assuring the integrity of the continuous matrix phase.

As the processing time is increased to 10 min, the extend and the dimensions of the reacted interphase grew. There are certain regions of the composite where a former ceramic grain is completely converted to reacted interphase. A closer look at this reacted interphase reveals a highly porous structure (Figure 3). The EDS analysis of the polymer region from 10 min sample revealed Ca and Al being present in the polymer matrix at much higher amounts
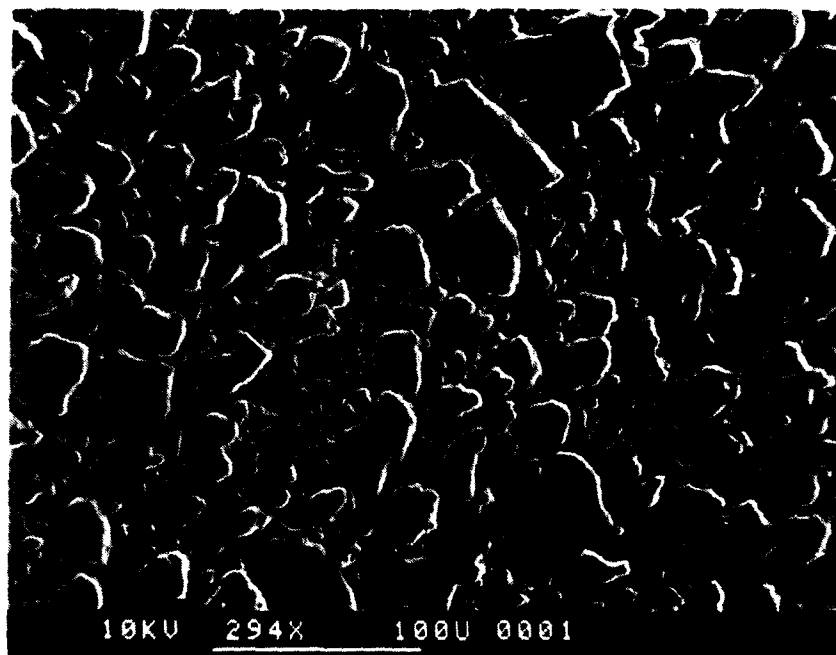
Figure 1. The SEM micrograph of aHAC-MDF composite processed in the internal high shear mixer. The Microstructure is free of macro defects.

Figure 2. The microstructure of the HAC-MDF composite that has been porcessed in an internal high shear mixer for 2 min. The mechanical deformation lines in the polymer matrix are arrowed.

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than impurity levels. Another feature that appeared in a 10 min processed sample is that although the polymer still showed mechanical deformation (flow) lines, it also showed tears and holes developing in the matrix (Figure 4). The tears may be the result of the enforced mechanical deformation upon a polymer which is now cross linked by the ceramic species and thereby losing its soft and easily flowing nature. The investigations on samples processed at longer times is underway.

The changes shown within the PVA matrix agree very well with changes in viscoelastic behavior shown by McHugh. The tears shown in Figure 4 are very small and qualify as "micro-defects". The porous nature of interphase region was not observed earlier, and may be caused by the different shearing conditions used in the present study. These pores are only 10-20 nm in diameter and are therefore microporous in nature.

When processing times are too long macro-defects are reintroduced into the material. Coalescence of the micropores and ultimate failure of the interphase apparently accounts for this. These observations nicely complements our work reported last year on in-situ straining experiments by TEM. Under tensile straining in the AEI/Kratos EM-7 high voltage microscope at Argonne National Laboratory we were able to demonstrate that failure occurred preferentially at the interphase.

We have thus clearly demonstrated that the interphase develops during processing. Crack propagation occurs preferentially through this region and may take a rather tortuous path. Consequently, the micro-defects observed in the polymer phase may not be able to become active. We believe the presence of the interphase region is a critical element in true MDF behavior.

3.1.2 Cement-Polymer Reactions. In the first year of the project we concentrated on developing model systems to discuss the chemical reactions that might be occurring between cement and polymer, in the interphase. We chose to use XPS because of its good spatial resolution and ability for depth profiling. However, the sensitive nature of the system required the use of very pure constituents both polymer and cement. This recessitated the synthesis of the major constituent $Ca_2Al_2O_4$ by a chemical route to avoid contamination by repeated grinding required in conventional synthesis by sintering. The method chosen was the Pecchini process[4] and represented the first time this approach had been used to synthesize hydraulic cement compounds. It has now been adopted by our colleagues working in the NSF Center for Advanced Cement-

Figure 3. The microstructure of the sample processed in the high shear mixer for 10 min. The interphase region is very highly porous. Some of the grains have completely reacted in to an interphase region (arrowed)

Figure 4. The microstructure of the HAC-MDF composite that has been porcessed in an internal high shear mixer for 10 min. The tears and the holes developing in the polymer matrix are arrowed. The micro graph also shows the the porous nature of the reacted interphase.

Based Materials. By this route it was possible to prepare crystalline $CaAl_2O_4$ powders of high purity and reactivity by calcination at 800°C. A detailed examination of the chemical and physical characteristics of the crystalline powders was completed. In addition a TEM study of the crystal growth kinetics from the initial amorphous matrix has been performed.

These $CaAl_2O_4$ powders were then sent to construct a model system with PVA to mimic the MDF cement. XPS analysis of the interphase region developed in the model revealed that there is a chemical reaction between cement and polymer. The appearance of a small Al-O-C peak is evidence of a chemical reaction between the hydrated cement ad PVA chains.

3.2 Interfaces Between Polymers

Calendering of MDF cement to form sheets may give rise to polymer-polymer interfaces which could influence properties of MDF cements. Thus studies of hwo polymers interdiffuse at an interface were included to determine how such potential lamination defects could be eliminated.

3.2.1 Reptation Theory. Over 20 years ago deGennes[5] developed the reptation theory which considers that individual polymer chains move primarily along their own contours in a snakelike fashion. Since its inception this model has been invoked to explain polymer properties based on polymer viscosity and diffusion, by both theoreticians and experimentalists alike. However a definitive statement regarding its validity has been missing. Experiments were conducted on model monodisperse polystyrene polymers which were selectively deuterated. Interdiffusion was studied as a function of annealing temperature and annealing time with neutron reflectivity and secondary ions mass spectroscopy. The results were compared with the minor chain model which was developed in our group several years ago and our recent computer simulation. These simulations proved a powerful tool in isolating various sections of the chains (chain ends, chain centers) and analyzing their contribution to the movement of the entire chain. The results conformed to the expected values predicted by the reptation model. The beauty of these experiments is such that other polymer dynamics models cannot even qualitatively explain our results. Thus we present for the first time the definitive proof of 'reptation', the most important dynamics theory for polymers. The results of this study of interdiffusion at polymer interfaces are directly useful in predicting the structure of the interfaces which in turn effects properties such as development of strength, adhesion etc.

3.2.2 Fractal Structure. When diffusion occurs at an interface the concentration profile of a diffusing species varies smoothly as a function of the one-dimensional depth variable. However, in two dimensions the random nature of diffusion permits the formation of a complex interface with fractal characteristics. The nature of the interface joining two identical pieces of amorphous polymer have been studied using computer simulation. This is representative of internal weld lines in the PVA matrix during the calendering of an MDF cement sheet.

The analysis of the fractal nature of amorphous polymer diffusion fronts is complicated by the interpenetrated nature of the random-coil chains allowing several statistical segments to occupy a single lattice site. The computer simulation of polymer on 2-D or 3-D lattice sites was done in such a manner as to keep track of both the occupied sites and the total number of segments in multiple occupied sites. The connectivity under gradient percolation conditions was examined in terms of connected sites and the diffusion front identified as the boundary between connected and unconnected sites. Figure 5 shows one side of a typical interface simulated on a 2-D lattice. A reptation algorithm was used. The interface became fractal at diffusion distances are greater than the radius of gyration and at times greater than the reptation time.

3.2.3. Fracture Studies. These observations have been used to help explain fracture studies of incompatible polymer interfaces welded above the glass transition temperature. The development of fractal interfaces also occurs during the fracture of a viscous polymer fluid between two plates. Studies of this model system has lead to an understanding of how fracture parameters (fracture energy, critical load and critical displacement) are controlled by strain rate and non-Newtonian fluid behavior. This information should be of great benefit in future studies on the fracture characteristics of MDF cements, particularly the effects of moisture adsorption, which lead to severe strength loss.

3.3. Cross-linking Reactions in the Polymer Matrix

3.3.1 Aluminate Crosslinking. There is ample evidence that the polymer matrix is modified by the hydrating cement. The glass transition temperature is higher than that of a pure PVA film[5]; MDF processing cannot be applied to mixture of PVA with unreactive fillers,[6,7] the rheology of the cement-polymer mixture changes during mixing;[3] and metal ions are present in the PVA matrix.[1,2] The mechanism proposed by Groves and co-workers[8] that $Al(OH)_4^-$ provides covalent cross-linking of PVA chains, analogous to that of borates,[9] has been

widely accepted. While there is good experimental evidence for the latter, the former has not been proven. Our studies reported in our last annual report showed that Al(OH)$_4^-$ does not behave analogously to B(OH)$_4^-$ at room temperature. However, after heating at 65°C, PVA films treated with NaAl(OH)$_4$ did show the presence of Al-O-C bonds by XPS analysis. We proposed that an initial interaction between cement and polymer involves linking PVA chains by hydrogen bonding of Al(OH)$_4^-$ or amorphous Al(OH)$_3$. This comparatively weak interaction would account for the modest rheological changes that define "MDF processing" characteristics. When boric acid is used[6] the material stiffens too rapidly because of more effective cross-linking, which makes it more difficult to produce a material that is entirely free of macro-defects.

```
50471   # of chains: 40/ 40    Chain length: 100
Width of front: 30   Length of front: 1349/ 546
Mean X: 13.9:        Std. Error: 6.03     Df: 1.79   / 1.11
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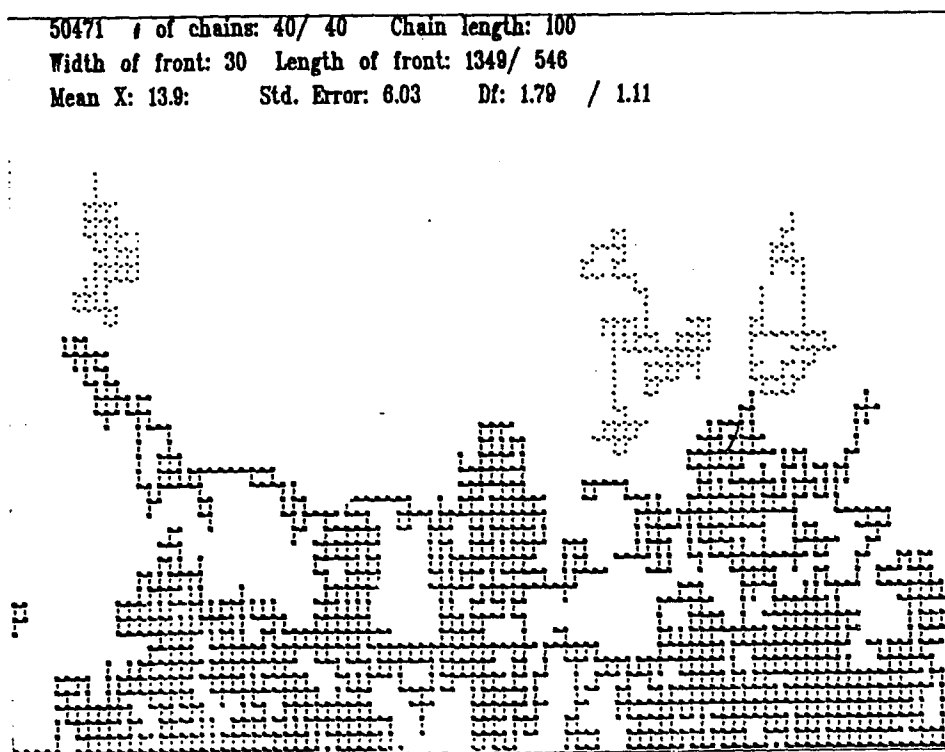

Figure 5. Polymer-polymer interface (one side) simulation on a 2-D lattice, formed by reptation of random-coil interpenetrated chains of length 100 steps.

3.3.2. Titanate Cross-linking.
Similar behavior is found with an organic titanium chelate compound [triethanolamino-TiOC$_3$H$_7$] is added to the mix. This compound is commercially available under the trade name Tyzor TE (DuPont de Nemours Co.). This material is added to MDF cement to improve water sensitivity[7] (see below), but the amount that can be added is limited by difficulties of processing. It has been shown that the titanium chelate rapidly gels a PVA solution even at room temperature. In this regard it behaves similarly to boric acid. XPS analysis of the gelled PVA showed a new signature for oxygen at 531.25 - 0.1 eV and one for carbon at 285.7 ± 0.1 eV. These shifts are similar to those observed for transition metal carboxylates and are thus consistent with the formation of a C-O-Ti-O-C complex. The water entrapped in the gelled PVA solution was still available for hydration of CaAl$_2$O$_4$ powders. It is thus proposed that a 3-D cage-like framework of PVA chains is created by random cross-links with Ti, as shown in Figure 6. Upon removal of the excess water by hydration and heating the three-dimensional structure is collapsed to water-resistant film.

3.3.3 Water Resistance.
Cross-linking is important both for developing "MDF processing" characteristics and adequate water resistance of the final material. PVA films are inherently hygroscopic unless they are cross-linked by metal ions or small disfunctional organic molecules.[10] Organic cross-linking reactions are catalyzed by hydrogen ions and thus do not proceed effectively in alkaline conditions. Metal ion cross-linking is well known, but, as discussed in the previous section, not easy to control. A desirable reaction scheme is proposed in Figure 7. If reaction (1) proceeds too rapidly n will be 1 or 0 and a high degree of partial cross-linking will occur (Eq. 2) and impede processing. This occurs with boric acid, where n = 0 initially, and with Tyzer TE where n may be 1. Complete cross-linking will occur on heating when final dealcoholation (or dehydration) can occur. If initial hydrolysis (Eq. 1) does not proceed readily then subsequent cross-linking will not be very effective. This appears to be the case when organosilane coupling agents are used,[6] since they work best in acidic environments. On the other hand complete hydrolysis in Eq. 1 would be satisfactory if partial cross-linking were confined to hydrogen bonding as we have proposed in the case of aluminum. Figure 7 emphasizes the need to provide only partial cross-linking for favorable processing characteristics, while full cross-linking is needed for good water resistance. The two reactions need to be decoupled so that they can be controlled independently.
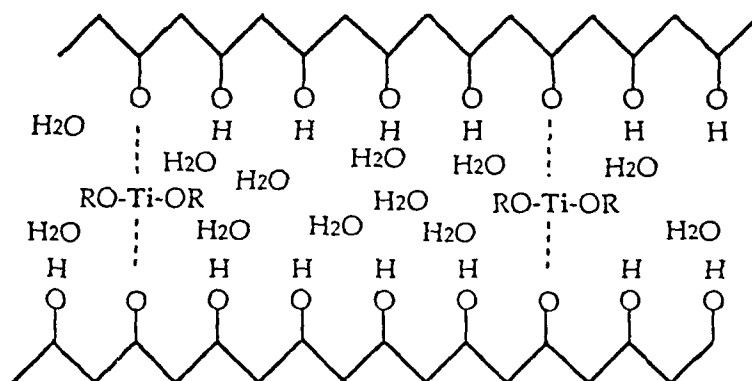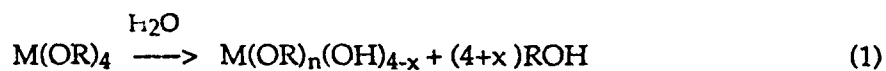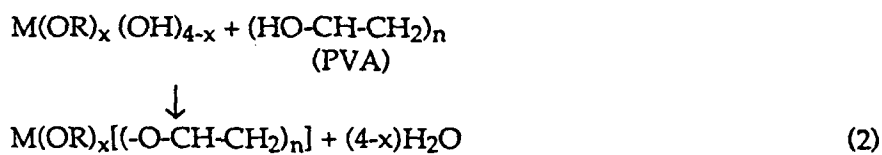
Figure 6. Two dimensional schematic model of the three dimensional cage structure of titanate cross couple PVA solution with the retained water of solution.

Initial Hydrolysis

$$M(OR)_4 \xrightarrow{\;H_2O\;} M(OR)_n(OH)_{4-x} + (4+x)ROH \qquad (1)$$

Partial Cross-linking

$$M(OR)_x(OH)_{4-x} + (HO\text{-}CH\text{-}CH_2)_n$$
$$(PVA)$$
$$\downarrow$$
$$M(OR)_x[(\text{-}O\text{-}CH\text{-}CH_2)_n] + (4\text{-}x)H_2O \qquad (2)$$

Complete Cross-linking

$$M(OR)_x[(\text{-}O\text{-}CH\text{-}CH_2)_n] + (HO\text{-}CH_2\text{-}CH_2)_n \qquad (3)$$
$$\downarrow$$
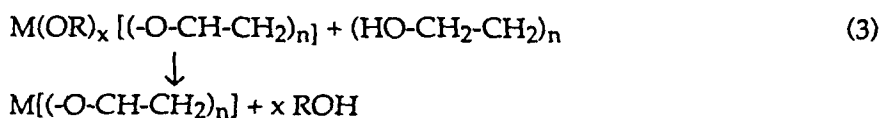$$M[(\text{-}O\text{-}CH\text{-}CH_2)_n] + x\,ROH$$

Figure 7. Proposed mechanism for cross-linking PVA in MDF cements.

3.4. Cement Hydration Reactions

3.4.1 Calcium Aluminates. The discussion in the previous sections indicates the importance of cement hydration during the development of the MDF microstructure. Unfortunately the reaction cannot be followed by x-ray diffraction because the overall reaction is not very extensive and well-crystalline hydration products are not formed. Thus, we have followed hydration using 27-Al NMR spectroscopy. This is the first systematic study of changes in the aluminum environment during hydration.

The experiments involved hydration of CA and Secar 71 in flowing dry nitrogen at temperatures from 4 to 70°C. The ^{27}Al NMR spectra clearly show the conversion of Al which is 4-coordinated by oxygen (Al(4)) in the anhydrous phases to 6-coordinated Al (Al(6)) in the hydrated compounds and provide a direct measure of the extent of reaction. The overall extent of hydration follows the typical autocatalytic kinetics of many hydration reactions, but interestingly the initial rate of reaction is greater at 4° than at 25°, apparently due to the formation of different phases. The spectra also contain a peak or peaks for Al(4) in a previously unobserved reaction intermediate (Figure 8), which the cross polarization spectra show to be hydrated. The maximum amount of this material, which is undetected by X-ray diffraction, is about 5%, quite large for a reaction intermediate. It may be a partially hydrated $CaAl_2O_4$ and $CaAl_4O_7$ which exists before these materials fully dissolve in the pore solution prior to reprecipitation as Al(6) in the final hydration products. Its structure, however, appears to be quite different from that of the hydrated $CaAl_2O_4$ present during the incubation period in some experiments.

Hydration in the presence of PVA changes the kinetics of reaction but does not alter the nature of the hydration products. The relatively large amount of hydrated Al(4) species, which is almost certainly amorphous or microcrystalline (or otherwise an x-ray diffraction pattern would be observed), is unusual. We speculate that it is probably amorphous calcium aluminate hydrate coating from which the latter hydration products crystallize. Such amorphous coatings have observed microscopically with hydrating $Ca_3Al_2O_6$.

This material likely forms part of the interphase region in MDF cements through interaction with PVA. In our studies reported after the first year we showed that whereas gibbsite [with Al(6)] precipitates from acidified $NaAl(OH)_4$ solutions, in the presence of PVA a solid with Al(4), Al(5) and Al(6) resonances

precipitates. Five coordinate aluminum can be found in some amorphous aluminum-containing phases.

3.4.2 Calcium Silicates. Subsequently we have turned our attention to examining the hydration of calcium silicates since NMR spectroscopic analysis has been shown to add a new dimension to hydration studies. It was of interest to see whether intermediate hydrated species are detectable in other cementitious system and whether they play a role the development of a Portland cement-based MDF microstructure. However, because the major hydration product is a amorphous calcium silicate hydrate (CSH) this system is much more difficult to study systematically. The work completed in this study has primarily been the application of new techniques to probe the nanostructure of CSH and interpret the resulting data.

The nanostructure of CSH has been a matter of speculation and investigation for nearly 50 years. CSH has a highly variable composition, and it is normally difficult to obtain as an isolated compound rather than a phase mixture. Our work is adding greatly to the understanding of CSH, because we have been able to form single-phase CSH not only by direct precipitation (which may not yield a compound like that in Portland cements) but also by hydration of a highly reactive β-dicalcium silicate and colloidal silica. For our work we have used ^{29}Si NMR and ^1H cross polarization methods used in previous investigations of CSH and in addition ^{17}O NMR, the ^1H cross polarization spin dynamics, and Ca X-ray adsorption spectroscopy (XAS). ^{17}O NMR provides a direct probe of the oxygen environments and is often a key to understanding any oxide based material. It can be used only for specially prepared, isotopically enriched samples. The cross polarization dynamics provides information about the motion of H-containing species, here water molecules and hydroxyl groups. Ca XAS provides structural information about the Ca environment similar to that provided by NMR for other elements by NMR than and because there is no financially feasible, NMR active Ca nucleide. The work was done at the Stanford Synchrotron Radiation Laboratory (SSRL).

Our initial work, involved formation of ^{17}O-enriched CSH and portlanide by hydration of β-Ca_2SiO_4 and precipitated CSH both in isotopically enriched water. This work showed that ^{17}O NMR signal for O's in Si-O-Ca, Si-O-Si, Ca-OH, and possibly Si-OH linkages can be readily detected and characterized. The isotopic labeling of the various sites in the reaction products involves transfer of oxygen atoms form the water to the solids and is consistent with a reaction

mechanism involving formation of a 5-coordinated Si reaction intermediate, proton transfer, and decomposition of the 5-coordinate state with labeled O remaining coordinated to the Si.

More recent and ongoing NMR work involves isotopic enrichment by the less expensive route of isotopic exchange of previously formed CSH in small amounts of enriched water (Figure 9). All of the sites exchange, indicating continuous dynamic equilibrium between the silicate structure and the water in the nano-porosity and consistent with the proposed reaction mechanism involving 5-coordinate Si.

A very significant consequence of having single phase materials to use is that we have for the first time directly determined the minimum concentration of Si-OH linkages needed in CSH, which is 0.4/Si. This value is essential for the development of realistic structural models of this material. We have been able to do this by comparison of structural formulae determined from chemical analyses and the polymerization of the CSH directly observed by ^{29}Si NMR. The ^{17}O NMR spectra also require the presence of such linkages and are consistent with the value determined.

The ^{29}Si-^{1}H cross polarization spin dynamics behavior of our CSH's indicates *rapid exchange* of hydrogen between OH groups and water molecules, as indicated by the rapid decay of the cross polarization intensity. This result is also clearly demonstrated by the poor signal/noise ratios of the ^{29}Si cross polarization spectra (indicating decoupling of the spin systems) and is consistent with the observed exchange of oxygen between the water and silicate structure.

The Ca XAS is to our knowledge the first of its type ever undertaken for cement materials. The initial experiments were done in May of 1993 and were quite difficult and time consuming. They demonstrated that the experiments are possible, that the hydration state does not effect the spectra significantly, that the spectra can provide structural information out to ca. 7 Å (clearly indicating that the structure is relatively well ordered on this scale but not the 100's of Å scale observed by X-ray diffraction), and that at least some of the CSH samples have a structure similar to that of 11Å tobermorite.
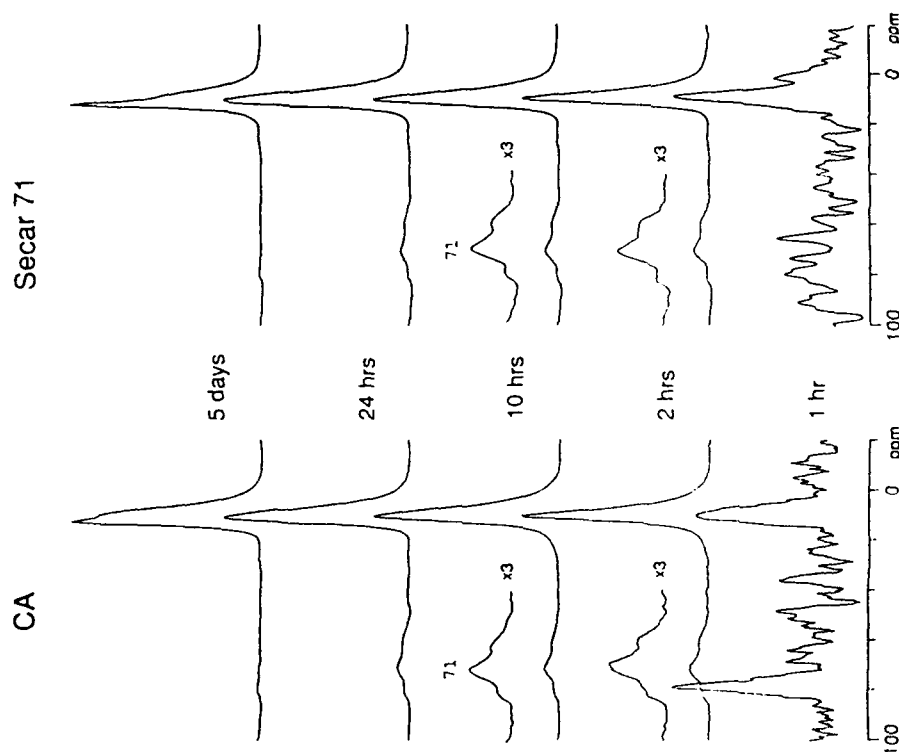
Figure 8. 27Al CPMAS spectra of reaction products for experiments with CaAl₂O₄ and Secar 71 at 50°C for the times indicated. Peaks for the Al(4)-containing reaction intermediate are shown vertically expanded 3x.
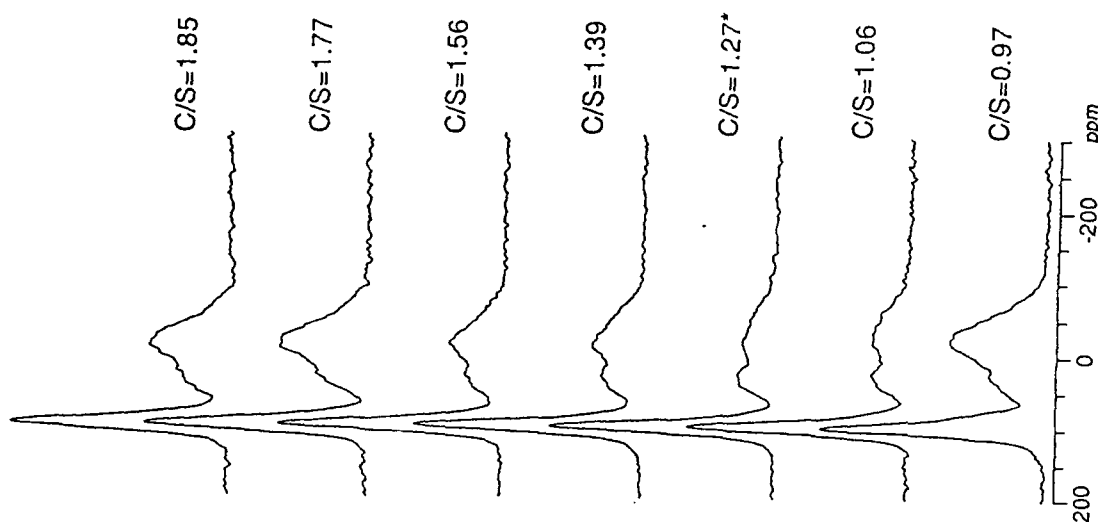
Figure 9. 17O MAS NMR spectra of C-S-H from hydration of β-Ca₂SiO₄-silica mixtures.

3.5 Intercalation of Polymers in Hydrates (Organoceramics)

In previous reports we described the intercalation of poly(vinyl alcohol) [PVA] between the layers of tetracalcium aluminate hydrate with the formula: $[Ca_2Al(OH)_6]_2(OH)_2 \bullet nH_2O$. The PVA chains was shown to be aligned between the inorganic lamellae of the layered double hydroxide as a bilayer. Although such intercalated complexes are known for small organic molecule, this was the first time a macro-molecule had been used. The complex is more thermally stable than either of its constituents and does not convert on heating to the thermodynamically stable phase $Ca_3Al_2O_6 \bullet 6H_2O$.

A change in lattice spacing on complex formation occurs only in the c-direction. Therefore it is possible that the nanocrystals of $Ca_2Al_2O_5 \bullet 8H_2O$ observed in the interphase region of MDF cement may actually be the PVA complex. $Ca_2Al_2O_5 \bullet 8H_2O$ is isostructural with tetracalcium aluminate hydrate and the a and b axes, which were used to identify the phase, are almost identical.

3.5.1 Reaction Variables

This unusual nanocomposite, which we have termed on "organoceramics", has properties unlike those of the separate components or simple mixtures. During the last year reaction variables were systematically varied in order to optimize the reaction for scale up of production for property measurements. The complex is precipitated from supersaturated $CaAl_2O_4$ solutions mixed with saturated CaO solutions containing PVA. Currently, the ratio of CaO solution (5°C):$CaAl_2O_4$ solution(RT) used in the synthesis of the organoceramic is 5 to 1. A number of experiments were done in which this ratio was varied. It was found that the formation of organoceramic is not affected by an increase in the amount of Ca^{+2} ions present in the solution (up to a 20% increase). However, increasing the amount of Al^{+3} ions in the solution had a dramatic effect on the product. Small increments in the Al^{+3} concentration (a few %), caused the formation of $Ca_2Al_2O_5 \bullet 8H_2O$. This was verified by both X-ray diffraction and elemental analysis. A Ca/Al ratio very near the theoretical value of two was obtained for the standard organoceramic runs, corresponding to pure tetracalcium aluminate. When the Al^{+3} ion concentration was increased, the Ca/Al ratio dropped with the formation of $Ca_2Al_2O_5 \bullet 8H_2O$. From this, we can conclude that the formation

of the tetracalcium aluminate organoceramic must be limited by the Al^{+3} ions in the solution, and that the complex probably does not form in MDF cements.

The precipitation of the organoceramic is not stoichiometric; residual calcium ions are always present in the reaction mixture. Measuring the solubilities of CaO and $CaAl_2O_4$ (via elemental and gravimetric techniques), we were able to calculate the minimum concentration ratio of calcium and aluminum ions required in solution to obtain organoceramic of pure tetracalcium aluminate. Measurements of this ratio ($[Ca^{+2}]/[Al^{+3}]$) varied from 4 to 4.5. This same ratio is observed for synthesis schemes using solutions of CaO and $CaAl_2O_4$ both made at 5°C, and for systems in which a 0.2M Al^{+3}/0.25M NaOH solution was used as the aluminum source. Ratios up to approximately 5.5 will form organoceramic but the overall yield of the batch decreases because the precipitation is limited by the concentration of the aluminum ions. Limitation of Al^{+3} also occurred at very slow rates of addition.

The precipitation of organoceramic is not dependent on the supersaturation of the $CaAl_2O_4$ solution with respect to 5°C. This is plainly seen by the success of the synthesis in which the $CaAl_2O_4$ solution is prepared at 5°C. Thus, the organoceramic must be thermodynamically favorable at 5°C.

3.5.2 Mechanical Properties. A preliminary study to determine the tensile strength of the organoceramic has been undertaken. A comparison was made between the organoceramic and tetracalcium aluminate hydrate treated with PVA and unmodified tetracalcium aluminate hydrate. Powders were mixed with additional PVA (conditioned at 100%rh for 7 days), pressed at 10,500 psi to make small tensile "dog-bone" specimens and annealed for 24 hrs. The specimens were tested in an Instron machine and the ultimate strength calculated. The results are shown in Table 1.

Sample	PVA Content (wt.%)	Composite (x:PVA)	Ultimate Tensile Strength (MPa)
Organoceramic	~36	0.5g:0.1g	16.83±2.28
Ceramic + Adsorbed PVA	~12	0.362g:0.238g	~7
Ceramic	0	0.3g:0.3g	0

The greater strengths with the organoceramic could be due to morphological differences between the solids. Alternatively, it could be due to entanglements of unbound PVA chains with chains that are firmly anchored in the organoceramic as shown in Figure 10, forming a stronger interfacial zone. Adsorbed PVA chains is not fixed in this way. In support of this view strength increases are observed on annealing in the range 50-70°C. This annealing would enhance chain entanglement.

3.5.3 Synthesis of Isotactic PVA. To better understand the interaction of the layers of tetracalcium aluminate hydrate we have targeted the synthesis of the organoceramic with isotactic PVA. Since there is no commercial source of isotactic PVA its synthesis was attempted. We selected t-butyl vinyl ether (tBVE), trimethyl silyl vinyl ether (TMSVE) and t-butyl-di-methyl silyl vinyl ether (tBDMSVE) as possible monomers. All of these monomers have been polymerized via cationic initiators (boron tribluoride etherate or tin(IV) chloride) to yield isotacticities of up to 79%. The ether side group can then be cleaved to yield PVA. Of these TMSVE was particularly attractive because the ether linkage is easily cleaved by methanol. Unfortunately, complication arise because fully hydrolyzed isotactic PVA is virtually insoluble in any solvent (including water). Solubility is critical to the organoceramic synthesis. To circumvent this problem, we attempted copolymerization of TMSVE with both tBDMSVE and tBVE. The trimethyl silyl groups of the copolymer could then be cleared to yield isotactic PVA with enough pendant groups (t-butyl or t-butyl-dimethyl silyl) to make it water soluble. Copolymerizations were run at numerous combinations of conditions (solvent, temperature, initiator, work-up) without appreciable yields. Another possibility lies in the partial deprotection poly(tBDMSVE) or poly(tBVE) to yield isotactic PVA with enough unhydrolyzed pendant groups to obtain solubility in water. Unfortunately this synthesis had not been successfully completed at the end of the project.
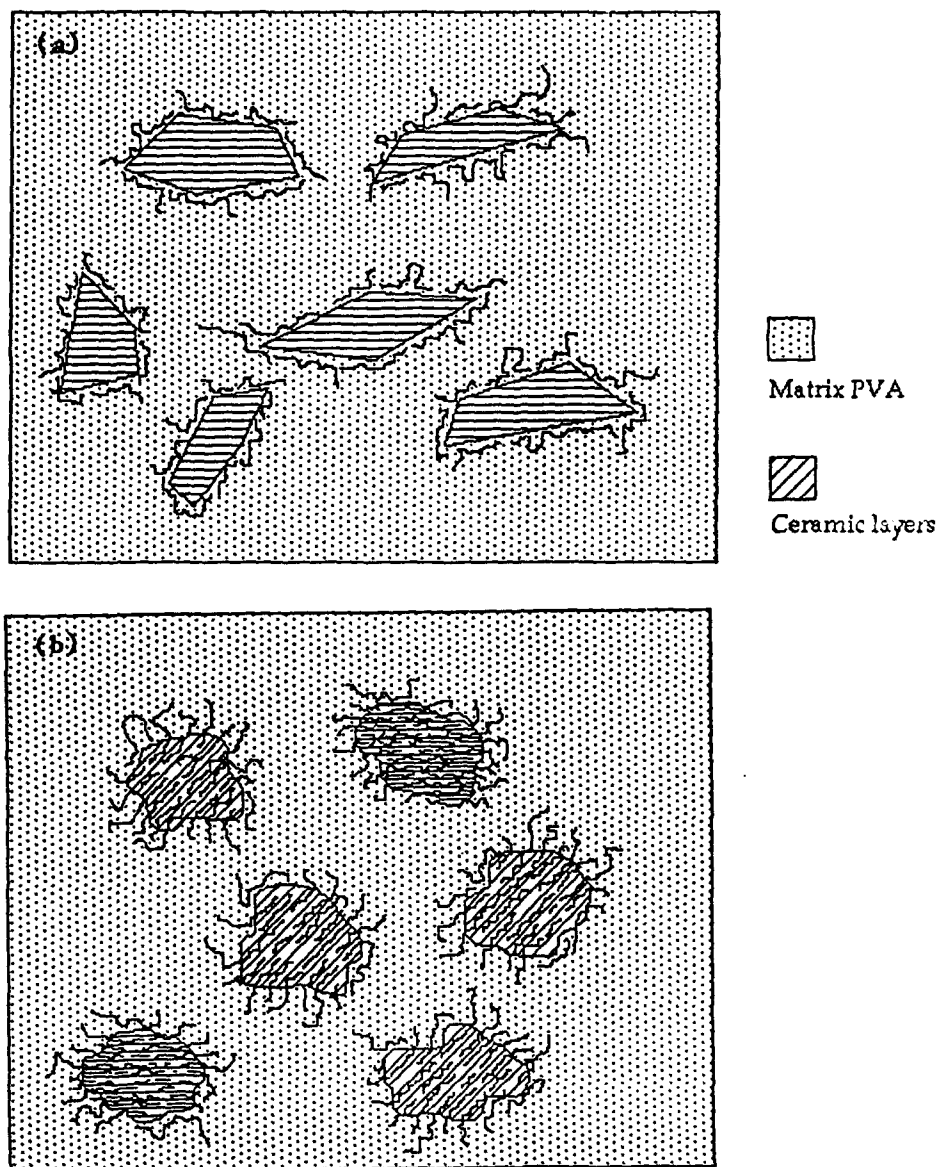
Figure 10. Schematic of ceramic PVA composite made with: (a) "modified ceramic" (adsorbed PVA), and (b) organoceramic.

3.6 References

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4. Publications

This list is an update from the Second Annual Report (May 1992).

4.1 Theses

P. B. Messersmith, "Synthesis and Characterization of Novel Polymer-Ceramic Nanocomposites:Organoceramic", (Ph.D).

P. G. Desai, "Cement-Polymer Interactions in Macro-Defect-Free Composites", (M.S.).

M. R. Van Landlingham, "Saffman-Taylor Model Fracture of a Fluid Between Two Plates", (M.S.).

4.2 Refereed Journals

O. O. Popoola and W. M. Kriven, "Interfacial Structure and Chemistry in a Ceramic/Polymer Composite Material", J. Mater. Res., 7 1545-1552 (1992).

M. A. Gulgun, O. O. Popoola and W. M. Kriven, "Chemical Synthesis and Characterization of Calcium Aluminate Powders", J. Amer. Ceram. Soc., accepted for publication.

T. P. Russell, V. R. Deline, W. D. Dozier, G. P. Felcher, G. Agrawal, R. P. Wool and J. W. Mays, "Direct Observation of Reptation at Polymer Interfaces", Nature, 365 pp. 235-237 (1993).

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X. Cong and R. J. Kirkpatrick, "Hydration of Calcium Aluminate Cements: A Solid-State ^{27}Al NMR Study", J. Amer. Ceram. Soc., Vol. 76, pp. 409-416 (1993).

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P. B. Messersmith and S. I. Stupp, "Synthesis and Nanocomposites: Organoceramics", J. Mater. Res., Vol. 7 pp. 2599 (1992).

4.3 Conference Proceedings

"Application of Ultramicrotomy to TEM Specimen Preparation of Particulate Inclusions and Composite Materials", O. O. Popoola, J. J. Cooper, B. P. Jakstys and W. M. Kriven, in Specimen Preparation for Transmission Electron Microscopy III, edited by R. Anderson, B. Tracy and J. Bravman. Mat. Res. Soc. Symp. Proc. Vol. 245, pp. 271-278 (1992).

"Preparation and Hydration Kienteics of Pure $CaAl_2O_4$", M. A. Gulgun, I. Nettleship, O. O. Popoola, W. M. Kriven and J. F. Young. In Advanced Cementitious Systems: Mechanisms and Properties, edited by F. P. Glasser, P. L. Pratt, T. O. Mason, J. F. Young and G. J. McCarthy, Mater. Res. Soc. Symp. Proc., Vol. 245, pp. 199-204, (1992).

"*In Situ* Transmission Electron Microscopy (TEM) Investigation of Fracture Mechanisms in a Calcium Aluminate MDF Cement", O. O. Popoola, W. M. Kriven and J. F. Young. In Advanced Cementitious Systems: Mechanisms and Properties, edited by F. P. Glasser, P. L. Pratt, T. O. Mason, J. F. Young and G. J. McCarthy, Mater. Res. Soc. Symp. Proc., Vol. 245, pp. 283-288, (1992).

P. G. Desai, J. F. Young and R. P. Wool, "Cross-Linking Reactions in Macro-Defect-Free Cement Composite", in Advanced Cementitious Systems:Mechansisms and Properties edited by F. P. Glasser, P. L. Pratt, T. O. Mason, J. F. Young and G. J. McCarthy, Mater. Res. Soc. Symp. Proc., Vol. 245, pp. 205-208, (1993).

P. B. Messersmith and S. I. Stupp, "Synthesis and Properties of Poly(vinyl alcohol)/Calcium Aluminate Nanocomposites", in Advanced Cementitious Systems:Mechansisms and Properties edited by F. P. Glasser, P. L. Pratt, T. O. Mason, J. F. Young and G. J. McCarthy, Mater. Res. Soc. Symp. Proc., Vol. 245, pp. 191-197 (1992).

R. J. Kirkpatrick and X. Cong, "An Introduction to ^{27}Al and ^{29}Si NMR Spectroscopy of Cements and Concretes", in Application of NMR Spectroscopy to Cement Science, edited by A. Grimmer and P. Colombet, (Gordon and Breach, in press).

4.4 Papers Submitted

"XPS Study of Bonding Between Polyvinyl Alcohol and a Titanate Cross Coupling Agent", M. A. Gulgun, W. M. Kriven and O. O. Popoola, J. Mater. Res., submitted.

M. R. Van Landingham and R. P. Wool, "Saffman-Taylor Model Fracture of a Polymer Fluid Between Two Plates", Macromolecules, submitted.