ISTANBUL TECHNICAL UNIVERSITY ★ INSTITUTE OF SCIENCE AND TECHNOLOGY

INVESTIGATIONS OF MOISTURE SENSITIVITY IN MACRO DEFECT FREE CEMENTS

PhD. Thesis by

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Department : Civil Engineering

Programme : Structural Engineering

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BÜYÜK BOŞLUKLARINDAN ARINDIRILMIŞ ÇİMENTO POLİMER KOMPOZİTLERİNİN SU ETKİSİ ALTINDAKİ DAVRANIŞLARININ İNCELENMESİ

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ÖZGÜR EKİNCİOĞLU
Civil Engineer, MSc.

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ABBREVIATIONS

$[Al(OH)_4]^-$	:	Tetrahydroxoaluminumate ion
$[B(OH)_4]^-$	:	Tetrahydroxyborate ion
A	:	Al_2O_3 - Aluminum oxide (Alumina) – Corundum
AA	:	Atomic absorption
ABS	:	Acrylonitrile-Butadiene-Styrene
AFM	:	Atomic force microscopy
AH_3	:	$Al_2O_3 3H_2O$ - Aluminate trihydrate-Gibbsite
ASTM	:	American Society for Testing and Materials
BSI	:	Béton spécial industriel–special industrial concrete
C	:	CaO
$C_{12}A_7$	:	$Ca_{12}Al_{14}O_{33}$-Mayenite
C_2AH_8	:	$2CaO.Al_2O_3.8H_2O$ – Dicalcium aluminate octahydrate
C_2AS	:	$2CaO.Al_2O_3.SiO_2$ – Dicalcium alumina silicate - Gehlenite
C_3A	:	$3CaO.Al_2O_3$ - Tricalcium aluminate
C_3AH_6	:	$3CaO.Al_2O_3.6H_2O$ - Tricalcium aluminate hexahydrate -Katoite - Hydrogarnet
$C_3H_5(OH)_3$	:	Glycerol
C_4AF	:	$4CaO.Al_2O_3.Fe_2O_3$ - Tetracalcium aluminoferrite
CA	:	$CaO.Al_2O_3$ - Monocalcium aluminate
CA_2	:	$CaO.2Al_2O_3$ - Monocalcium dialuminate – Grossite
CA_6	:	$CaO.6Al_2O_3$ - Monocalcium hexa-aluminate
CAC	:	Calcium aluminate cement
CAH_{10}	:	$CaO.Al_2O_3.10H_2O$- Calcium aluminate decahydrate
CaO	:	Calcium Oxide
CAPR	:	Calcium aluminate phenol resin
COONa	:	Sodium carboxylate
CRC	:	Compact reinforced composite
C-S-H	:	Calcium silicate hydrate
DC	:	Degree of crosslinking
DH	:	Degree of hydrolysis

DP : Degree of polymerization
DSC : Differential scanning calorimetry
DSP : Densified with small particles
DTA : Differential thermal analysis
DTG : Differential thermogravimetry
EDS : Energy dispersive spectrometry
F : Fe_2O_3 - Iron Oxide
FIZ : Fachsinformationzentrum
FTIR : Fourier transform infrared spectroscopy
GC : Gas chromatography
H : H_2O
H.P.L.C. : High performance liquid chromatography
$B(OH)_3$: H_3BO_3 - Boric acid
HAC : High aluminate cement
HPMC : Hydroxy propyl methyl cellulose
HREM : High resolution electron microscopy
ICDD : International centre for diffraction data
ICDS : Inorganic Crystal Structure Database
ICI : Imperial chemical industry
ICP : Inductively coupled plasma
ICP-AES : Inductively coupled plasma - atomic emission
ICP-MS : Inductively coupled plasma - mass spectroscopy
IR : Infrared
ITU : Istanbul Technical University
LC : Liquid chromatography
MAS : Magic angle spinning
MDF : Macro defect free
MIP : Mercury intrusion porosimetry
MOR : Modules of rupture
MPa : MegaPascal
MS : Mass spectroscopy
NIST : National institute of standards and technology
NMR : Nuclear magnetic resonance
OPC : Ordinary portland cement
PAA : Poly(acrylic acid)

PBA : Poly(butyl acrylate)

PC : Polymer concrete

PDF : Powder diffraction file

PE : Polyethylene

PEELS : Parallel electron energy loss spectrometry

PIC : Polymer impregnated concrete

PMC : Polymer modified concrete

PP : Polypropylene

PVA : Poly(vinyl alcohol) or poly(vinyl alcohol-co-vinyl acetate)

QXRD : Quantitative X-ray diffraction

RPC : Reactive powder concrete

S : SiO_2

SAFB : Sulfoaluminate ferrite belite

SEM : Scanning electron microscopy

SIFCON : Slurry infiltrated fiber concrete

SO_3^{-2} : Sulphite

TEM : Transmission electron microscopy

TG - TGA : Thermogravimetric analysis

TOC : Total organic carbon

UIUC : University of Illinois at Urbana-Champaign

UV-VIS : Ultraviolet-visible spectrophotometry

XRD : X-ray diffraction

XRF : X-ray fluorescence

β-C_2S : $2CaO.SiO_2$ - Dicalcium silicate - Belite

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LIST OF SYMBOLS

2γ	:	Fracture surface energy
A	:	Radius of support circle, mm.
a	:	Half of the critical crack length
B	:	Radius of loaded area or ram tip, mm.
C	:	Radius of specimen, mm.
D	:	Interplanar spacing
d	:	Thickness of the specimen, mm.
E	:	Young modulus
G_{max}	:	Dynamic storage modulus
H_0	:	Half of the nip gap
I/I_o	:	Relative intensities
K	:	Kelvin
N	:	Concentration of crosslinks
^oC	:	Celsius
^oF	:	Fahrenheit
P	:	Failure load, N.
p/c	:	Polymer/cement
R	:	Real gas constant
r	:	Radius of the rolls
S	:	Biaxial flexural strength or modulus of rupture (MOR), MPa.
$\overline{S}$	:	Mean value of biaxial flexural strength or MOR, MPa.
T	:	Temperature
U_0	:	Average speed of rolls U_1 and U_2
U_1	:	Speed of front roll
U_2	:	Speed of back roll
V	:	Coefficient of variation
w/c	:	Water/cement
γ	:	Rate of shear
γ_{max}	:	The maximum shear rate
δ	:	Geometric constant
ε	:	Dimensionless variable
ε_1	:	Dimensionless value describing the exit point, x_1, where material

detaches from the slower roll at thickness, $2h_1$

η	:	Dimensionless variable
λ	:	Dimensionless variable
σ	:	Standard deviation
σ_f	:	Tensile cracking stress at the moment of fracture
υ	:	Poisson ratio.
φ	:	Crosslink functionality
Ω	:	Electrical resistivity

INVESTIGATIONS OF MOISTURE SENSITIVITY IN MACRO DEFECT FREE CEMENTS

SUMMARY

Macro-Defect Free (MDF) Cements, which are cement-polymer composites, have been developed and patented by the scientists from Imperial Chemical Industry (ICI) in order to increase especially the flexural strength of cementious materials by decreasing large voids at the early 1980's in London. These composite materials are produced by adding small amount of polymer and water into the cement and processed in a method inspired by rubber production. Composite is passed between two roller mills repeatedly in different speeds. High shear forces eliminate the macro voids in the material during this step which is the most important part of the production. Subsequently, composite is cured under moderate temperature and pressure which also plays an important role for decreasing the voids. It is believed that polymer fills the voids under pressure at this step.

The most important property of these composites is their unusually high flexural strength. Although, generally more than 80% by weight of this composite is cement, it has 20-30 times higher flexural strength than conventional cement paste. 150-300 MPa flexural strengths are easily achieved which are close to the strength of ordinary steel and it was a very important development if we compare it with ordinary cement paste which has only 5-10 MPa flexural strength. Inventors of the MDF cements attributed this high flexural strength to the elimination of macro voids during processing. However, further studies proved that crosslinking reactions between the ions of cement and polymer chains are more important to obtain such high flexural strengths.

Different cement and polymer types can be used for the production of this composite material. However, the highest flexural strengths are obtained when calcium aluminate cements (CAC) and poly(vinyl alcohol-co-vinyl acetate) (PVA) copolymers are used. Ordinary portland cement (OPC) and poly(acrylamid) combination has the second highest flexural strength. On the other hand, this composite has serious durability problems under water effect. Significant amount of swelling are observed and the strength of this composite decreases in water storage even in very short time.

In this study, MDF cements were produced by using CAC-PVA copolymers and effects of ingredients as well as some additives to the water sensitivity were investigated in 5 different parts. Effects of ingredients and process parameters on the production were investigated and production process was optimized in the first part of the study. Secondly, seven different types of PVAs were used for the production of MDF cements and the water sensitivity of produced composites was investigated. Hydrolysis degrees of these PVAs were changed between 79.4 and 99.1 mole%. Production was successful with five of these seven PVAs. However, all of them were affected from water in different ratios. Modified production processes were also

followed in this part and PVA copolymers were used in water solution at high temperatures in order to increase the solubility of used polymers. Most suitable PVA was a partially hydrolysed PVA. MDF cements were also produced with four different types of CACs. The Al_2O_3 content was changed between 42% and 79% in CACs and effects of Al_2O_3 change on strength and water sensitivity were investigated. It was found that optimum Al_2O_3 content should be between 49% and 70%. Cement, which has 79% Al_2O_3 content, was the most unsuitable cement type for the production of MDF cements. In the fourth part of the study, different MDF composites were prepared by using a different polymer or without a polymer or cement. Aim of the last part was investigating the effect of different additives such as nanosilica, epoxy resin and a vinylic adhesive on the properties of MDF cements.

MDF ÇİMENTOLARIN SU ETKİSİ ALTINDAKİ DAVRANIŞLARININ İNCELENMESİ

ÖZET

Literatürde macro-defect-free (MDF) cement olarak belirtilen, çimento-polimer kompoziti veya MDF çimento olarak adlandırabileceğimiz malzeme, 1980'li yılların başında Londra'da Kraliyet Kimya Enstitüsü'ndeki (Imperial Chemical Industry) bilim adamları tarafından çimento esaslı malzemelerin yapısındaki büyük boşlukların oranını düşürerek özellikle eğilme dayanımlarının artırılabilmesi amacıyla geliştirilmiş ve patenti alınmıştır. Bu kompozitler; çimentoya az miktarda polimer ve su eklenmesi ve geleneksel çimento hamuru üretiminden farklı olarak kauçuk üretiminde de kullanılan, iki çelik merdanenin (kalender) arasından farklı hızlarda defalarca geçirilmesi suretiyle üretilir. Üretimin en önemli aşaması olan bu bölümde malzeme yüksek kesme kuvvetlerine maruz kalmaktadır ve bu sayede malzemenin yapısındaki büyük boşluklar yok edilmektedir. Daha sonra kompozitin ortalama basınç ve sıcaklık altında kür edilmesi de yine bu boşlukların yok edilmesinde büyük rol oynamaktadır. Polimerlerin basınç altında boşlukları doldurduğu düşünülmektedir.

Bu kompozitlerin en önemli özeliği çok yüksek eğilme dayanımlarına sahip olmasıdır. Her ne kadar, bu kompozitler genelde ağırlıkça % 80'den fazla oranda çimento içerse de, geleneksel çimento hamurlarına göre 20-30 kat daha fazla eğilme dayanımına sahiptirler. Bu sayede 150-300 MPa düzeyinde eğilme dayanımları rahatlıkla elde edilebilmekte ve nerede ise çeliğin eğilme dayanımına yaklaşılmaktadır. Bu değerler, 5-10 MPa eğilme dayanımına sahip normal çimento hamuru ile karşılaştırıldığında bunun ne kadar önemli bir ilerleme olduğu daha iyi anlaşılabilir. MDF çimentonun mucitleri bu yüksek eğilme dayanımlarını üretim esnasında uygulanan yöntemlerin malzeme içindeki büyük boşlukları yok etmesine bağlamıştır. Fakat daha sonra yapılan çalışmalar göstermiştir ki, çimento iyonları ile polimer zincirleri arasında oluşan çapraz bağ reaksiyonları da yüksek eğilme dayanımlarının elde edilmesinde çok önemli katkı sağlamaktadır.

Çimento-polimer kompozitlerinin üretilmesinde farklı polimer ve çimento tipleri kullanılabilir. Ancak en yüksek eğilme dayanımları alüminli çimentolar ve poli(vinil alkol-ko-vinil asetat) (PVA) kopolimerleri kullanıldığında elde edilmektedir. Portland çimentosu ve poliakrilamit kombinasyonu ile oluşturulan kompozit ikinci en yüksek eğilme dayanımına sahiptir. Bununla birlikte, bu kompozitler su ile temas etmeleri halinde çok ciddi dayanıklılık problemleri göstermektedirler. Kısa sürelerde dahi suya maruz kalan numunelerde önemli miktarlarda şişme ve dayanımlarında azalma gözlenmektedir.

Bu çalışmada, alüminli çimento ve PVA kopolimerleri ile MDF çimentoları üretilmiş ve içerdikleri malzemelerdeki değişimler ile üretim sırasında karışıma eklenen katkıların, bu kompozitlerin suya karşı davranışlarını nasıl etkiledikleri 5 farklı bölümde incelenmiştir. İlk bölümde, karışımda kullanılan malzemeler ve üretim

sırasında yapılan işlemlerin etkileri incelenmiş ve üretim yöntemi optimize edilmiştir. Ikinci olarak, yedi farkli PVA kopolimeri MDF çimento üretiminde kullanılmış ve üretilen kompozitlerin suya karşı dayanımları incelenmiştir. Hidroliz dereceleri % 79.4 ile % 99.1 arasındaki oranlarda değişen bu yedi PVA kopolimerleri ile yapılan üretimlerin beş tanesi başarılı olmuştur. Ancak bu üretimlerin tümünde, farklı oranlarda da olsa, su etkisi altında dayanımlarda düşme gözlenmiştir. Bu bölümde ayrıca PVA kopolimerlerinin karışıma sulu çözelti halinde ve ısıtılarak katıldığı bir yöntem de denenmiştir. Bu sayede polimerin su içerisinde daha fazla çözünmesi amaçlanmıştır. En uygun PVA kısmi hidrolize PVA olmuştur. Üçüncü bölümde, MDF çimentolar Al_2O_3 içerikleri % 42 ile % 79 arasında değişen 4 farklı tipte alüminli çimento kullanılarak üretilmiş ve Al_2O_3 içeriğindeki değişimin bu malzemelerin dayanımlarına ve su etkisi altında dayanıklılıkları üzerine etkileri araştırılmıştır. En uygun Al_2O_3 içeriğinin % 49 ile % 70 arasında olduğu tespit edilirken; % 79 Al_2O_3 içeriği olan çimento, MDF çimento üretimi için en uygun olmayan çimento tipi olarak tespit edilmiştir. Çalışmanın dördüncü bölümünde, farklı bir polimer kullanarak ya da hiç polimer veya çimento kullanmadan MDF kompozitleri üretimiştir. Beşinci ve son bölümde ise nanosilica, epoxy resin ve vinilik adhesive gibi katkıların MDF çimentoların özellikleri üzerine etkileri incelenmiştir.

1 INTRODUCTION

1.1 General

Material made from inorganic hydraulic cement has become the most important structural material especially after Joseph Aspdin, who took its patent in 1824, because of its low cost, widespread availability of raw materials, and easiness to shape of resulting materials. However, in the traditional usage of cement in concrete, more water is needed to be added to obtain a workable mixture than the necessary amount for hydration of cement and adding high amount of water makes the material more porous and greatly reduces its mechanical properties, especially in tension. A lot of studies were conducted in order to decrease the porosity, and hence to increase the strength of cementious materials; but none of them were successful to prevent the formation of macro voids in the material.

On the other hand, at the beginning of 1980s, Birchall et al. (1981, 1983) have developed a new cement-polymer composite in which pore ratio was notably decreased and consequently not only compressive strength but also tensile strength was increased. This new composite material is called “Macro Defect Free (MDF) Cement” by its inventors because of lack of macro voids. Water/cement ratio could be decreased to very low degrees in this composite with respect to other cement based materials. Generally, pore ratio increases in low w/c ratios in cement based materials because of improper compaction, but in this composite, pore ratio can be decreased to very low levels under high shear stresses by using two roller mills, like calendar type machine, which is widely used in rubber industry. Cement and a suitable polymer are mixed in a planetary mixer and this mixture is passed through roller mills repeatedly in this process. The reasons of the low pore content in this composite are explained with both low water/cement ratio and the production process used. After processing at roller mills, the composite is cured under moderate temperature and molded under pressure as a final step, which is necessary for obtaining such high strengths. Thus, tensile strength is reached up to 200-300 MPa levels which are close to the strength of ordinary steel. In this way it becomes

possible to increase the tensile strength of a cement based material more than 20 times.

Birchall et al. attributed the high flexural strengths of this composite to the elimination of macro voids during the production process and named this material as macro defect free cement as explained above, but further studies (Rodger et al., 1985; Popoola et al., 1991) showed that it is not the only reason which causes such high flexural strengths. Crosslinking reactions between polymer and cement, and also the pressing the material after production at moderate temperature and pressure are playing important roles in the achievement of high strengths. Therefore, this composite is also known as an organo-cement composite, a polymer cement composite or a high flexural strength polymer-cement composite in literature besides macro defect free cement.

In spite of their amazingly high flexural strength, serious durability problems can be observed in MDF cements when they are stored in water. Decrease in strength more than 50% and surface deterioriation can be observed after immersion in water for 7 days or more. This water sensitivity is the most important problem which limits using of these composites as a commercial product before solving this problem. For this reason, most of the researchs have been focused on the solutions of durability problems of MDF composites. Some researchers (Russell, 1991; Desai, 1992; Atkinson and Walsh, 1986; Lewis and Boyer, 1995; Pushpalal et al., 1997; Mojumdar et al., 2004; Chowhurry, 2004; etc) made some improvements, but none of them seems acceptable enough for the industrial applications yet.

This problem of MDF composite is a very complex one involving knowledge in different domains of science that could be solved only in the frame of multidisciplinary teams formed by engineers and chemists. Only this kind of cooperation could improve the understanding of phenomena that take place during the MDF cement synthesis and allows the control and tailor of MDF properties.

1.2 Organization of Content

Investigating Macro Defect Free Cements and their water sensitivity is the subject of this thesis. Effect of ingredients and different parameters as well as using different additives on the properties of MDF cements were investigated for this purpose.

Experimental studies can be divided in five parts. Studies I, II, III and IV were completed at the University of Illinois at Urbana-Champaign (UIUC) and the fifth study were conducted at Istanbul Technical University (ITU).

In the first part of the study, the production of MDF cements were tried by the help of previous studies especially completed at the University of Illinois at Urbana-Champaign (UIUC) and also effect of ingredients and process parameters on the MDF composite properties were investigated. These tests were called as pre-tests and production process tried to be optimized with respect to the ingredients and process parameters. In the second part of the study, MDF cements were produced with 7 different types of poly(vinyl alcohol-co-vinyl acetate) (PVA) copolymers and effects of hydrolysis degrees (between 79.6% and 99.1%) on the mechanical properties of MDF cements were investigated. After that, the influence of aluminate cement type on MDF properties was investigated in the third part. Although, mostly the alumina cements which have 70% Al_2O_3 content were preferred for the production of MDF cements (Birchall et al., 1983; Russell, 1991; Desai, 1990; Desai, 1992), there is not enough study about investigating the effect of Al_2O_3 content on the moisture sensitivity of MDF cements. Al_2O_3 content of used alumina cements was changed between 42% and 79%. Producing MDF cements without using any polymer and cement or with the addition of a different polymer or an additive was the subject of fourth part. Effects of using different additives such as epoxy resin, nanosilica and a self-reticulated vinylic adhesive during the production of MDF cements was investigated at the fifth and last part of the study.

2 STRENGTH OF CEMENT BASED MATERIALS

Increasing the strength of cement based materials is a high priority subject area in the field of Civil Engineering and pore content should be decreased in order to increase strength because of an inverse relationship between strength and porosity. The development of cement technology may be studied as a function of strength improvement of the hydrated mix of a mortar with respect to the chronological period studied, as indicated in Figure 2.1. Period 1 on this graph plots the era of meso-portland cement whilst period 2 is the transitional stage with the beginning of quality control procedures leading to period 3 which represents normal portland cement (Blezard, 2004).

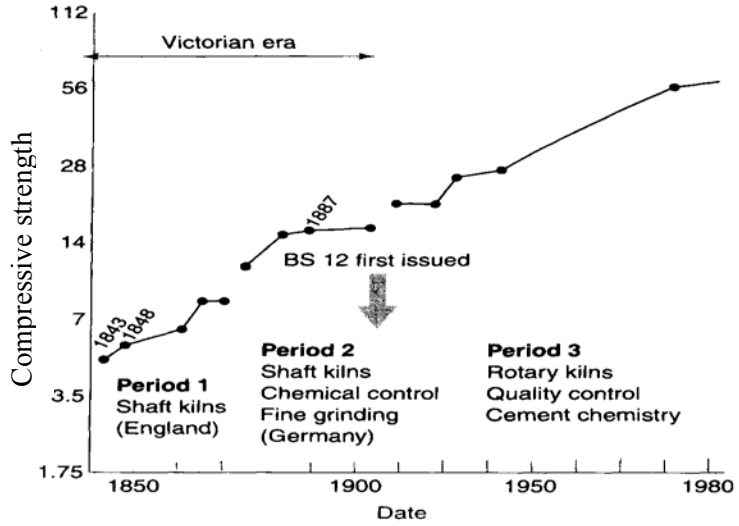


Figure 2.1: Stages of technological improvement; compressive strength of portland cement mortar (1:3 by weight at 28 days stored in water). Note the compressive strength scale units are not linear (Blezard, 2004)

Cement based materials such as concrete have very low strength under tension with respect to compression because very low energy needed for the inititation and growth of cracks. On the contrary, more energy is needed to form and to extend cracks in compression. Therefore, cement based materials have high strength under compression whereas have low strength under tension. The ratio between uniaxial compression and tension is generally in the range 8 to 14. Concrete elements mostly designed under compressive stress and tensile stresses are generally ignored.

However, a combination of tensile, compressive and shear stresses usually determines the strength when concrete is subjected to flexural loads, such as in highway pavements. The w/c ratios were decreased with the help of superplasticizers and also new processing techniques were introduced which caused to obtain high strength materials, hence cement technology has been witnessed to innovation of high strength-high performance cement-based composites especially in last 3 decades. These materials were defined using acronyms such as: Densified with small particle systems (DSP), compact reinforced composite (CRC) macro defect free (MDF) cements, reactive powder concrete (RPC), slurry infiltrated fiber concrete (SIFCON), béton spécial industriel–special industrial concrete (BSI). The main result obtained from the development of these materials is the optimum combination of high strength and ductility/toughness, approaching the structural properties of steel. Figure 2.2 shows the improving trends on cement based materials based on strength and toughness.

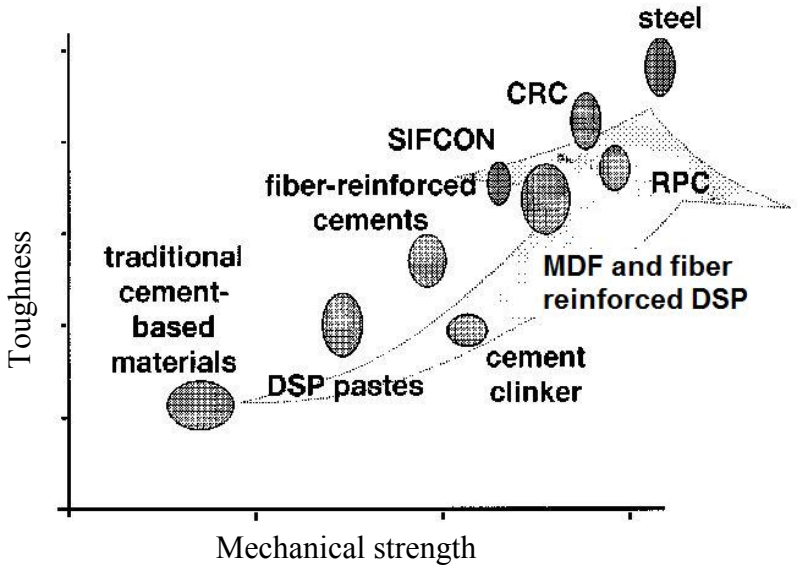


Figure 2.2: New trends of cement based materials (Guerrini, 2000)

2.1 Classification of Pores in Cement Based Materials

Upon hydration of the cement grains, a matrix of an amorphous hydrate gel along with crystallites of hydrated products is formed around the remaining unreacted grains. For the calcium-silicate based ordinary portland cement (OPC) pastes the gel matrix is composed of an amorphous calcium silicate hydrate, C-S-H, with crystallites of calcium hydroxide, CH. Similarly for calcium aluminate cement (CAC), an $Al_2O_3.3H_2O$ (AH_3) amorphous gel is formed with crystalline hydrates of

$CaO.Al_2O_3.10H_2O$ (CAH_{10}), $2CaO.Al_2O_3.8H_2O$ (C_2AH_8), or $3CaO.Al_2O_3.6H_2O$ (C_3AH_6) depending on temperature (see section 3.1.1.3). Also the pores are present in the microstructure of hardened cement pastes resulting from 1) poor packing and agglomeration of the cement grains, 2) air entrapped during mixing and forming, 3) small capillary pores (mesopores) between the hydrated particles, and 4) micropores associated with the amorphous colloidal products. Hence, the pore size distribution in hardened cement paste is quite broad. Pores can be classified, according to Alford (1984), by size and origin as summarized in Table 2.1. Mesopores of the hydrated matrix is the major contributor to the total pore volume of mature cement paste and is strongly dependent on the water/cement ratio (Russell, 1991).

Table 2.1: Classification of pore sizes and origin in hardened cement paste (Russel, 1991)

Pore Size	Pore Origin
10 μm-2 mm	Large voids left by poor cracking and agglomeration of cement grains: air bubles
1-10 μm	İntersitial holes between cement grains not filled by hydrated product: air bubles
0.1-1 μm	Capillary pores (mesopores) between hydrate crystallites
1 nm-0.1 μm	Micropores of the colloidal amorphous hydrate

2.2 Relationship between Strength and Porosity

The most important factor affecting the strength is porosity (pore ratio) in cement based composites (concrete, mortar, cement paste, etc.). Previous works on the fracture of cement have been concerned with compressive failure and with attempts to relate total volume porosity to compressive strength. From such studies, empirical laws such as those of Feret, Abrams, Powers, Bolomey and Graf have been derived. However, the mode of failure in compression is complex and the relationship of compressive strength to porosity is unlikely to be adequately described by a single equation (Birchall et al., 1981).

Most of the materials contain some defects and propagation of these initial defects results in failure of a structure. Concrete is a relatively brittle material, therefore, mechanical behavior of concrete is influenced by crack propagation. The fracture strength of concrete is controlled by the size of the largest flaw. It is thus not

surprising that attemps are being made to apply the concepts of fracture mechanics to quantify the resistance to cracking in cementitious composites (Shah et al., 1995).

The field of fracture mechanics originated in the 1920s with A.A. Griffith's work on fracture of brittle materials such as glass. According to Equation 2.1, as crack length is increase by a factor of four, the remote fracture stress is reduced by one-half. Therefore, it is expected that materials highly dependent on the presence and size of small cracks, or flaws (Philips and Struble, 2006).

$$\sigma_f = \sqrt{\frac{2E\gamma}{\pi a}} \qquad \textbf{(2.1)}$$

σ_f = Tensile cracking stress at the moment of fracture

E= Young's modulus

2γ =Fracture surface energy

a=Half of the critical crack length

2.3 Processes for Reducing Porosity in Concrete

Because of the flocculated behavior of the cement particles and workability problems, high amount of water above the desired amount for hydration is needed to be added which creates large voids and high porosity after curing. Therefore, the reduction of porosity has become a major goal in the processing of cement based materials and several methods have been developed to achieve this reduction. Table 2.2 lists the compressive and flexural strengths of different cement based materials (Falkner, 1989).

Table 2.2: Compressive and flexural strengths of different cement based materials

Processing Technique	Compressive Strength (MPa)	Flexural Strength (MPa)
Normal Strength Concrete	20-60	4-8
High Strength Concrete	60-115	6-10
Polymer impregnation	100-150	12-30
Densified small particles (DSP)	300-500	30-50
Reactive Powder Concrete	200-800	50-140
Macro Defect Free Cement (MDF)	400	150-300

Water/cement ratio is used to represent the porosity in order to explain the relation between porosity and strength. Amount of water, hence, water/cement ratio has been tried to be reduced by using superplasticizers in order to increase concrete strength without adversely affecting the concrete workability. In a recently developed application, which is called as self compacting concrete, high workability has been aimed even at low water/cement ratios. On the other hand, using polymers other than superplasticizers in the concrete technology is another developed method for reducing porosity and increasing strength. In this method, polymer resins are not only used as a binder but also impregnated into the hardened concrete or latex and emulsion-based polymers can be added into the concrete during mixture. In the so-called DSP (densified systems containing homogeneously arranged ultrafine particles) materials, the use of low w/c ratios (0.12-0.22), special aggregates, including fibres, and special processing conditions allows compressive strengths around 300 MPa to be obtained, with good resistance to abrasion and chemical attack. The particles of silica fume, being much finer than those of the cement, partially fill the spaces between the cement grains, and this, together with a superplasticizer, allows the latter to pack more uniformly (Taylor, 1997). The properties were attributed to combination of all effects. Reactive powder concrete is another successful application especially for increasing compressive strength b adjusting particle size. Unfortunately, effects of these methods over the material's tensile and flexural strength are limited. The tensile or flexural strengths of the cementitious materials, in general, about one-tenth of the compressive strengths, as in normal cement pastes or concretes (Taylor, 1997).

Opposite to all these methods, flexural strength is very high at macro defect free cements; more than 300 MPa flexural strengths are achieved in this method, which is nearly close to the strength of ordinary steels. Birchall et al. (1983) showed that samples of the same cement composition with the same amount of porosity but processed differently had flexural strengths varying by a factor of six. He postulated that the dominating factor for the strength of cements is the largest flaw size with the porosity of the system also being a factor. The simple empirical models based on porosity volume such as Feret, Bolomey and Graff models ignore the broad distribution and morphology of pores occuring in real cement pastes (Russell, 1991).

3 MACRO DEFECT FREE (MDF) CEMENTS

Macro Defect Free (MDF) cements, which are cement-polymer composites, have been innovated and patented by Birchall et al. (1981, 1983) from Imperial Chemical Industries (ICI) in England. Birchall et al. produced these materials by using cement, water and a water soluble polymer. Less than 25% water (generally 10-15%) and 1-15% polymer (generally 5-7%) were used for the production in addition to cement. Cement, polymer and water were mixed by using calendering machine and high shear forces were applied to the material in this way.

Achievement of very high flexural strengths is the most important advantage of this new material. Birchall et al. (1983) used different cements and polymers to obtain the highest flexural strength. They conducted series of tests by using poly(vinyl alcohol-co-vinyl acetate) copolymers (PVA), poly(acrylamide), poly(vinyl pyrollidone), poly(ethylene oxide), or hydroxypropyl methyl cellulose as a polymer and alumina cement and portland cement as a cement. The highest flexural strengths were obtained with the mixture of calcium aluminate cement and PVA while the second highest were obtained with ordinary portland cement (OPC) and poly(acrylamid). Birchall et al. (1983) had reached 177 MPa flexural strengths and it was a very important development if we compare it with ordinary cement paste which has only 5-10 MPa flexural strength. Further researches proved that conclusion and more than 300 MPa flexural strengths were obtained (Russell, 1991; Desai, 1992) which are close to the strength of ordinary steel.

This new composite material was named as macro defect free cements by Birchall et al. (1983) because of lack of macro voids. In addition, this material is also called as organo-cement composites, polymer cement composites or high flexural strength polymer-cement composites in the literature, because, the polymer has an important affect over the properties of this composite.

Inventors of MDF cements had attributed the high flexural strength of these composites to the elimination of macro voids in the material during high shear mixing process, and they thought that the polymer was a rheological aid and inert

filler. But now, we know that it is not the only reason to obtain high flexural strength. These high strengths are obtained by incorporating a water soluble polymer such as PVA in the cement and then treating the dough produced by pressure moulding, extrusion or calendaring (as in plastics and paper technology). Some researchers were also tried to obtain MDF cement without polymer by using the same procedure but high flexural strengths could not achieved. Therefore, polymer is not just a rheological aid. Probably these polymer chains are crosslinking with some ions of cements and they supply high flexural strength, as mentioned previously in Part 1.1.

On the other hand, serious durability problems were observed when these composites were contacted with water. Physical detoriation starts in few days and they lost sometimes more than half of their initial strength only in 1 week. There were some improvements on the water sensitivity of these composites but nobody found a satisfactory solution for preventing the strength loss of MDF cements in contact with water yet. Understanding the relation between inorganic cement and organic polymer in production of MDF cements is very important and it is not well understood yet. First of all, we need to investigate the materials which were used for the production of MDF cements.

3.1 Materials Used for the Production of MDF Cements

Cement, polymer and water are three main components of MDF cements. In addition, glycerol and some crosslinking additives can be added for different purposes. Birchall et al. (1983) used 60-70% cement, 1-15% polymer and less than 25% water by volume for the production of MDF cements. A proper water soluble polymer is necessary for the production of MDF cements. Previous studies showed that PVA copolymers and alumina cements are the most suitable components for the production of MDF cements. However, Pushpalal et al. (1997) have also proposed alcohol soluble polymers for this purpose.

Different cements, polymers and additives have been tested for the production of MDF cements. Table 3.1 lists the materials which were used for the production of MDF cements in literature. Some of them made some improvements for the moisture resistance of MDF cements but none of them seems acceptable enough yet. Using some of these materials for the production of MDF will be discussed more detail in Part 4.

Table 3.1: Polymers, cements and additives which were used for the production of MDF cement

Polymers	Cements	Additives
PVA with different hydrolysis and polymerization degrees (Birchall et al., 1983; etc.)	Calcium Aluminate Cement (Birchall et al., 1983; etc)	Glycerol, glycerin
Poly(acrylamid) (Sinclair, 1985; Poon, 1998; Santos, 1999; etc.)	Portland Cement (Sinclair and Groves, 1985; Santos, 1999)	Alkali metal silicate (Na_2O, K_2O) (Lynn et al, 1992)
Thermosetting acrylic resin (Brown, 1996)	Slag-modified cement (Santos et al., 1999)	Gypsum (Brown, 1996)
Phenol resin (Pushpalal et al., 1997; Pushpalal et al., 1999; Walberer and McHugh, 1998; etc.)		Activated carbon (Chowdhury, 2004a; Chowdhury, 2004b)
Hydroxy prophyl methyl cellulose (hpmc) (Eden and Bailey, 1984; Drabik et al., 1994, Drabik et al., 1999, etc.)		Organotitanete cross linking additive (Liutkus and Kovac, 1988)
Sodium polyphosphate glass (poly-P) (Drabik et al., 1999, Drabik et al. 2001; Mojumdar, 2001)		Silica fume (Santos et al., 1999)
		$CaCl_2$, $ZnCl_2$ (Poon et al., 1998)
		styrene/acrylonitrile co-polymer (SACP) (Mojumdar et al., 2004)

First of all, the properties of polymer and cement and their interaction should be examined in order to understand the reasons behind the high flexural strength and water sensitivity of MDF cements.

3.1.1 Cements

Cement, which comprises generally more than 80% by weight, is the main component of the MDF cements. Calcium aluminate cements (CAC) are more preferred cement type than portland cements or other types of cements for the production of MDF cements. Because, high flexural strengths of MDF cements are obtained by using this type of cement. Second most widely used cement type is the

portland cement. Slag modified cements are also used in some applications but the results showed that CACs are the best for producing MDF cements.

According to Sinclair and Groves (1985) and Santos (1999), MDF cements produced with ordinary portland cement and poly(acrylamide) are less sensitive against water when they are compared with the calcium aluminate cement (CAC)-poly(vinyl alcohol-co-vinyl acetate) (PVA) systems; however, the highest flexural strengths were always obtained with CAC-PVA combination. Therefore, researches about MDF cements mostly concentrated on CAC-PVA systems.

3.1.1.1 Calcium aluminate cements (CAC)

Calcium aluminate cement (CAC), which is also known as alumina cement or high alumina cement, was developed for sulphate resistant applications while it also supplies high early strength and resistance to high temperatures. CACs can also be used for the production of macro-defect-free cements and it is reported that MDF prepared with CAC gives more strength than the other cements (Birchall et al., 1983). It is considered that strong crosslinking reactions take place between Al ions and polymer chains in MDF (Rodger et al., 1984; Rodger et al., 1985; Popoola et al., 1991; and Bonapasta et al., 2000).

Main reactive phases of calcium aluminate cements are lime (CaO) and alumina (Al_2O_3) compounds whereas ordinary portland cements (OPC) are based mainly upon lime and silica (SiO_2) phases. Fe_2O_3, FeO, SiO_2, TiO_2, MgO, K_2O, Na_2O and SO_3 can also be found in minor amounts in the composition of CACs. Typical compositions of different calcium aluminate cements can be seen in Table 3.2.

Table 3.2: Typical compositions of calcium aluminate cements (mass percentages) (Taylor, 1997)

Type of cements	Al_2O_3	CaO	Fe_2O_3	FeO	SiO_2	TiO_2	MgO	K_2O+Na_2O	SO_3
Ciment Fondu	38-40	37-39	15-18	3-6	3-5	2-4	<1.5	<0.4	<0.2
40% Alumina	40-45	42-48	<10	<5	5-8	~2	<1.5	<0.4	<0.2
50% Alumina	49-55	34-39	<3.5	<1.5	4-6	~2	~1	<0.4	<0.3
50% Al_2O_3 (low Fe)	50-55	36-38	<2	<1	4-6	~2	~1	<0.4	<0.3
70% Alumina	69-72	27-29	<0.3	<0.2	<0.8	<0.1	<0.3	<0.5	<0.3
80% Alumina	79-82	17-20	<0.25	<0.2	<0.4	<0.1	<0.2	<0.7	<0.2

3.1.1.2 Phases and structure of calcium aluminate cements

Main phases of four different calcium aluminate cements which differ in their Al_2O_3 content between 40% and 80% can be seen in Table 3.3. Used cement chemistry nomenclature was A=Al_2O_3; C=CaO; F=Fe_2O_3; H=H_2O; S=SiO_2; $\bar{S}$=SO_3;. Thus CA_2=CaO.2Al_2O_3 and C_2S=2CaO.SiO_2.

Table 3.3: Typical compositions of calcium aluminate cements (Struble, 2006)

	40% Al_2O_3	**50% Al_2O_3**	**70% Al_2O_3**	**80% Al_2O_3**
CA	Major	Major	Major	Major
CA_2	Trace	Minor	Major	Minor
A	----	Minor	Minor	Major
$C_{12}A_7$	Trace	Minor	Trace	Trace
C_4AF	Major	----	----	----
FeO	Minor	----	----	----
Pleochroite	Minor	----	----	----
β-C_2S	Minor	Minor	----	----
C_2AS	Minor	Minor	----	----

The lime-alumina phase diagram (Figure 3.1), which was first published by Rankin and Wright in 1915 and developed by other researchers, shows the presence of five calcium aluminate compounds C_3A, $C_{12}A_7$, CA, CA_2 and CA_6.

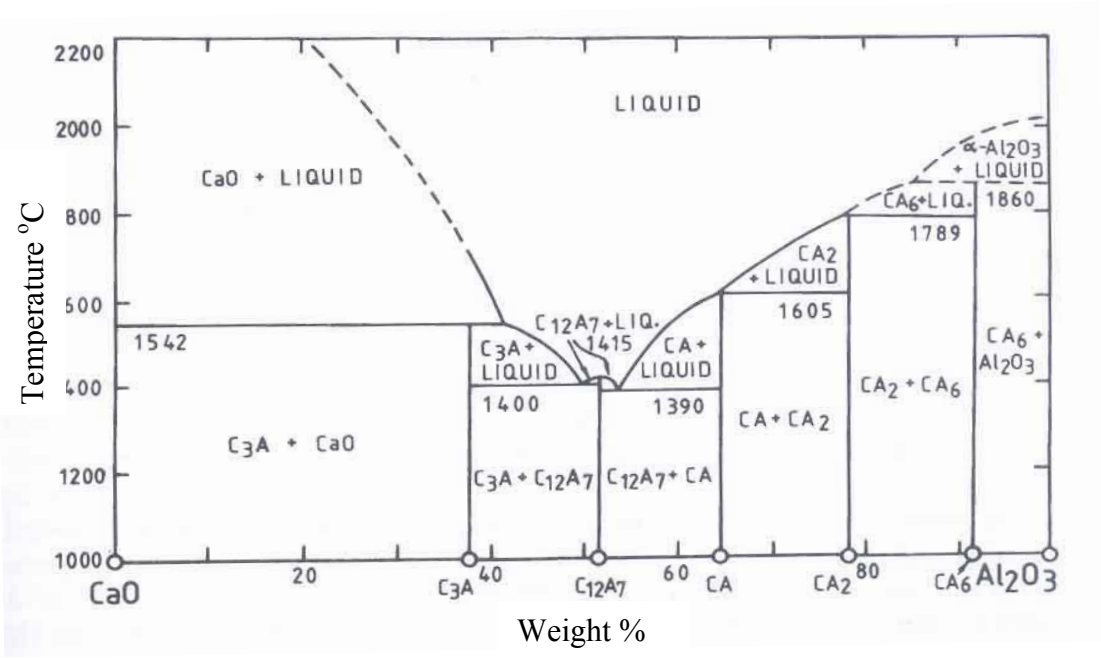


Figure 3.1: The lime-alumina binary phase diagram (Taylor, 1997)

As a rule, the reactivity of calcium aluminates increases as lime content increases, making C_3A the most reactive compound of these compounds as can be seen from the phase diagram. This is because the dissolution and re-crystallisation reactions are much quicker for compounds of increasing lime content. However, refractory property of the calcium aluminate compound increases when the alumina content increased (phases on the right having higher melting points) (Ceram Res. Ltd., 2007).

- **Calcium Mono-Aluminate (CA)**

Calcium mono-aluminate (CA), which has a monoclinic unit cell, is the principal hydraulic mineral present in calcium aluminate cement. Its hydration contributes to the high early strength of CACs. Figure 3.2 shows a model of its crystal structure (Myers, 2007a).

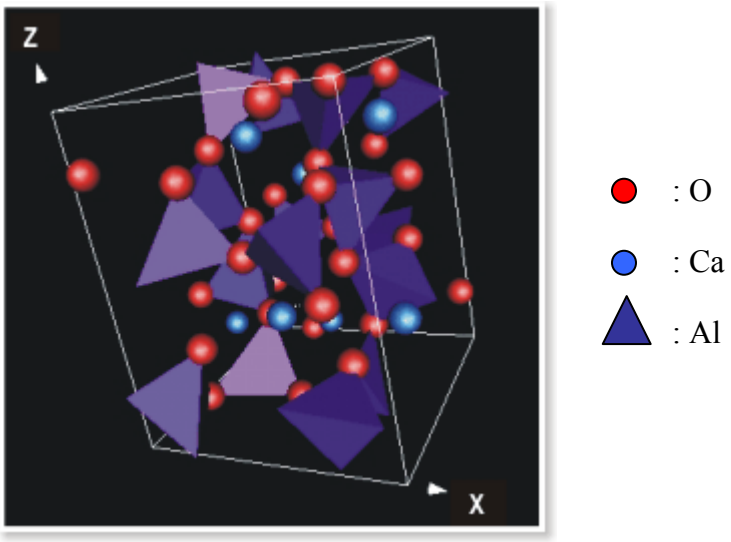


Figure 3.2: Crystal structure of calcium mono-aluminate (Myers, 2007a)

- **Calcium Di-Aluminate-Grossite (CA_2)**

Calcium di-aluminate or grossite (CA_2) has a monoclinic structure similar to CA. However, CA_2 phase tends to be more refractory in nature than CA, and less reactive to water. The hydration of CA_2 is reported to be accelerated at higher temperature and also in the presence of CA. CA_2 hydrating on its own imparts a lower strength than CA after 24 hours of curing. Grossite's crystal structure is shown in Figure 3.3 (Myers, 2007a).

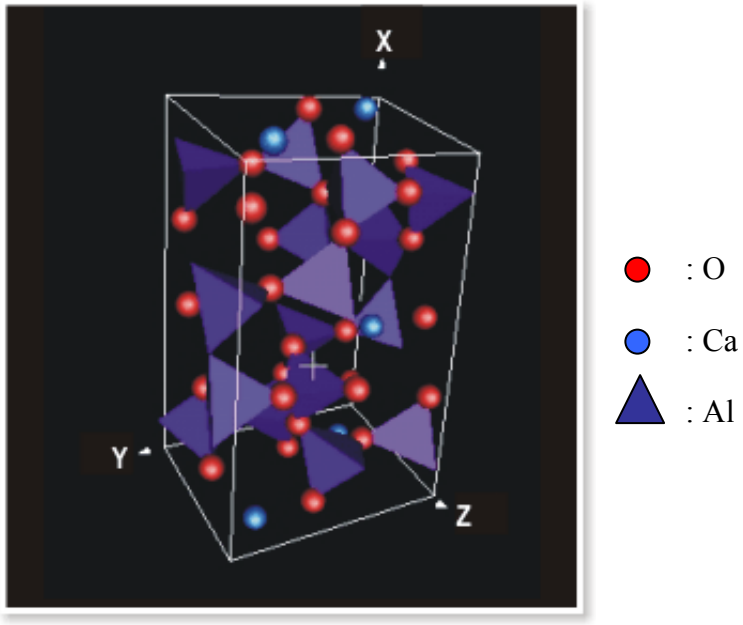


Figure 3.3: Crystal structure of calcium di-aluminate (grossite) (Myers, 2007a)

• **Dodecacalcium Hepta-Aluminate–Mayenite ($C_{12}A_7$)**

Dodeca-calcium hepta-aluminate or mayenite ($C_{12}A_7$) is the most reactive of all calcium aluminate species occurring in CACs, and hydrates very rapidly in contrast to CA and CA_2. Due to this fact, the amount of mayenite contained in calcium aluminate is very carefully regulated by manufacturers (Myers, 2007a).

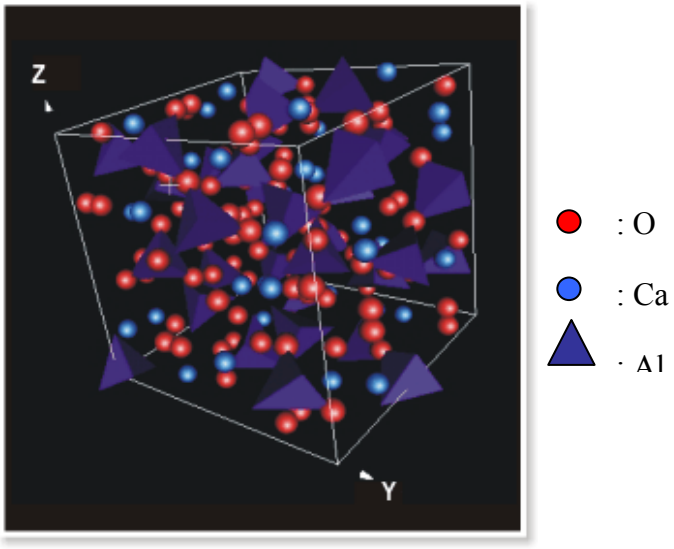


Figure 3.4: Crystal structure of mayenite (Myers, 2007a)

• **Other Calcium Aluminate Phases**

Calcium hexa-aluminate (CA_6) is non-hydraulic and more refractory than the other phases; having a melting point of 1870°C. CA_6 is formed in refractory castable products when they are heated to high temperatures. Tri-calcium aluminate (C_3A) is

the most reactive phase of all calcium-aluminate phases. However, it is only present in portland cements (Myers, 2007a).

3.1.1.3 Phases and structure of calcium aluminate hydrates

There are three fundamental calcium aluminate hydrates that are formed during the hydration of CAC. These are two meta-stable phases, CAH_{10} and C_2AH_8, and the stable phase C_3AH_6 (hydrogarnet or katoite). Further to these species, alumina tri-hydrate (AH_3) phases often occur during the hydration, these could be either as an amorphous gel or the crystalline phase gibbsite (Myers, 2007b).

- **Calcium Aluminate Decahydrate (CAH_{10})**

Calcium aluminate decahydrate (CAH_{10}) is a meta-stable hydrate and it is typically formed when calcium aluminates are mixed with water at temperatures below 20°C. CAH_{10} has a deformed-orthorhombic unit cell, which can be seen in Figure 3.5. CAH_{10} forms hexagonal platelets of poorly crystallised material making its identification by X-ray diffraction (XRD) often difficult. However, when CAH_{10} is heated, it will dehydrate between 120°C and 130°C with an endothermic reaction. Thus, it can easily be detected using differential thermal analysis (DTA). (Myers, 2007b).

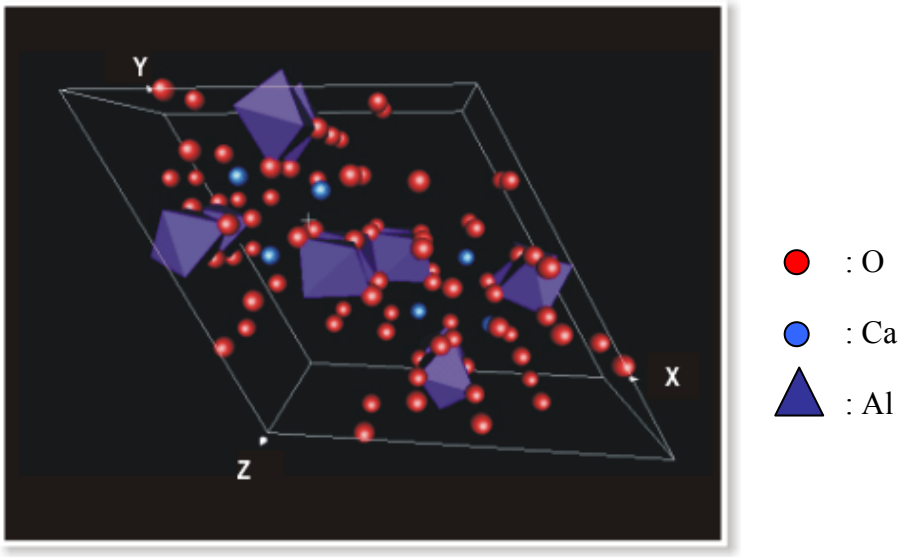


Figure 3.5: Crystal structure of CAH_{10} (Myers, 2007b)

- **Dicalcium Aluminate Octahydrate (C_2AH_8)**

Dicalcium aluminate octahydrate (C_2AH_8) is another meta-stable calcium aluminate hydrate. C_2AH_8 occurs in the temperature range 21°C - 30°C and it dehydrates in the

region of 210°C to 230°C with a characteristic endothermic peak. It tends to precipitate out of solution as a thin hexagonal platelet similar to CAH_{10} (Myers, 2007b).

• **Tricalcium Aluminate Hexahydrate (C_3AH_6) – Katoite**

Tri-calcium aluminate hexahydrate or hydrogarnet (katoite) is the most stable of all calcium aluminate hydrates. It has a cubic unit cell, which can be seen in Figure 3.6. C_3AH_6 occurs at higher ambient temperatures and dehydrates between 300 and 350°C, forming first $C_3AH_{1.5}$ before undergoing complete dehydration around 500°C. It will not undergo transformation into other hydrates like CAH_{10} and C_2AH_8 (Myers, 2007b).

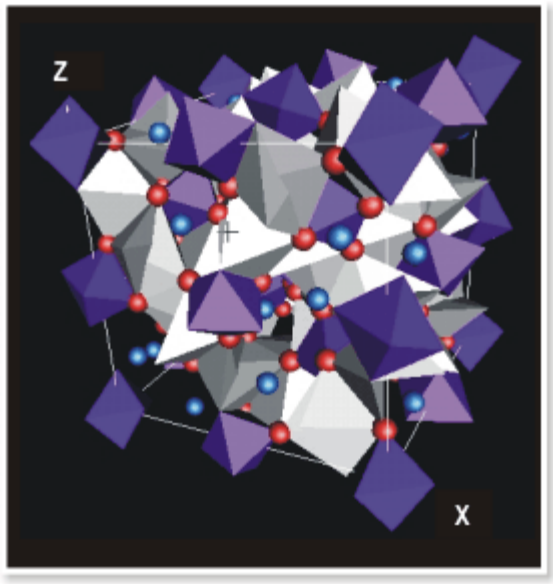


Figure 3.6: Crystal structure of C_3AH_6 (Myers, 2007b)

3.1.1.4 Formation of hydrated species and conversion

The formation of the hydrated species is very temperature dependent. Certain hydrates are formed at specific temperatures**.** CAH_{10} is formed at lower temperatures typically below 20°C. In the intermediate temperature, ranges between 21 and 30°C, C_2AH_8 is formed. Under conditions of elevated temperature, C_3AH_6 is formed, which is the most thermodynamically stable and the least soluble of the calcium aluminate hydrates. In addition to the hydrates formed at intermediate temperatures crystalline gibbsite (AH_3) is formed. Figure 3.7 shows the hydration pathway of the CA phase (Myers, 2007c).

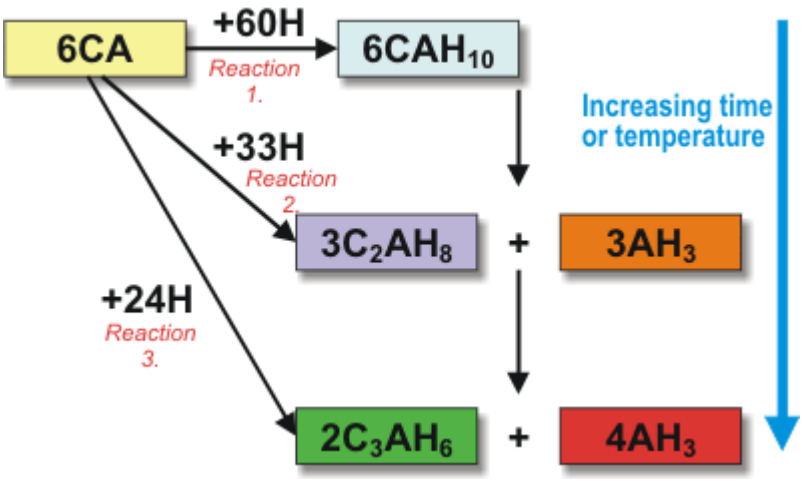


Figure 3.7: Hydration pathway of calcium mono-aluminate (Myers, 2007c)

CAH_{10} and C_2AH_8 transform into the hydrogarnet phase (C_3AH_6) with long periods of time or at elevated temperatures due to their meta-stable nature. This reaction is known as conversion. Conversion is initiated by the nucleation of C_3AH_6 and takes place in solution. There is a 52.5% reduction in the transformation from CAH_{10} to C_3AH_6, and during the change from C_2AH_8 to C_3AH_6 there is 33.7% reduction. Because of these changes, the porosity increases and strength decreases. Another effect of conversion is the release of water from the hydrates. A major impact of this is increase in porosity and shrinkage, which decreases mechanical strength. Conversion is a very important subject in the field of calcium aluminate cements and the phenomenon has been responsible for the failure of many buildings and bridges (Myers, 2007c).

3.1.1.5 Methods for the determination of phases in cement

Various techniques are used for determining the phases or hydration products of cement or cement based materials. Information about these methods is given in this part. Some of these techniques are also summarized in Table 3.4.

Table 3.4: Principal methods for the determination of portland cement clinker composition (Glasser, 2004)

Method	Applications area
Direct methods	
X-ray powder diffraction	Relates X-ray reflection intensity to phase content
Optical microscopy	Requires polished and etched thin section of clinker
Scanning electron microscopy with analysis	Closely related to optical microscopy; more expensive but also capable of automation; more versatile since chemical differences can also be measured
Supplementary methods	
Selective dissolution	Chemical free-lime determination is a widely used example; other methods are occasionally used. Requires judicious selection of reagents
Thermal analysis	Determination of thermally active phases in mixtures, e.g. gypsum content by thermogravimetry
Indirect methods	
Bogue calculation	Converts chemical analysis to potential phase composition; does not actually require measurements on a clinker, so useful for trial calculations
Hybrid methods	
Modified Bogue-type calculation	Uses Bogue-type calculation but additionally incorporates experimentally determined corrections, e.g. for chemically determined free lime, Ca contained in residual anhydrite, and solid solution corrections, using realistic formulae

- **X-Ray Diffraction**

"Powder X-ray Diffraction (XRD) is one of the primary techniques used by mineralogists and solid state chemists to examine the crystalline phases of unknown solids. This technique takes a sample of the material and places a powdered sample in a holder, then the sample is illuminated with x-rays of a fixed wave-length and the intensity of the reflected radiation is recorded using a goniometer. Obtained data is then analyzed for the reflection angle to calculate the inter-atomic spacing (D value in Angstrom units - 10^{-8} cm). The intensity (I) is measured to discriminate (using I ratios) the various D spacings and the results are compared with the powder diffraction file (pdf) to identify possible matches" (Barthelmy, 2005).

"Powder diffraction patterns are compiled from journals, the International Centre for Diffraction Data (ICDD) Grant-in-aid Program, other grants and scientific contributions. The patterns are edited for correctness, and reviewed for quality and uniqueness by various experts of the field. Subfile mark assignment was also conducted by the editors. The PDF currently (2001 release) consists of 51 sets of data

and 136895 patterns (over 87500 experimental and 49000 patterns calculated from the ICSD (Inorganic Crystal Structure Database maintained by Fachsinformationzentrum (FIZ) in Karlsruhe and National Institute of Standards and Technology (NIST)). The file covers ceramic mineral, metal/alloy, organic and other inorganic crystalline materials. The PDF is subdivided into various subfiles, such as inorganic, mineral, organic, metal/alloy, common phases, ICSD, forensic, education, zeolite, explosive, superconductors, cement, corrosion, polymer, detergent, pigment, pharmaceutical, ceramics, and a separate subfile for the NBS patterns" (Wong-Ng et al., 2001)

It has long been recognised that X-ray diffraction (QXRD) offers great potential for the quantitative analysis of cement and clinker phases. Unlike optical methods, which only accept physically small and possibly unrepresentative samples, it is easier to obtain representative bulk samples for X-ray diffraction. However, QXRD does present a number of potential pitfalls. Struble (1983, 1991) has suggested that the difficulties of achieving quantitative analysis are of two types: those inherent to QXRD itself and those which are peculiar to cement clinker (Glasser, 2004). ASTM developed a standard (ASTM C 1365-06) recently for the determination of the proportion by mass of individual phases in portland cement and portland cement clinker using X-Ray powder diffraction analysis.

The present state of the art summarised by Glasser (2004) as follows: "Satisfactory quantitative procedures presently exist for determining the amounts of MgO (periclase) and C_3A, both cubic and orthorhombic, in clinker. Ferrite determination is satisfactory but perhaps less accurate due to its variable composition and associated complexities. Problems associated with quantitative determination of C_3S and C_2S are, as yet, not fully resolved although some workers claim to have developed satisfactory procedures. Clinker from a particular plant may well present fewer problems of consistent analysis than clinkers made at different plants, from different raw materials and with different processing conditions, the consequences of which are that the suite of clinkers may contain different polymorphic variants of C_3S and C_2S. Other minor clinker phases which can probably be determined quantitatively include alkali sulfates, calcium langbeinite, free lime (CaO), the calcium sulfates (gypsum, anhydrite) and calcium carbonate (calcite, aragonite)".

- **Scanning Electron Microscopy**

"The advent of image analysis, coupled with scanning electron microscopy (SEM), opens new possibilities for the quantitative analysis of clinker. Like the optical microscope, SEM examination of suitably prepared specimens will reveal a wealth of detail on the clinker microstructure. The interaction of the electron beam with the specimen can be used to generate additional information. Three signals are useful: the low-energy secondary electrons, used to image surface topography; high-energy backscattered electrons and X-rays. The backscattered electron images are sensitive to the mean atomic number of the surfaces and give chemical contrast to the image - useful for rapid phase identification and point counting techniques, similar to those described for optical microscopy - while the X-rays can be analysed with a suitable detector system, also giving a chemical image. The X-ray image of the surface may be qualitative or, with suitable calibration of X-ray production, quantitative. The interstitial phases of clinker are often difficult to resolve by optical microscopy, the useful magnification limit of which is 500-1000x. However, even relatively inexpensive scanning electron microscopes give good analytical resolution in the range up to 2000x, which assists greatly in analysing the fine-grained interstitial phases, mainly aluminate and ferrite" (Glasser, 2004).

- **Miscellaneous Techniques**

"For bulk analysis, the majority of the world's cement plants probably use XRF (X-ray fluorescence). The equipment is expensive to buy but is rapid and, moreover, accommodates either solid or liquid samples. It can determine quantitatively all major elements likely to be present in cement raw materials and clinkers, with the exception of water and CO_2."

"Some plants still use wet chemistry for clinker and raw material analyses although traditional gravimetric and volumetric methods are often partly supplanted by more modern methods, usually using electrical detection or spectrophotometry. Examples include solution ion chromatography and atomic absorption (AA), respectively. The latter requires a liquid sample which is aspirated directly into a flame or, for greater sensitivity, into a heated graphite furnace. The method also requires a source of radiation characteristic of the element sought, e.g. a calcium lamp is required for a calcium determination. AA is also suitable for major element determination but analytes may require high dilutions to come within the working range of the

instrument, i.e. the range in which response is a linear function of composition. Interferences are most commonly encountered with the easily ionised elements, for example sodium and potassium and, for this reason, many laboratories continue to determine alkalis by the simple but robust method of flame photometry, using AA for the other elements. Many AA instruments can be operated in the flame photometry mode."

"Neither AA nor XRF will distinguish the oxidation state of a species; for example, they will not distinguish between Fe^{+2} and Fe^{+3}. Classical methods are still employed for the determination of oxidation state but, alternatively, polarography or ion chromatography may be used provided the balance of oxidation states remains stable upon dissolution. Both cation and anion-detecting columns are available for ion chromatography; the latter is particularly useful for anions, e.g. Cl^-, CO_3^- and SO_4^{-2}, which are either not detectable or only poorly detected by other techniques."

"Emission spectroscopy, with the advent of improved ionisation and detector systems, has had a new lease of life for the determination of trace or ultratrace elements. Basically, the technique accepts solid samples which are vaporised using arc discharge, spark or plasma. Stable plasmas, comprised mainly of argon, are sustained by inductively coupling the hot cloud of ionised gas to an electrically driven radio-frequency coil, hence the further development of ICP (inductively coupled plasma). ICP is best suited to the analysis of liquid samples which are directly injected into the plasma. The concentrations of numerous atoms can be measured directly and simultaneously by atomic emission (ICP-AES) or indirectly by coupled mass spectroscopy (ICP-MS). Both can have high sensitivities; for example, ICP-MS may have detection limits in the part-per-billion (ppb) or sub-ppb (parts per 10^9) range but, since the response curve of the MS detector is linear over many orders of magnitude concentrations, the method is also suitable for major element determinations, A limitation is that the total solids content of solutions aspirated into the plasma needs to be kept low."

"Gas chromatography (GC) and liquid chromatography (LC) have also been increasingly used. The choice of detector systems depends on the nature of the analysis: detector systems based on infrared (IR) or fourier transform infrared (FTIR), nuclear magnetic resonance (NMR) and mass spectroscopy (MS) are all commercially available."

"The nature and condition of the surfaces or near-surface layers of clinker phases may influence their reactivity. Two closely related techniques, electron spectroscopy for chemical analysis (ESCA) and X-ray photoelectron spectroscopy (XPS), have been developed which are particularly suited to the analysis of solid surfaces. Bombardment of the surface by X-rays releases photoelectrons which are detected and analysed according to kinetic energy. This reveals details of bonding of individual atom species: oxygen, calcium, silicon, etc. Unfortunately, hydrogen cannot be detected. The technique has, however, been useful in distinguishing the oxidation state of elements such as sulphur and iron in the near-surface layers of clinker minerals."

"NMR may also be used as a bulk technique. The principal nuclei in cement clinkers which are NMR sensitive include ^{29}Si, ^{27}Al and ^{13}C. The technique senses the bonding of the particular atom: thus monomeric silicon, SiO_4^{4-}, can be distinguished from dimeric and other more highly polymerised states of silicon. For example, the isolated tetrahedral which occur in both Ca_2SiO_4 and Ca_3SiO_5 can be distinguished from more polymerized silicon occurring in rankinite, $Ca_3Si_2O_7$. The selection of experimental conditions for the analysis of solids and interpretation of results are not straightforward and, moreover, the presence of iron degrades the quality of the signal. Much of the work on cements has therefore had to be carried out on pure (or nearly so) single phases or, for clinkers, using white cement clinkers low in iron."

"Clinker components and batches may also be analysed by thermal methods. The development of simultaneous differential thermal analysis (DTA) and thermogravimetric analysers (TGA) have simplified the correlation of results from these two complimentary techniques. Many modern DTA-TGA systems have relatively small gas volumes, so that when gas is evolved in the course of reaction it is also possible to apply evolved gas analysis (EGA): both chromatographic and mass spectroscopic techniques can be used for analysis. Species-specific electrochemical or optical sensors are also available if it is known what gas is being sought. In this way, the chemical nature of the gas species and amount of each component can be determined" (Glasser, 2004).

3.1.1.6 The hydration of aluminous cement with added poly(vinyl alcohol-co-vinyl acetate)

Edmonds and Majumdar (1989) studied the hydration of Secar 71 high alumina cement with added poly(vinyl alcohol-co-vinyl acetate). They used four types of polymers for the production of macro-defect-free cements. The polymers were abbreviated as KH, GH, GL and NH. The first three were partially hydrolysed poly(vinyl alcohol-co-vinyl acetates); NH was almost pure poly(vinyl alcohol). The course of the hydration reaction was followed using conduction calorimetry, X-ray diffraction, electron probe microanalysis and infrared spectroscopy. Figure 3.8 shows the conduction calorimeter output from pure Secar and Secar+polymer (ratio:10+1) mixtures using KH, GH and NH polymers, hydrated at 20°C. The polymer mixtures gave much lower, broader peaks than the pure Secar, and the total heat output was reduced from 270 to about 220 kJ per kilogram of dry solid. With the partially hydrolysed acetates KH and GH, there are two calorimeter peaks at about 6 and 36 h. With KH the first peak was the higher one, while with GH the two are about equal in intensity. Between these times, the hydrating material was flexible, with a dry, rubbery texture. After the second peak they became brittle. The fully hydrated NH polymer gave only the second peak and did not go through a flexible phase.

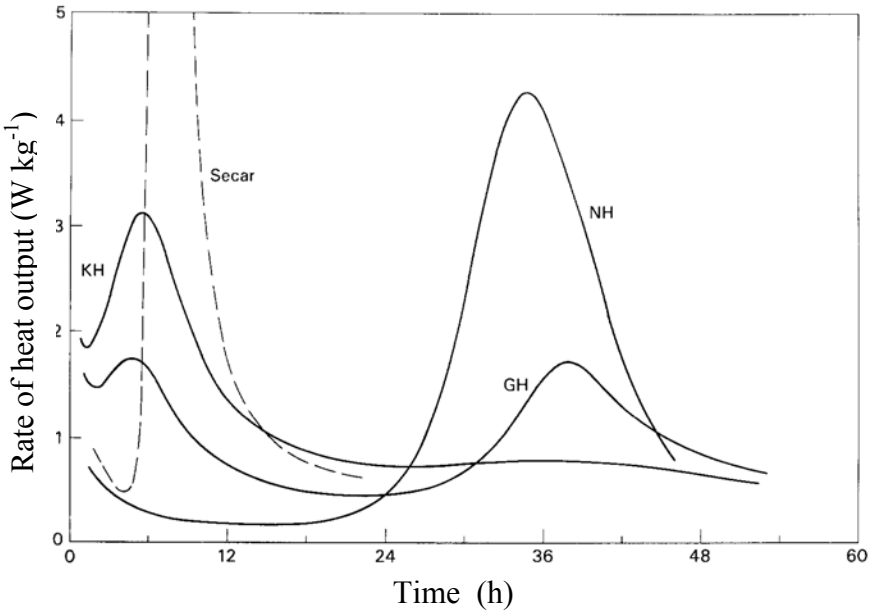


Figure 3.8: Conduction calorimeter output from Secar + polymer (ratio: 10 + 1) mixes and from pure Secar, at 20 ^{o}C (Edmonds and Majumdar, 1989)

The most interesting feature of the X-ray results was that crystalline hydrates are formed very slowly and in small quantities. With pure Secar, slightly more CA and CA_2 are consumed and a large quantity of CAH_{10} is produced. Such crystalline hydrates as do form in the polymer mixes tend to be calcium-rich; thus the KH mix gave C_3AH_6 but no CAH_{10} and the NH mix gave CAH_{10}, C_2AH_8 and C_3AH_6. With pure Secar C_2AH_8 is not formed at 20°C and C_3AH_6 occured only after long periods by conversion of CAH_{10}. Table 3.5 shows the composition of secar+polymer (ratio: 10 + 1) mixes after 3 days hydration (Edmonds and Majumdar, 1989). It appears that the presence of polymer inhibits the formation of crystalline calcium aluminate hydrates.

Table 3.5: Composition (%) of Secar + polymer (ratio: 10 + 1) mixes hydrated for 3 days at 20 ^{O}C (Edmonds and Majumdar, 1989)

	CA	CA_2	C_2AH_8	C_3AH_6	CAH_{10}
KH	20	38	0	0	0
GH	16	33	0	1	0
NH	15	31	3	1	4
pure Secar*	14	30	0	0	24

*Hydrated for 24 h

3.1.2 Polymers

3.1.2.1 Historical development

History of the plastics industry is recognized as having its beginnings in 1868 with the synthesis of cellulose nitrate. It was started with the shortage of ivory from which billiard balls were made. The manufacturer of these balls, seeking another production method, sponsored a competition. John Wesley Hyatt (in the U.S.) mixed pyroxin made from cotton (a natural polymer) and nitric acid with camphor. The result was cellulose nitrate, which he called celluloid. Hyatt, whose independent discovery of celluloid, was the first to take out patents for this discovery. Cellulose nitrate was derived from cellulose, a natural polymer. However, the first truly man-made plastic came 41 years later (in 1909) when Dr. Leo Hendrick Baekeland developed phenol–formaldehyde plastics (phenolics), the source of such diverse materials as electric iron and cookware handles, grinding wheels, and electrical plugs. Other polymers —

cellulose acetate (toothbrushes, combs, cutlery handles, eyeglass frames); urea–formaldehyde (buttons, electrical accessories); poly(vinyl chloride) (flooring, upholstery, wire and cable insulation, shower curtains); and nylon (toothbrush bristles, stockings, surgical sutures) —followed in the 1920s (Ebewele, 2000).

Table 3.6 gives a list of some plastics, their year of introduction, and some of their applications. “The pace of development of plastics, which was slow up to the 1920s, picked up considerable momentum in the 1930s and the 1940s. The first generation of man-made polymers was the result of empirical activities; the main focus was on chemical composition with virtually no attention paid to structure. However, during the first half of the 20th century, extensive organic and physical developments led to the first understanding of the structural concept of polymers– long chains or a network of covalently bonded molecules. In this regard, the classic works of the German chemist Hermann Staudinger on poly(oxymethylene) and rubber and of the American chemists W. T. Carothers on nylon stand out clearly. Staudinger first proposed the theory that polymers were composed of giant molecules, and he coined the word macromolecule to describe them. Carothers discovered nylon, and his fundamental research (through which nylon was actually discovered) contributed considerably to the elucidation of the nature of polymers. His classification of polymers as condensation or addition polymers persists today.” (Ebewele, 2000).

“In the 1930s, acrylic resins (signs and glazing); polystyrene (toys, packaging and housewares industries); and melamine resins (dishware, kitchen countertops, paints) were introduced. Poly(ethylene), now one of the most important plastics in the world, was developed because of the wartime need for better-quality insulating materials for such applications as radar cable. Thermosetting polyester resins (now used for boatbuilding) were developed for military use. The terpolymer acrylonitrile-butadiene-styrene (ABS), (telephone handsets, luggage, safety helmets, etc.) owes its origins to research work emanating from the wartime crash program on large-scale production of synthetic rubber.”

Table 3.6: Introductions of plastics materials (Ebewele, 2000)

Date	Material	Typical Use
1868	Cellulose nitrate	Eyeglass frames
1909	Phenol–formaldehyde	Telephone handsets, knobs, handles
1919	Casein	Knitting needles
1926	Alkyds	Electrical insulators
1927	Cellulose acetate	Toothbrushes, packaging
1927	Poly(vinyl chloride)	Raincoats, flooring
1929	Urea–formaldehyde	Lighting fixtures, electrical switches
1935	Ethyl cellulose	Flashlight cases
1936	Poly(acrylonitrile)	Brush backs, displays
1936	Poly(vinyl acetate)	Flashbulb lining, adhesives
1938	Cellulose acetate butyrate	Irrigation pipe
1938	Poly(styrene)	Kitchenwares, toys
1938	Nylon (polyamide)	Gears, fibers, films
1938	Poly(vinyl acetal)	Safety glass interlayer
1939	Poly(vinylidene chloride)	Auto seat covers, films, paper, coatings
1939	Melamine–formaldehyde	Tableware
1942	Polyester (cross-linkable)	Boat hulls
1942	Poly(ethylene) (low density)	Squeezable bottles
1943	Fluoropolymers	Industrial gaskets, slip coatings
1943	Silicone	Rubber goods
1945	Cellulose propionate	Automatic pens and pencils
1947	Epoxies	Tools and jigs
1948	Acrylonitrile-butadiene-styrene copolymer	Luggage, radio and television cabinets
1949	Allylic	Electrical connectors
1954	Poly(urethane)	Foam cushions
1956	Acetal resin	Automotive parts
1957	Polypropylene safety helmets	Safety helmets, carpet fiber
1957	Poly(carbonate)	Appliance parts

Table 3.7: (continued) Introductions of plastics materials (Ebewele, 2000)

1959	Chlorinated polyether	Valves and fittings
1962	Phenoxy resin	Adhesives, coatings
1962	Polyallomer	Typewriter cases
1964	Ionomer resins	Skin packages, moldings
1964	Poly(phenylene oxide)	Battery cases, high temperature moldings
1964	Polyimide	Bearings, high temperature films and wire coatings
1964	Ethylene–vinyl acetate	Heavy gauge flexible sheeting
1965	Polybutene	Films
1965	Polysulfone	Electrical/electronic parts
1970	Thermoplastic polyester	Electrical/electronic parts
1971	Hydroxy acrylates	Contact lenses
1973	Poly(butylene)	Piping
1974	Aromatic polyamides	High-strength tire cord
1975	Nitrile barrier resins	Containers

"The 1960s and 1970s witnessed the introduction of new plastics: thermoplastic polyesters (exterior automotive parts, bottles); high-barrier nitrile resins; and the so-called high-temperature plastics, including such materials as poly(phenylene sulfide), poly(ether sulfone), etc. The high-temperature plastics were initially developed to meet the demands of the aerospace and aircraft industries. Today, however, they have moved into commercial areas that require their ability to operate continuously at high temperatures" (Ebewele, 2000).

"In recent years, as a result of better understanding of polymer structure–property relationships, introduction of new polymerization techniques, and availability of new and low-cost monomers, the concept of a truly tailor-made polymer has become a reality. Today, it is possible to create polymers from different elements with almost any quality desired in an end product. Some polymers are similar to existing conventional materials but with greater economic values, some represent significant improvements over existing materials, and some can only be described as unique materials with characteristics unlike any previously known to man. Polymer materials can be produced in the form of solid plastics, fibers, elastomers, or foams.

They may be hard or soft or may be films, coatings, or adhesives. They can be made porous or nonporous or can melt with heat or set with heat" (Ebewele, 2000).

3.1.2.2 Polymer modification of cement and concrete

Polymer modification for cement mortar and concrete is dated back to the patents of Cresson (1923) and Lefebure (1924). Since then, many polymer modified systems have been developed and currently in use in the construction industry for improving the properties such as strength, deformability, adhesion, waterproofness and durability of cement mortar and concrete (Ohama, 1998). Polymer based admixtures which can be used as cement modifier were classified by Ohama (1998) as shown in Figure 3.9.

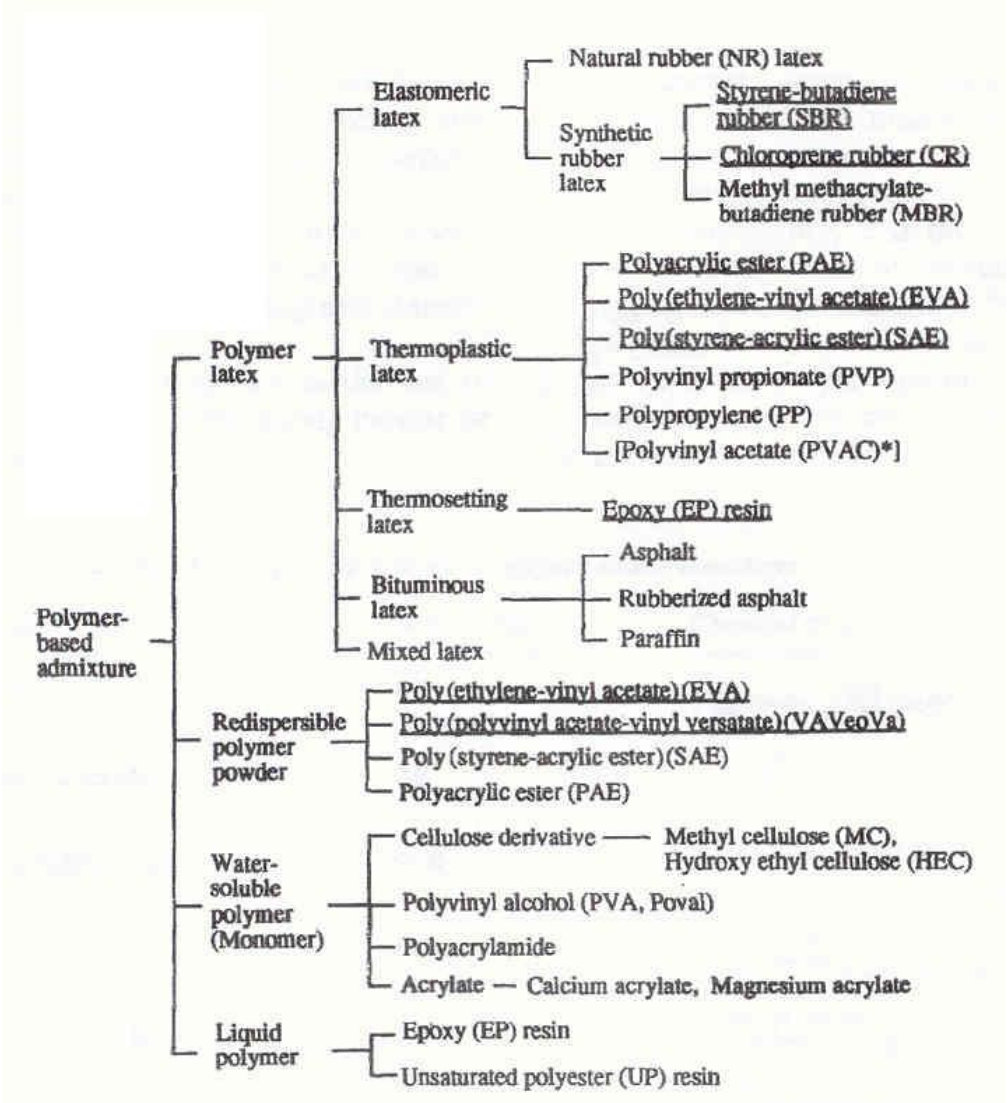


Figure 3.9: Classification of polymer-based (or polymeric) admixtures. *At present, PVA is not used because of its very poor water resistance (Ohama, 1998)

Polymers are used in concrete too and these polymer-cement composites can be classified as polymer impregnated concrete (PIC), polymer concrete (PC), and polymer modified concrete (PMC).

"PIC was produced by impregnating hydrated portland cement concrete with a low viscosity monomer, usually methyl methacrylate, which was subsequently polymerized by radiation or thermal catalytic techniques. PIC typically developed compressive strengths three to four times greater than the concrete from which it was made, had corresponding increases in tensile and flexural strength, and had excellent durability, particularly freezing and thawing and acid resistance, due to its extremely low permeability. Inexplicably, the modulus of elasticity was 50-100% higher than normal concrete even though the modulus of the polymer is no more than 10% of the concrete modulus. With such outstanding properties, many applications for PIC were forecast, including bridge decks, pipes, and conduits for aggressive fluids, floor tile, building cladding, hazardous waste containment, post-tensioned beams and slabs, and stay-in-place formwork" (Fowler, 1999).

"PC consists of aggregate with a polymer binder and contains no portland cement or water. Poly(ester-styrene), acrylics and epoxies have been the most widely used monomers/resins, but vinyl ester, furan, and urethane, have also been used. Sulphur is also considered to be a polymer and sulphur concrete has been used for applications requiring high acid resistance" (Fowler, 1999).

"PMC consists of portland cement concrete with a polymer modifier such as acrylic or styrene-butadiene latex (SBR), poly(vinyl alcohol-co-vinyl acetate), and ethylene vinyl acetate. From a construction standpoint PMC has the desirable attribute of being very similar to conventional portland cement concrete technology. The amount of polymer is usually in the range of 10±20% of the portland cement binder. There are only a few polymers suitable for adding to concrete; most polymers would produce poor quality PMC" (Fowler, 1999).

3.1.2.3 Using polymers for the production of MDF cements

The polymer have at least 3 functions in MDF cements: (1) it acts as a rheological aid and coating individual cement particles (2) it acts as pore filler, in voids between unreacted cement grains, and (3) it interacts chemically with the cement hydration products to form an integral microstructural feature referred to as the interphase region (Desai, 1994).

Birchall et al. (1983) proposed the water soluble or redispersible polymers as the most suitable polymers for MDF cement production. However, Pushpalal et al. (1997) succeeded to produce MDF cements with alcohol soluble polymers like phenol resin precursors instead of water soluble polymers. Poly(vinyl alcohol-co-vinyl acetate) copolymers, poly(acrylamide) and cellulosic products are the most preferred polymers for the production of MDF cements. Especially PVA copolymers are preferred for this purpose and in order to understand the reasons behind the strength loss in contact with water, the properties of PVA should be examined.

3.1.3 Poly(vinyl alcohol-co-vinyl acetate) (PVA)

Poly(vinyl alcohol) is commercially manufactured through the hydrolysis of poly(vinyl alcohol-co-vinyl acetate). First of all, poly(vinyl acetate) is produced by the polymerization processes of monomer vinyl acetate, which is reacted with NaOH and methanol in order to obtain poly(vinyl alcohol). But, this reaction can be controlled and when it is terminated some acetate groups may remain on the polymer. Then this copolymer of poly(vinyl alcohol) and poly(vinyl acetate) is called as poly(vinyl alcohol-co-vinyl acetate) and has different hydrolysis degrees. Production steps of poly(vinyl alcohol-co-vinyl acetate) can be seen in Figure 3.10.

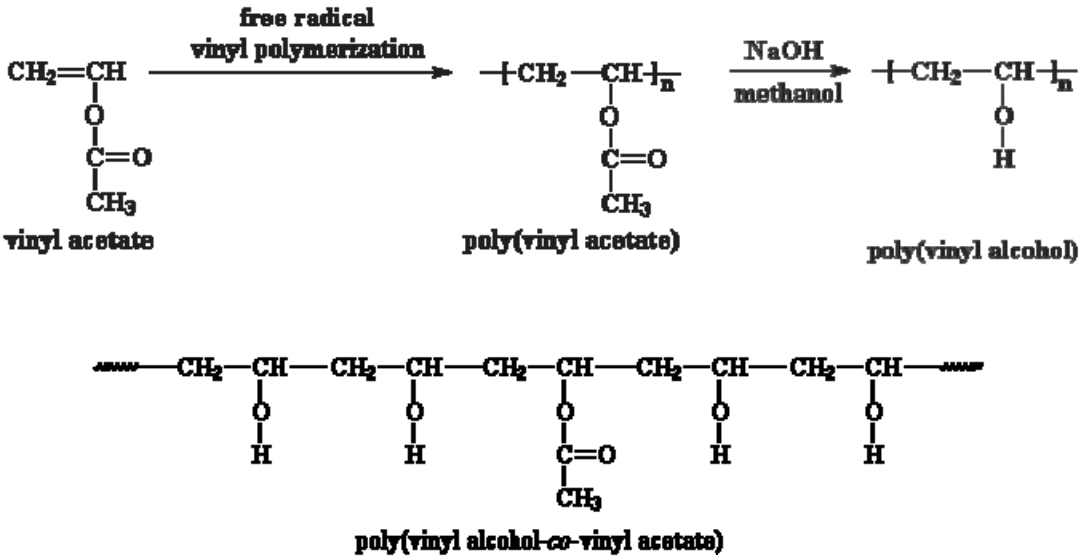


Figure 3.10: Production steps of poly(vinyl alcohol-co-vinyl acetate) (Macrogalleria, 2008)

This copolymer is the most widely used polymer for the production of MDF, and it shows different characteristics, because alcohol groups are hydrophilic while acetate groups are hydrophobic. So when the copolymer is put in water, it turns into a ball.

The alcohol repeat units are on the outer side of this ball-like molecule, while the acetate groups are on the inner side of the ball, as shown in Figure 3.11 (Macrogalleria, 2008).

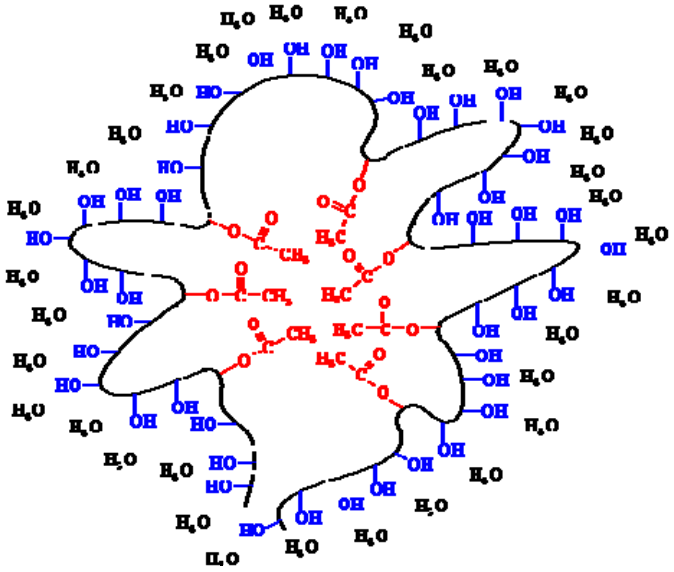


Figure 3.11: Shape of PVA copolymers in contact with water (Macrogalleria, 2008)

Table 3.7 summarizes representative properties of poly(vinyl alcohol) in the different forms in which the material is available commercially. These properties vary slightly with the grade of polymer-degree of hydrolysis, solution viscosity, and content of residuals, each of which, to a small extent, depends on the details of the method of manufacture. Unless otherwise stated, the data refer to fully hydrolysed (98-99%) unplasticized polymer in powder or granular form (Finch, 1992).

Table 3.7: General properties of poly(vinyl alcohol) (Finch, 1992)

Property	Data	Comments
Colour	White to ivory	
Storage stability	Indefinite in dry	
Light stability	Excellent	
Flammability	Burns similarly to paper	
Thermal Stability	Depends on temperature	Gradual discoloration above 100°C Darkens rapidly above 150°C Decomposes rapidly above 200°C
Effect of weak acids	Softens or dissolves	
Effect of strong acids	Dissolves or decomposes	
Effect of weak alkali	Softens or dissolves	
Effect of strong alkali	Softens or dissolves	
Effect of organic solvents	Generally resistant	
Refractive index	1.52-1.55	Anhydrous polymer
Specific gravity	1.23-1.31	Increases with degree of crystallinity
Specific volume pH of 4% aqueous solution	0.75-0.85	
Specific heat	1.65-1.67 J (gK)	
Thermal conductivity	~2	
Mean coefficient of thermal expansion ($x10^{-5}$/°C)	7-10	At 0-45°C
Heat sealing temperature (°C)	160-210	Unplasticized polymer
Glass transition temperature (°C)	85	98-99% hydrolysed
	58	87-89% hydrolysed
Melting point (°C)	230	98-99% hydrolysed
	180	87-89% hydrolysed
Degree of crystallinity	0-0.54	Increases with heat treatment and degree of hydrolysis
Moisture vapour permeability at 20-25 (°C)	500-550	10^{-9} gxcm/cm^{2}xhxtorr
Tensile strength (MPa)	65-110	98-99% hydrolysed: increases with heat treatment (decrease in crystallinity, decrease in humidity, and increase in molecular weight)
	25-80	87-89% hydrolysed: increases with molecular weight and with decrease in humidity
Elongation (%)	0-300	Increases with humidity (plasticized film)
	0-600	
Electrical resistivity (Ω cm)	$3.1\text{-}3.8x10^{-7}$	

3.1.3.1 Saponification of poly(vinyl acetate) to poly(vinyl alcohol)

The conversion of poly(vinyl acetate) to poly(vinyl alcohol) is the heart of any poly(vinyl alcohol) process. There are many different processes practised commercially, but all have several common features. In each, an ester exchange reaction is carried between poly(vinyl acetate) and a primary alcohol, most commonly methanol, and a second phase is formed. It is the formation of this second phase that necessitates a large amount of the mechanical equipment found in poly(vinyl alcohol) plants (Finch, 1992).

3.1.3.2 Effect of the degree of polymerization (DP) and degree of hydrolysis (DH) of PVA on MDF cements

Degree of polymerization (DP) and degree of hydrolysis (DH) of a PVA are highly affecting its properties. Hydrolysis degrees of a PVA are more affecting the moisture absorption property than polymerization degree as seen in Table 3.8.

Table 3.8: Effect of degree of polymerization (DP) and degree of hydrolysis (DH) at the properties of PVA (Kuraray, 2004)

	Polymerization degree		Hydrolysis degree	
	High 1700-2400	Low 500-600	High 98-99	Low 87-89
Solubility	↓	↑	↓	↑
viscosity of aqueous solution	↑	↓	↑	↓
Film strength	↑	↓	↑	↓
moisture absorption property	↓	↑	↓	↑

↓↑: Higher efficiency of performance
↓↑: Normal efficiency of performance

PVAs with high hydrolysis degrees have very less moisture absorption. In other words, MDF cements may less sensitive to water if they will be produced with high hydrolysis degrees PVAs. On the other hand, high hydrolysis degrees PVAs are less soluble at room temperature and this less solubility may prevent the production of MDF cements. However, solubility of PVA copolymers can be increased while

heating. Effect of heating to the solubility of PVA with respect to the hydrolysis degree can be seen in Figure 3.12.

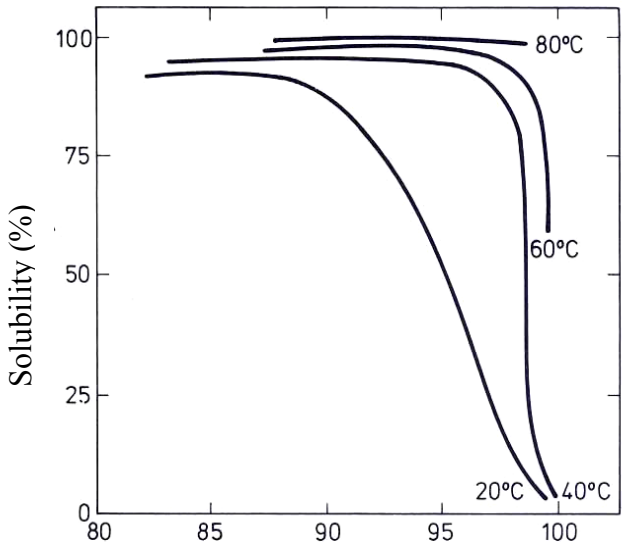
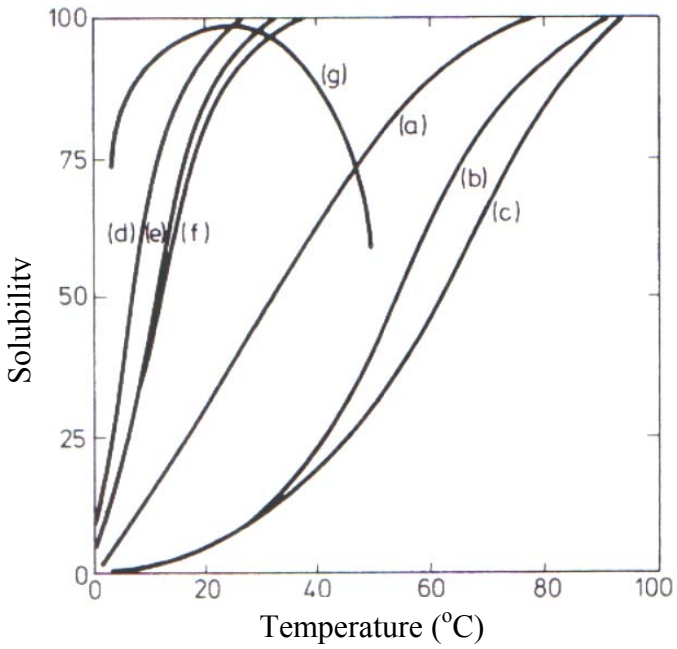


Figure 3.12: Effect of temperature on the solubility and degree of hydrolysis of PVA with d.p.=1750 (Finch, 1992)

Figure 3.13 shows the water solubility of various hydrolyzed grades and degree of polymerization as a function of temperature. Fully hydrolyzed grades of PVA are slightly soluble at room temperature whereas 78-90 mole% hydrolyzed grades are soluble at 20°C. While the hydroxyl groups along the polymer chain have a strong affinity for water, the limited solubility of the fully hydrolyzed grades at room temperature is caused by strong hydrogen bonding between the intra and intermolecular OH groups. The residual acetate groups in 78-90 mole% hydrolyzed PVA are hydrophobic and weaken the intra and intermolecular bonding, thereby increasing the water solubility at 20°C. As the concentration of acetate groups increases, the solubility at high temperatures decreases (Russell, 1991).



	D. of Hydrolsis (mole%)	D. of Polymerization
(a)	98-99	500-600
(b)	98-99	1700-1800
(c)	98-99	2400-2500
(d)	87-89	500-600
(e)	87-89	1700-1800
(f)	87-89	2400-2500
(g)	78-81	2000-2100

Figure 3.13: Water solubility versus temperature for various grades of poly(vinyl alcohol-co-vinyl acetate) (Finch, 1992)

All grades of PVA are highly hygroscopic owing to the strong polar hydroxyl side groups. Figure 3.14 shows the equilibrium moisture content at 20°C with increasing relative humidity (RH) of a fully hydrolyzed PVA film cast from an aqueous solution and dried at 50°C. From 0-50% RH the equilibrium moisture content increases linearly, above 60% RH it climbs rapidly, and rises very rapidly above 90% RH.

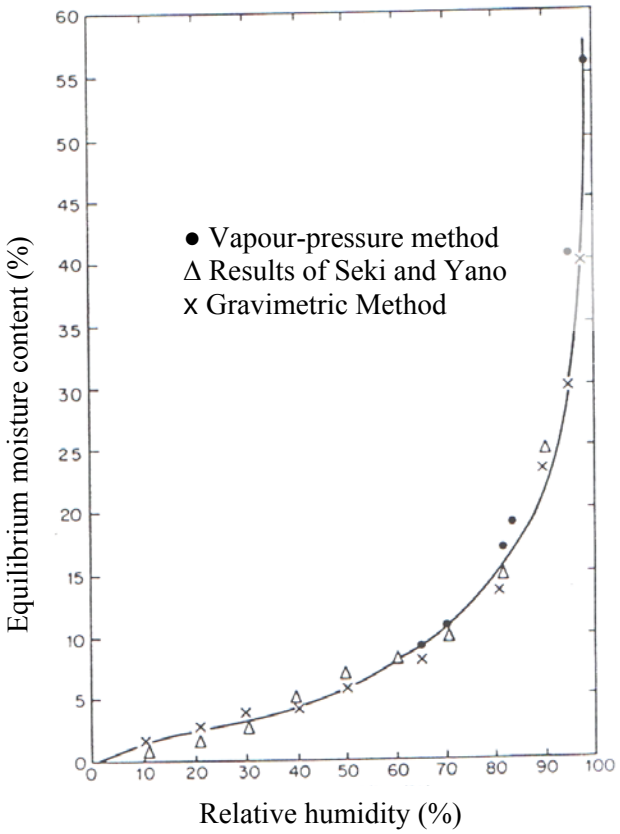


Figure 3.14: Equilibrium moisture content versus relative humidity at 20°C for a PVA film dried at 50°C (DP=1750, 99.9 mole% hydrolyzed) (Finch, 1973)

3.1.3.3 Crosslinking of PVA

Chemical and physical crosslinkings are the 2 ways of crosslinking of PVA. For example repeated cycles of freezing and thawing are a physical crosslinking method but it is easier to destroy physical crosslinkings than to the chemical crosslinkings. For example, cryogels are thermo reversible and it means they are stable up to 60°C due to the melting of crystals (Patachia, 2008). On the other hand, chemical crosslinking of linear polymers may provide feasible routes for the improvement of the mechanical properties and thermal stability. Several crosslinking methods have been published for different uses, since as a rule, all multifunctional compounds capable of reacting with hydroxyl groups can be used to obtain tridimensional networks in PVA. Crosslinked PVA found a very promising application in the preparation of biomedical materials and of magnetic-field-sensitive gels (Krumova, 2000).

The effect of crosslinking of poly(vinyl alcohol)s is generally to reduce water sensitivity and increase the stability in solution, usually with a marked increase in viscosity. Many different products have been developed by using such effects,

although the chemistry and formation methods of the used polymers are broadly similar.

The crosslinking is usually carried out by reaction with organic compounds, notably aldehydes, difunctional aldehydes or aldehyde-containing cross-linking resins. Alternatively, inorganic compounds in aqueous solution may be employed, such as boric acid or its salts, cupric acetate or other Group 1B salts, multivalent salts such as zinc or aluminum salts, and titanium compounds. Boric acid, H_3BO_3, alone does not introduce croos-links in poly(vinyl alcohol) solutions, but gelation does take place in the presence of cations. Chromates or dichromates have also been used for this purpose, sometimes in systems with photosensitive functions (Finch, 1992).

Crosslinking density can be measured using dynamical mechanical analysis (DMA) by calculating Mc, the (number) average molar mass of elastically effective chains (between crosslinks), according to the equation 3.1 derived from the theory of rubber elasticity (De Groote et al., 2004).

$$E=3nRT \qquad \textbf{(3.1)}$$

- E is Young's Modulus.
- n is the number of network chain segments per unit volume.
- R is the real gas constant.
- T is temperature

As underlined by Pascault et al. (2002), rubber elasticity is a rough method for crosslinking density determination but is the only one available on a practical level (De Groote et al., 2004). However, there are other physical approaches of entropic elasticity, especially the theory of phantom networks (Erman and Mark, 2005), in which the crosslinks freely fluctuate around their mean position. The above relationship then becomes:

$$E = 3RT(\upsilon_e - n) \qquad \text{(Pascault et al., 2002)} \qquad \textbf{(3.2)}$$

where n is the concentration of crosslinks. Thus,

$$E = 3RT\upsilon_e\left(1-\frac{2}{\varphi}\right) \qquad \text{(Pascault et al., 2002)} \qquad \textbf{(3.3)}$$

where φ is the crosslink functionality.

• **Chemical Crosslinking of PVA**

There are very different ways of crosslinking PVA chemically such as using boric acid or borate, glutaraldehyde, Cu^{+2}, beta radiation, gamma radiation etc. These are very efficient ways of crosslinking PVA but possible degredation reactions and toxicity are the disadvantages of these reactions (Patachia et al., 2007; Patachia et al., 2006; Patachia, 2003).

The polymer can be cross-linked by any difunctional agent that will condense with organic hydroxyl groups. The most important of these cross-linking agents are probably the aldehydes and these can be seen in Table 3.9.

Table 3.9: Aldehydes used as crosslinking agents with polymers (Finch, 1992)

Monoaldehydes	**Dialdehydes**
Formaldehyde, H.CHO	Glyoxal, $(CHO)_2$
Acetaaldehyde, CH_3.CHO	Glutaraldehyde, $CH_2(CHO)_2$
Propionaldehyde, $CH_3.CH_2.CHO$	Succinic dialdehyde, $(CH_2.CHO)_2$
Butyraldehyde, C_3H_7.CHO, and higher aldehydes	Terephthalaldehyde, $OHC.C_6H_4.CHO$
Furfuraldehyde	Aldehyde-containing resins, such as trimethylol melamine and other reaction products of formaldehyde with amines
Benzaldehyde, C_6H_5.CHO	Each of which form cross-linked polymers with decreased water solubility, forming gels

Heterogeneous acetalization of poly(vinyl alcohol) with formaldehyde, hydroxyacetaldehyde, and cloroacetaldehyde is accompanied by intermolecular cross-linking. This is not observed with acetalization by acetaldehyde, propionaldehyde, butyraldehyde, or benzaldehyde. The cross-linked polymer show lower rates of hydrolysis than those not cross-linked. Cross-linked PVAs can also be obtained by treatment with other organic compounds, including: Dicarboxylic acids, such as maleic or oxalic acids, and malonic, succinic and citric acids, poly(acrolein), mono- and di-isocynates, forming substituted carbamates, divinyl sulphate and other divinyl esters, glycidyl and other difunctional methacrylates; and with inorganic compounds, including: Boric acid and borates, germanic acids and germanates, titanium salts and esters, chromates and vanadates, cupric salts and other Group IB salts (Finch, 1992).

The statistical thermodynamic theory of the swelling of chemically cross-linked poly(vinyl alcohol) hydrogels, using formaldehyde or glutaraldehyde, has been studied extensively. It was shown that the character of the overall chemical potential change compared with polymer composition was independent of conditions of gel preparation, polymer solution concentration, degree of crosslinking, chemical nature of the crosslinking agent, and the solvent system employed. However, with poly(vinyl alcohol) water gels (where the gel is hydrogen bonded), there is a divergence from the theoretically predicted behavior. Gels prepared by a similar method, using an aqueous solution of poly(vinyl alcohol) with narrow molecular weight distribution (mol. wt=110000) crosslinked with glutaraldehyde, were studied by dynamic light scattering. Results suggest that these gels, with crosslinking linear flexible chains formed with glutaraldehyde in aqueous solution, differ significantly from the semi-dilute solutions from which they were prepared. Solutions show a slow hydrodynamic relaxation, which disappears on crosslinking, as well as the characteristic fast relaxation due to the network. At similar concentrations, the dynamic correlation length of the gel is about twice that of the corresponding solution, even with crosslinks amounting only to about 1% of the monomer weight. The swelling behavior of these hydrogels is described by the James-Guth theory, indicating that the logarithmic term in the network-dependent component of the overall change in free energy does not have a significant role (Finch, 1992).

The properties of the borate crosslinked poly(vinyl alcohol) gels depend on six variables: Cation-boron ratios, poly(vinyl alcohol) aqueous solution concentration, borate concentration, solution temperature, poly(vinyl alcohol) molecular weight, and degree of hydrolysis (acetate content) of the poly(vinyl alcohol). Basic crosslinking reaction of PVA and borate can be seen in Figure 3.15 (Finch, 1992).

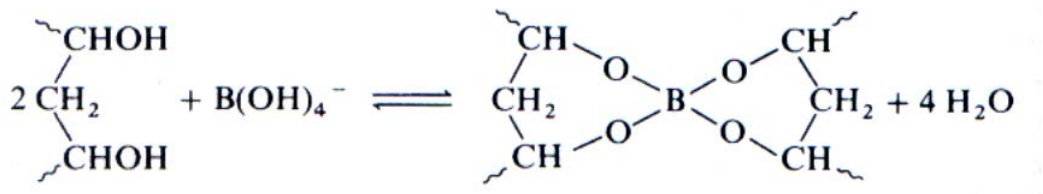


Figure 3.15: The basic crosslinking reaction of borate and poly(vinyl alcohol) (Finch, 1992)

A study of the dynamic mechanical properties of borate-crosslinked poly(vinyl alcohol) gels (using 98-99.7 mole% hydrolyzed polymers, with a range of

viscosities) suggested that boric acid does not introduce crosslinks into solutions, but gelation occurs in the presence of cations. It is concluded that cross-link density increases with borate concentration until steric hindrance occurs, but the efficiency of cross-linking decreases with borate concentration (Finch, 1992).

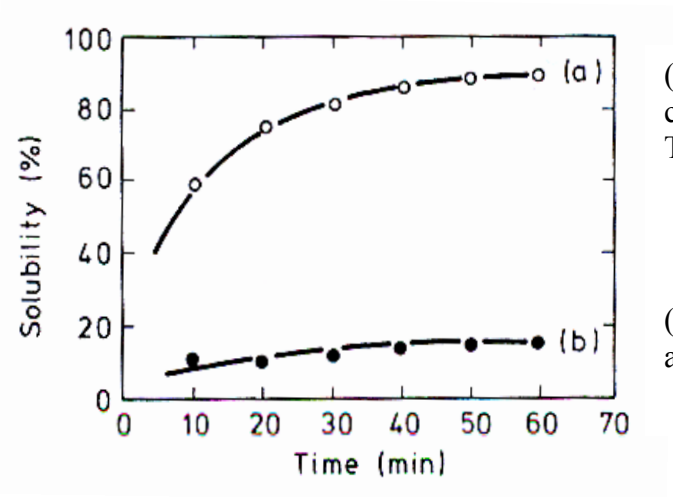
3.1.3.4 Modification of PVA by copolymerization

The endowment of new functionality to poly(vinyl alcohol)s is another reason for producing poly(vinyl alcohol-co-vinyl acetate) copolymers industrially. Ethylene-vinyl alcohol copolymers are a good example, as these have been produced industrially since 1973 and used widely in food packaging because of excellent oxygen gas barrier properties of the copolymers. Other properties found in poly(vinyl alcohol-co-vinyl acetate) copolymers are an increase in affinity to various substances such as inorganic salts and polar compounds, in surface activity, and in interaction with each other, depending on the hydrophobic bonds in the copolymers. Improved water resistance of the resulting copolymer film is also desirable, although the copolymer must be water soluble before use. To obtain poly(vinyl alcohol-co-vinyl acetate) copolymers with these properties, vinyl acetate must be copolymerized with various monomers; some of these are less than suitable from the point of view of obtaining homogeneous copolymer compositions since the monomer reactivity ratios, r_1, r_2, are widely different from each other. Therefore, it can be difficult to obtain homogenous copolymer compositions in industrial production (Finch, 1992).

3.1.3.5 Modification of PVA containing carboxylic groups

The solubiltiy of poly(vinyl alcohol) in water depends on its degree of polymerization and of saponification: the effect of the latter especially is significant. The hydroxyl groups of PVA have a strong affinity for water, but strong hydrogen bonding between the intra- and intermolecular hydroxyl groups greatly inhibits its solubility in water. Consequently, partially hydrolysed poly(vinyl alcohol-co-vinyl acetate) ($\leq$98 mole% saponification) is insoluble in cold water and must be heated to at least 70°C to dissolve completely. The residual acetate groups are essentially hydrophobic and weaken hydrogen bonding of adjoining hydroxyl groups. Consequently, partially hydrolysed poly(vinyl alcohol-co-vinyl acetate) (~88 mole% hydrolysed) is soluble in cold water.

Poly(vinyl alcohol) containing carboxylic acid has several different characteristics, compared with conventional (non-ionic) poly(vinyl alcohol)s. The incorporation of carboxyl groups (COONa) into the PVA incresases the solubility in water because of their anionic and hydrophilic characteristics. Figure 3.16 shows the rate of water solubility. Poly(vinyl alcohol)s containing carboxylic acid with a <3 mole% amount of COONa have a much superior solubility in cold water to conventional poly(vinyl alcohol) (Finch, 1992).



(a) Poly(vinyl alcohol) containing carboxylic acid: T-330H

(b) Conventional poly(vinyl alcohol) (d.p.=1800)

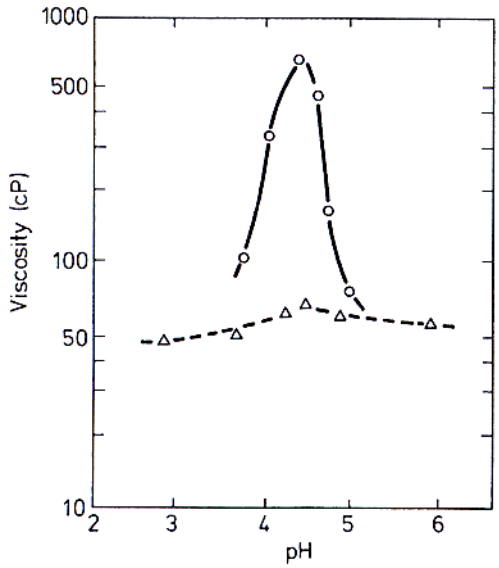
Figure 3.16: Rate of water solubility of 98~99% hydrolysed poly(vinyl alcohol)s (8% solution at 40°C) (Finch, 1992)

- **Applications**

Poly(vinyl alcohol) containing small amount of carboxyl groups has the characteristic property that the groups interact, or react with metal ions to form cross-links, and so increase the water solubility of the copolymer, and react with compounds containing epoxy, amino and similar groups which undergo cross-linking.

Figure 3.17 shows the changes in the aqueous solution viscosity of poly(vinyl alcohol)s containing carboxyl groups, in the presence of aluminum sulphate over a range of pH. The aqueous solution viscosity of the modified poly(vinyl alcohol) increases significantly in the pH range of 4~5, while the conventional poly(vinyl alcohol) remains almost constant. This significant increase in aqueous solution viscosity appears to be due to formation of ionic cross-links between aluminum ions and carboxyl ions. Greater concentration of modified poly(vinyl alcohol) means higher viscosity. Poly(vinyl alcohol)s containing carboxyl groups can be used in the paper industry as surface sizing agents, since aluminum sulphate is used as a

retention aid, at a pH of 4.5, so that the aqueous solution viscosity of poly(vinyl alcohol) containing carboxyl groups increases significantly on the paper surface, resulting in improved barrier properties in the paper (Finch, 1992).



○ : Carboxyl modified polyvinyl alcohol, d.p.=1750, 98.5 % hydrolysed

△ : Conventional polyvinyl alcohol, d.p.=1750, 98.5 % hydrolysed

Figure 3.17: Relation between pH and viscosity of 5% aqueous solution containing 0.3% aluminum sulphate (Finch, 1992)

Poly(vinyl alcohol) containing carboxyl groups can be used to prevent permeation of the silicone peeling agent into the paper, by undercoating with modified poly(vinyl alcohol) before commencing silicone/coating.

The mechanism of the barrier property obtained from coating the poly(vinyl alcohol) containing carboxyl groups is believed to be that the aqueous solution viscosity of the modified poly(vinyl alcohol) coated on paper increases, by reacting with aluminum ions on the paper surface, to prevent permeation of the polymer into the inside of the paper, and the polymer effectively fills up the porous paper surface (Finch, 1992).

3.1.3.6 Modification of PVA containing acetoacetyl groups

- **Preparation**

Two methods were reported for the preparation of poly(vinyl alcohol)s containing acetoacetyl groups. First one is the reaction of poly(vinyl alcohol) with diketene and the second is ester interchange of poly(vinyl alcohol) with acetoacetate (Figure 3.18). Some of these polymers are offered by Nippon Gohsei as the Gohsefimer Z series (Finch, 1992).

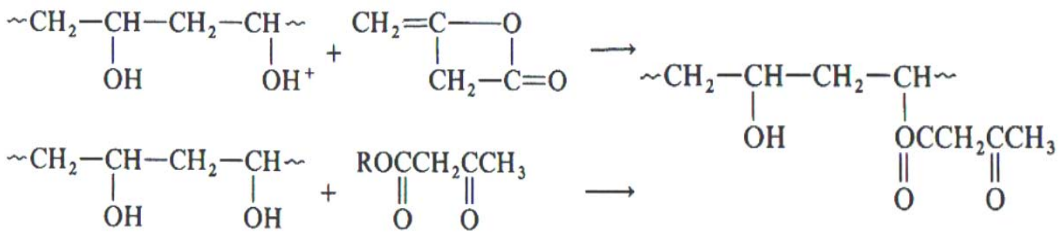


Figure 3.18: Modification of PVA with acetoacetyl (Finch, 1992)

- **Properties**

Insolubilization of film and gelation of aqueous solutions also take place by the cross-linking reaction of the acetoacetyl groups with reageants such as formalin, glyoxal, and amino-resin precondensates of urea or melamine with formalin. Table 3.10 shows results of studies on the hot water resistance of cross-linked poly(vinyl alcohol) films.

The characteristics of these polymers are:

a) The storage stability is good.

b) They have hot water resistance and an increased waterproof strength with heat treatment processing in compounding using specific waterproof agents.

c) They show water resistance in adhesive applications.

d) They have a marked effect as emulsifiers for poly(vinyl acetate) emulsions, especially on the water resistance of poly(vinyl acetate) emulsions used in wood adhesives, with significant improvement in adhesion of wood.

Table 3.10: Water resistance of modified poly(vinyl alcohol) films (Finch, 1992)

		Parts					
Composition	Poly(vinyl alcohol) containing acetoacetyl groups*	100	100	100			
	Conventional poly(vinyl alcohol)*				100	100	100
	Amino resin		5			5	
	Glyoxal			5			5
Hot water resistance	Insolubilization degree (%)	0	85	84	0	0	0

*: d.p.=1200; 99 mole% hydrolysed
Hot treatment of film: 100°C for 5 min.
Hot water resistance: in water at 80°C for 1 h.

• **Applications**

Several applications of poly(vinyl alcohol)s containing acetoacetyl groups have been suggested in the patent literature, including;

a) in textile manufacture, in finishing, caseproofing, and dyeing,

b) in paper manufacture, for general paper strength increase, and as a binder and coating agent for heat sensitive recording paper, giving an increase in water resistance,

c) as an emulsifying agent for water resistant poly(vinyl acetate) emulsion. The emulsions obtained are useful for adhesives, especially wood adhesives, textile finishes, coating materials, and cement compounds,

d) as a flocculating agent for particles suspended in aqeous solution,

e) in methods for immobilization of enzymes (Finch, 1992).

3.1.3.7 Effect of glycols

The properties of pure PVA can be modified by the addition of plasticizing constituents, and glycol based plasticizers are generally used to prevent PVA films from becoming hard and brittle at low humidities. The selection of an appropriate plasticizer for PVA is based on its dissolving temperature and its cloud point. The dissolving temperature is a measure of the plasticizer's ability to disrupt the bonds between poly(vinyl alcohol) chains, thus producing a solution. Conversely, the cloud point is the temperature at which the bonds between the PVA molecules are stronger than those between the plasticizer and PVA molecules. Above this point the polymer precipitates. Therefore, plasticizers which have a low cloud point will interact strongly with PVA. Table 3.11 lists some of the glycol based plasticizers and their characteristics. Ethylene glycol exhibits the strongest plasticization effect but glycerol is most commonly used because of its higher boiling point and associated lower vapor pressure (Boyer, 1993).

Table 3.11: Properties of glycols used as plasticizers for PVA (Boyer, 1993)

Glycol	Melting Point Depression (°C)	Boiling Point (°C)	Dissolving Temperature (°C)	Cloud Point (°C)
Ethylene glycol	-	197	140	110
Trimethylene glycol	-	214	160	130
Tetramethylene glycol	-	235	<200	150
Pentamethylene glycol	-	239	190	175
Hexamethylene glycol	-	250	160	190
Propylene glycol	-	187	190	150
Glycerol	25	290	160	120
2,3-butane diol	-	184	240	175
1,3-butane diol	-	204	185	175
Diethylene glycol	10	245	210	160
Triethylene glycol	8	278	210	185

Measured at 30 wt% plasticizer content

Glycerol is a colorless, odorless, viscous liquid with the formula $HOCH_2CH(OH)CH_2OH$ ($C_3H_5(OH)_3$) and it is also called glycerin. It is commenly used for the production of MDF cements as a plasticizer. A glycerol concentration of 15 wt% reduces the glass transition temperature to 20°C at 0% rh, as shown in Figure 3.19.

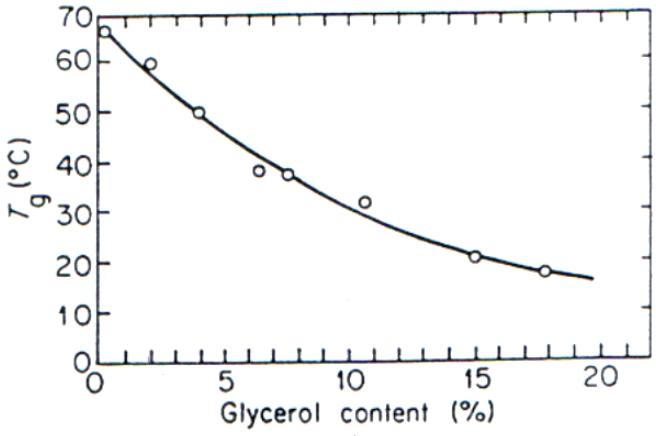


Figure 3.19: Effect of glycerol concentration (wt%) on the glass transition temperature of PVA (Finch, 1973)

The mechanism of plasticization by glycerol is two fold: a direct effect of glycerine with PVA, and an indirect effect through the increase of the hygroscopicity of the PVA film. The combined effect is shown in Figure 3.20 for 0, 6.39 and 17.7 wt%

glycerol. At a concentration of 6.39 wt% glycerol, T_g is lowered to 20°C with a moisture content of 2.5% (or 25% rh at equilibrium at 20°C) (Russel, 1991).

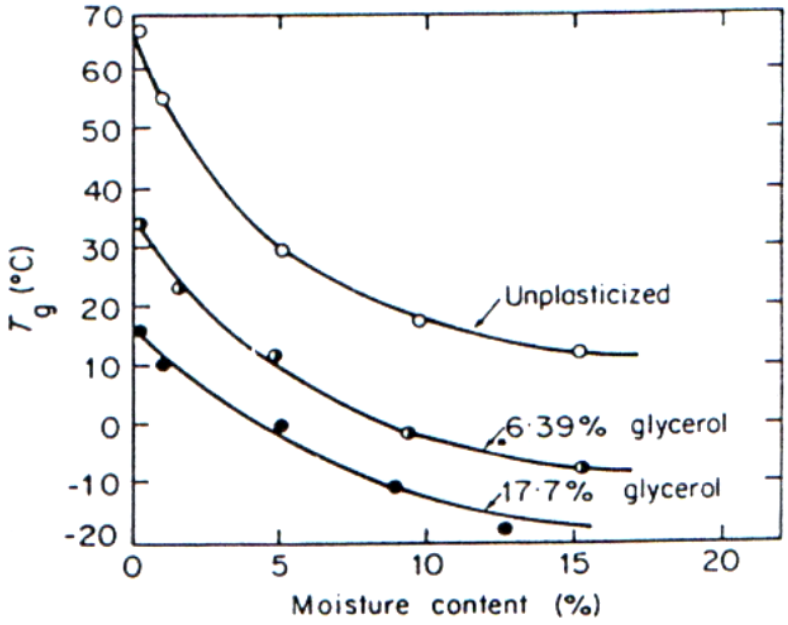


Figure 3.20: Glass transition temperature versus moisture content of PVA films with 0, 6.39 and 17.7 wt% glycerol as a plasticizer (Finch, 1973)

In the CAC-PVA system, the use of glycerol as a plasticizer was found to be an aid in air removal. Lowering the glass transition temperature, T_g, of the PVA reduces the change in viscosity of the system as the polymer matrix dehydrates allowing for air removal to occur before setting (Russell, 1991).

3.2 Production of MDF Cements

MDF cements were first produced by Birchall et al. (1981, 1983) at the beginning of 1980s. Cement, polymer and water were added seperately into a planetary mixer and mixed until a damp, granular crumble was obtained. Then high shear forces were applied to the mixture for eliminating the large voids. The high shearing action is achieved by compounding the composition in two roller mills. The composition is passed repeatedly through the nip between the rolls of the mill in different speeds. This process dispers the cement grains in the polymer matrix and rapidly produces rubbery, cohesive dough. Subsequently, the dough is calendered into a flexible sheet and molded by pressure-curing.

Pressing the sheet at low pressures (3-5 MPa) and temperature of 80°C for ten minutes removes entraped air from compounding according to Boyle's law (i.e.

$P_1V_1=P_2V_2$) as shown in Figure 3.21 and initiates cement hydration to form a dense, rigid body. Application of heat in addition to pressure accelerates the hydration of the cement and stiffening the dough (Russell, 1991). Full strength development is achieved by further curing of the sheet at temperatures up to 80°C for 24 hours. This process causes a reduction of porosity as a result of polymer contraction.

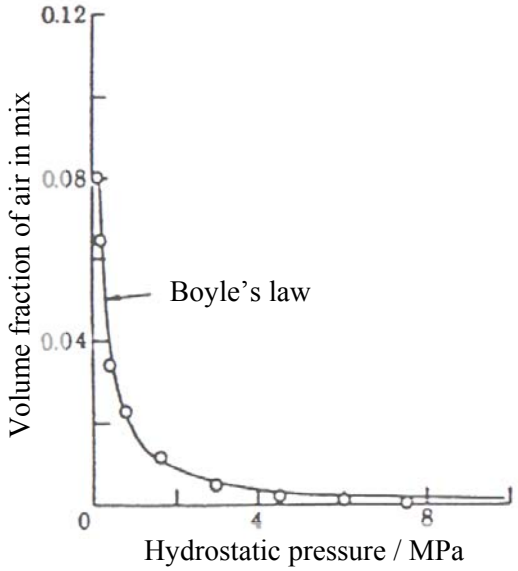


Figure 3.21: Effects of hydrostatic pressure on reducing volume of entrapped air in MDF cement. Circles represent results from composition of 100 parts HAC, 16 parts water and 3 parts HPMC. Solid line is Boyle's law

Birchall's production method by applying high shear was generally accepted for the standard MDF production procedure by other researchers or slightly modified according to materials or used machines. MDF production had been optimized at University of Illinois at Urbana Champaign between 1989 and 2000. Approximately 15 MSc and PhD theses were completed at this university between those years. Most of them used the same production method optimized by Russell (1991). More than 300 MPa flexural strengths were achieved with that method. Typical production steps can be seen in Figure 3.22.

Alternatively for more intricate shapes, the composite can be vacuum mixed-extruded or vacuum mixed-injection molded. Parts made by these processing routes are fully degassed and do not require pressure curing to achieve high strengths (Russell, 1991).

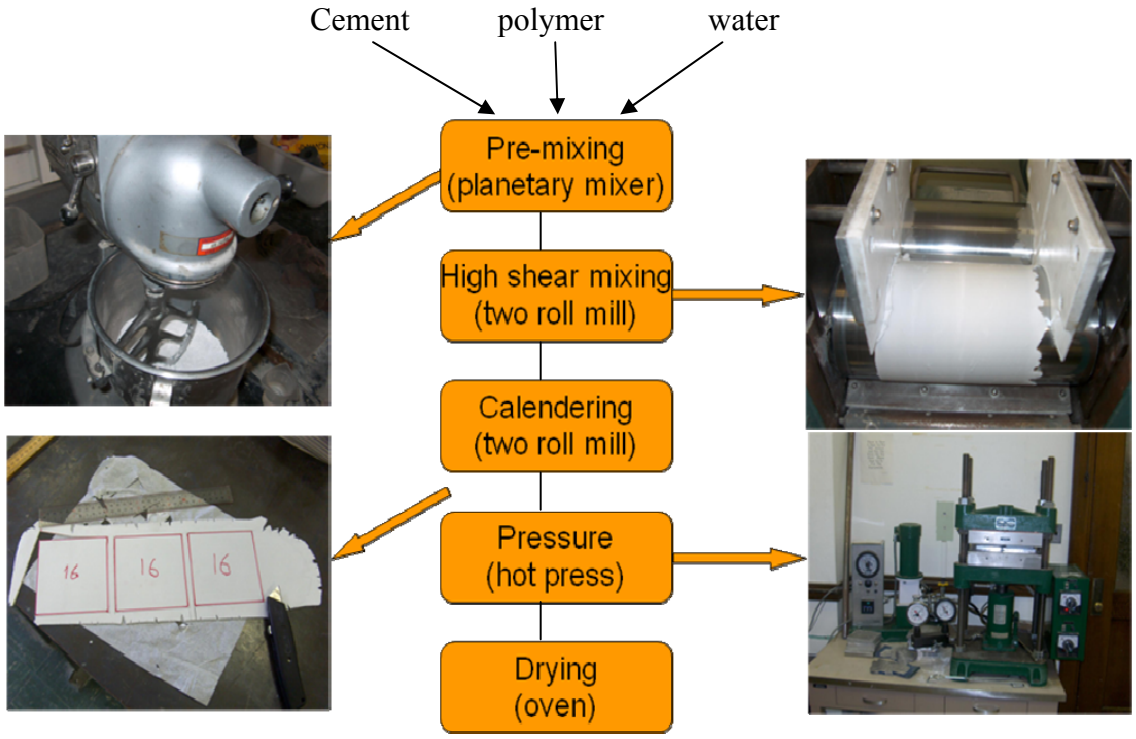


Figure 3.22: Schematical representation of production steps of MDF cements

On the other hand, Tan (1992) introduced a new way using Banbury mixer and MDF cements were successfully produced in this way too. Tan used Banbury type mixer for high shearing. High shear mixing was carried out in a Haake Rheocord System 90 (Haake, Paramus, NJ) with a water cooled/heated banbury type internal mixer attachment. The mixing head was coupled to a drive unit via a torque transducer which measures the torque required to maintain a pair of delta conical rotors at a given mixing rate. The rotors rotate in opposite directions and the right rotor spins 1.5 times faster than the left (Figure 3.23).

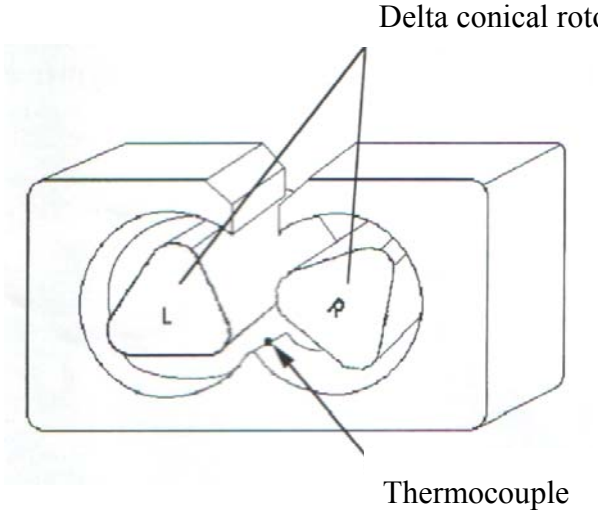


Figure 3.23: Banbury mixing chamber with delta conical rotors (Gulgun et al., 1995)

Tan (1992) described a “windows of processibility”. Figure 3.24 shows a generic torque-mixing time plot from the Banbury mixer-torque rheometer. An important contribution of Tan’s work was the definition of a "processing window," extending from the initial measurement of torque to the second torque maxima, which can be used to compare the effects of different compositions and properties on the processing of MDF cement pastes. If the material is overprocessed during fabrication, voids (macro-defects) can be reintroduced into the paste, resulting in degraded mechanical properties (Lewis and Boyer, 1995).

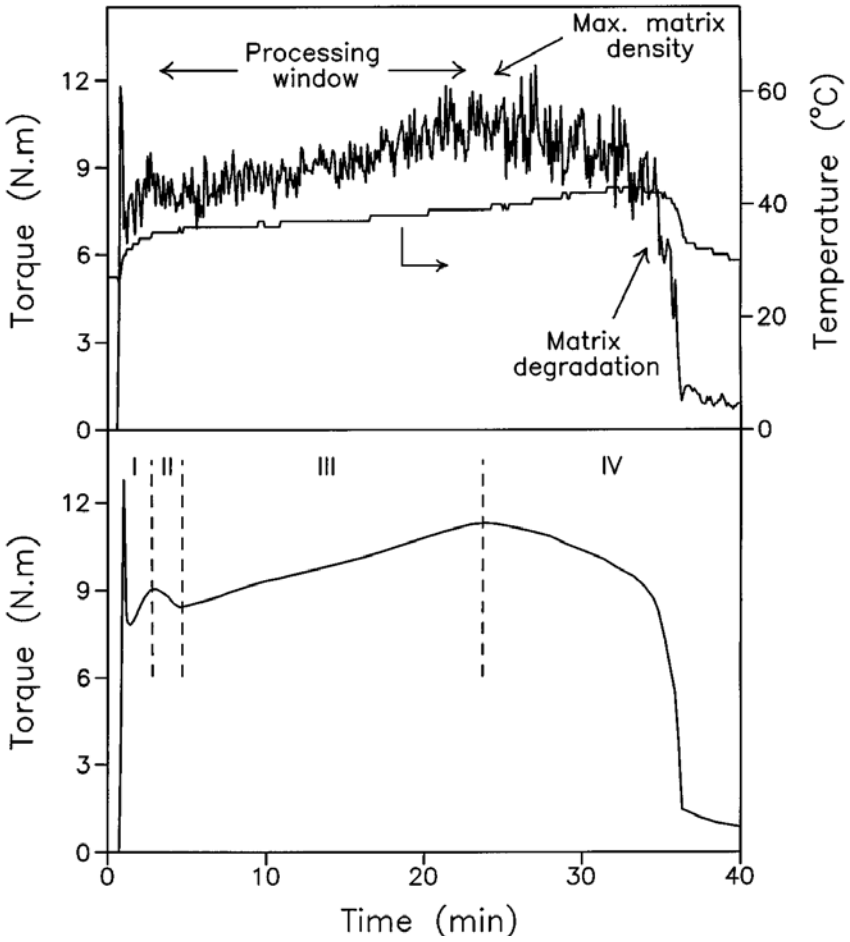


Figure 3.24: Torque and temperature versus mixing time plot of MDF processed at 75 rpm with initial sample temperature at 27 ^{o}C. The bottom plot delineates the specific regions of the mixing curve. Dotted lines denote regions described in text (Tan et al. 1996)

The torque curve has been categorized into four distinct regions. Region I denotes the transformation of the MDF formulation from a damp powder to a paste. The first maximum following the initial spike in the torque curve marks the completion of paste formation. Once formed, the paste begins to flow in region II, and hence, the torque declines. Degradation of the PVA chains may also contribute to the decrease

in mixing torque levels. Region III shows a monotonic increase in the torque, and is associated with the development of the polymer-particle network. The second apex at the end of region III is what is known as the "point of maximum crosslink density", where matrix density is maximized. Beyond this point, the network begins to degrade and the paste ultimately reverts back to a powder form at the end of region IV. Thus, the material exists as a completed, nondeteriorated paste only in regions II and III. Therefore, regions II and III combined are referred to as the "window of processibility" within which paste properties are optimum (Tan et al., 1996).

Di Maggio et al. (1997) produced MDF specimens by using PVA and alumina cements and modified with steel, polyethylene (PE) and poly(vinylalcohol) (PVA) fibres. They concluded that, despite their cost and the unavailability of short fibres, PE fibres are preferable to PVA ones, because of the higher improvement of the toughness, the fracture behaviour and better elastic modulus/radius of fiber (E/r) ratio. The PE fibre CAC-MDF composite showed the most relevant improvement of toughness, which could be related to the peculiar features of the PE fiber-cement interface.

Walberer and McHugh (1998) produced MDF cements by using CAC and a methanol soluble resole-type of phenol formaldehyde resin. Materials were similar to those of Pushpalal et al. (1997) but they used the production technique of Tan (1992). Banbury type mixer was used to mix the compound. They modified the initial resin pH before combining it with ceramic phases during mixing. They reported that the acceleration of mixing due either to high pH or low pH environment was detrimental to flexural strength development. High flexural strength was obtained as 168 MPa with CAC-standard resin composite. Since the high pH paste structure was likely dominated by interactions of resin and cement particles and the low pH paste structure was dominated by polymerized resin, these results suggest that the optimum high strength structure is achieved with a balance of both types of structures. They concluded that an optimum high strength microstructure can be formed when the phenol resin was simultaneously allowed to polymerize and ionically interact with the cement particles during paste processing.

Santos et al. (1999) produced MDF cements by using portland cement and slag modifed cement and used 4 different types of PVA with distinct degrees of hydrolysis and average molecular weight as polymer. They also tried to add silica

fume to the mixture. Materials were processed in three different forms: hand mixtures, compaction pressure (2 MPa) after hand mixtures and calendered with compaction pressure. MDF sheets could not obtain with hand mixtures. One of the four types of PVA did not provide MDF even processing the sample using calendaring machine. According to the results, MDF cements were obtained using PVAs with low hydrolysis degree (87 mole%), independently of the molecular weight. For PVAs with high hydrolysis degree, MDF cements were obtained only if the molecular weight is low. Only the PVA type which has high degree of hydrolysis did not provide MDF cement, even by calendering. Both cement types tested provided MDFs but they concluded that materials prepared using portland Type I cement were not significantly affected by humidity according to Vickers hardness measurements. Addition of silica fume has a negative effect on the acid resistance. This is a surprising observation, since in concrete technology the use of silica fume usually produces a good quality concrete. Their results indicate that silica fume does not play the same role in MDF as it does in conventional concrete.

3.2.1 Estimation of Shear Rate on the Two-Roll Mill

The generalized equation for the rate of shear based on the geometric configuration shown in Figure 3.25 is given by (Russell, 1991):

$$\gamma = \frac{6U_0}{\delta h_0}\left[\frac{\eta(\varepsilon_1^2 - \varepsilon^2)}{(1+\varepsilon^2)^3} + \frac{\lambda\delta}{6(1+\varepsilon^2)}\right] \qquad \textbf{(3.4)}$$

where:

γ :rate of shear

U_0=average speed of rolls U_1 and U_2

h_0:half of the nip gap

r:radius of the rolls

λ :(U_1-U_2)/2U_0, dimensionless variable

$\delta = \sqrt{\frac{2h_0}{r}}$, geometric constant

$\eta = \frac{y}{\sqrt{2rh_0}}$, dimensionless variable

$\varepsilon = \frac{x}{\sqrt{2rh_0}}$, dimensionless variable

$\varepsilon_1 = \frac{x_1}{\sqrt{2rh_0}} = \sqrt{\frac{h_1}{h_0} - 1}$, dimensionless value describing the exit point x_1 where material detaches from the slower roll at thickness $2h_1$.

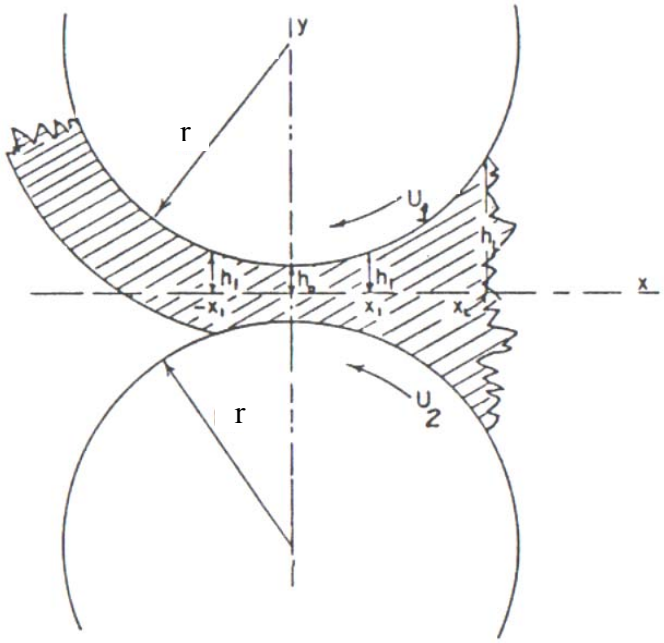


Figure 3.25: Geometric representation of two-roll mill

The maximum shear rate occurs at the nip gap of the roll surface (i.e. x=0, y=h_0):

$$\gamma_{max} = \frac{3U_0}{h_0}\left[\varepsilon_1^2 + \frac{\lambda}{3}\right] \quad \text{(Russell, 1991)} \qquad \textbf{(3.5)}$$

ε_1^2, the point at which the material detaches from the slower roll, was estimated by calculating the ratio of the thickness of the material exiting from the rolls and the nip gap, i.e. h_1/h_0. Values varied from 1.2 to 1.4 when measured. For symmetrical two-roll milling, Middleman has shown the ratio to have a specific value of 1.226. Using this value and replacing the dimensionless variable λ, the equation used to estimate the maximum shear rate is given by:

$$\gamma_{max} = \frac{3U_0}{h_0}\left[0.226 + \frac{U_1 - U_2}{6U_0}\right] \quad \text{(Russell, 1991)} \qquad \textbf{(3.6)}$$

The shear rate is controlled by three parameters: the gap between the rolls, the speed of the rolls, and the relative speeds of the rolls (roll speed ratio or friction ratio) (Russell, 1991).

3.2.2 Step by Step Procedure for the Production of MDF Cements

Production of MDF cements was optimized at UIUC for alumina cement and Gohsenol KH 17 type PVA (Desai, 1990; Russell, 1991 and Desai, 1992 etc.). Production steps can be divided in four parts like preliminary steps, planetary mixer, two roller mills, and hot pressing steps. The following production steps were also applied for pretests which can be seen in Part 4.1 and slightly modified after those pretests.

3.2.2.1 Preliminary steps

- Platens of press were pre-heated to 80°C (176°F).
- Chiller of the twin roll mill was set to 15-16°C (60°F).

3.2.2.2 Planetary mixer

- Cement and PVA were dry blended for two minutes prior to the addition of mixture of water and glycerol at a speed rate 1.
- After adding of water and glycerol, the batch was mixed for two minutes at medium speed (speed rate 2) until a damp, granular mix was formed.
- The cohesive solid material was scraped off the bowl in 30 seconds and then blended for an additional 1 minute at a speed rate 2.

3.2.2.3 Two roller mills

- Nip gap was set to 0.25 mm and side guards were aparted to 14 cm (5.5 inches).
- Two roller mills were turned on and speeds of the rolls were set to 36:30 (front:back)
- Powder was passed through, nip gap was increased two turn (to 0.49 mm), and folded and passed through again.
- Speeds of the rollers were changed to 54:27 and shear mixed for 15 seconds.
- Sheet was rotated 90° and shear mixed for another 15 seconds.
- Speeds of the rollers were changed to 36:30 and nip gap was increased 8 turns (to 1.66 mm)
- Sheet was passed through 4 times folding triple and rotating 90° each time.
- Side guards were moved out, nip gap was closed two turns (to 1.49 mm), and speeds of the rollers were changed to 30:30.
- Batch was passed through twice without folding or rotating.

- Sheet was cut into desired dimensions.

3.2.2.4 Hot press

- Cement sheets were placed between 2 pieces of Mylar (0.25-mm thick) and then were placed in hot press for 10 minutes at 5 MPa.
- Sheets were taken out of hot press and Mylar was pulled off of cement.
- Stiffened composite sheet was cured between two new sheets of Mylar and two 1.27 cm thick plates of aluminum for 24 hours at 80°C in a forced-air oven.

3.3 Properties of MDF Cements

MDF cements can be produced with different cement and polymer types and their properties largely depend on the used materials. MDF cements produced with CAC and water soluble PVA or alcohol soluble phenol resin precursor have unique properties and can be accepted as the most suitable materials for the production of MDF cements. Table 3.12 shows the properties of OPC, CAC-PVA MDF and CAPR MDF.

These cement-polymer composites have very high flexural strengths and it is the most important feature of these materials. The MDF cement specimens produced by Birchall et al. had reached 177 MPa of flexural strength while some other researchers (Russell, 1991; Desai, 1990 and Desai, 1992) achieved around 300 MPa flexural strengths, which are nearly equal to the strength of ordinary steel and this was a very important development when compared with ordinary cement paste which has only 5-10 MPa flexural strength.

Table 3.12: Typical properties of OPC and MDF cement composites

Property	OPC	CAC-PVA MDF*	CAPR MDF**
Flexural Strength, MPa	5-10	150-300	120-200
Compressive Strength, MPa	40-60	380	300
Young's Modulus, GPa	20-30	40-50	32-45
Poisson's ratio			0.24
Fracture Energy, J/m^2	20	200-500	
Fracture Toughness, $MPA.m^{1/2}$	0,5	3,0	
Density, g/cm^3	2,3	2,5	2.2-2.3
Porosity	25%	<1%	
Thermal exp. (C^{-1})	$10\text{-}20x10^{-6}$	$9,7x10^{-6}$ (25-100°C)	$17.8x10^{-6}$ (20-300°C)
Thermal conduct. $W/m\ ^0K$	2	1	0.8
D.C. Resistivity, Ω.cm		10^{12}	$10^{13}\text{-}10^{14}$
Stres intensity factor ($MPam^{1/2}$)			1.8-3.3
Weibull Modulus		20-40	
Oxygen permeability		10^{-6}	
Dielectric breakdown voltage, kV/mm		9	
Dielectric constant		7.8 (1 MHz)	9 (1 kHz) 6 (10 kHz)
Dissipation factor (1 MHz)		0.023	
Acoustical tan δ		0.1	
Q factor		40	

* : Polymer was PVA and the cement was alumina cement. (Russell, 1991)
** :Polymer was phenol resin and the cement was alumina cement. (Pushpalal et al., 1999)

Liutkus et al. (1988) used polysiloxanes for the production of MDF cements. The preferred polysiloxanes employed in their invention were polydimethyl siloxanes having the silanol terminal groups. They proposed that the presence of the silanol terminated polysiloxane significantly improved the thermal stability of the cement, as well as significantly reduced its dielectric constant. They also proposed that additional thermal stability and reduction of dielectric constant of the cement can also be achieved by incorporation of coupling agents to the cement matrix. These can

be either of the organofunctional titanates or organofunctional silanes category. Preferred subcategories are the quaternized pyrophosphato titanates, and the alkoxysilanes.

Chandrashekhar and Shafer (1989) produced MDF cements with calcium alumina cements and PVA copolymers and investigated the effect of polymer impregnation. First of all, MDF cements were heated at 500°C for 5 to 6 hours to completely remove the water and the original polymer (PVA) and then stored in vacuum at 150°C to prevent reabsorption of moisture. Then methyl methacrylate and some high-strength, heat resistant novolac epoxies were impregnated to these MDF cements. They proposed that this process improved their properties such as low dielectric constant, high resistivity, good flexural strengths and good temperature range of stability.

Di Maggio et al. (1998) used alkali resistant discontinuous fiber for the production of MDF cements. Fibers preferred for their invention were organic artificial fibers such as poly(ethylene) (PE), poly(propylene) (PP) (optionally fibrillated poly(propylene)) and poly(vinyl alcohol) (PVA) fibers. According to results, even if the breaking resistance of materials decreased by addition of fibers with respect to the standard specimen, both the impact strength and the fracture energy of the specimens with poly(vinyl alcohol) (PVA) and poly(propylene) fibers were observed to remarkably increase. In the case of comparison samples the decrease in resistance is not compensated by an increase in fracture energy.

3.4 Durability of MDF Cements

In spite of their amazingly high flexural strengths, these composites have serious durability problems under the effect of water which limit their usage as a commercial product before solving this problem. Their flexural strength decreases sometimes more than half of their initial strength when they are in contact with water. Physical changes of MDF cement specimens stored in desiccator and water for 1 week shown in Figure 3.26. Physical detoriation even can be seen visually. Therefore, most of the researches about MDF cements have been focused on their water sensitivity. Some researchers (Russell, 1991; Desai, 1992; Atkinson and Walsh, 1986; Lewis and Boyer, 1995; Pushpalal et al., 1997; Mojumdar et al., 2004; Chowhurry, 2004; etc.)

made some improvements, but none of them seems acceptable enough for this purpose.

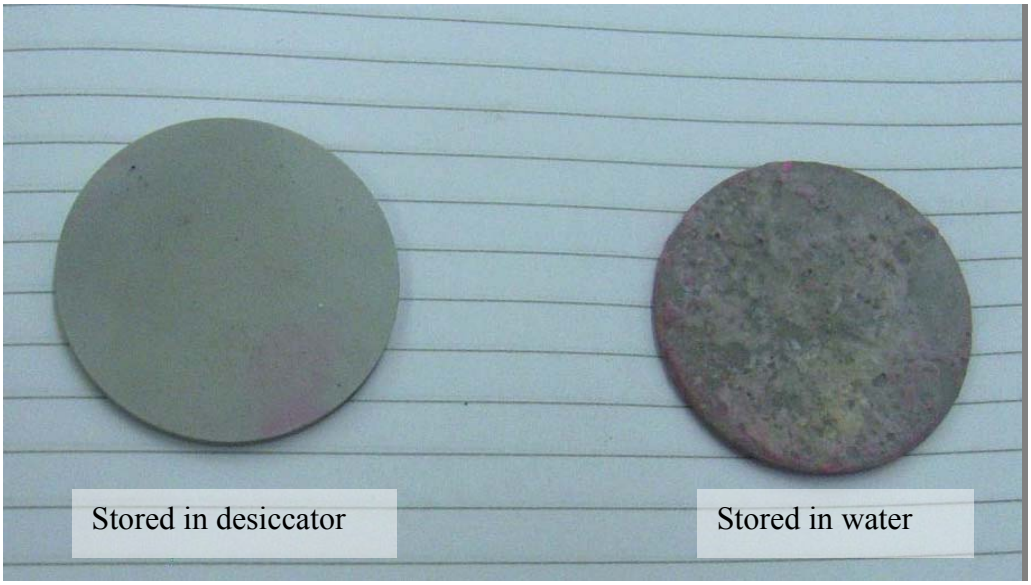


Figure 3.26: Physical appearances of MDF cements after storing in different conditions for 1 week

Atkinson et al. (1986) produced MDF specimens with the same procedure of Birchall et al. (1983). MDF cement sheet was cut into specimens suitable for flexural strength testing after production. One-third of the specimens were allowed to air-dry, one-third were immersed in water (at 20°C) for 3 days and the remaining third was immersed in 3% aqueous boric acid (H_3BO_3) for 3 days and then rinsed in water. Strengths were then measured by 3-point bending. Flexural strengths were 120, 61 and 84.4 MPa for the specimens tested dry, wet and treated with boric acid respectively. According to their invention the extent to which the flexural strength of products decreases in contact with water was reduced by treatment with an aqueous solution of boric acid or a borate although the recovery was only 19%.

Titchell et al., (1991) investigated the effect of water immersion, heat and gamma irradiaton of CAC- and OPC-based MDF cements. CAC MDFs are significantly stronger than OPC-based MDFs and they both degraded by immersion in water. The CAC system showed no sign of any recovery of strength with prolonged exposure whereas the OPC system did. Heating the specimens at 110°C decreased the strength but CAC MDFs were more severely affected by the heat than the OPC based MDFs. Gamma irradiation was also more damaging to the CAC-based MDFs according to their results. This may be because of the responsibility of the polymer for a greater degree of binding in the CAC system.

Ohama et al. (1993) produced MDF cements by using ordinary portland cement, poly(acrylamide) and a poly(alkylaryl) sulfonate-type water reducing agent with various polymer-cement ratios and water reducing agent contents at a constant water-cement ratio of 15%. They investigated the effects of curing conditions on the water resistance of MDF cements and recommended that the autoclave cure after moist and heat cure is most effective for improving the water resistance of MDF cements using a water-soluble polymer.

Lynn et al. (1992) used a water-soluble alkali metal silicate in their invention. This may for example be potassium or lithium or other silicate but sodium silicates are preferred. They found that compositions comprising one or more reactive fillers (e.g. pozzolanic materials) and one or more alkali metal silicates can be used to make high strength MDF cementitious products having both good water and thermal stability. Their advices are as follows:

Higher viscosity silicates give particularly good results in terms of strength of the resulting product. It is therefore preferred that the alkali metal silicate has a viscosity of at least 500 centipoise, more preferably at least 1000 centipoise and still more preferably a 2000 centipoise and over. Preferred examples of suitable pozzolanic materials for use in the invention include pulverised fuel ash (PFA) and blast furnace slag. Other possible reactive fillers include underburnt clays and shales; burnt gaize; rice husk; bauxite waste (a by-product of aluminum production); natural pozzolans such as volcanic ashes; and silica fume. The reactive fillers for use in the invention preferably contain calcium as one of the cations present, for improved water stability. In view of its lower calcium content, silica fume is advantageously used in combination with one or more calcium-containing reactive filers.

Desai et al. (1994) investigated the effects of reducing the unreacted cement content on the processing, structure, and moisture sensitivity of CAC-PVA based macro-defect-free (MDF) composites through both computer simulations and experiments. According to their hypothesis, the bulk polymer provides a pathway for water absorption and transport, but this process alone is not responsible for the observed strength loss during moisture exposure. They proposed that strength loss of MDF cements is affected by further hydration of unreacted cement grains, which leads to an accelerated deterioration of the performance properties of MDF materials. In addition, they suggested that the keys to optimizing the microstructural design of

MDF cements are to minimize their unreacted cement content and to eliminate their pathway for moisture transport. They tried to replace CAC with alumina (Al_2O_3) for decreasing the unreacted cement content. An increase in the amount of alumina (Al_2O_3) substitution resulted in a decrease in the unreacted cement content in the as-cured composites from 68.1 vol.% to 14.9 vol.%. They proposed that strength degradation upon exposure to moisture was affected by unreacted cement content, with the 25:75 CAC:Al_2O_3 composite exhibiting superior moisture resistivity.

Lewis et al. (1994) investigated the effect of binder distribution on the moisture absorption kinetics of macro defect free cements. They used hard-core/soft shell continuum percolation model to simulate the microstructure of MDF cement (Figure 3.27). A fundamental understanding of how moisture is transported from the sample surface to its interior through the binder phase tried to be clarified in their study. Through computer modeling, they tried to show that both polymer and interphase regions form percolative pathways through the MDF microstructure. They concluded that although the interphase regions form a percolative pathway through the MDF cement microstructure, their contribution to the transport of moisture is limited. In contrast, the bulk polymer regions have a significant effect on moisture absorption, providing the dominant transport pathway. They also suggested according to the knowledge gained from their work that modifying the binder phase of MDF cement such that the interphase to bulk PVA ratio increases should yield materials with improved moisture resistivity. In such samples, a nonpercolative distribution of bulk PVA would result, thereby inhibiting moisture transport to their interior.

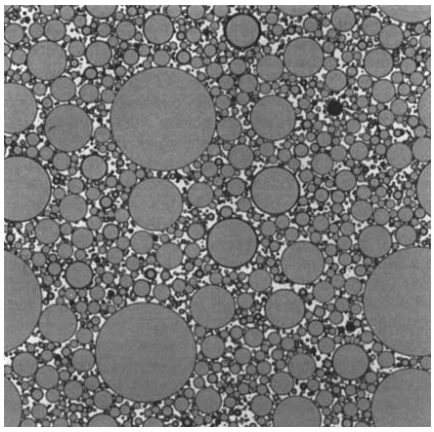


Figure 3.27: Two-dimensional view of the simulated MDF cement microstructure, where the unreacted cement grains (hard cores) are shown in gray, the interphase regions (soft shells) are shown in black, and the bulk PVA matrix is shown in white (Lewis et al., 1994)

Lewis and Boyer (1995) investigated the effects of an organotitanate cross-linking additive (triethanolamine titanate with the commercial name of Tyzor® TE) on the processing and moisture sensitivity of macro-defect-free (MDF) cements. They preferred coating cement particles in a special process opposite to Desai (1990) and Gulgun (1996) who also added the same crosslinking additive in bulk to the starting batch composition or during shear mixing. It was estimated that 6 wt% (by weight of the cement powder) of the additive was adsorbed. Initial flexural strengths of the organotitanate-modified MDF cement samples were lower than the standard MDF samples processed under identical conditions because of similar processing times during their high shear mixing and calendaring steps. These steps had been optimized for the standard MDF cement samples and processing in the same way led to a 65% reduction in the processing window for the modified pastes as compared to the standard MDF cement pastes. However, the organotitanate-modified MDF cement samples exhibited improved moisture resistance as compared to the standard samples when exposed to 100% relative humidity at 22°C. The most significant result was that the modified samples retained nearly 100% of their initial strength after 200 days of exposure to these conditions, whereas the strength of the standard MDF samples was decreased by approximately 45%. However, this composite has less initial strength with respect to standard MDF specimens. The cross-linking of PVA by triethanolamine titanate is reported to be initiated above 100°C or in high pH (pH 6 to 10) environments but the high temperature and high alkaline environment is destructive for PVA. Lewis and Boyer (1995) also proposed that triethanolamine titanate was not an ideal additive due to its chemical reactivity with PVA under ambient conditions although crosslinking the polymer phase is a promising approach to minimizing the moisture sensitivity of MDF cement system.

Brown (1996) used thermosetting acrylic resin and gypsum for the production of MDF cements. 100 parts by weight of alumina cement, 10 to 100 parts by weight of an aqueous polymer precursor emulsion (Component A), and 15 to 600 parts by weight of a hemi-hydrate gypsum (Component B) were mixed in his product. Component A preferably comprises a thermosetting acrylic resin, and Component B is preferably an alpha-hemihydrate gypsum or an anhydrous or retarded plaster. He proposed that aggregates, reinforcing materials or other additives may be incorporated into the product. The product is preferably prepared by mixing together

Component A and the alumina cement to form a precursor slurry, then mixing together the precursor slurry and Component B, and allowing the mixture to cure. He prepared 5 diferent specimens and decided that the combined alumina cement and gypsum product of his invention can be used to provide a water and weather resistant render that can be applied using traditional plastering methods or projection spraying.

Pushpalal et al. (1997) tried to produce MDF cements by using an alcohol soluble polymer instead of water soluble polymers and they succesfully produced MDF cements although final flexural strength was lower (123 MPa) than CAC-PVA MDF systems. They used resole type phenol resin precursor for the production of MDF. The precursor was essentially anhydrous and soluble in methanol and contains 58 to 62 wt% of nonvolatile matter. The strength loss of the phenol resin-alumina cement composite after immersion in water at 20°C for one year was 9%, and the elastic modulus remains almost unchanged. Phenol resin-alumina cement composite specimens have reached 0.12% expansion level and accumulated 0.82% of water after immersion in water at 20°C for one year. These are very small values in comparison with ordinary MDF cements. However, standard specimens soaked in water at 40°C, 60°C and 80°C showed a higher strength loss which increases with the increasing temperature of the water. The slight deterioration in water at 20°C and the large deterioration in hot water were attributed to further hydration of unreacted high alumina cement through absorption of water allowing crack growth in the polymer cement interface.

Poon et al. (1998) used poly(acrylamid) and OPC for the production of MDF cements and investigated the effect of adding silica fume, $CaCl_2$ and $ZnCl_2$ on the microstructure and stability of MDF in water. All the samples suffered a 50-60% decrease in strength after 1 day immersion in water, except for the sample dosed with 1 M $ZnCl_2$ solution. The sample prepared with 1 M $ZnCl_2$ solution had the lowest initial strength (34 MPa) and immersion in water resulted in almost a total loss of strength as the sample turned plastic. Strengths were partially recovered by continued immersion for 7 and 14 days and same recovery had been observed too in their earlier study (Poon and Groves, 1988) for OPC based MDF cements. They explained this strength recovery by further hydration of OPC which releases more Ca and Si to render a more stable gel matrix. They judged from the expansion and

microchemistry data that the samples with less Si content in its polymer matrix suffered more swelling and proposed that an icrease in Si concentration results in improved water stability.

Rodrigues and Joekes (1998) used PVA in solution instead of in bulk at the production of MDF cements. Hydrolysis degrees of PVA were between 87-89% and the concentration of the PVA solutions varied from 1.0 to 5.0% w/v. In mixed films, sodium silicate solution from 0 to 5.0% v/v was added to aqueous PVA solutions. To prepare the mixed films containing cement, the cement was added to a freshly prepared solution of PVA and sodium silicate. They called this process as "in situ" reticulation of polymer and proposed that the hydrophilicity of PVA is reduced. The amount of PVA needed in order to obtain MDF cements was only 1% in relation to cement weight, without loss of rheology of the paste according to them. The micro hardness of test specimens so prepared made them believe that the dependence between high relative humidity and mechanical properties can be eliminated. However, using lower amount of polymer may decrease the mechanical properties of composite.

Drabik et al. (1999) used hydroxypropylmethyl cellulose (hpmc) and poly(phosphate) (poly-p) as polymer and C_4AF, C_4A_3S and $C_4AF+C_4A_3\overline{S}+C_2S$ as binder. They investigated the mass and phase changes of MDF materials when exposed to moisture by using thermoanalytical methods. In MDF samples exposed to attack by moisture, thermoanalytical methods revealed the formation of secondary C-(A,F)-$\overline{S}$ hydrates and $CaCO_3$ only. The amounts of these materials were substantially supressed when the original material contains poly-p. They proposed that thermoanalytical studies allow a clear distinction of the regions and phases within MDF samples that are resistant (cross-linked sections of clinker hydrates with polymers) or unresistant (regions free of polymers) to uptake of moisture.

Delucchi and Cerisola (2001) produced MDF cements with PVA and 3 types of alumina cement and investigated the influence of the application of various organic coatings. Al_2O_3 contents of alumina cements were approximately 39, 41 and 70%. The results showed that the cement with the highest Al_2O_3 percentage had the lowest degredation after prolonged immersion. Porosity was measured approximately 1% in that composite. Organic coatings were low solvent epoxy resin, epoxy hydroalcoholic solution, water based epoxy resin, epoxy resin, poly(urethane-

aliphatic) and fluoropolymer solution. The application of surface coatings to the MDF cement resulted in a lower weight increase of the specimens during immersion in water; the different rates of water uptake reflected the water permeability properties of the coatings evaluated through EIS measurements, suggesting the compatibility of the coatings tested with the selected MDF cement. Epoxy hydroalcoholic solution had the highest water intake while fluoropolymer solution had the lowest.

Drabik et al. (2001) and Mojumdar (2001) used sulfoaluminate ferrite belite (SAFB) clinker premixed with portland cement in mass ratio 85:15 as binder and hydroxypropylmethyl cellulose (HPMC) or sodium poly(phosphate) (poly-P) as polymer for the production of MDF cements and investigated the effect of moisture. It appears that these two studies are nearly identical to each other; therefore, they are evaluated together. Their aim was to follow the effect of portland cement in the raw mixture and subsequent moisture resistance. They collected information from the mass changes, thermogravimetry (TG) and differential thermal analysis (DTA). They concluded that the most important improvement of moisture resistance of MDF materials was achieved in probes containing poly-P. In addition, delayed dried according to mass change results and the addition of portland cement in the raw mix also improved the moisture resistance of MDF cements. However, they did not conduct any mechanical tests.

Drabik and Slade (2004) tried to determine the level of moisture resistance of the compacted MDF tablets by the atomic structure of the cross-links. They used portland cement and sulfo-aluminate-ferrite belite (SAFB) clinker blended with portland cement ratio in mass 85:15 as binder and hydroxy-propylmethyl cellulose (HPMC) and poly(phosphate) glass (poly-p) as polymer for the production of MDF cements, similar to an other study of the first author (Drabik et al., 2001). It is generally accepted that moisture enters into MDF material by diffusion through the polymer-containing interface and difuses to the residual cement particles, with the consequence that the hydrate destroys the interphase region and ultimately degrades the original interface and the binding matrix. Therefore they tried to explore the relationship of atomic-level structure (cross-links) to moisture resistance of MDF materials in the system PC-SAFB clinker-HPMC-poly-P–water. They used ^{27}Al, ^{13}C, ^{31}P high resolution MAS NMR, ^{57}Fe Mossbauer and thermal (TG/DTA) analyses to

investigate the microstructure. They concluded from the comparison of the effects of HPMC and poly-P that the compactness of Al(Fe)-O-P cross-linked interfaces (developed by extensive reaction between the cement and the poly(phosphate)) increased the intrinsic density and lowered the moisture sensitivity by reducing the interfacial transport routes for moisture. Further improvement is achieved by the delay of drying of the samples after the original syntheses.

Mojumdar et al. (2004) used poly(butyl acrylate) (PBA), styrene/acrylonitrile co-polymer (SACP) and sodium poly(phosphate) (poly-P) for the production of MDF cements. Processing of MDF cements was similar to the earlier study of first author (Mojumdar, 2001). The only difference was the addition of Al_2O_3 (10%) and the type of polymers used. The most important improvement of moisture resistance of MDF cements is achieved in materials containing PBA, delayed dried and 5 MPa pressure applied for 3 h. The lower mass change was the evidence of higher moisture resistance.

Chowdhury (2004a) investigated the role of activated carbon in moisture-blocking capability of MDF cements. The polymer is required for strength in MDF formulations, but it also acts as a conduit for moisture uptake. Therefore, he believed that the solution is based on rendering the polymer hydrophobic by the use of activated carbon in an MDF cement formulation comprising ordinary portland cement (mixture of calcium, iron and alumino-silicates), silica and a vinyl polymer. He proposed that incorporation of activated carbon as an additive in an MDF cement formulation containing a vinyl polymer has been found to satisfy the aim of MDF cements for producing a moisture-blocking durable cement material. Comperative results by thermal analysis for carbon and non-carbon samples exposed to conditions of high humidity have verified total moisture resistance for carbonated samples. High voltage polarizability of only the carbonated samples signifies formation of a new entity in these samples that is absent in regular cement with the polymer alone. X-ray diffraction analysis and SEM pictures have provided further evidence of low initial hydration which is a characteristic of MDF cements.

Chowdhury (2004b) took also a patent for using activated carbon at the production of MDF cements. He proposed that the moisture content can be reduced or eliminated and also the voids can be reduced or eliminated in finished cement products. Although higher carbon content is contemplated, some initial studies have indicated

that higher carbon content can make the cement brittle. Generally, more carbon content higher than 50% is detrimental. On the other hand, mechanical tests were not conducted in order to give the strength of specimens in this study.

3.5 Microstructure of MDF Cements

Birchall et al. (1981) had thought that the polymer was a rheological aid at the production of MDF cements. A major function of the polymer was believed to develop a plastic mass during a process of high shear mixing from the mixture containing relatively little water. However, further studies (Eden and Bailey, 1984; Rodger et al., 1984; Rodger et al., 1985) showed that the removal of pores, either large or colloidal, is not the principal mechanism for obtaining such high strengths and polymer must also be interacting in some way with the cement. It was impossible to obtain such high strengths without using polymer even using the high shear process. In addition, experiments by Desai et al. (1992) with dilute and semidilute PVA solutions have shown that, even under the high pH conditions associated with cement hydration, the $Al(OH)^-_4$ ions do not crosslink the dissolved PVA. Thus, MDF-type reactions do not take place in the absence of strong mechanical agitation such as shear mixing (Tan et al., 1996). After that, some other studies (Sinclair and Groves, 1984; Poon and Groves, 1988; Kriven and Popoola, 1991; Popoola et al., 1991; Lewis and Kriven, 1993, Gulgun et al., 1995; Tan et al., 1996; Maggio et al., 2001; Bonapasta et al. 2001) had been conducted in order to understand the microstructure and the interaction between cement and polymer.

Birchall et al. (1981) produced OPC pastes and MDF cements and measured the flexural strengths and related these results through the Griffith equation to the sizes of the largest natural or artifically-introduced pores within the material. Flexural strength results versus flaw size can be seen in Figure 3.28. They investigated the porosity of the samples by mercury porosimetry and quantitative microscopy methods. Mercury porosimetry showed only 0.1% volume porosity above 15 μm diameter while it was detected as 5% by quantitative microscopy. Pore volume was far greater using quantitative microscopy than that given by mercury porosimetry, presumably because the mercury method cannot distinguish the pore diameter from the pore entrance diameter, or because some pores are effectively closed. They proposed that the results fitted the Griffith theory reasonably well.

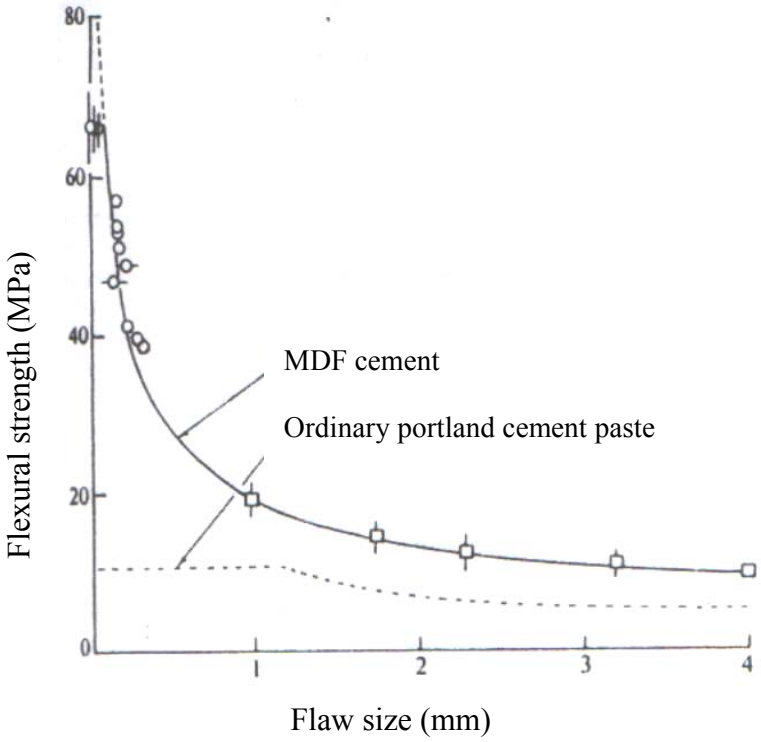


Figure 3.28: Results of flexural testing of notched MDF cement compared with ordinary portland cement paste (Birchall et al., 1981)

Sinclair and Groves (1984) prepared two different MDF systems with CAC-PVA and OPC-poly(acrylamide) and investigated their microstructure with transmission electron microscopy (TEM). They concluded that the normal crystalline hydrates of conventional calcium aluminate cement were absent in CAC MDF cements but a small quantity of polymer gel containing cement cations acted as the cementing phase. A thin rim of a material had been observed surrounding CA grains. However, OPC MDF cements contain the normal hydration products, CH, AFt and CSH, intimately mixed with the polymer matrix.

Sinclair and Groves (1985) produced MDF specimens by using same procedure with Birchall et al. (1983). They used OPC and CAC as cement for the production of MDF cement and compared them with each other. The polymer was poly(acrylamide) for OPC-based MDF cements and PVA for CAC-based MDF cements. Although both CAC- and OPC-based MDF cements were processed in a similar manner, the calcium aluminate cements yield higher flexural strength by a factor of 2 or 3 than those of OPC. In addition, water treatment decreased the strength of CAC-based MDF cements about 50% but OPC-based MDF cements appear to be less affected by a similar treatment.

They also examined the microstructures using transmission electron microscopy (TEM) of ion-beam thinned sections of pastes together with optical microscopy and X-ray diffraction, and compared with more conventional pastes. One of the most striking features of CAC- and OPC-based MDF cements when viewed through an optical microscope was the lack of defects such as air bubbles, cracks etc, which normally occur in cement pastes cast at higher water/solid ratios. An extremely fine porosity was present in the interstitial low contrast material on a scale of less than 0.01 μm at CAC-based MDF cements while it was 0.1 μm at OPC-based MDF. Furthermore, the amount of porous material is clearly much greater in OPC-based MDF than in CAC-based MDF. OPC-based MDF cements contain the normal hydration products CH and AFt, whereas CAC-based cement does not display any crystalline hydrate phases. CAC displays large grains of CA and CA_2 and normal crystalline hydration products of CA and CA_2, i.e. C_2AH_8 and CAH_{10}, were not found by either XRD or TEM in these CAC-based MDF cements. Therefore, the loss of strength of CAC-based MDF cements cannot be attributed to the conversion reaction of a conventional high alumina cement paste since the hexagonal hydrates CAH_{10} and C_2AH_8 are not initially present. They proposed that the loss in strength may be attributable to direct reaction of CA and CA_2 grains to form C_3AH_6 and gibbsite.

Dunster and Parsonage (1988) compared the silicate anion distribution in the macro defect free cements in which ordinary portland cement (OPC) was used for the production. They used the technique of trimethylsilylation where the silicate phases are converted into stable Q_xM_y poly(organosiloxane)s (with Q = $SiO_{4/2}$, M = $(CH_3)_3$ SiO_2). Two different MDF cement samples and one OPC paste were produced. First MDF cement consisted of OPC and PVA with the w/c ratio of 0.12 and the second MDF cement consisted of OPC and HPMC with the w/c ratio of 0.14 and OPC paste prepared with the w/c ratio of 0.47. The Q_xM_y poly(organosiloxane)s were analysed by high performance liquid chromatography (h.p.l.c.) and interfacial polymeric material and MDF cement samples were analysed using the following techniques: elemental analysis, ^{29}Si NMR, infrared spectroscop, DTA and DTG. Their work has confirmed the low degree of hydration of MDF cement pastes which contrasts with the much greater degree of hydration achieved in conventional portland cement pastes according to them.

Poon and Groves (1988) investigated the effect of microstructure on the water stability of MDF cements which was produced by OPC and poly(acrylamide). They concluded that flexural strength increased with the increase on polymer content but higher polymer content caused higher strength loss in water. They also concluded that the initially lost strength can be recovered by prolonged immersion up to 14 or 21 days. They replaced OPC with pulverized fly ash at 30% but it did not affect the strength.

Kriven and Popoola (1991) investigated the effect of poly(vinyl alcohol-co-vinyl acetate) (PVA) on the hydration behavior of monocalcium aluminate (CA). The polymer apparently reduced the number of hydration product nucleation sites according to their SEM and TEM images and EDS analyses. They explained the effects of PVA on nucleation and growth of the hydrates in three steps: (i) the viscosity change of the solution as the polymer progressively dissolve in water and calcium and aluminate ions are released into solution. (ii) ionic interactions between the calcium and the aluminate ions and the functional groups of the polymer chain (iii) steric effects if the polymer is intercalated into the crystal structures.

First Rodger et al. (1985) and then Kriven and Popoola (1991) suggested that the absence of the expected Ca-hydrate, in this case C_3AH_6, in the MDF microstructure could be due either to "nucleation site poisoning" by the polymer, or to a lack of sufficient water in the system for the conversion reactions. Results of Tan et al. (1996) with high amounts of water suggest that nucleation site poisoning may be a more plausible explanation.

Popoola et al. (1991) investigated the microstructure and microchemistry of MDF cements by using transmission electron microscopy (TEM), scanning electron microscopy (SEM), high resolution electron microscopy (HREM), energy dispersive spectrometry (EDS) and parallel electron energy loss spectrometry (PEELS). The expected hydration product at the processing temperature is $Ca_3Al_2O_6.6H_20$ (C_3AH_6), and sufficient moisture is available to facilitate the conversion of $Ca_2Al_2O_5.8H_2O$ (C_2AH_8) to $Ca_3AI_2O_6.6H_2O$ (C_3AH_6). However, the presence of the polymer phase in the amorphous interphase region, as evidenced by the PEELS spectrum, apparently inhibits this conversion. $Ca_2Al_2O_5.8H_2O$ has a layered structure which is isostructural with $Ca_4Al_2O_5.13H_20$. The intercalation of organic molecules with the latter has been to result in lattice swelling in the crystallographic

direction and to stabilize the structure above 80°C with respect to $Ca_3Al_2O_6.6H_2O$. It was considered that incorporation of organic additives into the hydrate lattices could be responsible for preventing the transformation to $Ca_3Al_2O_6.6H_2O$ (Young, 1970). Poly(vinyl alcohol) has been shown to intercalate in $Ca_4Al_2O_5.13H_2O$ and decrease its degree of crystallinity by Messersmith and Stupp (1992). It is thus suggested that partial intercalation of the polymer chain favors the formation of $Ca_2Al_2O_5.8H_2O$ within the interphase region, but the exact mechanisms involved are yet to be elucidated. SEM studies have suggested that the fracture of MDF cement can occur at the ceramic/polymer interface, inside the polymer phase, or transgranularly across the ceramic grains, depending on relative humidity. In dry tests the interphase/ceramic or interphase/polymer interfaces may be possible sites for crack nucleation. Water interaction with MDF proceeds by polymer swelling and interphase dissolution. The rate at which water diffuses across the interphase can determine the strength. Moreover, the conversion of $Ca_2Al_2O_5.8H_2O$ to $Ca_3Al_2O_6.6H_2O$ is accompanied by about 10% volume shrinkage and can create microporosity in the microstructure. While polymer swelling can be reversed by drying the sample, interphase dissolution is most likely an irreversible process. In dry tests, the strength of the ceramic/interphase and interphase/polymer interfaces may determine the failure mechanisms of MDF cements.

Lewis and Kriven (1993) discussed microstructure-property relationships in MDF cements. The binder distribution in MDF cement was varied by heating samples to temperatures between 125°C and 400°C. Chemically bonded water was removed from the system at 125°C, while PVA and water were removed simultaneously at higher temperatures. A bimodal pore-size distribution develops as increasing amounts of binder were removed from the composite, as shown in Figure 3.29.

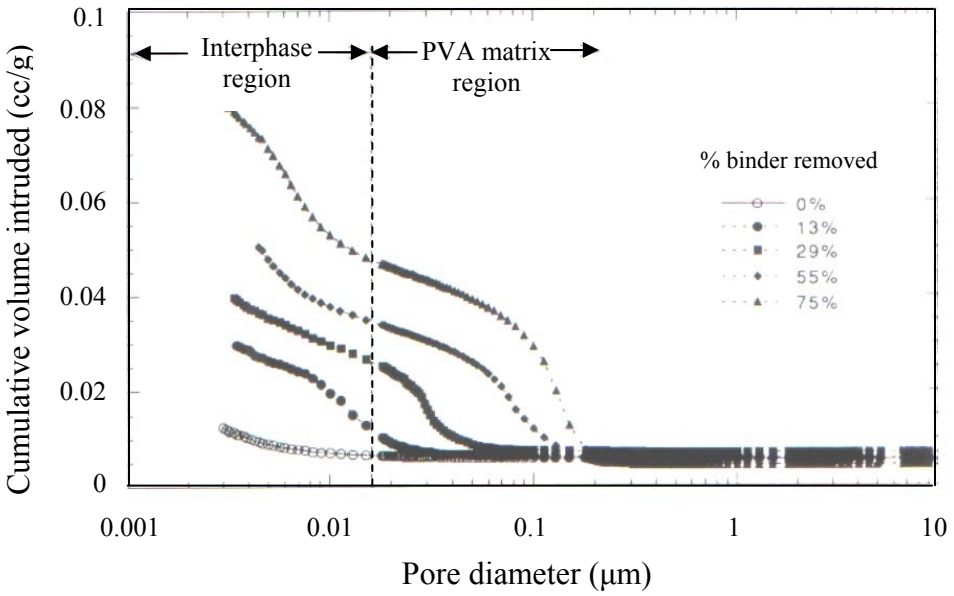


Figure 3.29: Pore development of heat treated MDF cements as a function of binder removed (Lewis and Kriven, 1993)

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 (Figure 3.30). This situation indicates that the interphase regions are highly resistant to moisture transport, and that the predominant transport pathway is through the bulk PVA matrix (Lewis and Kriven, 1993).

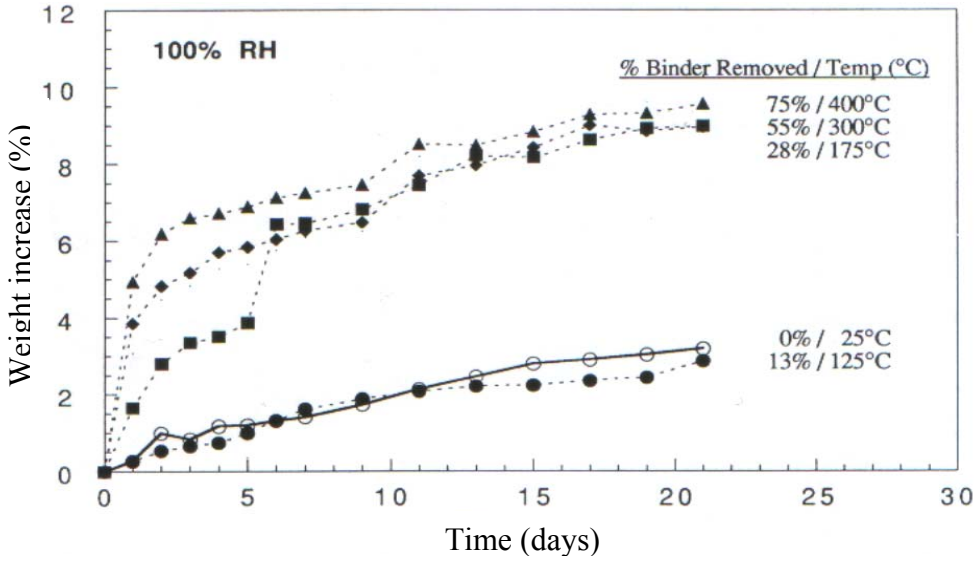


Figure 3.30: Moisture absorption behavior of heat treated MDF cements as a function of binder removed (Lewis and Kriven, 1993)

Additionally, Figure 3.31 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-sclae 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 (Lewis and Kriven, 1993).

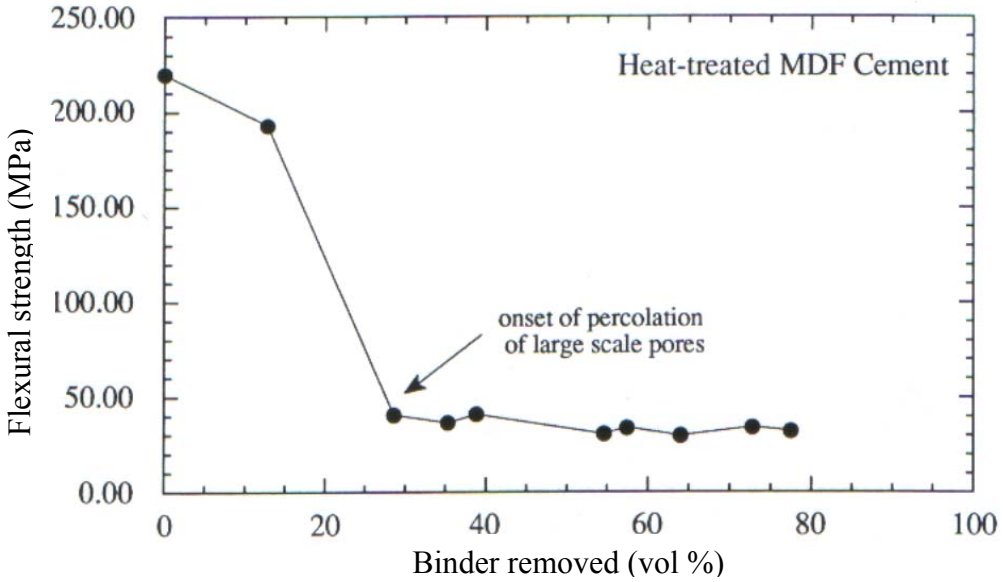


Figure 3.31: Flexural strength of heat treated MDF cements as a function of binder removed (Lewis and Kriven, 1993)

Drabik et al. (1994) prepared MDF cements representing selected compositions in the system $4CaO.Al_2O_3.Fe_2O_3$-$4CaO.3Al_2O_3.SO_3$-hpmc-H_2O and examined these samples using X-ray powder diffraction (XRD), thermogravimetry (TG), differential thermogravimetry (DTG), differential thermal analysis (DTA) and ^{27}Al magic-angle-spinning nuclear magnetic resonance (MAS NMR) spectroscopy. They concluded that the presence of hpmc inhibits the formation of crystalline products in the system C_4AF-C_4A_3S-hpmc-H, and an amorphous phase is formed. Inhibition of the conversion has also been reported previously in high alumina cement-poly(vinyl alcohol) MDF cements (Rodger et al., 1985; Edmonds and Majumdar, 1989; and Popoola et al., 1991).

Bortzmeyer et al. (1995) investigated the mechanical properties of macro-defect free cements with the help of fracture mechanics and rheology; transmission electron microscopy (TEM) and scanning electron microscopy (SEM). They concluded that MDF cements show very high fracture strengths due to both a high stres intensity

factor and a small critical defect size. The critical defect size is also a very important parameter affecting the mechanical properties, as is well known. Changing the processing variables (for examples, molecular weight of polymer or pressing temperature) may have an influence on both critical stress intensity factor (K_{IC}) and critical defect size (a_c), leading to complicated evolutions of the tensile strength according to them.

Gulgun et al. (1995) and Tan et al. (1996) investigated the affect of mixing time and mixing rate to the microstructure of CAC-PVA MDF composite and concluded that mechanically induced chemical reactions during mixing are responsible for the composite microstructure formation and resultant properties of the hardened matrix.

Comotti et al. (1997) studied the macrodefect free composites based on alumina cement and a poly(vinyl alcohol-co-vinl acetate) (PVA) copolymer by ^{13}C cross-polarization magic-angle-spinning nuclear magnetic resonance (CP MAS NMR). By observing ^{13}C NMR nuclei to measure hydrogen relaxation times in different molecular neighbourhoods they proposed that they determined the organic-inorganic phase interaction. In addition, an analysis of the intramolecular hydrogen bonds showed a stronger modification in the sample containing $CaAl_2O_4$ (CA) than in that containing $Ca_3Al_2O_6$ (C_3A). From the spectra, they have seen the deacetylation, and proposed that there was interaction between acetate groups and the calcium and aluminum ions.

Di Maggio et al. (2001) investigated the microstructure and its effect on the properties of MDF cements by using transmission electron microscope (TEM), X-Ray spectroscopy (EDXS), dynamical mechanical analysis (DMA) and flexural strength tests. They prepared MDF cements with three different cements which differ in their Al_2O_3 percent. Two of them were alumina cement while the last one was OPC. Since all of the materials had been processed under similar conditions, any differences existing in their properties should be the consequence of the chemical interactions between the cement ions and polymer which occured during the MDF cement processing procedure. The flexural strength decreased as the alumina content were reduced and calcia and silica contents were increased. In the comparison of the mechanical properties of the three composites, the differences can be attributed to crosslink bonds, although other effects have to be taken into account. They also

concluded that the cross-link density and the covalent character increase further upon heating.

Bonapasta et al. (2001) investigated the interaction of Ca ions with the carboxylate anions of one or two poly(acrylic acid) (PAA) chains by first theoretical methods. Their results indicated the formation of a stable CaO_4 complex which involves the -COO- groups of two different polymer chains. This gives support to the existence of a quite efficient cross-linking of the PAA chains because the Ca ion is anchored to four points of two PAA chains. Further, the CaO_4 fragment should be flexible enough to permit PAA cross-linking even in the presence of local deformations. The results also suggested that the PAA cross-linking is more efficient than that realized in the case of the PVA polymer, where a Ca ion is anchored to two points of two PVA chains. Theoretical investigations of the microchemical reactions between the organic and inorganic phases in MDF composites suggested the following relative strengths of the polymer-chain cross-linking: Al-PVA > Ca-PVA and Ca-PAA > Ca-PVA. The different strength of the polymer-chain cross-linking is certainly related to the mechanical properties of MDF materials. However, the above results cannot be directly related to the strength of those materials. In fact, other effects must be taken into account, e.g., the effects of processing where crosslinking may have opposite effects on the final mechanical strength of the MDF material.

3.5.1 Interaction Hypothesis between Cement and Polymer and Crosslinking Theory

There have been two main hypotheses on the nature of chemical interaction between the cement and the polymer: one suggests that the hydroxyl groups of PVA crosslink with the aluminate ions ($[Al(OH)_4]^-$) released by the hydrating cement, analogous to PVA-borate ion ($[B(OH)_4]^-$) crosslinking reaction (Rodger et al., 1984; Rodger et al., 1985; Popoola et al., 1991 and Bonapasta et al., 2000), and the other suggests that $Al(OH)_3$ precipitating from supersaturated solution forms strong coordinate bonding with the hydroxyl groups of the PVA (Desai, 1992). In an extension of the latter hyphothesis, it has been suggested that some of these weaker bonds possibly convert to stronger ionic/covalent bonds (Al-O-C) during curing at elevated temperature (~80-100°C) (Desai, 1997). The latter hypothesis seems less acceptable, although additional research is needed to fully resolve this issue.

It is well known that the borate ion $[B(OH)_4]^-$ is able to form complexes with certain poly(hydroxyl) compounds such as glycerol, mannitol or sugars and it is known that orthoboric acid H_3BO_3 reacts with poly(vinyl alcohol) in the presence of a base to form a completely glassy crosslinked polymer phase. The aluminate ion $[AI(OH)_4]$- has a very similar tetrahedral structure and may react in an analogous way. Reactions of PVA with hydrated calcium aluminate cement were first described by Rodger et al. (1984, 1985) and they proposed that the behavior of the polymer is more complex than being an inert rheological aid. They studied the evidence of polymer-cement interactions provided by calorimetry, solution chemistry and infrared spectroscopy. When water was added into the cement and partially hydrolyzed poly(vinyl alcohol-co-vinl acetate) mixture, the rising pH caused the hydrolysis of the acetate groups, leaving poly(vinyl alcohol) in solution with acetate ions, which subsequently reacted with calcium ions to form calcium acetate. Then the metal ions in the solution crosslinked with the poly(vinyl alcohol) chains; which made the polymer matrix rubbery and thus allowed the physical processing to continue as the cement-polymer mix attains plasticine-like consistency. The polymer also coordinated with metal ions on the surface of the cement grains producing a cohesive matrix which linked the anhydrous particles. This reaction scheme with the modification of Desai can be see in Figure 3.32.

Rodger et al. (1985) investigated the both poly(acrylamid)-OPC based MDF cements and PVA-HAC based MDF cements. They studied the evidence of polymer-cement interactions provided by calorimetry, solution chemistry and infrared spectroscopy. According to the results of calorimetry (Figure 3.33), as the concentrations of PVA added increases the retarding effect is reduced and an earlier peak begins to appear. This early peak increases in height as the PVA addition increases whilst the later peak, which corresponds to calcium aluminate hydrate formation, decreases. If a similar quantity of PVA is mixed with inert filler, e.g. sand, neither peak occurs, and we can conclude that this early peak is due to the interaction between the polymer and ions released from the cement.

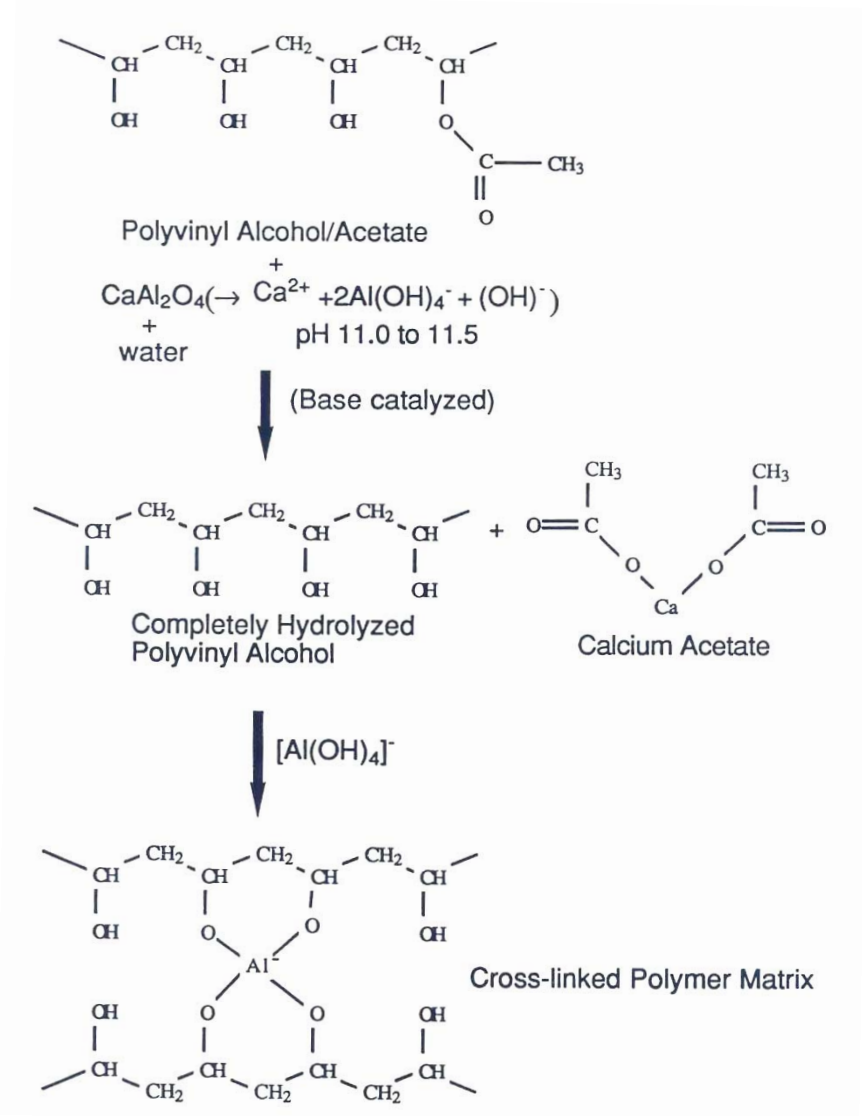


Figure 3.32: Schematic representation of the calcium aluminate cement with PVA in the presence of water (Desai, 1992)

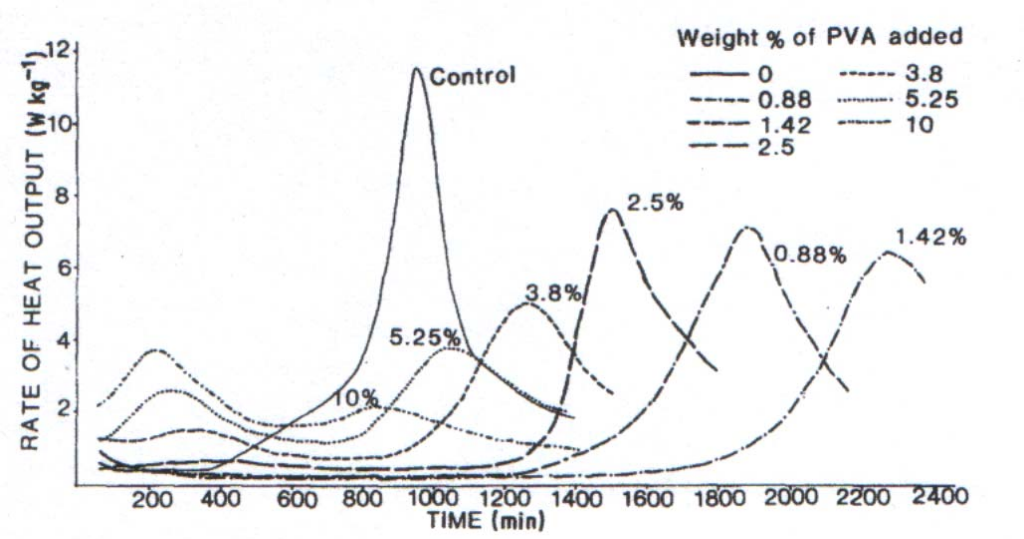


Figure 3.33: Heat evalution against time curves for control and Secar 71 pastes treated with poly(vinyl alcohol co-vinyl acetate), w/c=0.5 (Rodger et al., 1985)

XRD traces of hydrating paste containing 5 wt% PVA show no evidence of the crystalline hydrates, CAH_{10} or C_2AH_8, after the first exotherm (i.e. at 600 min). However, after the second isotherm (at 1500 min) peaks corresponding to C_2AH_8 appear. Thus the second isotherm may be identified as due to the formation of calcium aluminate hydrates whilst the first may correspond to the interaction between the polymer addition and the cement.

Crosslinking between Al ions and polymer chains were also supported by other studies. Popoola et al. (1991) pointed that significantly more aluminum than calcium was present in the polymer phase. This situation supports the hypothesis that aluminum is acting as a cross-linking agent in the polymer matrix.

Bonapasta et al. (2000) have been investigated the crosslinking of PVA chains by Al ions by ab initio theoretical methods. It has been assumed that the reaction of calcium aluminates with water leads to the formation of $Al(OH)_4^-$ molecules which are involved in the polycondensation reactions. The Car-Parrinello method has been used to estimate the energies released in these reactions as well as to investigate the equilibrium geometries, the electronic charge distributions, and the chemical bonding of several model systems where an Al ion is tetrahedrally coordinated with four O atoms. In these systems, the Al^{+3} ion is bonded with zero, one and two PVA chains. (see the structures of the $Al(OH)_4^-$ molecule and of the Al-PVA(I) and Al-PVA(II) models shown in parts a, b and c of Figure 3.34, respectively). The strength of the Al-O bonds has been investigated both for the equilibrium geometry and for distorted geometries of the Al-PVA(I) model to evaluate the effects of deformations of the PVA chains on the stability of cross-linking. Accordingly, the higher theoretical stability of the Al-PVA(II) model with respect to the model I supports the role of these ions in determining the properties of MDF cements. Bonapasta et al. stated that their results strongly support the existence of cross-linking of PVA chains by Al ions.

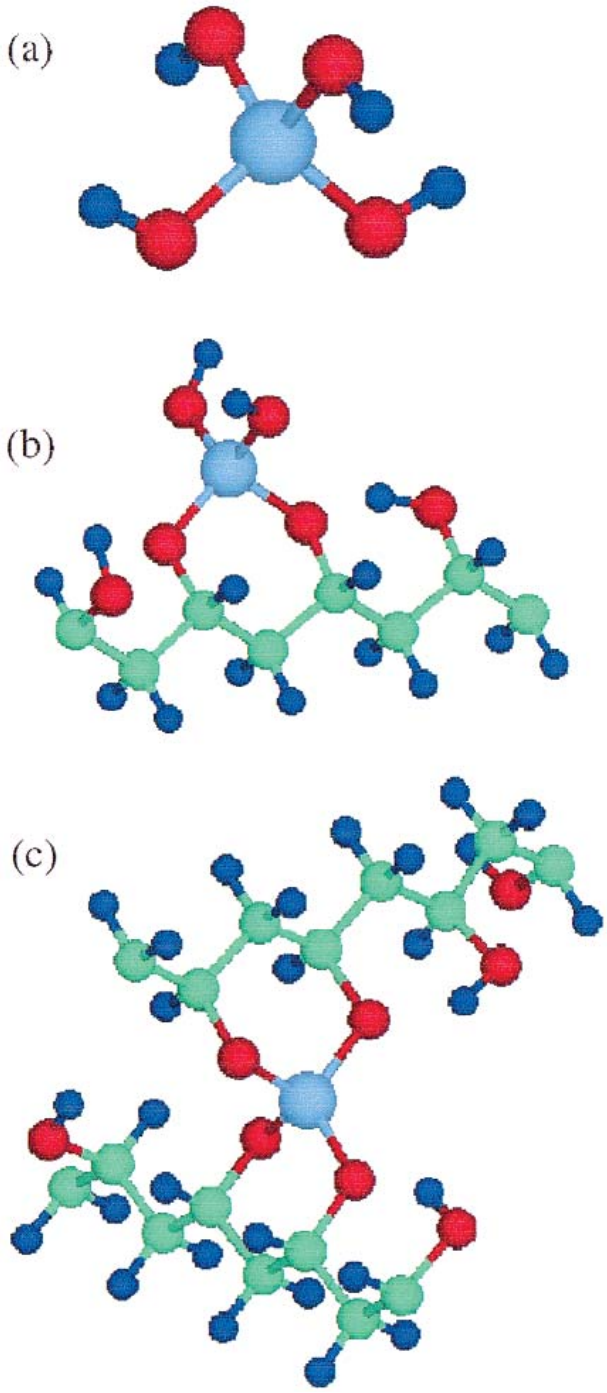


Figure 3.34:(a) Structure of the $Al(OH)_4^-$ complex; (b) structure of the Al-PVA(I) system; and (c) structure of the Al-PVA(II) system. In the Al-PVA(II) system a cross-linking is realized by an Al ion tetrahedrally coordinated with four O atoms of two PVA chains. In the calculations, the fragments of the PVA chains shown in the figure are repeated along the chain axis to simulate chains of infinite length. The Al, C, O, and H atoms are identified by the colors cyan, green, red, and blue, respectively (Bonapasta et al, 2000)

Bonapasta et al. (2002) investigated the cross-linking of poly(vinyl alcohol) (PVA) chains by Ca ions with first-principle theoretical methods and compared with a

previously investigated case of cross-linking of poly(acrylic acid) (PAA) chains. Present results support the existence of a Ca-PAA cross-linking that is significantly stronger and more efficient than that realized in the case of the Ca-PVA systems. This result implies that the Ca-O bonds involved in the cross-linking of the PVA and PAA chains are affected by the different functional groups present in the two polymer chains and agrees with the improvement of the mechanical properties observed when the PVA polymer is replaced by the PAA polymer in portland-cement-based MDFs. The achieved results also indicated that the Ca-polymer interactions may have significant effects on the mechanical properties of the above MDFs as well as on their processing. They suggested the following scale of relative strength for the cross-linking of the polymer chains: Al-PVA > Ca-PAA > Ca-PVA according to the results of their present and previous studies (Bonapasta et al., 2000; Bonapasta et al., 2001) on the interaction of metallic ions with PVA and PAA chains.

3.6 Applications of MDF Cements

High-strength cement-based materials developed recently are being used to explore new applications that have not been occupied hitherto by traditional cement and concrete technology. High flexural strength has not been a familiar property to conventional cement products; thus, there is no established position of MDF cements in modern industries. The relatively high cost of these materials has limited their use in civil and architectural applications that are very common for cements. Searching for new applications in the areas presently dictated by metal, plastics, and ceramics is a challenging task to cement scientists and engineers.

However, a novel processing method of high-strength cement-based materials led to the production of metal-like thin sheets at least 20 times stronger than ordinary cement paste but, unlike metals, they are intrinsically brittle. Metals have high moduli. They are ductile, allowing them to be formed by deformation processes. Plastics are nearly as strong as metals. They are easy to shape; complicated parts performing several functions can be molded from plastics in a single operation. The large elastic deflections allow the design of plastic components that snap together, making assembly fast and cheap. However, properties of plastics are highly dependent on temperature, so that the plastics are tough and flexible at 20°C, but may be brittle at the 4°C of a household refrigerator. They creep even at room

temperature, meaning that plastic components are deformed under a load with time. Ceramics are stiff, hard, and abrasion resistant; they retain their strength up to a high temperature but are difficult to machine. Despite this, high-strength cement-polymer composites combine the attractive properties of ceramics and plastics while avoiding some of their drawbacks. They are light and strong, and they can be made tough by introducing fibers. Unlike metals, they are resistant to corrosion. Unlike ceramics, cement-polymer composites can be cured at lower temperatures with great freedom in making desired shapes at room temperature. Unlike plastics, they show a wide range of temperature stability. In addition, there are some global issues such as the social demand to minimize environmental damage to save energy, and to reuse rather than discard (Pushpalal et al., 1999).

Figure 3.35 shows thermal insulation plates made by the calcium aluminate phenol resin (CAPR) composite for a hydraulic pressing machine. This machine is utilized for injection molding of plastic parts for earphones, and it is necessary to keep pressing molds at 60°C continuously. Thermal insulation plate is used between the mold and the pressure drum as shown in Figure 3.36. The plates were faced with a high degree of precision to fit the clearance between the mold and the pressure drum and were drilled to facilitate assembling. The CAPR plates are relatively easy to face and drill compared to ceramics and thermoplastics. Besides low thermal conductivity, these plates are lower in creep deformation under the elevated temperatures (Pushpalal et al., 1999).

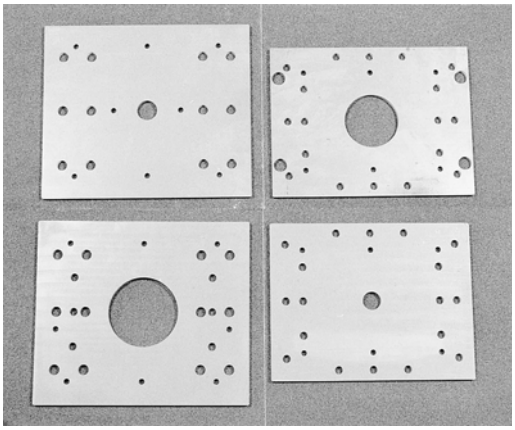


Figure 3.35: Four types of thermal insulation plates made by CAPR composite. Holes with various diameters facilitate assembling (Pushpalal et al., 1999)

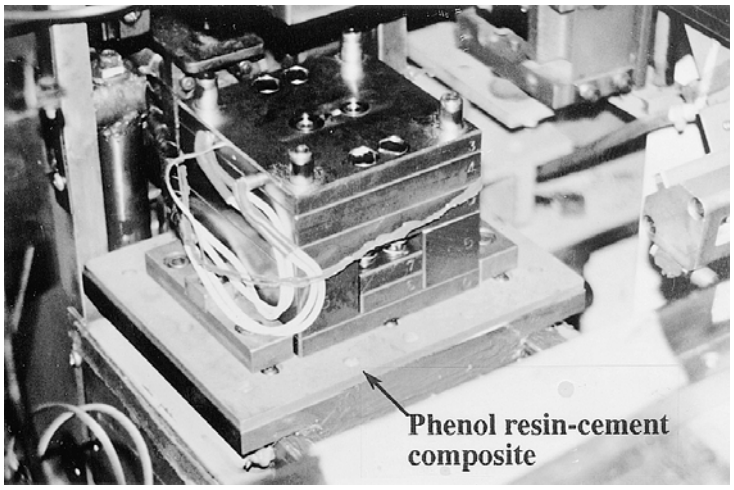


Figure 3.36:CAPR composite insulators in operation in an injection molding machine (Pushpalal et al., 1999)

Figure 3.37 shows a cutaway view of a lightweight honeycomb thermal insulation panel for the floor, roof, and wall panels in the building industry. The panel consists of two 1.2- to 1.8-mm thick CAPR composite. Outer sheets separated by a 25-mm thick layer of less dense aluminum core. Face sheets are stuck to the honeycomb using epoxy-type adhesives. The faces satisfactorily bear in-plane loading and any transverse bending stresses. The load-deflection patterns of honeycomb panels with the CAPR faces and the aluminum faces, both having equal overall thickness. The CAPR composite-faced panel is as strong as the aluminum-faced panel, but it is lower in deflection and has no permanent deformation under the loading as indicated in Figure 3.38. One interesting result is that the CAPR composite emits far-infrared rays into the atmosphere when heated, which may be an indispensable property of the material for some applications (Pushpalal et al., 1999).

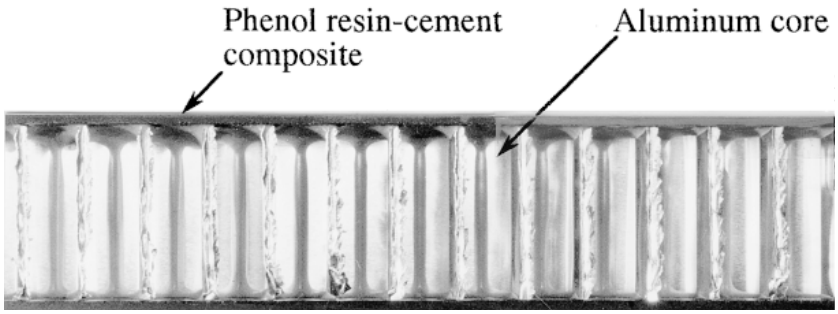


Figure 3.37: Cutaway view of a lightweight honeycomb thermal insulation panel. Facing plates were made by the CAPR composite (Pushpalal et al., 1999)

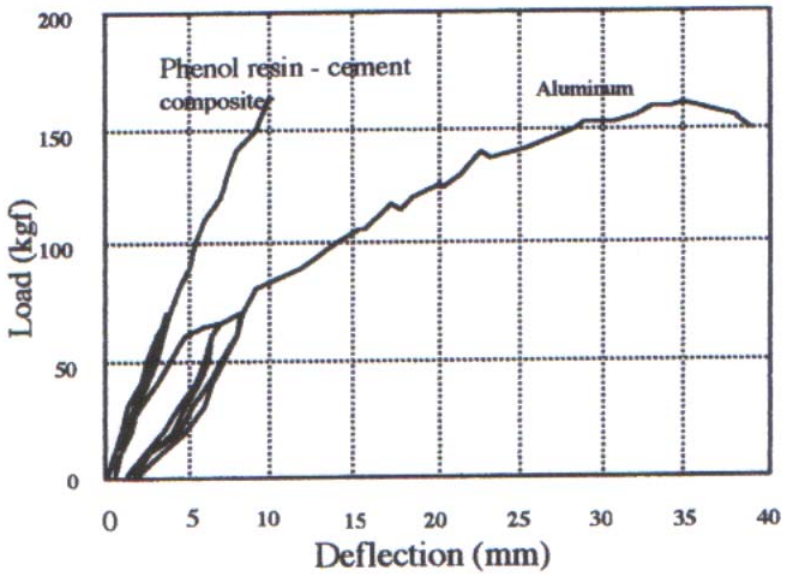


Figure 3.38: The load-deflection response of honeycomb panels with the cement faces and the aluminum faces (Pushpalal et al., 1999)

CAPR sheets, which has 120 MPa flexural strength and 2-mm thick, were placed in 15-mm thick wooden molds and fresh mortar was poured into the mold so that they harden together to make a united body. This strengthening method can be satisfactorily applied when making thin and lightweight cement membranes instead of steel or fiber-reinforced plastic (FRP) embedments, which make handling difficult. Figure 3.39 shows a cutaway view of a 15-mm thick, lightweight double-deck floor panel.

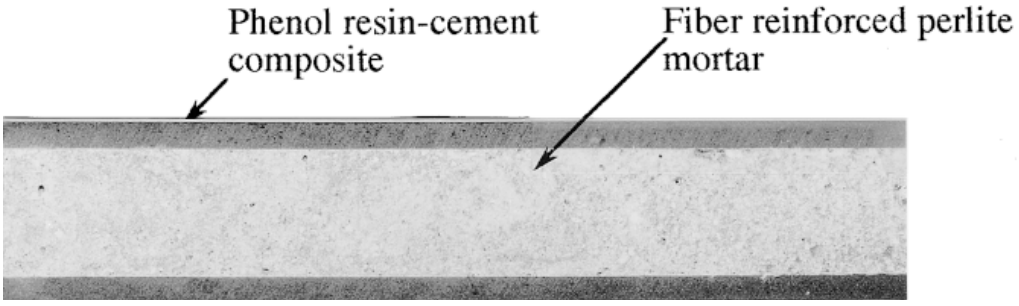


Figure 3.39: Cutaway view of a lightweight double-deck floor panel. Two-millimeter thick CAPR sheets are used in the top and bottom for reinforcement (Pushpalal et al., 1999)

A solar car with a 3600x700x900 mm body was made by Pushpalal et al. (1999), and this car was run in a solar car rally to study the feasibility of utilizing cements in the transportation industry. A side view of the solar car is shown in Figure 3.40.

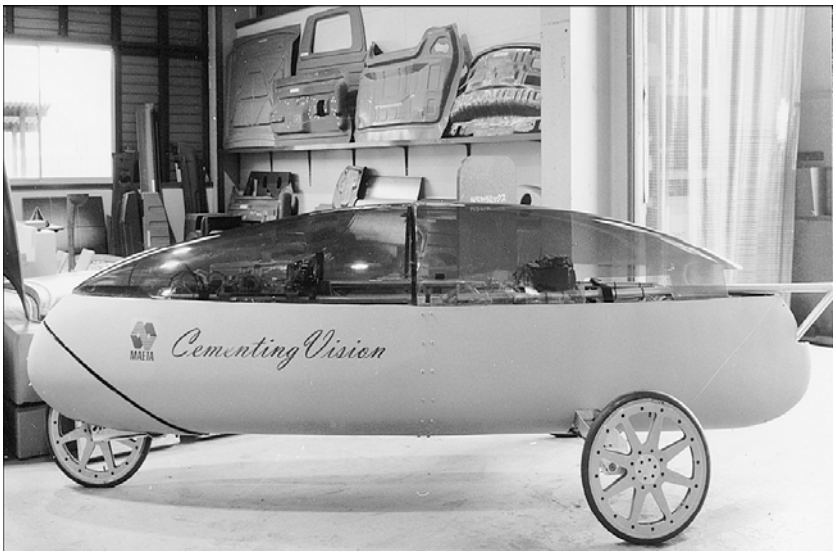


Figure 3.40: View of the solar-powered car in which the body is made by the CAPR composite (Pushpalal et al., 1999)

Possible application areas of MDF cements according to Alford and Birchall (1984), Russell (1991) and Pushpalal et al. (1999) can be summarized as follows;

Roof tiles and roofing slates

Domestic and industrial flooring tiles

Wall tiles, paneling for walls, ceilings

Corrugated sheeting, e.g. for fencing and roofing

Molded castings for electromagnetic interference screening

Extruded piping

Electronic packaging

Ballistic armor plating

Liquid cryogenic containers

Acoustical damping panels

Thermal insolators

4 EXPERIMENTAL STUDIES

4.1 Experimental Study I: Investigations of Ingredients and Process Parameters (Pre-tests)

4.1.1 Materials

The cement used in this study was calcium aluminate cement which was produced by Lafarge firm with the commercial name of Secar 71. Al_2O_3 content was 70% and CaO content was 29.2% of this cement. Technical properties of Secar 71 can be seen in Table 4.16 and Table 4.17.

The polymer used in this study was partially hydrolyzed poly(vinyl alcohol-co-vinyl acetate) copolymer, and its commercial name was Gohsenol KH-17, and it's produced by Nippon Gohsei. This polymer has 79.4 mole% hydrolysis degree and it was the most widely used PVA type for the production of MDF cements in literature (Birchall et al., 1983; Russell, 1991; Desai, 1992; etc.). The properties of Gohsenol KH17 can be seen in Table 4.4. Small amount of glycerol (1% of PVA by weight) was also added into the mixture for plasticizing unless it is not mentioned.

4.1.2 Mix Design

Twenty different MDF cement batches were prepared. Amounts of the materials were same for all batches except number 17, 18 and 19. Compositions of these batches can bee seen in Table 4.1. Water/cement (w/c) was 0.11 and polymer/cement (p/c) was 0.07 by weight unless it is not mentioned.

Table 4.1: Compositions of the specimens for pretests except mix no: 17, 18, and 19

Material	Density (g/cm^3)	Weight		Volume	
		(g)	(%)	(cm^3)	(%)
CAC	2.93	120	84.2	40.96	67
PVA	1.3	8.4	5.9	6.46	10
Glycerol	1.26	0.84	0.6	0.67	1
Water	1	13.2	9.3	13.20	22
Total	-	***142.44***	***100***	***61.28***	***100***

Aim of these tests was learning the production processes, getting used to the production steps, understanding the effects of different parameters and optimizing the production method with respect to results. Investigated parameters were mixing duration and speed at the planetary mixer, working width of the roller mills, effects of glycerol addition, hot pressing, heating at oven, folding 2 or 3 times of the sheet at the last step of calendering, cooling temperature of the calendering machine, hot press temperature, amount of PVA, amount of water and adding activated carbon.

Only mixing duration and the speed of planetary mixer were changed for the batches 1-7. Then mixing method of number 6 was accepted as standard method and rest of the batches were mixed at planetary mixer with the same method and other parameters were changed in order to see their effects. Brief definitions of each production are given below.

Number 1: CAC, PVA, glycerol and water were blended together in a planetary mixer at a speed setting of 2 for 15 seconds. The cohesive solid material were scraped off the bowl and then blended for an additional 3 minutes at a speed rate 2.

Number 2: CAC, PVA and glycerol were dry blended for two minutes prior to the addition of water at a speed rate 1. After adding of water, the batch was mixed for three minutes at medium speed (speed rate 2) until a damp, granular mix formed.

Number 3: CAC, PVA and glycerol were dry blended for one minute prior to the addition of water at a speed rate 1. After adding of water, the batch was mixed for three minutes at medium speed (speed rate 2) until a damp, granular mix formed.

Number 4: CAC, PVA and glycerol were dry blended for one minute prior to the addition of water at a speed rate 1. After adding of water, the batch was mixed for two minutes at medium speed (speed rate 2) until a damp, granular mix formed.

Number 5: CAC, PVA and glycerol were dry blended for one minute prior to the addition of water at a speed rate 1. After adding of water, the batch was mixed for two minutes at high speed (speed rate 3) until a damp, granular mix formed. It is necessary to cover the bowl during this step to prevent loss of material.

Number 6: CAC, PVA and glycerol were dry blended for one minute prior to the addition of water at a speed rate 1. After adding of water, the batch was mixed for one minute at medium speed (speed rate 2) until a damp, granular mix formed. The cohesive solid material is scraped off the bowl in 30 seconds and then was blended for an additional 1 minute at a speed rate 2.

Number 7: CAC and PVA were dry blended for one minute prior to the addition of water at a speed rate 1. Mixture of water and glycerol were added, the batch was mixed for two minutes at medium speed (speed rate 2)

Number 8: Same mixing procedure with number 6, but the working width did not narrowed to the 14 cm.

Number 9: Same mixing procedure with number 6, but different type of glycerol was used.

Number 10: Same mixing procedure with number 6, but glycerol was used two times more.

Number 11: Same mixing procedure with number 6, but MDF sheets were put directly to the oven without using hot press.

Number 12: Same mixing procedure with number 6, but MDF sheets weren't put to the oven after hot pressing.

Number 13: Same mixing procedure with number 6, but MDF sheets were folded 2 times instead of 3 at the final step of the calendering machine.

Number 14: Same mixing procedure with number 6, but chiller was adjusted to 10°C (50°F) in order to cool down the calendering machine.

Number 15: Same mixing procedure with number 6, but chiller was adjusted to 21°C (70°F) in order to cool down the calendaring machine.

Number 16: Same mixing procedure with number 6, but hot press machine was adjusted to 100°C (212°F) instead of 80°C (176°F).

Number 17: Same mixing procedure with number 6, but 6 g PVA was used instead of 8.4 g. (p/c=0.05 instead of 0.07).

Number 18: Same mixing procedure with number 6, but 15.6 g water was used instead of 13.2 g. (w/c=0.13 instead of 0.11).

Number 19: Same mixing procedure with number 6, but activated carbon was added to the mixture as 10% of cement by weight.

Number 20: Same mixing procedure with number 6, but 3 MPa pressure was applied in hot press machine instead of 5 MPa.

4.1.3 Production Procedure

Conventional production method optimized at UIUC (Part 3.2.2) was used for these pre-tests. Model of the used planetary mixer was Hobart which has 3 different speeds (Figure 4.1). After mixing the ingredients at planetary mixer, the mix was fed into

the rolls of two-roll mill (model no: TAH 4.00, 6x15 inch (15.2x38.1 cm), and serial no: 69562 laboratory mill, Stanat Mfg,, Westbury, Long Island, NY). Roller mills can be seen in Figure 4.2.

Figure 4.1: Mixing the materials in a planetary mixer

Figure 4.2: Calendering machine with two roller mills and cooling system

The mix was processed in different speeds and nip gaps at roller mills according to the steps mentioned in Part 3.2.2.3 unless it is not mentioned. Subsequently, 2 different 100x100x1.7 mm sheets were trimmed with a knife after production. Then these sheets were pressed at 80°C and 5 MPa for 10 minutes between 2 sheets of 0.25-mm thick Mylar® polyester sheets and 12-mm thick aluminum plates. The Mylar® sheets were used as a non-stick surface as well as to produce a smooth finish on the MDF sample. Hot press machine (Figure 4.3) has a capacity of 25 tons

hydraulic press with 300x300 mm electrically heated platens and automatic temperature, timer and pressure controllers, Model 2518, Carver Press Co., Menomonee Falls, WI.

Figure 4.3: Hot press machine

The specimens with 100x100x1.7 mm sizes were then cured in a forced-air oven at 80°C for 24 hours between two sheets of Mylar® and aluminum plates. The aim of covering the specimens with Mylar® and aluminum plates was to reduce warping of the specimens. Approximately 7-9 circular specimens were core drilled from each of these 100x100x1.7 mm sheets with a Delta model diamond core (Figure 4.4). 24 hours later except for the batch number 19. Mineral oil was used as a coolant to avoid exposure to water. Finally, specimens were cleaned using methyl alcohol or acetone to remove the mineral oil from the surface of the specimens.

Figure 4.4: Core drilling machine used to prepare circular specimens from MDF sheets

Half of the specimens were stored in water for 6 days while the other half were stored in a desiccator using silica gel as the desiccant. All specimens were taken their containers and subjected to biaxial flexural strength tests 7 days later after their production.

4.1.4 Biaxial Flexural Strength Test Results for Pretests

Biaxial flexural test method which involves supporting a plate on three or more points at bottom surface and loads on upper central point was first described by Wachtman et al. (1972) and ASTM published a standard in 1978 according to their drawings and proposals. Specimens were supported symetrically at three points, 120° apart on a 25.40-mm circle in the fixture. The load is applied at the center of the disc with a 1.60-mm diameter piston. Russell et al. (1991) compared this indirect tensile test method with the most common 3 or 4 point bending test method and concluded that the biaxial flexure strength results were 15-20% higher than the 3 and 4 point bending tests respectively.

Biaxial flexural strength tests were conducted over each sample both stored in water and desiccator according to ASTM F394 (1996). More information about biaxial flexural strength test and calculations can be found in Appendix A.

Typically five specimens for each sample condition were tested. Avearge values of biaxial flexural strengths ($\overline{S}$), standard deviations (σ) and coefficient of variations (V) of each mixture were calculated and the results can be seen in Table 4.2 and Figure 4.5. Dry strength means the strength of specimens which were stored in desiccator and wet strength is the strength of specimens which were stored in water. In addition, all test results of each specimen can be found in Appendix B.

Table 4.2: Biaxial flexural strength test results of pretests for 7-days

	DRY STRENGTH			WET STRENGTH		
Batch No	$\bar{S}$ (MPa)	σ (MPa)	V (%)	$\bar{S}$ (MPa)	σ (MPa)	V (%)
1	209	31	15	151	21	14
2	228	15	7	138	37	27
3	217	23	11	128	13	10
4	195	18	9	175	13	7
5	162	10	7	116	33	28
6	194	26	13	83	21	26
7	243	15	6	113	20	18
8	196	17	9	134	23	17
9	185	9	5	116	15	13
10	220	15	7	94	11	12
11	114	7	6	23	6	24
12	226	22	10	74	23	30
13	189	21	11	117	9	8
14	199	10	5	93	25	27
15	209	17	8	122	42	35
16	220	16	7	136	23	17
17	129	17	14	68	17	25
18	205	22	11	125	35	28
19	8	-	-	22	-	-
20	179	31	17	118	21	18

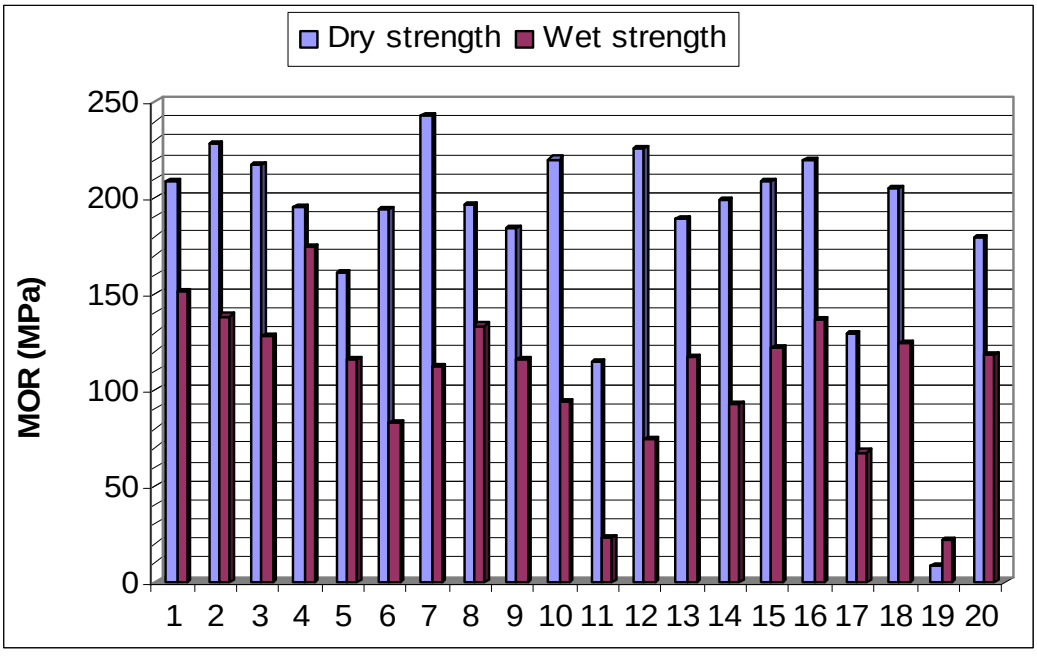


Figure 4.5: Biaxial flexural strength test results of pre-tests for 7 days

4.1.4.1 Effect of mixing duration and mixing speeds

Cement, polymer, water and glycerol were first mixed at planetary mixer in order to obtain a more homogeneous mixture and different durations and speeds can be applied during this step. Seven different mixtures were prepared in order to investigate the effect of different mixing time and speeds. Mixing time was changing between 3-5 minutes and 3 different speeds (1:slow, 2:medium, 3:fast) were applied Differences on mixing durations and speeds can be seen in Table 4.3. These tests were conducted in order to find better mixing time and speed.

Table 4.3: Differences on mixing times and speeds for the numbers 1-7

Mixture No.	Mixing time 1 (min)	Speed Rate 1	Mixing time 2 (min)	Speed rate 2	Mixing time 3 (min)	Speed rate 3	Total mixing time (min)
1	25 sec	2	3	2	-	-	3 m. 25 s.
2	2	1	3	2	-	-	5
3	1	1	3	2	-	-	4
4	1	1	2	2	-	-	3
5	1	1	2	3	-	-	3
6	1	1	1	2	1	2	3
7	1	1	2	2	-	-	3

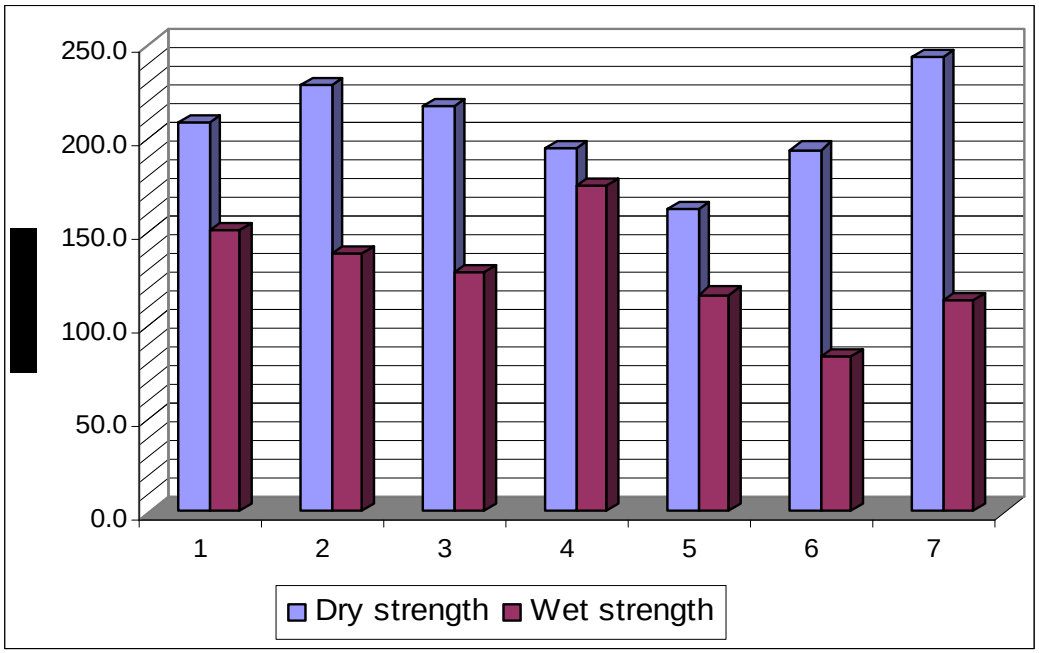


Figure 4.6: Effect of mixing time to the flexural strength of MDF cements

Biaxial flexural strengths of these 7 batches in dry and wet conditions can be seen in Figure 4.6. Only mixing times and speeds were changed in these batches. Number 7 has the highest dry strength (243 MPa) while the number 5 has the lowest flexural strength (162 MPa). Glycerol was not added to the dry mixture in number 7, it was added in a water solution. Therefore, adding glycerol to the mixture in a water solution looks like a better procedure. In addition, if we look at first 6 batches, higher mixing times caused the higher strengths. According to these pretest results, mixing duration was chosen as 5 minutes (number 2) for further productions (this was same with Russell, 1991), adding glycerol in water solution like in number 7.

4.1.4.2 Effect of glycerol

Effect of glycerol can be seen in Figure 4.7. Glycerol was added to the mixture two times more in number 10 (20% of PVA by weight) according to number 6 (10% of PVA by weight). Flexural strength increased 13% in both dry and wet conditions although standard deviation was higher. Effect of glycerol was already explained in Part 3.1.3 and glycerol amount is chosen 10% of PVA amount similar to other researchers (Russell, 1991; Desai, 1992; Boyer, 1993; Gulgun, 1996; etc)

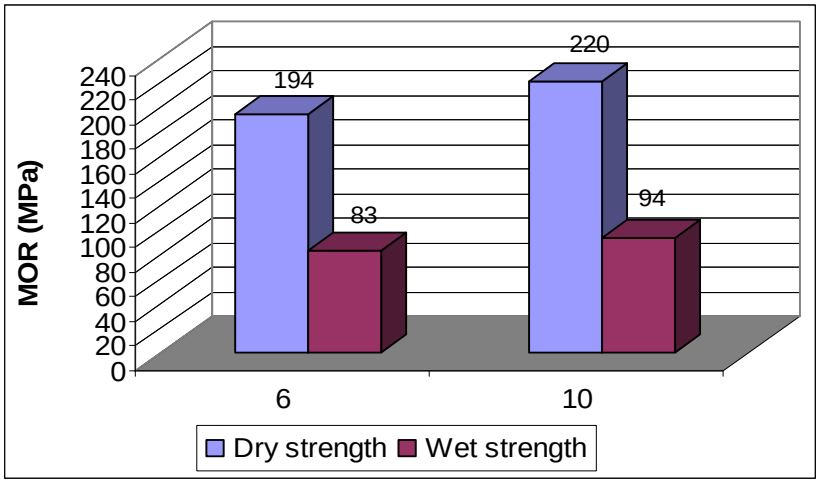


Figure 4.7: Effect of glycerol amount to the flexural strength of MDF cements

4.1.4.3 Effect of hot pressing

Effect of hot pressing can be seen in Figure 4.8. If we compare number 6 (hot press procedure was applied) and number 11 (hot press procedure was not applied), there is 42% decrease in dry condition and 72% decrease in wet condition. Therefore, hot press is an important procedure to obtain high strengths in both conditions. It is believed that polymer fills the voids during this process.

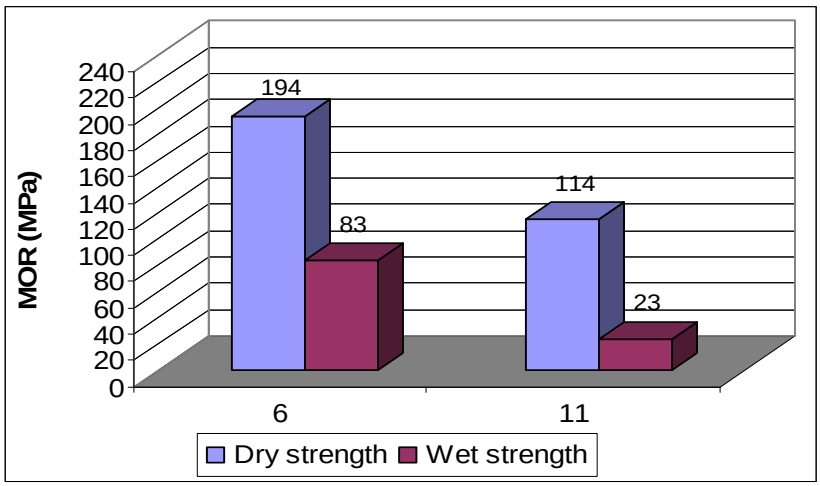


Figure 4.8: Effect of hot pressing to the flexural strength of MDF cements

Effect of pressure during hot press can be seen in Figure 4.9. If we compare number 6 (5 MPa hot press applied) with number 20 (3 MPa hot press was applied), there is 8% decrease in dry condition but 42% increase in wet condition. 3 MPa looks like better to increase wet strength but, coefficient of variation was high in these results. Applying 5 MPa pressure is accepted for further productions similar to other researchers (Birchall et al., 1983; Russell, 1991; Desai, 1992; Boyer, 1993; Gulgun, 1996; etc).

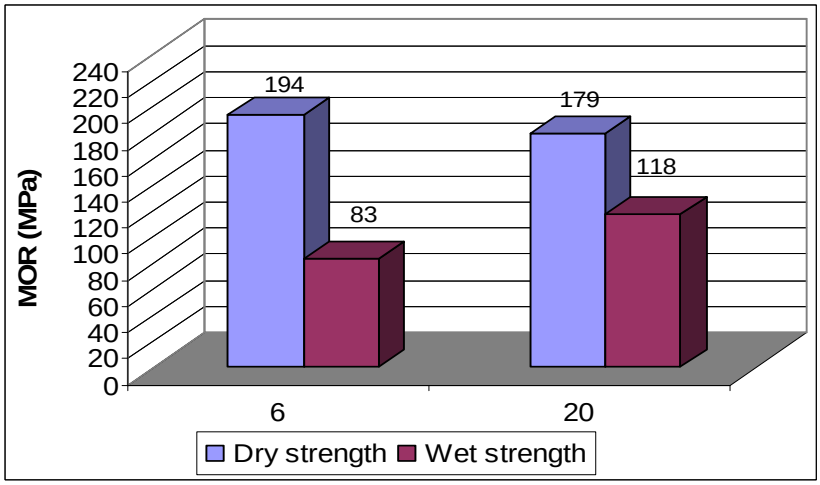


Figure 4.9: Effect of pressure during hot press to the flexural strength of MDF cements

4.1.4.4 Effect of hot press temperature

Effect of temperature during hot pressing can be seen in Figure 4.10. If we compare number 6 (80°C was applied) and number 16 (100°C was applied), there is 13% increase in dry condition and 65% increase in wet condition. Therefore, applying 100°C during hot press looks like a better solution, but coefficient of variation was high at wet strength and high temperature can be harmful for polymer. Wet strength

of number 16 was 56.1 MPa at 28 days which makes us dubious about the result of 7 days wet strength. Because of all these reasons, hot press temperature was accepted 80°C similar to previous researchers.

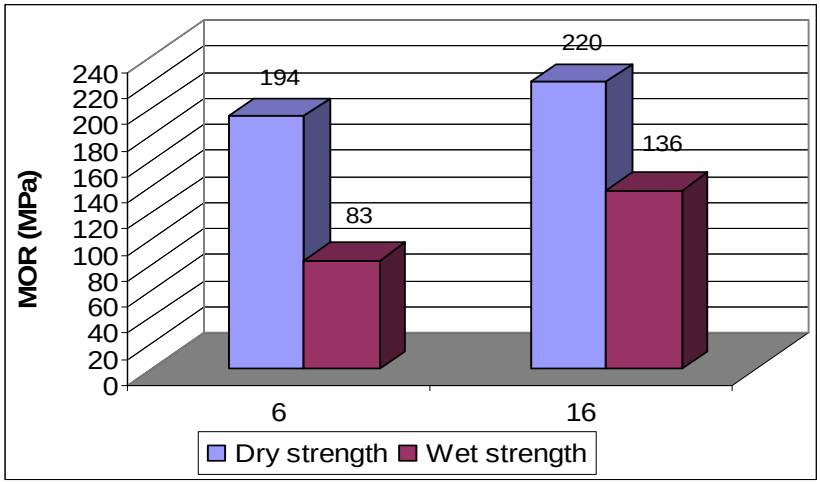


Figure 4.10: Effect of temperature during hot press to the flexural strength of MDF cements

4.1.4.5 Effect of oven

Effect of using oven during curing can be seen in Figure 4.11. If we compare number 6 (specimens stored at oven at 80°C for 24 hours after hot press) and number 12 (specimens directly put to the desiccator just after hot press), there is 16% increase in dry condition but 10% decrease in wet conditions. Hot cure at oven is an important step for the production of MDF cements.

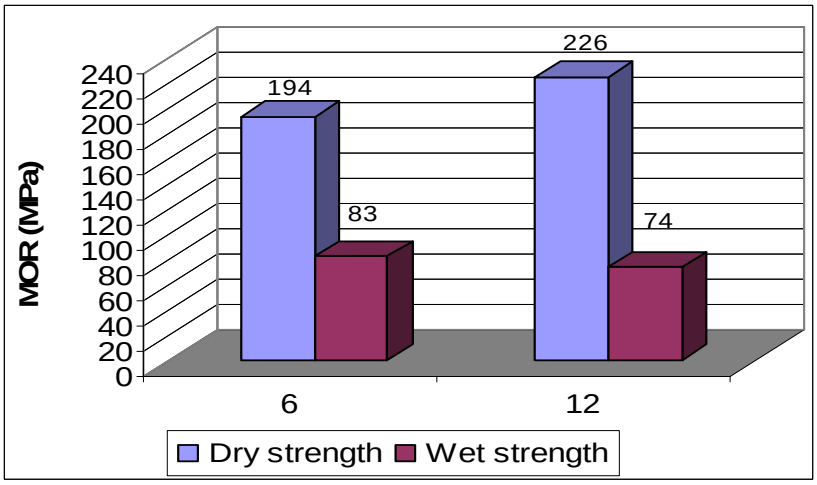


Figure 4.11: Effect of curing at oven to the flexural strength of MDF cements

4.1.4.6 Effect of the number of the folding the sheets

MDF cements were folded 2 or 3 times at the last step of calendering. These tests were conducted in order to see the effects of folding. Test results can be seen in

Figure 4.12. Folding sheets 2 or 3 times during calendaring is not so important, because Number 6 and Number 13 gave nearly same results.

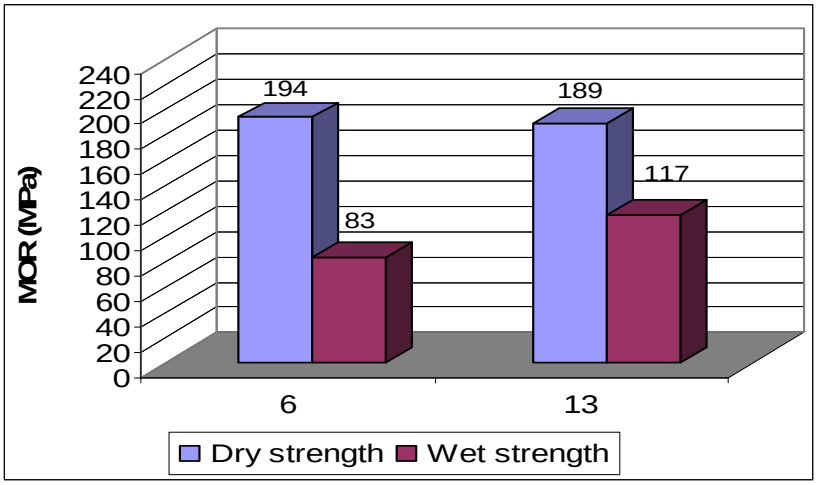


Figure 4.12: Effect of folding sheets to the flexural strength of MDF cements

4.1.4.7 Effect of cooling water temperature

Roller mills were generally cooled down during production in order to prevent any adverse effect of high temperature. Therefore, chiller was adjusted to 3 different temperatures during MDF cement preperation in order to see the effects of temperature on mechanical properties. Test results can be seen in Figure 4.13. There is very little difference between these 3 batches. 60°F (15.5°C) is accepted for further productions like in other researches (Russel, 1991; Desai, 1992; Desai 1997; Boyer, 1993; etc.).

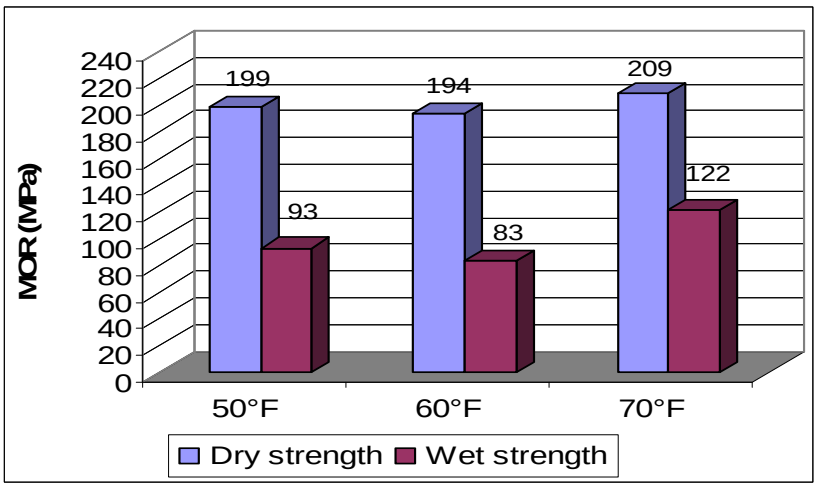


Figure 4.13: Effect of cooling temperature to the flexural strength of MDF cements

4.1.4.8 Effect of PVA amount

Effect of PVA amount can be seen in Figure 4.14. If we compare number 6 (PVA/cement:0.07) and number 17 (PVA/cement: 0.05), there is a 44% decrease in

dry condition and 19% decrease in wet condition. Russell (1991) and other researchers already optimized these amounts, and using 0.07% PVA/cement ratio looks better solution. Using 0.07% PVA/cement ratio is accepted for further productions.

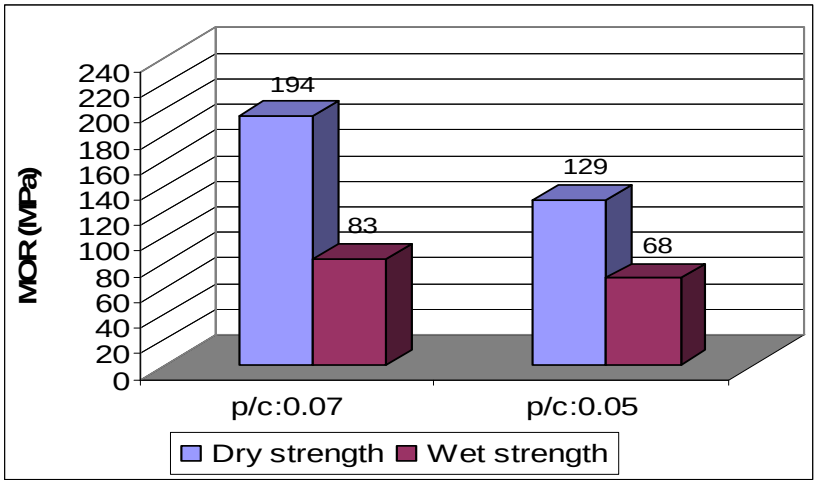


Figure 4.14: Effect of PVA amount to the flexural strength of MDF cements

4.1.4.9 Effect of water amount

If we compare number 6 (water/cement:0.11) and number 18 (water/cement:0.13), there is 5% increase in dry condition and 50% increase in wet condition (Figure 4.15). But, it wasn't easy to produce MDF cement with 0.13 water/cement and MDF sheets passed from roller mills several times more, because it wasn't easy to peel of the sheet from roller mills. 1 more high shear process was applied and waited for drying. This procedure was already optimized for 0.11 w/c by Russell (1991), using 0.13 w/c may need a little bit different procedure. Because of the difficulty of the production with 0.13 w/c, 0.11 w/c was chosen for further productions.

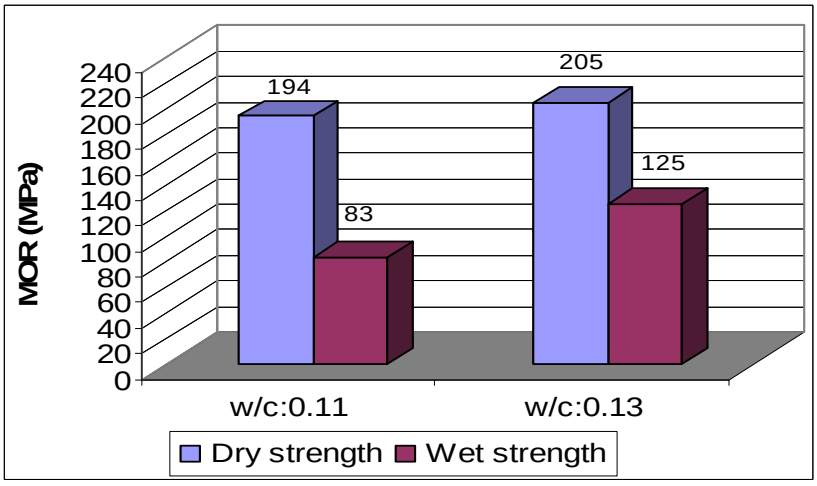


Figure 4.15: Effect of water content to the flexural strength of MDF cements

4.1.4.10 Effect of activated carbon

Adding activated carbon (10% of cement weight) decreased both dry and wet strengths (Figure 4.16). It was not easy to produce MDF sheets using activated carbon, temperature of the material increased very much during high shear process, (same thing was happened when portland cement was used), so it may need a different procedure for production. Only 2 circular specimens were obtained with activated carbon.

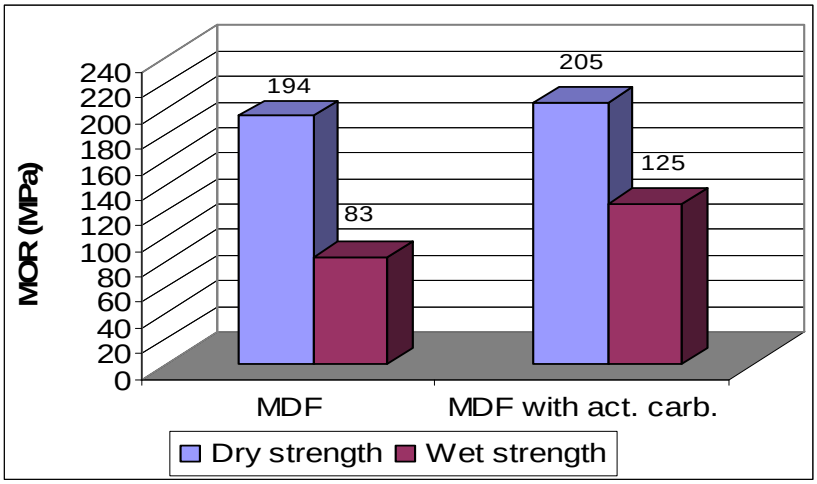


Figure 4.16: Effect of activated carbon to the flexural strength of MDF cements

4.1.4.11 Conclusions for pretests

Production method of MDF cements mentioned in Part 3.2.2 was slightly modified according to the results of these pretests. Most of the process was not changed, and the only difference was changing the mixing step at planetary mixer. This new production method (Part 4.1.5) is accepted as standard procedure for further productions. This method will be applied for all subsequent processing of samples produced at UIUC unless otherwise mentioned. More combinations could be tried than these 20 mixtures, but searching the effects of different parameters is not the aim of this study. This process was already developed by Birchall et al. (1983) and optimized by Russell (1991). Therefore, these 20 mixtures were enough in order to be sure about the effects of these parameters and get used to production method of MDF cements.

4.1.5 Optimized Procedure for the Production of MDF Cements

Preliminary steps:

- Platens of press were pre-heated to 80°C (176°F).

- Chiller of the twin roll mill was set to 15-16°C (60°F).

Planetary mixer:

- Cement, PVA and glycerol were dry blended for one minute prior to the addition of water at a speed rate 1.
- After adding of water, the batch was mixed for one minute at medium speed (speed rate 2) until a damp, granular mix was formed.
- The cohesive solid material was scraped off the bowl in 30 seconds and then blended for an additional 1 minute at a speed rate 2.

Two roller mill:

- Nip gap was set to 0.25 mm and side guards were aparted to 14 cm (5.5 inches).
- Two roller mills were turned on and speeds of the rolls were set to 36:30 (front:back)
- Powder was passed through, nip gap was increased two turn (to 0.49 mm), and folded and passed through again.
- Speeds of the rollers were changed to 54:27 and shear mixed for 15 seconds.
- Sheet was rotated 90° and shear mixed for another 15 seconds.
- Speeds of the rollers were changed to 36:30 and nip gap was increased 8 turns (to 1.66 mm)
- Sheet was passed through 4 times folding triple and rotating 90° each time.
- Side guards were moved out, nip gap was closed two turns (to 1.49 mm), and speeds of the rollers were changed to 30:30.
- Batch was passed through twice without folding or rotating.
- Sheet was cut into desired dimensions.

Hot press:

- Cement sheets were placed between 2 pieces of Mylar (0.25-mm thick) and then were placed in hot press for 10 minutes at 5 MPa.
- Sheets were taken out of hot press and Mylar was pulled off of cement.
- Stiffened composite sheet was cured between two new sheets of Mylar and two 1.27 cm thick plates of aluminum for 24 hours at 80°C in a forced-air oven.

Cutting Procedure

- Circular specimens were core drilled from each sheet with 31.75-mm inner diameter diamond core one day after the production.
- Half of the specimens were stored in water while the other half were stored in a desiccator using silica gel as desiccant until the test date.

4.2 Experimental Study II: Effect of Hydrolysis Degree of PVA on the Properties of MDF Cements

Poly(vinyl alcohol-co-vinyl acetate) copolymers are the most preferred polymers in production of macro defect free (MDF) cements. Birchall et al. (1983) had proposed the Gohsenol KH17 which has approximately 80 mole% hydrolysis degree as the most suitable polymer in his patent. If we look at the 25-year history of MDF cements this type of PVA was the most commonly used polymer in production of MDF cements. The properties of PVA are mostly determined by their polymerization and hydrolysis degrees. PVA, which has high degree of hydrolysis, show less moisture absorption (Table 3.8), but a previous attempt (Santos et al., 1999) to produce MDF with high hydrolysis degree polymers were unsuccessful, due to their low solubility at room temperature. However, they can be made more soluble by heating up to 80°C (Figure 3.12). Nowadays, polymer technology is growing very fast and 20th century is called as polymer age as well as space or nuclear age. Everyday new types of polymers are introduced to industrial use, including PVAs that are more soluble at room temperature. These types of PVAs are modified with some other groups such as carboxyl or acetoacetyl. The purpose of this study was to investigate the effect of new type PVAs which are modified and high hydrolysis degrees at the moisture sensitivity of MDF cements.

4.2.1 Materials

In this study, the possibility of macro defect free (MDF) cement production was tested by using 7 different type of PVA. Their hydrolysis degrees were changed between 79.6 and 99.1 mole%. Properties of PVA copolymers, which have different degree of hydrolysis, can be seen in Table 4.4. Only N300 type PVA was fully hydrolyzed while KH17 and GH20R were partially hydrolyzed. Other types were

modified with some other groups like carboxyl or acetoacetyl in order to make them more soluble even at room temperature.

Table 4.4: Properties of PVAs used for the production of MDF cements

Product Name	Hydrolysis degree (mole%)	Viscosity4% (mPa-s)	pH	Feature
KH17	79.6	36.2	5.5	Partially Hydrolyzed
GH 20R	87.1	46.5	5.5	Partially Hydrolyzed
Z 320	92.7	22.3	4.7	Acetoacetylated
T 330	96.0	30.0	7.0	Carboxylated
Z 410	97.9	51.7	4.9	Acetoacetylated
N 300	98.4	27.8	5.9	Fully Hydrolyzed
Z 100	99.1	5.4	5.0	Acetoacetylated

Calcium aluminate cement was the product of Lafarge firm with the commercial name of Secar 71 and has 70% Al_2O_3 and 29.2% CaO in composition. More information about this cement can be found in Table 4.16 and Table 4.17. Small amounts of water between 11-20% of cement weight were used and a small amount of glycerol (1% of PVA by weight) was also added into the mixture for plasticizing.

4.2.2 Mix Design

Fifty three different mixtures were prepared by using seven different types of PVA and three different production methods. The polymer-cement ratio (p/c) was generally 0.07 but it decreased to 0.04 especially when second production method was used. The water -cement ratio (w/c) was changing between 0.11 and 0.20. A typical composition for w/c=0.11 and p/c=0.07 can be seen in Table 4.5.

Table 4.5: Compositions of the specimens

Material	Density (g/cm^3)	Weight		Volume	
		(g)	(%)	(cm^3)	(%)
CAC	2.93	120	84.2	40.96	67
PVA	1.3	8.4	5.9	6.46	10
Glycerol	1.26	0.84	0.6	0.67	1
Water	1	13.2	9.3	13.20	22
Total	-	***142.44***	***100***	***61.28***	***100***

MDF specimens were prepared in 3 different methods. In the first method, optimized production process was followed, and it was same with the method mentioned in Part 4.1.5. A modified procedure was also developed in order to increase the solubility of PVA. PVAs were mixed with water and heated up to 70-90°C depending on the type of PVA in this second method. This PVA solution was mixed with cement and glycerol in a planetary mixer and the same procedure was applied after that. MDF cements were successfully produced with this method too. Amine type adipyl hydrazide (AH) was also used for the production of MDF in order to increase their crosslinking capacity as a third production method. Z type PVAs are known with their increasing crosslinking capacity when they used with aldehydes or amines. Estimated crosslinking reaction of Gohsefimer Z with di-amine can be seen in Figure 4.17.

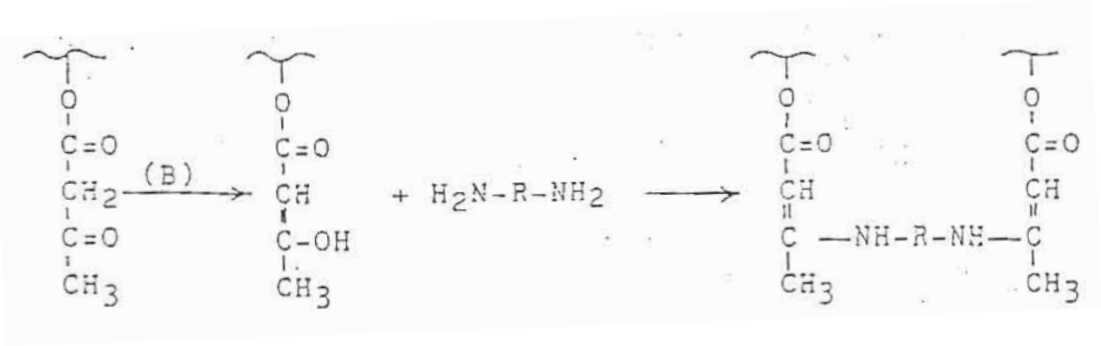


Figure 4.17: Crosslinking reaction of Z type PVA with di-amine (Nippon Gohsei, 2006)

These production methods can be summarized as follows:

1st method: Conventional production method optimized in previous part. This method can be seen in Part 4.1.5.

2nd method: Similar with first method. Only difference was preheating the polymer up to 70-90°C before adding into the mixture in order to increase the solubility of PVA.

3rd method: Similar with first method. Only difference was adding adipyl hydrazide crosslinking agent into the mixture. This method was only used with Z type polymers.

Mixtures were coded depending on the polymer type and production method. For example, polymer was Gohsenol GH 20 and 2nd production method was used at mixture GH 20-2. Mixture KH17-23 shows that used polymer was Gohsenol KH17,

and 2nd and 3rd production methods used at the same time which means polymer heated and adipyl hydrazide added to the mixture. There are some mixtures with the same mixture code it means that same productions were followed for those batches in order to see the reproducibility of the results.

4.2.3 Production Methods

MDF cements were produced by using the same machines and procedures mentioned in the previous study (Part 4.1.3). Production was successful with 5 of these PVAs. Resultant product produced with a partially hydrolyzed PVA can be seen in Figure 4.18. However, MDF cements could not be produced neither with an almost fully hydrolyzed PVA (N300), which has 98.4 mole% hydrolysis degree nor with a carboxylated PVA, which has 96 mole% hydrolysis degree even with the modified procedure in different w/c and p/c ratios. It was very hard to pass thorough materials between roller mills and temperature of the mixtures increased. The dough tended to debond from the faster roll and knitted poorly upon calendaring into a sheet with a tendency to crumble. The obtained products by using carboxylated PVA (T 330) and fully hydrolyzed PVA (N 300) can be seen in Figure 4.19.

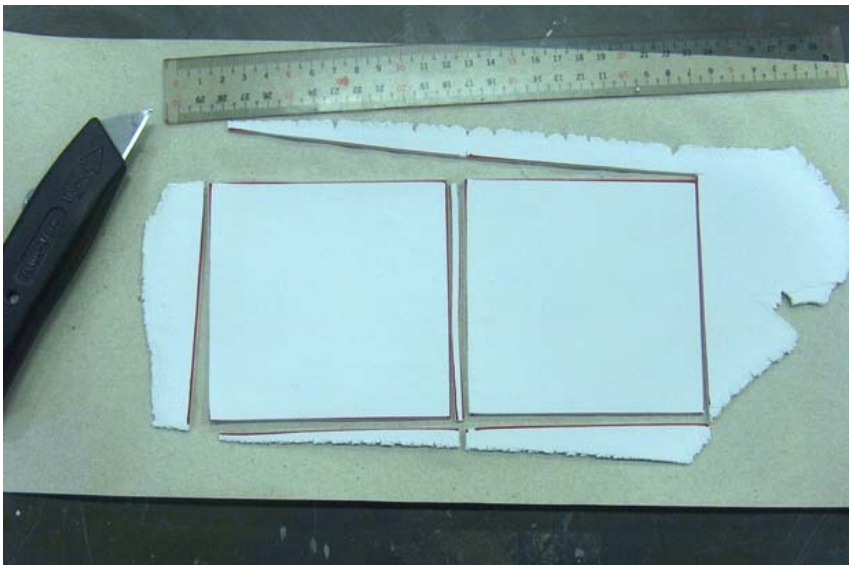
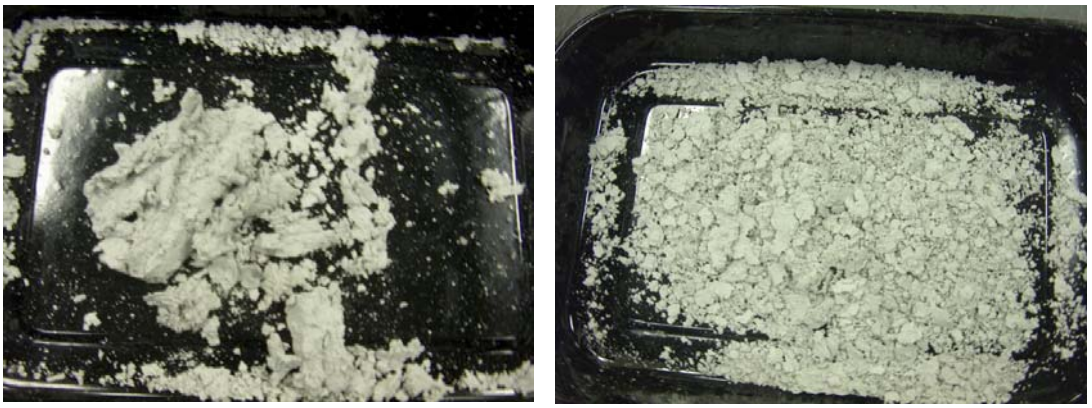


Figure 4.18:MDF cement production with a partially hydrolyzed PVA (KH17)



(a) (b)

Figure 4.19:MDF cement production with a) carboxylated PVA (T330)-w/c:0.25-p/c:0.05 b) fully hydrolyzed PVA (N 300)-w/c:0.30-p/c:0.05

4.2.4 Biaxial Flexural Strength Tests

After production of MDF sheets with the methods mentioned in Part 4.2.2, circular specimens were drilled from each sheet with diamond core. Then the specimens were seperated to two groups and half of the specimens were stored in water while the other half were stored in a desiccator using silica gel as desiccant. Biaxial flexural strength test was conducted for each specimen according to ASTM F-394 (1978-reapproved 1996). An Instron model universal testing machine equipped with a 1 kN load cell was used to test the specimens with a cross-head speed of 0.5 mm/min. More information about this test and calculations can be seen in Appendix A. Dry strength means the strength of specimens which were stored in desiccator while the wet strength is the strength of specimens which were stored in water.

4.2.4.1 Biaxial flexural strength results for 7 days

Biaxial flexural strength tests were conducted for these specimens at 7 and 28 days after production. Average biaxial flexural strength results ($\overline{S}$) of each batch and standard deviations (σ) as well as coefficient of variations (V) for 7 days can be seen in Table 4.6 and all results for each specimen can be found in Appendix C.

MDF cements could not be produced for mix numbers 8, 23, 24, 32 and 36 due to their low w/c ratios. The surface of the sheets were glossy and very hot to touch during high shear processes in most of them. Edges of the sheets were crumbly, cracked, and easily teared. In addition, MDF cements could not be produced for mix numbers 40-53 due to the reasons explained in Part 4.2.3.

Table 4.6: Biaxial flexural strength test results for KH17, GH20, Z320, Z410, Z100, T330 and N300 at 7 days

				Dry Strength			Wet Strength		
Mixture No.	**Mixture Code**	**w/c**	**p/c**	$\overline{S}$ **(MPa)**	σ **(MPa)**	**V (%)**	$\overline{S}$ **(MPa)**	σ **(MPa)**	**V (%)**
1	KH17-1	0.11	0.07	199	31	16	109	47	43
2	KH17-1	0.11	0.07	197	16	8	96	14	15
3	KH17-2	0.11	0.07	167	49	30	65	3	5
4	KH17-2	0.12	0.058	177	12	7	77	41	53
5	KH17-2	0.125	0.042	120	5	4	46	2	4
6	KH17-23	0.122	0.04	119	38	32	33	5	16
7	KH17-23	0.113	0.056	168	14	8	54	11	20
8	GH20-1	0.11	0.07	-	-	-	-	-	-
9	GH20-1	0.11	0.07	41	6	15	36	5	13
10	GH20-1	0.13	0.05	122	37	31	59	1	2
11	GH20-1	0.13	0.07	142	24	17	61	8	13
12	GH20-1	0.13	0.07	172	35	21	114	16	14
13	GH20-1	0.15	0.07	161	28	18	72	15	21
14	GH20-1	0.15	0.07	128	6	5	114	14	13
15	GH20-1	0.15	0.07	144	15	10	57	6	11
16	GH20-1	0.17	0.07	198	26	13	64	18	27
17	GH20-2	0.13	0.07	147	36	25	47	9	18
18	GH20-2	0.134	0.067	177	17	9	49	6	12
19	GH20-2	0.139	0.069	181	10	6	57	1	2
20	Z320-1	0.15	0.07	151	25	16	41	6	14
21	Z320-2	0.15	0.07	170	10	6	47	59	126
22	Z320-3	0.15	0.07	141	10	7	47	10	21
23	Z410-1	0.15	0.07	-	-	-	-	-	-
24	Z410-1	0.15	0.07	-	-	-	-	-	-
25	Z410-1	0.15	0.07	48	-	-	-	-	-
26	Z410-1	0.17	0.05	151	51	34	61	2	3
27	Z410-1	0.17	0.07	82	7	8	75	9	11
28	Z410-1	0.2	0.07	119	19	16	35	5	14
29	Z410-2	0.2	0.07	141	23	16	47	4	8
30	Z410-3	0.2	0.05	74	12	16	23	2	9
31	Z410-3	0.2	0.07	102	17	17	29	8	28
32	Z100-1	0.11	0.07	-	-	-	-	-	-
33	Z100-1	0.15	0.07	95	12	13	15	3	17
34	Z100-1	0.15	0.07	161	18	11	32	5	15
35	Z100-2	0.13	0.07	181	8	5	75	12	15
36	Z100-2	0.15	0.07	-	-	-	-	-	-
37	Z100-3	0.15	0.07	136	4	3	20	1	5
38	Z100-3	0.15	0.07	90	23	25	23	2	8
39	Z100-3	0.15	0.07	119	14	12	31	4	12
40	T330-1	0.11	0.07	-	-	-	-	-	-
41	T330-1	0.15	0.07	-	-	-	-	-	-
42	T330-1	0.17	0.07	-	-	-	-	-	-
43	T330-1	0.19	0.07	-	-	-	-	-	-
44	T330-1	0.21	0.05	-	-	-	-	-	-
45	T330-1	0.23	0.05	-	-	-	-	-	-
46	T330-1	0.25	0.05	-	-	-	-	-	-

Table 4.7: (continued) Biaxial flexural strength test results for KH17, GH20, Z320, Z410, Z100, T330 and N300 at 7 days

Mixture No.	Mixture Code	w/c	p/c	Dry Strength			Wet Strength		
				$\overline{S}$ (MPa)	σ (MPa)	V (%)	$\overline{S}$ (MPa)	σ (MPa)	V (%)
47	N300-1	0.15	0.07	-	-	-	-	-	-
48	N300-2	0.15	0.07	-	-	-	-	-	-
49	N300-1	0.17	0.07	-	-	-	-	-	-
50	N300-1	0.18	0.07	-	-	-	-	-	-
51	N300-1	0.2	0.05	-	-	-	-	-	-
52	N300-2	0.2	0.05	-	-	-	-	-	-
53	N300-1	0.3	0.05	-	-	-	-	-	-

Flexural strengths of the specimens which were stored in dry conditions for 7 days and decrease in strength after storing at water for 7 days can be seen in Figure 4.20. Hydrolysis degrees of the PVAs were increasing from left to right on the graphics of Figure 4.20 and Figure 4.21.

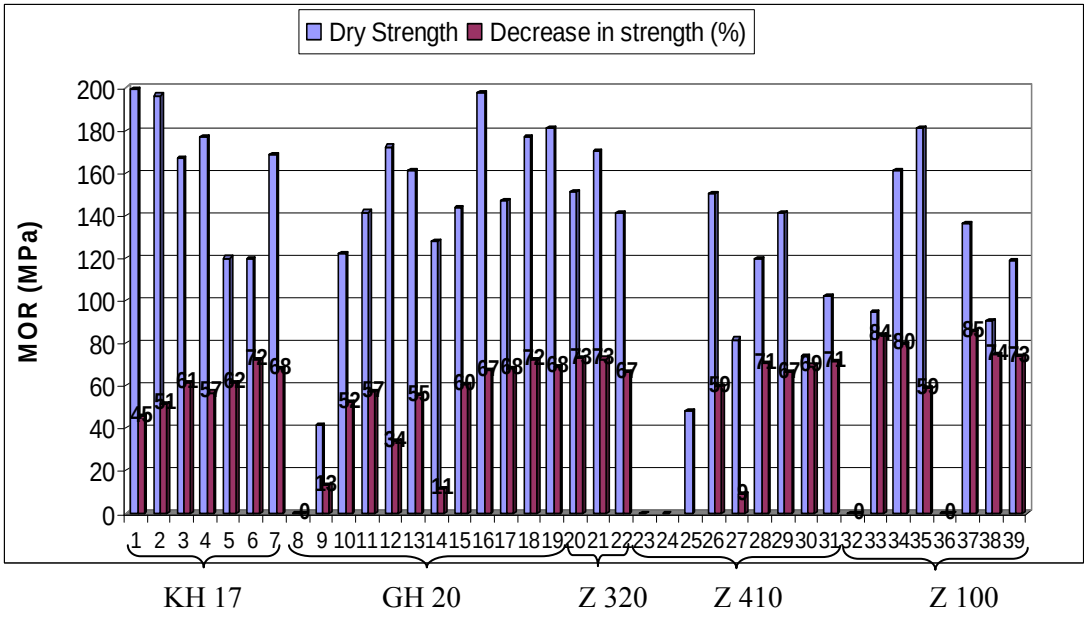


Figure 4.20: Dry strength and decrease in strength of the specimens at 7 days produced with different PVAs

The highest flexural strengths were obtained on mixtures 1 (KH17-1) and 16 (GH20-1). Flexural strengths of these mixtures were 199 and 198 respectively. Partially hdrolyzed PVAs were used in both mixtures. In addition to these mixtures high flexural strengths were obtained with modified procedure (2nd method) too. The 3rd highest flexural strengths were obtained on mixtures number 19 (GH20-2) and 35 (Z100-2), which were 181 MPa in both mixtures. The lowest flexural strengths were

41, 48 and 74 MPa for the mixtures 9 (GH20-1), 25 (Z410-1) and 30 (Z410-3), respectively.

When the specimens were immersed in water, a whitening of the entire surface of the specimens was observed which appeared to be a very thin layer of hydration products. In addition, these products sometimes released to the water and developed an oily film over the surface of the water. Decreases in strengths in water ranged between 11% (mixture no. 14/GH20-1) and 85% (mixture no. 37/Z100-3); the former decrease was a very promising result. However, the same decrease ratio was not observed on similar batches prepared for the confirmation; the decreases were 55% and 60% for mixture no. 13/GH20-1 and mixture no. 15/GH20-1, respectively. Another promising result was mixture no. 9 (GH20-1). Decrease was only 13% on this mixture, however, strengths were very low in dry and wet conditions (41 and 36 MPa, respectively). Processing was very difficult due to its very low w/c ratio (0.11). This mixture can not be classified as MDF cement because of its very low strength.

Specimens produced with the 2nd method have smoother surface with respect to the specimens produced with conventional method (1st method). However, this 2nd method did not cause significant difference in the strength or water resistivity of specimens or slightly decreased the results.

Another important point is that decrease in strengths was higher when high hydrolysis degress PVAs (Z320, Z410 and Z100) were used compared to partially hydrolysed PVAs (KH17 and GH20). However, their surface was very smooth and visible degredation were not observed in water storage, contrary to partially hydrolysed PVAs, and an oily film on the surface of the water was not observed. The decrease in strength was approximately 50-55% when partially hydrolysed PVAs was used. On the other hand, 70% or more decrease was observed with acetoacetylated PVAs.

4.2.4.2 Biaxial flexural strength results for 28 days

Average values of biaxial flexural strengths ($\overline{S}$), standard deviations (σ) and coefficient of variations (V) of the specimens which were stored in dry and wet conditions for 28 days can be seen in Table 4.8 and dry strength and the decrease in strength can be seen in Figure 4.21. Test results of each specimen can be seen in Appendix C.

Table 4.8: 28 days biaxial flexural strength test results for KH17, GH20, Z320, Z410 and Z100

Mixture No.	Mixture Code	w/c	p/c	Dry Strength			Wet Strength		
				$\overline{S}$ (MPa)	σ (MPa)	V (%)	$\overline{S}$ (MPa)	σ (MPa)	V (%)
1	KH17-1	0.11	0.07	208	39	19	64	12	19
2	KH17-1	0.11	0.07	187	11	6	58	16	28
3	KH17-2	0.11	0.07	156	16	10	56		
4	KH17-2	0.12	0.058	146	9	6	64	4	7
5	KH17-2	0.125	0.042	137	9	7	59	7	11
6	KH17-23	0.122	0.04	73	5	7	39	8	20
7	KH17-23	0.113	0.056	150	29	19	65	1	2
10	GH20-1	0.13	0.05	110	27	25	52	6	11
11	GH20-1	0.13	0.07	138	80	58	62	6	9
12	GH20-1	0.13	0.07	218	47	22	65	3	5
14	GH20-1	0.15	0.07	127	6	5	53	8	16
15	GH20-1	0.15	0.07	131	26	20	58	6	10
16	GH20-1	0.17	0.07	183	19	11	58	9	15
17	GH20-2	0.13	0.07	124	25	20	47	7	15
18	GH20-2	0.134	0.067	228	19	9	45	8	17
19	GH20-2	0.139	0.069	194	28	14	43	7	17
20	Z320-1	0.15	0.07	164	6	4	30	0	2
21	Z320-2	0.15	0.07	156	28	18	48	5	11
22	Z320-3	0.15	0.07	154	23	15	39	4	10
27	Z410-1	0.17	0.07	67	5	7	26		
28	Z410-1	0.2	0.07	136	14	10	33	2	5
29	Z410-2	0.2	0.07	165	7	5	50	4	7
31	Z410-3	0.2	0.07	118	10	8	28	3	10
34	Z100-1	0.15	0.07	161	25	15	45	17	38
35	Z100-2	0.13	0.07	194	7	4	36	1	3

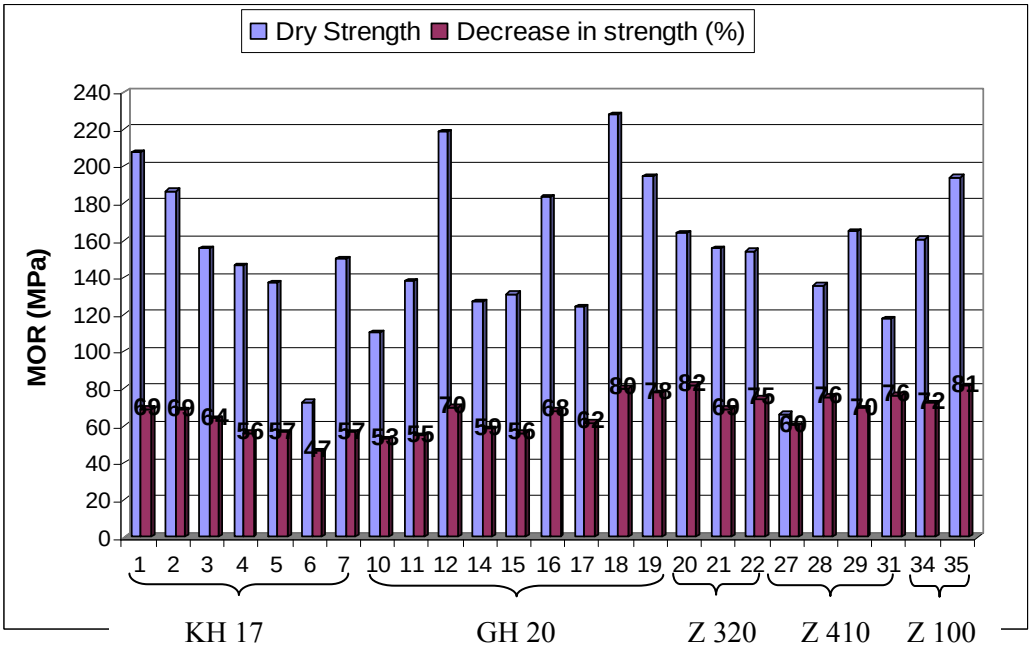


Figure 4.21: Dry strength and decrease in strength of the specimens at 28 days produced with different PVAs

The highest dry flexural strengths were 228, 218 and 208 for mixture numbers 18 (GH20-2), 12 (GH20-1) and 1 (KH17-1), respectively. These PVAs were both partially hydrolysed PVAs. The highest flexural strength was obtained with the specimen prepared with heating the PVA (2nd method). However, the decrease in strength was very high for this specimen (80%).

Decreases in strengths ranged between 47% (mixture no. 6/KH17-23) and 82% (mixture no. 20/Z320-1). However, dry strength of mixture no. 6 was only 73 MPa which is the 2nd lowest strength of all batches after mix no. 27/Z410-1 (67 MPa).

There was no significant difference on the results of 7 and 28 days. However, dry strengths were increased slightly while wet strengths were decreased. Similarly to the results of 7 days, decrease in strengths was higher when high hydrolysis degress PVAs (Z320, Z410 and Z100) used compared to partially hydrolysed PVAs (KH17 and GH20). Decreases in strength were approximately 55-65% when partially hydrolysed PVAs were used. On the other hand, decreases ranged between 70% and 82% when acetoacetylated PVAs were used.

Adding adipyl hydrazide to the mixtures for increasing the crosslinking capacity of PVAs (3rd method) did not change the results significantly. For example, dry flexural strengths were 164, 156 and 154 and decrease in strengths were 82, 69 and 75, respectively for mixture no. 20 (Z320-1), 21 (Z320-2) and 22 (Z320-3)

4.2.5 Weight and Thickness Differences

MDF cements were produced by using 5 different types of PVAs in order to see the change on their weight and thickness. Each PVA shows different characteristics and it was not easy to produce them while using same w/c ratios. The most suitable w/c ratios were determined according to the previous productions. Productions of the specimens were conducted by using these optimum w/c ratios for each PVA type by using the optimized method mentioned in Part 4.1.5. Optimum w/c ratios for each PVA can be seen in Table 4.9.

Table 4.9: Optimum w/c ratios for CAC-MDF specimens produced with different PVAs

Polymer	w/c
KH 17	0.11
GH 20	0.13
Z 100	0.13
Z 320	0.15
Z410	0.2

Table 4.10: Weight and thickness change results for CAC-MDF specimens produced with different PVA

		Weight (g)			Thickness (mm)		
Polymer Type	**Specimen no**	**2 days**	**8 days**	**28 days**	**2 days**	**8 days**	**28 days**
KH 17	1	4.82	4.89	4.97	1.708	1.813	1.899
	2	5.07	5.11	5.16	1.7	1.733	1.847
	3	4.95	5.06	5.19	1.731	1.807	1.952
	4	4.94	4.99	4.97	1.671	1.729	1.8
	5	4.65	4.7	4.61	1.652	1.715	1.812
GH 20	1	5.27	5.48	5.53	1.876	1.999	2.056
	2	5.31	5.46	5.5	1.839	1.933	2.009
	3	5.51	5.67	5.76	1.837	1.929	2.026
	4	5.22	5.42	5.47	1.845	1.954	2.045
	5	5.49	5.76	5.72	1.872	1.972	2.1
Z 100	1	4.97	5.28	5.32	1.832	1.913	1.98
	2	5.29	5.73	5.81	1.861	1.959	2.012
	3	3.33	3.56	3.67	1.837	2.016	2.09
	4	3.69	3.9	4.02	1.774	1.97	2.052
	5	3.41	3.56	3.63	1.788	2.018	2.07
Z 320	1	5.49	5.72	5.75	1.936	2.006	2.061
	2	5.38	5.66	5.69	1.922	2.026	2.082
	3	5.4	5.64	5.66	1.957	2.045	2.116
	4	5.53	5.79	5.8	1.889	1.978	2.068
	5	5.06	5.34	5.29	1.854	1.955	2.063
Z 410	1	4.76	5.13	5.2	1.781	1.817	1.875
	2	4.08	4.29	4.36	1.491	1.578	1.634
	3	4.12	4.35	4.41	1.493	1.572	1.63
	4	4.87	5.16	5.25	1.861	1.95	2.006
	5	4.76	5.11	5.17	1.85	1.915	1.992

First measurement was made in the next day after production, just before putting the specimens into water. Measurements were also made 7 and 28 days after immersion in water. The results can be seen in Table 4.10. Comparison of weight change with strength loss can be seen in Figure 4.22 while the comparison of thickness change can be seen in Figure 4.23.

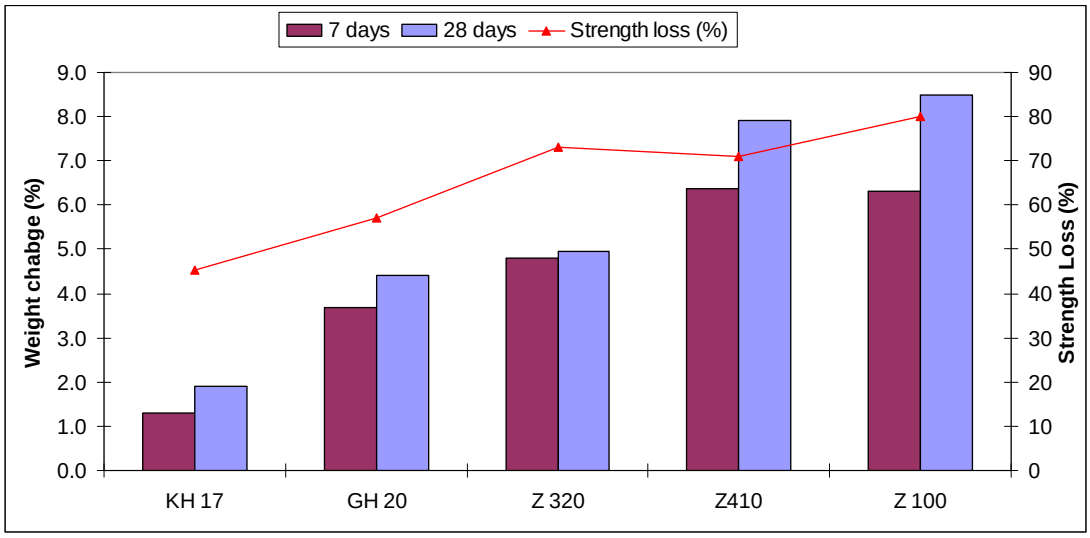


Figure 4.22: Comparison of weight change with strength loss

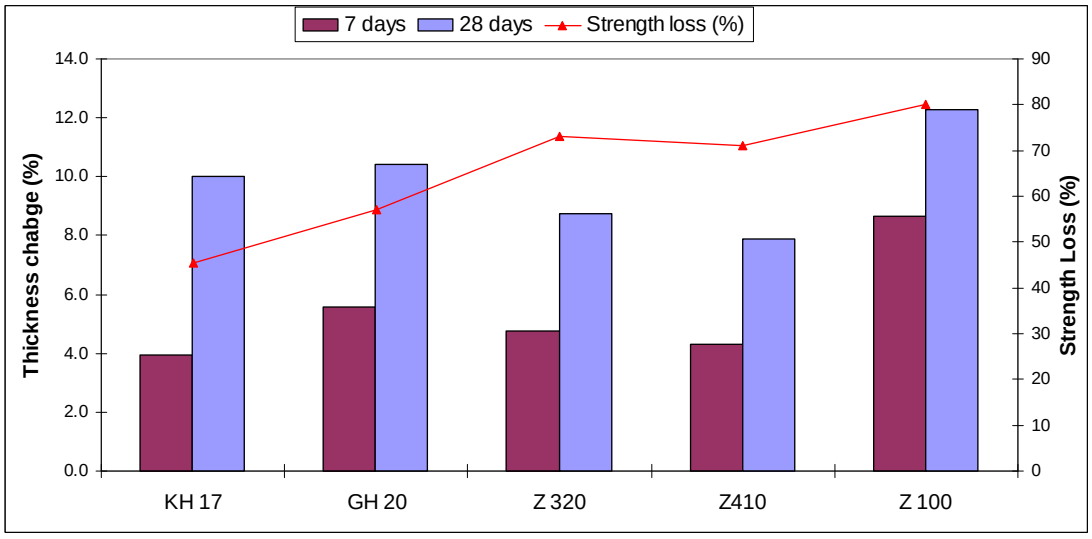


Figure 4.23: Comparison of thickness change with strength loss

There is a pretty good relationship between strength loss and weight increase according to the Figure 4.22, which means a higher increase in weight with a higher strength loss. Another point is that hydrolysis degrees of PVAs are increasing from left to right in this graphic which proves the lower hydrolysis degrees PVAs more suitable for the production of MDF cements. The loss in strength, swelling and weight change of CAC-PVA composites upon immersion in water were due to the hydrophilic nature of the PVA matrix. When water is absorbed by the PVA matrix, swelling of the composite occurs, allowing water to migrate to the polymer-cement interface and destroying the bonding.

4.2.6 Analysis of Storing Water

Gohsenol KH 17 was found as the most suitable poly(vinyl alcohol-co-vinyl acetate) copolymer for the production of MDF cements while the Gohsefimer Z 100 was found as the worst copolymer from the previous results according to their highest flexural strengths and loss on strength in contact with water. For this reason, we decided to analyze the storing water of both specimens in order to find what were releasing.

4.2.6.1 Preparation of specimens

Macro Defect Free cement specimens were produced by using two different PVAs (Gohsenol KH 17 and Gohsefimer Z 100) and the cement was Secar 71 type calcium aluminate cement which has a 70% Al_2O_3 content. Properties of the polymers and cement can be seen in Table 4.4, Table 4.16 and Table 4.17. Two different 10x10x1.7 cm MDF specimens were produced by using each PVA and cylindrical specimens were cut by using diamond saw one day later after production. Half of the cylindirical specimens were stored at water for additional 6 days and the others stored at desiccators. Specimens were taken from water 7 days after production date and the water solutions were sent to the Illinois Waste Management and Research Center for Total Organic Carbon and Al-Ca determination tests. In addition to these two solutions, blank water was also sent to the research center for comparison. The purpose of these tests was finding the amount of released elements in water.

1st Solution (KH 17):

This solution called as KH 17 because of the PVA used in the production. Water/cement was 0.11 and polymer/cement was 0.07. 9 cylindrical specimens were cut by using diamond saw one day later after production. 5 of them stored at water for additional 6 days and 4 of them stored at desiccators using silica gel as desiccant. Total weight of the specimens which were stored at water was 17 g. and the total weight of water was 120 g. Compositions of the MDF specimens which were produced by using KH 17 can be seen in Table 4.11.

Table 4.11: Composition of the MDF specimens produced with Gohsenol KH 17

Material	Density (g/cm^3)	Weight		Volume	
		(g)	(%)	(cm^3)	(%)
CAC	2.93	120	84.2	40.96	67
Gohsenol KH 17	1.3	8.4	5.9	6.46	10
Glycerol	1.26	0.84	0.6	0.67	1
Water	1	13.2	9.3	13.20	22
Total	-	***142.44***	***100***	***61.28***	***100***

2nd Solution (Z 100):

This solution called as Z 100 because of the PVA used in the production. Water/cement was 0.15 and polymer/cement was 0.07. Seven cylindrical specimens were cut by using diamond saw one day later after production. Five of them stored at water for additional 6 days and two of them stored at desiccators. Total weight of the specimens which were stored at water was 15.6 g. and the total weight of water was 120 g. Compositions of the MDF specimens which were produced by using Z 100 can be seen in Table 4.12.

Table 4.12: Compositions of the MDF specimens produced with Gohsefimer Z 100

Material	Density (g/cm^3)	Weight		Volume	
		(g)	(%)	(cm^3)	(%)
CAC	2.93	150	82.9	51.2	64.3
Gohsefimer Z100	1.3	10.5	5.8	8.1	10.2
Glycerol	1.26	1.05	0.6	0.8	1
Water	1	19.5	10.8	19.5	24.5
Total	-	*181.05*	***100***	79.6	100

3rd Solution (Blank water):

120 g tap water were sent to the research center in order to compare the results and finding the amount of released elements into water. Storing conditions of the 1st and 3rd solution can be seen in Figure 4.24.

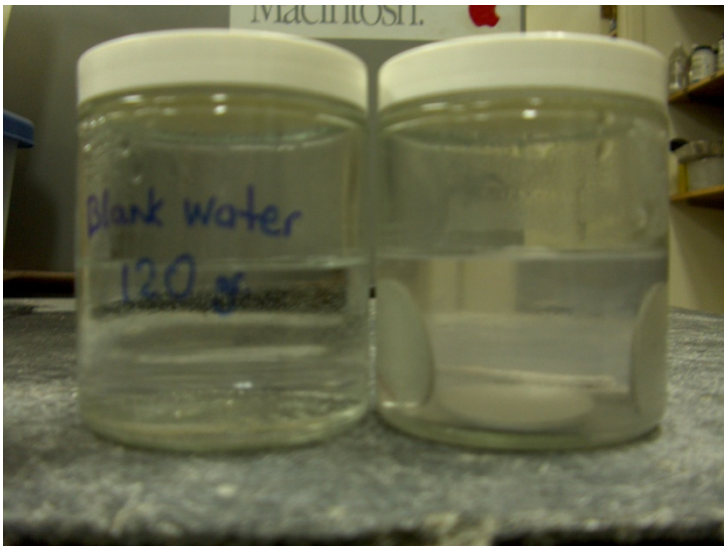


Figure 4.24: Storing conditions of test specimens for water analysis tests

4.2.6.2 Water analysis results

Raw data of 3 different water specimens which were taken from Illinois Waste Management and Research Center can be seen in Appendix D. Al was determined by Inductively Coupled Plasma Mass Spectrometry and Ca was determined by Atomic Absorption Spectrometry. The main results of these tests can be seen in Table 4.13. According to these results Al, Ca and total organic carbon (TOC) were released to the water in different rates. Presence of the TOC shows that some part of PVA copolymers were released to the water. In addition, presences of Al and Ca show that some of the cement was released to the water.

Table 4.13: Water analysis results of all specimens

Sample Code	TOC (ppm)	Al (mg/L)	Ca (mg/L)
KH 17	280	140	360
Z 100	190	230	110
Blank	1.8	< 0.02	14

4.2.6.3 Calculations of the released total organic carbon (TOC), Al and Ca amounts at water

We need to make some assumptions before calculating the ratios of these materials in solution. These assumptions and calculations are:

- Structural unit of PVA: C_2H_40 (fully hdrolysed)
- Molecular weight of structural unit of PVA:2x12+4x1+16=44 g

- Weight of carbon in a structural unit of PVA: 2x12=24 g
- Weight of KH 17 type MDF specimens calculated from recipe :

  KH:17: 100 g cement+7 g PVA+11 g water+0.7 g glycerol=119 g MDF

  Z 100: 100 g cement+7 g PVA+15 g water+0.7 g glycerol=123 g MDF

- Weight of PVA in an MDF specimen: 7 g.
- Weight of water solution for tests: 120 g
- Weight of specimens stored at water:

  KH 17: 17 g

  Z 100: 15.6 g

- Molecular weight of Al_2O_3 :27x2+16x3=54+48=102 g.
- Molecular weight of CaO : 40+16=56 g.
- 102x0.7+56x0.3=71.4 Al_2O_3+16.8 CaO =88.2 g. cement
- 71.4x54/102=37.8 g. Al (in a 88.2 g cement)
- 16.8x40/56=12 g. Ca (in a 88.2 g cement)

Note: Gohsenol KH 17 and Gohsefimer Z 100 are not fully hydrolysed PVAs and they have acetate groups too but the difference is minor and it will not affect the results significantly. This difference was neglected and the molecular weights of structural unit of PVA copolymers were accepted as 44 gr.

Released C, Al and Ca ratios to the water are calculated by using these calculations and assumptions.

1st solution: KH 17

$$\frac{280\text{x}10^{-6}\text{g C in solution}}{\text{ml solution}}\text{x}\frac{44\text{g PVA}}{24\text{g C}}\text{x}\frac{119\text{g MDF}}{7\text{g PVA}}\text{x}\frac{120\text{g solution}}{17\text{g MDF}}=0.062\ \frac{\text{g C in solution}}{\text{g C in polymer}}$$

$$\frac{0.14\text{g Al in solution}}{1000\text{ ml solution}}\text{x}\frac{88.2\text{g cement}}{37.8\text{g Al}}\text{x}\frac{119\text{g MDF}}{100\text{g cement}}\text{x}\frac{120\text{g solution}}{17\text{g MDF}}=0.003\ \frac{\text{g Al in solution}}{\text{g Al in cement}}$$

$$\frac{0.36\text{g Ca in solution}}{1000\text{ ml solution}}\text{x}\frac{88.2\text{g cement}}{12\text{g Ca}}\text{x}\frac{119\text{g MDF}}{100\text{g cement}}\text{x}\frac{120\text{g solution}}{17\text{g MDF}}=0.022\ \frac{\text{g Ca in solution}}{\text{g Ca in cement}}$$

2nd solution: Z100

$$\frac{190\text{x}10^{-6}\text{g C in solution}}{\text{ml solution}} \text{x} \frac{44\text{g PVA}}{24\text{g C}} \text{x} \frac{123\text{g MDF}}{7\text{g PVA}} \text{x} \frac{120\text{g solution}}{15.6\text{g MDF}} = 0.047 \frac{\text{g C in solution}}{\text{g C in polymer}}$$

$$\frac{0.23\text{g Al in solution}}{1000\text{ ml solution}} \text{x} \frac{88.2\text{g cement}}{37.8\text{g Al}} \text{x} \frac{123\text{g MDF}}{100\text{g cement}} \text{x} \frac{120\text{g solution}}{15.6\text{g MDF}} = 0.005 \frac{\text{g Al in solution}}{\text{g Al in cement}}$$

$$\frac{0.11\text{g Ca in solution}}{1000\text{ ml solution}} \text{x} \frac{88.2\text{g cement}}{12\text{g Ca}} \text{x} \frac{123\text{g MDF}}{100\text{g cement}} \text{x} \frac{120\text{g solution}}{15.6\text{g MDF}} = 0.008 \frac{\text{g Ca in solution}}{\text{g Ca in cement}}$$

Released C, Al and Ca percents were calculated and can be seen in Table 4.14 and Figure 4.25. Released Al ratio is higher in solution 2 compared to the solution 1 while the released C and Ca is lower. Less Al in solution 1 is most likely because of higher crosslinking ratio and these results support the crosslinking hypothesis between Al and PVA chains.

Table 4.14: Comparing flexural strengths and released amounts of C, Al and Ca

Test specimens	Polymer type	Flexural strength-dry (MPa)	Flexural strength-wet (MPa)	Decrease in strength (%)	Released C (%)	Released Al (%)	Released Ca (%)
Solution 1	KH 17	256	107	58	6.2	0.3	2.2
Solution 2	Z 100	193	37	80	4.7	0.5	0.8
Solution 3	Blank	-	-	-	-	-	-

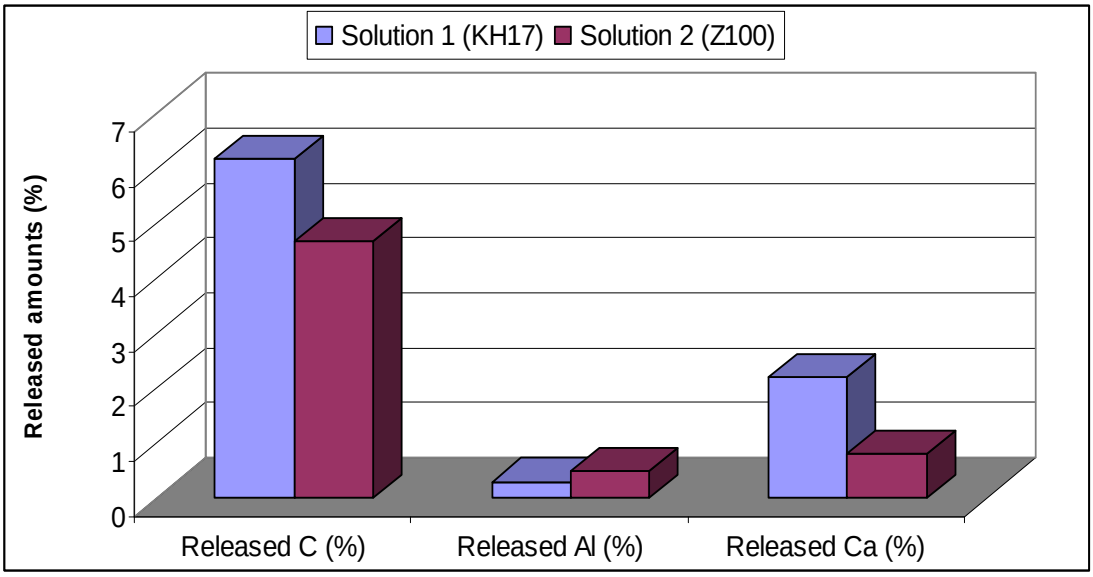


Figure 4.25: Bar graphics of released C, Al and Ca

4.2.7 ^{27}Al Magic Angle Spinning Nuclear Magnetic Resonance (MAS-NMR) Tests

^{27}Al MAS NMR tests were conducted in order to find any evidence of crosslinking between Al ions and PVA. 3 different types of specimens prepared for this purpose. First of all, a standard MDF cement composition was prepared. Secondly, a cement paste without PVA were prepared and last of all, MDF tried to be produced without cement. Since it was impossible to produce and calender MDF cements without addition of cement, $NaAlO_2$ and Al_2O_3 were added into the mixture. A sheet form was obtained after several trying and changing the amounts of materials but its strength was very low comparing with MDF cements. This was the same composite with mixture number 16 mentioned in Part 4.4.1. They were broken even with hand which makes measuring the flexural strength difficult. Compositions of these specimens can be seen in Table 4.15.

Table 4.15: Compositions of the specimens subjected to NMR tests

	MDF	**Cement paste**	**MDF with $NaAlO_2$ and α-Al_2O_3 (without cement)**
PVA	7	-	8
Secar 71	100	100	-
Water	11	11	42
$NaAlO_2$	-	-	10
Al_2O_3	-	-	100

Test results can be seen in Figure 4.26. CA and CA_2 are the initial phases of Secar 71 type alumina cements. More information about phases and hydration products of cement can be find in Part 3.1.1. Interestingly, no hydration product were observed for cement paste and there was a huge amount of $Al(OH)_3$ in third sample comparing to first sample (MDF) because of the used materials.

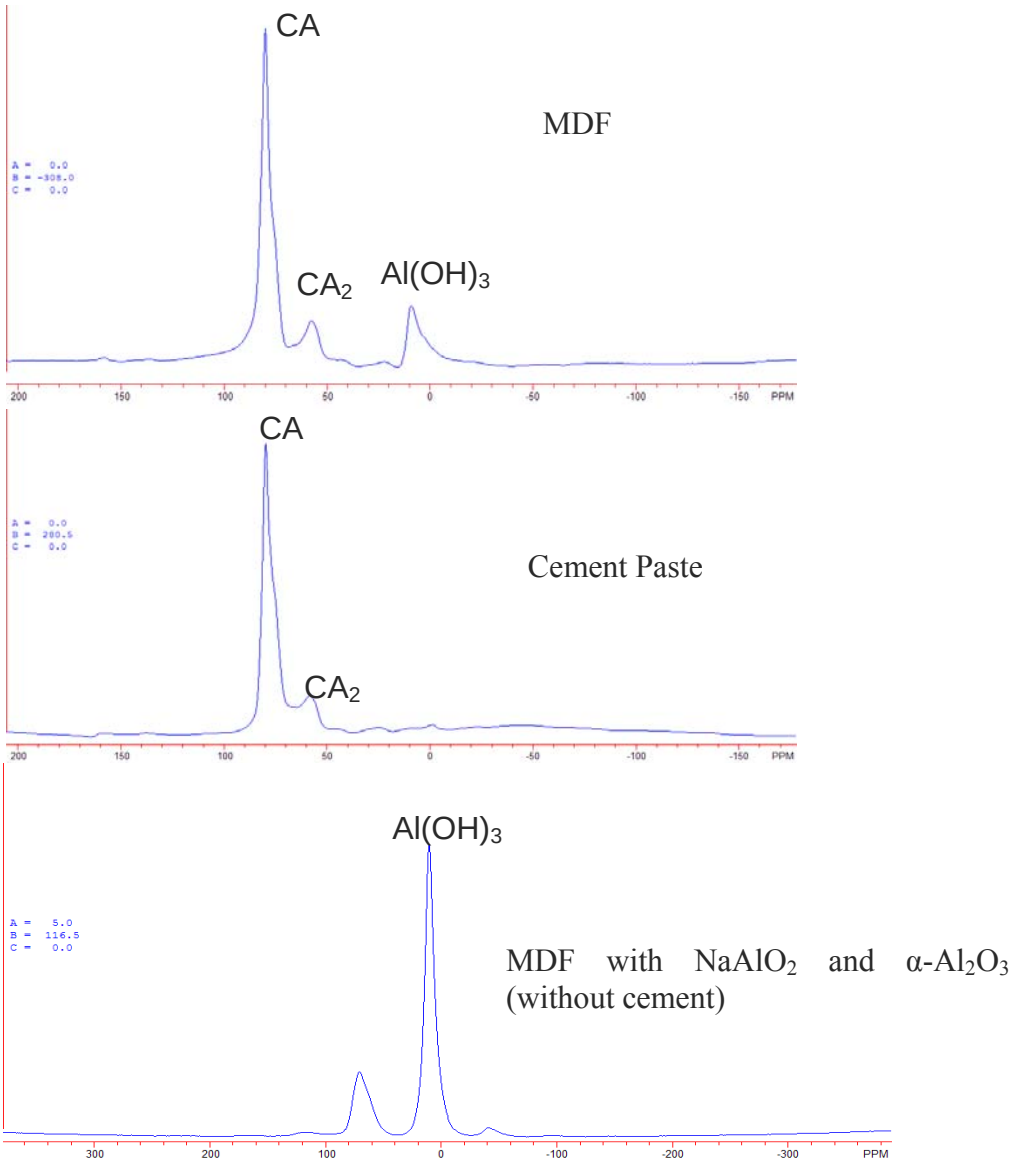


Figure 4.26: ^{27}Al MAS NMR tests

4.2.8 Conclusions for Part II

- MDF cements can be successfully produced with 5 out of 7 different hydrolyzed PVAs, sometimes with modified procedures.
- MDF cements can not be produced with fully hydrolyzed PVA or carboxylated PVA.
- All specimens were affected from moisture and lost a part of its initial strength. However, the PVA at the lowest hydrolysis degree (79,6 mole%) gave the lowest strength loss. Paralel results were obtained in weight and thickness change tests.
- Increasing degree of hydrolysis of PVAs increased the strength loss of MDF specimens which were stored in water.

- Preheating the polymer before mixing (specimens coded with -2) in order to obtain a homogeneous mixture did not change flexural strengths and strength loss significantly.
- Using an amine type crosslinker (adipyl hydrazide) with Z type PVAs did not make any change on the moisture sensitivity of MDF cements.
- MDF cements can also be produced by using $NaAlO_2$ and Al_2O_3 instead of alumina cement with similar MDF production procedure but this material can not be classified as MDF cements because of its very low strength.

4.3 Experimental Study III: Effect of Alumina Content in Calcium Aluminate Cements (CAC) on the Properties of MDF Cements

4.3.1 Materials

MDF cements were produced with 4 different types of calcium aluminate cements in this study. Their alumina contents ranged between 42% and 79%. Chemical compositions of these cements which were provided by the producer can be seen in Table 4.16 and the physical properties can be seen in Table 4.17.

Table 4.16: Chemical compositions of calcium aluminate cements used for the production of MDF cements

Cement Type	Alumina % (Al_2O_3)	Calcium Oxide % (CaO)	Ferric Oxide % (Fe_2O_3)	Silica (SiO_2)
Ciment Fondu	42.29	35.05	14.05	4.52
Secar 41	48.86	34.89	7.16	5.56
Secar 71	70.0	29.2	-	-
Secar 80	78.95	19.57	-	-

Table 4.17: Physical properties of calcium aluminate cements used for the production of MDF cements

Cement Type	Blaine (cm^2/g)	Loss on ignition (%)	Initial set time (min)	Final set time (min)
Ciment Fondu	4033	0.98	145	160
Secar 41	4249	0.56	250	275
Secar 71	3986	0.1	200	255
Secar 80	*	-	90	115

*: Blaine specific surface area and loss on ignition was not written for this cement type in its quality certificate but fineness of this cement is high and it should be over 8000 according to product data sheet.

PVA copolymer which has 79.6 mole% hydrolysis degree and 5.5 pH ratio was used in this study (Gohsenol KH-17). It was determined as the most suitable PVA for the

production of MDF cements in the previous study. Properties of Gohsenol KH-17 can be seen in Table 4.4. Small amounts of glycerol, which is 10% of PVA by weight, were also added into the mixtures.

4.3.2 Mix Design

Twenty eight different batches were prepared in order to produce MDF cements, which differ in their water contents. Water/cement was changing between 0.09 and 0.19 while the polymer/cement was kept constant at 0.07. Typical mix proportion of MDF cements can be seen in Table 4.18. These batches were coded with respect to their Al_2O_3 content. It was impossible to obtain MDF sheets only in 5 batches (49-7, 79-4, 79-5, 79-6 and 79-7) due to the lack of coherence at low w/c ratios.

Table 4.18: Typical mix proportion of MDF cements

Material	Parts by weight (%)	Parts by volume (%)
CAC	79-86	58-70
PVA	6	9-11
Glycerol	1	0.9-1.1
Water	8-15	18-32
Total	***116.7-126.7***	***100***

4.3.3 Production Procedure

Optimized production method (Part 4.1.5) was followed for the production of specimens. However, the dough became more rubbery and pliable with increasing water and it was difficult to peel of from roller mills during calendaring because of gummy and tacky structure. Therefore, production time was longer and mixtures were folded and passed thorough roller mills several times more instead of only 4 times during calendering. Resultant products can be seen in Figure 4.27 for each cement type. 8 circular specimens were drilled from each sheet with diamond core. Subsequently, the specimens were seperated to two groups and half of the specimens were stored in water while the other half were stored in a desiccator using silica gel as desiccant in for 28 days in order to see the effect of water on mechanical strength.

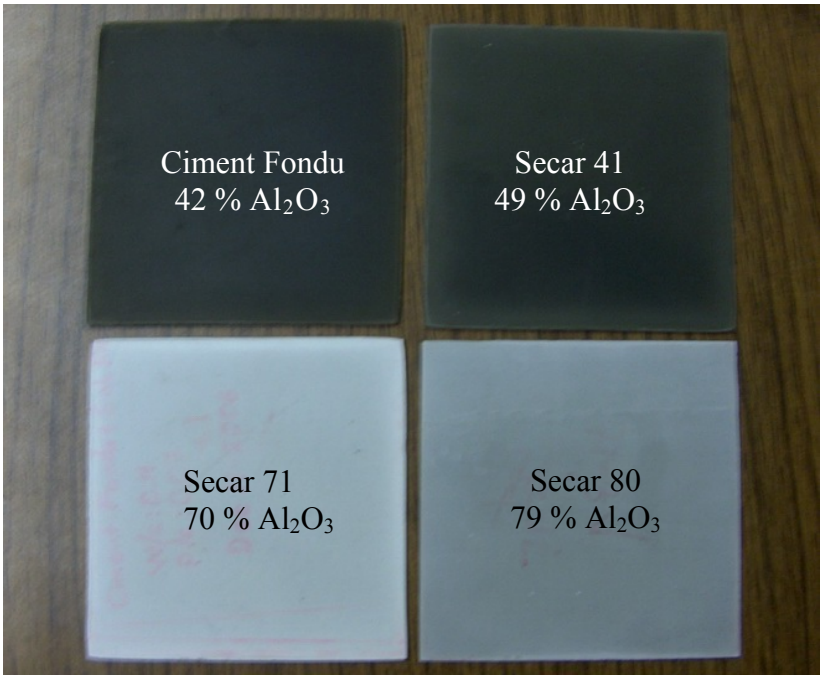


Figure 4.27: MDF cement specimens produced with different CACs

4.3.4 Biaxial Flexural Strength Tests

Biaxial flexural strength tests were carried out on both water stored and dry specimens for 7 and 28 days according to ASTM F-394 (1978-reapproved 1996). An Instron model universal testing machine equipped with a 1 kN load cell was used to test the specimens with a cross-head speed of 0.5 mm/min. More information about this test can be seen in Appendix A and test results of each specimen can be found in Appendix E. Dry strength means the strength of specimens stored in desiccator while the wet strength is the strength of specimens stored in water.

4.3.4.1 Biaxial flexural strength results for 7 days.

Average biaxial flexural strength results ($\overline{S}$) of each batch and standard deviations (σ) as well as coefficient of variations (V) in dry and wet conditions after keeping the specimens in desiccator and water for 7 days can be seen in Table 4.19. Dry strength means the flexural strength of specimens that were stored in desiccator and wet strength is the flexural strength of specimens that were stored in water. Figure 4.28 shows the dry strengths and decreases in strength after storing in water. Al_2O_3 content of these cements are increasing from left to right in this graphic.

Table 4.19: Biaxial flexural strength test results for different CAC at 7 days

Cement type	Codes	w/c	Dry Strength			Wet Strength		
			$\overline{S}$ (MPa)	σ (MPa)	V (%)	$\overline{S}$ (MPa)	σ (MPa)	V (%)
Ciment Fondu	42-1	0.19	169	30	18	87	5	6
Ciment Fondu	42-2	0.17	194	14	7	124	8	7
Ciment Fondu	42-3	0.15	206	18	9	175	25	14
Ciment Fondu	42-4	0.13	220	19	9	180	18	10
Ciment Fondu	42-5	0.11	233	17	7	179	29	17
Ciment Fondu	42-6	0.10	235	25	11	124	27	22
Ciment Fondu	42-7	0.09	206	19	9	126	27	21
Secar 41	49-1	0.19	205	13	6	130	12	9
Secar 41	49-2	0.17	178	8	5	108	6	6
Secar 41	49-3	0.15	213	17	8	142	4	3
Secar 41	49-4	0.13	216	16	7	161	30	18
Secar 41	49-5	0.11	238	12	5	180	46	27
Secar 41	49-6	0.10	221	21	10	143	21	14
Secar 41	49-7	0.09	-	-	-	-	-	-
Secar 71	70-1	0.19	187	11	6	127	16	13
Secar 71	70-2	0.17	209	26	13	170	45	27
Secar 71	70-3	0.15	257	8	3	193	21	11
Secar 71	70-4	0.13	248	7	3	199	15	8
Secar 71	70-5	0.11	248	19	8	191	36	19
Secar 71	70-6	0.10	243	22	9	169	34	20
Secar 71	70-7	0.09	174	26	15	87	19	22
Secar 80	79-1	0.19	70	18	26	15	3	22
Secar 80	79-2	0.17	105	6	6	17	6	33
Secar 80	79-3	0.15	85	5	6	44	1	2
Secar 80	79-4	0.13	-	-	-	-	-	-
Secar 80	79-5	0.11	-	-	-	-	-	-
Secar 80	79-6	0.10	-	-	-	-	-	-
Secar 80	79-7	0.09	-	-	-	-	-	-

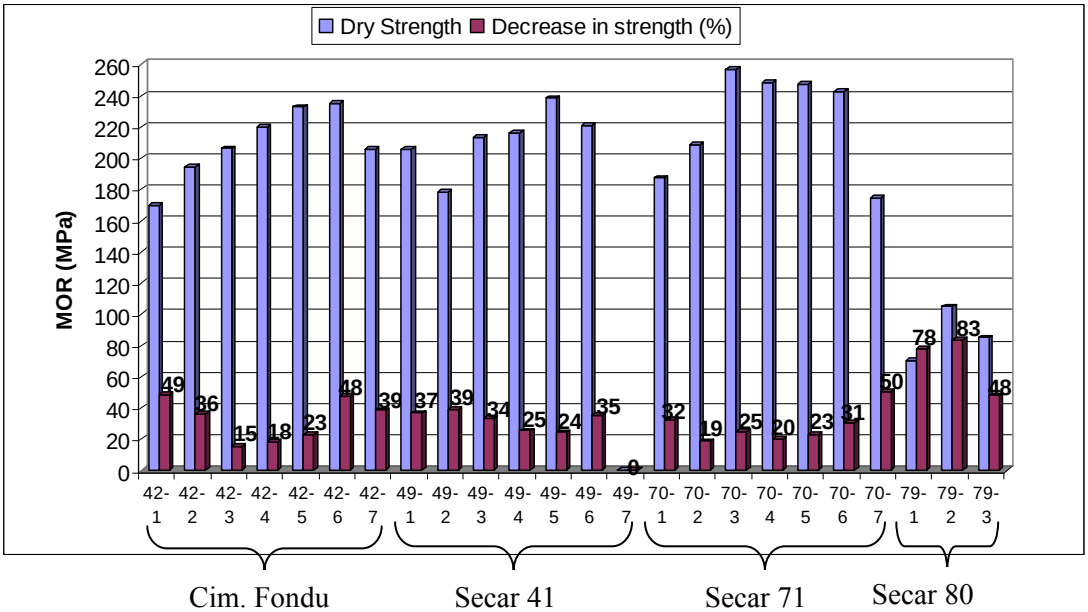


Figure 4.28: Biaxial flexural strength test results at 7 days

The highest flexural strengths in dry condition were 257, 248 and 248 MPa for mix numbers 70-3, 70-4 and 70-5, respectively and these were achieved with Secar 71 which has 70% Al_2O_3 content. All batches prepared with Secar 71 gave the highest flexural strengths with respect to other compositions in same w/c ratios except with the 0.19 w/c ratio.

The lowest flexural strengths were 70, 85 and 105 MPa for mix numbers 79-1, 79-3 and 79-2 respectively and these were achieved with Secar 80 which has 79% Al_2O_3 content. It was difficult to process with this cement type even in higher w/c ratios.

Decreases in strengths ranged between 15% (CF-3) and 83% (80-2). Lower decreases in strength was generally obtained with w/c ratios between 0.11 and 0.15.

4.3.4.2 Biaxial flexural strength results for 28 days

Average biaxial flexural strength results ($\overline{S}$) of each batch and standard deviations (σ) as well as coefficient of variations (V) in dry and wet conditions after keeping the specimens in desiccator and water for 7 days can be seen in Table 4.20. Dry strength means the flexural strength of specimens, which were stored in desiccator and wet strength is the flexural strength of specimens which were stored in water. Figure 4.29 shows the dry strengths and decreases in strength after storing at water. Al_2O_3 content of these cements are increasing from left to right in this graphic.

The highest flexural strengths of the specimens which were stored in dry conditions, were 268, 264 and 258 MPa for 71-5, 71-3 and 71-4 respectively. These results were obtained with Secar 71 similar to the results of 7 days.

The lowest flexural strengths of the specimens, which were stored in dry conditions, were 71, 109 and 122 MPa for 79-1, 79-2 and 79-3 respectively. These results were obtained with Secar 80 similar to the results of 7 days.

Dry strengths obtained with Ciment Fondu and Secar 41 were very similar to each other in same w/c ratios. In addition, decreases in strengths ranged between 56% (41-1) and 66% (71-4) except for the MDF cements produced with Secar 80. Decreases in strengths was approximately 80% for Secar 80.

Table 4.20: Biaxial flexural strength test results for different CAC at 28 days

Cement type	Codes	w/c	Dry Strength			Wet Strength		
			$\overline{S}$ (MPa)	σ (MPa)	V (%)	$\overline{S}$ (MPa)	σ (MPa)	V (%)
Ciment Fondu	42-1	0.19	170	15	9	59	11	19
Ciment Fondu	42-2	0.17	191	8	4	59	17	29
Ciment Fondu	42-3	0.15	215	8	4	67	9	13
Ciment Fondu	42-4	0.13	206	12	6	77	4	5
Ciment Fondu	42-5	0.11	234	22	10	84	19	23
Ciment Fondu	42-6	0.10	243	10	4	90	13	14
Ciment Fondu	42-7	0.09	183	26	14	70	1	2
Secar 41	49-1	0.19	185	10	6	81	1	1
Secar 41	49-2	0.17	176	13	7	75	3	5
Secar 41	49-3	0.15	201	19	10	77	9	12
Secar 41	49-4	0.13	212	12	6	72	15	20
Secar 41	49-5	0.11	244	15	6	95	18	19
Secar 41	49-6	0.10	212	10	5	100	12	12
Secar 41	49-7	0.09	-	-	-	-	-	-
Secar 71	70-1	0.19	195	21	11	80	8	10
Secar 71	70-2	0.17	252	10	4	87	23	26
Secar 71	70-3	0.15	264	13	5	99	15	15
Secar 71	70-4	0.13	258	16	6	88	9	10
Secar 71	70-5	0.11	268	27	10	95	35	36
Secar 71	70-6	0.10	244	18	7	106	11	10
Secar 71	70-7	0.09	183	11	6	79	3	4
Secar 80	79-1	0.19	71	12	17	14	1	9
Secar 80	79-2	0.17	109	2	2	23	14	60
Secar 80	79-3	0.15	122	0	0	38	0	1
Secar 80	79-4	0.13	-	-	-	-	-	-
Secar 80	79-5	0.11	-	-	-	-	-	-
Secar 80	79-6	0.10	-	-	-	-	-	-
Secar 80	79-7	0.09	-	-	-	-	-	-

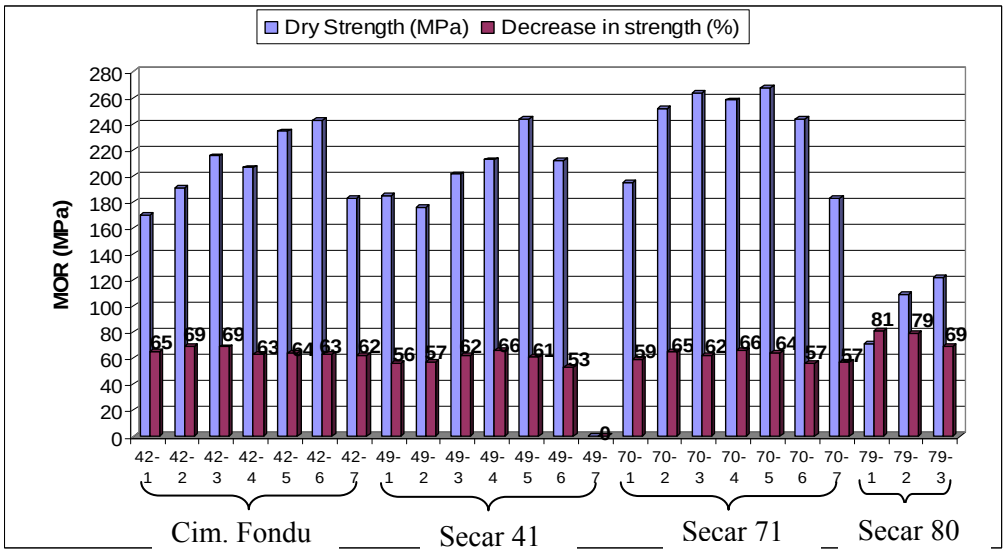


Figure 4.29: Biaxial flexural strength test results at 28 days

On the other hand, dry strengths of 7 and 28 days look almost identical. This situation can be seen better at Figure 4.30. Alumina cements are known as with their high early strength and it is obvious that MDF cements were already reached to their highest flexural strengths in 7 days. However, their wet strengths continue to drop until 28 days too (Figure 4.31) and this lost almost double compared to 7 days.

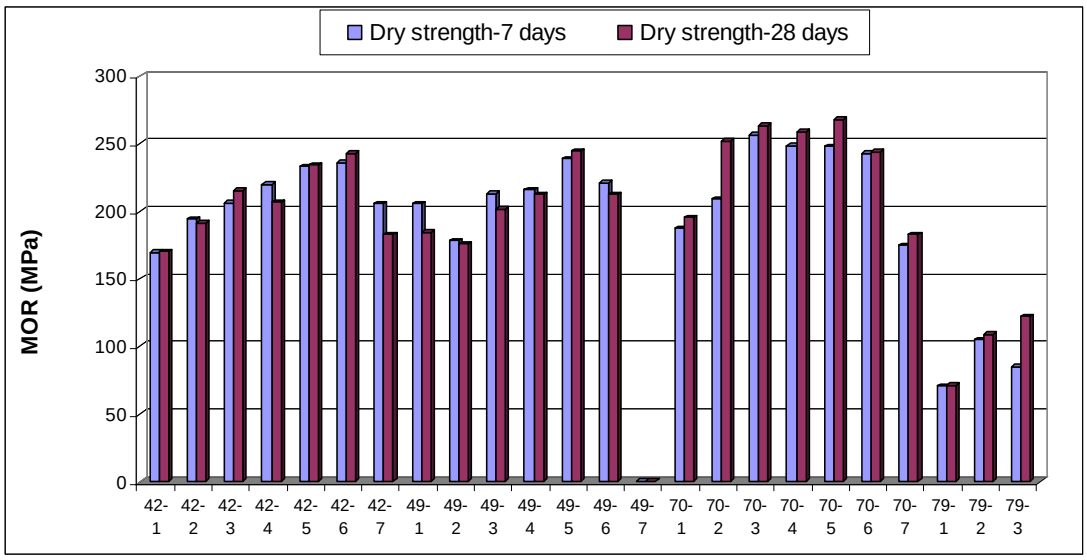


Figure 4.30: Dry strengths of MDF specimens at 7 and 28 days

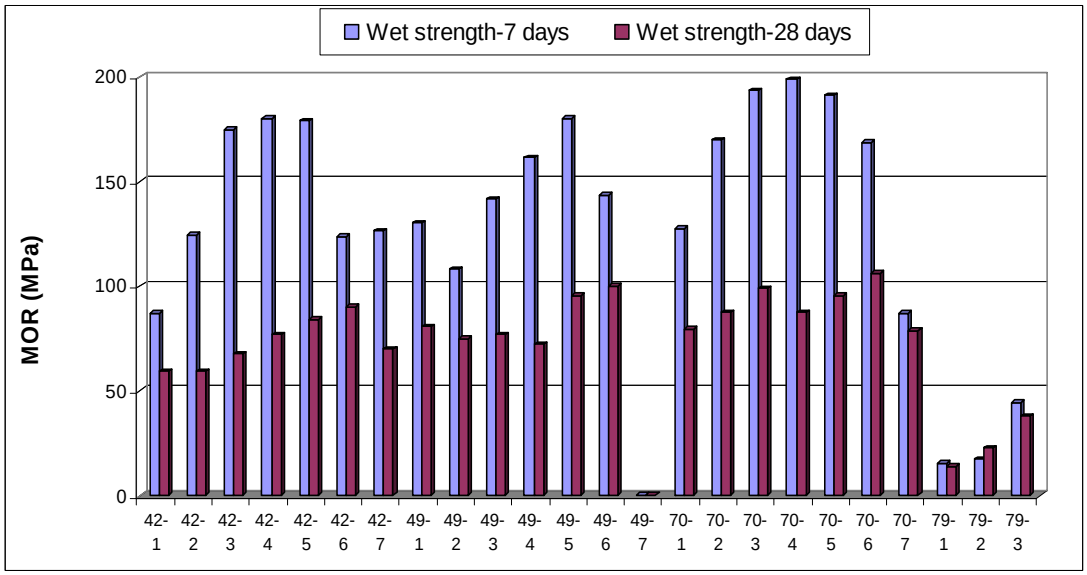


Figure 4.31: Wet strengths of MDF specimens at 7 and 28 days

All these results showed that composties produced with Secar 80 cement have the lowest flexural strengths between the cements tested, which may be due to the high content of alumina in this cement (79%). It seems that crosslinking of Al ions with polymer did not fully complete. Another important point is that Secar 80 has smaller particle size compared to other cement types and this maybe the other reason for

these low strengths. It was very hard to produce MDF cements in low w/c ratios with that cement type because of its smaller particle size. Kendall suggested that the strength of the MDF cement systems is no longer pore size controlled, but controlled by the size of the largest grain caused by poor adhesion or elastic mismatch with the polymer matrix (Russell, 1991), although it was opposite in our case. This strength drop is most probably because of the used production process. This process was optimized for Secar 71 and it may not fit for Secar 80 because of its different particle size.

Secar 80 also caused the highest strength losses in water storage. It seems that Secar 71 cement, which contains 70% alumina, performs slightly better than the other cements tested in flexure; even with this cement it was possible to obtain flexural strengths over 250 MPa. However, all composites produced with all types of alumina cements are sensitive to water and show strength loss over 50% after 28 days water storage. The variation of strength loss with w/c ratio is exhibited in Figure 4.32. This figure shows that lower w/c ratios have lower strength losses in water comparing to higher w/c ratios. However, the strength loss was over 50% even for the least w/c.

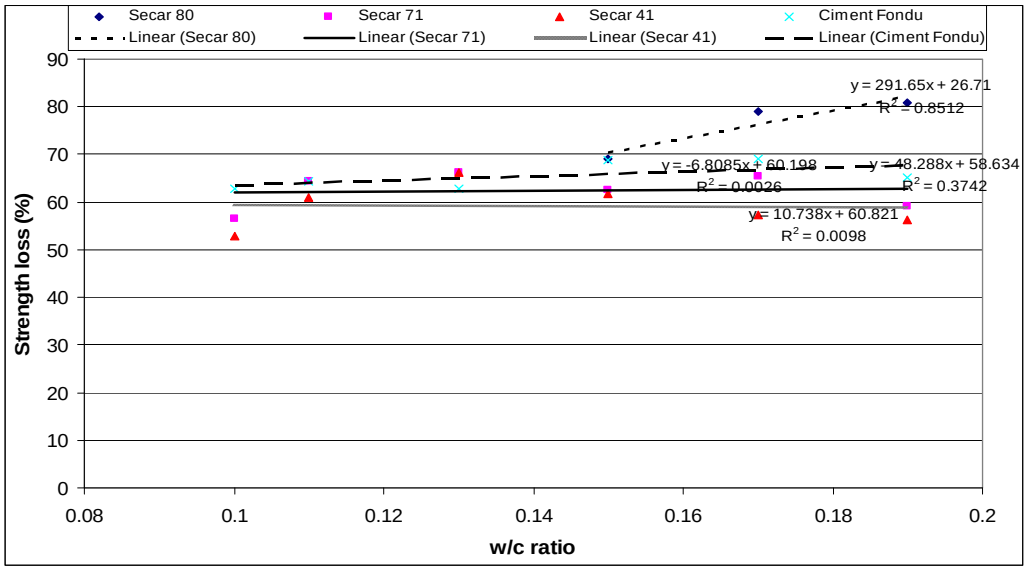


Figure 4.32: Strength loss versus water/cement ratio for 28 days water storage

Strength loss is also plotted against Al_2O_3 content of alumina cements in Figure 4.33. It seems that there is a minimum strength loss between 49% and 70% alumina contents. These results are in good agreement with the results of Delucchi and Cerisola (2001). They were proposed that the highest Al_2O_3 percentage had the lowest degredation after prolonged immersion by using cements up to 70% alumina content.

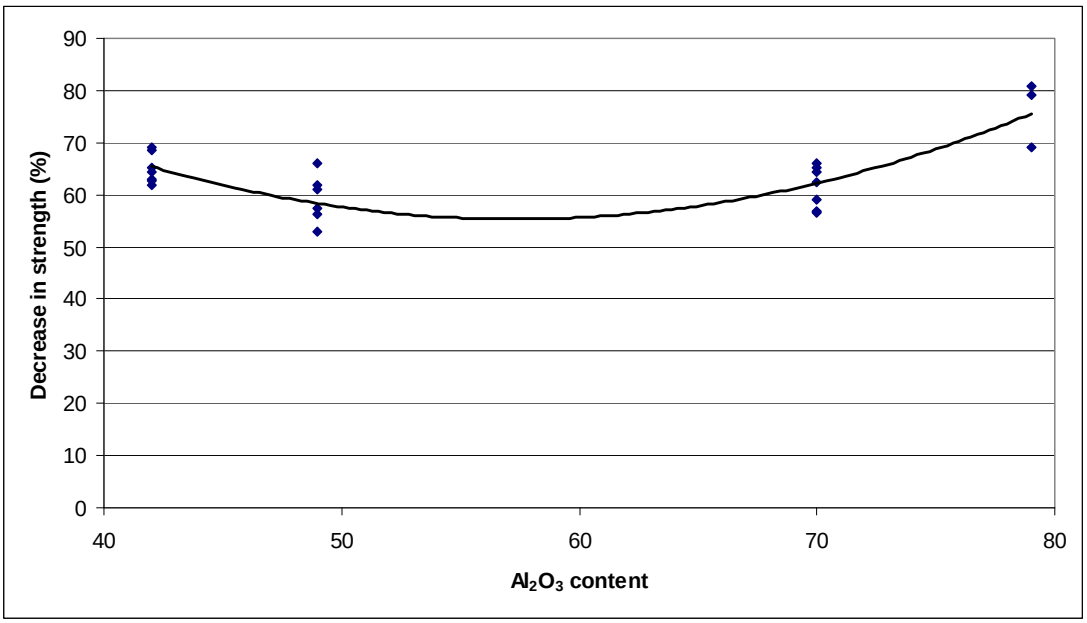


Figure 4.33: Strength loss versus Al_2O_3 content for 28 days water storage (w/c changes between 0.09 and 0.19)

4.3.5 X-Ray Diffraction Analysis

The aim of these tests was comparing the phases between unhydrated cement and MDF cement and finding the hydration products of MDF cements if there are any.

4.3.5.1 Specimen preparation for X-Ray diffraction analysis

XRD analysis were conducted on Rigaku model X-ray diffractometer (Figure 4.34). 8 different specimens were prepared for tests. Four of them were alumina cements and the other four were MDF cements prepared by using each cement type. These specimens were:

1. Ciment Fondu
2. MDF produced with Ciment Fondu
3. Secar 41
4. MDF produced with Secar 41
5. Secar 71
6. MDF produced with Secar 71
7. Secar 80
8. MDF produced with Secar 80

MDF cement specimens prepared 7 days before the tests and stored in desiccator until test date. Subsequently, MDF cement specimens were grinded with pestle in order to decrease the particle size. Specimens were packed with minimal force for smooth, planar surface and placed inside the machine.

Figure 4.34: Rigaku model X-ray diffractometer

4.3.5.2 Test results of X-Ray diffraction analysis

Specimens analysed qualitatively. All peaks tried to match with phases by using Jade software. Entire process was repeated until all peaks have been assigned. Results of Secar 71 and MDF produced with Secar 71 can be seen in Figure 4.35 and Figure 4.36. All other results are given in Appendix F after assignment of peaks.

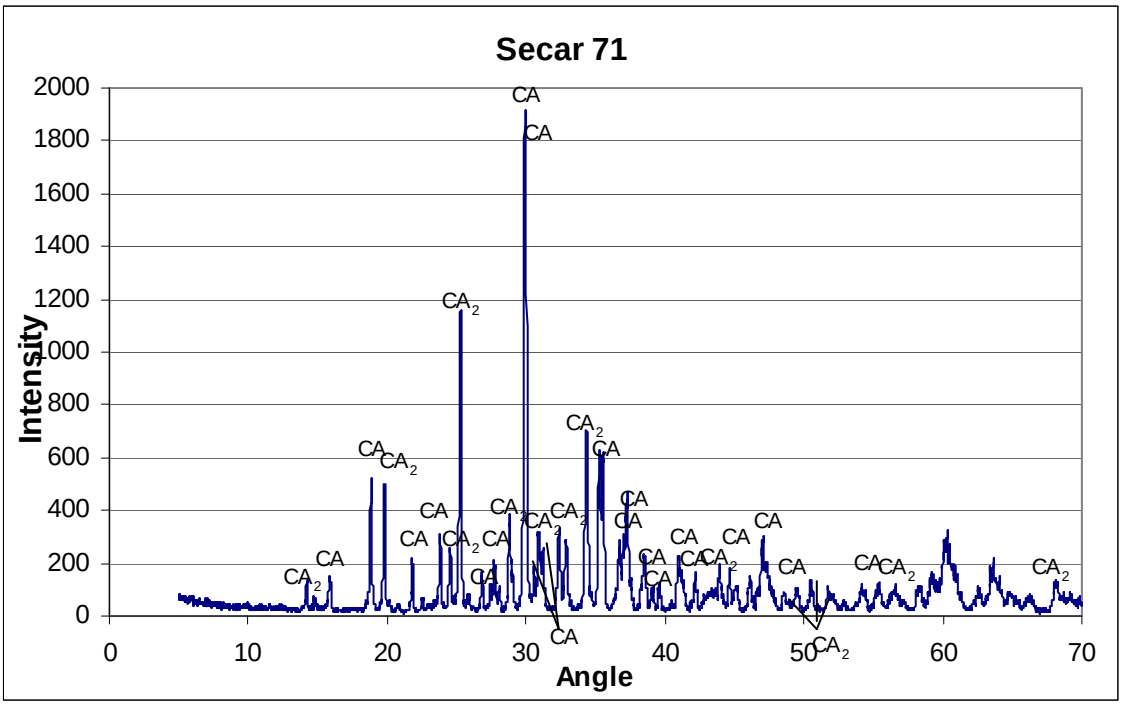


Figure 4.35:X-ray diffraction of Secar 71

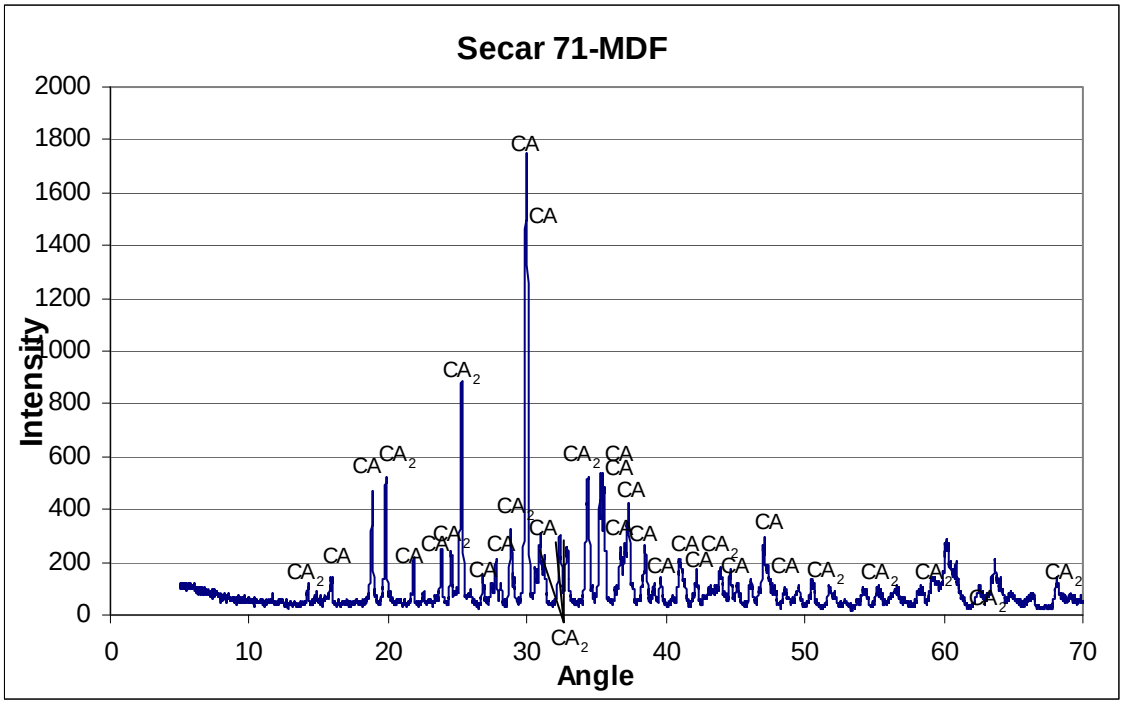


Figure 4.36:X-ray diffraction of MDF cement produced with Secar 71

In the comparison of the results of each cement type with each MDF cements, there is not any significant difference. Intensities of patterns slightly decreae but it may be because of PVA addition of MDF cements. Cement specimens were unhydrated but MDF cement specimens were hydrated with 0.11 w/c and cured under 80°C for 24 hours. Hydration products of alumina cements are C_3AH_6, C_2AH_8, CAH_{10} and AH_3 in general, and the expected hydration product at this high temperature was the former one, which is in hexagonal form and stable (for more information see Part 3.1.1.4) We couldn't find any evidence of hydration products. Although, around angle 10 and the left of angle 10 there are some increase on intensities and hydration products may be concentrated on that area. It seems that PVA prevents the formation of hydration products on MDF cements which is in good aggreement with the previous researchers (Sinclair and Groves, 1984; Sinclair and Groves, 1985; Edmonds and Mojumdar, 1989; Popoola et al., 1991; Drabik et al., 1994). It was considered that incorporation of organic additives into the hydrate lattices could be responsible for preventing the transformation to C_3AH_6 (Young, 1970).

4.3.6 Morphological Investigation of MDF 71 and MDF 80

MDF cements were produced with Secar 71 and Secar 80, which contained the lowest Al_2O_3 content (70%) and the highest Al_2O_3 (79%) content, respectively, and coded with respect to their cement type (MDF 71 and MDF 80). Gohsenol KH17

type PVA were used in the production of both specimens. Polymer/cement were kept constant at 0.07 but their water/cement were 0.10 and 0.17, respectively. Properties of the used cements and PVA can be seen in Table 4.4, Table 4.16 and Table 4.17. These specimens were sent to the Transilvania University of Brasov for morphological investigation. Atomic Force Microscopy (AFM), Contact Angle and Fourier Transform Infrared Spectroscopy (FTIR) tests were conducted over these specimens.

These cement types were the best and worst cement types for the production of MDF cements with respect to the mechanical test results (Part 4.3.4). Biaxial flexural strength test results of these specimens stored in water and desiccator for 28 days can be seen in Table 4.21.

Table 4.21: Biaxial flexural strength results of MDF specimens

MDF composite	w/c	p/c	Dry Strength (MPa)	Wet Strength (MPa)
MDF 71	0.10	0.07	244	106
MDF 80	0.17	0,07	109	23

4.3.6.1 Atomic force microscopy (AFM) tests

Surface morphology and roughness of the cement sample were examined by using Atomic Force Microscopy (AFM, NT-MDT model NTGRA PRIMA EC). The images were taken in semicontact mode with silicone cantilever (CSG 10, force constant 0.15 N/m, tip radius 10 nm). The root-mean-square (RMS) roughness was calculated with the AFM manufacturer's provided software on images of 20x20 μm^2 scan size.

Figure 4.37 shows the surface 3D images used for roughness calculation for MDF 71 and MDF 80. The experiments proved that the MDF 80 surface has a higher roughness compared with MDF 71. Average roughness was 221 nm for MDF 71 and 360 nm for MDF 80. This affirmation can be correlated with biaxial flexural strength tests and contact angle determinations.

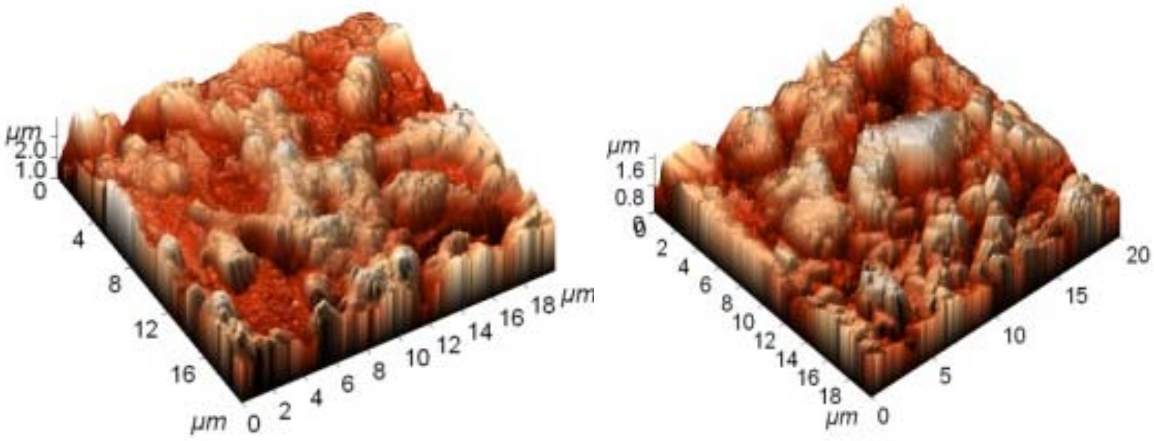


Figure 4.37:AFM image for 20x20 μm^2 scan size; a) MDF 71, average roughness: 221 nm b) MDF 80, average roughness: 360 nm

4.3.6.2 Contact angle tests

The contact angle of a liquid drop with a solid surface is a consequence of intermolecular interactions. It is strongly dependent on the liquid nature and solid interface characteristics (porosity and hydrophilicity). Contact angle determinations (θ angle) tests were performed by using an OCA-20 Contact Angle System (Data Physics Instruments). Testing liquid, with known polarity and surface tension, was ultra pure water. The obtained results are presented in Figure 4.38.

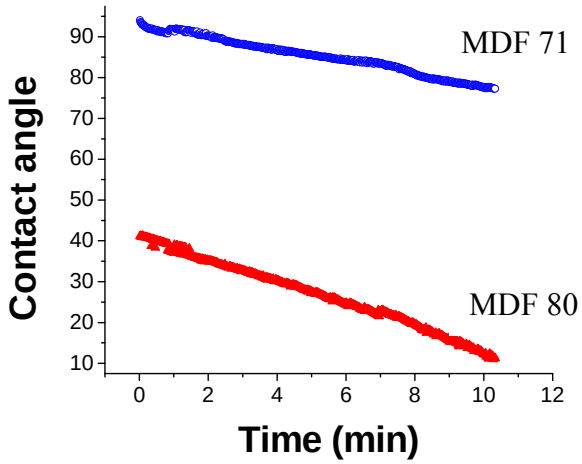


Figure 4.38: Time dependence of contact angle between water and studied MDF cements

It could be noted that the contact angle decreases in time, linearly, showing different slopes. Fitting the experimental data, the following equations that describes the kinetic of water absorption into the MDF cements, have been obtained:

- for Secar 71: θ=93.00881-1.50154 t; R= 0.99462
- for Secar 80: θ=41.12895-2.7714 t; R= 0.99759

The free term from the equations indicates the MDF cements hydrophilicity. Therefore, it could be concluded that MDF cements obtained by using Secar 71 are more hydrophobic in comparison with those obtained with Secar 80.

In addition, the higher slope obtained for the curve describing the contact angle modification in time, in case of Secar 80, indicates a higher porosity of this cement by comparing with that obtained by Secar 71. These results are in good agreement with those obtained by AFM.

The obtained data are in good correlation with biaxial flexural strength results for MDF cements in dry and wet conditions. A clear dependence of mechanical resistance and MDF cements morphology could be established: the lower roughness, porosity and hydrophilicity, the higher flexural strength.

4.3.6.3 Fourier transform infrared spectroscopy (FTIR) tests

Fourier Transform Infrared Spectroscopy (FTIR) was used to characterize the presence of specific chemical groups in the materials. FTIR spectra were obtained in the range of wavenumber from 4000 to 650 cm^{-1} using a Perkin-Elmer spectrophotometer. The FTIR spectra were normalized and major vibration bands were associated with chemical groups. These tests were conducted over MDF composites produced with Secar 71 and Secar 80 and called as MDF 71 and MDF 80. Third specimen was pure Gohsenol KH 17. The purpose of these tests was finding any evidence of crosslinking due to the change on pattern. Test result can be seen in Figure 4.39.

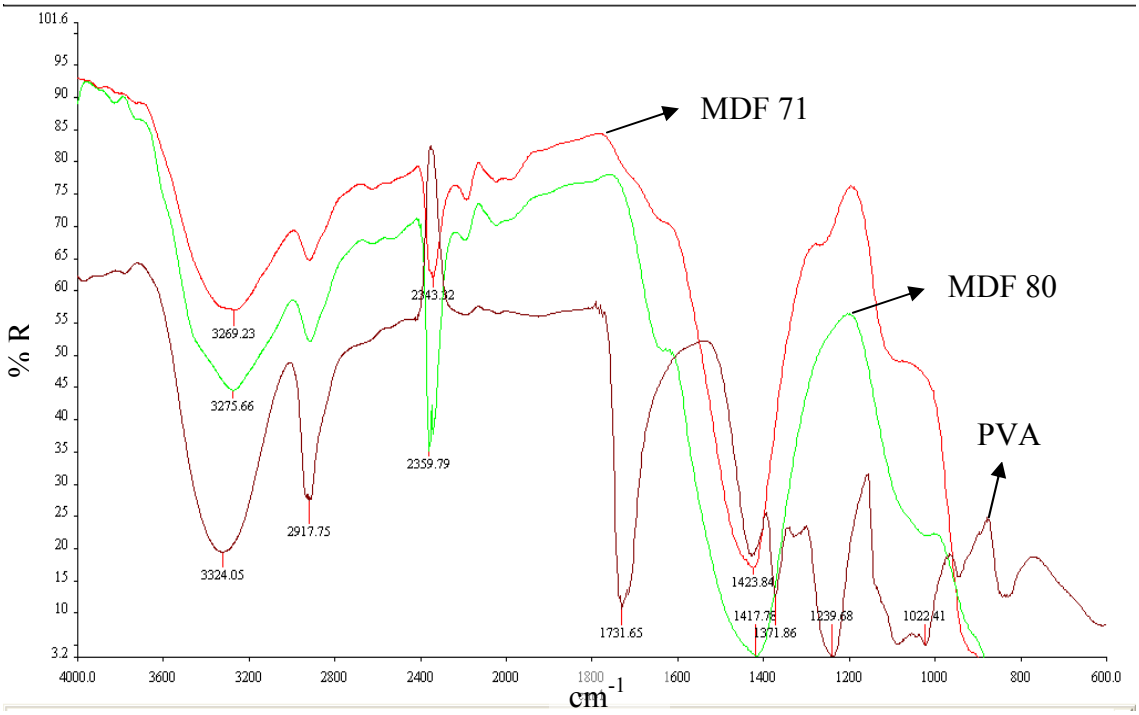


Figure 4.39:FTIR spectra for MDF 71, MDF 80 and PVA (KH17)

Regarding PVA, first major band, observed between 3550 and 3200 cm^{-1} is linked to the stretching of O-H bonds involved in the intermolecular and intramolecular hydrogen bonds. The vibrational band observed between 2840-3000 cm^{-1} refers to the stretching of C-H bonds from alkyl groups and the peaks between 1750-1720 cm^{-1} corresponds to C=O and C-O bonds from acetate group.

The relative intensity of the vibration band from 1141 cm^{-1} could be correlated to the cristalinity of PVA. The C-O-C groups determine an absorption band in the region 1150-1085 cm^{-1}. The band situated between 1461-1417 cm^{-1} is due to CH_2 groups (Herman et al., 2007).

The specific bands from the spectra of MDF 71 and MDF 80 were as follows: the absorption band from 3270 cm^{-1} representing the O-H stretching vibration in its hydrates (Sugma et al., 2002) and the band situated between 2840-3000 cm^{-1} could be correlated to the stretching C-H bond from the alkyl groups provided by PVA. The intensity of these two bands is much smaller than the homologue bands corresponding to PVA.

During hydration the following reactions are possible:

$$CaO \cdot Al_2O_3 + 4H_2O \rightarrow Ca^{2+} + 2Al(OH)_4^-$$

$$2CaO \cdot Al_2O_3 \cdot SiO_2 + 5H_2O + OH^- \rightarrow Ca^{2+} + 2Al(OH)_4^- + H_3SiO_4^-$$

The band from 1630 cm^{-1} that can be seen in both types of cements, can be assigned to formation of polymer-Al complex (the vibration of C-O-Al bond). It could be noticed that the intensity of this band is higher for MDF 80 in comparison with MDF 71, in good agreement with the higher Al_2O_3 amount of this type of cement.

The band detected near to 1420 cm^{-1} could be attributed to the stretching vibration of CO_3 in the calcite (Sugma et al., 2002) and the weak absorption band from 1090 cm^{-1} observed for MDF 71 is probably due to Al-O-H bonds.

Also, absorption band from 1630 cm^{-1} suggests the PVA cross-linking by aluminum ions in good agreement with the proposed mechanism of Desai (1992) in Figure 3.32.

It could be noticed that the peak observed at 1350 cm^{-1} corresponding to the acetate group in case of PVA, disappeared for both types of MDF cement. This fact demonstrates that the acetate groups are eliminated due to the hydrolysis reaction. Disappearance of acetate groups could be noticed too, for MDF cements obtained by Secar 71 and Secar 80 through total or partial decrease of the intensity of band situated to 1239 cm^{-1} in the PVA spectra. This mentioned band is attributed to C-H wagging from CH_3 groups that belongs to acetate groups.

The ratio of band intensities (height) from 3324 cm^{-1} (due to OH groups) and 2917 cm^{-1} (due to -CH_2- groups) was calculated and the results are presented in Table 4.22.

Table 4.22: The ratio of band intensities between 3324 cm^{-1} and 2917 cm^{-1}

Sample code	Ratio obtained
PVA	1.72
MDF 71	3.75
MDF 80	3.60

It could be observed an increase of these ratios for MDF 71 and MDF 80 in comparison to PVA, due to the hydrolysis process which has as effect the formation of supplementary OH groups provided from hydroxides and PVA respectively.

The absorption band from 1020 cm^{-1} observed for MDF 80 can be ascribed to the non-reacted CACs, such as: $2CaO \cdot Al_2O_3 \cdot SiO_2$; $CaO \cdot Al_2O_3$; SiO_2 ; $3Al_2O_3 \cdot 2\ SiO_2$; Al_2O_3 (Sugma et al., 2002).

4.3.7 Thermogravimetric Analysis (TA) and Differential Thermal Analysis (DTA) Tests

Thermogravimetric Analysis (TA) and Differential Thermal Analysis (DTA) tests were conducted over 10 different specimens by using NETZSCH STA 409 model Simultaneous Thermal Analyzer. Four of the specimens were alumina cements, and other four were macro defect free cements. Another specimen was PVA (Gohsenol KH17) and the last specimen was cement paste. These specimens can be seen in Table 4.23. MDF cements were prepared by using alumina cements, water, glycerol and Gohsenol KH 17 type PVA with the method mentioned in Part 4.1.5. Properties of the used cements and PVA can be seen in Table 4.4, Table 4.16 and Table 4.17. The purpose of these thermal analysis tests was finding any evidence of crosslinking due to the change on thermal pattern and comparing the each MDF system with respect to their cement type.

Table 4.23: Materials used for thermal analysis tests

Specimen No	Materials	Material Types
1	Ciment Fondu	Alumina Cements
2	Secar 41	
3	Secar 71	
4	Secar 80	
5	MDF Fondu	MDF Cements
6	MDF 41	
7	MDF 71	
8	MDF 80	
9	Gohsenol KH 17	PVA
10	Cement Paste	Secar 71+Water

4.3.7.1 TA and DTA tests results

Graphics of all tested specimens can be seen in Appendix G. According to these results, decresases on mass ranged between 9.27% and 13% for each MDF cement with respect to used cement type. Decreases were 9.27% for MDF 71, 10% for MDF 41, 10.4% for Ciment Fondu and 13% for MDF 80. Appareantly, polymer phases of MDF cements were caused these decreases in mass since there is no decrease in the mass of aluminate cements. These results are in good aggrement with the results of biaxial flexural strengths and the highest flexural strengths were obtained in the same order. MDF 80 were also showed earlier change on DTA results.

4.3.8 Conclusions for Part III

- MDF cements can be successfully produced with 4 different types of alumina cements.
- Dry strength results were almost same for 7 and 28 days but wet strengths were continued to decrease until 28 days.
- The highest biaxial flexural strength was obtained as 268 MPa on the composite coded as 70-5, which was prepared by high alumina cement with 70% Al_2O_3 content and at a water/cement of 0.11.
- The lowest biaxial flexural strength was 71 MPa and belongs to the composite coded as 79-1 which was prepared with 79% Al_2O_3 content cement at water/cement of 0.19.
- Flexural strengths of all specimens decreased between 53 and 81% after storing in water for 28 days.
- It seems that there is an optimum alumina content between 49-70% for minimum strength loss in water.
- For high level of Al_2O_3 (79%), the production of MDF becomes harder and the level of strength drops while strength loss increases comparing with other cements.
- There were no significant difference on the results of XRD for each cement and MDF cement type and no hydration product were observed. It seems that PVA prevents the formation of hydration products on MDF cements which is in good aggreement with the previous researchers.
- Average roughnes was low and contact angle was higher for MDF 71 comparing to MDF 80, which means that MDF 71 has less affinity for water.
- Decresases on mass ranged between 9.27% and 13% for each MDF cement with respect to used cement type according to the results of TA. These results are in good aggrement with the results of biaxial flexural strengths and the highest flexural strengths were obtained in the same order.

4.4 Experimental Study IV: Investigation of Different Parameters on the Production of MDF Cements

In this part, effect of different parameters on the production of MDF cements were investigated. First of all, production of MDF cements was tried without cement or

polymer. A composite was obtained without using a cement though it was very weak on strength, but production was not possible on roller mills without using polymer. After that, MDF cements were produced with a different resin and a different polymer. Used resin was poly(amide-epichlorohydrin) and the polymer was poly(ethylene oxide).

4.4.1 Producing MDF Cements without Using Cement

Production of MDF cements was tried without using CAC. First of all, only $NaAlO_2$ was used instead of CAC but these attempts were unsuccessful and then α-Al_2O_3 was also added in different amounts in order to combine the material. Aim of this study was to see if PVA crosslinks in $NaAlO_2$ solution, if so, does this crosslinking prevent or reduce water adsorption and swelling? 11 different mixtures were prepared with $NaAlO_2$. Used PVA was Gohsenol KH 17 and its properties can be seen in Table 4.4. Compositions of these mixtures can be seen in Table 4.24.

Table 4.24: Compositions of mixtures prepared with $NaAlO_2$

Mixture no.	PVA (g)	$NaAlO_2$ (g)	Water (g)
1	3.5	1.5	5.5
2	3.5	2.5	5.5
3	3.5	1.5	11.0
4	3.5	1.5	11.0
5	3.5	1.5	55.5
6	3.5	1.5	11.0
7	3.5	1.5	36.4
8	3.5	-	36.4
9	7.0	10.0	20.0
10	7.0	10.0	20.0
11	5.0	10.0	15.0

As can be seen from Table 4.24, some mixtures look same but their mixing order was different. These mixing procedures are:

- **Mixture no. 1, 2 and 4:** $NaAlO_2$ was added to water. Mixture was shaked 30 seconds after waiting 2 minutes, which looked like milk. PVA was added to the mixture and shaked until mixed well.
- **Mixture no. 3:** 1.5 g $NaAlO_2$ was added to 5.5 g water and shaked 30 seconds, it became like milk, and its colour turned to yellow about 5 min. later (a). 3.5 g PVA added to the 5.5 g water, it solidify immediately (b). Mixture a added to

the mixture b, but these two mixtures didn't mix well. Because, mixture b was nearly solid and mixture a stayed over mixture b.

- **Mixture no. 5:** 1.5 g $NaAlO_2$ was added to 5.5 g water and shaked 30 seconds, it became like milk, and its colour turned to transparent yellow in a few min (mix a). 3.5 g PVA added to the 50 g water slowly and stirred-up about 5 minutes, it partly rubberized, partly solved (mix b). then 10 min later mixture a added to the mixture b, it become rubberize (soft gel).
- **Mixture no. 6:** 1.5 g $NaAlO_2$ was added to 3.5 gr PVA and tube shaked. 11 gr. water added to dry mixture, it become very strong gel in 1 minute.
- **Mixture no. 7:** 26.4 g water and 3.5 g. PVA was mixed during heating up to 80°C (mix a). 11 g water and 1.5 g $NaAlO_2$ were also mixed in a different container (mix b). Mixture b was added to the mixture a.
- **Mixture no. 8:** 26.4 g water and 3.5 g. PVA was mixed during heating up to 80°C (mix a). 11 g water were added to this mixture. This mixture has low viscosity, less sticky, less white and more transparent compared to mixture no. 7.
- **Mixture no. 9:** 7 g PVA and 10 g water were mixed in a glass tub (mix a), and it gelled as expected. Better solutions can be prepared by adding more water but adding more water makes the MDF production harder on roller mills. 10 g $NaAlO_2$ and 10 g water mixed in a glass tub (mix b). These 2 mixes were mixed and it became more stiff very quickly. Gel phase and $NaAlO_2$+water could not be mixed neither stirring nor in planetary mixer. Thus, it is not possible to produce MDF with this mixture. This mixture can be seen at Figure 4.40.

Figure 4.40: Mixing gel phase and $NaAlO_2$+water mixture in a planetary mixer for mixture no. 9

- **Mixture no. 10:** Same amounts were used with mixture no. 9, but mixtures were heated during stirring. No difference was observed in this mixture too.
- **Mixture no. 11:** 5 gr PVA and 15 gr water were mixed in a glass tub while heating and stirring. This flowable gel and $NaAlO_2$ were mixed in a planetary mixer. Final product can be seen in Figure 4.41. It was not possible to produce MDF with this material.

Figure 4.41: Mixing gel phase and $NaAlO_2$ in a planetary mixer for mixture no. 11

It was impossible to produce MDF cements with all these mixtures. Their gel behaviour makes them unsuitable for high shear process on two roller mills. It was also impossible to obtain them in a sheet form with hand mixture.

After that, adding α-Al_2O_3 to the mixture was decided to increase the powder form and decrease the gelling effect of PVA with respect to our observations from previous mixtures. These mixtures can be seen in Table 4.25. Water was mixed with PVA and $NaAlO_2$ at different containers. For this reason, water was given in 2 different coloums.

Table 4.25: Compositions of mixtures prepared with $NaAlO_2$ and α-Al_2O_3

Mixture no.	PVA (g)	Water mixed with PVA (g)	$NaAlO_2$ (g)	Water mixed with $NaAlO_2$ (g)	α-Al_2O_3	CAC (g)
12	7	15	10	-	100	-
13	7	20	10	-	100	-
14	10	40	10	20	80	20
15	10	40	10	40	70	30
16	10	40	10	10	100	-
17	10	40	5	10	100	-
18	10	40	-	10	100	-

Brief definitions of these mixtures are:

- **Mixture no. 12:** PVA and water were mixed and heated up to 70-75°C. 18.5 g of total 22 g of PVA-water solution was used for the production of MDF. Mixing this gel and other ingredients were tried at planetary mixer but it was impossible.

- **Mixture no. 13:** Same procedure were applied with mixture no. 12. 23 g of total 27 g of PVA-water solution was used for the production of MDF. Mixing this gel and other ingredients were tried at planetary mixer but it was impossible.

- **Mixture no. 14:** Same procedure were applied with mixture no. 12. 44 g of total 50 g of PVA-water solution was used for the production of MDF. Mixing this gel and other ingredients were tried at planetary mixer with the addition of extra 20 g of water, but it was impossible.

- **Mixture no. 15:** Same procedure were applied with mixture no. 12. 45 g of total 50 g of PVA-water solution was used for the production of MDF. Mixing this gel and other ingredients were tried at planetary mixer with the addition of extra 40 g of water, but it was impossible. Mixture no. 14 and 15 was quiet successful compared to 12 and 13 but again a sheet form could not be produced. Final product can be seen at Figure 4.42.

Figure 4.42: Final product of mixture no. 15

- **Mixture no. 16:** PVA and water were mixed and heated up to 70-75°C. 40 g of total 50 g of PVA-water solution was used for the production of MDF. Mixing this gel and other ingredients were tried at planetary mixer with the addition of extra 10 g of water, but it was impossible. Calendering process were applied and obtained material were subjected to conventional hot press and oven cure.

- **Mixture no. 17:** Same procedure were applied with mixture no. 16. Only difference was adding 5 g of extra water instead of 10 g.

- **Mixture no. 18:** Same procedure were applied with mixture no. 16. Only difference was adding no extra water.

As a conclusion, it was possible to produce MDF cements without using CAC for mixtures 16, 17 and 18. However, they were very weak samples compared to real MDF cements even it was possible to break them with hand. Since it was difficult to apply flexural tests to these specimens, their weight change were calculated under 100% moisture conditions. Different pieces from mixtures 16, 17 and 18 were stored at water for 1 week and the increase on their weight were calculated. Average results for each mixture can be seen in Table 4.26. This is 6-8 times more if we compare these results with the weight increase of conventional MDF cements which is generally around 2-3%. More detailed study of weight increase of MDF cements produced with different PVA can be seen in Part 4.2.5.

Table 4.26: Average weight increase of specimens, which were produced without cement, after subjected to 100% humid condition for 1 week

Mixture no.	Weight increase (%)
16	18
17	21
18	25

4.4.2 Producing MDF Cements without Using Polymer

MDF cements were tried to be produced without using any polymer. 3 attempts had been made for this purpose. These mixes can be seen in Table 4.27. Secar 71 type alumina cement which has 70% Al_2O_3 content mixed with water in a planetary mixer. Then this crumble type mixture tried to be obtain in a sheet form at calendaring machine. It was impossible to join all the pieces of mixture in any of the recipies tested.

Table 4.27: Mix proportions of cement-water mixes

No	1	2	3
Cement	120	100	100
Water	13.6	18	33
w/c	0.11	0.18	0.33

Mixtures was hardly passed through between roller mills in mixtures 1 and 2. Mixture was divided into many little pieces. Turning of the roller mills was so difficult and the production process was stopped in order to prevent any damage to calendering machine. On the other hand, 3rd mixture became too slurry which also make it impossible to obtain material in a sheet form. As conclusion, a polymer is necessary to convert the mixture into gel form to resist high shearing during production process.

4.4.3 Using a Poly(amide-epichlorohydrin) Resin for the Production of MDF Cements

Kymene® 557H is a wet-strength resin and a trademark of Hercules firm. Hercules Incorporated produces an many alkaline curing, water soluble, cationic, thermo-setting resins. Chief among these is as a functional additive to paper to impart the property of wet strength. When added to the wet end of the papermaking process, these resins are absorbed onto the pulp fibers and fines. As the paper is dried, the resins crosslink with cellulose to form an insoluble network within the structure of the sheet. This family of resins exhibits similar reactivity with a number of other organic materials including; carboxylated and hydroxylated latexes, poly(vinyl alcohol), carboxymethylcellulose, alginate, poly(acrylate), guar gum, and starch (Hercules Inc., 2006a). Typical properties of Kymene® 557H can be seen in Table 4.28.

Table 4.28: Typical properties of Kymene® 557H (Hercules Inc., 2006b)

Typical properties	
Appaearance	Pale amber liquid
Active material (%)	12.5
Density (g/cc)	1.03
Viscosity (cP) at 21°C	40-60
Freze point	-1°C
pH	4.6-4.9
Shelf life (days)	90

Kymene® 557H resin is a water-soluble, poly(amide-epichlorohydrin) crosslinking polymer that reacts with active hydrogen groups, such as carboxyl, hydroxyl, and amino functional groups. Many water-soluble polymeric materials with such groups are insolubilized in the presence of Kymene® 557H resin when cast as films and dried at elevated temperatures. Polymers having carboxyl groups are generally the

most reactive and insolubilize even at room temperature. The rate and degree of insolubilization are influenced by several variables such as molecular weight of the water-soluble polymer, reactivity of the active-hydrogen group, concentration of Kymene® 557H resin and temperature of cure (Hercules Inc., 2006b).

4.4.3.1 Test results of MDF cements produced with poly(amide-epichlorohydrin) resin

The aim of using poly(amide-epichlorohydrin) crosslinking polymer for the production of MDF cements was insolubilizing the PVA and making the composite more water resistant. At first, MDF cements were tried to be produced without PVA too but it was impossible to produce MDF cement with only Kymene® 557H. The mixture could not pass between roller mills and poured over mills very carefully in little amounts. Material was seperated into very little pieces and it was impossible to combine it into a sheet form. Machine was stopped in order to prevent any damage to calendaring machine. Therefore, MDF cements were produced by using Kymene® 557H and with different hydrolysis degrees of PVAs for this purpose. Kymene® 557H was added to the mixture 20% of PVA amount by weight during mixing at the planetary mixer. The cement used in this study was Lafarge product Secar 71 calcium aluminate cement. Its Al_2O_3 content was 70% and CaO content was 29.2%. The PVAs used in this study were Gohsenol KH17, Gohsenol GH 20 and Gohsenol N 300 and their hydrolysis degrees were 79.6, 87.1 and 98.4% respectively. The properties of the used cement and PVAs can be seen in Table 4.16, Table 4.17 and Table 4.4, respectively. Typical composition of a batch can be seen in Table 4.29.

Table 4.29: Composition of the specimens produced with Kymene® 557H

Material	Density (g/cm^3)	Weight		Volume	
		(g)	(%)	(cm^3)	(%)
CAC	2.93	120	83.3	40.96	65
PVA	1.3	8.4	5.8	6.46	10
Kymene® 557H	1.03	1.68	1.2	1.63	3
Glycerol	1.26	0.84	0.6	0.67	1
Water	1	13.2	9.1	13.20	21
Total		***144.12***	***100***	***62.91***	***100***

Half of the specimens were stored in water while other half were stored in a desiccator using silica gel as desiccant until the test date. Biaxial flexural strength tests were conducted over these specimens at 7 days and flexural strengths under wet and dry conditions were calculated. Test results can be seen in Table 4.30 and Appendix H.

Table 4.30: Biaxial flexural strength test results of MDF cements produced with Kymene® 557H

Polymer type	w/c	p/c	Dry Strength			Wet Strength		
			$\overline{S}$ (MPa)	σ (MPa)	V (%)	$\overline{S}$ (MPa)	σ (MPa)	V (%)
KH17+557	0.11	0.07	197	31	16	115	37	32
GH20+557	0.11	0.07	95	15	16	42	5	12
N300+557	0.15	0.07	-	-	-	-	-	-

It was observed in previous productions that temperature was increasing during productions especially with fully hydrolysed PVA and this was preventing to obtain composite in a sheet form. Addition of Kymene® 557H decreased temperature during production with KH17, GH 20 and N300 but even in this condition it was impossible to produce MDF cements with fully hydrolysed PVA (N300) even with the addition of Kymene® 557H. MDF cements were successfully produced with Gohsenol KH 17 and Gohsenol GH 20R with the addition of Kymene® 557H but there was no significant difference on water resistivity and flexural strength.

4.4.4 Using a Poly(ethylene oxide) Polymer for the Production of MDF Cements

Polyox™ WSR 301 is a nonionic, high molecular weight water-soluble poly(ethylene oxide) polymer and a product of Dow Chemical company. Viscosity of Polyox™ WSR 301 is 5 cPs in 1% aqueous solution and its pH is 9.2. It has white color and used for the production in powder form. Composition of Polyox™ WSR 301 can be seen in Table 4.31 and some properties can be seen in Table 4.32.

Table 4.31: General composition of Polyox™ WSR 301

Components	Amount (% w/w)
Poly (ethylene oxide)	≥ 95%
Fumed silica (generic)	≤ 3%
Calcium as mixed salts	≤1%

Table 4.32: Physical properties and functional contributions of Polyox^{TM} WSR 301

Selected Physical Properties	Functional Contributions
White, free-flowing powder	Nonionic water-soluble polymer that serves as a foam enhancer and slip agent in hair care and skin care products
Approximate molecular weight: 4,000,000	Slip and drag reduction properties help products apply smoothly and leave hair and skin feeling silky
	Improves foam density and fullness without affecting foam height or cleansing
Viscosity of 1% aqueous solution: 1,650 – 5,500 cPs	Compatible with a wide range of surfactants
	contributes secondary thickening

4.4.4.1 Test results of MDF cements produced with poly(ethylene oxide)

Three different MDF cement compositions were prepared by using Polyox^{TM} WSR 301. The cement used in this study was Lafarge product Secar 71 calcium aluminate cement. Its Al_2O_3 content was 70% and CaO content was 29.2%. Other properties of this cement can be seen in Table 4.16 and Table 4.17. Average values of 7 and 28 days biaxial flexural strength tests can be seen in Table 4.33 and Table 4.34. Test results for each specimen can be seen in Appendix I.

Table 4.33: 7 days biaxial flexural strength test results of MDF cements produced with Polyox^{TM} WSR 301

Polymer type	w/c	p/c	Dry Strength			Wet Strength		
			$\overline{S}$ (MPa)	σ (MPa)	V (%)	$\overline{S}$ (MPa)	σ (MPa)	V (%)
Polyox11	0.11	0.088	14.3	11.1	77.8	7.8	-	-
Polyox10	0.10	0.07	10.2	1.5	14.7	5.1	0.4	7.9
Polyox9	0.09	0.07	15.0	3.6	23.8	5.8	0.7	12.5

Table 4.34: 28 days biaxial flexural strength test results of MDF cements produced by using Polyox^{TM} WSR 301

Polymer type	w/c	p/c	Dry Strength			Wet Strength		
			$\overline{S}$ (MPa)	σ (MPa)	V (%)	$\overline{S}$ (MPa)	σ (MPa)	V (%)
Polyox10	0.10	0.07	22	0	2	7	1	10
Polyox9	0.09	0.07	11	2	20	8	1	10

It was hard to produce MDF cements by using this polymer because of lack of coherence during high shear process. High shear applied several times more than the standard production procedure mentioned in Part 4.1.3. Flexural strength was very low comparing to PVA-CAC MDF composites and it was also highly affected from

water which makes this polymer unsuitable for the production of MDF cements according to our results.

4.5 Experimental Study V: Effect of Different Additives on the Properties of MDF Cements

All of the previous experimental studies were conducted at United States of America (USA) by using the machines and laboratories of UIUC. New machines, such as planetary mixer, calendering machine, hot press, core drilling machine, oven and a new biaxial flexural strength test fixture were designed and produced succesfully in Turkey and all productions in this part were conducted by using these new machines at Istanbul Technical University. Information about the used machines can be find in Part 4.5.1.3.

4.5.1 Optimization Studies

First of all, optimization studies were conducted since the new machines have different properties and dimensions. 34 different batches were prepared for the investigation of different parameters and to find the highest flexural strengths and less strength drop in contact with water. A constant production procedure was determined with the help of Part 4.1.5. This production step was consist of 17 steps:

Preliminary steps:

1. Platens of press were pre-heated to 80°C (176°F).

Planetary mixer:

2. Cement and PVA were dry blended for one minute prior to the addition of mixture of water and glycerol at a speed rate 1.
3. After adding of water, the batch was mixed for one minutes at medium speed (speed rate 1) until a damp, granular mix was formed.
4. The cohesive solid material was scraped off the bowl in 30 seconds and then blended for an additional 1 minute at a speed rate 2.

Two roll mill:

5. Nip gap was set to 0.25 mm and side guards 15 cm apart.
6. Two roller mills were turned on and speeds of the rollers were set to 25:20 (front:back), passing powder through.

7. Powder was passed through, nip gap was increased to 0.50 mm and folded and passed through again.
8. Speeds of the rollers were changed to 40:20 and shear mixed for 15 seconds.
9. Sheet was rotated 90^0 and shear mixed for another 15 seconds.
10. Speeds of the rollers were changed to 25:20 and nip gap was increased to 2.00 mm
11. Sheet was passed through 10 times folding triple and rotating 90° each time.
12. Side guards were moved out, nip gap were closed to 1.50 mm and speeds of the rollers were changed to 20:20.
13. Batch was passed through twice without folding or rotating.
14. Sheet was cut into desired dimensions.

Hot press:

15. Cement sheets were placed between 2 pieces of Mylar (0.25-mm thick) and then were placed in hot press for 10 minutes at 5 MPa.
16. Sheets were taken out of hot press and Mylar was pulled off of cement.
17. Stiffened composite sheet was cured between two new sheets of mylar and two plates of steel for 24 hours at 80°C. in a forced-air oven.

4.5.1.1 Materials

PVA copolymer which has 88 mole% hydrolysis degree and an alumina cement which is known with the commercial name of Isidac 40 (Al_2O_3: 40%) were used for the productions. Typical properties of this cement can be seen in Table 4.35.

Table 4.35: Properties of the used cement for optimization studies

Chemical Properties	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**CaO**	**MgO**	**SO_3**	**Loss on ignition**
	4.20	40.10	16.55	36.10	0.80	0.02	0.3
Physical Properties	**Density (g/cm^3)**		**Initial set (min)**	**Final set (min)**	**Blaine specific surface (cm^2/g)**		
	3.22		300	310	3300		
Mechanical Properties	**Flexural Strength (MPa)**			**Compressive Strength (MPa)**			
	6 hours	24 hours	28 days	6 hours	24 hours	28 days	
	4.2	9.3	10.8	30.0	82.0	109.0	

4.5.1.2 Mixtures

Thirty four different mixtures were prepared. Different parameters such as nip gap, number of passing materials at different steps, w/c and p/c were changed in the production of mixtures. Compositions of these specimens can be seen in Table 4.36.

Table 4.36: Compositions of the batches for optimization studies

Mix no.	Cement (g)	Water (g)	PVA (g)	Glycerol (g)	w/c	p/c	gly/p
1	150	19.5	7.5	-	0.13	0.05	-
2	150	19.5	7.5	-	0.13	0.05	-
3	150	19.5	7.5	-	0.13	0.05	-
4	150	19.5	7.5	-	0.13	0.05	-
5	300	39	15	-	0.13	0.05	-
6	300	39	15	-	0.13	0.05	-
7	300	39	15	-	0.13	0.05	-
8	300	39	15	-	0.13	0.05	-
9	300	39	15	-	0.13	0.05	-
10	300	39	15	-	0.13	0.05	-
11	300	39	15	1.5	0.13	0.05	0.1
12	300	39	15	2.25	0.13	0.05	0.15
13	300	39	15	3	0.13	0.05	0.2
14	341	44	17	3	0.13	0.05	0.176
15	300	39	15	3	0.13	0.05	0.2
16	300	39	15	3	0.13	0.05	0.2
17	300	39	15	3	0.13	0.05	0.2
18	300	39	15	3	0.13	0.05	0.2
19	150	16.5	10.5	-	0.11	0.07	-
20	300	36	21	3	0.12	0.07	0.143
21	150	19.5	10.5	-	0.13	0.07	-
22	300	42	21	4.2	0.14	0.07	0.2
23	300	33	18	3.6	0.11	0.06	0.2
24	300	36	18	3.6	0.12	0.06	0.2
25	300	39	18	3.6	0.13	0.06	0.2
26	300	42	18	3.6	0.14	0.06	0.2
27	300	33	15	3	0.11	0.05	0.2
28	300	36	15	3	0.12	0.05	0.2
29	300	39	15	3	0.13	0.05	0.2
30	300	42	15	3	0.14	0.05	0.2
31	300	33	12	2.4	0.11	0.04	0.2
32	300	36	12	2.4	0.12	0.04	0.2
33	300	39	12	2.4	0.13	0.04	0.2
34	300	42	12	2.4	0.14	0.04	0.2

These optimization studies can be divided in 2 parts. At the first part, w/c was 0.13 and p/c was 0.05 for mix numbers between 1 and 18. Different parameters were changed in these 18 batches. Then all these parameters were kept constant and p/c

and w/c were changed in order to find the most suitable p/c and w/c ratios on the mixture numbers 19 and 34. Information about these differences between mixtures can be seen in Table 4.37.

Table 4.37: Changed parameters for optimization studies

Mix no.	w/c	p/c	Repeat of 6^{th} step	Repeat of 7^{th} step	Repeat of 9^{th} step	Nip gap at 10^{th} step
1	0.13	0.05	1	1	1	1.7
2	0.13	0.05	1	-	1	1.7
3	0.13	0.05	-	1	1	2
4	0.13	0.05	1	1	1	2
5	0.13	0.05	2	-	1	2
6	0.13	0.05	-	2	1	2
7	0.13	0.05	2	2	1	2
8	0.13	0.05	3	3	1	2
9	0.13	0.05	2	2	1	1.7
10	0.13	0.05	2	2	2	2
11	0.13	0.05	2	1	1	2
12	0.13	0.05	1	2	1	2
13	0.13	0.05	2	2	1	2
14	0.13	0.05	2	2	1	2.25
15	0.13	0.05	2	2	1	2.75
16	0.13	0.05	2	2	1	3
17	0.13	0.05	2	2	1	1.7
18	0.13	0.05	2	2	1*	1.7
19	0.11	0.07	2	2	1	2
20	0.12	0.07	2	2	1	1.7
21	0.13	0.07	2	2	1	2
22	0.14	0.07	2	2	1	2
23	0.11	0.06	2	2	1	2
24	0.12	0.06	2	2	1	2
25	0.13	0.06	2	2	1	2
26	0.14	0.06	2	2	1	2
27	0.11	0.05	2	2	1	2
28	0.12	0.05	2	2	1	2
29	0.13	0.05	2	2	1	2.5
30	0.14	0.05	2	2	1	2
31	0.11	0.04	2	2	1	2
32	0.12	0.04	2	2	1	2
33	0.13	0.04	2	2	1	2
34	0.14	0.04	2	2	1	2

*:Front roll was adjusted 40 rpm and back roll was 10 rpm.

4.5.1.3 Production procedure

Production of these 34 batches were conducted by using 17 steps, which were mentioned in Part 4.5.1 in regarding to the changes mentioned in Table 4.37. Model of the used planetary mixer was Teknodinamik which has 2 different speeds (140-280 rpm). This mixer can be seen in Figure 4.43. After mixing the materials in planetary mixer, the mix was fed into the rolls of two-roller mill which was produced by Deniz Makina in 2007 (Figure 4.44).

Figure 4.43: Planetary mixer

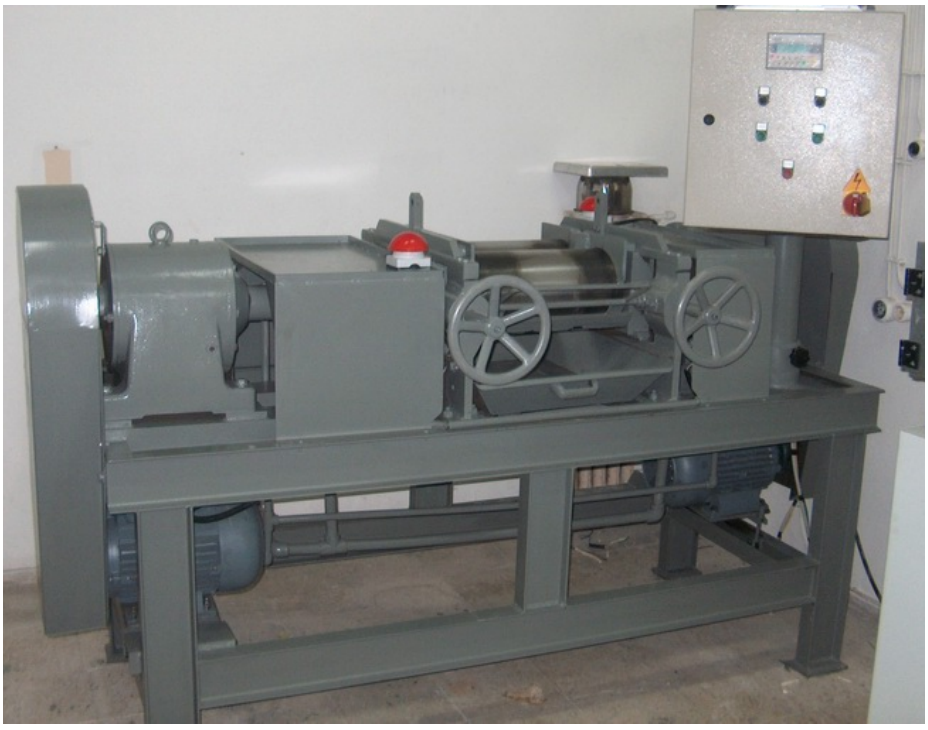


Figure 4.44: Calendering machine with two roller mills

Properties of the roller mills with the comparison of previously used mills at UIUC can be seen in Table 4.38. Maximum rate of shear in different steps of processing on twin-roll mill were also calculated according to equation 3.4 of Part 3.2.1. Table 4.39 summarizes the process conditions of the mills used at UIUC and ITU.

Table 4.38: Properties of the roller mills used in UIUC and ITU

	Diameter of rolls (cm)	**Length of rolls (cm)**	**Min speed (rpm)**	**Max speed (rpm)**
Roller mills of UIUC	15.24	38.1	17.2	34.4
Roller mills of ITU	21.5	42.0	3	40

Table 4.39: Process parameters of the roller mills

	Process Step	**Nip gap (mm)**	**Roll speed front/back (cm/sec)**	**Est. max rate of shear (sec^{-1})**
UIUC	Initial shearing	0.25	18/15	1015
		0.49		518
	High shearing	0.49	28/14	867
	Calendering	1.66	18/15	153
		1.49	15/15	137
ITU	Initial shearing	0.25	28/22.5	1590
		0.50		795
	High shearing	0.50	45/22.5	1365
	Calendering	1.7	28/22.5	199
		1.5	22.5/22.5	203

Four different 100x100x1.9 mm sheets were trimmed with a knife after production. Then these sheets were pressed at 80°C and 5 MPa for 10 minutes between 2 sheets of nylon and steel plates. Nylon sheets were used as a non-stick surface as well as to produce a smooth finish on the MDF sample. Hot press machine (Figure 4.45) has a capacity of 15 tons hydraulic press with 350x400 mm electrically heated platens and automatic temperature, timer and pressure controllers. This machine was produced by Alsa Lab. in 2007.

Figure 4.45: Hot press machine

The specimens with 100x100x1.9 mm sizes were then cured in an oven (Nuve FN model 500, max temp:150 and automatic time and temperature controlled) at 80°C for 24 hours between 2 sheets of nylon and steel plates. Used oven can be seen in Figure 4.46. The aim of covering the specimens with steel plates was to reduce warping of the specimens.

Figure 4.46: Oven used for hot curing

Approximately 20 circular specimens were drilled from each of these sheets with a core machine (Promax PM 70281 Power 750 W Chuck 16 mm, 16 speed, 160-3000 rpm.) 24 hours later. Grinding oil was used as a coolant to avoid exposure to water. This machine can be seen in Figure 4.47.

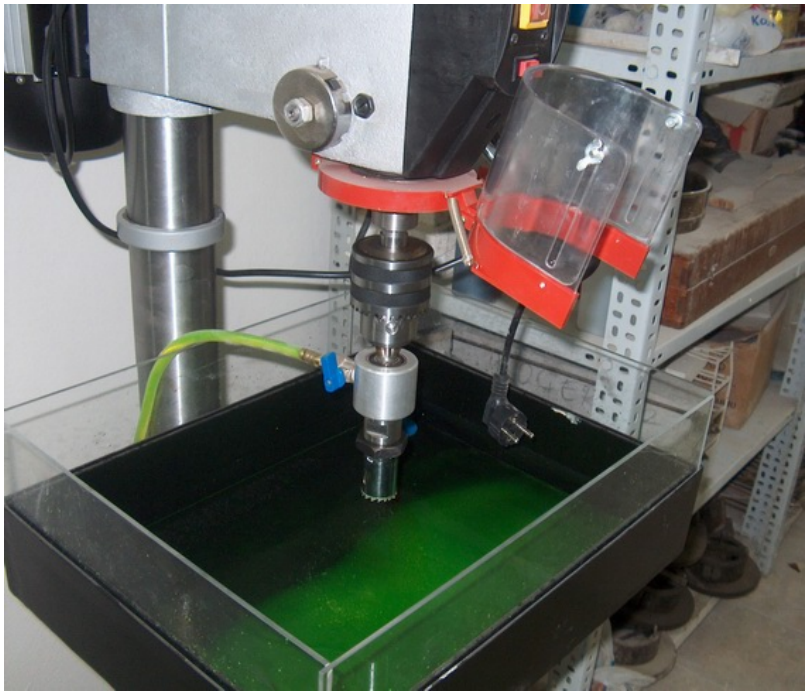


Figure 4.47: Core drilling machine used to prepare circular specimens from MDF sheets

Half of the specimens were stored in water for 6 days while the other half were stored in a desiccator using silica gel as the dessicant. All specimens were taken their containers and subjected to biaxial flexural strength tests 7 and 28 days later after their production.

4.5.1.4 Biaxial flexural strength tests

Biaxial flexural strength tests were carried out on both water stored and dry specimens for 7 and 28 days according to ASTM F-394 (1978-reapproved 1996). An Instron 5500R model universal testing machine was used to test the specimens with a cross-head speed of 0.1 mm/min. Test setup can be seen in Figure 4.48, more information about this test method can be seen in Appendix A, and the test results of each specimen can be found in Appendix J.

Figure 4.48: Biaxial flexural strength test setup

Biaxial flexural strength results for 7 days

Average biaxial flexural strength results ($\overline{S}$) and standard deviations (σ) as well as coefficient of variations (V) for each batch were calculated and given in Table 4.40 for 7 days. Flexural strengths of the specimens stored in dry conditions and their strength loss for 7 days water storage can be seen in Figure 4.49. The highest flexural strengths in dry condition were 156 and 154 for mix numbers 20 and 18, respectively. However, their strength loss was also the highest which were 74 and 72%. Nip gap at the 10^{th} step of production was 1.7 mm in both mixtures.

Table 4.40: 7 days biaxial flexural strength test results of optimization studies

Mixture Code	w/c	p/c	Dry Strength			Wet Strength		
			$\overline{S}$ (MPa)	σ (MPa)	V (%)	$\overline{S}$ (MPa)	σ (MPa)	V (%)
1	0.13	0.05	149	13	9	47	4	8
2	0.13	0.05	143	13	9	43	10	22
3	0.13	0.05	130	26	20	49	8	17
4	0.13	0.05	123	17	14	52	10	20
5	0.13	0.05	122	10	8	46	17	37
6	0.13	0.05	138	5	3	56	11	19
7	0.13	0.05	130	10	7	47	5	10
8	0.13	0.05	108	8	7	54	6	10
9	0.13	0.05	99	10	10	44	10	22
10	0.13	0.05	134	8	6	51	8	16
11	0.13	0.05	120	26	21	50	10	20
12	0.13	0.05	97	23	24	41	8	20
13	0.13	0.05	109	13	12	50	16	32
14	0.13	0.05	115	19	16	55	6	10
15	0.13	0.05	98	12	12	71	10	14
16	0.13	0.05	98	17	17	46	15	31
17	0.13	0.05	132	15	11	63	4	7
18	0.13	0.05	154	17	11	39	10	24
19	0.11	0.07	59	5	9	36	4	12
20	0.12	0.07	156	22	14	43	23	54
21	0.13	0.07	38	7	17	24	13	55
22	0.14	0.07	105	17	16	45	6	13
23	0.11	0.06	111	23	21	54	18	34
24	0.12	0.06	129	10	8	60	7	12
25	0.13	0.06	138	17	12	58	10	17
26	0.14	0.06	109	19	18	58	5	8
27	0.11	0.05	112	21	19	53	25	47
28	0.12	0.05	124	16	13	48	18	36
29	0.13	0.05	114	14	13	82	15	18
30	0.14	0.05	120	13	11	48	11	22
31	0.11	0.04	-	-	-	-	-	-
32	0.12	0.04	93	16	17	50	9	18
33	0.13	0.04	113	7	6	49	8	17
34	0.14	0.04	122	11	9	62	6	10

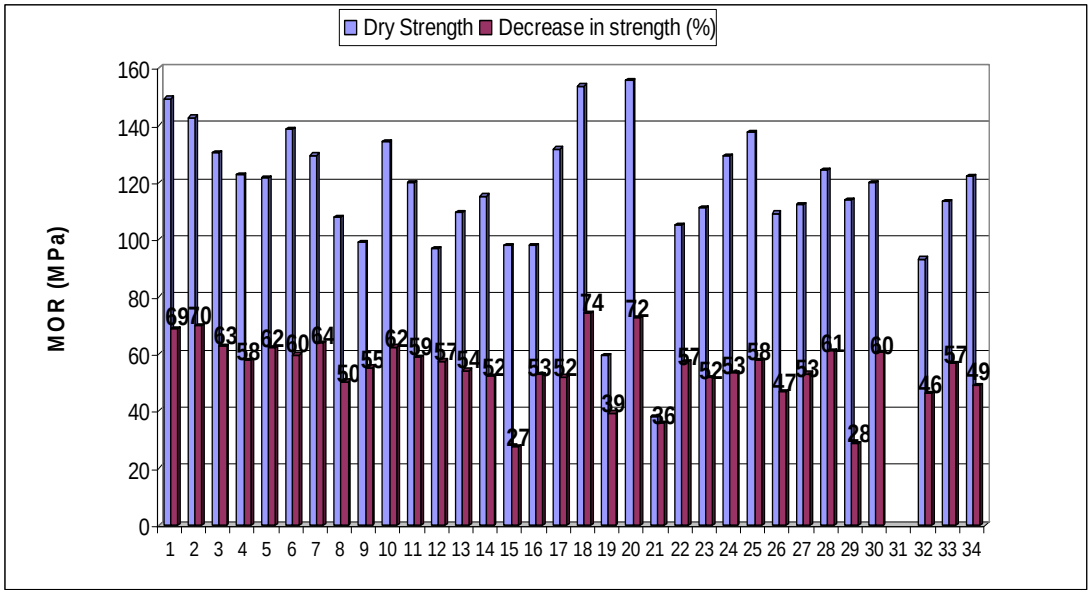


Figure 4.49: Dry biaxial flexural strengths and decrease in strengths for 7 days

According to our observations, it was easier to process when the material passed through rolls 2 times at 6th and 7th steps. Biaxial flexural strength results of mix numbers 4,8 and 10 also supported our belief.

Our other observation was about the nip gap distance. When the nip gap distance was increased from 2 to 3 mm gradually, strengths were tending to decrease on mix numbers 13, 14, 15 and 16. Dry flexural strengths of mixture numbers 15 and 16 was 98 MPa and this was the second lowest result after mixture number 12 which has 97 MPa.

On the comparison of mix numbers between 19 and 34 in which only w/c and p/c ratios were changed and process parameters were kept constant. Mix numbers 19 and 21 were produced without glycerol and they were not taken into consideration.

The highest flexural strengths were 156 (w/c:0.12, p/c:0.07), 138 (w/c:0.13, p/c:0.06) and 129 MPa (w/c:0.12, p/c:0.06) for mix numbers 20, 25 and 24, respectively. The lowest flexural strengths were 93 (w/c:0.12, p/c:0.04), 105 (w/c:0.14, p/c:0.07) and 109 MPa(w/c:0.14, p/c:0.06) for mix numbers 32, 22 and 26, respectively.

Decreases in strengths in wet storage ranged between 27% (mix no. 15) and 74% (mix no. 18). There were no systematic relations with these parameters (different p/c and w/c ratios) and strength loss.

Optimum w/c can be accepted as 0.12 or 0.13 and optimum p/c can be accepted as 0.06 or 0.07 in comparison of these results. However, these results are higly depended on the used polymer and its hydrolysis degree.

Biaxial flexural strength results for 28 days

Average biaxial flexural strength results ($\overline{S}$) and standard deviations (σ) as well as coefficient of variations (V) for each batch were calculated and given in Table 4.41 for 28 days.

Table 4.41: 28 days biaxial flexural strength test results of optimization studies

Mixture Code	w/c	p/c	Dry Strength			Wet Strength		
			$\overline{S}$ (MPa)	σ (MPa)	V (%)	$\overline{S}$ (MPa)	σ (MPa)	V (%)
1	0.13	0.05	146	23	16	55	6	11
2	0.13	0.05	141	13	9	59	10	17
3	0.13	0.05	-	-	-	-	-	-
4	0.13	0.05	-	-	-	-	-	-
5	0.13	0.05	146	28	19	39	13	34
6	0.13	0.05	153	16	10	34	10	30
7	0.13	0.05	134	12	9	32	1	3
8	0.13	0.05	129	15	12	49	8	17
9	0.13	0.05	133	27	20	25	8	32
10	0.13	0.05	156	31	20	27	26	96
11	0.13	0.05	136	6	4	41	9	22
12	0.13	0.05	113	30	27	28	5	17
13	0.13	0.05	82	14	16	42	10	23
14	0.13	0.05	106	18	17	44	6	14
15	0.13	0.05	104	20	20	50	2	3
16	0.13	0.05	97	10	10	32	2	6
17	0.13	0.05	139	20	14	46	4	9
18	0.13	0.05	102	19	19	33	2	7
19	0.11	0.07	59	5	9	36	5	14
20	0.12	0.07	132	15	12	37	3	9
21	0.13	0.07	38	7	17	24	3	12
22	0.14	0.07	107	26	24	30	2	7
23	0.11	0.06	120	13	11	53	7	14
24	0.12	0.06	143	20	14	49	48	99
25	0.13	0.06	129	23	18	43	27	62
26	0.14	0.06	120	18	15	41	32	79
27	0.11	0.05	102	25	24	44	36	83
28	0.12	0.05	120	10	8	46	35	75
29	0.13	0.05	109	32	29	46	6	13
30	0.14	0.05	106	22	21	31	27	87
31	0.11	0.04	-	-	-	-	-	-
32	0.12	0.04	96	16	17	39	15	40
33	0.13	0.04	108	5	4	41	32	77
34	0.14	0.04	117	11	9	51	24	47

Flexural strengths of the specimens stored in dry conditions and their strength loss for 28 days water storage can be seen in Figure 4.50. The highest flexural strengths in dry condition were 156, 153 and 146 MPa for mix numbers 10, 6, 5 and 1 respectively. Nip gap at the 10th step of production was 2 mm in 3 of these mixtures.

The lowest flexural strengths were 82, 97 and 104 MPa for mix numbers 13, 16 and 15, respectively. However, the result of mixture 13 was considerably lower compared to it's 7 days result and it was not taken into consideration. Nip gap at 10th step was 2.75 mm and 3 mm for the mix numbers 15 and 16.

Decreases in strengths in wet storage ranged between 49% (mix no. 13) and 83% (mix no. 10). There was no systematic relation with these parameters and strength loss.

On the comparison of mix numbers between 19 and 34 in which only w/c and p/c ratios were changed and process parameters were kept constant. The highest flexural strengths were 143 (w/c:0.12, p/c:0.06), 132 (w/c:0.12, p/c:0.07) and 129 MPa (w/c:0.13, p/c:0.06). The lowest flexural strengths were 96 (w/c:0.12, p/c:0.04), 102 (w/c:0.11, p/c:0.05), 106 MPa (w/c:0.14, p/c:0.05). Mix numbers 19 and 21 were produced without glycerol and they were not taken into consideration. Optimum w/c can be accepted as 0.12 or 0.13 and optimum p/c can be accepted as 0.06 or 0.07. These results confirmed our conclusion which we made before according to 7 days results.

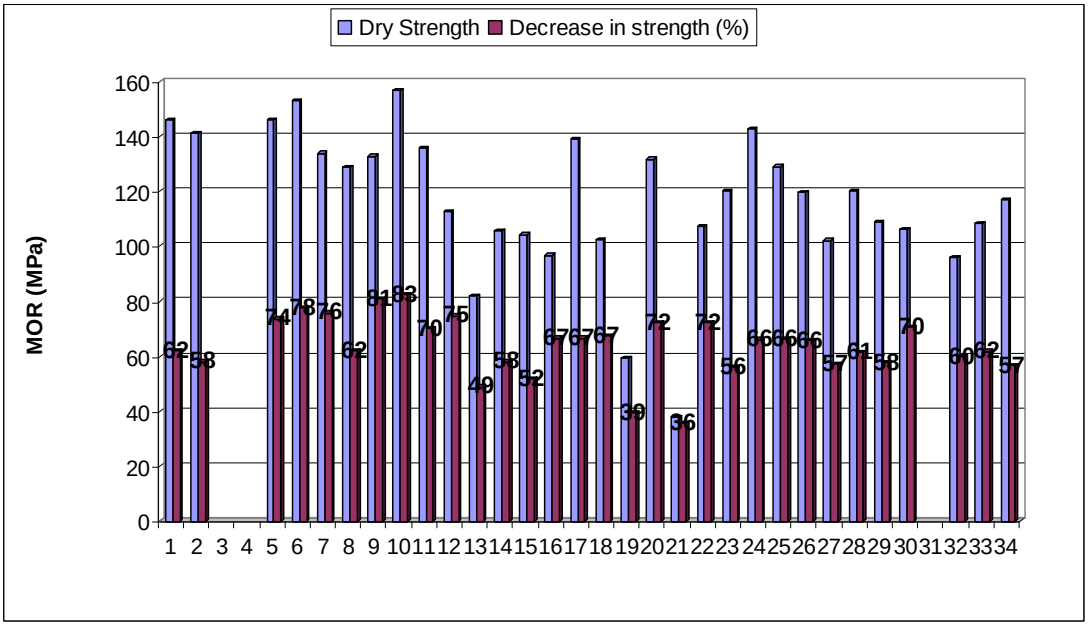


Figure 4.50:28 days dry biaxial flexural strengths and decrease in strengths

4.5.1.5 Interpretation of test results

Nip gap, number of passing during intial shearing, number of high shear and speed of rolls were changed in batch numbers 1-18 while p/c was 0.05 and w/c was 0.13. Therefore these 18 batches should be compared with each other. Our conclusions abouts these batches are:

- Repeating the 6^{th} and 7^{th} steps 2 times caused better strength results and production was also easier in this way.
- Increasing the nip gap more than 2 mm at the 10^{th} production step was decreased the strength results.
- Decreasing the speed of back roll from 20 rpm to 10 rpm during high shear process was increased the strength result for 7 days but decreased for 28 days considerably.
- Repeating the 9^{th} step (high shear process) 2 times increased the strength slightly.

Following batches (between 19 and 34) were produced in order to find better p/c and w/c ratios for processing. The w/c was changed between 0.11 and 0.14 while p/c was changed between 0.04 and 0.07. Using 0.12 or 0.13 w/c ratio and 0.06 or 0.07 p/c ratio gave the highest flexural strength according to both 7 and 28 days results. All these results and our observations during production were taken into consideration and a new optimized procedure determined for the production of MDF cements.

4.5.1.6 Optimized production procedure for the calendaring machine

This new production procedure was accepted as standard production procedure acccording to the previous results and experiences and this procedure will be used in the following productions.

Preliminary steps:

1. Platens of pres were pre-heated to 80°C.

Planetary mixer:

2. Cement and PVA were dry blended for one minute prior to the addition of mixture of water and glycerol at a speed rate 1.

3. After adding of water, the batch was mixed for one minutes at medium speed (speed rate 1) until a damp, granular mix was formed.
4. The cohesive solid material was scraped off the bowl in 30 seconds and then blended for an additional 1 minute at a speed rate 2.

Two roll mill:

5. Nip gap was set to 0.25 mm and side guards were aparted to 25 cm.
6. Two roller mills were turned on and speeds of the rollers were set to 25:20 (front:back)
7. Powder was passed through 2 times
8. Nip gap was increased to 0.50 mm folding and passing through 2 times again.
9. Speeds of the roller mills were changed to 40:20 and shear mixed for 15 seconds.
10. Sheet was rotated 90^0 and shear mixed for another 15 seconds.
11. Speeds of the rollers were changed to 25:20 and nip gap was increased to 1.70 mm.
12. Sheet was passed through 10 times folding triple and rotating 90° each time.
13. Side guards were moved out, nip gap was closed to 1.50 mm, speeds of the rollers were changed to 20:20.
14. Batch was passed through twice without folding or rotating.
15. Sheet was cut into desired dimensions.

Hot press:

16. Cement sheets were placed between 2 pieces of Mylar (0.25-mm thick) and then were placed in hot press for 10 minutes at 5 MPa.
17. Sheets were taken out of hot press and Mylar were pulled off of cement.
18. The stiffened composite sheet were cured between two new sheets of mylar and two plates of steel for 24 hours at 80°C in a forced-air oven.

4.5.2 Production of MDF Cements with Epoxy Resin

4.5.2.1 Materials

PVA copolymer with the commercial name of Gohsenol KH17 and produced by Nippon Gohsei was used for the production of MDF cements. Properties of the used PVA can be seen in Table 4.42.

Table 4.42: Properties of the used PVA

Product Name	Hydrolysis degree (mole%)	Viscosity4% (mPa-s)	pH	Feature
KH17	79.4	35.2	5.7	Partially Hydrolyzed

An alumina cement which is known with the commercial name of Isidac 40 (Al_2O_3: 40%) was used for the productions. Typical properties of this cement can be seen in Table 4.35. Small amount of glycerol, which is 10% by weight of PVA, was also used for plasticizing. In addition to these main ingredients, an epoxy resin was also added in different amounts. It is believed that epoxy resin will interact with PVA and decrease its water absorption.

D.E.R. 351 liquid epoxy resin is a low viscosity epoxy resin combining the performance properties of standard Bisphenol-A epoxy resin with the low viscosity of Bisphenol-F epoxy resin. Application areas are including solvent free coatings, tank- and pipe-linings, concrete reinforcements but also floorings, adhesives, electrical insulation and filament winding. Properties of epoxy resin can be seen in Table 4.43.

Table 4.43: Typical properties of diglycidyl ether of bisphenol A-F epoxy resin

Density (g/cm^3)	EEW (g/eq)	Viscosity (mPa.s at 25 °C)	Appareance
1.1-1.18	169-181	4500-6500	Between liquid and half-solid

4.5.2.2 Mixtures

First of all, five different batches were produced by using epoxy resin and coded according to their epoxy resin content. Main difference on the composition of these batches was the amount of epoxy resin. Epoxy resin was used between 0 and 10% of cement weight in these batches. The w/c was kept constant at 0.11 and p/c was 0.07 in all productions. Glycerol was used at 10% of PVA by weight. These mixtures can be seen in Table 4.44. Subsequently, an additional five samples were produced and subjected to biaxial flexural strength tests to determine if the promising results were reproducible.

Table 4.44: Compositions of the batches produced with epoxy resin

Mix no.	epoxy/ cement (%)	Cement (g)	Water (g)	PVA (g)	Glycerol (g)	Epoxy (g)
B0	0	300	33	21	2.1	0
B1	1	300	33	21	2.1	3
B3	3	300	33	21	2.1	9
B5	5	300	33	21	2.1	15
B10	10	300	33	21	2.1	30

4.5.2.3 Production procedure

Optimized production method (Part 4.5.1.6) was followed for the production of specimens. More information about production procedures can be found in Part 4.5.1.3. Twenty circular specimens were drilled from the sheets of each batch with diamond core. Subsequently, the specimens were separated into two groups and half of the specimens were stored in water while the other half were stored in a desiccator using silica gel as desiccant for 7 and 28 days in order to see the effect of water on flexural strength.

4.5.2.4 Biaxial flexural strength tests

Biaxial flexural strength tests were carried out on both water stored and dry specimens for 7 days according to ASTM F-394 (1978-reapproved 1996). An Instron 5500R model universal testing machine was used to test the specimens with a cross-head speed of 0.1 mm/min. More information about this test can be seen in Appendix A. Average values of biaxial flexural strength results ($\overline{S}$) and standard deviations (σ) as well as coefficient of variations (V) for each batch were calculated and given in Table 4.45 and results of each specimen can be seen in Appendix K. Dry strength means the strength of specimens stored in desiccator while the wet strength is the strength of specimens stored in water.

Table 4.45: 7 days biaxial flexural strength test results of MDF specimens produced with epoxy resin

Mixture Code	Dry Strength			Wet Strength		
	$\overline{S}$ (MPa)	σ (MPa)	V (%)	$\overline{S}$ (MPa)	Σ (MPa)	V (%)
B0	135	7	5	80	25	32
B1	113	18	16	100	33	33
B3	111	11	10	79	20	26
B5	103	16	16	80	27	34
B10	65	7	10	62	6	10

Dry strengths and decreases in strengths in wet storage can be seen in Figure 4.51, there was a constant decrease with the increasing amount of epoxy resin. However, the decrease in strength was very low especially with the addition of 1 and 10% epoxy resin. These were very promising results for preventing the water sensitivity of MDF cements. However, coefficient of variations were high especially in water stored samples. In order to find if theses results were reproducible, additional 5 samples were produced and subjected to biaxial flexural strength tests.

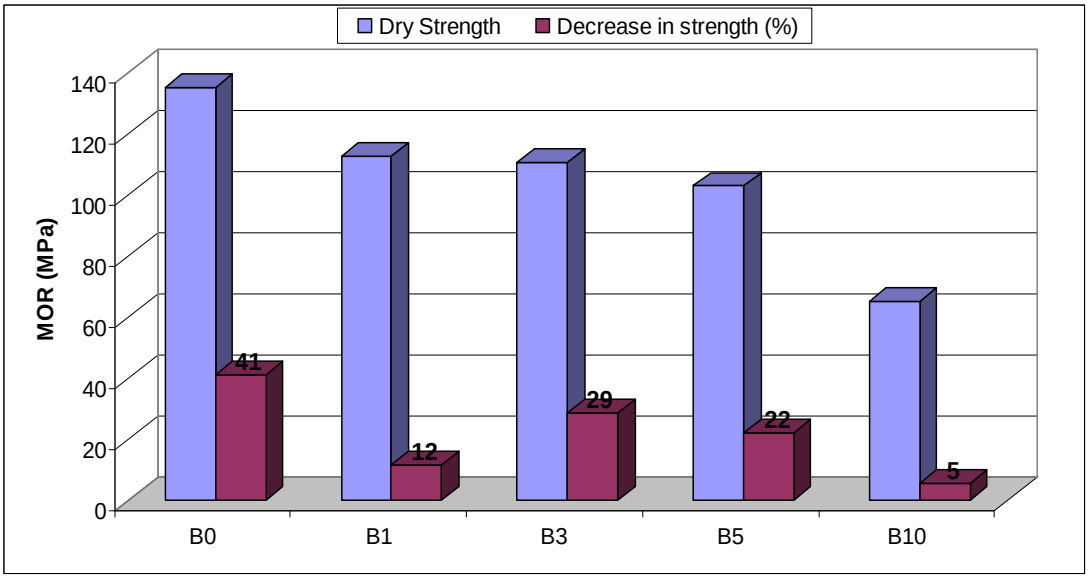


Figure 4.51:7 days dry strengths and decrease in strengths of MDF specimens produced with epoxy resin

4.5.2.5 Additional biaxial flexural strength tests for reproducibility

Additional 5 different batches were prepared with the same epoxy resin. Epoxy/cement was changed between 0.5 and 4%. The w/c was kept constant at 0.11 and p/c was 0.07 in all productions and glycerol was used 10% of PVA by weight similar to previous productions. Composition of these batches can be seen in Table 4.46.

Table 4.46: Compositions of the new batches produced with epoxy resin

Mix no.	epoxy/ cement (%)	Cement (g)	Water (g)	PVA (g)	Glycerol (g)	Epoxy (g)
B0.5	0.5	300	33	21	2.1	1.5
B1	1	300	33	21	2.1	3
B1.5	1.5	300	33	21	2.1	4.5
B2	2	300	33	21	2.1	6
B4	4	300	33	21	2.1	12

Same production procedures were followed with the previous batches and biaxial flexural strength tests were conducted similarly. Test results are given in Table 4.47 and the results of each specimen can be seen in Appendix K.

Table 4.47: 7 days biaxial flexural strength test results of MDF specimens produced with epoxy resin for reproducibility

Mixture Code	Dry Strength			Wet Strength		
	$\bar{S}$ (MPa)	σ (MPa)	V (%)	$\bar{S}$ (MPa)	σ (MPa)	V (%)
B05	115	17	14	80	8	10
B1	125	9	7	63	17	28
B1,5	125	16	12	74	33	45
B2	121	24	20	68	15	23
B4	96	8	9	49	19	40

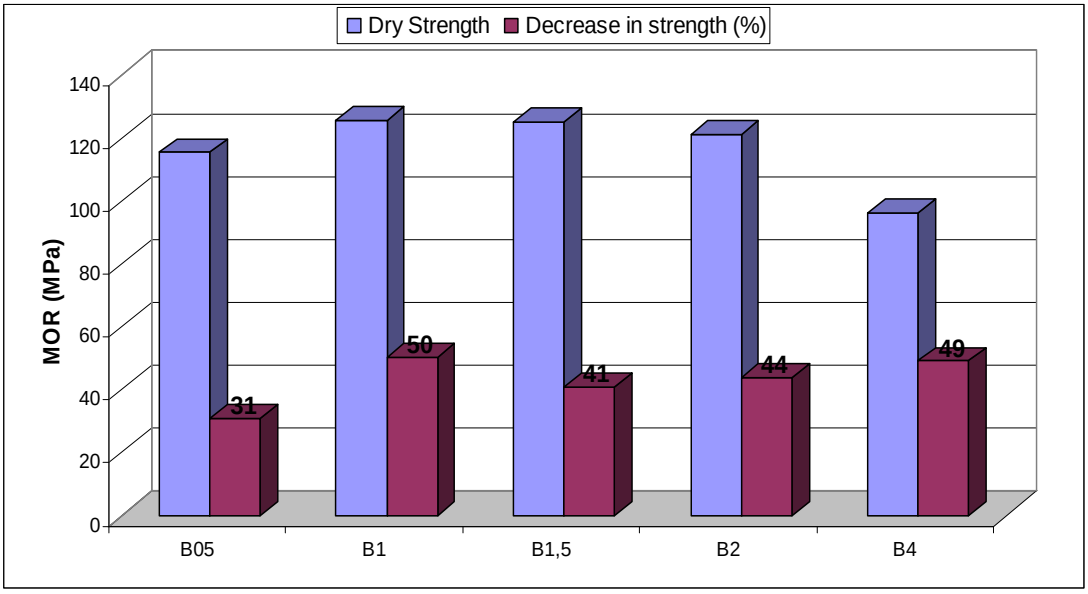


Figure 4.52:7 days dry strengths and decrease in strengths of MDF specimens produced with epoxy resin for reproducibility

Figure 4.52 shows dry strengths and decreases in strengths in water storage. Dry strengths were approximately same for close w/c ratios. However, the decrease in strength was min 31% for batch no B05 and 50% for batch no B1. These were higher compared to our previous promising results and it could not confirmed that used epoxy resin decreasing the water sensitivity of MDF cements.

4.5.3 Production of MDF Cements with Nanosilica

4.5.3.1 Materials

PVA copolymer with the commercial name of Gohsenol KH17 and produced by Nippon Gohsei was used for the production of MDF cements. Properties of the used PVA can be seen in Table 4.42. An alumina cement which is known with the commercial name of Isidac 40 (Al_2O_3: 40%) was used for the productions. Typical properties of this cement can be seen in Table 4.35. Small amount of glycerol, which is 10% by weight of PVA, was also used for plasticizing. In addition to these main ingredients, nanosilica was also added in different amounts.

Used nanosilica is known with the commercial name of Cembinder® 8 and produced by Eka Chemicals. CEMBINDER® 8 is based on amorphous silicondioxide. The product is defined as a polydispersion of silicon dioxide particles in water. The active compound is an inorganic, highly reactive, water based colloidal silica. Typical properties of CEMBINDER® 8 can be seen in Table 4.48.

Table 4.48: Typical properties of CEMBINDER® 8

Density, g/cm^3 (20°C)	pH	Viscosity (cP)	Solid content (wt%)	Appearance
1.4	9.5	<15	50	Opalescent, no smell or taste

The addition rate of CEMBINDER® 8 is adviced as 0.1 to 1.5% by weight of cement by the producer. Normally the addition is around 0.5% in a concrete with a w/c of 0.3 - 0.5. Due to specific conditions and demands other addition rates may be appropriate.

4.5.3.2 Mixtures

First of all, nine different batches were prepared. Main difference on the composition of these batches was the amount of nanosilica. Nanosilica was used between 0 and 4% of cement weight in these batches. The w/c was kept constant at 0.11 and p/c was 0.07 in all productions. Glycerol was used at 10% of PVA by weight. These mixtures can be seen in Table 4.49. Nanosilica was in 50% water solution. Therefore, water content was decreased in order to keep to w/c constant in all batches. Subsequently,

an additional seven samples were produced and subjected to biaxial flexural strength tests to determine if the promising results were reproducible.

Table 4.49: Compositions of the batches produced with nanosilica

Mix no.	Nanosilica/ cement (%)	Cement (g)	Water (g)	PVA (g)	Glycerol (g)	Nanosilica (g)
N0	0	300	33	21	2.1	0
N005	0.5	300	33	21	2.1	1.5
N010	1	300	33	21	2.1	3
N015	1.5	300	33	21	2.1	4.5
N020	2	300	33	21	2.1	6
N025	2.5	300	33	21	2.1	7.5
N030	3	300	33	21	2.1	9
N035	3.5	300	33	21	2.1	10.5
N040	4	300	33	21	2.1	12

4.5.3.3 Production procedure

Optimized production method (Part 4.5.1.6) was followed for the production of specimens. More information about production can be found in Part 4.5.1.3. Twenty circular specimens were drilled from the sheets of each batch with diamond core. Subsequently, the specimens were seperated two groups and half of the specimens were stored in water while the other half were stored in a desiccator using silica gel as desiccant for 7 and 28 days in order to see the effect of water on flexural strength.

4.5.3.4 Biaxial flexural strength tests

Biaxial flexural strength tests were carried out on both water stored and dry specimens for 7 days according to ASTM F-394 (1978-reapproved 1996). An Instron 5500R model universal testing machine was used to test the specimens with a cross-head speed of 0.1 mm/min. More information about this test can be seen in Appendix A. Average values of biaxial flexural strength results ($\overline{S}$) and standard deviations (σ) as well as coefficient of variations (V) for each batch were calculated and given in Table 4.50 and results of each specimen can be seen in Appendix L. Dry strength means the strength of specimens stored in desiccator while the wet strength is the strength of specimens stored in water.

Table 4.50: 7 days biaxial flexural strength test results of MDF specimens produced with nanosilica

Mixture Code	Dry Strength			Wet Strength		
	$\overline{S}$ (MPa)	σ (MPa)	V (%)	$\overline{S}$ (MPa)	σ (MPa)	V (%)
N0	134	20	15	81	30	37
N005	115	16	14	67	30	45
N010	139	8	6	110	52	47
N015	127	11	9	100	31	31
N020	122	23	19	110	32	29
N025	140	19	13	97	30	31
N030	142	15	11	90	20	23
N035	116	19	16	71	15	21
N040	117	17	15	98	20	20

Dry strengths and decreases in strengths in water storage can be seen in Figure 4.53. The decrease in strength was only 10% when 2% (by cement weight) nanosilica was used. Results were also promising when 1%, 1.5% and 4% nanosilica were used. An additional seven samples were produced and subjected to biaxial flexural strength tests to determine if the promising results of Table 4.50 was reproducible.

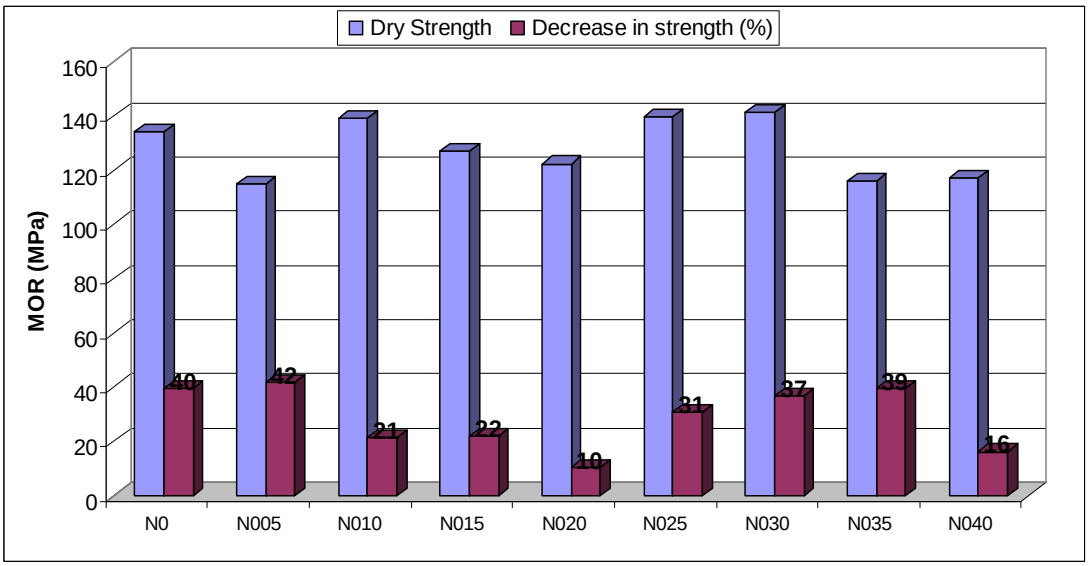


Figure 4.53:7 days dry strengths and decrease in strengths of MDF specimens produced with nanosilica

4.5.3.5 Additional biaxial flexural strength tests for reproducibility

Additional 7 different batches were prepared with nanosilica. Nanosilica/cement was changed between 1 and 3% since the promising results were obtained with the addition of nanosilica around 1-2% in the previous part. Compositions of these batches can be seen in Table 4.51.

Table 4.51: Compositions of the new batches produced with nanosilica

Mix no.	Nanosilica/ cement (%)	Cement (g)	Water (g)	PVA (g)	Glycerol (g)	Nanosilica (g)
N1	1	300	33	21	2.1	3.0
N1.5	1.5	300	33	21	2.1	4.5
N1.8	1.8	300	33	21	2.1	5.4
N2	2.0	300	33	21	2.1	6.0
N2.2	2.2	300	33	21	2.1	6.6
N2.5	2.5	300	33	21	2.1	7.5
N3	3.0	300	33	21	2.1	9.0

Same production procedures were followed with the previous batches and biaxial flexural strength tests were conducted similarly. Test results are given in Table 4.52 and the results of each specimen can be seen in Appendix L.

Table 4.52: 7 days biaxial flexural strength test results of MDF specimens produced with nanosilica for reproducibility

Mixture Code	Dry Strength			Wet Strength		
	$\overline{S}$ (MPa)	σ (MPa)	V (%)	$\overline{S}$ (MPa)	σ (MPa)	V (%)
N1	153	13	8	90	14	15
N1.5	148	11	7	89	35	39
N1.8	128	11	8	71	32	45
N2	128	19	15	80	28	35
N2.2	128	20	16	51	16	32
N2.5	136	23	17	97	35	37
N3	125	14	11	96	10	11

Dry strengths and decrease in strengths can be seen in Figure 4.54. The most promising result was obtained on the batch N3. The decrease in strength was 23% with the addition of 3% nanosilica on this batch. Although these results are not as good as the previous results, using nanosilica as an additive for the production of MDF cements slightly decreased the water sensitivity of this material.

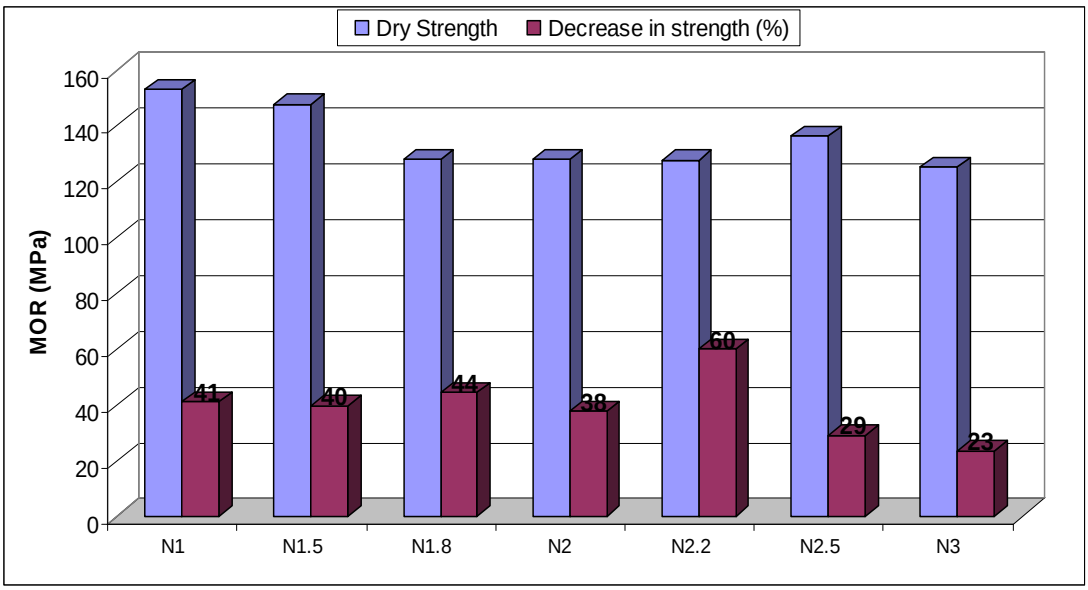


Figure 4.54:7 days dry strengths and decrease in strengths of MDF specimens produced with nanosilica for reproducubility

4.5.4 Production of MDF Cements with Self-reticulated Vinylic Adhesive

4.5.4.1 Materials

PVA copolymer with the commercial name of Gohsenol KH17 and produced by Nippon Gohsei was used for the production of MDF cements. Properties of the used PVA can be seen in Table 4.42. An alumina cement which is known with the commercial name of Isidac 40 (Al_2O_3)was used for the productions. Typical properties of this cement can be seen in Table 4.35. Small amount of glycerol, which is 10% by weight of PVA, was also used for plasticizing. In addition to these main ingredients, Steron K3 which is a self-reticulated vinylic adhesive was used in different amounts. Density of adhesive was 1.069 g/cm^3, viscosity was 5720 cp and solid content was 52.52%.

4.5.4.2 Mixtures

Seven different batches were prepared. Main difference on the composition of these batches was the amount of viniylic adhesive. It was used between 0 and 10% of cement by weight in these batches. The w/c was kept constant at 0.11 and p/c was 0.07 in all productions. Glycerol was used 10% of PVA by weight. These mixtures can be seen in Table 4.53. Adhesive was approximately 50% in water solution. Therefore, water content was decreased in order to keep to w/c constant in all

batches. Subsequently, an additional seven samples were produced and subjected to biaxial flexural strength tests to determine if the promising results was reproducible.

Table 4.53: Compositions of the batches produced with vinylic adhesive

Mix no.	adhesive/ cement (%)	Cement (g)	Water (g)	PVA (g)	Glycerol (g)	Adhesive (g)
SK0	0	300	33	21	2.1	0
SK0.1	0.1	300	33	21	2.1	0.3
SK0.5	0.5	300	33	21	2.1	1.5
SK1	1	300	33	21	2.1	3
SK3	3	300	33	21	2.1	9
SK5	5	300	33	21	2.1	15
SK10	10	300	33	21	2.1	30

4.5.4.3 Production procedure

Optimized production method (Part 4.5.1.6) was followed for the production of specimens. More information about production can be find in Part 4.5.1.3. Twenty circular specimens were drilled from the sheets of each batch with diamond core. Subsequently, the specimens were seperated two groups and half of the specimens were stored in water while the other half were stored in a desiccator using silica gel as desiccant for 7 days in order to see the effect of water on flexural strength.

4.5.4.4 Biaxial flexural strength tests

Biaxial flexural strength tests were carried out on both water stored and dry specimens for 7 days according to ASTM F-394 (1978-reapproved 1996). An Instron 5500R model universal testing machine was used to test the specimens with a cross-head speed of 0.1 mm/min. More information about this test can be seen in Appendix A. Average values of biaxial flexural strength results ($\overline{S}$) and standard deviations (σ) as well as coefficient of variations (V) for each batch were calculated and given in Table 4.54 and results of each specimen can be seen in Appendix M. Dry strength means the strength of specimens stored in desiccator while the wet strength is the strength of specimens stored in water.

Table 4.54: 7 days biaxial flexural strength test results produced with vinylic adhesive

Mixture Code	Dry Strength			Wet Strength		
	$\bar{S}$ (MPa)	σ (MPa)	V (%)	$\bar{S}$ (MPa)	σ (MPa)	V (%)
SK0	120	12	10	60	14	24
SK0.1	116	17	14	84	16	19
SK0.5	114	14	12	54	13	24
SK1	134	14	10	74	14	19
SK3	120	6	5	41	11	26
SK5	115	9	8	30	11	37
SK10	137	10	8	29	4	13

Dry strengths and decrease in strengths can be seen in Figure 4.55. As can be sen from the figure, dry strength did not change significantly with the addition of vinylic adhesive, even the highest flexural strengths obtained with the addition of 1% (SK1) and 10% (SK10) vinylic adhesive. Decreases in strength ranged from 28% to 79% and decrease was increasing with the increase in vinylic adhesive content.

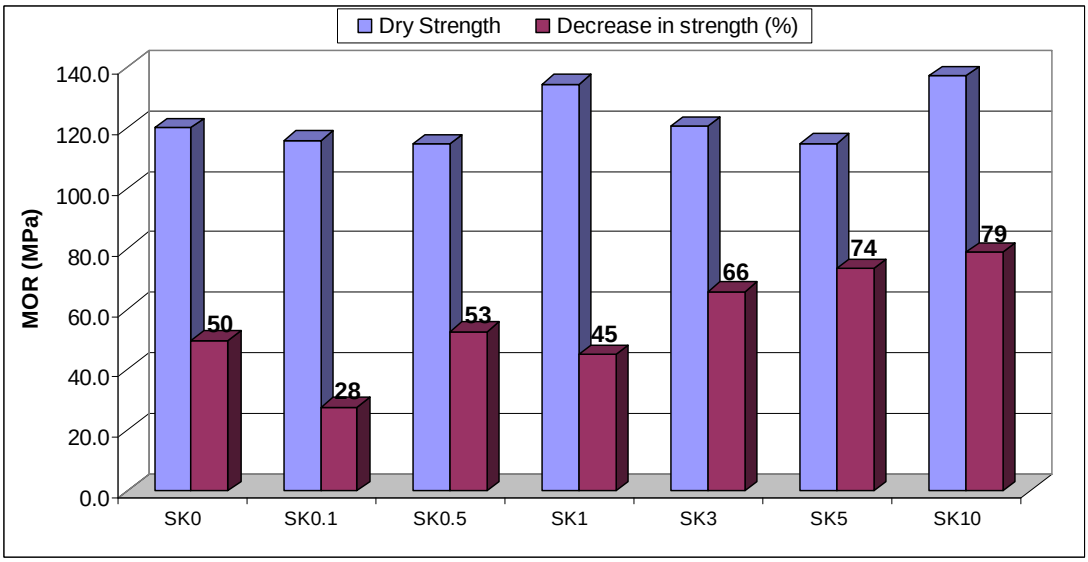


Figure 4.55:7 days dry strengths and decrease in strengths of MDF specimens produced with vinylic adhesive

5 GENERAL CONCLUSIONS

The main objective of this study is to investigate the water sensitivity of MDF cements. These investigations were completed in 5 different parts and their results and conclusions were already given in involved parts. In this chapter, general results of these studies are summarized. Some future work topics that can be investigated to better understand the subject are also pointed out.

5.1 Investigation of Ingredients and Process Parameters

Production method of MDF cements were first described by Birchall et al. (1983) and developed by other researchers. Since the properties of used machines and the used materials can be changed, a new optimized method was necessary before starting productions. Therefore, first studies were conducted for determining a constant production procedure and production processes were optimized both UIUC and ITU with respect to used machines. In addition, effect of different parameters such as ingredients and changing the process parameters of the production of MDF cements were also investigated in this part. Optimized production procedure for the machines of UIUC can be seen in Part 4.1.5 and for the machines of ITU can be seen in Part 4.5.1.6.

5.2 Effect of Hydrolysis Degree of PVA on the Properties of MDF Cements

Hydolysis degrees of PVA are highly affecting the properties such as moisture absorption and solubility. Therefore, the effects of hydrolysis degrees of PVAs, which were changing between 79.4 and 99.1 mole%, on the properties of MDF cement were investigated.

- Partially hydrolyzed PVAs showed higher flexural strengths and lower strength decrease in water storage with comparing to acetoacetylated PVAs.

- A modified production procedure was also developed in which PVAs were dissolved in water under high temperature previous before production of MDF. PVA copolymers were heated up to 90°C during preparation of these solutions in order to

increase the solubility. MDF cements were successfully produced with that procedure and smoother surfaces were obtained. However, effect of this method on the mechanical properties and durability of MDF cements was insignificant.

- MDF cements were not able to be produced with fully hydrolyzed or carboxylated PVAs even with the modified procedure.

- An amine type crosslinking agent (adipyly hydrazide) was used for the production of MDF cements with acetoacetylated PVAs. However, its effect was insignificant on the properties of MDF cements.

- Different MDF cements were swelling in different degress when they were exposed to water. This swelling behavior is causing serious problems in microstructure and sharp decreases are observed in flexural strengths. Weight and thickness changes of MDF cements were also investigated in this part and a pretty good relationship between strength loss and weight change were found. Wieght increases ranged between 1.9 and 8.5% with respect to used PVA.

- Depending on the obtained results in this study, the most suitable PVA was determined as partially hydrolyzed PVAs which has 79.4 mole% hydrolysis degree and the worst PVA was acetoacetylated one, which has 99.1% hydrolysis degree.

- The best and the worst MDFs were prepared and stored in water to find the leaching elements in water for 1 week and the water was analysed. Dissolved Al was lower and the C and Ca were higher when the best MDF composition was used comparing with the worst one. This can be because of higher crosslinking ratio of Al ions with PVA molecules in the best MDF composition, which makes the cement more stable.

- MAS-NMR tests were also conducted for MDF cements, cement paste and MDF without cement. CA and CA_2 were the initial phases of used alumina cements and interestingly no hydration products were observed for cement paste which makes the comparison difficult. Only observed hydration product of MDF cement was $Al(OH)_3$.

5.3 Effect of Alumina Content in Calcium Aluminate Cements (CAC) on the Properties of MDF Cements

- MDF cements were produced with 4 different types of alumina cements which differ in their Al_2O_3 content. The Al_2O_3 contents were 41, 49, 70 and 79%.

- The most suitable alumina cement type was determined as the one which has 70% Al_2O_3 content in comparing both the highest flexural strengths and lower strength decrease after water storage. However, 41 and 49% Al_2O_3 contents were also very suitable for the production of MDF cements and their results were only slightly lower than the first one.

- MDF cements produced with the cement which has 79% Al_2O_3 content showed totally different properties comparing with other cement types. It was the most unsuitable alumina cement type for the production. It may be because of smaller particle size or higher Al content of this cement. Al content probably was higher than the necessary amount for crosslinking the polymer chains.

- Optimum Al_2O_3 content can be expected between 49 and 70%. It would be interesting to search whether there exists an optimum Al_2O_3 content around 60%.

- X-Ray diffraction analyses were also conducted for 4 alumina cement types and 4 MDF cement types. There were no hydration products for MDF cements. This was an interesting result because, hydration products of alumina cements were C_3AH_6, C_2AH_8, CAH_{10} and AH_3 and expected hydration product was especially stable and hexagonal C_3AH_6 at that temperature. This result was also observed by other reserchers. It can be true that XRD method may not be appropiate for MDF cements.

- Morphological investigation of the best (MDF 71) and the worst (MDF 80) MDF cements were conducted by using AFM and contact angle methods. The obtained data are in good correlation with biaxial flexural strenght results for MDF cements in dry conditions. A clear dependence of mechanical resistance and MDF cements morphology could be established: the lower roughness, porosity and hydrophilicity, the higher flexural strength.

- Thermogravimetric Analysis (TA) and Differential Thermal Analysis (DTA) tests were conducted for 4 types of alumina cements, 4 types of MDF cements, a cement

paste and a PVA. TA results are in good correlation with biaxial flexural strength tests.

5.4 Investigation of Different Parameters on the Production of MDF Cements

- MDF cements were produced without cement. $NaAlO_2$ and Al_2O_3 were used instead of alumina cement. Production was successful but its strength was very low. Weight increase of these composites ranged between 18-25% which is very high in comparing with the results of original MDF cements.

- MDF cement production without using any polymer by using the same processes was unsuccessful.

- MDF cements were also produced with the additon of poly(amide-epichlorohydrin) resin. This resin were added to the mixture 20% of PVA weight. However, effect of this resin on flexural strength and water resistivity was insignificant.

- Last of all, MDF cements were produced by using poly(ethylene oxide) polymer instead of poly(vinyl alcohol-co-vinyl acetate) copolymer. Composites were produced by using same processes, however, their strength was very low comparing to original MDF cements.

5.5 Effet of Using Different Additives for the Production of MDF Cements

- Using different additives on the properties of MDF cements were investigated in this part. Used additives were an epoxy resin, nanosilica and a vinylic adhesive. All additives were helpful for increasing the properties of MDF cements when they are used in different amounts depending on the used additive. The most promising results were obtained with nanosilica.

- Increasing the ratio of epoxy resin up to 10% decreased dry flexural strengths. However, decrease in strengths under exposure of water were very low when used epoxy was 1 and 10% of cement weight.

- Increasing the ratio of nanosilica up to 4% did not decrease the dry flexural strengths. In addition, decreases in strengths under water exposure were only 10-20% when nanosilica was used in 1, 1.5, 2 and 4% by cement weight.

- Increasing the ratio of vinylic adhesive up to 10% did not decrease the dry flexural strengths. However, decrease in strengths were very high in water storage. Using 0.1% vinylic adhesive decreased the strength loss from 50% to 28%.

- Some additional tests were also conducted for confirming the promising results of especially nanosilica and epoxy resin. Although the results were lower compared to the previous tests, these additives were helpful on increasing the properties of MDF cements. More detailed study should be conducted for determining the most suitable amounts and production methods when these additives were used.

As a conclusion, it can be said that these composites are produced by using inorganic cement and an organic polymer and their properties make these composites very important with respect to mechanical behavior, especially flexural strengths, However, their water sensitivity prevents the usage of them in industry before solving this problem. It is necessary to know both materials in more detail in order to produce advanced materials. Polymer technology is growing very fast and our age sometimes called as polymer age as well as space and electronic age. Civil engineers don't have enough knowledge about polymers and polymer experts don't have enough knowledge about inorganic part. New advanced materials which are expected from industry can be produced with a multidisciplinary work of both experts in the future.

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APPENDIX A

Information about Biaxial Flexural Strength Test

Biaxial flexural strengths of the specimens were measured according to ASTM F 394 – 78 (Reapproved 1996) in this thesis. An Instron model universal testing machine equipped with a 1 kN load cell was used to test the specimens with a cross-head speed of 0.5 mm/min at University of Illinois at Urbana-Champaign (UIUC). Similarly, an Instron model universal testing machine equipped with a 10 kN load cell was used to test the specimens with a cross-head speed of 0.5 mm/min at Istanbul Technical University (ITU).

- The formula for calculating flexural strength is:

$$S = -0.2387P(X - Y)/d^2$$

where;

$X=(1+\upsilon)\ln(B/c)^2+[(1-\upsilon)/2](B/c)^2$

$Y=(1+\upsilon)[1+\ln(A/c)^2]+(1-\upsilon)(A/c)^2$

S:Biaxial Flexural Strength or MOR, MPa.

P:Failure Load, N.

υ:Poisson Ratio.

d:Thickness of the specimen, mm.

A:Radius of support circle, mm.

B:Radius of loaded area or ram tip, mm.

c:Radius of specimen, mm.

Note: Poisson ratio was accepted as 0.23 for all specimens.

- $\overline{s} = (S_1+S_2+S_3+\ldots\ldots S_n)/n$

where;

$\overline{S}$ = Mean value of biaxial flexure strength for the lot (psi or MPa),

S_1, S_2, etc., are individual specimen strength values (psi or MPa), and

n=number of specimens

- Estimated standard deviation are calculated σ of *S* for the test lot from the equation:

$\sigma = ([S_1 - \bar{s}]^2 + [S_2 - \bar{s}]^2 + [S_3 - \bar{s}]^2 + \ldots\ldots\ldots + [S_n - \bar{s}]^2)/(n-1))^{0.5}$

- Coefficient of variation *V* of *S* are calculated for the test lot from the equation:

$V,\% = (100\sigma/\bar{s})$

Figure A.1: Biaxial flexural strength test apparatus

APPENDIX B

Biaxial Flexural Strength Test Results for Pre-Tests

20 pretest results are given in this appendix.

A:Radius of support circle was 12.5 mm in all tests calculated in this appendix

B:Radius of ram tip was 0.8 mm in all tests calculated in this appendix.

υ:Poisson Ratio was taken as 0.23 in all tests calculated in this appendix.

Table B.1: Biaxial flexural strength test results for pre-tests

Mixture no.	Condition	Specimen number	Thickness (mm)	Diameter (mm)	Radius (mm)	P(N)	S (MPa)
1	Dry	1	1.7	31.7	15.85	319.4	**223.5**
		2	1.7	31.7	15.85	219.7	**153.7**
		3	1.7	31.2	15.60	336.3	**235.7**
		4	1.7	30.7	15.35	256.4	**180.0**
		5	1.7	31.7	15.85	299.8	**209.7**
		6	1.7	31.7	15.85	340.9	**238.5**
		7	1.7	31.5	15.75	311.7	**218.2**
	Wet	8	2.0	31.7	15.85	252.1	**127.4**
		9	2.1	31.2	15.60	306.0	**140.5**
		10	2.1	31.7	15.85	294.3	**134.9**
		11	2.0	31.5	15.75	317.2	**160.4**
		12	2.0	31.6	15.80	0.0	**0.0**
		13	2.2	31.5	15.75	373.2	**156.0**
		14	1.9	31.5	15.75	332.2	**186.2**
2	Dry	1	1.7	31.4	15.70	324.3	**227.1**
		2	1.7	31.4	15.70	331.6	**232.2**
		3	1.7	31.4	15.70	298.1	**208.8**
		4	1.7	31.5	15.75	358.5	**251.0**
		5	1.7	31.5	15.75	318.7	**223.1**
	Wet	6	2.2	32.0	16.00	235.1	**98.1**
		7	2.2	32.0	16.00	234.0	**97.6**
		8	2.0	31.3	15.65	316.7	**160.3**
		9	1.9	31.7	15.85	306.6	**171.7**
		10	2.0	31.9	15.95	325.4	**164.4**

Table B.1: (continued) Biaxial flexural strength test results for pre-tests

Mixture no.	Condition	Specimen number	Thickness (mm)	Diameter (mm)	Radius (mm)	P(N)	S (MPa)
3	Dry	1	1.7	31.7	15.85	264.1	**184.8**
		2	1.7	31.3	15.65	306.6	**214.8**
		3	1.7	31.6	15.80	362.4	**253.6**
		4	1.7	31.6	15.80	340.8	**238.5**
		5	1.7	31.5	15.75	302.3	**211.6**
		6	1.7	31.5	15.75	308.3	**215.8**
		7	1.7	31.7	15.85	288.7	**202.0**
	Wet	8	2.0	31.7	15.85	257.7	**130.3**
		9	2.0	31.9	15.95	230.8	**116.6**
		10	2.0	31.8	15.90	242.8	**122.7**
		11	2.0	31.8	15.90	290.2	**146.6**
		12	2.0	31.8	15.90	214.9	**108.6**
		13	2.0	31.7	15.85	277.2	**140.1**
		14	1.9	31.7	15.85	239.7	**134.2**
4	Dry	1	1.7	31.4	15.70	241.9	**169.4**
		2	1.7	31.4	15.70	264.2	**185.0**
		3	1.7	31.8	15.90	283.0	**197.9**
		4	1.7	31.5	15.75	304.4	**213.1**
		5	1.7	31.6	15.80	298.3	**208.8**
	Wet	6	1.8	31.6	15.80	277.1	**173.0**
		7	1.8	31.7	15.85	-	**-**
		8	1.8	31.7	15.85	263.3	**164.3**
		9	1.8	31.8	15.90	279.9	**174.6**
		10	1.8	31.7	15.85	264.0	**164.7**
		11	1.8	31.6	15.80	313.7	**195.8**
5	Dry	1	1.8	30.0	15.00	254.0	**159.5***
		2	1.8	31.5	15.75	276.3	**172.5**
		3	1.8	31.5	15.75	270.7	**169.0**
		4	1.8	31.9	15.95	264.6	**165.0**
		5	1.9	31.5	15.75	259.8	**145.6**
		6	1.8	31.4	15.70	239.8	**149.8**
		7	1.8	31.5	15.75	262.6	**164.0**
		8	1.9	31.4	15.70	307.1	**172.2**
		9	1.9	31.6	15.80	274.4	**153.7**
	Wet	10	1.9	31.6	15.80	253.4	**142.0**
		11	2.0	31.7	15.85	206.5	**104.4**
		12	1.9	31.7	15.85	274.7	**153.8**
		13	2.0	31.6	15.80	92.9	**46.9**
		14	2.0	31.8	15.90	140.6	**71.0***
		15	1.9	31.8	15.90	135.7	**76.0***
		16	1.9	31.8	15.90	197.5	**110.6**

Table B.1: (continued) Biaxial flexural strength test results for pre-tests

Mixture no.	Condition	Specimen number	Thickness (mm)	Diameter (mm)	Radius (mm)	P(N)	S (MPa)
6	Dry	1	1.6	31.9	15.95	280.3	**221.2**
		2	1.7	31.0	15.50	264.0	**185.2***
		3	1.7	31.5	15.75	300.2	**210.2**
		4	1.7	31.5	15.75	238.3	**166.8**
		5	1.7	31.5	15.75	252.7	**176.9**
	Wet	6	1.9	31.7	15.85	207.4	**116.2**
		7	2.0	31.8	15.90	170.8	**86.3**
		8	2.0	32.0	16.00	150.4	**75.9**
		9	2.0	31.8	15.90	151.9	**76.8**
		10	2.0	31.7	15.85	116.4	**58.8**
7	Dry	1	1.7	31.6	15.80	365.7	**255.9**
		2	1.7	31.6	15.80	338.4	**236.8**
		3	1.7	31.7	15.85	361.0	**252.6**
		4	1.7	31.7	15.85	359.7	**251.6**
		5	1.8	31.9	15.95	352.3	**219.7**
	Wet	6	2.2	32.1	16.05	304.6	**127.1**
		7	2.1	31.9	15.95	268.5	**123.0**
		8	2.1	31.7	15.85	255.1	**117.0**
		9	2.2	31.7	15.85	200.0	**83.5**
		10	2.2	31.8	15.90	-	**-**
8	Dry	1	1.6	31.8	15.90	225.5	**178.0**
		2	1.6	31.7	15.85	273.8	**216.2**
		3	1.6	31.6	15.80	459.5	**363.0****
		4	1.6	31.7	15.85	257.7	**203.5**
		5	1.7	31.8	15.90	268.5	**187.8**
	Wet	6	1.9	31.8	15.90	282.0	**157.9**
		7	2.0	31.9	15.95	116.2	**58.7***
		8	1.9	31.8	15.90	232.9	**130.4**
		9	2.0	31.8	15.90	135.9	**68.7***
		10	2.0	31.6	15.80	222.0	**112.3**
9	Dry	1	1.7	31.6	15.80	268.9	**188.2**
		2	1.6	31.8	15.90	237.5	**187.5**
		3	1.7	31.7	15.85	255.8	**179.0**
		4	1.7	31.9	15.95	281.0	**196.4**
		5	1.7	31.6	15.80	245.9	**172.1**
	Wet	6	2.1	32.0	16.00	289.2	**132.4**
		7	2.0	31.7	15.85	218.5	**110.4**
		8	2.0	32.1	16.05	215.2	**108.6**
		9	2.1	32.0	16.00	211.2	**96.7**
		10	2.0	31.9	15.95	258.5	**130.6**

Table B.1: (continued) Biaxial flexural strength test results for pre-tests

Mixture no.	Condition	Specimen number	Thickness (mm)	Diameter (mm)	Radius (mm)	P(N)	S (MPa)
10	Dry	1	2.0	31.7	15.85	442.6	**223.7**
		2	2.0	31.5	15.75	468.1	**236.8**
		3	2.0	31.5	15.75	399.6	**202.1**
		4	2.0	31.8	15.90	411.9	**208.1**
		5	2.0	32.0	16.00	457.5	**231.0**
	Wet	6	2.7	31.9	15.95	340.7	**94.4**
		7	2.6	31.9	15.95	331.2	**99.0**
		8	2.5	31.9	15.95	232.0	**75.0**
		9	2.6	31.9	15.95	346.3	**103.5**
		10	2.7	31.9	15.95	349.5	**96.9**
11	Dry	1	2.0	31.7	15.85	233.9	**118.2**
		2	2.0	31.5	15.75	230.4	**116.5**
		3	2.0	31.6	15.80	239.9	**121.3**
		4	2.0	31.6	15.80	218.5	**110.5**
		5	2.0	31.8	15.90	206.8	**104.5**
	Wet	6	2.7	31.9	15.95	51.4	**14.2***
		7	2.5	32.1	16.05	59.8	**19.3**
		8	2.3	32.4	16.20	47.3	**18.0***
		9	2.4	32.0	16.00	46.1	**16.2***
		10	2.3	32.0	16.00	71.2	**27.2**
12	Dry	1	1.7	31.4	15.70	327.1	**229.1**
		2	1.8	31.5	15.75	336.5	**210.1**
		3	1.7	31.8	15.90	293.1	**205.0**
		4	1.7	31.4	15.70	318.8	**223.3**
		5	1.7	31.4	15.70	372.2	**260.7**
	Wet	6	2.3	31.8	15.90	129.8	**49.6**
		7	2.0	32.0	16.00	152.3	**76.9**
		8	2.0	31.7	15.85	218.3	**110.3**
		9	2.0	32.1	16.05	136.9	**69.1**
		10	2.0	32.1	16.05	129.8	**65.5**
13	Dry	1	1.7	31.6	15.80	241.1	**168.7**
		2	1.7	31.5	15.75	308.4	**215.9**
		3	1.7	31.6	15.80	283.3	**198.3**
		4	1.7	31.7	15.85	239.9	**167.8**
		5	1.7	31.5	15.75	277.4	**194.2**
	Wet	6	1.9	31.8	15.90	191.6	**107.3**
		7	2.0	31.7	15.85	241.2	**121.9**
		8	1.9	31.7	15.85	231.5	**129.7**
		9	1.9	31.7	15.85	204.2	**114.4**
		10	1.9	31.9	15.95	197.6	**110.6**

Table B.1: (continued) Biaxial flexural strength test results for pre-tests

Mixture no.	Condition	Specimen number	Thickness (mm)	Diameter (mm)	Radius (mm)	P(N)	S (MPa)
14	Dry	1	1.7	31.5	15.75	280.1	**196.1**
		2	1.7	31.7	15.85	263.6	**184.4**
		3	1.7	31.6	15.80	282.7	**197.8**
		4	1.7	31.6	15.80	297.2	**208.0**
		5	1.7	31.6	15.80	297.3	**208.1**
	Wet	6	1.9	31.5	15.75	196.6	**110.2**
		7	1.9	31.5	15.75	212.9	**119.3**
		8	2.0	31.8	15.90	119.7	**60.5**
		9	2.0	31.4	15.70	196.8	**99.6**
		10	2.0	31.5	15.75	146.4	**74.1**
15	Dry	1	1.7	31.6	15.80	302.0	**211.4**
		2	1.7	31.5	15.75	261.9	**183.4**
		3	1.7	31.4	15.70	313.5	**219.6**
		4	1.7	31.4	15.70	-	**-**
		5	1.7	31.5	15.75	315.1	**220.6**
	Wet	6	2.0	32.0	16.00	194.7	**98.3**
		7	2.0	31.6	15.80	124.1	**62.7**
		8	1.9	31.5	15.75	250.8	**140.6**
		9	1.9	31.7	15.85	238.8	**133.7**
		10	1.9	31.5	15.75	307.5	**172.3**
16	Dry	1	1.7	31.5	15.75	301.1	**210.8**
		2	1.7	31.5	15.75	306.4	**214.5**
		3	1.7	31.5	15.75	290.8	**203.6**
		4	1.7	31.5	15.75	325.4	**227.8**
		5	1.7	31.5	15.75	346.5	**242.6**
	Wet	6	1.9	31.6	15.80	257.5	**144.3**
		7	2.0	31.7	15.85	287.7	**145.4**
		8	2.0	31.7	15.85	262.9	**132.9**
		9	2.0	31.5	15.75	197.4	**99.8**
		10	1.8	31.6	15.80	255.6	**159.6**
17	Dry	1	1.7	31.5	15.75	167.7	**117.4**
		2	1.7	31.5	15.75	169.2	**118.5**
		3	1.7	31.4	15.70	218.8	**153.2**
		4	1.7	31.5	15.75	163.3	**114.3**
		5	1.7	31.5	15.75	202.1	**141.5**
	Wet	6	2.0	31.7	15.85	87.4	**44.2**
		7	1.8	31.7	15.85	137.1	**85.6**
		8	1.9	31.7	15.85	102.3	**57.3**
		9	1.9	31.6	15.80	141.6	**79.3**
		10	1.9	31.8	15.90	127.7	**71.5**

Table B.1: (continued) Biaxial flexural strength test results for pre-tests

Mixture no.	Condition	Specimen number	Thickness (mm)	Diameter (mm)	Radius (mm)	P(N)	S (MPa)
18	Dry	1	1.5	31.6	15.80	210.2	**189.0**
		2	1.6	31.7	15.85	289.2	**228.4**
		3	1.5	31.5	15.75	242.0	**217.6**
		4	1.6	31.4	15.70	232.5	**183.8**
	Wet	5	1.8	31.5	15.75	206.2	**128.8**
		6	1.9	31.8	15.90	134.3	**75.2**
		7	1.7	31.7	15.85	223.6	**156.4**
		8	1.9	31.9	15.95	246.9	**138.2**
19	Dry	1	2.0	31.7	15.85	16.2	**8.2**
	Wet	2	2.7	31.7	15.85	78.8	**21.9**
20	Dry	1	1.8	31.5	15.75	245.0	**153.0**
		2	1.7	31.5	15.75	266.1	**186.3**
		3	1.8	31.5	15.75	242.7	**151.6**
		4	1.7	31.5	15.75	253.3	**177.3**
		5	1.7	31.5	15.75	324.8	**227.4**
	Wet	6	2.0	31.6	15.80	210.9	**106.6**
		7	1.9	31.6	15.80	200.5	**112.3**
		8	1.9	31.5	15.75	235.1	**131.8**
		9	2.0	31.5	15.75	289.2	**146.3**
		10	1.9	31.8	15.90	163.9	**91.8**

* These specimen were damaged/deformed before the experiment therefore the test results of these specimen are not taken into consideration during the calculations.

** This result is not taken into consideration due to extraordinary standard deviation.

APPENDIX C

Table C.1: 7 days biaxial flexural strength test results for MDF cements prepared with different PVAs

Mixture no.	Condition	Specimen number	Thickness (mm)	Diameter (mm)	Radius (mm)	P(N)	S (MPa)
1	Dry	1	1.7	31.7	15.85	316.3	**221.3**
		2	1.8	31.5	15.75	265.0	**165.5**
		3	1.7	31.6	15.80	307.4	**215.1**
		4	1.7	31.7	15.85	236.2	**165.2**
		5	1.7	31.5	15.75	327.6	**229.4**
	Wet	6	1.7	31.8	15.90	235.4	**164.6**
		7	1.9	31.9	15.95	106.5	**59.6**
		8	1.9	31.7	15.85	120.6	**67.5**
		9	1.9	31.7	15.85	184.0	**103.1**
		10	1.9	31.7	15.85	267.2	**149.6**
2	Dry	1	1.6	31.6	15.80	260.1	**205.5**
		2	1.6	31.6	15.80	276.1	**218.1**
		3	1.6	31.6	15.80	264.1	**208.7**
		4	1.6	31.6	15.80	232.3	**183.5**
		5	1.6	31.5	15.75	233.7	**184.7**
		6	1.6	31.5	15.75	226.5	**179.0**
	Wet	7	1.7	31.6	15.80	134.0	**93.8**
		8	1.7	31.6	15.80	107.5	**75.2**
		9	1.7	31.6	15.80	134.0	**93.8**
		10	1.7	31.7	15.85	134.4	**94.0**
		11	1.7	31.7	15.85	171.3	**119.8**
		12	1.7	31.7	15.85	141.6	**99.1**
3	Dry	1	1.8	31.6	15.80	323.4	**201.9**
		2	1.9	31.6	15.80	235.7	**132.1**
	Wet	3	1.9	31.9	15.95	111.5	**62.4**
		4	1.8	31.8	15.90	107.4	**67.0**
4	Dry	1	1.7	31.6	15.80	248.0	**173.6**
		2	1.7	31.6	15.80	239.0	**167.3**
		3	1.7	31.6	15.80	271.0	**189.7**
	Wet	4	1.7	31.6	15.80	150.3	**105.2**
		5	1.7	31.6	15.80	68.4	**47.8**
		6	1.7	31.7	15.85	-	**-**
5	Dry	1	1.7	31.5	15.75	169.8	**118.9**
		2	1.7	31.5	15.75	164.9	**115.4**
		3	1.6	31.6	15.80	159.0	**125.6**
	Wet	4	1.7	31.7	15.85	64.3	**44.9**
		5	1.7	31.7	15.85	67.6	**47.3**

Table C.1: (continued) 7 days biaxial flexural strength test results for MDF cements prepared with different PVAs

Mixture no.	Condition	Specimen number	Thickness (mm)	Diameter (mm)	Radius (mm)	P(N)	S (MPa)
6	Dry	1	1.6	31.6	15.80	153.2	**121.0**
		2	1.6	31.5	15.75	101.2	**80.0**
		3	1.5	31.5	15.75	174.1	**156.6**
	Wet	4	1.5	31.8	15.90	40.9	**36.7**
		5	1.6	31.7	15.85	37.2	**29.3**
7	Dry	1	1.7	31.6	15.80	253.8	**177.6**
		2	1.7	31.6	15.80	229.4	**160.5**
		3	1.7	31.6	15.80	218.2	**152.7**
		4	1.7	31.6	15.80	261.4	**182.9**
	Wet	5	1.7	31.9	15.95	92.7	**64.8**
		6	1.8	31.7	15.85	69.4	**43.3**
		7	1.7	31.9	15.95	77.1	**53.9**
9	Dry	1	1.9	31.6	15.80	-	**-**
		2	1.9	31.5	15.75	81.1	**45.4**
		3	1.9	31.4	15.70	65.7	**36.9**
	Wet	4	2.0	31.8	15.90	62.6	**31.7**
		5	2.0	31.8	15.90	80.9	**40.9**
		6	2.0	31.8	15.90	69.5	**35.1**
10	Dry	1	1.8	31.7	15.85	167.5	**104.5**
		2	1.7	31.6	15.80	235.4	**164.7**
		3	1.7	31.7	15.85	137.7	**96.3**
	Wet	4	1.8	31.7	15.85	92.2	**57.5**
		5	1.8	31.8	15.90	95.3	**59.5**
		6	1.8	31.9	15.95	94.9	**59.2**
11	Dry	1	1.8	31.5	15.75	-	**-**
		2	1.8	31.6	15.80	272.1	**169.9**
		3	1.8	31.6	15.80	202.5	**126.4**
		4	1.9	31.6	15.80	229.4	**128.5**
	Wet	5	1.8	31.8	15.90	101.9	**63.6**
		6	1.9	32.0	16.00	118.4	**66.2**
		7	1.9	31.9	15.95	87.4	**48.9**
		8	1.9	31.9	15.95	117.6	**65.8**
12	Dry	1	2.2	31.6	15.80	366.0	**152.9**
		2	2.2	31.6	15.80	333.4	**139.3**
		3	2.2	31.6	15.80	424.5	**177.4**
		4	2.2	31.6	15.80	526.7	**220.1**
	Wet	5	2.2	31.7	15.85	316.3	**132.1**
		6	2.2	31.6	15.80	293.6	**122.7**
		7	2.3	31.6	15.80	248.4	**95.0**
		8	2.2	31.7	15.85	257.7	**107.6**

Table C.1: (continued) 7 days biaxial flexural strength test results for MDF cements prepared with different PVAs

Mixture no.	Condition	Specimen number	Thickness (mm)	Diameter (mm)	Radius (mm)	P(N)	S (MPa)
13	Dry	1	1.7	31.6	15.80	189.9	**132.9**
		2	1.7	31.5	15.75	301.2	**210.9**
		3	1.8	31.5	15.75	222.1	**138.7**
		4	1.8	31.5	15.75	276.3	**172.5**
		5	1.8	31.5	15.75	244.7	**152.8**
		6	1.8	31.5	15.75	255.3	**159.4**
	Wet	7	2.1	31.6	15.80	149.3	**68.5**
		8	2.0	31.7	15.85	152.7	**77.2**
		9	2.0	31.8	15.90	124.5	**62.9**
		10	2.0	31.7	15.85	182.0	**92.0**
		11	2.1	31.9	15.95	108.9	**49.9**
		12	1.9	31.8	15.90	148.5	**83.1**
14	Dry	1	1.8	31.5	15.75	218.9	**136.7**
		2	1.8	31.5	15.75	206.0	**128.6**
		3	1.8	31.5	15.75	206.7	**129.1**
		4	1.8	31.5	15.75	191.2	**119.4**
		5	1.8	31.5	15.75	200.7	**125.3**
	Wet	6	1.9	31.7	15.85	197.2	**110.4**
		7	1.9	31.7	15.85	186.4	**104.4**
		8	1.9	31.7	15.85	185.2	**103.7**
		9	1.8	31.7	15.85	221.7	**138.3**
		10	1.9	31.7	15.85	198.2	**111.0**
15	Dry	1	1.8	31.1	15.55	212.7	**133.0**
		2	1.8	31.5	15.75	259.0	**161.7**
		3	1.8	31.6	15.80	209.2	**130.6**
		4	1.9	31.5	15.75	269.2	**150.9**
	Wet	5	2.1	31.9	15.95	114.2	**52.3**
		6	2.0	31.9	15.95	116.3	**58.7**
		7	2.0	31.9	15.95	104.6	**52.8**
		8	2.0	32.0	16.00	129.8	**65.5**
16	Dry	1	1.9	31.7	15.85	313.5	**175.6**
		2	1.8	31.6	15.80	348.4	**217.5**
		3	1.8	31.6	15.80	282.2	**176.2**
		4	1.9	31.6	15.80	-	**-**
		5	1.9	31.6	15.80	398.9	**223.5**
	Wet	6	1.9	31.9	15.95	146.7	**82.1**
		7	2.1	31.8	15.90	184.9	**84.7**
		8	2.1	32.0	16.00	120.8	**55.3**
		9	2.1	32.0	16.00	101.7	**46.6**
		10	2.1	32.0	16.00	117.1	**53.6**

Table C.1: (continued) 7 days biaxial flexural strength test results for MDF cements prepared with different PVAs

Mixture no.	Condition	Specimen number	Thickness (mm)	Diameter (mm)	Radius (mm)	P(N)	S (MPa)
17	Dry	1	1.7	31.6	15.80	260.1	**182.0**
		2	1.8	31.6	15.80	213.5	**133.3**
		3	1.8	31.6	15.80	271.3	**169.4**
		4	1.8	31.7	15.85	145.6	**90.9**
		5	1.8	31.6	15.80	254.4	**158.8**
	Wet	6	2.0	32.0	16.00	65.8	**33.2**
		7	1.9	32.1	16.05	98.8	**55.3**
		8	1.9	32.0	16.00	79.3	**44.4**
		9	1.8	32.1	16.05	83.6	**52.1**
		10	1.9	31.9	15.95	89.8	**50.2**
18	Dry	1	1.8	31.6	15.80	290.3	**181.2**
		2	1.8	31.5	15.75	241.0	**150.5**
		3	1.8	31.6	15.80	283.2	**176.8**
		4	1.8	31.5	15.75	313.2	**195.6**
		5	1.8	31.5	15.75	292.5	**182.7**
	Wet	6	1.9	32.0	16.00	90.6	**50.7**
		7	1.9	32.0	16.00	97.0	**54.3**
		8	1.9	32.0	16.00	72.3	**40.5**
		9	2.0	32.0	16.00	103.2	**52.1**
19	Dry	1	1.8	31.6	15.80	279.1	**174.2**
		2	1.8	31.6	15.80	311.4	**194.4**
		3	1.8	31.5	15.75	274.8	**171.6**
		4	1.8	31.6	15.80	296.5	**185.1**
	Wet	5	2.0	31.9	15.95	110.3	**55.7**
		6	2.0	31.8	15.90	114.4	**57.8**
		7	1.8	31.9	15.95	91.2	**56.9**
		8	1.8	31.9	15.95	93.8	**58.5**
20	Dry	1	2.0	31.5	15.75	231.8	**117.2**
		2	1.9	31.6	15.80	331.2	**185.6**
		3	1.9	31.5	15.75	283.7	**159.0**
		4	1.9	31.5	15.75	263.4	**147.6**
		5	1.9	31.5	15.75	261.0	**146.3**
	Wet	6	2.0	31.8	15.90	80.7	**40.8**
		7	2.0	31.8	15.90	82.4	**41.6**
		8	2.0	31.8	15.90	97.1	**49.1**
		9	2.0	31.9	15.95	66.2	**33.5**
		10	2.0	31.8	15.90	76.3	**38.5**
21	Dry	1	1.9	31.5	15.75	286.3	**160.5**
		2	1.9	31.5	15.75	294.3	**164.9**
		3	1.9	31.6	15.80	326.7	**183.0**
		4	1.9	31.6	15.80	292.6	**163.9**
		5	1.9	31.6	15.80	318.9	**178.7**
	Wet	6	1.9	32.0	16.00	95.3	**53.3**
		7	2.0	32.0	16.00	92.5	**46.7**
		8	2.0	32.0	16.00	94.2	**47.6**
		9	2.0	32.1	16.05	84.6	**42.7**
		10	2.0	32.1	16.05	86.1	**43.5**

Table C.1: (continued) 7 days biaxial flexural strength test results for MDF cements prepared with different PVAs

Mixture no.	Condition	Specimen Number	Thickness (mm)	Diameter (mm)	Radius (mm)	P(N)	S (MPa)
22	Dry	1	1.9	31.5	15.75	265.5	**148.8**
		2	2.0	31.5	15.75	259.8	**131.4**
		3	1.9	31.5	15.75	268.3	**150.4**
		4	2.0	31.5	15.75	263.2	**133.1**
	Wet	5	2.2	31.9	15.95	85.9	**35.8**
		6	2.1	31.9	15.95	115.0	**52.7**
		7	2.1	31.8	15.90	115.1	**52.8**
		8	2.0	31.9	15.95	122.7	**62.0**
25	Dry	1	1.9	31.5	15.75	85.4	**47.9**
26	Dry	1	1.9	31.5	15.75	282.8	**186.8**
		2	2.0	31.6	15.80	237.9	**-**
		3	2.0	31.6	15.80	261.0	**114.2**
	Wet	4	1.9	31.6	15.80	222.4	**60.0**
		5	1.8	31.6	15.80	140.0	**62.2**
27	Dry	1	1.9	31.6	15.80	154.3	**86.4**
		2	1.9	31.6	15.80	137.3	**76.9**
	Wet	3	1.9	31.9	15.95	122.7	**68.7**
		4	1.8	31.7	15.85	129.4	**80.7**
28	Dry	1	2.0	31.6	15.80	271.0	**137.0**
		2	2.0	31.6	15.80	188.9	**95.5**
		3	2.0	31.6	15.80	226.5	**114.5**
		4	2.0	31.6	15.80	258.6	**130.8**
	Wet	5	2.0	31.9	15.95	82.5	**41.6**
		6	2.0	31.9	15.95	70.0	**35.4**
		7	2.0	31.9	15.95	59.9	**30.3**
		8	2.0	31.9	15.95	65.3	**33.0**
29	Dry	1	2.1	31.5	15.75	243.8	**111.9**
		2	2.1	31.6	15.80	328.5	**150.7**
		3	2.0	31.6	15.80	326.2	**164.9**
		4	2.0	31.7	15.85	271.0	**137.0**
	Wet	5	2.0	31.7	15.85	99.7	**50.4**
		6	2.1	31.7	15.85	103.5	**47.5**
		7	2.0	31.8	15.90	96.9	**49.0**
		8	2.0	31.9	15.95	82.5	**41.7**
30	Dry	1	2.0	31.5	15.75	180.1	**91.1**
		2	2.0	31.5	15.75	128.7	**65.1**
		3	2.0	31.5	15.75	148.1	**74.9**
		4	2.0	31.6	15.80	129.5	**65.5**
	Wet	5	2.2	32.0	16.00	53.8	**22.4**
		6	2.0	32.0	16.00	41.5	**20.9**
		7	2.0	31.9	15.95	49.6	**25.0**
31	Dry	1	2.0	31.6	15.80	246.9	**124.8**
		2	2.0	31.6	15.80	195.2	**98.7**
		3	2.0	31.6	15.80	165.0	**83.4**
		4	2.0	31.6	15.80	199.0	**100.6**
	Wet	5	2.0	31.8	15.90	61.7	**31.2**
		6	2.0	31.8	15.90	34.8	**17.6**
		7	2.1	31.8	15.90	72.0	**33.0**
		8	2.0	31.8	15.90	71.6	**36.2**

Table C.1: (continued) 7 days biaxial flexural strength test results for MDF cements prepared with different PVAs

Mixture no.	Condition	Specimen number	Thickness (mm)	Diameter (mm)	Radius (mm)	P(N)	S (MPa)
33	Dry	1	1.7	31.7	15.85	155.4	**108.7**
		2	1.8	31.8	15.90	136.6	**85.2**
		3	1.8	31.6	15.80	145.5	**90.8**
	Wet	4	1.9	31.9	15.95	24.3	**13.6**
		5	1.9	32.0	16.00	30.7	**17.2**
34	Dry	1	1.7	31.5	15.75	209.5	**146.7**
		2	1.8	31.6	15.80	247.2	**154.3**
		3	1.8	31.5	15.75	234.7	**146.6**
		4	1.7	31.5	15.75	270.0	**189.0**
		5	1.7	31.5	15.75	242.8	**170.0**
	Wet	6	1.8	31.7	15.85	41.6	**26.0**
		7	1.8	31.7	15.85	63.1	**39.3**
		8	1.8	31.7	15.85	49.6	**30.9**
		9	1.9	31.8	15.90	56.8	**31.8**
		10	1.9	31.8	15.90	60.0	**33.6**
35	Dry	1	1.6	31.7	15.85	241.4	**190.7**
		2	1.7	31.6	15.80	250.8	**175.5**
		3	1.7	31.6	15.80	253.6	**177.5**
	Wet	4	1.8	32.0	16.00	107.2	**66.8**
		5	1.8	32.0	16.00	133.4	**83.2**

Table C.2: 28 days biaxial flexural strength test results for MDF cements prepared with different PVAs

Mixture no.	Condition	Specimen number	Thickness (mm)	Diameter (mm)	Radius (mm)	P(N)	S (MPa)
1	Dry	1	1.7	31.5	15.75	356.6	**249.7**
		2	1.7	31.5	15.75	252.7	**176.9**
		3	1.7	31.5	15.75	331.0	**231.7**
		4	1.7	31.5	15.75	246.3	**172.4**
	Wet	5	2.0	31.8	15.90	119.6	**60.4**
		6	2.0	31.8	15.90	127.7	**64.5**
		7	2.0	32.0	16.00	101.8	**51.4**
		8	2.0	31.8	15.90	159.3	**80.5**
2	Dry	1	1.6	31.5	15.75	234.2	**185.1**
		2	1.7	31.6	15.80	285.8	**200.0**
		3	1.7	31.5	15.75	245.3	**171.7**
		4	1.7	31.7	15.85	258.3	**180.7**
		5	1.6	31.6	15.80	247.5	**195.5**
	Wet	6	2.0	32.0	16.00	158.8	**80.2**
		7	2.1	31.9	15.95	153.4	**70.3**
		8	2.1	32.0	16.00	96.7	**44.3**
		9	2.1	32.1	16.05	107.0	**49.0**
		10	2.0	32.0	16.00	92.2	**46.6**
3	Dry	1	1.8	31.5	15.75	267.6	**167.1**
		2	1.8	31.6	15.80	231.6	**144.6**
	Wet	3	2.0	32.0	16.00	111.7	**56.4**
4	Dry	1	1.7	31.6	15.80	204.2	**142.9**
		2	1.7	31.6	15.80	199.7	**139.8**
		3	1.7	31.7	15.85	224.1	**156.8**
	Wet	4	1.7	31.9	15.95	99.3	**69.4**
		5	1.7	31.9	15.95	89.7	**62.7**
		6	1.8	31.9	15.95	97.6	**60.9**
5	Dry	1	1.6	31.5	15.75	181.4	**143.4**
		2	1.6	31.5	15.75	165.4	**130.7**
	Wet	3	1.6	31.6	15.80	80.7	**63.7**
		4	1.7	31.8	15.90	77.8	**54.4**
6	Dry	1	1.6	31.5	15.75	87.2	**68.9**
		2	1.6	31.5	15.75	96.6	**76.4**
	Wet	3	1.7	31.9	15.95	47.4	**33.1**
		4	1.6	31.8	15.90	56.1	**44.3**
7	Dry	1	1.7	31.5	15.75	250.3	**175.2**
		2	1.7	31.6	15.80	223.5	**156.4**
		3	1.7	31.5	15.75	170.1	**119.1**
	Wet	4	1.7	32.0	16.00	94.1	**65.7**
		5	1.8	32.0	16.00	101.8	**63.5**
		6	1.8	32.1	16.05	104.5	**65.1**
10	Dry	1	1.8	31.5	15.75	129.4	**80.8**
		2	1.8	31.5	15.75	183.9	**114.8**
		3	1.7	31.5	15.75	192.3	**134.6**
	Wet	4	2.1	32.0	16.00	126.9	**58.1**
		5	2.1	32.0	16.00	103.3	**47.3**
		6	2.2	32.1	16.05	118.6	**49.5**

Table C.2: (continued) 28 days biaxial flexural strength test results for MDF cements prepared different with PVAs

Mixture no.	Condition	Specimen number	Thickness (mm)	Diameter (mm)	Radius (mm)	P(N)	S (MPa)
11	Dry	1	1.8	31.5	15.75	0.0	**0.0**
		2	1.8	31.5	15.75	223.6	**139.6**
		3	1.8	31.5	15.75	218.8	**136.6**
	Wet	4	2.2	32.2	16.10	138.6	**57.8**
		5	2.2	32.4	16.20	145.8	**60.8**
		6	2.2	32.1	16.05	164.7	**68.7**
12	Dry	1	2.1	31.7	15.85	408.2	**187.1**
		2	2.1	31.5	15.75	425.2	**195.1**
		3	2.0	31.6	15.80	539.7	**272.9**
	Wet	4	2.3	31.9	15.95	176.4	**67.4**
		5	2.3	31.9	15.95	164.7	**62.9**
14	Dry	1	1.7	31.5	15.75	180.1	**126.1**
		2	1.7	31.5	15.75	174.1	**121.9**
		3	1.8	31.5	15.75	213.5	**133.3**
	Wet	4	1.8	31.7	15.85	93.7	**58.5**
		5	1.9	31.7	15.85	83.8	**46.9**
15	Dry	1	1.7	31.4	15.70	203.6	**142.6**
		2	1.8	31.5	15.75	163.0	**101.8**
		3	1.8	31.6	15.80	239.4	**149.4**
	Wet	4	1.9	32.2	16.10	110.2	**61.6**
		5	2.0	32.2	16.10	106.2	**53.6**
16	Dry	1	1.9	31.5	15.75	354.1	**198.5**
		2	1.9	31.5	15.75	358.3	**200.8**
		3	1.9	31.5	15.75	304.0	**170.4**
		4	1.9	31.5	15.75	290.6	**162.9**
	Wet	5	2.3	32.1	16.05	146.8	**56.0**
		6	2.3	32.2	16.10	182.9	**69.8**
		7	2.4	32.1	16.05	170.5	**59.8**
		8	2.4	32.0	16.00	137.3	**48.1**
17	Dry	1	1.9	31.5	15.75	180.3	**101.7**
		2	1.9	31.6	15.80	283.9	**151.3**
		3	1.9	31.5	15.75	215.9	**119.4**
	Wet	4	2.1	31.9	15.95	102.2	**45.0**
		5	2.1	32.2	16.10	94.1	**41.9**
		6	2.1	32.1	16.05	120.9	**55.3**
18	Dry	1	1.7	31.5	15.75	349.9	**245.0**
		2	1.7	31.5	15.75	342.6	**239.9**
		3	1.8	31.5	15.75	361.5	**225.7**
		4	1.8	31.5	15.75	322.8	**201.6**
	Wet	5	1.8	31.9	15.95	81.3	**50.7**
		6	1.8	31.9	15.95	55.7	**34.7**
		7	1.9	32.0	16.00	91.0	**50.9**
		8	1.8	31.9	15.95	73.0	**45.5**

Table C.2: (continued) 28 days biaxial flexural strength test results for MDF cements prepared with different PVAs

Mixture no.	Condition	Specimen number	Thickness (mm)	Diameter (mm)	Radius (mm)	P(N)	S (MPa)
19	Dry	1	1.8	31.6	15.80	303.8	**189.6**
		2	1.7	31.6	15.80	312.7	**218.8**
		3	1.8	31.6	15.80	251.2	**156.8**
		4	1.7	31.6	15.80	302.7	**211.8**
	Wet	5	1.8	32.0	16.00	75.3	**47.0**
		6	1.8	31.6	15.80	55.4	**34.6**
		7	1.8	31.7	15.85	74.8	**46.7**
20	Dry	1	1.9	31.5	15.75	284.7	**159.6**
		2	1.9	31.5	15.75	301.1	**168.8**
	Wet	3	1.9	31.8	15.90	52.3	**29.3**
		4	2.0	31.8	15.90	59.2	**29.9**
21	Dry	1	1.9	31.5	15.75	227.5	**128.3**
		2	1.9	31.6	15.80	290.2	**154.7**
		3	1.9	31.5	15.75	333.8	**184.5**
	Wet	4	2.1	31.9	15.95	121.4	**53.4**
		5	2.1	32.2	16.10	105.7	**47.1**
		6	2.1	32.1	16.05	93.8	**42.9**
22	Dry	1	1.8	31.4	15.70	205.5	**128.4**
		2	1.9	31.6	15.80	308.3	**172.7**
		3	1.9	31.5	15.75	289.2	**162.1**
	Wet	4	2.0	32.0	16.00	67.9	**34.3**
		5	1.8	32.0	16.00	65.6	**40.9**
		6	1.9	32.1	16.05	74.1	**41.4**
27	Dry	1	2.0	31.6	15.80	125.2	**63.3**
		2	1.9	31.6	15.80	124.4	**69.7**
	Wet	3	1.8	31.9	15.95	42.3	**26.4**
28	Dry	1	2.0	31.5	15.75	263.9	**133.5**
		2	2.0	31.6	15.80	256.2	**129.5**
		3	1.9	31.6	15.80	277.5	**155.5**
		4	1.9	31.6	15.80	222.9	**124.9**
	Wet	5	1.9	32.0	16.00	61.4	**34.3**
		6	1.9	32.0	16.00	55.4	**31.0**
		7	1.9	31.9	15.95	60.4	**33.8**
29	Dry	1	1.9	31.6	15.80	284.8	**159.6**
		2	2.0	31.6	15.80	336.4	**170.1**
		3	2.0	31.5	15.75	-	**-**
	Wet	4	2.3	31.9	15.95	136.9	**52.3**
		5	2.3	32.0	16.00	123.8	**47.3**
31	Dry	1	2.1	31.6	15.80	235.5	**108.0**
		2	2.0	31.6	15.80	252.1	**127.5**
		3	1.9	31.6	15.80	209.1	**117.2**
	Wet	4	2.1	31.8	15.90	64.9	**29.7**
		5	2.0	31.9	15.95	48.8	**24.7**
		6	2.0	31.9	15.95	57.4	**29.0**

Table C.2: (continued) 28 days biaxial flexural strength test results for MDF cements prepared with different PVAs

Mixture no.	Condition	Specimen number	Thickness (mm)	Diameter (mm)	Radius (mm)	P(N)	S (MPa)
34	Dry	1	1.7	31.5	15.75	260.2	**182.2**
		2	1.7	31.6	15.80	234.9	**164.4**
		3	1.6	31.6	15.80	216.7	**171.2**
		4	1.7	31.5	15.75	179.7	**125.8**
	Wet	5	1.8	31.8	15.90	69.4	**43.3**
		6	1.8	31.6	15.80	45.8	**28.6**
		7	1.8	31.6	15.80	100.1	**62.5**
35	Dry	1	1.6	31.6	15.80	248.9	**199.1**
		2	1.7	31.6	15.80	278.8	**189.1**
	Wet	3	1.9	32.2	16.10	63.9	**35.3**
		4	1.9	32.2	16.10	66.2	**36.9**

APPENDIX D

Water analysis results of KH 17 and blank water

Client / Project:	Macro Defect Free Cements	WMRC Run# 1106-11
Samples Submitted By:	Ozgur Ekincioglu	Date Samples Completed: 12/04/06
Date Samples Submitted:	16.11.2006	Instrument: Carbon Analyzer, Inductively Coupled Plasma Mass Spectroscopy
Analyst:	M. Wilcoxon and Brent Panno	

Client Sample Number	WMRC # 06-	TOC (ppm)	Al (mg/L)	Ca (mg/L)
KH 17	2673	280	140	360
Blank	2674	1,8	< 0.02	14

Note: Sample 2673 was filtered through a 0.45 μm PTFE membrane prior to analysis for TOC.

QA/QC Report

Client Sample Number	WMRC # 06-	TOC (ppm)	Al (mg/L)	Ca (mg/L)
Sample	2673	267	140	358
Duplicate		284	136	354
RPD (%)		6	3	1
Spike		390	320	570
Recovery (%)		102	93	104
Check Standard (200 ppm)		194	-	-
Check Standard (200 ppm)		191	-	-
RPD (%)		2	-	-

Group Leader: Teresa Chow

To: Ozgur Ekincioglu

Xc: T. Chow, M. Wilcoxon, M. Piwoni

Water analysis results of Z 100

Client / Project:	Macro Defect Free Cements		
Samples Submitted By:	Ozgur Ekincioglu	WMRC Run# 1206-03	
Date Samples Submitted:	27.12.2006	Date Samples Completed:	1/8/06
Analyst:	M. Wilcoxon	Instrument: Carbon Analyzer	

Client Sample Number	WMRC # 06-	TOC (mg/L)	Al (mg/L)	Ca (mg/L)
Z100	2695	190	230	110

QA/QC Report

Client Sample Number	WMRC # 06-	TOC (mg/L)	Al (mg/L)	Ca (mg/L)
Z100	2695	193	230	110
Duplicate		174	230	110
Triplicate		193	NA	NA
RSD (%)		6	0,1	0,1
Spike		322	701	227
Recovery (%)		109	118	99
Check Standard (TOC 200 ppm)		202	NA	5.3
		202	NA	6,2
RPD (%)		0,4	NA	86

NA: Not Applicable

Group Leader: Teresa Chow

To: Ozgur Ekincioglu
Xc: T. Chow, M. Wilcoxon, M. Piwoni

APPENDIX E

Table E.1: 7 days biaxial flexural strength test results for MDF cements prepared with different CACs

Mixture no.	Condition	Specimen number	Thickness (mm)	Diameter (mm)	Radius (mm)	P(N)	S (MPa)
42-1	Dry	1	1.7	31.8	15.90	232.3	**159.8**
		2	1.6	31.7	15.85	246.8	**191.8**
		3	1.7	31.6	15.80	196.8	**131.3**
		4	1.6	31.8	15.90	255.8	**194.8**
	Wet	5	1.8	31.9	15.95	125.9	**83.0**
		6	1.7	31.9	15.95	134.8	**94.2**
		7	1.8	31.9	15.95	133.2	**84.2**
		8	1.8	31.9	15.95	142.8	**87.0**
42-2	Dry	1	1.9	31.6	15.80	309.5	**176.2**
		2	1.9	31.6	15.80	346.1	**200.6**
		3	1.8	31.6	15.80	322.2	**191.0**
		4	1.8	31.6	15.80	322.7	**208.6**
	Wet	5	1.9	31.9	15.95	217.6	**118.8**
		6	1.9	31.9	15.95	235.0	**136.2**
		7	1.8	31.9	15.95	197.3	**118.8**
		8	1.8	32.0	16.00	202.6	**123.0**
42-3	Dry	1	1.8	31.7	15.85	324.2	**199.6**
		2	1.8	31.6	15.80	310.0	**192.0**
		3	1.8	31.6	15.80	366.9	**227.0**
	Wet	4	1.8	32.0	16.00	290.4	**180.6**
		5	1.8	31.7	15.85	319.3	**196.2**
		6	1.8	31.8	15.90	225.5	**147.5**
42-4	Dry	1	1.8	31.7	15.85	282.8	**181.1**
		2	1.8	31.7	15.85	355.6	**232.6**
		3	1.7	31.7	15.85	284.7	**194.3**
		4	1.7	31.6	15.80	323.0	**223.4**
		5	1.8	31.6	15.80	365.2	**228.0**
		6	1.7	31.6	15.80	323.4	**226.3**
		7	1.7	31.7	15.85	360.8	**252.4**
		8	1.8	31.6	15.80	352.3	**219.9**
	Wet	9	1.8	31.7	15.85	294.7	**185.3**
		10	1.7	31.9	15.95	212.0	**146.1**
		11	1.7	31.9	15.95	292.1	**196.1**
		12	1.7	31.8	15.90	226.6	**165.6**
		13	1.8	31.8	15.90	282.8	**176.4**
		14	1.8	31.7	15.85	314.4	**196.2**
		15	1.8	31.9	15.92	280.7	**175.1**
		16	1.8	31.9	15.95	322.6	**201.2**

Table E.1: (continued) 7 days biaxial flexural strength test results for MDF cements prepared with different CACs

Mixture no.	Condition	Specimen number	Thickness (mm)	Diameter (mm)	Radius (mm)	P(N)	S (MPa)
42-5	Dry	1	1.7	31.7	15.85	358.9	**245.0**
		2	1.7	31.7	15.85	342.5	**226.4**
		3	1.7	31.7	15.85	330.5	**231.5**
		4	1.7	31.6	15.80	338.3	**231.6**
		5	1.8	31.7	15.85	370.8	**231.4**
		6	1.8	31.6	15.80	388.6	**242.6**
		7	1.8	31.7	15.85	411.8	**257.0**
		8	1.9	31.7	15.85	351.0	**196.6**
	Wet	9	1.7	31.7	15.85	338.9	**241.6**
		10	1.8	31.7	15.85	313.6	**201.5**
		11	1.8	31.8	15.90	266.3	**166.9**
		12	1.7	31.7	15.85	311.7	**218.1**
		13	1.8	31.8	15.90	297.0	**185.3**
		14	1.9	31.7	15.85	266.3	**149.1**
		15	1.9	31.7	15.85	266.6	**149.3**
		16	1.9	31.8	15.92	213.4	**119.5**
42-6	Dry	1	1.9	31.6	15.80	373.6	**209.3**
		2	1.8	31.6	15.80	372.2	**232.3**
		3	1.9	31.7	15.85	411.2	**230.3**
		4	1.8	31.7	15.85	432.7	**270.0**
	Wet	5	1.9	31.7	15.85	290.3	**162.6**
		6	2.0	31.8	15.90	202.0	**102.1**
		7	2.0	31.7	15.85	218.4	**110.4**
		8	2.0	31.7	15.85	235.9	**119.2**
42-7	Dry	1	1.9	31.7	15.85	303.4	**179.2**
		2	1.9	31.7	15.85	377.0	**222.7**
		3	1.9	31.8	15.90	387.3	**216.8**
		4	1.8	31.6	15.80	325.6	**203.3**
	Wet	5	2.0	31.9	15.95	172.7	**87.2**
		6	1.9	31.9	15.95	263.0	**147.2**
		7	2.0	31.8	15.90	243.9	**129.6**
		8	2.0	31.7	15.85	265.1	**141.0**
49-1	Dry	1	2.2	31.6	15.80	488.2	**196.3**
		2	2.1	31.6	15.80	452.3	**214.5**
	Wet	3	1.7	31.8	15.90	179.2	**121.9**
		4	2.6	31.8	15.90	464.6	**138.4**
49-2	Dry	1	1.7	31.6	15.80	257.1	**175.6**
		2	1.7	31.7	15.85	267.1	**184.5**
		3	1.7	31.8	15.90	261.0	**188.5**
		4	1.7	31.6	15.80	236.6	**167.5**
		5	1.7	31.6	15.80	255.5	**173.9**
	Wet	6	1.7	31.8	15.90	173.0	**115.2**
		7	1.7	31.7	15.85	144.9	**102.5**
		8	1.8	31.8	15.90	-	**-**
		9	1.8	31.8	15.90	162.8	**106.8**
		10	1.7	31.7	15.85	-	**-**

Table E.1: (continued) 7 days biaxial flexural strength test results for MDF cements prepared with different CACs

Mixture no.	Condition	Specimen number	Thickness (mm)	Diameter (mm)	Radius (mm)	P(N)	S (MPa)
49-3	Dry	1	1.6	31.6	15.80	283.4	**211.8**
		2	1.7	31.6	15.80	277.3	**196.8**
		3	1.7	31.6	15.80	314.4	**230.8**
	Wet	4	1.7	31.7	15.85	209.8	**142.7**
		5	1.7	31.7	15.85	216.7	**145.4**
		6	1.7	31.7	15.85	199.9	**136.9**
49-4	Dry	1	1.7	31.6	15.80	260.3	**182.6**
		2	1.6	31.6	15.80	272.8	**229.7**
		3	1.6	31.6	15.80	276.7	**222.2**
		4	1.6	31.6	15.80	258.5	**214.3**
		5	1.7	31.7	15.85	301.0	**210.6**
		6	1.7	31.7	15.85	302.1	**211.3**
		7	1.7	31.6	15.80	315.8	**231.8**
		8	1.7	31.7	15.85	305.8	**224.4**
	Wet	9	1.7	31.8	15.90	223.5	**147.7**
		10	1.7	31.8	15.90	239.2	**176.9**
		11	1.7	31.8	15.90	326.6	**227.6**
		12	1.7	31.8	15.90	214.6	**145.8**
		13	1.7	31.8	15.90	251.9	**176.2**
		14	1.8	31.9	15.95	223.1	**139.1**
		15	1.8	31.7	15.85	243.8	**152.1**
		16	1.8	31.7	15.85	191.5	**125.0**
49-5	Dry	1	1.8	31.7	15.85	372.7	**233.9**
		2	1.8	31.6	15.80	393.5	**246.7**
		3	1.8	31.6	15.80	395.9	**243.9**
		4	1.8	31.6	15.80	397.5	**242.7**
		5	1.8	31.7	15.85	376.7	**235.1**
		6	1.8	31.7	15.85	384.0	**239.6**
		7	1.8	31.7	15.85	408.1	**254.7**
		8	1.8	31.6	15.80	338.5	**211.3**
	Wet	9	1.9	31.7	15.85	-	-
		10	1.8	31.7	15.85	411.6	**258.9**
		11	1.9	31.7	15.85	319.7	**182.7**
		12	1.9	31.7	15.85	327.2	**189.0**
		13	1.8	31.7	15.85	342.1	**213.5**
		14	1.9	31.8	15.90	219.4	**122.8**
		15	2.0	31.8	15.90	327.0	**165.2**
		16	2.0	31.8	15.90	197.4	**99.7**
49-6	Dry	1	1.9	31.8	15.90	370.7	**207.5**
		2	1.9	31.8	15.90	357.4	**200.1**
		3	1.9	31.7	15.85	417.7	**246.8**
		4	1.9	31.7	15.85	390.3	**230.6**
	Wet	5	2.0	31.8	15.90	300.3	**159.6**
		6	1.9	31.7	15.85	280.2	**156.9**
		7	2.0	31.8	15.90	281.4	**142.2**
		8	2.0	31.8	15.90	226.6	**114.5**

Table E.1: (continued) 7 days biaxial flexural strength test results for MDF cements prepared with different CACs

Mixture no.	Condition	Specimen number	Thickness (mm)	Diameter (mm)	Radius (mm)	P(N)	S (MPa)
70-1	Dry	1	1.6	31.7	15.85	234.3	**191.7**
		2	1.6	31.7	15.85	229.6	**186.7**
		3	1.5	31.7	15.85	229.9	**198.3**
		4	1.6	31.6	15.80	205.6	**172.9**
	Wet	5	1.6	31.9	15.95	132.2	**103.8**
		6	1.5	31.8	15.90	155.6	**135.6**
		7	1.5	31.8	15.90	155.7	**139.3**
		8	1.5	31.8	15.90	145.6	**130.3**
70-2	Dry	1	1.7	31.7	15.85	279.3	**197.9**
		2	1.6	31.8	15.90	295.4	**238.9**
		3	1.7	31.7	15.85	-	**-**
		4	1.7	31.7	15.85	268.1	**190.0**
	Wet	5	1.7	31.8	15.90	242.7	**176.5**
		6	1.7	31.8	15.90	266.3	**191.2**
		7	1.8	31.9	15.95	160.7	**104.9**
		8	1.6	31.7	15.85	272.0	**207.0**
70-3	Dry	1	1.7	31.7	15.85	367.3	**248.7**
		2	1.7	31.8	15.90	343.5	**250.7**
		3	1.7	31.7	15.85	384.2	**260.4**
		4	1.7	31.7	15.85	367.2	**266.5**
	Wet	5	1.8	31.8	15.90	267.8	**163.6**
		6	1.8	31.7	15.85	314.4	**202.7**
		7	1.7	31.7	15.85	293.3	**195.0**
		8	1.7	31.7	15.85	314.6	**212.0**
70-4	Dry	1	1.7	31.7	15.85	360.1	**255.5**
		2	1.7	31.7	15.85	341.3	**240.5**
		3	1.6	31.7	15.85	334.3	**252.2**
		4	1.7	31.7	15.85	345.9	**244.9**
	Wet	5	1.7	31.8	15.90	297.7	**208.2**
		6	1.6	31.8	15.90	268.5	**199.6**
		7	1.8	31.8	15.90	272.6	**177.1**
		8	1.7	31.7	15.85	288.8	**210.1**
70-5	Dry	1	1.7	31.7	15.85	332.6	**233.0**
		2	1.7	31.7	15.85	360.2	**243.3**
		3	1.6	31.7	15.85	363.0	**274.9**
		4	1.7	31.7	15.85	362.1	**239.3**
	Wet	5	1.7	31.8	15.90	300.6	**204.2**
		6	1.8	31.8	15.90	330.1	**206.1**
		7	1.8	31.8	15.90	333.8	**217.3**
		8	1.8	31.7	15.85	225.5	**137.3**
70-6	Dry	1	1.8	31.7	15.85	423.6	**265.8**
		2	1.8	31.7	15.85	424.9	**257.6**
		3	1.8	31.7	15.85	354.7	**221.3**
		4	1.9	31.7	15.85	384.2	**226.2**
	Wet	5	1.8	31.8	15.90	323.8	**196.1**
		6	1.9	31.9	15.95	296.6	**174.0**
		7	1.9	31.8	15.90	213.2	**120.1**
		8	1.8	31.8	15.90	306.0	**184.5**

Table E.1: (continued) 7 days biaxial flexural strength test results for MDF cements prepared with different CACs

Mixture no.	Condition	Specimen number	Thickness (mm)	Diameter (mm)	Radius (mm)	P(N)	S (MPa)
70-7	Dry	1	1.9	31.7	15.85	309.7	**182.0**
		2	1.9	31.7	15.85	256.3	**143.7**
		3	1.8	31.7	15.85	345.7	**204.7**
		4	1.9	31.7	15.85	291.2	**167.6**
	Wet	5	2.0	31.9	15.95	197.8	**104.5**
		6	2.0	31.9	15.95	144.3	**75.4**
		7	1.9	31.9	15.95	191.4	**102.5**
		8	2.0	31.9	15.95	128.3	**65.7**
79-1	Dry	1	2.0	31.6	15.80	106.9	**55.7**
		2	2.0	31.6	15.80	109.4	**55.4**
		3	2.0	31.6	15.80	150.9	**78.2**
		4	1.9	31.6	15.80	157.3	**91.9**
	Wet	5	2.0	31.9	15.95	29.5	**14.6**
		6	2.0	31.9	15.95	27.7	**13.4**
		7	2.0	31.8	15.90	41.9	**20.6**
		8	2.2	31.8	15.90	36.7	**16.0**
		9	2.1	31.9	15.95	24.9	**11.8**
79-2	Dry	1	1.8	31.6	15.80	167.3	**101.5**
		2	1.8	31.6	15.80	161.4	**100.9**
		3	1.8	31.6	15.80	179.7	**112.3**
		4	1.8	31.6	15.80	-	**-**
	Wet	5	2.0	31.7	15.85	29.6	**15.4**
		6	1.9	31.8	15.90	24.1	**12.9**
		7	2.0	31.8	15.90	51.2	**25.9**
		8	2.0	31.8	15.90	30.1	**15.3**
79-3	Dry	1	1.9	31.6	15.80	135.1	**79.5**
		2	1.9	31.6	15.80	148.7	**87.8**
		3	1.8	31.6	15.80	144.7	**88.0**
	Wet	4	2.1	32.0	16.00	93.5	**44.9**
		5	2.0	32.0	16.00	87.0	**43.6**

Table E.2: 28 days biaxial flexural strength test results for MDF cements prepared with different CACs

Mixture no.	Condition	Specimen number	Thickness (mm)	Diameter (mm)	Radius (mm)	P(N)	S (MPa)
42-1	Dry	1	1.7	31.5	15.75	213.9	**158.2**
		2	1.7	31.7	15.85	239.7	**172.9**
		3	1.7	31.6	15.80	220.6	**159.6**
		4	1.6	31.6	15.80	225.1	**189.5**
	Wet	5	1.8	32.1	16.05	73.4	**46.1**
		6	1.7	32.2	16.10	98.6	**65.3**
		7	1.7	32.0	16.00	88.9	**66.0**
42-2	Dry	1	1.9	31.6	15.80	317.5	**183.8**
		2	1.8	31.7	15.85	325.0	**194.9**
		3	1.8	31.7	15.85	321.6	**200.7**
		4	1.9	31.7	15.85	320.2	**185.1**
	Wet	5	2.0	32.5	16.25	99.2	**50.8**
		6	2.0	32.5	16.25	95.1	**48.2**
		7	1.9	32.1	16.05	147.3	**78.9**
42-3	Dry	1	1.7	31.7	15.85	324.2	**219.5**
		2	1.8	31.7	15.85	322.7	**205.7**
		3	1.8	31.7	15.85	352.9	**221.0**
	Wet	4	1.9	32.1	16.05	133.6	**77.6**
		5	1.9	32.4	16.20	119.3	**64.3**
		6	1.9	32.3	16.15	112.9	**60.5**
42-4	Dry	1	1.7	31.6	15.80	236.4	**175.4**
		2	1.7	31.6	15.80	274.5	**194.6**
		3	1.7	31.6	15.80	319.2	**212.0**
		4	1.8	31.6	15.80	359.7	**224.5**
		5	1.8	31.7	15.85	358.2	**223.5**
		6	1.8	31.7	15.85	343.0	**214.0**
		7	1.8	31.6	15.80	342.0	**213.5**
	Wet	8	1.8	32.0	16.00	112.8	**70.9**
		9	1.8	32.3	16.15	104.0	**62.8**
		10	1.8	32.2	16.10	109.9	**67.0**
		11	2.0	32.1	16.05	165.3	**83.4**
		12	2.0	32.3	16.15	158.8	**83.4**
		13	1.9	32.1	16.05	157.1	**87.9**
		14	1.9	32.1	16.05	163.7	**91.6**

Table E.2: (continued) 28 days biaxial flexural strength test results for MDF cements prepared with different CACs

Mixture no.	Condition	Specimen number	Thickness (mm)	Diameter (mm)	Radius (mm)	P(N)	S (MPa)
42-5	Dry	1	1.7	31.7	15.85	268.8	**179.3**
		2	1.8	31.7	15.85	353.4	**229.4**
		3	1.8	31.8	15.90	360.3	**236.7**
		4	1.8	31.6	15.80	358.6	**232.8**
		5	1.7	31.6	15.80	358.7	**251.0**
		6	1.7	31.7	15.85	388.4	**271.7**
		7	1.8	31.6	15.80	388.5	**232.1**
		8	1.8	31.6	15.80	386.8	**241.5**
	Wet	9	1.9	32.0	16.00	134.9	**78.9**
		10	1.8	32.1	16.05	135.3	**80.0**
		11	1.8	32.0	16.00	154.5	**96.5**
		12	2.0	32.0	16.00	157.2	**79.4**
		13	1.9	32.0	16.00	220.1	**123.1**
		14	2.0	32.4	16.20	115.2	**58.1**
		15	2.0	32.6	16.30	137.1	**69.1**
42-6	Dry	1	1.9	31.7	15.85	423.1	**237.0**
		2	1.9	31.7	15.85	425.4	**238.3**
		3	1.9	31.7	15.85	424.5	**237.7**
		4	1.8	31.7	15.85	414.3	**258.5**
	Wet	5	2.0	31.9	15.95	196.1	**99.1**
		6	2.0	32.0	16.00	202.0	**102.0**
		7	2.0	32.1	16.05	167.8	**84.7**
		8	2.0	32.0	16.00	148.5	**75.0**
42-7	Dry	1	1.9	31.7	15.85	368.6	**206.4**
		2	1.9	31.7	15.85	276.2	**154.7**
		3	1.8	31.7	15.85	327.0	**204.1**
		4	1.9	31.7	15.85	296.1	**165.8**
	Wet	5	2.1	32.1	16.05	154.1	**70.6**
		6	2.1	32.1	16.05	149.0	**68.2**
		7	2.0	32.0	16.00	139.6	**70.5**
49-1	Dry	1	2.6	31.6	15.80	578.1	**177.2**
		2	2.4	31.6	15.80	540.6	**191.9**
	Wet	3	2.0	32.0	16.00	151.4	**80.3**
		4	2.3	32.1	16.05	211.6	**81.1**
49-2	Dry	1	1.7	31.8	15.90	270.4	**190.4**
		2	1.7	31.6	15.80	242.3	**171.2**
		3	1.7	31.6	15.80	234.4	**160.6**
		4	1.6	31.6	15.80	242.3	**180.4**
	Wet	5	1.8	32.2	16.10	116.9	**71.7**
		6	1.8	32.2	16.10	121.7	**75.0**
		7	1.8	32.2	16.10	130.9	**84.5**
		8	1.8	32.2	16.10	104.5	**68.2**
49-3	Dry	1	1.7	31.6	15.80	275.3	**201.6**
		2	1.6	31.6	15.80	263.8	**220.7**
		3	1.7	31.7	15.85	273.1	**182.2**
	Wet	4	1.9	32.3	16.15	117.1	**68.5**
		5	1.6	32.1	16.05	110.8	**86.6**
		6	1.7	32.0	16.00	101.7	**75.4**

Table E.2: (continued) 28 days biaxial flexural strength test results for MDF cements prepared with different CACs

Mixture no.	Condition	Specimen number	Thickness (mm)	Diameter (mm)	Radius (mm)	P(N)	S (MPa)
49-4	Dry	1	1.7	31.8	15.90	296.7	**212.0**
		2	1.7	31.6	15.80	268.6	**188.0**
		3	1.6	31.6	15.80	282.1	**209.8**
		4	1.6	31.9	15.95	295.5	**233.2**
		5	1.6	31.7	15.85	282.1	**222.8**
		6	1.7	31.7	15.85	296.7	**207.6**
		7	1.7	31.6	15.80	318.6	**223.0**
	Wet	8	1.8	32.2	16.10	119.9	**78.1**
		9	1.8	32.2	16.10	103.5	**61.1**
		10	1.8	32.1	16.05	135.9	**88.6**
		11	1.8	32.4	16.20	127.7	**79.5**
		12	1.8	32.4	16.20	119.1	**74.1**
		13	1.8	32.4	16.20	81.7	**50.8**
49-5	Dry	1	1.8	31.7	15.85	365.9	**230.9**
		2	1.8	31.7	15.85	415.0	**271.5**
		3	1.8	31.7	15.85	398.4	**250.6**
		4	1.7	31.7	15.85	401.9	**267.8**
		5	1.8	31.8	15.90	364.0	**227.1**
		6	1.8	31.7	15.85	380.0	**237.1**
		7	1.8	31.7	15.85	396.9	**247.7**
		8	1.8	31.7	15.85	354.9	**221.5**
	Wet	9	1.9	32.0	16.00	172.4	**96.8**
		10	1.9	32.0	16.00	189.8	**102.2**
		11	1.8	31.9	15.95	204.4	**123.0**
		12	1.9	31.8	15.90	245.3	**143.0**
		13	2.0	32.3	16.15	121.9	**61.5**
		14	1.9	32.1	16.05	143.3	**80.1**
		15	1.9	32.1	16.05	167.7	**93.8**
		16	2.0	32.1	16.05	125.9	**63.5**
49-6	Dry	1	1.9	31.7	15.85	401.3	**224.8**
		2	1.9	31.7	15.85	381.9	**213.9**
		3	1.9	31.7	15.85	371.6	**208.1**
		4	1.9	31.6	15.80	360.2	**201.8**
	Wet	5	2.0	32.0	16.00	184.7	**93.3**
		6	1.9	32.1	16.05	167.6	**93.7**
		7	1.9	31.9	15.95	169.3	**94.8**
		8	1.9	32.1	16.05	211.1	**118.1**
70-1	Dry	1	1.6	31.6	15.80	218.6	**172.7**
		2	1.5	31.6	15.80	213.7	**192.1**
		3	1.5	31.7	15.85	213.8	**192.1**
		4	1.5	31.7	15.85	248.7	**223.5**
	Wet	5	1.7	32.2	16.10	125.5	**87.6**
		6	1.7	32.1	16.05	117.1	**81.8**
		7	1.7	32.2	16.10	98.2	**68.6**
		8	1.6	32.0	16.00	101.9	**80.4**

Table E.2: (continued) 28 days biaxial flexural strength test results for MDF cements prepared with different CACs

Mixture no.	Condition	Specimen number	Thickness (mm)	Diameter (mm)	Radius (mm)	P(N)	S (MPa)
70-2	Dry	1	1.6	31.6	15.80	327.5	**258.7**
		2	1.6	31.6	15.80	329.0	**259.9**
		3	1.6	31.6	15.80	317.0	**250.4**
		4	1.6	31.7	15.85	302.9	**239.2**
	Wet	5	1.8	32.2	16.10	111.7	**69.6**
		6	1.8	32.2	16.10	124.3	**77.4**
		7	1.8	32.2	16.10	131.0	**81.6**
		8	1.7	32.1	16.05	173.3	**121.1**
70-3	Dry	1	1.7	31.7	15.85	377.7	**264.2**
		2	1.7	31.6	15.80	380.8	**266.5**
		3	1.7	31.7	15.85	351.5	**245.9**
		4	1.7	31.7	15.84	396.5	**277.4**
	Wet	5	1.9	32.1	16.05	141.8	**79.3**
		6	1.8	32.1	16.05	160.8	**100.2**
		7	1.8	32.1	16.05	184.8	**115.2**
		8	1.8	32.1	16.05	162.3	**101.1**
70-4	Dry	1	1.6	31.7	15.85	330.9	**261.3**
		2	1.6	31.6	15.80	312.4	**246.8**
		3	1.6	31.7	15.85	354.8	**280.2**
		4	1.7	31.6	15.81	350.4	**245.2**
	Wet	5	1.9	32.1	16.05	135.5	**75.8**
		6	1.8	32.1	16.05	146.0	**91.0**
		7	1.8	32.1	16.07	155.2	**96.7**
		8	1.8	32.1	16.05	139.0	**86.6**
70-5	Dry	1	1.7	31.6	15.80	369.3	**258.5**
		2	1.7	31.8	15.89	350.0	**244.8**
		3	1.6	31.7	15.83	388.7	**307.0**
		4	1.7	31.7	15.83	374.7	**262.2**
	Wet	5	1.9	32.2	16.10	117.4	**65.6**
		6	1.7	32.1	16.05	207.2	**144.8**
		7	1.8	32.2	16.10	153.3	**91.4**
		8	1.9	32.2	16.10	139.3	**79.5**
70-6	Dry	1	1.8	31.7	15.84	409.0	**255.2**
		2	1.8	31.7	15.84	347.0	**216.6**
		3	1.8	31.7	15.85	404.1	**252.2**
		4	1.8	31.7	15.84	402.9	**251.4**
	Wet	5	1.9	32.1	16.05	162.7	**91.0**
		6	1.8	32.1	16.05	180.8	**112.7**
		7	1.9	32.1	16.05	190.0	**106.3**
		8	1.8	32.1	16.05	183.3	**114.2**
70-7	Dry	1	1.9	31.7	15.85	331.1	**189.4**
		2	1.9	31.6	15.80	291.9	**167.0**
		3	1.9	31.7	15.85	312.6	**182.7**
		4	1.8	31.6	15.80	306.9	**191.6**
	Wet	5	2.0	32.1	16.05	148.6	**75.0**
		6	1.9	32.1	16.05	146.6	**82.0**
		7	1.9	32.1	16.05	143.8	**80.4**
		8	2.0	32.1	16.05	152.9	**77.2**

Table E.2: (continued) 28 days biaxial flexural strength test results for MDF cements prepared with different CACs

Mixture no.	Condition	Specimen number	Thickness (mm)	Diameter (mm)	Radius (mm)	P(N)	S (MPa)
79-1	Dry	1	2.0	31.6	15.80	123.4	**61.0**
		2	2.1	31.6	15.80	158.4	**75.2**
		3	1.9	31.6	15.80	114.9	**62.1**
		4	2.0	31.6	15.80	179.3	**87.1**
	Wet	5	2.2	32.2	16.10	32.1	**13.3**
		6	2.1	32.2	16.10	28.1	**12.7**
		7	2.2	32.2	16.10	35.3	**15.2**
79-2	Dry	1	1.8	31.6	15.80	175.1	**108.3**
		2	1.8	31.6	15.80	167.9	**105.0**
		3	1.8	31.7	15.85	169.3	**106.0**
		4	1.8	31.6	15.80	181.7	**115.2**
	Wet	5	2.1	31.9	15.95	30.1	**13.9**
		6	2.0	32.0	16.00	77.3	**38.5**
		7	2.1	32.0	16.00	34.7	**15.7**
79-3	Dry	1	1.8	31.6	15.80	-	**-**
		2	1.8	31.6	15.80	198.7	**121.9**
	Wet	3	2.0	31.9	15.95	74.4	**37.9**
		4	2.0	32.0	16.00	75.0	**37.5**

APPENDIX F

X-ray Diffraction Test Results

All tests were conducted on Rigaku Model X-Ray Diffrectometer. Subsequently, patterns were matched with crystalline phases by using Jade Software.

Used notations in this part are:

CA: $CaAl_2O_4$: Calcium Aluminum Oxide

CA_2: $CaAl_4O_7$:Grossite

Ca': $Ca_3Al_2O_6$: Calcium Aluminum Oxide

$C_{12}A_7$:$Ca_{12}Al_{14}O_{33}$:Mayenite

C_3A: $Ca_3Al_2O_6$: Tri Calcium Aluminate

C_2AS:$Ca_2Al_2SiO_7$: Gehlenite

A:Al_2O_3: Corundum

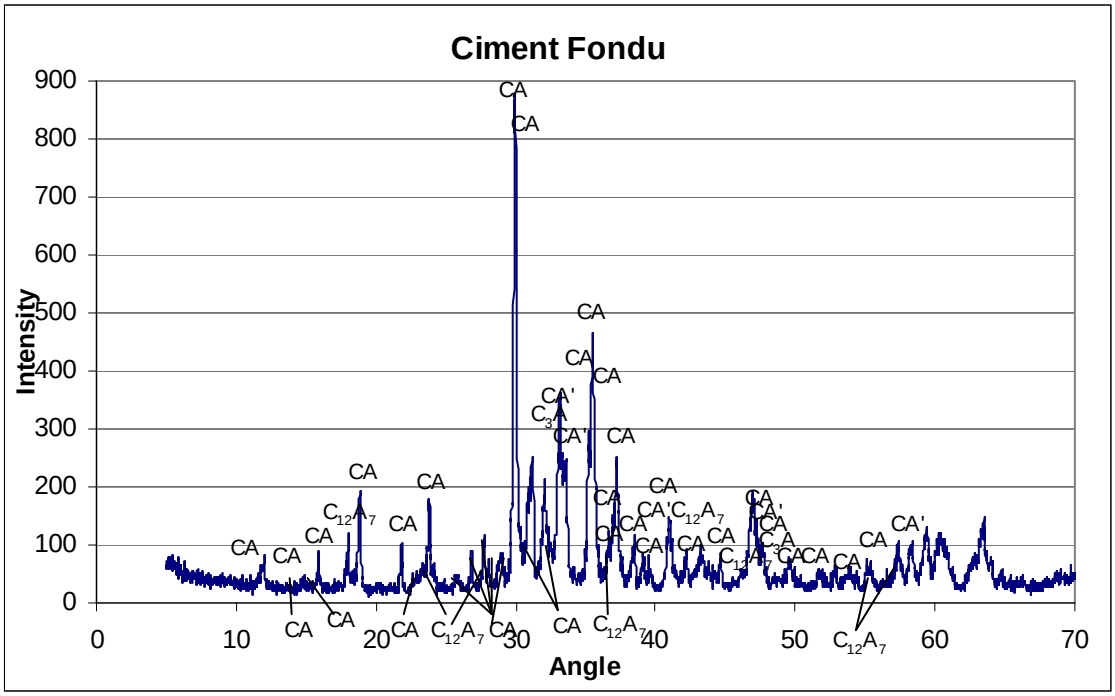

Figure F.1: X-Ray diffraction of ciment fondu

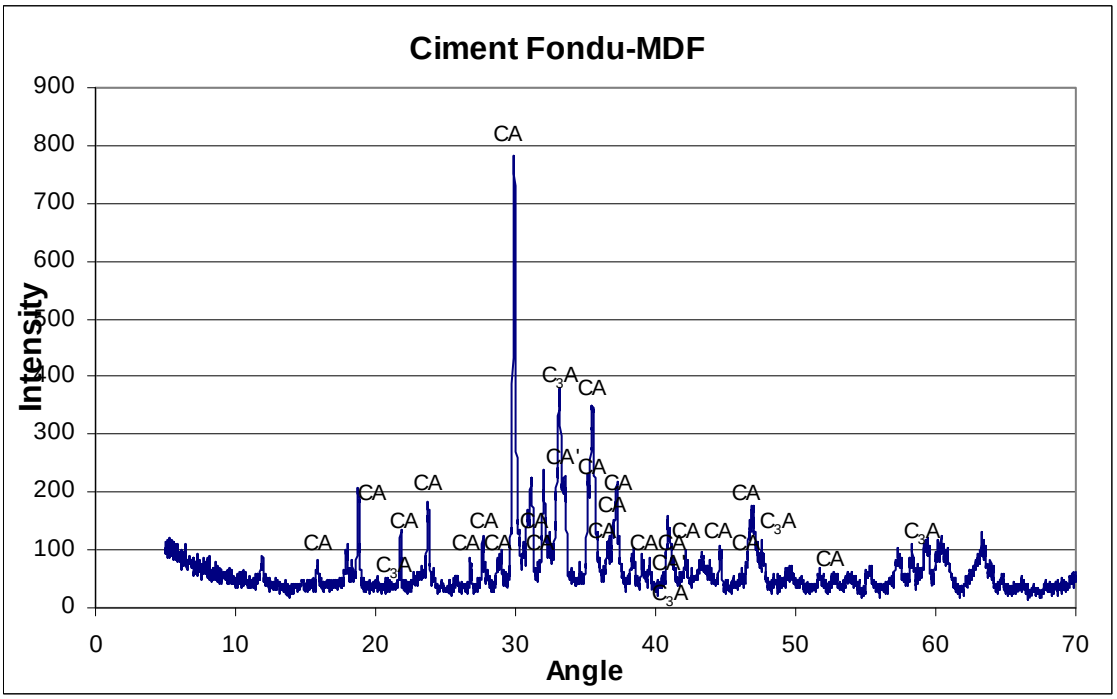

Figure F.2: X-Ray diffraction of MDF cement produced with ciment fondu

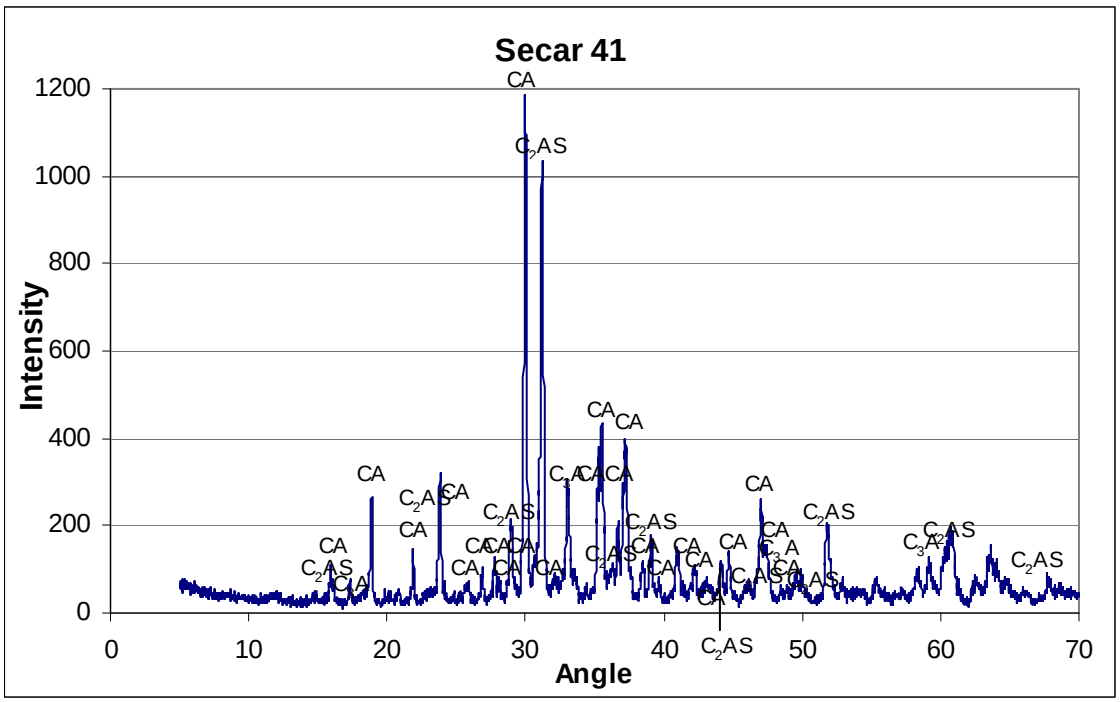

Figure F.3: X-Ray diffraction of Secar 41

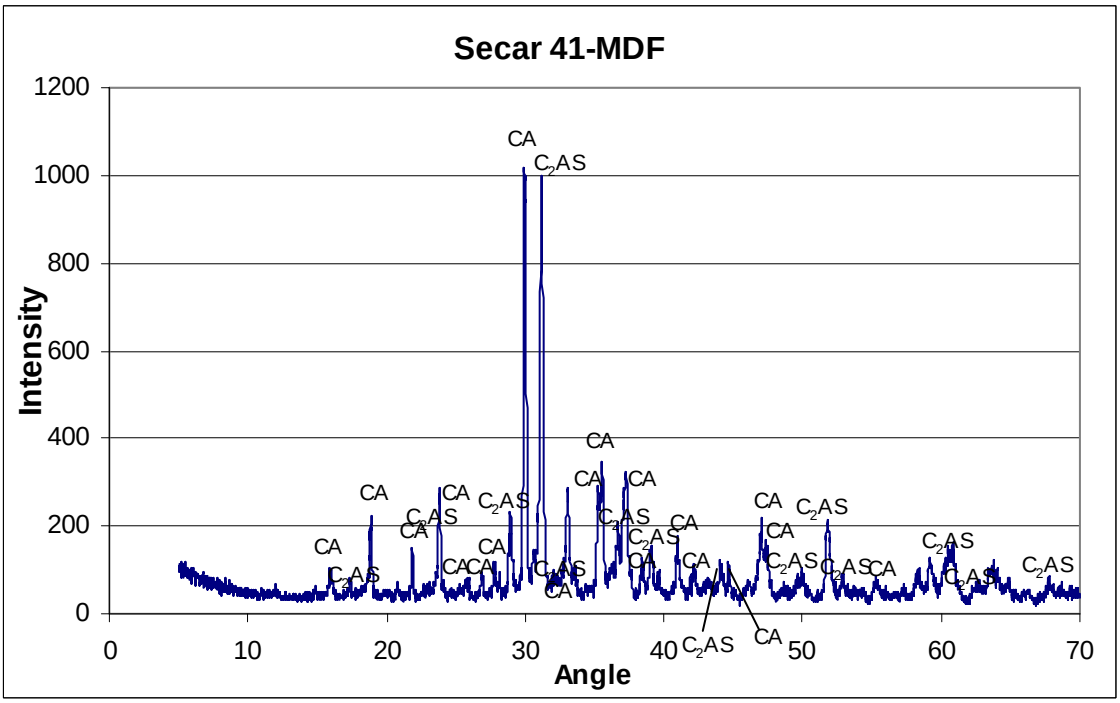

Figure F.4: X-Ray diffraction of MDF cement produced with Secar 41

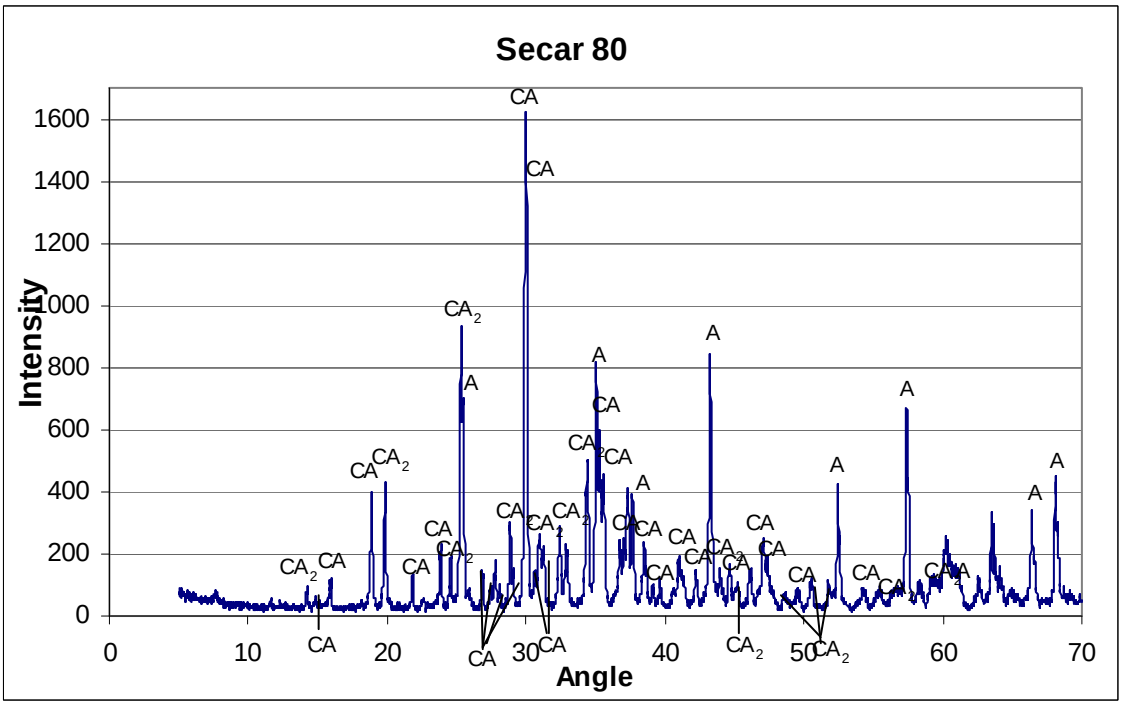

Figure F.5: X-Ray diffraction of Secar 80

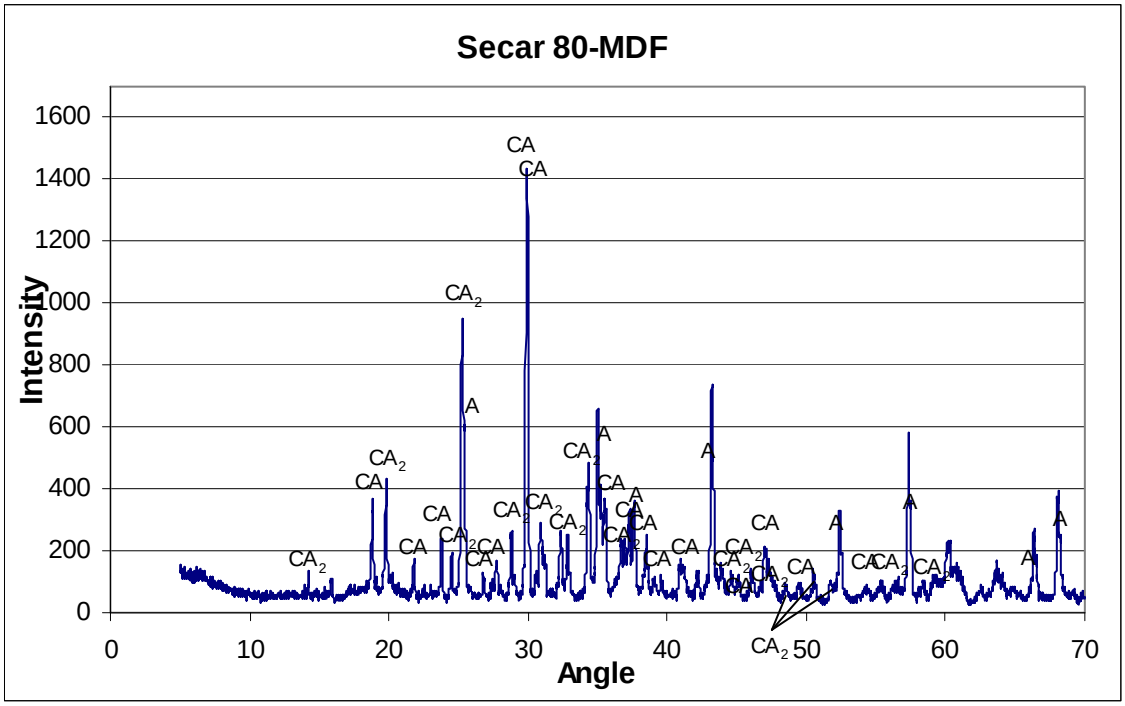

Figure F.6: X-Ray diffraction of MDF cement produced with Secar 80

APPENDIX G

Thermogravimetric Analysis (TA) and Differential Thermal Analysis (DTA) Test Results

Table G.1: Materials used for thermal analysis tests

Specimen No	Materials	Material Types
1	Ciment Fondu	Alumina Cements
2	Secar 41	
3	Secar 71	
4	Secar 80	
5	MDF Fondu	MDF cements
6	MDF 41	
7	MDF 71	
8	MDF 80	
9	Gohsenol KH 17	PVA
10	Cement Paste	Secar 71+Water

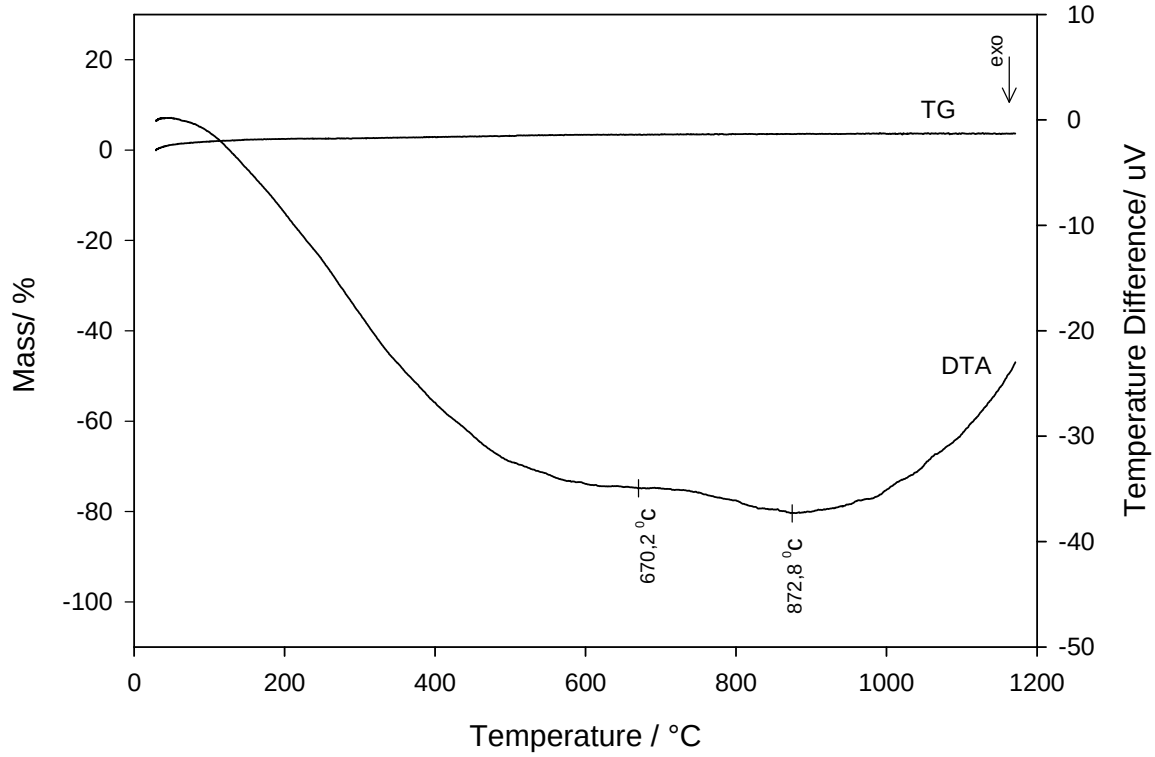

Figure G.1: TA and DTA results of Ciment Fondu

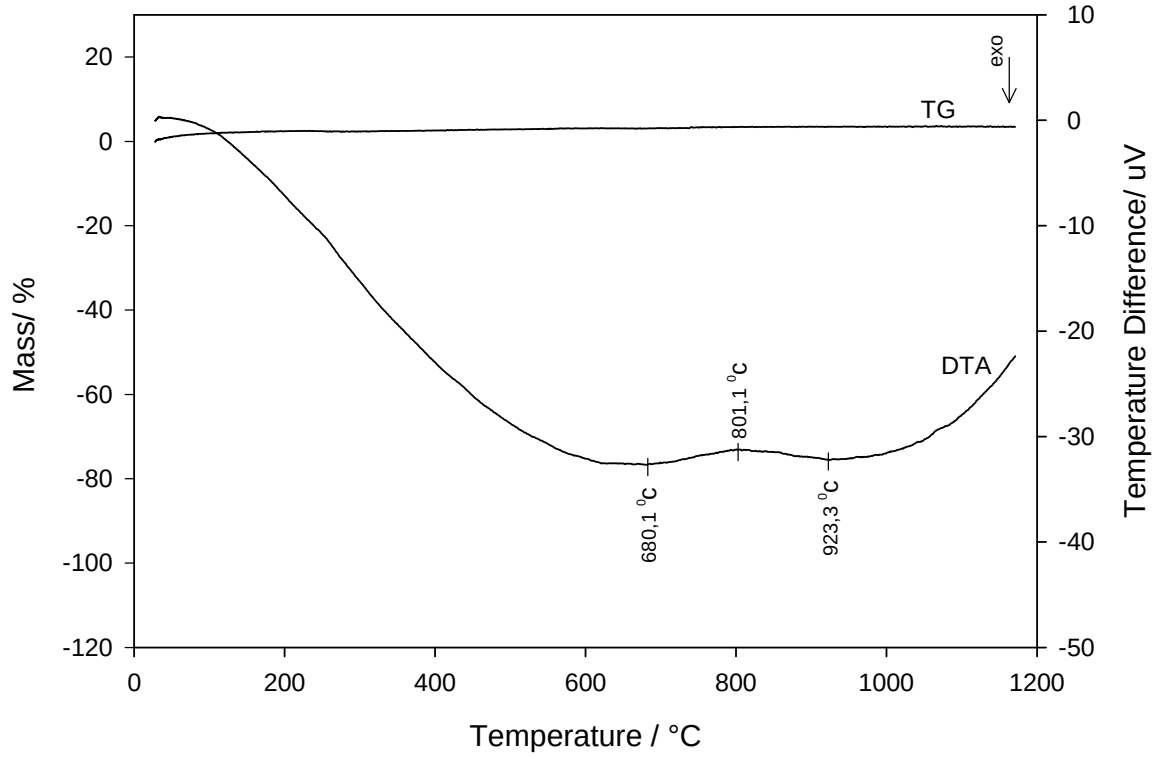

Figure G.2: TA and DTA results of Secar 41

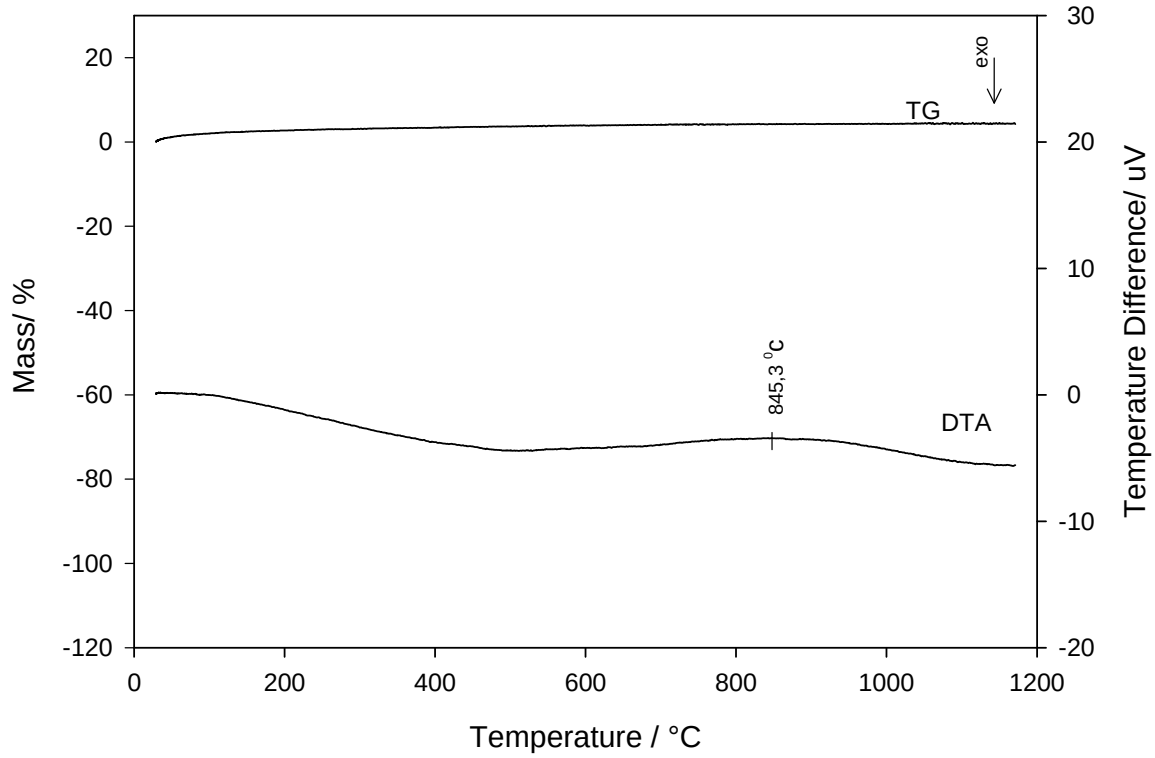

Figure G.3: TA and DTA results of Secar 71

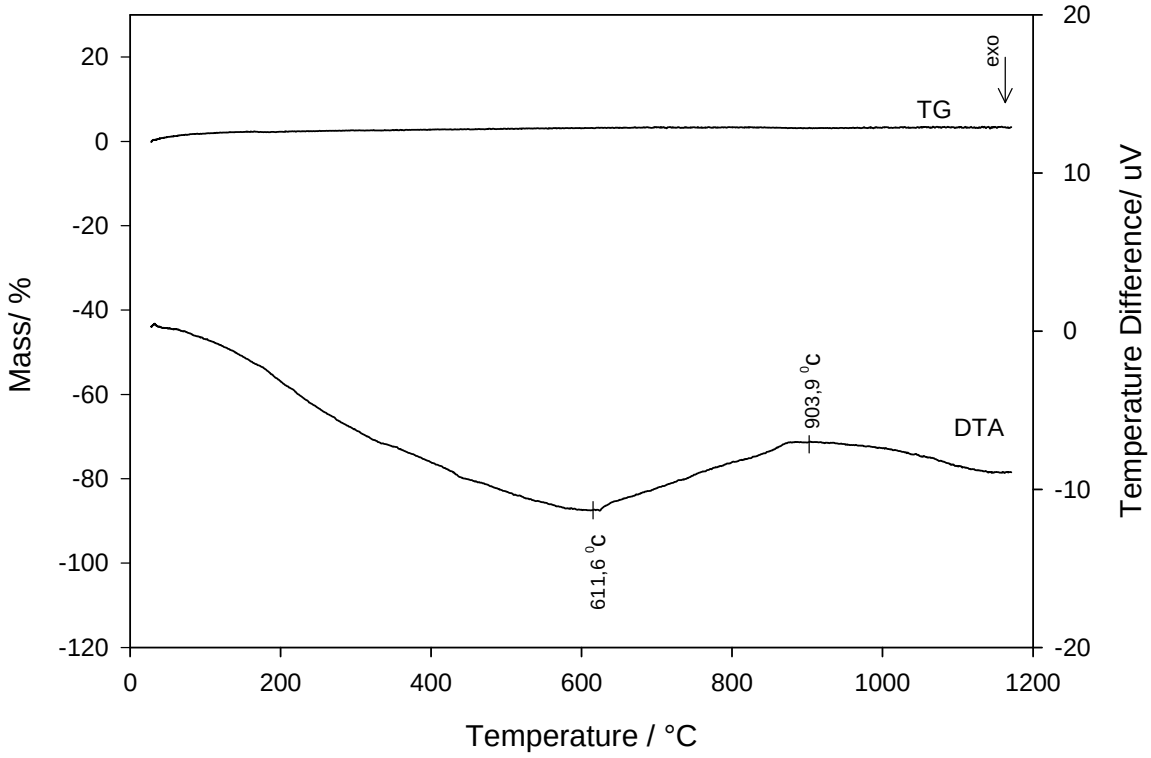

Figure G.4: TA and DTA results of Secar 80

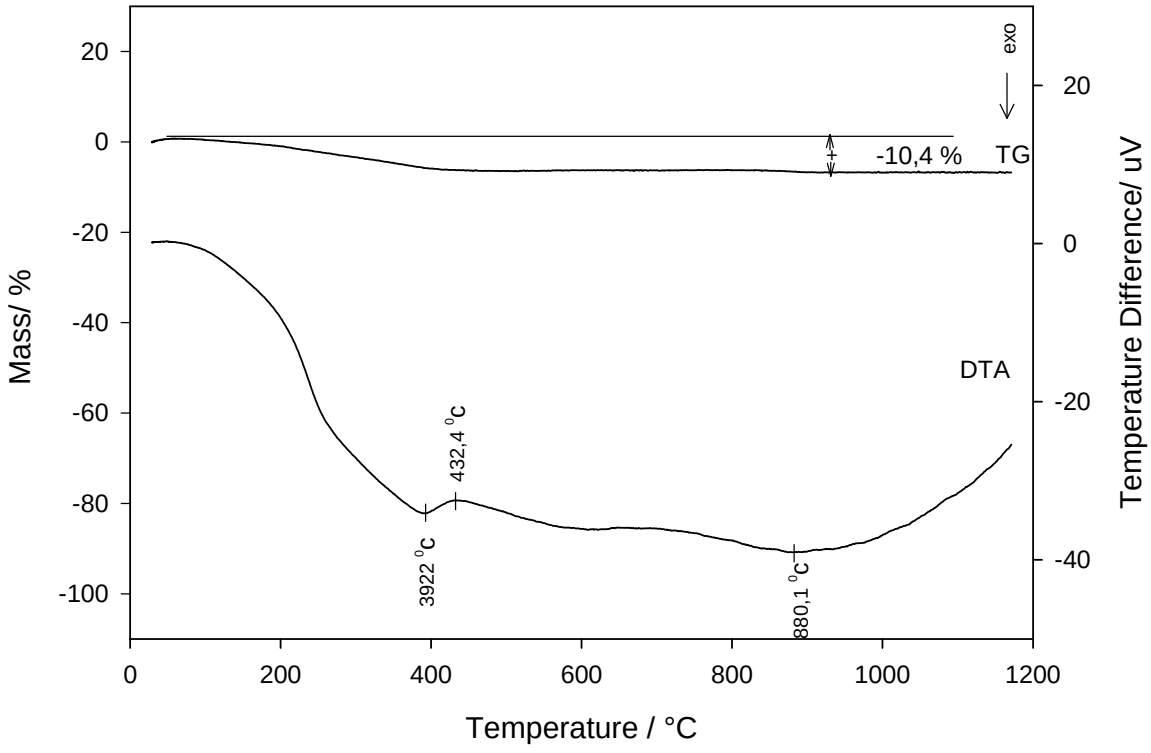

Figure G.5: TA and DTA results of MDF Fondu

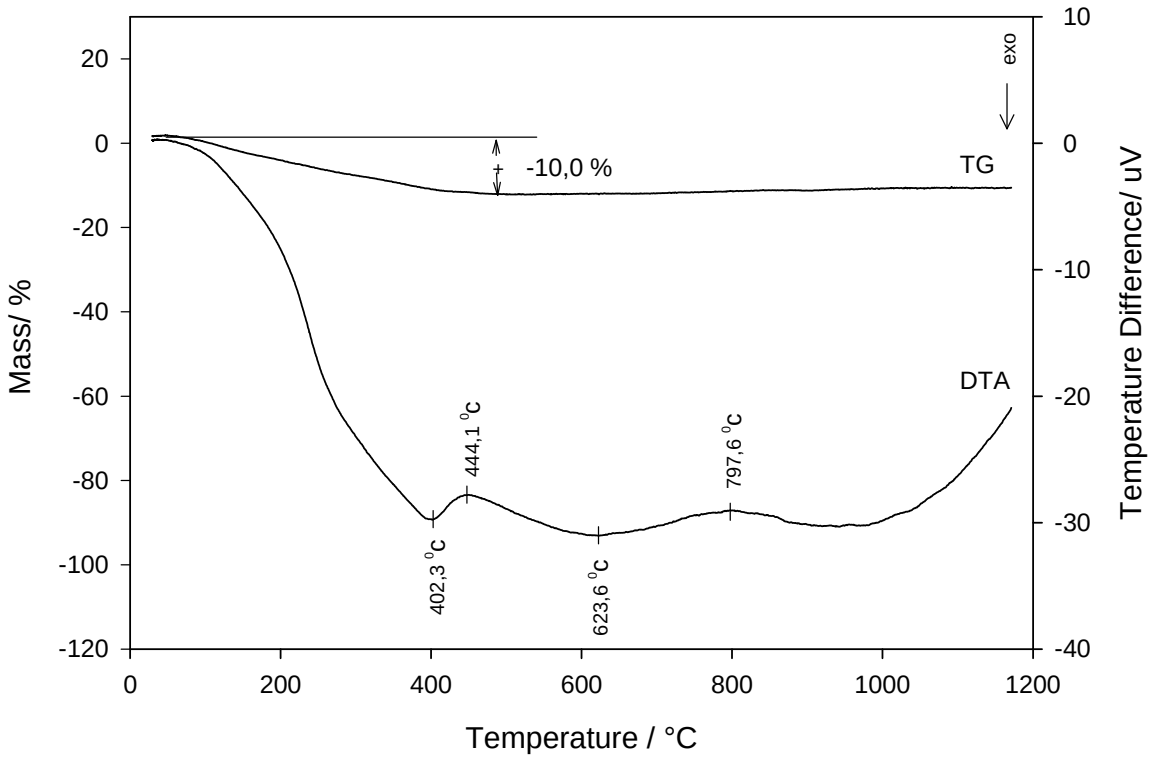

Figure G.6: TA and DTA results of MDF 41

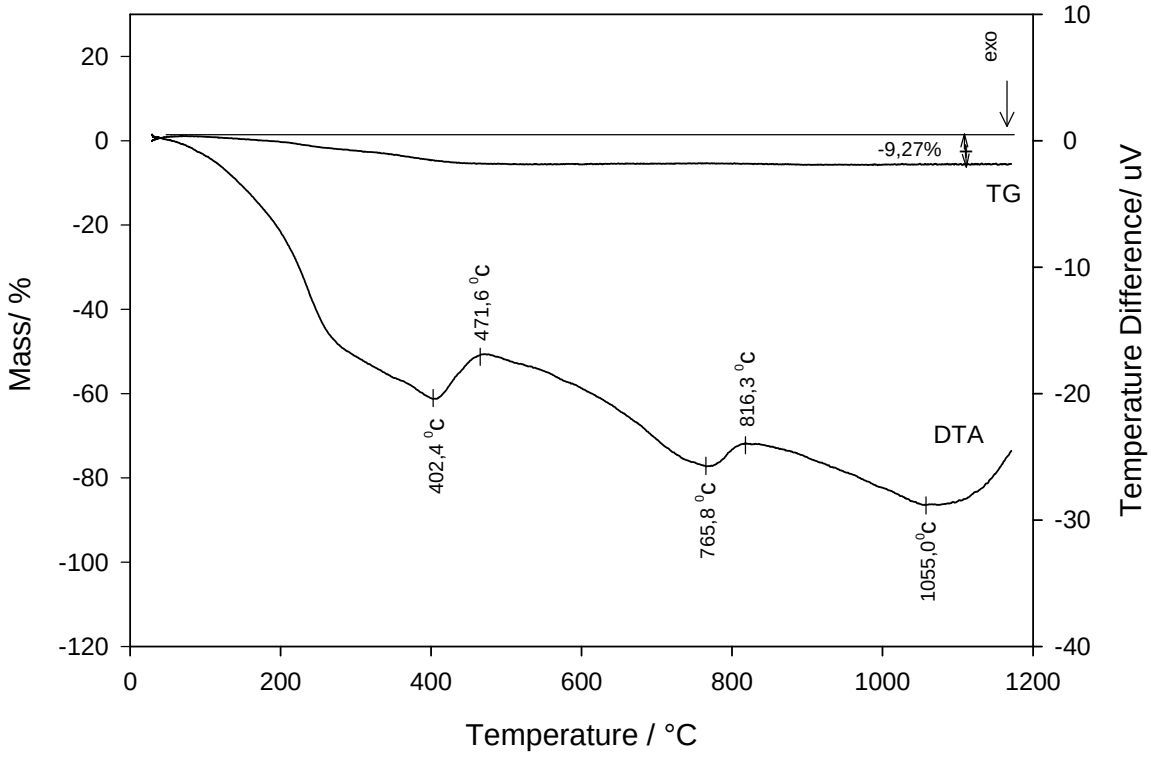

Figure G.7: TA and DTA results of MDF 71

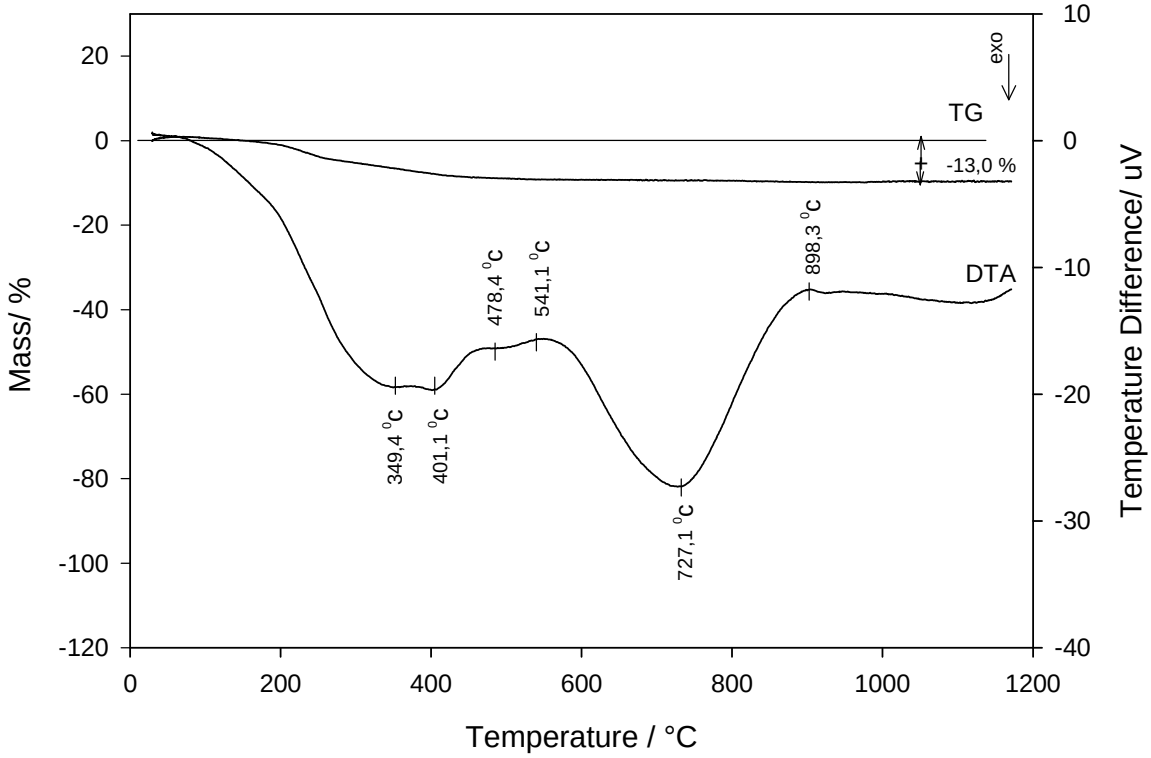

Figure G.8: TA and DTA results of MDF 80

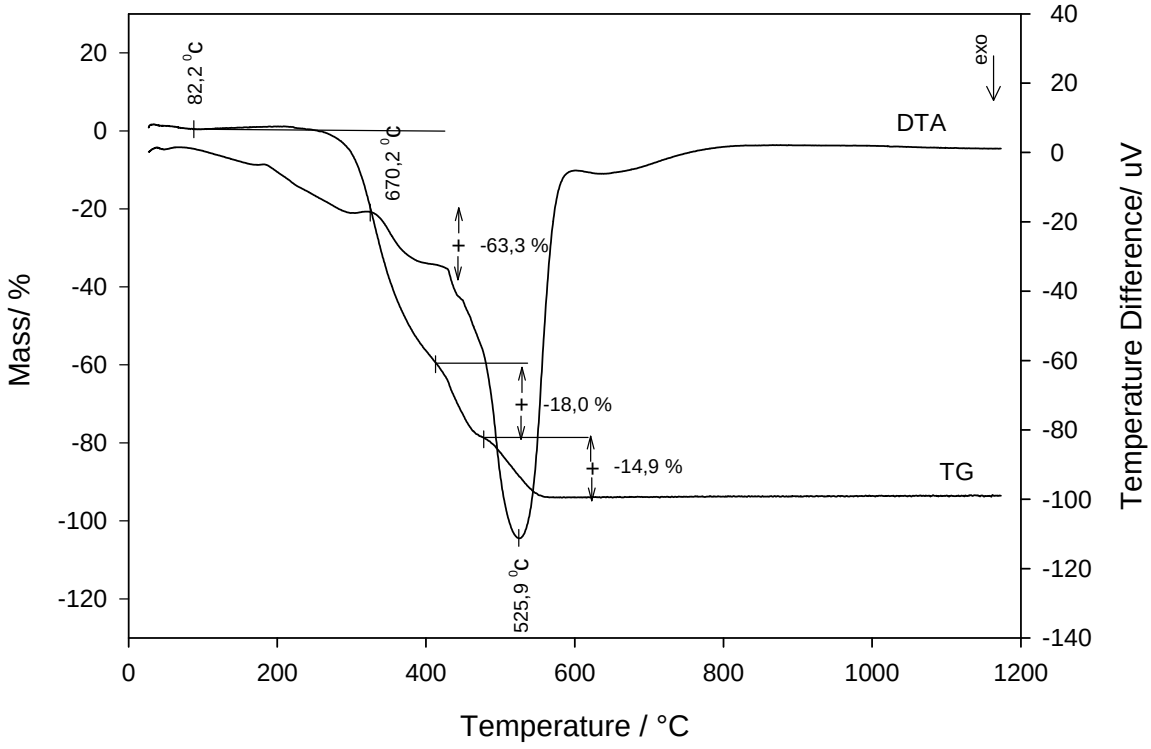

Figure G.9: TA and DTA results of Gohsenol KH 17

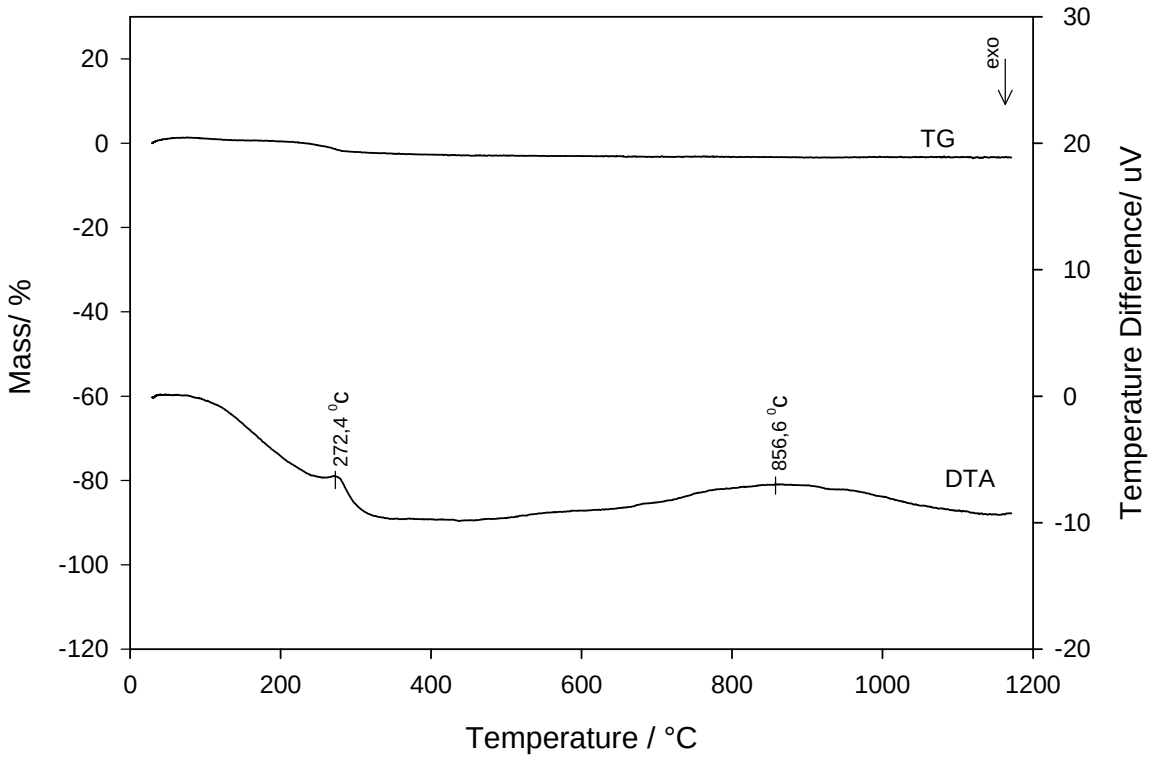

Figure G.10: TA and DTA results of Cement Paste

APPENDIX H

Table H.1: 7 days biaxial flexural strength test results for MDF cements prepared with Kymene® 557H

Mixture no.	Condition	Specimen number	Thickness (mm)	Diameter (mm)	Radius (mm)	P(N)	S (MPa)
KH17	Dry	1	1.7	31.4	15.70	282.8	**198.1**
		2	1.7	31.5	15.75	237.9	**166.6**
		3	1.6	31.4	15.70	261.0	**206.4**
		4	1.6	31.7	15.85	308.9	**244.0**
		5	1.7	31.5	15.75	244.9	**171.5**
	Wet	6	1.7	31.6	15.80	222.4	**155.6**
		7	1.8	31.6	15.80	140.0	**87.4**
		8	1.8	31.5	15.75	126.8	**79.2**
		9	1.8	31.5	15.75	160.8	**100.4**
		10	1.7	31.5	15.75	221.1	**154.8**
GH20	Dry	1	1.8	31.6	15.80	165.2	**103.1**
		2	1.8	31.5	15.75	150.1	**93.7**
		3	1.8	31.6	15.80	165.3	**103.2**
		4	1.9	31.5	15.75	123.9	**69.4**
		5	1.8	31.6	15.80	168.1	**104.9**
	Wet	6	1.9	31.9	15.95	62.7	**35.1**
		7	1.8	31.9	15.95	67.1	**41.9**
		8	1.9	31.9	15.95	78.5	**44.0**
		9	1.9	31.9	15.95	84.9	**47.5**

APPENDIX I

Table I.1: 7 days biaxial flexural strength test results for MDF cements prepared with polyox

Mixture no.	Condition	Specimen number	Thickness (mm)	Diameter (mm)	Radius (mm)	P(N)	S (MPa)
Polyox 11	Dry	1	2.0	31.5	15.75	20.16	**10.2**
		2	1.9	31.5	15.75	10.31	**5.8**
		3	1.9	31.5	15.75	47.89	**26.8**
	Wet	4*	3.0	32.4	16.20	-	**-**
		5	3.5	32.4	16.20	47.44	**7.8**
Polyox 10	Dry	1	1.8	31.5	15.75	18.02	**11.3**
		2	1.9	31.5	15.75	19.42	**10.9**
		3	1.9	31.5	15.75	19.14	**10.7**
		4	1.9	31.5	15.75	14.26	**8.0**
	Wet	5	3.9	32.5	16.25	35.08	**4.7**
		6	3.7	32.4	16.20	37.59	**5.5**
		7	3.7	32.1	16.05	36.11	**5.3**
		8	3.7	32.1	16.05	33.22	**4.9**
Polyox 9	Dry	1	1.9	31.4	15.70	23.06	**12.9**
		2	1.9	31.5	15.75	20.41	**11.4**
		3	1.9	31.5	15.75	34.71	**19.5**
		4	1.9	31.6	15.80	28.81	**16.1**
	Wet	5	3.8	32.4	16.20	33.69	**4.7**
		6	3.8	32.4	16.20	43.8	**6.1**
		7	3.7	32.2	16.10	42.75	**6.3**
		8	3.6	32.2	16.10	38.28	**6.0**

* These specimen were damaged/deformed during test and the test results of this specimen could not calculated.

Table I.2: 28 days biaxial flexural strength test results for MDF cements prepared with polyox

Mixture no.	Condition	Specimen number	Thickness (mm)	Diameter (mm)	Radius (mm)	P(N)	S (MPa)
Polyox 10	Dry	1	1.9	31.4	15.7	40.59	**22.8**
		2	1.9	31.5	15.75	39.4	**22.1**
		3*	1.9	31.6	15.8	-	**-**
	Wet	4	3.2	32.1	16.05	29.45	**5.8**
		5	3.5	32.2	16.1	42.59	**7.0**
		6	3.5	32.0	16	42.35	**7.0**
Polyox 9	Dry	1	1.8	31.6	15.8	16.2	**10.1**
		2	1.8	31.5	15.75	13.6	**8.5**
		3	1.9	31.5	15.75	23.1	**12.9**
		4	1.8	31.5	15.75	21.11	**13.2**
	Wet	5	3.4	32.6	16.3	48.46	**8.4**
		6	3.6	32.2	16.1	43.16	**6.7**
		7	3.6	32.5	16.25	45.83	**7.1**
		8	3.4	32.6	16.3	44.97	**7.8**

* These specimen were damaged/deformed during test and the test results of this specimen could not calculated.

APPENDIX J

Table J.1: 7 days biaxial flexural strength test results of optimization studies

Mixture no.	Condition	Specimen number	Thickness (mm)	Diameter (mm)	Radius (mm)	P(N)	S (MPa)
1	Dry	1	2.0	27.9	13.95	326.1	**158.7**
		2	2.0	27.6	13.82	335.2	**158.5**
		3	2.0	27.8	13.90	273.8	**132.0**
		4	2.0	27.7	13.84	343.4	**169.0**
		5	2.0	27.7	13.86	302.4	**140.1**
	Wet	6	2.1	27.9	13.95	105.9	**46.6**
		7	2.0	28.0	13.98	94.0	**43.9**
		8	2.1	28.1	14.04	102.6	**44.7**
		9	2.1	27.8	13.89	117.5	**52.3**
2	Dry	1	1.8	28.0	14.00	212.0	**123.7**
		2	1.9	27.7	13.84	284.3	**150.6**
		3	1.7	27.8	13.91	253.9	**158.7**
		4	1.7	27.9	13.97	218.6	**136.6**
		5	1.8	27.9	13.97	242.4	**144.7**
	Wet	6	1.9	28.2	14.11	96.0	**48.1**
		7	1.9	28.1	14.06	97.8	**49.6**
		8	1.8	28.3	14.13	55.6	**32.1**
3	Dry	1	1.9	27.6	13.78	264.1	**142.9**
		2	1.8	27.5	13.76	215.4	**121.8**
		3	1.8	27.5	13.75	-	**-**
		4	1.9	27.7	13.84	171.7	**89.0**
		5	1.8	27.7	13.85	259.2	**148.1**
		6	1.7	27.5	13.75	236.7	**149.9**
	Wet	7	2.1	28.0	14.00	107.7	**47.4**
		8	1.9	27.9	13.96	106.3	**58.1**
		9	1.9	28.0	14.01	107.0	**56.6**
		10	2.1	28.1	14.03	94.7	**40.1**
		11	2.1	27.8	13.88	95.8	**41.4**
4	Dry	1	1.8	27.8	13.88	201.8	**123.3**
		2	1.7	27.6	13.80	169.3	**113.7**
		3	1.8	27.7	13.85	171.9	**101.5**
		4	2.2	27.9	13.93	322.5	**130.5**
		5	2.2	27.9	13.96	374.4	**150.1**
		6	1.9	27.9	13.94	212.9	**116.3**
	Wet	7	1.9	28.1	14.07	113.6	**59.4**
		8	1.8	27.8	13.91	91.9	**50.8**
		9	2.0	27.8	13.92	70.2	**34.5**
		10	2.4	27.9	13.94	169.3	**55.9**
		11	1.8	27.8	13.90	103.1	**58.2**

Table J.1: (continued) 7 days biaxial flexural strength test results of optimization studies

Mixture no.	Condition	Specimen number	Thickness (mm)	Diameter (mm)	Radius (mm)	P(N)	S (MPa)
5	Dry	1	2.1	27.7	13.83	263.2	**109.6**
		2	2.2	27.6	13.82	289.8	**117.4**
		3	2.2	27.6	13.78	315.5	**127.8**
		4	2.2	27.4	13.70	301.3	**117.8**
		5	2.3	27.4	13.71	368.7	**135.3**
	Wet	6	2.2	27.5	13.77	177.3	**69.3**
		7	2.3	27.6	13.82	130.2	**46.5**
		8	2.3	27.7	13.87	112.6	**40.5**
		9	2.3	27.6	13.82	81.9	**28.7**
		10	2.2	27.7	13.83	122.8	**46.2**
6	Dry	1	2.3	27.4	13.71	365.0	**132.7**
		2	2.3	27.4	13.72	403.3	**139.2**
		3	2.2	27.3	13.65	355.0	**138.8**
		4	2.2	27.4	13.71	357.4	**135.9**
		5	2.2	27.5	13.77	386.7	**145.7**
	Wet	6	2.4	27.6	13.79	178.0	**59.4**
		7	2.4	27.7	13.83	132.8	**44.2**
		8	2.4	27.7	13.87	141.5	**45.6**
		9	2.3	27.7	13.83	190.7	**68.7**
		10	2.3	27.5	13.77	180.3	**62.2**
7	Dry	1	1.9	27.5	13.76	250.0	**127.0**
		2	1.8	27.4	13.72	214.7	**122.8**
		3	1.9	27.5	13.75	236.4	**120.1**
		4	1.9	27.2	13.62	280.2	**144.0**
		5	2.1	27.4	13.72	300.8	**134.1**
	Wet	6	2.0	28.0	14.01	92.9	**45.2**
		7	1.9	27.8	13.92	102.8	**51.1**
		8	1.9	27.9	13.93	102.0	**51.7**
		9	2.0	28.0	14.01	96.8	**45.2**
		10	2.3	27.7	13.86	111.6	**40.9**
8	Dry	1	1.9	27.3	13.67	234.0	**116.6**
		2	1.9	27.4	13.72	221.0	**111.2**
		3	2.0	27.4	13.71	202.2	**94.7**
		4	2.0	27.4	13.72	228.5	**108.1**
		5	2.0	27.5	13.76	227.7	**107.7**
	Wet	6	2.0	27.7	13.84	113.1	**52.9**
		7	2.1	27.8	13.88	113.8	**48.8**
		8	2.0	27.7	13.87	132.4	**60.7**
		9	2.1	27.8	13.89	111.9	**47.9**
		10	2.0	27.8	13.90	119.4	**57.5**

Table J.1: (continued) 7 days biaxial flexural strength test results of optimization studies

Mixture no.	Condition	Specimen number	Thickness (mm)	Diameter (mm)	Radius (mm)	P(N)	S (MPa)
9	Dry	1	1.9	27.4	13.69	186.9	**93.1**
		2	1.9	27.5	13.73	173.4	**89.0**
		3	1.9	27.4	13.71	180.4	**92.7**
		4	1.9	27.5	13.77	217.2	**109.2**
		5	1.9	27.7	13.83	214.5	**111.2**
	Wet	6	2.0	27.6	13.82	95.9	**44.0**
		7	1.9	28.0	14.00	80.3	**43.4**
		8	1.9	27.7	13.85	62.3	**33.0**
		9	1.9	27.6	13.80	108.3	**56.7**
10	Dry	1	2.1	27.7	13.83	298.6	**127.9**
		2	2.1	27.7	13.84	314.1	**132.1**
		3	2.1	27.4	13.69	332.1	**142.5**
	Wet	4	2.3	28.2	14.11	117.6	**42.3**
		5	2.2	27.9	13.94	157.2	**63.0**
		6	2.3	28.0	14.00	123.4	**45.6**
		7	2.2	27.9	13.95	130.0	**48.4**
		8	2.2	28.1	14.04	140.0	**53.6**
11	Dry	1	1.8	27.5	13.76	202.9	**120.0**
		2	1.8	27.6	13.80	223.7	**136.8**
		3	1.8	27.5	13.77	216.3	**125.0**
		4	1.8	27.6	13.80	255.1	**141.1**
		5	1.7	27.6	13.80	123.8	**76.6**
	Wet	6	1.8	27.7	13.84	76.2	**42.6**
		7	1.8	27.8	13.88	101.2	**56.5**
		8	1.8	27.5	13.77	100.6	**60.1**
		9	1.8	27.7	13.87	91.3	**50.5**
		10	1.8	27.7	13.84	95.2	**55.0**
12	Dry	1	1.7	27.5	13.76	155.6	**103.3**
		2	1.6	27.6	13.79	160.4	**115.9**
		3	1.7	27.6	13.80	126.3	**81.9**
		4	1.6	27.6	13.80	91.0	**64.9**
		5	1.6	27.5	13.76	169.6	**118.1**
	Wet	6	1.7	27.7	13.83	52.6	**34.5**
		7	1.7	27.7	13.86	67.4	**44.7**
		8	1.7	27.6	13.81	81.0	**53.7**
		9	1.7	27.8	13.91	60.9	**40.4**
		10	1.8	27.9	13.93	56.6	**33.1**
13	Dry	1	1.7	27.6	13.80	172.9	**118.9**
		2	1.7	27.5	13.77	150.5	**101.1**
		3	1.7	27.6	13.78	176.4	**115.7**
		4	1.7	27.7	13.83	181.7	**120.5**
		5	1.7	27.5	13.77	140.0	**91.8**
	Wet	6	1.8	27.7	13.87	87.6	**49.5**
		7	1.9	27.6	13.80	77.8	**39.5**
		8	1.9	27.7	13.85	77.3	**42.2**
		9	1.9	27.8	13.90	86.5	**78.0**
		10	1.9	27.9	13.97	81.0	**41.1**

Table J.1: (continued) 7 days biaxial flexural strength test results of optimization studies

Mixture no.	Condition	Specimen number	Thickness (mm)	Diameter (mm)	Radius (mm)	P(N)	S (MPa)
14	Dry	1	1.6	27.6	13.80	147.9	**110.9**
		2	1.7	27.4	13.70	201.0	**136.7**
		3	1.6	27.5	13.76	118.0	**86.3**
		4	1.6	27.5	13.75	163.5	**118.2**
		5	1.6	27.5	13.76	169.9	**124.3**
	Wet	6	1.9	27.7	13.84	84.5	**46.2**
		7	1.8	27.8	13.91	102.2	**61.0**
		8	1.7	27.7	13.87	90.3	**58.4**
		9	1.8	27.6	13.82	94.4	**55.2**
		10	1.8	27.8	13.88	94.2	**55.0**
15	Dry	1	2.1	27.8	13.89	268.9	**113.0**
		2	2.2	27.9	13.93	237.3	**96.0**
		3	2.1	28.0	14.02	205.1	**87.8**
		4	2.1	27.7	13.85	254.7	**108.1**
		5	2.1	27.9	13.93	199.6	**85.5**
	Wet	6	2.3	27.7	13.84	200.0	**70.1**
		7	2.1	28.0	13.99	178.8	**75.8**
		8	2.2	28.0	13.99	147.8	**55.1**
		9	2.1	27.9	13.97	173.4	**72.2**
		10	2.2	28.0	13.99	208.7	**82.8**
16	Dry	1	1.6	27.9	13.93	152.4	**115.7**
		2	1.6	28.0	13.99	124.7	**88.8**
		3	1.7	27.8	13.91	180.7	**115.6**
		4	1.7	28.0	13.99	114.8	**78.8**
		5	1.6	27.7	13.86	122.0	**90.3**
	Wet	6	1.8	27.9	13.97	53.6	**30.3**
		7	1.7	28.0	14.01	84.5	**57.3**
		8	1.8	28.0	13.99	54.5	**32.2**
		9	1.7	27.9	13.96	92.1	**62.5**
		10	1.8	27.7	13.86	86.0	**49.1**
17	Dry	1	2.0	27.8	13.89	245.5	**117.1**
		2	2.0	27.8	13.89	290.1	**133.0**
		3	2.0	27.8	13.92	308.3	**148.6**
		4	2.1	27.9	13.95	267.0	**116.5**
		5	2.1	27.8	13.88	338.4	**143.6**
	Wet	6	2.1	27.9	13.93	138.1	**57.5**
		7	2.1	28.2	14.10	151.8	**63.1**
		8	2.1	27.9	13.94	149.7	**62.9**
		9	2.0	28.0	14.01	138.3	**63.3**
		10	2.1	28.2	14.09	157.0	**69.8**

Table J.1: (continued) 7 days biaxial flexural strength test results of optimization studies

Mixture no.	Condition	Specimen number	Thickness (mm)	Diameter (mm)	Radius (mm)	P(N)	S (MPa)
18	Dry	1	1.6	27.5	13.74	200.5	**146.8**
		2	1.6	27.8	13.88	190.2	**140.8**
		3	1.6	27.6	13.82	209.4	**153.1**
		4	1.6	27.9	13.97	203.4	**144.9**
		5	1.6	27.5	13.77	250.1	**183.0**
	Wet	6	1.8	28.0	13.99	64.7	**37.3**
		7	1.8	27.8	13.88	84.6	**48.3**
		8	1.8	27.9	13.97	47.0	**26.2**
		9	1.7	27.9	13.94	55.0	**36.0**
		10	1.7	27.9	13.97	76.0	**49.1**
19	Dry	1	2.4	28.2	14.08	176.4	**55.8**
		2	2.3	27.9	13.94	191.8	**65.5**
		3	2.2	27.7	13.83	148.1	**56.3**
	Wet	4	2.6	27.7	13.86	109.8	**30.9**
		5	2.6	27.6	13.82	136.5	**38.1**
		6	2.7	27.6	13.82	149.0	**38.8**
20	Dry	1	1.9	27.6	13.79	270.6	**138.9**
		2	2.0	27.7	13.83	320.4	**156.1**
		3	2.0	27.9	13.97	268.2	**129.2**
		4	1.9	28.0	14.01	354.8	**183.7**
		5	1.8	27.8	13.92	307.5	**169.9**
	Wet	6	2.1	27.9	13.97	145.0	**59.2**
		7	2.1	28.0	13.98	163.2	**72.6**
		8	2.1	28.1	14.07	97.0	**39.9**
		9	2.2	28.0	13.98	41.6	**15.6**
		10	2.2	28.4	14.22	71.8	**27.2**
21	Dry	1	2.5	27.5	13.73	159.0	**46.2**
		2	2.5	27.4	13.72	150.6	**43.7**
		3	2.6	27.6	13.78	125.6	**35.3**
		4	2.6	27.4	13.68	116.1	**33.5**
		5	2.6	28.1	14.05	111.7	**31.1**
	Wet	6	2.7	28.0	14.00	56.8	**14.9**
		7	2.7	28.0	14.00	42.1	**10.9**
		8	2.6	28.3	14.16	130.8	**35.0**
		9	2.7	28.5	14.23	146.1	**36.8**
22	Dry	1	1.6	27.9	13.93	122.1	**88.1**
		2	1.5	27.8	13.90	138.9	**111.0**
		3	1.5	27.9	13.96	118.4	**94.6**
		4	1.6	28.1	14.03	174.4	**130.5**
		5	1.6	28.4	14.20	129.5	**100.6**
	Wet	6	1.8	28.3	14.15	68.0	**41.0**
		7	1.7	28.3	14.15	66.2	**41.8**
		8	1.7	28.2	14.08	78.9	**54.1**
		9	1.7	28.4	14.18	60.5	**40.5**
		10	1.7	28.3	14.17	73.5	**48.0**

Table J.1: (continued) 7 days biaxial flexural strength test results of optimization studies

Mixture no.	Condition	Specimen number	Thickness (mm)	Diameter (mm)	Radius (mm)	P(N)	S (MPa)
23	Dry	1	2.1	27.7	13.84	303.7	**133.9**
		2	2.0	27.6	13.81	266.6	**122.3**
		3	2.2	27.9	13.97	189.4	**73.2**
		4	2.1	27.8	13.90	274.2	**118.6**
		5	2.3	28.1	14.06	293.2	**108.2**
	Wet	6	2.2	27.9	13.95	178.0	**67.5**
		7	2.2	28.0	14.01	185.0	**71.5**
		8	2.3	28.4	14.18	97.6	**35.6**
		9	2.2	28.1	14.03	164.0	**61.1**
		10	2.3	28.1	14.03	89.9	**32.3**
24	Dry	1	1.8	27.7	13.84	233.1	**130.3**
		2	1.8	27.6	13.78	228.0	**126.1**
		3	1.8	27.9	13.94	190.9	**115.2**
		4	1.8	28.0	13.99	244.6	**144.3**
		5	1.8	27.9	13.93	231.1	**130.5**
	Wet	6	2.0	27.9	13.96	-	**-**
		7	2.0	28.1	14.03	140.8	**69.2**
		8	1.9	28.0	14.01	119.0	**61.6**
		9	1.9	28.1	14.03	114.6	**59.3**
		10	2.0	28.0	14.02	104.8	**51.5**
25	Dry	1	1.7	27.3	13.64	198.1	**128.5**
		2	1.7	27.6	13.78	232.4	**159.9**
		3	1.7	27.6	13.80	228.4	**149.8**
		4	1.7	27.6	13.80	179.2	**118.9**
		5	1.6	27.8	13.90	183.9	**131.1**
	Wet	6	1.7	27.9	13.95	98.9	**61.1**
		7	1.7	28.4	14.20	106.5	**65.6**
		8	1.8	27.8	13.91	121.6	**68.7**
		9	1.8	28.1	14.03	85.8	**47.4**
		10	1.8	28.2	14.08	85.8	**47.9**
26	Dry	1	2.0	27.9	13.93	205.1	**94.0**
		2	2.0	28.0	14.01	183.6	**89.3**
		3	1.9	28.1	14.05	252.3	**126.5**
		4	1.9	27.9	13.95	246.3	**131.7**
		5	2.0	27.8	13.89	228.9	**103.9**
	Wet	6	2.0	28.2	14.08	114.8	**52.5**
		7	2.0	28.1	14.07	124.1	**60.3**
		8	2.0	28.2	14.11	113.7	**53.6**
		9	1.9	28.3	14.14	122.6	**60.8**
		10	2.1	28.1	14.07	151.4	**62.9**

Table J.1: (continued) 7 days biaxial flexural strength test results of optimization studies

Mixture no.	Condition	Specimen number	Thickness (mm)	Diameter (mm)	Radius (mm)	P(N)	S (MPa)
27	Dry	1	2.2	28.0	14.00	338.7	**129.6**
		2	2.2	27.9	13.95	257.8	**100.5**
		3	2.3	28.0	14.02	323.3	**117.2**
		4	2.5	27.8	13.92	271.8	**82.0**
		5	2.2	27.8	13.90	343.7	**131.6**
	Wet	6	2.5	28.1	14.06	191.5	**55.9**
		7	2.7	27.9	13.94	107.9	**28.5**
		8	2.8	28.1	14.05	103.1	**25.5**
		9	2.3	28.0	14.00	213.9	**75.6**
		10	2.3	28.1	14.04	220.5	**77.9**
28	Dry	1	1.7	28.0	13.99	201.2	**124.3**
		2	1.6	28.0	13.99	213.4	**150.1**
		3	1.7	27.9	13.97	178.1	**117.9**
		4	1.7	27.9	13.94	168.3	**105.2**
		5	1.7	28.2	14.09	191.4	**123.7**
	Wet	6	1.8	28.0	14.01	102.6	**58.5**
		7	2.0	28.1	14.05	51.8	**24.7**
		8	1.9	27.9	13.97	114.7	**59.4**
		9	1.9	27.9	13.97	121.9	**64.5**
		10	1.9	28.2	14.12	65.8	**34.7**
29	Dry	1	2.0	27.7	13.84	270.6	**127.9**
		2	2.0	27.7	13.86	250.7	**118.5**
		3	2.0	27.7	13.87	213.2	**96.8**
		4	2.0	27.7	13.84	272.1	**126.1**
		5	2.0	27.9	13.94	215.8	**100.9**
	Wet	6	2.0	27.8	13.92	206.8	**96.7**
		7	2.1	27.9	13.94	161.3	**68.4**
		8	2.0	28.0	13.98	150.4	**70.3**
		9	2.1	27.7	13.83	180.6	**73.8**
		10	2.0	28.2	14.08	217.6	**98.6**
30	Dry	1	1.7	27.9	13.97	156.7	**97.9**
		2	1.7	27.8	13.89	186.1	**123.4**
		3	1.5	27.9	13.94	167.7	**134.0**
		4	1.7	28.0	13.99	181.2	**118.6**
		5	1.6	28.1	14.04	167.4	**125.3**
	Wet	6	1.8	28.1	14.06	68.9	**40.2**
		7	1.8	27.9	13.97	107.4	**64.8**
		8	1.8	27.9	13.96	69.2	**39.9**
		9	1.8	28.1	14.05	86.7	**50.0**
		10	1.9	28.4	14.21	81.6	**42.6**
32	Dry	1	2.1	28.0	14.01	270.8	**110.5**
		2	2.1	27.9	13.93	176.2	**73.3**
		3	2.1	27.9	13.95	242.6	**99.1**
		4	2.4	27.9	13.93	270.3	**90.0**
	Wet	5	2.4	27.8	13.89	153.9	**50.8**
		6	2.4	27.9	13.94	113.8	**37.6**
		7	2.2	28.2	14.08	147.4	**55.4**
		8	2.2	28.1	14.07	153.7	**57.2**

Table J.1: (continued) 7 days biaxial flexural strength test results of optimization studies

Mixture no.	Condition	Specimen number	Thickness (mm)	Diameter (mm)	Radius (mm)	P(N)	S (MPa)
33	Dry	1	1.7	27.9	13.97	162.7	**105.2**
		2	1.7	28.0	14.02	161.7	**107.1**
		3	1.7	28.0	13.98	179.4	**120.2**
		4	1.6	28.0	13.98	158.9	**113.2**
		5	1.6	28.0	13.99	163.9	**121.2**
	Wet	6	1.8	27.9	13.96	83.9	**49.5**
		7	1.7	28.1	14.05	88.7	**58.7**
		8	1.8	27.9	13.93	91.9	**53.7**
		9	1.9	28.0	14.01	88.3	**47.7**
		10	1.8	28.3	14.13	63.9	**36.0**
34	Dry	1	2.1	27.8	13.91	317.3	**135.9**
		2	2.2	27.9	13.94	290.9	**112.4**
		3	2.1	27.7	13.84	299.2	**122.3**
		4	2.2	27.6	13.81	279.9	**110.3**
		5	2.1	27.9	13.93	310.7	**129.3**
	Wet	6	2.2	27.8	13.92	160.1	**60.8**
		7	2.2	27.9	13.97	174.4	**65.0**
		8	2.2	28.0	13.99	146.6	**57.7**
		9	2.2	28.0	14.00	151.2	**56.3**
		10	2.2	28.0	14.00	191.1	**71.2**

Table J.2: 28 days biaxial flexural strength test results of optimization studies

Mixture no.	Condition	Specimen number	Thickness (mm)	Diameter (mm)	Radius (mm)	P(N)	S (MPa)
1	Dry	1	2.0	27.8	13.90	301.9	**142.6**
		2	1.9	27.5	13.75	330.9	**169.9**
		3	2.0	27.6	13.80	261.2	**124.8**
	Wet	4	2.2	27.4	13.70	136.8	**55.0**
		5	2.2	27.8	13.90	123.3	**49.0**
		6	2.1	27.7	13.85	144.8	**61.4**
2	Dry	1	1.8	27.6	13.79	271.2	**150.0**
		2	1.8	27.6	13.78	225.8	**132.0**
	Wet	3	2.1	28.3	14.15	129.7	**56.0**
		4	2.0	27.9	13.93	144.5	**70.4**
		5	2.0	27.8	13.90	110.2	**51.5**
5	Dry	1	2.2	27.8	13.90	398.3	**152.6**
		2	2.2	27.5	13.74	346.9	**135.5**
		3	2.3	27.6	13.78	285.5	**102.9**
		4	2.2	27.7	13.86	450.1	**177.2**
		5	2.3	27.4	13.71	433.0	**160.3**
	Wet	6	2.5	28.0	14.01	103.5	**32.2**
		7	2.4	28.0	13.98	120.3	**40.0**
		8	2.6	28.2	14.09	89.8	**25.6**
		9	2.2	27.8	13.89	149.5	**56.3**
		10	2.4	28.0	14.00	74.6	**24.4**
6	Dry	1	2.3	27.7	13.85	490.8	**173.6**
		2	2.3	27.5	13.76	373.9	**131.2**
		3	2.3	27.6	13.82	451.3	**159.7**
		4	2.2	27.5	13.77	410.1	**154.4**
		5	2.3	27.7	13.83	413.3	**145.0**
	Wet	6	2.5	28.1	14.06	91.9	**26.6**
		7	2.4	28.1	14.05	95.1	**31.1**
		8	2.6	27.9	13.97	119.0	**34.2**
		9	2.4	28.1	14.05	154.0	**51.7**
		10	2.6	27.9	13.97	94.1	**26.6**
7	Dry	1	2.1	27.6	13.80	197.9	**81.7**
		2	1.9	27.5	13.74	246.3	**123.9**
		3	1.9	27.4	13.71	268.7	**138.0**
		4	1.9	27.4	13.70	290.5	**149.2**
		5	1.9	27.5	13.75	226.0	**123.7**
	Wet	6	2.2	27.9	13.95	82.2	**32.6**
		7	2.2	27.9	13.97	83.2	**32.7**
		8	2.3	28.2	14.09	91.3	**33.1**
		9	2.2	28.0	13.98	87.6	**32.9**
		10	2.2	28.1	14.04	78.5	**30.9**

Table J.2: (continued) 28 days biaxial flexural strength test results of optimization studies

Mixture no.	Condition	Specimen number	Thickness (mm)	Diameter (mm)	Radius (mm)	P(N)	S (MPa)
8	Dry	1	1.9	27.5	13.73	254.5	**128.0**
		2	1.9	27.6	13.78	223.3	**114.6**
		3	2.0	27.5	13.73	275.8	**135.9**
		4	1.9	27.6	13.82	298.3	**149.9**
		5	2.0	27.5	13.76	232.4	**114.5**
	Wet	6	2.1	27.7	13.87	123.7	**53.5**
		7	2.2	27.9	13.95	92.2	**35.3**
		8	2.1	27.9	13.96	126.8	**55.9**
		9	2.1	27.8	13.90	110.6	**46.9**
		10	2.1	27.9	13.94	127.7	**52.1**
9	Dry	1	2.0	27.5	13.73	205.5	**100.2**
		2	1.8	27.5	13.74	267.9	**163.9**
		3	1.8	27.6	13.80	244.0	**142.6**
		4	1.8	27.5	13.73	278.1	**157.3**
		5	1.9	27.5	13.74	226.2	**123.8**
	Wet	6	2.1	27.8	13.91	59.9	**26.7**
		7	2.0	27.8	13.89	71.7	**35.3**
		8	2.0	28.1	14.05	32.7	**15.8**
		9	2.1	28.0	13.99	55.6	**23.8**
10	Dry	1	1.9	27.7	13.86	362.8	**186.1**
		2	2.0	27.8	13.88	339.0	**157.0**
		3	1.9	27.4	13.72	376.5	**187.4**
		4	1.9	27.4	13.72	219.8	**115.3**
		5	1.9	27.5	13.74	257.6	**136.5**
	Wet	6	2.3	27.9	13.94	91.0	**33.0**
		7	2.2	27.9	13.94	132.9	**53.8**
		8	2.2	27.7	13.83	-	**-**
		9	2.3	28.0	13.99	-	**-**
		10	2.1	27.7	13.85	115.2	**49.9**
11	Dry	1	1.7	27.6	13.80	207.7	**137.8**
		2	1.7	27.5	13.73	201.2	**138.5**
		3	1.7	27.6	13.78	195.4	**131.2**
		4	1.6	27.6	13.80	204.6	**142.4**
		5	1.7	27.5	13.74	193.3	**128.3**
	Wet	6	1.9	27.7	13.83	91.5	**47.0**
		7	2.0	28.0	13.98	73.1	**34.2**
		8	1.9	28.0	13.98	79.9	**41.4**
		9	1.9	28.0	13.98	78.9	**41.3**
		10	1.9	27.7	13.83	74.2	**39.3**
12	Dry	1	1.5	27.4	13.70	166.2	**148.1**
		2	1.4	27.3	13.63	84.0	**75.9**
		3	1.5	27.4	13.69	164.5	**138.9**
		4	1.5	27.5	13.74	110.8	**96.1**
		5	1.5	27.3	13.67	120.9	**103.5**
	Wet	6	1.8	27.9	13.96	42.1	**23.7**
		7	1.8	27.7	13.83	53.3	**30.5**
		8	1.8	27.9	13.94	56.2	**34.3**
		9	1.9	27.8	13.91	46.6	**25.5**

Table J.2: (continued) 28 days biaxial flexural strength test results of optimization studies

Mixture no.	Condition	Specimen number	Thickness (mm)	Diameter (mm)	Radius (mm)	P(N)	S (MPa)
13	Dry	1	1.8	27.5	13.77	111.4	**67.4**
		2	1.8	27.6	13.81	169.0	**99.9**
		3	1.7	27.5	13.77	126.3	**78.2**
		4	1.8	27.6	13.82	149.8	**82.8**
		5	2.0	27.8	13.91	64.8	**31.2**
	Wet	6	2.0	27.6	13.79	85.9	**42.3**
		7	1.9	28.1	14.04	65.4	**54.8**
		8	2.0	27.8	13.89	82.0	**39.5**
		9	1.8	27.5	13.77	111.4	**67.4**
14	Dry	1	1.7	27.6	13.81	125.8	**82.5**
		2	1.7	27.6	13.82	203.4	**127.2**
		3	1.8	27.7	13.83	186.3	**111.3**
		4	1.7	27.6	13.81	166.7	**114.6**
		5	1.7	27.6	13.82	141.6	**92.8**
	Wet	6	1.8	27.8	13.89	85.7	**49.5**
		7	1.8	28.0	13.99	61.1	**35.7**
		8	1.9	27.8	13.88	85.1	**45.0**
		9	1.8	27.8	13.89	80.3	**47.4**
15	Dry	1	2.0	27.9	13.96	265.7	**121.7**
		2	2.1	28.4	14.18	198.3	**83.9**
		3	2.0	28.3	14.13	226.1	**106.6**
		4	2.1	27.8	13.91	193.1	**82.7**
		5	2.1	27.9	13.95	294.1	**125.9**
	Wet	6	2.3	27.9	13.97	140.4	**51.4**
		7	2.3	28.2	14.09	131.8	**48.6**
		8	2.3	28.1	14.07	141.5	**50.4**
		9	2.2	28.1	14.05	120.1	**48.5**
		10	2.3	28.0	14.02	140.4	**51.8**
16	Dry	1	1.6	27.7	13.87	131.1	**95.9**
		2	1.6	28.0	13.98	121.8	**85.7**
		3	1.5	27.6	13.80	109.5	**88.7**
		4	1.5	28.0	14.00	129.0	**107.1**
		5	1.6	27.8	13.91	152.1	**105.8**
	Wet	6	2.0	28.2	14.11	61.7	**30.3**
		7	1.8	28.1	14.06	56.3	**31.1**
		8	1.9	27.9	13.94	63.0	**34.1**
		9	1.8	28.1	14.04	59.0	**33.6**
17	Dry	1	1.9	27.6	13.82	319.0	**167.2**
		2	2.0	27.8	13.92	312.8	**146.3**
		3	2.0	27.7	13.86	297.6	**133.8**
		4	2.1	27.5	13.75	306.3	**133.9**
		5	2.0	27.7	13.83	244.5	**113.3**
	Wet	6	2.2	27.9	13.95	134.1	**51.8**
		7	2.2	28.0	14.00	104.8	**41.2**
		8	2.0	28.1	14.07	109.5	**49.2**
		9	2.2	28.4	14.20	117.0	**45.1**
		10	2.3	28.0	14.00	126.0	**44.5**

Table J.2: (continued) 28 days biaxial flexural strength test results of optimization studies

Mixture no.	Condition	Specimen number	Thickness (mm)	Diameter (mm)	Radius (mm)	P(N)	S (MPa)
18	Dry	1	1.7	27.7	13.83	131.2	**82.1**
		2	1.7	27.7	13.87	136.1	**85.1**
		3	1.8	27.7	13.87	171.0	**101.0**
		4	1.7	28.0	13.98	189.1	**118.2**
		5	1.7	27.7	13.83	187.8	**124.5**
	Wet	6	2.0	27.9	13.96	64.7	**30.3**
		7	2.1	28.2	14.12	71.4	**31.1**
		8	2.0	28.0	14.00	76.6	**35.8**
		9	2.0	27.9	13.96	73.1	**34.9**
		10	1.9	28.2	14.12	66.6	**34.4**
19	Dry	1	2.4	28.2	14.08	176.4	**55.8**
		2	2.3	27.9	13.94	191.8	**65.5**
		3	2.2	27.7	13.83	148.1	**56.3**
	Wet	4	2.6	27.7	13.86	109.8	**30.9**
		5	2.6	27.6	13.82	136.5	**38.1**
		6	2.7	27.6	13.82	149.0	**38.8**
20	Dry	1	2.1	28.0	14.02	334.9	**138.0**
		2	2.1	27.9	13.94	353.0	**144.2**
		3	2.1	27.8	13.91	250.1	**105.1**
		4	2.1	27.6	13.80	324.7	**135.3**
		5	2.1	27.5	13.73	304.3	**135.7**
	Wet	6	2.3	28.4	14.19	119.1	**40.6**
		7	2.4	28.2	14.12	121.9	**38.6**
		8	2.4	28.3	14.15	115.5	**37.1**
		9	2.4	28.5	14.23	98.1	**31.8**
		10	2.4	28.0	14.02	104.4	**35.0**
21	Dry	1	2.5	27.5	13.73	159.0	**46.2**
		2	2.5	27.4	13.72	150.6	**43.7**
		3	2.6	27.6	13.78	125.6	**35.3**
		4	2.6	27.4	13.68	116.1	**33.5**
		5	2.6	28.1	14.05	111.7	**31.1**
	Wet	6	2.7	28.0	14.00	56.8	**14.9**
		7	2.7	28.0	14.00	42.1	**10.9**
		8	2.6	28.3	14.16	130.3	**34.9**
		9	2.7	28.5	14.23	146.0	**36.8**
22	Dry	1	1.6	27.8	13.88	105.1	**78.8**
		2	1.6	28.0	14.01	123.3	**85.7**
		3	1.6	28.1	14.05	178.0	**129.9**
		4	1.6	27.9	13.93	146.2	**104.2**
		5	1.5	28.0	14.00	174.9	**137.8**
	Wet	6	1.7	27.9	13.96	52.0	**32.5**
		7	1.8	28.0	13.99	55.2	**30.8**
		8	1.8	28.3	14.14	49.8	**27.7**
		9	1.8	28.2	14.09	54.0	**31.5**
		10	1.8	28.0	13.99	49.3	**27.5**

Table J.2: (continued) 28 days biaxial flexural strength test results of optimization studies

Mixture no.	Condition	Specimen number	Thickness (mm)	Diameter (mm)	Radius (mm)	P(N)	S (MPa)
23	Dry	1	2.1	27.9	13.94	320.6	**134.7**
		2	2.1	27.8	13.90	269.2	**113.1**
		3	2.1	27.9	13.96	308.4	**127.1**
		4	2.2	28.0	14.01	282.9	**105.4**
	Wet	5	2.2	28.1	14.07	154.5	**59.6**
		6	2.2	27.9	13.94	146.2	**57.0**
		7	2.3	27.9	13.95	141.8	**51.0**
		8	2.4	28.3	14.13	132.9	**43.5**
24	Dry	1	1.8	28.0	13.99	261.2	**152.4**
		2	1.8	27.9	13.95	197.8	**109.3**
		3	1.7	27.9	13.94	223.6	**139.7**
		4	1.7	28.0	14.00	248.0	**158.5**
		5	1.8	27.8	13.88	263.5	**153.9**
	Wet	6	2.0	28.0	14.02	107.4	**51.7**
		7	2.0	28.1	14.05	98.6	**47.9**
		8	2.0	28.1	14.04	106.3	**49.2**
		9	2.0	28.0	13.99	82.5	**40.2**
		10	2.0	28.0	13.99	116.3	**53.8**
25	Dry	1	1.7	28.0	13.99	246.5	**152.2**
		2	1.8	27.7	13.87	249.6	**152.5**
		3	1.9	27.9	13.95	201.3	**110.0**
		4	1.7	28.0	13.99	203.5	**127.1**
		5	1.8	27.9	13.95	169.6	**102.4**
	Wet	6	2.1	28.3	14.13	84.0	**37.3**
		7	2.0	28.3	14.15	90.7	**43.2**
		8	1.9	28.3	14.13	97.1	**48.7**
		9	2.0	28.1	14.05	93.9	**42.6**
		10	2.0	28.2	14.12	100.2	**45.0**
26	Dry	1	1.9	27.9	13.97	281.8	**147.5**
		2	1.9	28.0	14.00	195.9	**97.3**
		3	2.0	27.7	13.85	243.3	**119.8**
		4	1.9	28.0	13.99	243.6	**121.0**
		5	2.0	27.9	13.96	230.0	**111.9**
	Wet	6	2.1	28.3	14.15	86.1	**37.1**
		7	2.1	28.2	14.11	94.9	**39.1**
		8	2.1	28.2	14.08	103.5	**45.1**
		9	2.1	28.3	14.13	91.8	**39.6**
		10	2.1	28.4	14.22	99.1	**43.2**
27	Dry	1	2.2	27.8	13.92	346.2	**132.6**
		2	2.5	27.6	13.82	242.4	**74.4**
		3	2.4	28.1	14.07	287.3	**91.6**
		4	2.3	27.9	13.97	246.8	**88.8**
		5	2.1	27.9	13.94	293.0	**123.1**
	Wet	6	2.4	28.0	14.00	188.2	**60.1**
		7	2.4	28.0	13.99	103.6	**33.9**
		8	2.6	28.0	13.99	156.8	**44.7**
		9	2.6	28.0	13.98	145.1	**39.5**
		10	2.6	27.8	13.91	146.5	**40.8**

Table J.2: (continued) 28 days biaxial flexural strength test results of optimization studies

Mixture no.	Condition	Specimen number	Thickness (mm)	Diameter (mm)	Radius (mm)	P(N)	S (MPa)
28	Dry	1	1.8	27.7	13.85	189.7	**113.3**
		2	1.8	27.8	13.91	182.1	**106.3**
		3	1.7	28.0	14.01	201.7	**130.4**
		4	1.7	27.7	13.85	199.4	**127.7**
		5	1.7	28.0	14.02	199.4	**123.1**
	Wet	6	1.9	28.0	13.98	102.2	**51.3**
		7	2.0	28.2	14.08	86.7	**39.3**
		8	2.0	28.2	14.09	85.3	**41.9**
		9	1.9	28.2	14.09	104.3	**53.4**
		10	2.0	28.2	14.09	94.2	**45.8**
29	Dry	1	1.9	28.0	13.99	214.6	**106.6**
		2	1.9	27.8	13.89	275.0	**142.5**
		3	2.0	27.7	13.84	198.9	**96.9**
		4	2.0	28.0	14.01	135.0	**63.1**
		5	2.0	27.6	13.82	274.5	**135.1**
	Wet	6	2.2	28.0	14.01	96.3	**38.6**
		7	2.2	28.2	14.11	114.4	**45.8**
		8	2.1	28.2	14.08	101.9	**42.8**
		9	2.1	28.0	13.98	109.8	**47.0**
		10	2.2	27.9	13.95	139.9	**55.1**
30	Dry	1	1.7	27.7	13.84	181.1	**118.7**
		2	1.6	27.7	13.86	193.7	**134.8**
		3	1.6	27.8	13.88	106.6	**79.9**
		4	1.7	27.9	13.96	169.6	**104.7**
		5	1.7	28.0	13.99	141.2	**91.3**
	Wet	6	2.0	28.2	14.08	63.3	**29.5**
		7	1.9	28.0	14.00	54.9	**29.3**
		8	2.0	28.1	14.03	57.3	**28.1**
		9	1.8	28.2	14.10	58.2	**35.1**
		10	1.9	28.2	14.11	69.4	**34.4**
32	Dry	1	2.2	27.9	13.95	228.8	**91.7**
		2	2.4	27.6	13.80	248.7	**82.9**
		3	2.2	27.8	13.90	225.2	**89.5**
		4	2.2	27.8	13.89	302.5	**119.1**
	Wet	5	2.7	27.9	13.97	122.7	**32.7**
		6	2.6	27.8	13.88	75.7	**20.9**
		7	2.4	28.0	14.02	139.8	**43.9**
		8	2.2	27.8	13.92	147.7	**56.5**
33	Dry	1	1.7	27.8	13.90	175.8	**115.1**
		2	1.7	27.7	13.85	176.5	**110.3**
		3	1.7	27.9	13.96	157.5	**106.9**
		4	1.7	27.9	13.94	157.1	**102.9**
		5	1.7	28.0	14.00	168.4	**105.2**
	Wet	6	1.7	28.2	14.08	72.8	**44.9**
		7	1.9	28.1	14.05	81.3	**44.4**
		8	1.9	28.0	14.00	68.1	**37.2**
		9	1.9	28.1	14.06	73.9	**38.6**

Table J.2: (continued) 28 days biaxial flexural strength test results of optimization studies

Mixture no.	Condition	Specimen number	Thickness (mm)	Diameter (mm)	Radius (mm)	P(N)	S (MPa)
34	Dry	1	2.1	28.0	14.00	295.9	**130.3**
		2	2.1	27.9	13.94	287.5	**117.4**
		3	2.2	27.9	13.94	278.3	**109.5**
		4	2.1	27.7	13.85	285.3	**123.4**
		5	2.1	27.8	13.88	237.9	**102.9**
	Wet	6	2.2	27.9	13.94	127.7	**47.6**
		7	2.4	28.0	14.02	148.8	**49.5**
		8	2.3	27.9	13.94	140.6	**48.4**
		9	2.2	27.9	13.94	145.0	**55.0**
		10	2.2	27.9	13.96	138.9	**52.7**

APPENDIX K

Table K.1: 7 days biaxial flexural strength test results of MDF cements produced with epoxy resin

Mixture no.	Condition	Specimen number	Thickness (mm)	Diameter (mm)	Radius (mm)	P(N)	S (MPa)
B0	Dry	1	1.6	28.0	14.02	202.3	**140.6**
		2	1.6	28.1	14.03	187.6	**136.9**
		3	1.6	28.0	13.98	191.9	**138.4**
		4	1.7	28.1	14.05	185.0	**125.4**
	Wet	5	1.7	28.0	14.01	129.1	**80.6**
		6	1.7	28.1	14.04	153.8	**103.0**
		7	1.8	28.0	14.02	65.6	**37.8**
		8	1.7	28.0	14.01	140.8	**94.4**
		9	1.6	28.0	14.01	118.4	**82.3**
B1	Dry	1	2.0	28.0	13.98	245.2	**115.7**
		2	1.9	27.9	13.94	164.7	**82.7**
		3	2.0	28.0	14.01	261.1	**128.4**
		4	2.0	28.0	14.02	242.5	**114.5**
		5	2.0	28.0	14.01	271.9	**123.3**
	Wet	6	2.3	27.9	13.97	123.3	**45.1**
		7	2.1	28.0	13.99	281.6	**124.0**
		8	2.0	28.0	13.98	265.5	**127.9**
		9	2.1	27.9	13.94	237.3	**105.6**
		10	2.1	28.0	14.02	230.3	**95.8**
B3	Dry	1	1.7	28.0	13.98	181.0	**121.3**
		2	1.7	27.8	13.90	173.3	**116.3**
		3	1.7	27.8	13.90	150.9	**93.2**
		4	1.7	28.0	13.99	169.3	**108.2**
		5	1.7	28.0	14.01	171.0	**116.0**
	Wet	6	1.9	28.0	14.00	96.2	**52.5**
		7	1.8	27.9	13.94	117.9	**67.3**
		8	1.7	28.0	13.99	126.7	**78.2**
		9	1.8	27.9	13.95	155.9	**95.2**
		10	1.8	27.9	13.97	172.2	**102.8**
B5	Dry	1	1.7	27.9	13.97	158.0	**103.4**
		2	1.6	27.9	13.97	160.0	**115.4**
		3	1.7	27.9	13.95	113.8	**76.3**
		4	1.6	28.0	14.01	160.8	**116.0**
		5	1.6	27.8	13.88	144.7	**104.4**
	Wet	6	1.6	28.1	14.03	51.4	**38.5**
		7	1.7	28.0	14.01	138.9	**95.3**
		8	1.6	27.9	13.96	100.5	**74.3**
		9	1.6	28.1	14.04	113.7	**82.0**
		10	1.6	28.1	14.05	146.5	**111.1**

Table K.1: (continued) 7 days biaxial flexural strength test results of MDF cements produced with epoxy resin

Mixture no.	Condition	Specimen number	Thickness (mm)	Diameter (mm)	Radius (mm)	P(N)	S (MPa)
B10	Dry	1	1.6	27.9	13.94	97.8	**71.5**
		2	1.6	28.0	14.00	98.0	**71.5**
		3	1.5	27.8	13.90	72.2	**61.7**
		4	1.7	27.7	13.83	87.3	**55.9**
		5	1.6	28.0	13.99	95.3	**66.3**
	Wet	6	1.6	28.0	13.99	83.5	**58.1**
		7	1.7	27.9	13.93	85.8	**55.5**
		8	1.6	27.9	13.97	84.7	**58.9**
		9	1.6	28.1	14.04	91.5	**66.0**
		10	1.5	28.0	13.98	89.4	**70.5**

Table K.2: 7 days biaxial flexural strength test results of MDF cements produced with epoxy resin for reproducubility

Mixture no.	Condition	Specimen number	Thickness (mm)	Diameter (mm)	Radius (mm)	P(N)	S (MPa)
B05	Dry	1	1.7	27.9	13.94	158.1	**102.3**
		2	1.7	27.8	13.90	170.5	**113.0**
		3	1.7	27.8	13.89	141.5	**97.3**
		4	1.7	28.0	13.99	186.6	**128.1**
		5	1.6	28.0	13.98	206.2	**136.2**
	Wet	6	1.7	28.1	14.04	130.0	**87.1**
		7	1.7	28.1	14.07	115.9	**75.8**
		8	1.7	28.0	14.02	118.5	**73.1**
		9	1.7	28.1	14.04	116.9	**73.0**
		10	1.7	28.2	14.08	140.4	**88.7**
B1	Dry	1	1.7	27.9	13.97	195.7	**123.7**
		2	1.7	27.8	13.92	205.3	**128.3**
		3	1.7	27.8	13.90	214.9	**139.1**
		4	1.8	27.9	13.93	197.2	**120.4**
		5	1.7	27.9	13.95	187.3	**115.7**
	Wet	6	1.7	28.1	14.07	119.1	**73.5**
		7	1.8	28.0	14.02	91.8	**50.7**
		8	1.7	27.9	13.97	128.4	**85.1**
		9	1.9	28.1	14.06	79.8	**41.7**
		10	1.8	28.0	14.02	106.1	**61.9**
B1.5	Dry	1	2.0	27.8	13.90	271.1	**128.1**
		2	1.9	27.9	13.95	288.1	**143.1**
		3	1.9	27.9	13.96	263.2	**130.8**
		4	1.9	28.0	13.99	247.7	**123.0**
		5	2.0	28.0	14.02	213.4	**100.7**
	Wet	6	2.1	28.1	14.05	114.3	**48.4**
		7	2.0	27.9	13.93	122.3	**57.2**
		8	2.0	27.8	13.92	226.0	**103.6**
		9	2.0	27.8	13.90	250.3	**115.9**
		10	2.1	28.0	13.98	111.6	**45.5**
B2	Dry	1	2.0	28.0	13.98	239.3	**116.5**
		2	1.9	27.9	13.93	245.7	**123.3**
		3	2.0	27.9	13.97	281.9	**135.8**
		4	1.9	27.9	13.94	156.6	**83.8**
		5	1.8	27.8	13.91	257.1	**146.8**
	Wet	6	2.0	28.0	13.99	163.4	**77.9**
		7	2.0	28.0	14.01	109.2	**52.6**
		8	1.9	27.9	13.93	133.3	**67.6**
		9	1.9	27.8	13.90	177.7	**88.3**
		10	2.0	28.0	14.02	116.2	**53.7**

Table K.2: (continued) 7 days biaxial flexural strength test results of MDF cements produced with epoxy resin for reproducibility

Mixture no.	Condition	Specimen number	Thickness (mm)	Diameter (mm)	Radius (mm)	P(N)	S (MPa)
B4	Dry	1	1.7	27.8	13.88	147.3	**98.8**
		2	1.6	27.7	13.85	152.0	**108.4**
		3	1.7	27.9	13.93	132.6	**85.8**
		4	1.8	27.9	13.96	151.9	**91.7**
		5	1.8	27.9	13.96	156.7	**95.7**
	Wet	6	1.9	28.3	14.17	56.1	**28.4**
		7	1.7	27.9	13.97	88.9	**56.8**
		8	1.7	28.0	14.02	96.7	**61.1**
		9	1.7	28.0	13.98	108.4	**70.1**
		10	1.9	28.2	14.08	54.6	**28.3**

APPENDIX L

Table L.1: Biaxial flexural strength test results of MDF cements produced with nanosilica

Mixture no.	Condition	Specimen number	Thickness (mm)	Diameter (mm)	Radius (mm)	P(N)	S (MPa)
N0	Dry	1	2.1	27.9	13.97	315.7	**128.9**
		2	2.3	27.8	13.91	321.6	**111.8**
		3	2.2	28.0	13.98	409.4	**159.6**
		4	2.2	27.9	13.95	326.1	**121.5**
		5	2.1	27.9	13.96	356.2	**149.6**
	Wet	6	2.3	28.0	14.01	287.3	**100.6**
		7	2.4	28.0	14.01	191.3	**64.7**
		8	2.3	27.9	13.95	202.2	**70.9**
		9	2.4	28.0	14.02	137.8	**46.2**
		10	2.3	28.0	13.99	355.0	**122.2**
N005	Dry	1	2.0	28.0	13.98	301.4	**135.4**
		2	2.3	27.9	13.97	256.8	**92.3**
		3	2.1	27.6	13.80	276.2	**114.0**
		4	2.3	27.9	13.94	349.2	**124.5**
		5	2.1	27.8	13.89	249.1	**109.8**
	Wet	6	2.3	28.1	14.05	124.6	**43.2**
		7	2.2	27.9	13.93	216.0	**83.5**
		8	2.5	28.0	13.98	102.4	**30.4**
		9	2.1	27.7	13.86	255.5	**105.4**
		10	2.3	27.7	13.87	206.9	**73.8**
N010	Dry	1	2.0	27.9	13.94	281.0	**132.7**
		2	2.1	28.0	14.00	305.7	**130.8**
		3	1.9	28.0	14.02	296.7	**148.8**
		4	2.2	27.8	13.91	365.5	**146.5**
		5	2.2	28.1	14.05	346.2	**137.4**
	Wet	6	2.0	28.0	13.99	347.8	**165.9**
		7	2.1	28.1	14.03	286.5	**123.8**
		8	2.1	28.0	14.01	70.8	**30.3**
		9	2.0	27.8	13.91	305.1	**137.2**
		10	2.1	28.0	14.02	215.8	**90.6**
N015	Dry	1	2.0	27.8	13.91	237.3	**116.7**
		2	1.9	28.0	14.01	260.0	**139.0**
		3	1.9	27.9	13.97	233.5	**126.2**
		4	1.9	28.0	14.00	219.8	**116.2**
		5	1.8	27.9	13.97	240.3	**138.7**
	Wet	6	1.9	27.8	13.89	219.6	**117.5**
		7	1.8	28.0	13.99	204.3	**112.8**
		8	2.0	28.0	13.98	153.4	**71.7**
		9	2.1	27.9	13.93	141.8	**62.5**
		10	1.8	28.0	13.99	242.4	**133.8**

Table L.1: (continued) Biaxial flexural strength test results of MDF cements produced with nanosilica

Mixture no.	Condition	Specimen number	Thickness (mm)	Diameter (mm)	Radius (mm)	P(N)	S (MPa)
N020	Dry	1	1.9	27.8	13.90	204.1	**101.5**
		2	1.9	27.8	13.91	230.8	**123.5**
		3	2.0	28.1	14.04	245.8	**120.8**
		4	1.9	27.8	13.90	213.5	**106.2**
		5	1.8	27.9	13.95	277.9	**160.4**
	Wet	6	1.9	28.0	13.99	200.6	**102.8**
		7	2.0	28.0	14.02	189.1	**89.3**
		8	2.0	28.0	14.01	153.6	**71.8**
		9	1.9	27.8	13.89	275.5	**147.4**
		10	1.9	27.9	13.94	266.7	**138.2**
N025	Dry	1	1.9	27.8	13.89	244.5	**124.1**
		2	1.8	27.9	13.94	203.6	**117.5**
		3	1.8	28.0	13.99	261.9	**159.9**
		4	1.9	27.9	13.95	268.6	**140.6**
		5	1.7	27.9	13.96	253.1	**156.3**
	Wet	6	1.9	27.8	13.89	161.0	**82.6**
		7	1.8	28.0	14.01	250.6	**143.0**
		8	1.9	27.9	13.93	207.7	**112.3**
		9	2.0	27.9	13.94	144.1	**68.7**
		10	1.9	27.8	13.91	151.6	**78.6**
N030	Dry	1	1.8	28.0	13.98	251.5	**150.1**
		2	1.7	27.9	13.97	247.5	**154.6**
		3	1.7	28.2	14.10	237.2	**151.5**
		4	1.8	28.1	14.03	226.3	**133.5**
		5	1.9	28.0	14.00	235.7	**118.3**
	Wet	6	1.8	27.8	13.90	176.0	**102.8**
		7	1.9	28.0	14.02	159.0	**80.6**
		8	1.9	28.1	14.03	230.4	**119.3**
		9	1.9	28.0	14.01	144.2	**71.6**
		10	1.9	28.1	14.05	149.2	**74.8**
N035	Dry	1	2.1	27.9	13.95	271.1	**117.2**
		2	2.0	27.9	13.93	281.7	**137.2**
		3	2.0	27.6	13.81	285.8	**128.6**
		4	2.2	27.9	13.96	271.5	**109.8**
		5	2.1	27.7	13.86	205.5	**88.9**
	Wet	6	2.2	28.0	14.00	132.8	**51.3**
		7	2.1	28.0	13.99	136.5	**57.9**
		8	2.1	27.9	13.96	195.6	**79.9**
		9	2.0	27.8	13.91	190.6	**86.5**
		10	2.2	27.9	13.93	194.7	**77.3**
N040	Dry	1	2.1	27.8	13.91	304.6	**131.7**
		2	2.2	27.8	13.88	308.0	**124.7**
		3	2.2	27.9	13.94	295.3	**116.2**
		4	2.2	27.7	13.87	220.2	**87.5**
		5	2.1	27.8	13.91	283.4	**124.9**
	Wet	6	2.2	27.9	13.93	224.9	**88.5**
		7	2.2	27.9	13.96	216.4	**83.6**
		8	2.2	27.6	13.81	219.2	**83.3**
		9	2.2	27.6	13.81	326.0	**129.6**
		10	2.2	27.9	13.94	262.3	**106.1**

Table L.2: Biaxial flexural strength test results of MDF cements produced with nanosilica for reproducubility

Mixture no.	Condition	Specimen number	Thickness (mm)	Diameter (mm)	Radius (mm)	P(N)	S (MPa)
N1	Dry	1	2.1	27.9	13.93	377.9	**161.8**
		2	2.1	27.9	13.93	376.9	**158.3**
		3	2.1	27.9	13.97	314.8	**134.8**
		4	2.1	28.0	14.00	341.2	**144.6**
		5	2.1	27.9	13.93	390.4	**165.6**
	Wet	6	2.1	28.1	14.04	200.4	**84.9**
		7	2.2	28.0	14.01	177.4	**71.1**
		8	2.1	28.0	14.02	211.2	**90.4**
		9	2.1	27.9	13.93	239.0	**97.6**
		10	2.0	27.9	13.95	235.9	**107.0**
N1.5	Dry	1	2.1	28.0	14.00	335.3	**147.7**
		2	1.9	28.0	14.00	271.1	**144.9**
		3	1.9	27.9	13.95	330.4	**165.8**
		4	2.0	28.0	14.01	295.2	**139.3**
		5	2.0	27.9	13.95	298.6	**141.0**
	Wet	6	2.1	28.2	14.08	156.6	**66.3**
		7	2.0	28.0	14.01	301.2	**148.1**
		8	2.0	27.9	13.96	206.1	**93.5**
		9	2.1	28.1	14.03	175.3	**73.6**
		10	2.1	28.0	14.00	151.2	**64.1**
N1.8	Dry	1	2.2	28.0	14.00	333.0	**131.0**
		2	2.2	27.9	13.97	319.4	**129.2**
		3	2.2	28.0	14.01	356.2	**142.7**
		4	2.3	27.9	13.97	354.7	**123.2**
		5	2.3	27.9	13.93	330.9	**114.0**
	Wet	6	2.2	27.9	13.95	225.4	**88.7**
		7	2.4	28.0	14.02	148.7	**50.3**
		8	2.2	28.0	14.00	254.8	**96.6**
		9	2.4	28.2	14.11	76.9	**25.3**
		10	2.2	28.2	14.09	243.1	**94.7**
N2	Dry	1	2.1	27.9	13.96	325.2	**137.9**
		2	2.1	27.8	13.90	359.9	**148.4**
		3	2.1	27.8	13.90	235.4	**98.9**
		4	2.1	27.8	13.92	305.8	**133.5**
		5	2.1	27.9	13.93	289.0	**121.4**
	Wet	6	2.1	28.0	14.02	192.3	**83.1**
		7	2.2	27.7	13.86	102.1	**39.9**
		8	2.1	27.9	13.96	151.8	**65.0**
		9	2.0	27.9	13.95	241.4	**108.5**
		10	2.1	27.8	13.89	242.5	**102.9**

Table L.2: (continued) Biaxial flexural strength test results of MDF cements produced with nanosilica for reproducubility

Mixture no.	Condition	Specimen number	Thickness (mm)	Diameter (mm)	Radius (mm)	P(N)	S (MPa)
N2.2	Dry	1	1.6	28.0	13.98	214.2	**150.7**
		2	1.7	28.0	13.98	209.4	**129.3**
		3	1.8	28.0	14.00	225.8	**128.8**
		4	1.7	27.9	13.94	149.2	**95.4**
		5	1.7	27.9	13.97	216.5	**133.7**
	Wet	6	1.7	28.1	14.05	120.6	**78.9**
		7	1.9	27.9	13.97	85.1	**45.5**
		8	1.8	28.1	14.03	85.9	**50.1**
		9	1.9	28.0	14.02	70.0	**36.2**
		10	1.9	28.1	14.07	82.4	**44.5**
N2.5	Dry	1	2.0	27.7	13.85	332.1	**150.8**
		2	2.0	27.7	13.85	290.3	**133.2**
		3	2.0	27.9	13.96	214.5	**98.3**
		4	2.0	27.8	13.89	312.2	**152.0**
		5	2.0	27.9	13.95	305.8	**147.3**
	Wet	6	2.1	27.8	13.88	167.9	**73.3**
		7	2.0	27.8	13.91	239.0	**107.4**
		8	2.2	27.8	13.92	122.8	**49.2**
		9	2.0	27.9	13.93	251.5	**115.3**
		10	2.0	28.0	14.01	308.5	**138.5**
N3	Dry	1	2.1	27.7	13.86	304.4	**126.8**
		2	2.1	27.8	13.89	308.0	**128.2**
		3	2.2	27.8	13.88	300.1	**118.1**
		4	2.1	27.7	13.84	341.5	**145.0**
		5	2.2	27.8	13.92	270.2	**108.3**
	Wet	6	2.2	27.8	13.90	223.8	**88.9**
		7	2.2	27.7	13.87	252.0	**98.3**
		8	2.2	27.9	13.93	241.4	**95.0**
		9	2.2	27.8	13.92	215.6	**85.6**
		10	2.2	27.8	13.92	277.7	**112.4**

APPENDIX M

Table M.1: Biaxial flexural strength test results of MDF cements produced with vinylic adhesive

Mixture no.	Condition	Specimen number	Thickness (mm)	Diameter (mm)	Radius (mm)	P(N)	S (MPa)
SK0	Dry	1	1.9	27.9	13.94	253.5	**128.6**
		2	1.9	27.9	13.95	219.1	**113.5**
		3	2.1	27.8	13.91	283.9	**120.4**
		4	2.1	27.9	13.94	233.4	**103.9**
		5	2.0	27.9	13.93	273.8	**133.3**
	Wet	6	2.1	28.0	13.98	158.4	**69.1**
		7	2.0	28.0	14.00	166.9	**75.0**
		8	2.1	28.1	14.03	91.7	**37.8**
		9	2.0	27.8	13.90	124.2	**61.1**
		10	2.0	28.0	14.02	128.8	**58.4**
SK0.1	Dry	1	1.6	27.9	13.96	165.8	**115.3**
		2	1.6	27.8	13.91	159.4	**116.5**
		3	1.6	27.9	13.94	162.1	**112.7**
		4	1.6	27.8	13.92	199.8	**140.6**
		5	1.6	27.7	13.86	131.2	**93.5**
	Wet	6	1.8	28.0	14.02	94.0	**55.4**
		7	1.6	27.9	13.95	135.9	**95.7**
		8	1.7	27.9	13.93	135.6	**92.1**
		9	1.8	28.0	13.98	142.5	**85.0**
		10	1.7	27.9	13.94	143.6	**89.7**
SK0.5	Dry	1	1.6	27.8	13.89	173.4	**122.1**
		2	1.7	27.8	13.90	153.0	**103.9**
		3	1.6	27.8	13.91	164.4	**117.2**
		4	1.6	27.6	13.81	187.3	**132.0**
		5	1.7	27.8	13.90	145.9	**96.7**
	Wet	6	1.8	28.1	14.05	81.0	**47.2**
		7	1.6	28.0	14.01	109.8	**76.3**
		8	1.8	28.1	14.04	75.8	**44.2**
		9	1.7	28.1	14.05	73.1	**47.8**
		10	1.7	28.0	14.01	85.0	**54.9**
SK1	Dry	1	2.0	27.8	13.92	303.7	**143.5**
		2	2.1	27.8	13.89	300.1	**127.3**
		3	1.9	27.8	13.91	208.5	**112.7**
		4	2.0	27.9	13.95	296.6	**145.8**
		5	1.9	27.8	13.88	265.7	**142.2**
	Wet	6	2.1	28.0	14.00	171.1	**74.6**
		7	2.0	28.0	14.00	141.5	**66.8**
		8	2.0	28.0	14.00	134.4	**61.6**
		9	2.0	28.1	14.05	148.4	**67.3**
		10	2.0	28.1	14.03	215.9	**97.9**

Table M.1: (continued) Biaxial flexural strength test results of MDF cements produced with vinylic adhesive

Mixture no.	Condition	Specimen number	Thickness (mm)	Diameter (mm)	Radius (mm)	P(N)	S (MPa)
SK3	Dry	1	1.7	27.8	13.90	189.8	**118.7**
		2	1.7	27.9	13.97	167.5	**109.6**
		3	1.7	27.9	13.97	186.3	**124.9**
		4	1.7	27.8	13.89	185.2	**122.8**
		5	1.6	27.9	13.96	180.2	**125.3**
	Wet	6	1.7	28.3	14.16	60.4	**37.7**
		7	1.8	28.7	14.34	42.6	**23.5**
		8	1.8	28.2	14.10	84.2	**49.1**
		9	1.8	28.3	14.15	77.6	**47.3**
		10	1.8	28.1	14.07	82.7	**47.2**
SK5	Dry	1	1.9	27.9	13.96	188.1	**101.7**
		2	1.9	27.9	13.94	222.3	**117.7**
		3	1.9	27.8	13.91	207.8	**111.2**
		4	1.9	27.8	13.92	230.4	**116.9**
		5	1.8	27.8	13.92	221.0	**126.2**
	Wet	6	1.9	28.5	14.25	96.4	**48.3**
		7	2.1	28.7	14.34	53.0	**22.6**
		8	2.0	28.3	14.13	71.9	**34.6**
		9	2.0	28.4	14.21	52.1	**24.1**
		10	2.1	28.7	14.36	50.5	**22.4**
SK10	Dry	1	2.4	27.9	13.93	401.1	**132.4**
		2	2.4	28.1	14.04	370.9	**122.3**
		3	2.4	27.8	13.91	408.4	**138.3**
		4	2.3	27.9	13.96	405.7	**149.8**
		5	2.3	27.8	13.89	401.1	**141.9**
	Wet	6	2.8	28.7	14.37	120.9	**29.8**
		7	2.7	29.0	14.48	135.3	**35.1**
		8	2.8	28.9	14.43	110.7	**26.5**
		9	2.9	28.9	14.45	110.2	**25.1**
		10	2.7	28.6	14.28	116.3	**29.3**

APPENDIX N

Photographs

Figure N.1: Processing the materials on roller mills

Figure N.2: MDF composite before high shear process

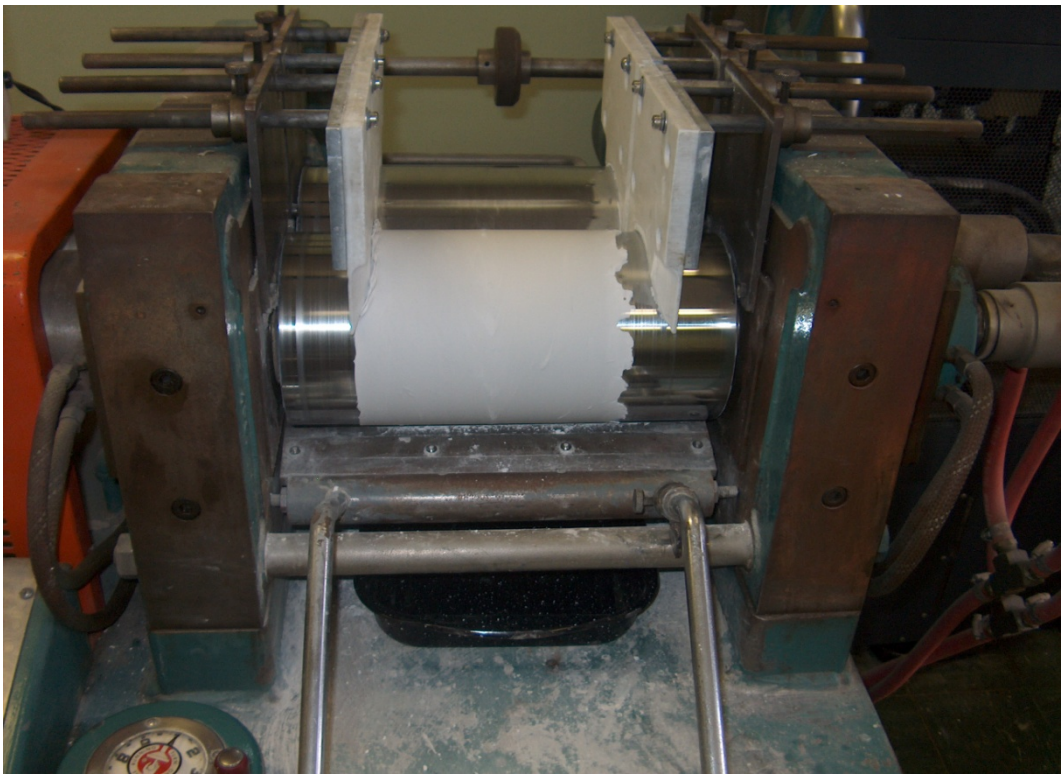

Figure N.3: MDF composite during high shear process

Figure N.4: MDF composite after high shear process

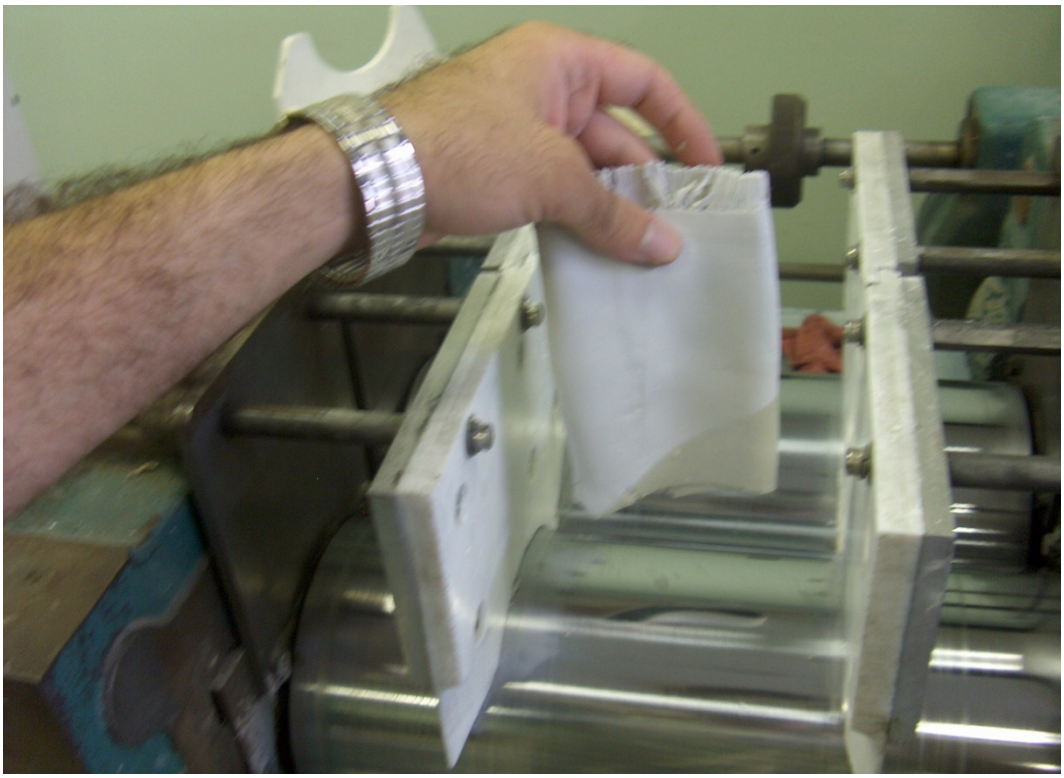

Figure N.5: MDF composite during calendering process

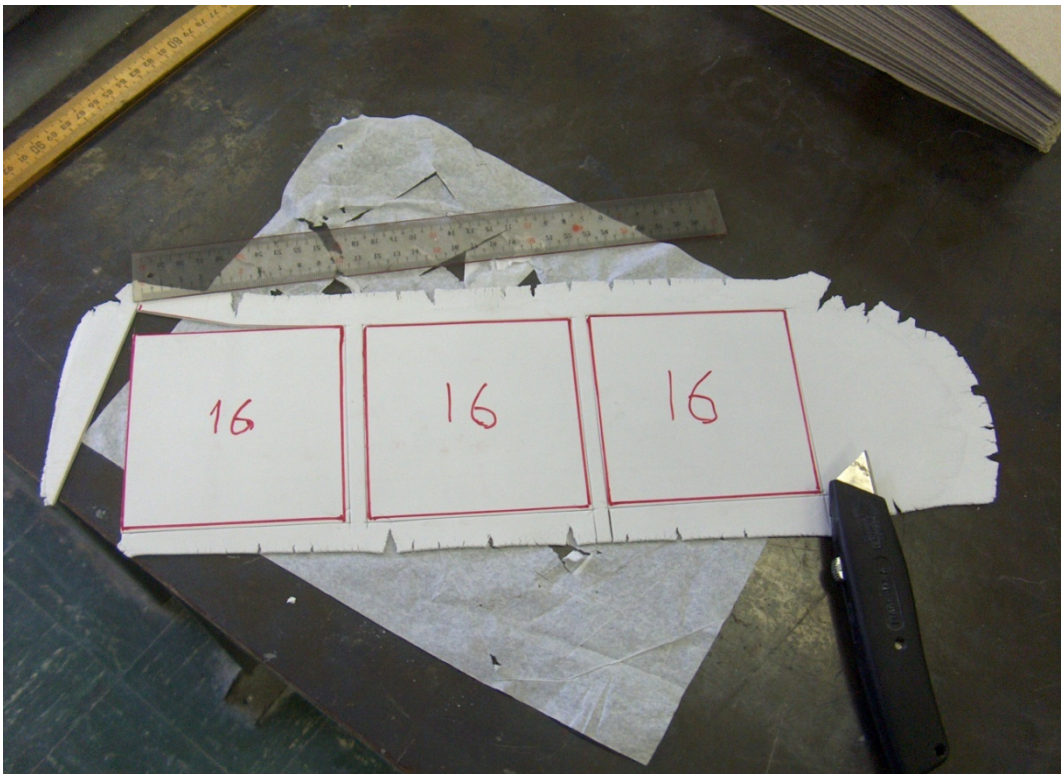

Figure N.6: MDF composite after calendering process

Figure N.7: Biaxial flexural strength test setup

Figure N.8: General view of the MDF cement production room of ITU

CURRICULUM VITAE

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Publications:

Papers in International Conferences

1. **Patachia, S., Moise, G., Özkul, M.H., Ekincioğlu, Ö., Croitoru, C.,** 2008. Morphologycal Characterization of High Alumina Cement Based Macro Defect Free Cements, *Bulletin of the Transilvania University of Brasov*, Vol. **1 (50)**, pp.251-254, ISSN 2065-2119.

2. **Patachia, S., Moise, G., Özkul, M.H., Ekincioğlu, Ö., Croitoru, C.,** 2008. Influence of the Obtaining Technology on the Macro Defect Free Cements Characteristics, Fourth International PhD Symposium in Engineering, Pecs, Hungary, Oct 20-21, **accepted**

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7. **Ekincioğlu, Ö., Özkul, M.H., Struble, L.J.,** 2007. A Case Study: Moisture Resistance of Macro Defect Free (MDF) Cements Produced With Different Polyvinyl Alcohol Copolymers, *Bulletin of the Transilvania University of Brasov*-Bramat 2007, Vol. **4**, Feb 22-24, Romania, pp. 331-336.

8. **Ekincioğlu, Ö., Özkul, M.H., Struble, L.J.,** 2006. Moisture Resistance of Macro-Defect-Free Cements, *Materials Science & Technology 2006, Symposium: Advances in Cement-Based Materials: Manufacture, Hydration, Admixture Interaction, Properties, and Degradation,* Oct 15-19, Cincinnati, Ohio, USA.

9. **Ekincioğlu, Ö., Özkul, M.H., Struble, L.J.,** 2006. Role of New PVA Systems to Improve the Moisture Resistance of Macro-Defect-Free Cements, Creating the Foundation for a New Generation, March 08-09**,** Center For Advanced Cement Based Materials, Evanston, Illinois, USA.

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10. **Ekincioğlu, Ö., Özkul, M.H., Struble, L.J.,** 2007. Farklı PVA'larla Üretilen Büyük Boşluklarından Arındırılmış Çimento-Polimer Kompozitlerinin Suya Karşı Dirençlerinin İncelenmesi, 7. Ulusal Beton Kongresi-Prof. Dr. Mehmet Uyan Anısına, Beton Teknolojisinde Gelişmeler ve Uygulamalar, TMMOB İnşaat Mühendisleri Odası, Nov 28-30, pp. 33-42 (in Turkish).

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11. **Ekincioğlu, Ö.,** 2002. Mechanical behavior of cement based composites reinforced with hybrid fibres, Sika Technical Bulletin, Vol **3**, Istanbul, pp. 10-17.