DEVELOPMENT OF HIGH PERFORMANCE SHRINKAGE RESISTANT CONCRETE, USING NOVEL SHRINKAGE COMPENSATING ADMIXTURES

by

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Certificate of Authorship / Originality

I certify that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of requirements for a degree except as fully acknowledged within the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature used are indicated in this thesis.

Pedram Hamedanimojarrad

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List of Abbreviations

APP	Ammonium Polyphosphates
AS	Australian Standards
ASTM	American Society for Testing and Materials
C_2S	Dicalcium Silicate
C_3A	Tricalcium Aluminate
C_3S	Tricalcium Silicate
C_4AF	Tetracalcium Aluminoferrite
CH	Calcium Hydroxide (Portlandite)
C-S-H	Calcium Silicate Hydrate
DTA	Differential Thermal Analysis
DTG	Differential Thermogravimetry
EnAPP	Encapsulated Ammonium Polyphosphates
HAp	Hydroxyapatite
HWR	High-range Water Reducer
ITZ	Interfacial Transition Zone
Ke	Keratin
LOI	Loss on Ignition
Me	Melamine
MePP	Melamine Polyphosphates
OPC	Ordinary Portland Cement
PE	Polyethylene
PVA	Polyvinyl Alcohol

RH	Relative Humidity
SCA	Shrinkage Compensating Admixture
SDT	Simultaneous Differential Thermal
SEM	Scanning Electron Microscopy
SRA	Shrinkage Reducing Admixture
TG	Thermogravimetry
TGA	Thermogravimetric Analysis
Wo	Wollastonite
w/b	Water / binder
w/c	Water / Cement
wt. %	Weight Percent

Abstract

Shrinkage in cementitious materials can bring about major durability issues, beginning with a crack in a restrained section. This phenomenon causes contraction and consequently tensile stresses in the sample, and since the concrete and all conventional cementitious materials are not capable enough to bear tensile stresses, they crack. In conventional concrete, the major contribution to shrinkage strain belongs to drying shrinkage. Therefore, reducing the amount of drying shrinkage in concrete and cement mortars can result in lower total shrinkage strain and therefore, lessen the risk of cracking and ion invasion into the sample.

Shrinkage reducing admixtures (SRA), expansive agents and fibres are currently used in research and industry, in order to reduce the amount of shrinkage in one or more aspects; or at least decrease the risk of shrinkage cracking. Having been used in industry, SRAs and many other shrinkage compensating admixtures have been showing adverse side effects on the physical and mechanical properties of concrete and cement mortars; such as strength reduction and change in rheology.

Therefore, this research project aimed to introduce, investigate and develop new drying shrinkage compensating admixtures with no or limited reduction in mechanical strength, in order to be used in mortar, concrete and cementing compounds. The methodology of current research project was based on examining engineering physical and mechanical properties of OPC mortar samples associated with the addition of these new admixtures. Cementitious material used in this research project was ordinary Portland cement (OPC) mortar instead of concrete samples, in which the coarse aggregates provide more resistant to any expansion or contraction.

Firstly, a novel chemical composition of polyphosphates, Ammonium Polyphosphates (APP) that was designed and produced in Science Faculty of UTS, was adopted in current research. Based on its unique composition, this agent was expected to produce a cementing product (binder) via reaction with calcium hydroxide in the mix, where can enhance mechanical characteristics of the cement mortar and at the same

time generate ammonia gas (or volatile amine, as an anti-corrosion product), and might end up in generating expansion in the mix.

APP was used as an admixture inside OPC mortar samples and resulted in less shrinkage strain and enhanced compressive strength and workability. However, after more investigation it was concluded that the shrinkage compensation of APP could not only be due to the ammonia agent, but it was mainly related to the robust structure of calcium polyphosphate as one of the primary products of APP and calcium hydroxide reaction. This assumption was tested by the means of expansion studies and microstructural tests, and then comprehensively explained in Chapter 4.

On the other hand, APP showed some undesirable aspects such as ammonia odour during mixing. This downside aspect of APP was firstly addressed by encapsulating APP with a superplasticiser, and then by changing the chemical composition of APP to melamine polyphosphate or even testing melamine as an admixture. Encapsulation did not eliminate the ammonia release from the mix completely, but remarkably reduced the rate of ammonia release. Other admixtures however, were subjected to different results, due to different behaviours involved in them, which were not similar to the mechanism of APP in cementitious materials.

As mentioned earlier, fibres are mainly known for their effects on crack resistance rather than their ability to limit the shrinkage. This dissertation has a close look at microfibres as shrinkage resistant admixtures, as expected to be more efficient for their micro-crack bridging. This micro-bridging parameter was supposed to lock in shrinkage immediately as soon as it begins due to moisture loss.

Therefore, polyethylene (PE) microfibre was tested and used as an addition to OPC mortar samples before mixing. Results showed reduction in drying shrinkage, workability and compressive strength. Reduction in moisture loss of PE reinforced specimens suggested that the hydrophobicity of PE microfibres make it a shrinkage reducing admixture, since with considering their dimensions, they can be located in a way to block capillary pores and accordingly avoid moisture loss. Whereas, loss in strength might reveal this phenomenon that PE microfibre could not be efficient in micro-bridging of particles under stress. Another conclusion was that micro-bridging is not the mechanism behind the shrinkage reduction of PE microfibre.

Another admixture used was microfibre of an inosilicate mineral, wollastonite. Its micro-bridging characteristics and its positive influence on some mechanical properties of concrete were the incentives for being used in this research. Wollastonite microfibre reduced the amount of drying shrinkage and for some concentrations; it even enhanced the compressive strength, with no adverse effect on workability. Behavioural test results showed that micro-bridging of wollastonite microfibre can possibly be a reason behind its shrinkage reduction.

Early age behaviour of these admixtures has also been investigated. Current early age experiments and the information that each can give, were studied. A simple experiment was adopted from the literature, and mortar specimens were cast using optimum concentrations of these admixtures. The specimens were stored in a controlled drying environment and monitored for 24 hours. The number of major cracks, the cracking time and the dimensions of cracks have been assessed and analysed. Based on these experiments, APP, PE microfibre and wollastonite microfibre can significantly reduce the number and the size of early age cracks in cementitious materials. APP modified mortar could also delay the cracking time significantly.

This dissertation concludes that APP, PE microfibre and wollastonite microfibre reduce the drying shrinkage and early age cracking potential. APP and wollastonite microfibre have no side effect in mechanical characteristics of OPC mortars. These admixtures not only reduce the drying shrinkage in a cementitious material, but also control the early age cracking. By examining some other chemical compositions of polyphosphates, this thesis concludes that there are still new shrinkage compensating admixtures and mechanisms, which need to be examined and introduced to the industry.

Throughout this PhD research project, a number of conference and journal articles were submitted and published, while there is also one article still under peer review. These publications have been listed under Appendix B of this dissertation and copies of published papers have been attached.

1 Introduction

1.1 Preface

Concrete is the most abundantly used construction material. Based on the amount of cement manufactured every year, it can be estimated that the present consumption of concrete in the world is of the order of 21 to 31 billion tonnes per year. Unlike many other materials, concrete is generally resistant to water and it can be formed in a variety of shapes and sizes. In addition, it is usually the most economical option for structural elements. These advantages have made the concrete a widespread construction material.

Structural and non-structural elements, such as dams, pavements, piles, foundations, footings, floors, beams, columns, roofs, exterior walls, and pipes, are frequently built with plain or reinforced concrete. ASTM terminology relating to concrete and concrete aggregates, C125 (2012) defines concrete as —a composite material that consists essentially of a binding medium within which are embedded particles or fragments of aggregate; in hydraulic-cement concrete, the binder is formed from a mixture of hydraulic cement and water”. In addition, mortar is a mixture of sand, cement, and water. It is considered to be similar to concrete, but without any coarse aggregate.

ASTM C125 also describes —hydraulic cement” as a material —that sets and hardens by chemical reaction with water and is capable of doing so under water”, or as Blezard (1998) describes cement is an adhesive substance capable of uniting fragments or masses of solid matter to a compact whole. The main hydraulic cement used in industry is —Portland Cement”. Portland cement or calcium silicate cement is produced by firing to partial fusion a well-homogenized and finely ground mixture of limestone or chalk (calcium carbonate) and an appropriate quantity of clay or shale, at a temperature of approximately 1500°C (Newman & Choo, 2003).

In addition, —granular material, such as sand, gravel, crushed stone, or iron blast-furnace slag” (ASTM-C125, 2012) are incorporated as the aggregate in concrete. In a conventional Portland cement concrete, aggregate has volume fraction of 70-80% and the remaining volume accommodates matrix of water, cementitious materials, admixtures and air voids (Helmuth & Detwiler, 2006).

Despite their positive factors in construction industry, cement-based materials can be subject to serviceability issues. These issues can vary from deterioration due to sulphate attack, to volume changes due to carbonation or moisture loss. In general, for most of these issues, cement hydration products are involved. Therefore, in order to study the materials aspect of concrete, it is essential to understand the process of cement hydration and its products.

1.2 Cement hydration

Immediately after ordinary Portland cement (OPC) contacts with water, an amorphous, colloidal gel layer, which is rich in alumina, silica, calcium and sulphate, forms on the surfaces of the cement grains (Taylor, 1997). Within a few minutes of cement hydration, the needle-shaped crystals of calcium trisulfoaluminate hydrate, called ettringite, first make their appearance. A few hours later, formation of calcium silicate hydrate (C-S-H) and calcium hydroxide (CH) results in high heat evolution. The CH forms massive prismatic crystals in the originally water-filled space, whereas, small fibrous crystals of C-S-H form a thickening layer around the cement grains.

The hydration of OPC involves the reaction of the anhydrous calcium silicate and aluminate phases with water to form hydrated phases. These solid hydrates occupy more space than the anhydrous particles and the result is a rigid interlocking mass whose porosity is a function of the ratio of water to cement (w/c) in the original mix. Due to its complexity, OPC hydration can be seen by reactions of 1- the silicate phases (C_3S and C_2S) and 2- the aluminate phases (C_3A and C_4AF) separately (Newman & Choo, 2003).

Before setting, two, and sometimes three, kinds of volume changes occur. Based on the phenomenon behind, these volume changes can be caused by settlement, bleeding and plastic shrinkage.

1.2.1 Hydration of silicates

Both C_3S and C_2S react with water to produce an amorphous C–S–H gel, which is the main bonding agent for sand and aggregate particles together in concrete. C_3S is much more reactive than C_2S and at temperature conditions of 20°C half of the C_3S present in typical cement will be hydrated by 3 days and 80% by 28 days. In contrast, the hydration of C_2S does not normally proceed substantially before 14 days of age. The following equations approximately summarize the hydration reactions (Newman & Choo, 2003):

$$C_3S + 4.3H \rightarrow C1.7SH_3 + 1.3CH$$

$$C_2S + 3.3H \rightarrow C1.7SH_3 + 0.3CH$$

1.2.2 Hydration of aluminates

The reactions of laboratory-prepared C_3A and C_4AF with water, alone or in the presence of calcium sulphate and calcium hydroxide, have been extensively studied (Odler, 1998). However, the findings should be interpreted with caution as the composition of the aluminate phases in industrial clinker differs considerably from that in synthetic preparations and hydration in cements is strongly influenced by the much larger quantity of silicates reacting, also by the presence of alkalis.

In the absence of soluble calcium sulphate, C_3A reacts rapidly to form the phases C_2AH_8 and C_4AH_{19}, which subsequently convert to C_2AH_6. This is a rapid and highly exothermic reaction.

If finely ground gypsum ($CaSO_4 \cdot 2H_2O$) or hemihydrate ($CaSO_4 \cdot 0.5H_2O$) is blended with the C_3A prior to mixing with water then the initial reactions are controlled by the formation of a protective layer of ettringite ($C_3A \cdot 3CS \cdot 32H$) on the surface of the C_3A crystals. The reaction can be summarized as:

$$C_3A + 3C + 3S + 32H \rightarrow C_3A \cdot 3CS \cdot 32H \text{ (ettringite)}$$

Notations S represent SO_3 and notations H represent H_2O. In most commercial Portland cements there will be insufficient sulphate available to sustain the formation of ettringite. When the available sulphate has been consumed, the ettringite reacts with C_3A to form a phase with a lower SO_3 content known as monosulphate:

$$C_3A \cdot 3CS \cdot 32H + 2C_3A + 4H \rightarrow 3(C_3A \cdot CS \cdot 12H)$$

Many studies have shown that the hydration of C_4AF (or more correctly the C_2 (A–F) solid solution) is analogous to that of C_3A but proceeds more slowly (Taylor, 1997). The iron enters into solid solution in the crystal structures of ettringite and monosulphate substituting for aluminium. In order to reflect the variable composition of ettringite and monosulphate formed by mixtures of C_3A and C_4AF they are referred to AFt (alumino-ferrite trisulphate hydrate) and AFm (alumino-ferrite monosulphate hydrate) phases, respectively.

The C–S–H gel which forms around the larger C_3S and C_2S grains is formed in situ and has a rather dense and featureless appearance when viewed using scanning electron microscopy (SEM) test (Newman & Choo, 2003).

SEM shows the crystals of $Ca(OH)_2$, AFm/AFt and also C–S–H with a foil- or sheet-like morphology, formed in what was originally water-filled space and also space occupied by the smaller cement grains and by interstitial material (C_3A and C_4AF) (Newman & Choo, 2003). The structure of the outer product is strongly influenced by the initial water-to-cement ratio, which in turn determines paste porosity and consequently strength development. The hydration of Portland cement involves exothermic reactions, i.e. releases heat.

The arrangement of cement hydration products in the matrix creates the structure of the cement-based materials. Durability of the cement-based material depends upon the quality of the microstructure of its cement paste matrix. Thus, the modern method of investigation has been dedicated to the study of concrete microstructure, particularly in hardened state.

1.3 Microstructure in hardened state

Characteristics of cementitious materials can be appraised through their macro- and microstructure. Application of transmission and scanning electron microscopy techniques has made it possible to resolve the microstructure of materials to a fraction of one micrometer and even further. However, the microstructure-property relationships in concrete are not yet fully developed, in particular the involving chemical reactions that happen during cement hydration.

The term macrostructure is generally used for the gross features visible to the human eye. At the macroscopic level, concrete is mostly reflected as a two-phase material, consisting of aggregate particles dispersed in a matrix of cement paste. While at the microscopic level, this categorisation is more complex, due to different unknown reactions of cement hydration.

Properties of hardened cement compositions (mortars and Concrete) are extremely influenced by the developed pores structure. The pores structure reflects the quality and quantity of the formed hydration products, and affects the strength characteristics and permeability of cementitious materials, which directly relates to the material's durability.

Mehta & Monteiro (2006) describe the three components of the concrete microstructure, namely, hydrated cement paste, aggregate, and interfacial transition zone between the cement paste and aggregate by: 1- Interfacial transition zone (ITZ), which represents a narrow region next to the particles of coarse aggregate. Existing as a thin shell, typically 10 to 50 μm thick around large aggregate, the ITZ is generally weaker than either of the two main components of concrete; thus, it exercises a far greater influence on the mechanical behaviour of concrete than is reflected by its volume fraction. 2- Each of the three phases is itself a multiphase in character. For instance, each aggregate particle may contain several minerals in addition to microcracks and voids. Similarly, both the bulk hydrated cement paste and the interfacial transition zone generally contain a heterogeneous distribution of different types and amounts of solid phases, pores, and microcracks, as will be described later. 3- The microstructure of concrete is not an intrinsic characteristic of the material because the two components of the microstructure, namely, the hydrated cement paste and ITZ, are subject to change with time, environmental humidity, and temperature.

In microstructure of mortar and concrete, when OPC is dispersed in water, the calcium sulphate and the high-temperature compounds of calcium begin to go into solution, and the liquid phase becomes rapidly saturated with various ionic species. As a result of interaction between calcium, sulphate, aluminate, and hydroxyl ions within a few minutes of cement hydration, the crystals of calcium trisulfoaluminate hydrate (ettringite) may appear. Then after few hours, the large crystals of CH and very small fibrous crystals of C-S-H replaces water and the dissolving cement particles in empty voids. After some days, depending on the alumina-to-sulphate ratio of the OPC, ettringite may become unstable and will decompose to form monosulfoaluminate hydrate, which has hexagonal plate morphology. Hexagonal-plate morphology is also the characteristic of calcium aluminate hydrates that are formed in the hydrated pastes of either under-sulphated or high-C_3A Portland cements. A scanning electron micrograph illustrating the typical morphology of phases prepared by mixing a calcium aluminate solution with calcium sulphate solution is shown in Figure 1. 1.

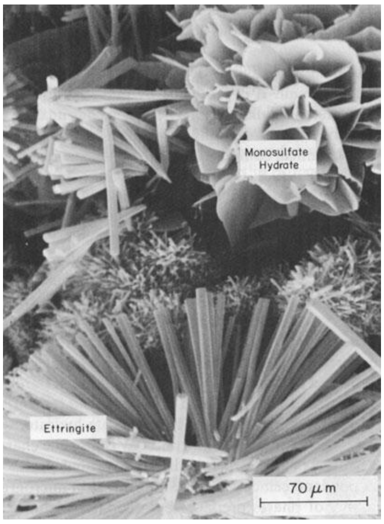


Figure 1. 1. Typical morphology of hydrated OPC phases (Courtesy to Mehta, 2006)

Generally, amounts and characteristics of the four principal solid phases in the hydrated cement paste that can be resolved by an electron microscope are introduced as follows:

Calcium silicate hydrate (C-S-H) builds 50 to 60% of the volume of solids in a completely hydrated Portland cement paste and is, therefore, the most important phase determining the properties of the paste. C-S-H is not a well-defined compound; the C/S ratio can vary between 1.5 and 2.0 and the structural water content varies even more. The morphology of C-S-H also varies from poorly crystalline fibres to reticular network. Due to their colloidal dimensions and a tendency to cluster, C-S-H crystals could only be resolved with the advent of electron microscopy. Although the exact structure of C-S-H is not known, several models have been proposed to explain the properties of the materials. Different models describe different structures for C-S-H (P.K. Mehta & Monteiro, 2006; Taylor, 1997).

Calcium hydroxide (CH) crystals (portlandite) constitute 20 to 25 percent of the volume of solids in the hydrated paste. Unlike C-S-H, calcium hydroxide is a compound with a definite stoichiometry, $Ca(OH)_2$. It also forms large crystals with distinctive hexagonal-prism morphology. Compared with C-S-H, the strength-contributing potential of CH is limited as a result of considerably lower surface area.

Calcium sulfoaluminates hydrates occupy 15 to 20 percent of the solid volume in the hydrated paste and, therefore, play only a minor role in the microstructure-property relationships. It also has been known that during the early stages of hydration the sulphate/alumina ionic ratio of the solution phase generally forms ettringite, which forms needle-shaped prismatic crystals. In pastes of OPC, ettringite eventually transforms to the monosulphate hydrate, which makes the concrete vulnerable to sulphate attack.

Finally, depending on the particle size distribution of the anhydrous cement and the degree of hydration, some unhydrated clinker grains may be found in the microstructure of hydrated cement pastes, even long after hydration. Clinker particles in modern Portland cement generally conform to the size range 1 to 50 μm. With the progress of the hydration process, the smaller particles dissolve first and disappear from the system, then the larger particles become smaller.

In microstructural point of view of mortar and concrete, these cementitious materials contain three major parts in their structure which are explained here: 1- Aggregate phase, 2- Cement paste which mainly contains C-S-H, CH, $C_6AS_3H_{32}$ (ettringite or C_4ASH_{18}) and Unhydrated clinker grains, and 3- Interfacial transition zone (ITZ) which is a small region next to particles of coarse aggregates with 10 to 50 µm thickness.

1.3.1 Voids in the hydrated cement paste

In addition to solids, the hydrated cement paste contains several types of voids which have important influences on its physical and mechanical properties. These voids also affect the shrinkage mechanism of cementitious materials. Based on their dimensions, these voids are generally introduced as:

Interlayer space in C-S-H- Powers (1968) assumed the width of the interlayer space within the C-S-H structure to be 18 Å and determined that it accounts for 28 percent porosity in solid C-S-H; however, Feldman and Sereda (1970) suggested that the space may vary from 5 to 25 Å. Nevertheless, this void size is too small to have any adverse effect on the strength and permeability of the hydrated cement paste. On the other hand, water in these small voids can be held by hydrogen bonding, and its removal under certain conditions may contribute to volume change.

Capillary voids- Capillary voids represent the space not filled by cement or the hydration products. In well-hydrated, low water-cement ratio pastes, the capillary voids may range from 10 to 50 nm; in high w/c ratio pastes, at early ages of hydration, the capillary voids may be as large as 3 to 5 µm. Capillary voids larger than 50 nm, referred to as macro-pores in modern literature, are probably more influential in determining the strength and impermeability characteristics, whereas voids smaller than 50 nm, referred to as micro-pores, play an important part in drying shrinkage and creep.

Air voids- Unlike capillary voids, which are irregular in shape, air voids are generally spherical. A small amount of air is usually trapped in the cement paste during concrete mixing. Entrapped air voids may be as large as 3 mm; entrained air voids usually range from 50 to 200 µm. Therefore, both the entrapped and entrained air voids in the hydrated cement paste are far bigger than the capillary voids, and are capable of adversely affecting the strength.

1.3.2 Water in the hydrated cement paste

Depending on the humidity of the environment and the porosity of the paste, the untreated cement paste is capable of holding a large amount of water. Like the solid and the void phases discussed above, water can exist in the hydrated cement paste in many forms. Water presents in the hydrated cement paste in the following states:

Capillary water is present in voids larger than about 50 Å. It may be considered to be the bulk water that is free from the influence of the attractive forces exerted by the solid surface. Actually, from the standpoint of the behaviour of capillary water in the hydrated cement paste, it is desirable to divide the capillary water into two categories: the water in large voids of the order of >50 nm (0.05 μm), which may be called free water because its removal does not cause any volume change, and the water held by capillary tension in small capillaries (5 to 50 nm), the removal of which may cause shrinkage of the system.

Adsorbed water is the water that is close to the solid surface. Under the influence of attractive forces, water molecules are physically adsorbed onto the surface of solids in the hydrated cement paste. It has been suggested that up to six molecular layers of water (15 Å) can be physically held by hydrogen bonding.

Since the bond energies of the individual water molecules can decrease with distance from the solid surface, a major portion of the adsorbed water can be lost when hydrated cement paste is dried to 30 percent relative humidity.

Interlayer water is associated with the C-S-H structure. It has been suggested (P.K. Mehta & Monteiro, 2006) that a monomolecular water layer between the layers of C-S-H is strongly held by hydrogen bonding. The interlayer water is lost only due to strong drying conditions i.e., below 11% relative humidity. Then the C-S-H structure shrinks considerably when the interlayer water is lost.

Chemically combined water is an integral part of the microstructure of various cement hydration products. This water is not lost on drying; it is evolved when the hydrates decompose on heating.

The actual water content of the paste depends on the ambient RH. In particular, capillary pores because of their comparatively large size, empty when the ambient relative humidity falls below about 45%, but water is absorbed in the gel pores even at very low ambient humidity.

Neville (1995) categorised water in hydrated cement paste based on their degrees of firmness. First is free water that is held in capillaries and is beyond the range of the surface forces of the solid paste; second one is gel water and the last one is chemically combined water forming a definite part of the hydrated compounds.

The water held by the surface forces of the gel particles is called adsorbed water, and the part of it, which is held between the surfaces of certain planes in a crystal is called interlayer or zeolitic water. Lattice water is that part of the water of crystallization, which is not chemically associated with the principal constituents of the lattice.

1.3.3 Microstructure and cement paste characteristics

Main engineering characteristics of hardened cementitious materials such as strength, dimensional stability, and durability are considerably manipulated by microstructural features such as type, amount, size and distribution of solids and voids.

Strength- Small crystals of C-S-H, and hexagonal calcium aluminate hydrates with their substantial surface areas and adhesive capabilities tend to bond strongly to each other and to low surface-area solids, such as CH, anhydrous clinker grains, and fine and coarse aggregates.

Dimensional stability- As soon as the cementitious materials are exposed to relative humidity less that 100%, they begin to lose moisture and shrink, as illustrated in Figure 1. 2 (L'Hermite, 1960). Based on Figure 1. 2, a saturated hydrated cement paste exposed to slightly less than 100% RH can lose a considerable amount of total evaporable water before undergoing any shrinkage.

As soon as the RH drops below 100 percent, the free water held in large cavities (e.g., >50 nm) begins to escape to the environment. Because the free water is not attached to the microstructure of the hydration products by any physical-chemical bonds, its loss is not typically accompanied by shrinkage. Once most of the free water has been lost, further loss of water results in considerable shrinkage. This phenomenon is attributed mainly to the loss of adsorbed water and the water held in small capillaries.

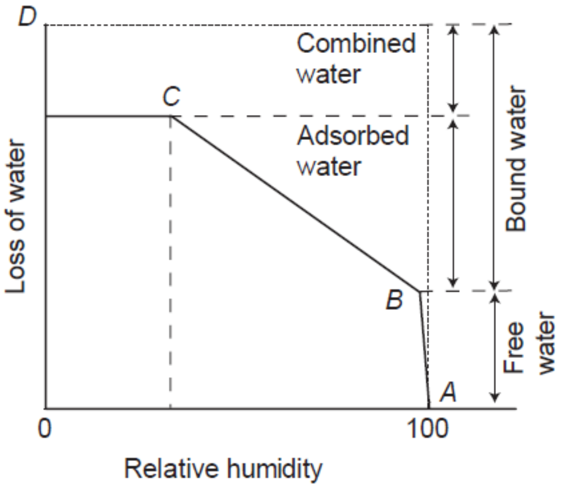


Figure 1. 2. Moisture loss due to change in relative humidity (L'Hermite, 1960)

When confined to narrow spaces between two solid surfaces, the adsorbed water causes disjoining pressure. The removal of the adsorbed water reduces the disjoining pressure and brings about shrinkage of the system. The interlayer water, present as a mono-molecular water film within the C-S-H layer structure, can also be removed due to severe drying conditions. Because the water in small capillaries (5 to 50 nm) exerts hydrostatic tension, its removal tends to induce a compressive stress on the solid walls of the capillary pore, thus also causing contraction of the system.

Durability- Impermeability, or watertightness, becomes a primary factor in determining the durability. Size and continuity of the pores in the microstructure of the solid would determine its permeability.

It has numerously been stated that w/c ratio and the degree of hydration determine the total capillary porosity, which decreases with the decreasing water-cement ratio and/or increasing degree of hydration (P.K. Mehta & Monteiro, 2006; Neville, 1995).

1.4 Shrinkage

Shrinkage of concrete is defined as time-dependent strain measured in an unloaded and unrestrained specimen at constant temperature (Kovler & Zhutovsky, 2006) and it is not meant to cover length change due to temperature variations (ACI, 2009a).

Shrinkage is assumed to approach a final value, as time approaches infinity (Kovler & Zhutovsky, 2006).

Cementitious materials can also shrink in fresh state. During this period, volume change occurs due to cement hydration, water evaporation, thermal change, absorption and bleeding which are all categorised as plastic shrinkage.

When a cementitious material is constantly stored at 100% RH or sunk under water, it adsorbs moisture and swells. When the change in volume by shrinkage or by swelling is restrained, stresses develop. In reinforced concrete structures, the restraint may be provided by the reinforcing steel, the supports or by the difference in volume change of various parts of the structure.

Drying shrinkage of concrete is dependent on the relative humidity, temperature, type and quantity of the binder, air content, the water content and water to cement ratio, the ratio of fine to coarse aggregate, the type, grading and quantity of the aggregate, admixtures, curing and the size and shape of the member (ACI, 2009a; Kovler & Zhutovsky, 2006). However, the difference between plastic shrinkage, autogenous shrinkage, chemical shrinkage and drying shrinkage should be considered.

Shrinkage, its mechanisms and its effects will be thoroughly discussed in Chapter 2.

1.4.1 Other physical and mechanical properties of concrete

Cement-based materials are usually assessed by their fresh state as well as hardened stated characterisations. Fresh state characteristics of concrete and mortar mainly include workability or flow, fresh density, setting time and air content. While, permeability, different mechanical strengths such as compressive, tensile and flexural, creep, shrinkage and its behaviour to attacking chemicals create its hardened state characters.

This research mainly studies on the shrinkage reduction of samples. Several causes result volume change in cementitious materials.

1.5 Research Objectives

The main aim of this research is to investigate and develop new drying shrinkage compensating materials for use in mortar, concrete and cementing systems, by examining engineering physical and mechanical properties associated with the addition of new agents.

The two principal objectives of this research are:

- To review current shrinkage compensating / reducing admixtures, then design new admixtures or reuse the current admixtures with potential of drying shrinkage reduction; and,
- To test and investigate their performance on shrinkage and other physical and mechanical properties of cementitious materials and to study their behaviour.

The research is the first attempt to use and study these new agents as shrinkage compensating materials in cement mortar or concrete samples. In addition, it is anticipated that the research outcomes will have international significance for concrete industry since the current shrinkage compensating materials and agents adversely affect the physical and mechanical properties of structural and non-structural concrete. Furthermore, the research adopts microstructural investigation techniques such as thermal analysis and scanning electron microscopy. This research also provides a broad view of the effects of new agents on concrete elements.

In order to achieve the research objectives, a combination of literature study and experimental curriculum, was conducted in three stages. Throughout the first stage of the research, the novel agents were designed, chosen and developed from their current application. A thorough study was carried out on each of them to assess their performance before initiation of experimental phase. During the second stage, supplied additives were assessed for their performance in drying shrinkage reduction and other fresh and hardened state properties of cement mortar, in an extensive experimental curriculum. Scanning electron microscopy (SEM) and thermal analysis were utilised in the third stage, in order to monitor new admixtures activities inside the microstructure of cement mortars. The early age (plastic) shrinkage and cracking of these agents have also been studied, using an optimum concentration of each additive.

1.6 Significance

Drying shrinkage mechanism, as a phenomenon, is not completely explained in published literature yet. However, there are number of materials and methods, which can decrease the amount of shrinkage, although approximately all of them adversely influence the mechanical characteristics of concrete. Research conducted to date on plastic and drying shrinkage has led to a general understanding of their mechanisms and their prevention mechanisms. On the other hand, long-term effects of shrinkage in cement-based materials have proved the viability of this type of admixtures for the development of novel cement-based construction materials. Current study contributes to the further development of shrinkage compensating agents, without comprising on engineering and mechanical properties of cement-based materials.

This research projects adopted and studied novel shrinkage compensating admixtures, which have never been studied. Enhancement of characteristics such as flow, compressive strength and resistant to cracking has been considered in the selection of admixtures and agents for current project.

In addition, this dissertation is a step forward in understanding shrinkage, its mechanism, and materials and methods that can prevent it.

1.7 Structure of the Thesis

The thesis has hitherto provided a general background on cement hydration, shrinkage and microstructure of cement-based materials.

Chapter 2 reports a state of the art and critical review on shrinkage in concrete and the mechanisms introduced for this complex phenomenon. Different forms of shrinkage have been differentiated in terms of their occurrence time, and mechanism behind.

This chapter also reports all the factors influencing shrinkage based on the findings from published literature. Current shrinkage reducing/compensating methods and materials have been thoroughly introduced, followed by discussing their influences on shrinkage as well as other aspects of cement-based materials. Furthermore, Chapter 2 also take a look at the sensibility of shrinkage mechanisms to the RH of the environment, which has been taken into account in experimental tests curriculum.

Chapter 3 outlines the research methodology by targeting the introduction of raw materials and experimental techniques in preparation, characterisation and evaluation for cement mortar samples in this study. In this regard, different experiments, which have been used in the project have been revealed.

Chapters 4 and 5 present the main additives investigated in this research work. Chapter 4 is a fundamental study assessing the performance of chemically involved additives when added to OPC mortar, such as ammonium polyphosphate and melamine polyphosphate. Investigation has been continued to find out the behaviour of shrinkage reduction of APP. Chapter 5 studies the performance of non-chemically involved additives in shrinkage reduction by utilising microfibres as an addition to the mix proportion. This chapter also endeavours to explain the phenomenon of micro-crack bridging of these microfibres as the cause for shrinkage reduction.

After obtaining promising results from some of the additives studied throughout Chapters 4 and 5, Chapter 6 examines the plastic shrinkage characteristics of cement mortars using the new agents. This chapter concludes in enhanced resistance to plastic shrinkage cracking in OPC mortars adopting APP, PE microfibre and wollastonite.

Summary and Conclusions relating the drying shrinkage reduction and resistance to plastic cracking of APP, PE microfibre and wollastonite are included in Chapter 7. Chapter 7 also endeavours to enlighten a research path for future studies in development of shrinkage compensating/reducing materials and methods.

References for all chapters are listed at the end of the thesis in the Bibliography section.

Thermal analysis and SEM experimental results of test specimens not presented elsewhere are contained in Appendix A. The various journal and conference publications submitted during the candidature of this thesis are also included in Appendix B.

1.8 Terminology Used in Current Thesis

This section endeavours to define and cover all specific terms used in this dissertation. These terms have been extensively used throughout the chapters and they are being defined in order to differentiate them from similar terms. Therefore, understanding them is necessary for this thesis.

- Admixture: A material other than water, aggregates, and cementitious materials, used as an ingredient in concrete, and added to the batch in controlled amounts immediately before or during mixing to produce some desired modification to the properties of the concrete (1478.1, 2000). Based on this definition from Australian Standards, shrinkage compensating admixtures, such as SRAs, expansive agents and even fibres can be categorised under this term.

- Shrinkage compensating admixture (SCA): A general term used in this dissertation for describing admixtures (defined earlier) which can compensate and/or reduce the amount of shrinkage, in any type. This should be distinguished from shrinkage reducing admixtures (SRA) which only reduce shrinkage by the means of decreasing the surface tension of water. On the other hand, all SRAs are SCA, but not all the SCAs are SRA.

- Mechanism (behaviour): The behaviour or mechanism of an admixture in a fresh or hardened cement-based material that can cause modified properties of cement-based material (in this thesis reduced or compensated shrinkage). This behaviour can contain chemical reactions or physical effects or both of them.

- Control mix: A batch of concrete mixed without the admixture under test (1478.1, 2000).

2 Shrinkage in concrete

2.1 Preface

Concrete and mortar as porous media generally deform when subjected to mechanical, thermal, or hygral actions (Acker & Ulm, 2001):

Mechanical actions are external forces, which applied at the surface or in the volume. Thermal actions are due to temperature variations applied internally or externally. Hygral actions, in which capillary tensions increase considerably as the largest pores are emptied, inducing compression of the solid skeleton. It can be subjected to strains induced from variations of the relative humidity of the environment, water ingress and from variations of the internal humidity (self-desiccation due to the hydration of the cement).

As concrete sets, its volume decreases due to the evacuation of water from the mix. Even after setting, as the concrete continues to evolve, its volume is subject to change with time. In addition, if concrete is restrained, which is commonly the case in engineering practice; tensile stresses develop which can result in cracking. This phenomenon is major concern for flat structures like highway pavements, industrial floors, and bridge decks.

American Concrete Institute (ACI) in a its report 209.1R-2 (2009a) describes shrinkage as the strain measured on a load-free concrete specimen. ACI obviously states that shrinkage does not include changes in length due to temperature variations, but depends on the environment and on the configuration and size of the specimen.

Shrinkage in cement-based materials leads to shrinkage cracking which has adverse effects on the serviceability of the structural members. In fact, shrinkage cracking is one of the most exasperating problems encountered by the construction industry. Although considerable amount of research has been carried out to understand shrinkage and avoid it, researches need to be conducted to fully understand all aspects of this complex phenomenon (Kovler & Zhutovsky, 2006).

Due to the recent advances in materials and chemicals, interdisciplinary research can be applied to develop high performance concretes, which are more resistant to shrinkage and at the same time possess enhanced mechanical properties.

Generally, concrete and cement mortar in different ambient conditions are subject to different types of volume changes in their service life.

2.2 Types of Shrinkage and expansion

Neville (1995) classified Autogenous shrinkage, swelling, drying shrinkage and carbonation shrinkage as the most important aspects of volume change which can happen throughout the service life of concrete. Neville (1995) explains that when cementitious material swells, the adsorbed water molecules act against the cohesive forces and tend to force the gel particles further apart. Swelling is accompanied by an increase in mass of the order of 1%. Expansion can also happen due to the hydration of crystalline MgO (periclase) or CaO, when present in significant amount in a Portland cement (Goodwin, 2006).

In terms of contraction, there are two types of volume changes in constant load situation, creep and shrinkage. The gradual increase in strain with time under a constant load is called creep (Goodwin, 2006). Mehta (2006) presented that a sustained external stress becomes the driving force for the movement of the physically adsorbed water and the water held in small capillaries. Thus, creep strain can occur even at 100% RH.

Concrete and mortar contain two major parts in their matrix: cement paste and aggregate. The former shrinks and the latter restrains shrinkage (Goodwin, 2006). Therefore, shrinkage in concrete specimens is expected to be less than shrinkage in mortar specimen, which is made up with similar mix design but without coarse aggregates.

As illustrated in Chapter 1, water exists in the hydrated cement paste in many forms. Mehta and Monteiro (2006) have presented a comprehensive classification of water and their contribution to shrinkage of cement-based materials. Capillary water, present in voids larger than about 50 Å is free from the influence of the attractive forces exerted by the solid surfaces. In fact, only the removal of water held by capillary tension in small capillaries (5 to 50 nm) can cause shrinkage of the system. A major portion of the adsorbed water can be lost when hydrated cement paste is dried to 30% RH. The loss of adsorbed water is responsible for the shrinkage of the hydrated cement paste. The C-S-H interlayer water is lost only due to very severe drying and then the C-S-H structure will shrink considerably. Eventually, chemically combined water is not expected to be lost on drying.

Literature survey represents different types of shrinkage:

Drying shrinkage- This type of shrinkage occurs in response to moisture loss. Withdrawal of water from concrete is due to storing in unsaturated air. For normal-strength concrete, it is the dominant part of shrinkage, so it is assumed that the entire shrinkage strain is from drying, and any contribution from autogenous shrinkage is neglected (ACI, 2009a). It is also seen that after returning the concrete or mortar into a saturated ambient the whole value of shrinkage is not reversible and a part of this movement is irreversible (Figure 2. 1).

As this type of shrinkage involves moisture movement, amount of drying strain depends on the size and shape of the specimen.

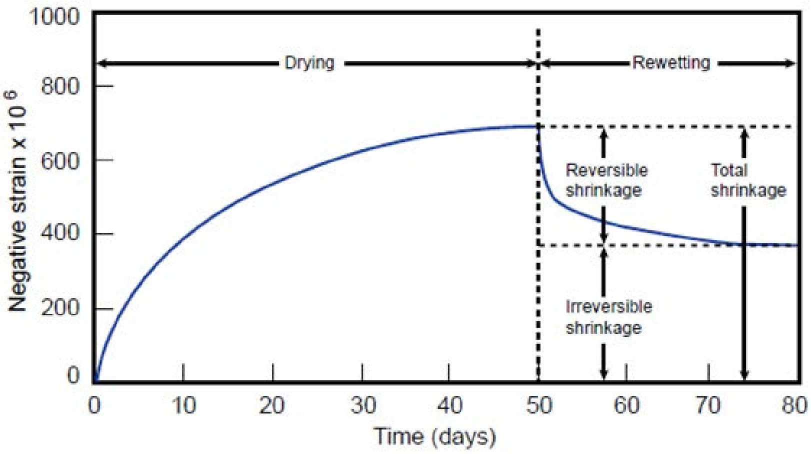


Figure 2. 1. Drying and rewetting of concrete, courtesy to Kumar Mehta & Monteiro (2006)

Autogenous shrinkage- This type is only associated with cement hydration, and environmental conditions do not affect it. It combines the mechanisms of chemical shrinkage and self-desiccation (Goodwin, 2006). Its magnitude is usually negligible for normal- strength concretes. However, for concrete with W/C ratio less than 0.40, autogenous shrinkage may be a significant contributor to the total measured shrinkage.

Neville (1995) also describes it as the consequence of withdrawal of water from the capillary pores by the hydration of the hitherto unhydrated cement, a process known as self-desiccation.

Autogenous shrinkage tends to increase at higher temperatures, with higher cement content, and possibly with finer cements, and with cements, which have a high C_3A and C_4AF content. Nevertheless, higher content of fly ash leads to lower autogenous shrinkage. The magnitude of shrinkage is affected by increase or decrease in disjoining pressure in poorly crystalline C-S-H and ettringite due to respective water absorption or water removal (Goodwin, 2006).

The onset of autogenous shrinkage becomes earlier as w/c decreases. Meanwhile, the cracks due to thermal stress and plastic shrinkage can hardly be independent of autogenous shrinkage (Tazawa & Miyazawa, 1995).

Carbonation shrinkage- It is the product of hydration in presence of CO_2. Chemical reaction of various cement hydration products with carbon dioxide is the origin of carbonation in concrete; however, it is limited to the surface of the concrete. The rate of carbonation is reported to be dependent on several factors such as porosity of specimens, size of specimen, RH, temperature, CO_2 concentration etc. (Goodwin, 2006).

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

The explained mechanisms of carbonation shrinkage still have some paradigms. $CaCO_3$ formation implicates volume increase. Powers (1962) has tried to explain this paradigm, however, this mechanism cannot completely explain all available experimental data (Kovler & Zhutovsky, 2006).

Plastic shrinkage- Several references (Neville, 1995) reported other kind of shrinkage as well, where water can be lost by evaporation from the surface of the concrete while it is still in the plastic state. Therefore, it is named as plastic shrinkage, as the concrete is still in plastic state.

The magnitude of plastic shrinkage is affected by the amount of water lost from the surface of the concrete, which is influenced by temperature, ambient RH, and wind velocity. However the rate of loss of water per se does not predict plastic shrinkage. If the amount of water lost per unit area exceeds the amount of water brought to the surface by bleeding, surface cracking can occur, resulting in plastic shrinkage cracking. Plastic shrinkage is more significant when the cement content of the mix is high or water to cement ratio is too low.

Figure 2. 2 presents a general view on initial expansion, shrinkage types and creep types on a normal strength cementitious material. This figure shows that the concrete undergoes autogenous shrinkage before even drying begins. Once drying commences at time t_0, drying shrinkage occurs and then, upon loading, both drying and basic creep occurs in the drying specimen (ACI, 2009a).

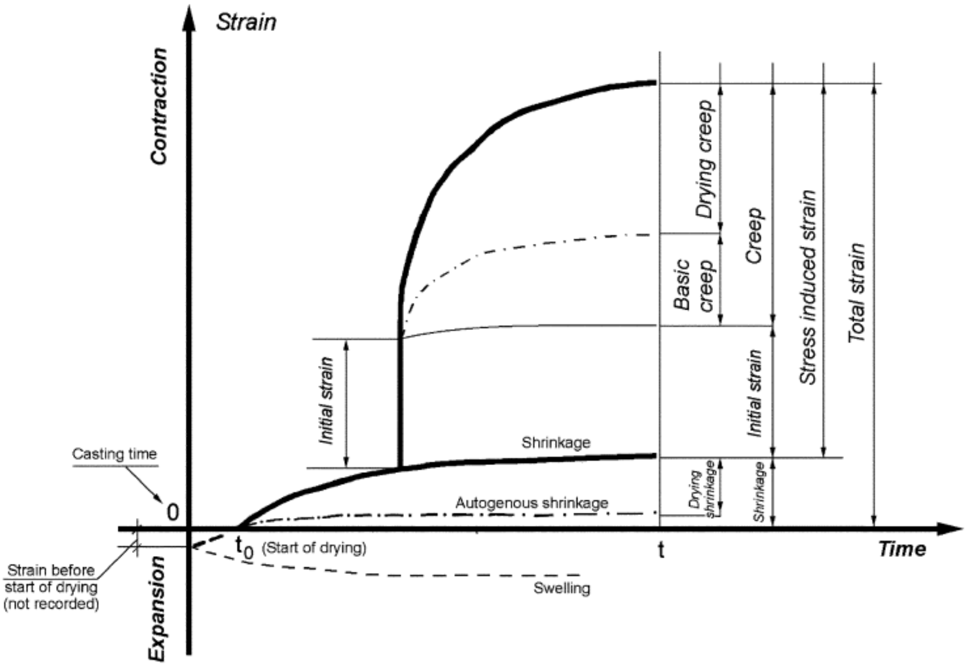


Figure 2. 2. Volume changes in concrete, from (ACI, 2009)

Shrinkage due to chemical reactions- Since cement hydration is an exothermic chemical reaction, temperature variation caused by that, produces volume changes and since volume of reactants typically differs from reaction products volume, volume changes due to chemical reactions are inevitable (Kovler & Zhutovsky, 2006).

Defined by Bazant and Wittmann (1982) and reviewed by Kovler and Zhutovsky (2006), shrinkage can also be viewed and then classified into 2 major categories: 1- shrinkage due to moisture changes and, 2- shrinkage due to chemical reactions. The latter category contains:

Hydration shrinkage- Cement hydration is not single chemical reaction, but complex set of quite a few reactions and each reaction has its own volume stoichiometry. During the hydration, two major calcium silicates in cement result mostly in two main products: C-S-H and calcium hydroxide (CH). Because the calcium silicates represent the bulk of Portland cement, the volumetric change that occurs during their hydration is the major contributor to hydration shrinkage. On the other hand, it is always seen that the resultant volume of cement paste is smaller than the volume of water and cement together. Albeit, there is still uncertainty about the precise magnitude of that reduction of the volume (Kovler & Zhutovsky, 2006). The chemical shrinkage depends on cement type, cement content and degree of hydration (F. H. Wittmann, 1982). The chemical shrinkage is usually larger than autogenous shrinkage.

Self desiccation- Self desiccation is the reduction in the internal RH of a sealed system when empty pores are generated, occurs as soon as the chemical shrinkage takes place at the time the cement paste matrix has developed a self-supportive skeleton.

Since the hydration products can form only in water-filled space, only a part of the water in the capillary system can be used for hydration and therefore enough water needs to be present both for the chemical reactions and for filling of gel pores (Kovler & Zhutovsky, 2006; Weber & Reinhardt, 1996). Thus, if the w/c is high enough, full hydration of cement is possible. Whereas, when the w/c is low, at some state of hydration there will not be enough water to saturate the solid surfaces of the capillary pores. Hence, the hydration stops commonly when the vapour pressure in the capillary pores falls below 80% of the saturation pressure. Furthermore, if concrete is completely sealed or isolated from a moisture source, self-desiccation is likely to happen.

On the other hand, if from external sources, water can enter into the hydrating cement paste, hydration will continue until there is not enough space left to accommodate hydration products. Consequently, when the concrete is continuously water cured, the capillary system will always be full of water so that hydration will proceed constantly (Aitcin, Neville, & Acker, 1997; Kovler & Zhutovsky, 2006).

Thermal shrinkage- Cement hydration is an exothermal reaction and produces heat energy. Furthermore, different mineral of cement liberate different amount of heat. A significant portion of the heat is released when concrete is still fresh and, thus thermal expansion is observed at this stage (Kovler & Zhutovsky, 2006). Later, as hydration rate declines, the temperature decreases and, as a consequence, the concrete undergoes thermal shrinkage and accordingly serious cracking (Kovler & Zhutovsky, 2006; Soroka, 1979; F. H. Wittmann, 1982).

In fact, the magnitude of thermal swelling and shrinkage is thoroughly dependent on the coefficient of thermal expansion. The thermal expansion coefficient of cement paste and its thermal shrinkage depend on the curing conditions and moisture content, of which both relate to RH (Meyers, 1950; F. Wittmann & Lukas, 1975).

Crystallization swelling- In fresh concrete, formed colloidal products and crystallized phases expand in the water filled spaces. Afterward, when solid skeleton is built further crystal growth continues and produces internal pressure and then swelling (Kovler & Zhutovsky, 2006; F. H. Wittmann, 1982). Although this expansion will be compensated by drying and autogenous shrinkage (ACI, 2009a).

Carbonation shrinkage- In the presence of water the calcium hydroxide, produced from hydration, reacts with atmospheric carbon dioxide and decreases the cement paste volume. Carbonation shrinkage is mainly affected by RH, CO_2 concentration, paste porosity and its moisture content (Soroka, 1979; F. H. Wittmann, 1982).

Shrinkage due to phase transitions- Some phases in hydrated cement paste, especially aluminate hydrates in high alumina cement, slowly undergo transition to a more stable form. This phase transition is accompanied by volume changes (Kovler & Zhutovsky, 2006; F. H. Wittmann, 1982).

Dehydration shrinkage- Some of the hydration products are not stable with respect to a decrease of RH, e.g., well-crystallized phases can lose their hydrate water at low RH. This loss of hydrate water is associated with volume change (Kovler & Zhutovsky, 2006; F. H. Wittmann, 1982).

2.3 Drying shrinkage

As mentioned earlier, for normal-strength cementitious material, the major contribution to shrinkage belongs to drying shrinkage. Therefore, the main concern of this research project is on drying shrinkage, considering if the drying shrinkage is reduced, the total amount of shrinkage can be proportioned.

Mehta and Monteiro (2006) proposed that the mechanisms that are responsible for drying shrinkage are also responsible for creep of hydrated cement paste. In fact, drying shrinkage and creep arise from the same source, i.e., the hydrated cement paste.

A saturated cement paste will not remain dimensionally stable when exposed to ambient humidity that is below saturation, mainly because the loss of physically adsorbed water from the paste results in a shrinkage strain. Similarly, when a hydrated cement paste is subjected to a sustained stress, depending on the magnitude and duration of applied stress, the C-S-H will lose a large amount of the physically adsorbed water, and the paste will show a creep strain. In short, both the drying shrinkage and creep strains in concrete are assumed to be related mainly to the removal of adsorbed water from the hydrated cement paste. The difference is that in one case the differential RH between concrete and the environment is the driving force, while in the other it is the sustained applied stress. Again, as stated before, a minor cause of the contraction of the system, either as a result of drying or applied stress is the removal of water held by hydrostatic tension in small capillaries (<50 nm) of the hydrated cement paste.

For studying the mechanism of shrinkage, it is needed to have another look at the different parts of concrete or mortar and types of water in hydrated cement paste.

2.3.1 Drying shrinkage mechanism

Essentially the change in the volume of drying concrete is not equal to the volume of water removed (Kovler & Zhutovsky, 2006). The loss of free water, which takes place first, causes little or no shrinkage. As drying continues, adsorbed water is removed and the change in the volume of unrestrained hydrated cement paste at that stage is equal approximately to the loss of a water layer one molecule thick from the surface of all gel particles.

The relation between the mass of water lost and shrinkage observed in Figure 2. 3 presented by Neville (1995), showing. In the situation of 100% cement content as no capillary water is present and only adsorbed water is removed. In the other mixes there are pulverized silica added and for workability reasons, required a higher w/c ratio, and therefore they contain capillary pores even when completely hydrated. Emptying of the capillaries causes a loss of water without shrinkage;

however once the capillary water has been lost, the removal of adsorbed water takes place and causes shrinkage in the same manner as in a neat cement paste.

This is also demonstrated in Figure 2. 4 by Mehta and Monteiro (2006), that after exposing specimens to environmental humidity, which is normally lower than 100%, the material begins to lose water and shrink in this order:

Free water in large cavities- Since this water is not attached to the microstructure of the hydration products, its loss would not be accompanied by shrinkage. This part of water loss occurs immediately after that humidity drops below 100% (Line AB in Figure 2. 4).

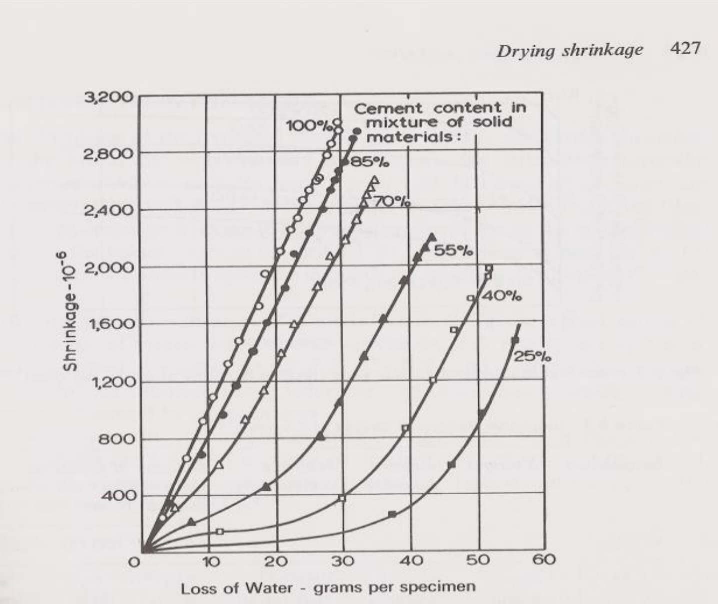


Figure 2. 3. Relation between shrinkage and moisture loss from cement-pulverized silica pastes cured for 7 days at 21°C and then dried, Courtesy to Neville (1995)

Loss of adsorbed water and water held in small capillaries- The adsorbed water usually causes disjoining pressure. The removal of the adsorbed water reduces the disjoining pressure and brings about shrinkage of the system (Line BC in Figure 2. 4).

Interlayer water: After severe drying shrinkage and it causes some kind of contraction.

Mechanisms and theories describing shrinkage and creep of concrete are complex and not fully understood yet (Tamtsia, Beaudoin, & Marchand, 2003).

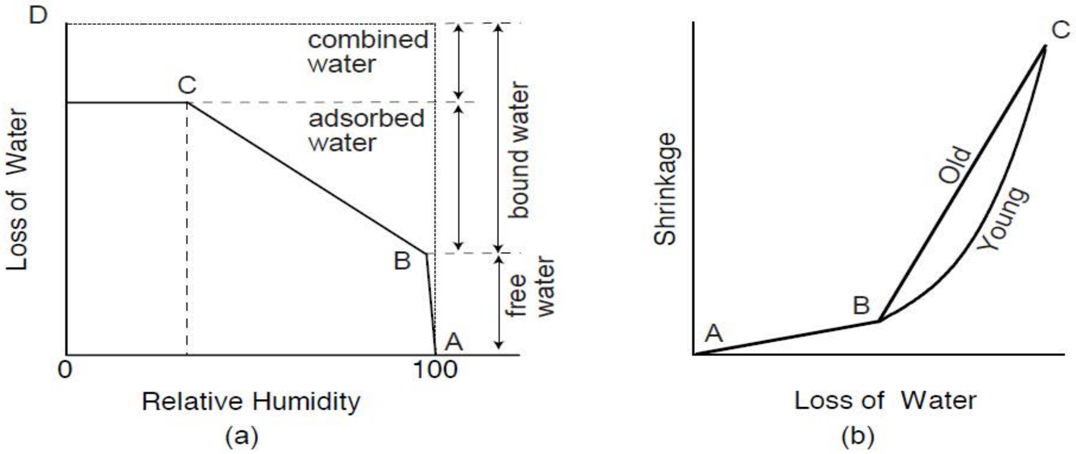


Figure 2. 4. Relation between relative humidity and loss of water, courtesy to P. K. Mehta and Monteiro (2006)

Furthermore, the drying process of concrete specimens or structures is a very slow phenomenon. That is due to the progression of the drying from the surface to the inner part of the material and this phenomenon results in an inhomogeneous distribution of shrinkage strains. Therefore, the surface zone, where the water can evaporate more rapidly, has a tendency to contract more than the bulk of the material (Benboudjema, Meftah, & Torrenti, 2007). This incompatibility leads to the stress redistribution in the material, tensile stresses at the surface zone and compressive ones in the bulk, following by micro-cracking of the cementitious material (Benboudjema, et al., 2007; Iding & Bresler, 1982). Consequently, these induced micro-cracking strains and stress redistribution affect any experimental measure of the drying shrinkage strain. Hence, the intrinsic shrinkage behaviour cannot be identified directly from the total measured strain.

2.3.1.1 **Capillary tension**

One of the first theories describing shrinkage states that the liquid phase of mixture is placed under stress in relation to its initial state. It has also been suggested that the stresses, which result in shrinkage, are capillary stresses (Kovler & Zhutovsky, 2006). The force in this case is proportional to the surface tension σ of the liquid that fills the capillaries and adversely proportional to the radii of curvature r_1 and r_2 of the menisci of liquid phase. As the water content diminishes, the radii do likewise and the capillary force increases.

When RH drops below 100%, or, in other words, vapour pressure is below saturated pressure, evaporation takes place.

The Kelvin-Laplace equation relates radius of curvature and RH:

$$\ln(RH) = \ln(\frac{P}{P_0}) = \frac{2\gamma V_m}{RTr}$$ **Equation 2. 1**

This equation is often related as Kelvin-Laplace equation. The implication of this equation is demonstrated in Figure 2. 5.

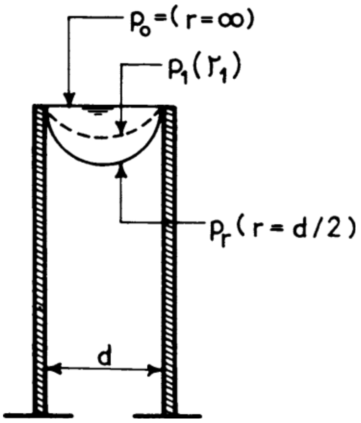


Figure 2. 5. Relation between radius of curvature and vapour pressure, Courtesy to Kovler & Zhutovsky (2006)

When RH is 100% ($P = P_0$), the water surface in the capillary is plane ($r = \infty$) and no evaporation takes place. With a decrease in relative humidity ($RH_1 = P_1/P_0$), water starts evaporating until a meniscus with radius of curvature r_1 corresponding to RH_1 in Kelvin-Laplace equation is formed. Further decrease in RH causes further evaporation with corresponding decrease in the curvature radius of the meniscus. The minimum radius of meniscus curvature is equal to the radius of the capillary. Therefore, if RH drops below relative humidity corresponding to the minimum meniscus curvature radius, evaporation takes place until all the water evaporates.

This is correct for the cylindrical capillary with constant diameter. However, in capillary pores of concrete that have certain size distribution, evaporation takes place until the biggest pores are emptied and meniscus is formed in the pores with radius equal to the meniscus curvature radius corresponding to the relative humidity. By this means, in concrete, pores that have radius lower that meniscus radius are filled by water and pores with bigger radius are empty. As was stated by Kelvin-Laplace equation, water in capillaries is under tension, i.e. under tensile stress. This tensile stress in capillary water must be balanced by compressive stress of the surrounding solid. Thus, emptying of capillary pores in cement paste by any drying or throughout chemical reaction will subject the paste to compressive stress, which in return; will result in volume decrease, i.e. shrinkage. OPC paste is considered to be viscoelastic material, therefore this volume change have both elastic and viscous, i.e. creep, components. Both components vary with age and water to binder (w/b) ratio.

Some literature suggest that capillary tension is of great importance mainly at relative humidity in the range of 50–100% , when others believe that this range is 35–100% (Kovler & Zhutovsky, 2006; T.C. Powers, 1965).

2.3.1.2 **Surface tension**

The other mechanism was suggested by Baˇzant and Wittmann and reported by Wu (1984) is applicable in the range of 5–50% RH. The driving force for shrinkage in this suggested mechanism is the surface tension of the liquid. As a result, the surface tends to contract and behaves like a stretched elastic skin (Kovler & Zhutovsky, 2006). The introduced surface tension induces compressive stress inside the mixture. In particles of colloidal size, such as the cement gel particles having large specific surface area, surface tension can induce huge compressive stresses of the order 250 MPa (Soroka, 1979).

The shrinkage strain (Δl/l), is directly related to the corresponding change in surface tension (γ) or, likewise, in surface energy. It was shown by Bangham (1931) and stated by Kovler & Zhutovsky (2006) that, in certain limits of RH, this relation is linear:

$$\frac{\Delta l}{l} = \lambda.\Delta\gamma$$

Equation 2. 2

The proportionality factor λ is a constant that is relevant to empty pores wall area, specific mass and the elasticity modulus of the material.

2.3.1.3 **Movement of interlayer water**

C-S-H particles of the cement gel are composed of laminar sheets, which large surface area having electrical charge attract highly polarized water molecules at interface up to few mono-layers apart (Kovler & Zhutovsky, 2006; F. H. Wittmann, 1982). Movement of this water into and out of layered C-S-H particles structure will affect spacing between the layers causing volume changes. Most researchers attribute shrinkage at relative humidity below 35–40% to this mechanism (Kovler & Zhutovsky, 2006). Wittman (1982) has illustrated effect of interlayer movement on volume change of C-S-H layers in Figure 2. 6.

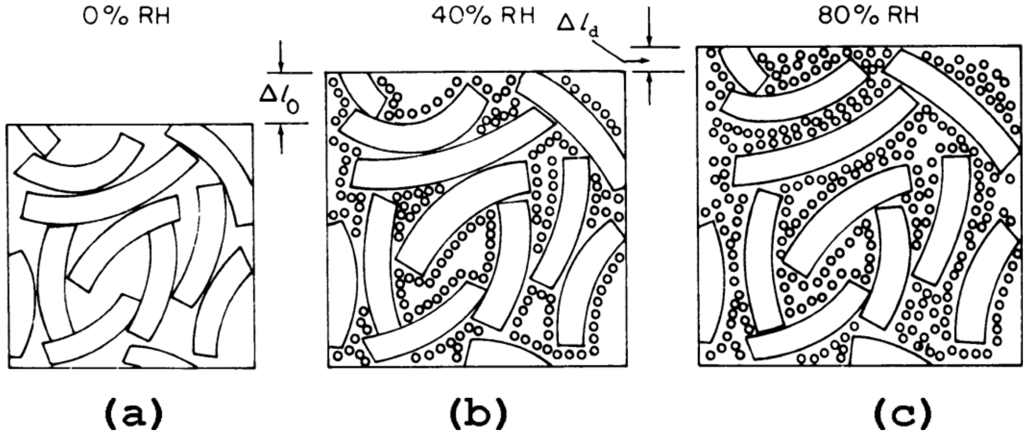


Figure 2. 6. Schematic illustration of different stages of interlayer water movement, courtesy to F.H. Wittmann (1982)

2.3.1.4 **Disjoining pressure**

By the adsorption of interlayer water, not only a repulsive force arises, but a decrease in attractive van der Waals' forces between solid layers can occur as well (Kovler & Zhutovsky, 2006). The net surface repulsion force and loss of attraction forces is usually called disjoining pressure or swelling pressure (Kovler & Zhutovsky, 2006; Visser, 1998), as illustrated in Figure 2. 7. This has been suggested that the removal of capillary water reduces the disjoining pressure and causes the shrinkage of hydrated cement paste on exposure to drying conditions (Goodwin, 2006).

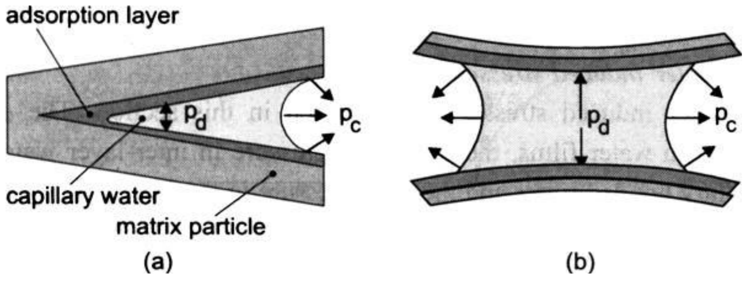


Figure 2. 7. Capillary pressure and induced disjoining pressure, courtesy to Visser (1998)

Disjoining pressures are initiated in the nano-pores by the repulsion between the adsorbed water molecules preventing the solid layers to come closer, while meniscuses in capillary pores lead to surface tensions at the liquid-solid interfaces tending to shrink the paste (F. H. Wittmann, 1982). These two conflicting driving forces depend largely on the variation of the degree of saturation of the material and RH of the environment. They are responsible for the micro-prestresses, which rise into the solid skeleton and are at the origin of the observed macroscopic shrinkage strain when the material dries.

Beltzung & Wittmann (2005) stated that disjoining pressure is clearly the dominant mechanism when humidity is above 50% RH. However, Kovler & Zhutovsky (2006) reported that based on Powers model this mechanism is valid over the whole range of relative humidity.

2.3.1.5 **Influence of RH on shrinkage mechanism**

As mentioned throughout the introduction of shrinkage mechanisms, appearance of one or another is strongly dependent on degree of saturation of the cement paste and RH of the environment. The degree of saturation and RH are genuinely connected since the equilibrium between adsorbed water and vapour pressure must exist. Indeed, any change in RH disturbs the equilibrium and causes evaporation or condensation, depending on whether RH is respectively decreased or increased.

Shrinkage and swelling typically happen by more than one mechanism; however there is some disagreement on which mechanism plays the most significant role at certain RH. In general, capillary pressure becomes the major contributor to shrinkage when pore water becomes continuous, whereas disjoining pressure is important at low degrees of saturation (Visser, 1998).

Kovler & Zhutovsky (2006) reported that most researchers attribute volume changes at RH above 40% to the capillary tension, whereas movement of interlayer water is considered responsible for the volume changes at RH below 35%. Nevertheless, there is not a complete agreement between researchers and some assume that variations in surface energy is the cause of shrinkage/swelling at RH below 40%, and some, on the contrary, believe that this mechanism is active at RH above 40%. Disjoining pressure is also controversial mechanism when explained by some to be responsible for the volume changes at higher RH, and some consider it is applicable at lower RH, and some completely reject this mechanism (Kovler & Zhutovsky, 2006). Therefore, as the main research conclusion, the range of RH between 40-50% is described as a border range between different mechanisms.

2.3.1.6 **Factors influencing drying shrinkage**

In practice, moisture movements in the hydrated cement paste, which essentially control the drying shrinkage and creep strains in concrete, are influenced by numerous simultaneously interacting factors.

The main factors affecting the magnitude and the rate of drying shrinkage includes the ratio of water to cement, ratio of aggregate to cement, elastic properties of aggregate, size and shape of specimens, temperature, type of cement, type of admixture used and curing and storage condition (ACI, 2009a; Kumar Mehta P. & M., 2006).

2.3.1.7 **Effect of mixture proportions**

The drying shrinkage of a given concrete mixture is governed by the shrinkage of the cement paste and the quantity and properties of the aggregate.

Quantity of aggregate- As the aggregate restrains shrinkage of the cement paste, the total volume of aggregate in a mixture, is extremely important on shrinkage amount. It has been reported by Pickett (1956) that shrinkage of concrete (S_C) is related to shrinkage of the cement paste (S_P) and the aggregate volumetric fraction (g) according to the below equation (Pickett, 1956):

$$S_C = S_P.(1-g)^n$$

Equation 2. 3

where n is variable between 1.2 - 1.7.

Size and grading of aggregate- In general, an increase in the maximum aggregate size, and concurrent decrease in paste content, will decrease drying shrinkage (ACI, 2009a). A rounder aggregate may result in a decreased paste content that will result in lower shrinkage.

Water content, cement content, and slump- Increasing the total cement and water content will tend to increase shrinkage, since the additional water or cement will decrease the aggregate content in a mixture. For instance, if increasing the slump is obtained through increasing the w/c or total paste content of the concrete, drying shrinkage increases consequently.

Elastic properties of aggregate- Since the aggregate restrains the shrinkage of cement paste, aggregate with a high modulus of elasticity will tend to impose a lower drying shrinkage than an aggregate with a low modulus of elasticity (Reichard & Standards, 1964).

Clay-containing aggregates- Aggregates containing clay minerals, such as breccia, usually result in an increase in drying shrinkage due to their high water demands (ACI, 2009a).

Lightweight aggregates- Lightweight aggregates often have potential to increase drying shrinkage of concrete; however, with appropriate selection of aggregates, lightweight concrete with moderate drying shrinkage is possible.

Cement characteristics- The chemistry of the cement plays a significant role in the shrinkage of cement paste and concrete. Roper (1974) found that cements with low quantities of sulphate may exhibit increased shrinkage. The shrinkage of concrete made with a high alumina content occurs more rapidly and on the other hand, finely ground cements result in greater shrinkage than coarser ground cements (ACI, 2009a).

Air content- When the total air content of the concrete is less than 8%, there is generally no effect on the magnitude of drying shrinkage (Davis & Troxell, 1954).

Admixtures- Although some admixtures such as shrinkage reducing admixtures (SRA), are specifically formulated to reduce different types of shrinkage (Nmai, Tomita, Hondo, & Buffenbarger, 1998), the effect of other admixtures on shrinkage depends on the type and use of admixture. The effect of admixtures on drying shrinkage is discussed by Brooks (1989; 1999) where extensive discussions are made relating to other changes that are commonly made when using these admixtures such as changes in cement content or water use. Compared with concrete having the same mixture proportions, the effect of various ingredients on the shrinkage of concrete determined by Brooks is shown as follows:

Water reducing or High range water reducing admixtures are reported to increase the drying shrinkage (J. Brooks & Jiang, 1997; J. J. Brooks, 1999). However, claimed by Ramachandran & Mailvaganam (1995), water reducers reduce the drying shrinkage, as they reduce the surface tension of capillary water and the water demand, in general.

Ground slag increases the drying shrinkage with increase in replacement amount (ACI, 2009a; Saito, Kinoshita, Umehara, & Yoshida, 2010).

Fly ash has shown no significant change. While as fly ash increases the hydration heat, it is supposed to increase thermal shrinkage (ACI, 2009a; Atiş, Kiliç, & Sevim, 2004; Gao, Lu, & Tang, 2009).

Silica fume (less than 7.5% replacement) is reported to decrease the drying shrinkage.

2.3.1.8 **Effect of environment**

The environment in which concrete is mixed, placed, and cured and to which it is exposed during its life has a significant effect on the drying of concrete (ACI, 2009a). Low RH, wind, and high temperatures tend to increase the rate of drying shrinkage and drying cracking.

Relative humidity (RH)- Shrinkage is principally affected by the RH of the air surrounding the concrete. Generally, the lower the RH, the higher the drying shrinkage. However, unrestrained concrete stored in water tends to swell.

For RH>50%, drying shrinkage strain is reported to be related to RH by following equation (ACI, 2009a):

$$Shrinkage \propto 1 - \left(\frac{RH}{100}\right)^b$$ **Equation 2.** 4

In which, b varies from 1 to 4.

Temperature: ACI 209 (2009a) has quoted an increase in ultimate shrinkage of approximately 15% for an increase of temperature from 23 to 60 °C at a constant RH.

2.3.1.9 **Effect of design and construction**

Period of curing- Extended periods of moist curing are believed to reduce the amount of drying shrinkage by 10 to 20%. Perenchio (1997) has shown that periods of curing greater than 4 to 8 days and less than 35 to 50 days may increase the drying shrinkage.

Heat and steam curing- Heat and steam curing can significantly reduce drying shrinkage of concrete by as much as 30% (ACI, 2009a).

Size and shape of specimen- Due to the slower rate of drying of the larger members, thick concrete members might shrink at a slower rate than thin concrete members (ACI, 2009a). The amount of shrinkage is generally assumed to be inversely proportional to the ratio of the volume of the specimen to its drying surface area, squared (Hansen & Mattock, 1966):

$$Shrinkage \propto \left(\frac{S}{V}\right)^2$$ **Equation 2. 5**

where V = volume, and S = surface area.

2.4 Shrinkage Compensating Methods

Researchers have introduced different materials and methods, in order to overcome the consequences of shrinkage in cement compounds. However, in most cases, these methods and materials come with their side effects on cementitious materials physical and mechanical characteristics. As the aim of current research is also developing of shrinkage compensating materials, which have fewer side effects on the concrete properties, reviewing the background of these methods and materials would be beneficial. Kovler & Zhutovsky (2006) have comprehensively summarized different methods introduced ever to industry as follows:

- Cement modification
- Expansive agents
- Admixtures reducing drying shrinkage
- Fibres
- Internal curing
- Surface treatment

2.4.1 Cement modification (expansive cement)

Cement modification can lead to lower autogenous shrinkage of OPC, when it contains higher belite (C_2S) content and lower contents of alite (C_3A) or celite (C_4AF) (Kovler & Zhutovsky, 2006). However, changing cement composition in order to reduce autogenous shrinkage will affect the compressive strength of the paste. Additionally, the increased gypsum content in cement, which causes autogenous expansion, and in consequence, it reduces the autogenous shrinkage.

The formation of ettringite and hydration of crystalline CaO are two mechanisms in cement modification, which are capable of causing disruptive expansion. Committee 223 of ACI (2009b) defines an expansive cement as a cement that when mixed with water forms a paste that, after setting, tends to increase in volume to a significantly greater degree than normal Portland cement paste. This committee also introduces expansive cement K, expansive cement M and expansive cement S, which are well-known in compensating for volume decrease due to shrinkage. The amount of expansion produced, is generally enough to offset the effect of tensile stress due to subsequent drying shrinkage (Goodwin, 2006). Figure 2. 8 illustrates the effect of cement paste expansion on length change of concrete samples (P.K. Mehta & Monteiro, 2006).

Odler (2000) stated that mostly the expansive stresses in hardening time are created by the formation of ettringite ($C_3A.3CS.32H$), and this phase is formed in the reaction of a constituent containing aluminium oxide with calcium sulphate, calcium oxide or hydroxide and water. Some of the other expansive cement are based on the formation of CH from calcium oxide, or magnesium hydroxide from magnesium oxide (Ivan Odler, 2000).

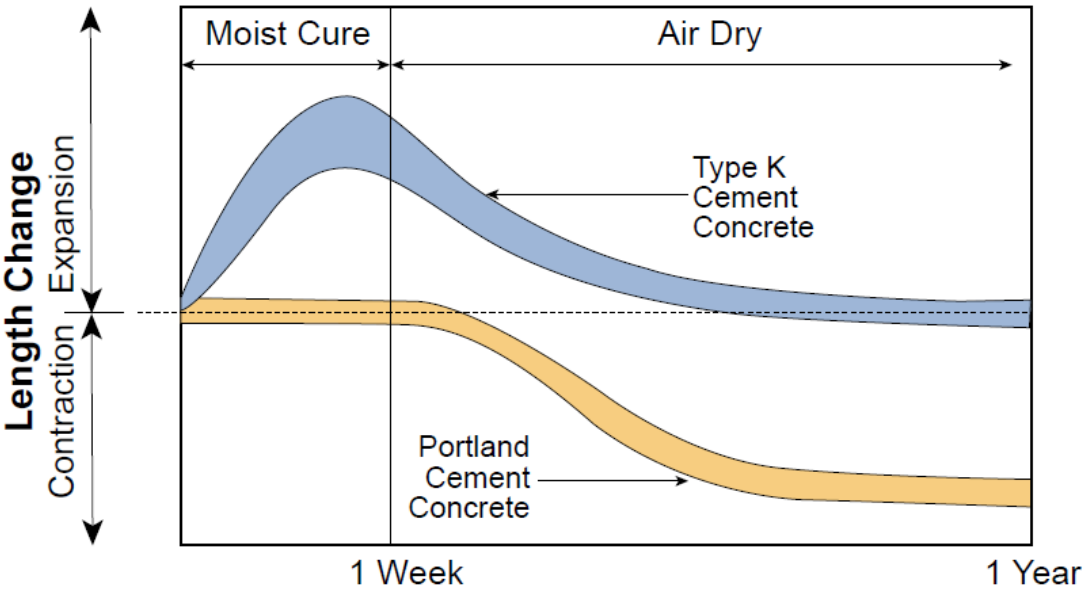


Figure 2. 8. Type K expansive cement, Courtesy to Mehta and Monteiro (2006)

In fact, there is not a distinguishing boundary line between the materials involved in ―cement modification” and ―expansive additives” in regards to mechanisms behind. For example, MgO (periclase) and CaO, when present in significant amounts in Portland cement, cause expansion and probably cracking. These two chemicals can be added to OPC during either manufacturing (cement modification) or concrete mixing (expansive additive). Nevertheless, only under autoclaving conditions (accelerated laboratory tests) is periclase known to hydrate and cause considerable expansion in cement pastes (Goodwin, 2006).

2.4.2 Expansive additives

Expansive additive can reduce total shrinkage in ordinary cement compounds. There are several types of mechanisms explaining the action of expansive additive.

Use of expansive additive in combination with high belite or low heat Portland cement can become more effective in shrinkage reduction (Kovler & Zhutovsky, 2006). Mailvaganam (1995) has summarized general classes of expansion producing admixtures as follows:

a. Admixtures, which control settlement and provide expansion in the plastic stage. These are gas generating materials.
b. Admixtures, which control plastic settlement and hardened shrinkage by providing expansion in both the plastic and hardened state. These are composed of calcium sulfo-aluminate and lime-based materials. This class shares materials with cement modification materials.
c. Admixtures, which do not control settlement but provide expansion only in the hardened state. They consist of granulated iron filings and chemicals that promote oxidation of iron in the presence of moisture and air.

Gas generating admixtures include:

- Single component admixtures consisting of a gas producing agent and other minor ingredients for bubble stability and acceleration of the gassing reaction or forming expansive products.
- And multi-component admixtures: which contain other chemical ingredients for water reduction and strength increase.
- A variety of metals and other materials are used as single component admixtures, such as Al, Mg or Zn which release hydrogen, H_20_2 which

liberates oxygen and certain forms of activated carbon or fluidized coke of which air is liberated.

Multi-component admixtures are generally used in structural grouting of machine base-plate and cementing of porous formation of oil wells. Commonly available commercial products combine two or more admixtures such as gas forming, workability aids, retarders, accelerators or supplementary cementing materials.

These admixtures might help reduce plastic or even autogenous shrinkage, but mortar and concrete containing gassing agents, generally produce higher drying shrinkage than ordinary concrete and mortar. Thus, it results in surface cracks and strength reduction.

Admixtures containing granulated iron filings cause expansion only after the mortar have been set and hardened. Two basic types, iron particles with rust promoting or rust inhibiting admixtures, are commonly used both under restrained and unrestrained conditions in grouting and flooring compositions, respectively.

Oxidation of the iron particles in the presence of rust promoting chemicals occurs in the first few days of hardening, causing sufficient volume increase to offset the settling that occurs before initial set. In compositions containing treated iron particles or those containing corrosion inhibiting admixtures, expansion is produced by the use of expansive cements such as type K cement or expansive calcium aluminate or lime based admixtures. Unlike the rust promoting types, these admixtures do not show significant expansion after 48 hours and, therefore, are not susceptible to disruptive expansion when exposed high moisture levels.

Calcium sulfo-aluminate (CSA) and lime-based expanding admixtures can provide a means of offsetting volume changes into hardened state shrinkage. These admixtures have already been introduced as cement modification agents, while in this section; they are described as expansive additives.

Using CSA and CaO, shrinkage compensation is obtained at lower addition rates, while chemical prestressing of the reinforcement is achieved at higher dosages. The most widely used single component, calcium sulfo-aluminate admixture is composed of 30% (C_4A_3S), 50% $CaS0_4$ and 20% CaO with small amounts of a glassy phase. Particles size is coarser than that of Portland cement.

Having reacted with water, CSA type admixtures form ettringite and expand. Expansion in the lime-based system is due to crystal growth and the pressure that results when CaO particle forms $Ca(OH)_2$.

Expansion of cement-based materials associated with ettringite formation is well recognised and has been being used for decades (P. K. Mehta, 1973; P. K. Mehta & Wang, 1982). Ettringite is a mineral phase high-sulphate calcium sulfo-aluminate ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 – 32H_2O$) and is well known as the product of the principal expansion-producing reaction in cements or admixtures (ACI, 2009b). The formation of limited amounts of this product may be considered acceptable; however, in some cements excessive amounts of formed ettringite may cause expansion and cracking of the hardened paste and should be avoided (I. Odler & Colán-Subauste, 1999). These authors believe that the extent of ettringite-related expansion depends on the conditions of curing and increases with increasing amounts of water taken up from the environment while ettringite is formed, indicating the participation of swelling phenomena in the expansion process.

Large number of research studies has been taken place about behaviour of these organic expansive admixtures and their effects on the cement-based mixtures. According to Wakeley (1987), salt-saturated concrete achieves only low levels of expansion if any. It was also shown that use of sodium citrates and specific curing conditions results in substantial expansion in concrete that is related to delayed ettringite formation. It implies that the slower the formation of a rigid structure, which is related to delay in ettringite formation, the more the concrete will expand.

Nagataki, and Gomi (1998) reported iron powder, aluminium powder, magnesia, calcium sulfo-aluminate ($CaO\text{-}A1_20_3\text{-}S0_3$) and calcium oxide (CaO) or other ettringite forming agents as expansive admixtures. Maltese, et al. (2005) observed that the use of calcium oxide based expansive agent, with propylene glycol ether based shrinkage reducing admixture, is effective in compensating drying shrinkage. However, Nagataki & Gomi (1998) and Sousa Ribeiro (1998) conclude that the mechanical strength decreases with the increase of the expansive constituents of the blend.

Expansion characteristics of MgO have recently been well-known. Chatterji (1995) concluded that delayed expansions, due to the presence of dead-burnt CaO or MgO, was based on the crystal growth pressure, and diffusion of Ca^{2+} and Mg^{2+} through the electrical double layer which forms around cement hydration products. In addition Nokken (2010) stated that MgO which is also called periclase can slowly hydrate to brucite ($Mg(OH)_2$), resulting in volume increase, leading to expansion and if not limited, to cracking.

Explained limitations related to expansive additives have prevented considerable application of these materials in concrete industry. However, they are still significantly used in grout or concrete repair material production.

2.4.3 Shrinkage reducing admixtures (SRA)

Shrinkage reducing admixtures have been proved to reduce different types of shrinkage. Autogenous shrinkage as well as plastic shrinkage can also be reduced using drying shrinkage reducing admixture (Kovler & Zhutovsky, 2006; Mora-Ruacho, Gettu, & Aguado, 2009). The experimental results, carried out by Lura, et al. (2007) depicted that the addition of SRA reduces the width of plastic cracks in mortars exposed to evaporation immediately after casting.

SRAs are believed to directly affect the surface tension of capillary pore water, resulting in a decrease of shrinkage made by surface tension mechanism. Although, SRA reduces the surface tension of pore fluid when added up to a threshold concentration (Rajabipour, Sant, & Weiss, 2008). Reducing the surface tension in the pore fluid, SRA is reported to reduce plastic shrinkage by: 1- evaporation rate reduction, 2- settlement reduction, and 3- reduction in the stresses that develop at the surface of the mortar (Lura, et al., 2007).

SRAs can also reduce the evaporation rate of water from the porous structure of mortar or concrete and consequently, increase the achieved degree of hydration (Dale P. Bentz, 2005).

It has also been reported that the SRA has an effect to retard the hydration process of Portland cement under normal condition (He, Li, Chen, & Liang, 2006). This observation is in agreement with exhibited lower early strength in concrete containing SRA (Folliard & Berke, 1997).

SRAs reduce the surface tension of pore fluid when only added up to a certain threshold concentration (e.g., 7.5% by weight of cement). Beyond this critical threshold, any further addition of SRA results in accumulation of surfactant molecules within the bulk solution rather than the solution–air interface. As such, beyond the critical threshold, further reduction in pore fluid's surface tension becomes marginal (Rajabipour, et al., 2008).

Rajabipour et al. (2008) also found that the addition of SRA reduces the polarity of mixing water, resulting in reduction of alkali concentration in pore fluid. However, a higher alkali concentration can be attained when SRA is added after the initial mixing of paste. The reduced alkalinity of the pore fluid has a direct impact on the rate of cement hydration and can contribute to retardation in hydration and strength development of concrete containing SRA.

On the other hand, as hydration continues or when the concrete is exposed to drying environment, the SRA concentration in pore fluid has been shown to increase (Rajabipour, et al., 2008). In another study, Weiss et al. (2008) reported higher RH in sealed specimens than sealed control mixes.

In drying specimens, the surface tension of the pore solution is related to the size of the pores, from which the water is lost at different RH (Kovler & Zhutovsky, 2006). Specimens containing SRA lose water in smaller pores than conventional mixtures at the same RH (Weiss, et al., 2008). Based on this observation Weiss et al. (2008) concluded that the shrinkage in mixtures containing SRA is dominated by capillary stress over a smaller RH range than in control mixtures (Weiss, et al., 2008).

2.4.4 Fibres

Fibres for use in cement-based materials are commonly accepted for their immediate effects in shrinkage cracking resistance, rather than long-term shrinkage reduction.

To date, there have been several types of fibres introduced and adopted by the construction industry. Bentur & Mindess (2007) have listed them as:

- Steel fibres

- Glass fibres
- Asbestos fibres
- Natural fibres
- Synthetic fibres
    - Polypropylene (PP)
    - Polyethylene (PE)
    - Acrylic
    - Polyester
    - Nylon
    - Carbon
    - Aramid
    - Polyvinyl alcohol (PVA)

There have been a large number of research projects on the effects of fibres on the properties of cement compounds. In following paragraphs, some of them in regards to shrinkage of cement-based materials are summarised.

Pelisser et al. (2010b), from their experimental results, concluded that the addition of short PP fibres (12-15mm) to the mortar mix was efficient in preventing considerably crack formation due to plastic shrinkage. Sivakumar et al. (2007) stated that in hybrid fibre combinations, the steel–polyester combination could provide a significant reduction in cracking, compared to plain concrete, but steel–glass combination did not perform as well as other combinations. Eventually, Mesbah et al. (1999) reported that cast iron fibres were more efficient than PP fibres in reducing cracking, although the use of both types contributed to delaying the overall development of cracks.

On the other hand, Kayali et al. (1999) reported higher drying shrinkage strain for lightweight aggregate concretes reinforced with PP or steel fibres, compared to plain concrete. Aly et al. (2008) also observed increased shrinkage strain and increased permeability occurring in concrete incorporating fibres. They carried out their tests using 0.05-0.5% of PP fibre.

Vegetable fibres as natural fibres have also been used as reinforcing component. Toledo et al. (2005) carried out shrinkage measurement tests and stated that free plastic shrinkage could be reduced by the inclusion of 0.2% by volume of 25 mm short sisal fibres in cement mortar. These authors also reported that addition of 0.2% volume fraction of 25 mm sisal and coconut fibres, could delay the initial cracking for restrained plastic shrinkage and effectively controls crack development at the early age of composite. Soroushian and Ravanbakhsh (1998) have also employed cellulose fibres at 0.06% volume fraction, and found 78% reduction in plastic shrinkage crack area relative to plain conventional concrete. Boghossian and Wegner (2008) studied the influence of flax fibres and showed that when flax fibres were added at a volume fraction of 0.1%, the total projected area of cracks forming on the surface of specimens within the first 24 hours was reduced by more than 95% relative to plain mortar specimens, and maximum crack widths were reduced by more than 90% to less than 0.18 mm. In addition, flax fibres at all volume fractions and lengths tested were found to have minor effects on the amount of free plastic shrinkage experienced within the first 24 hours after moulding.

Chen & Chung (1996) indicated that the use of 0.19% by volume short carbon fibres (0.5% of the cement weight) in silica fume modified concrete results in 84% decrease in drying shrinkage strain after 14 days storage in air. The authors also stated that carbon fibres dominated the silica fume in lowering the drying shrinkage and increasing the flexural toughness. Eventually as they illustrated, the addition of fibres decreased the compressive strength as well as chemical attack resistance, due to the increase in air content.

Passuello et al. (2009) used PVA fibres in two different sizes, i.e. 8mm and 30mm in length, incorporated with SRA. Their tests resulted in that addition of fibres did not greatly modify the cracking time, but reduced the crack width by about 70% in the case of long fibres, and by almost 90% with short fibres. They also reported a small reduction in free shrinkage of samples with both size of fibres.

About the geometry of fibres, Banthia & Gupta (2006) tested sets of PP fibres 6.35-12.5 mm, and found that longer fibres and finer fibres were more effective in reducing crack areas and crack widths.

2.4.5 Internal curing

Internal curing is a newly developed method in concrete technology. The term internal curing implies introduction to the concrete mixture of a new component, which will serve as curing agent. In this relation, internal curing can be classified into two categories: water adding, when curing agent performs as water container slowly releasing water, and non-water adding, when curing agent intends in delay or prevent loss of water present in the system.

Water-adding internal curing is considered to be a more effective method in reducing autogenous shrinkage than non-water adding, since it directly affects the cause of autogenous shrinkage, namely self-desiccation (Zhutovsky, Kovler, & Bentur, 2002).

Internal curing, as well as external curing, can be classified into two categories (Kovler & Zhutovsky, 2006):

1- Internal sealing, when the curing agent is intended to delay or prevent loss of water from the hardening concrete, and

2- Internal water curing, when the curing agent performs as a water reservoir, which gradually releases water. Super absorbing polymers (SAP) is an example of these materials which as internal water reservoir, acts as a curing agent by gradually releasing absorbed water during the hydration process (Craeye, Geirnaert, & Schutter, 2010). This was also reported that by adding super absorbing polymers into the high performance concrete as an internal curing agent, and by adding additional curing water to the concrete mixture, the chemical shrinkage and the self-desiccation during hydration of the concrete is counteracted and thus the autogenous shrinkage of the HPC can be significantly reduced (Craeye, et al., 2010). These polymers can absorb very large quantities of water during concrete mixing, and once the initial free water has been consumed by the hydration reactions, the water absorbed by the SAP will be gradually released. However, the addition of SAP also leads to a significant reduction of mechanical strength and modulus of elasticity. On the other hand, a higher addition of SAP leads towards a higher creep deformation.

Internal curing is a novel method in shrinkage reduction, and it has been studied by a large number of researchers recently (Akcay & Tasdemir, 2010; A. Bentur, Igarashi, & Kovler, 2001; Dale P. Bentz, 2009; Dale P. Bentz & AÃ¯tcin, 2008; D. P. Bentz & Snyder, 1999; Craeye, et al., 2010; Daniel Cusson & Hoogeveen, 2008; D. Cusson, Lounis, & Daigle, 2010; Johansen, Millard, Mezencevova, Garas, & Kurtis, 2009; Kawashima & Shah, 2011; Nestle, et al., 2009; Sahmaran, Lachemi, Hossain, & Li, 2009; Zhutovsky, et al., 2002). Experimental results have shown that the use of pre-soaked light weight aggregates as water reservoirs effectively mitigates the autogenous shrinkage of concrete (Akcay & Tasdemir, 2010). The incorporation of internal curing in engineered cementitious composites by the addition of saturated fine lightweight aggregate is very beneficial in controlling the development of autogenous shrinkage of a high performance concrete. A reduction of 67% in autogenous shrinkage relative to control specimens at 28 days can be attained with a 20% substitution of silica sand by saturated lightweight aggregate. An additional benefit of drying shrinkage reduction of 37% relative to control specimens at 90 days, has also been reported (Sahmaran, et al., 2009).

Many researchers have also reported the advantages of using pre-saturated light weight aggregate in high performance concrete and high strength concrete (A. Bentur, et al., 2001; Craeye, et al., 2010; Daniel Cusson & Hoogeveen, 2008; D. Cusson, et al., 2010).

2.4.6 Other methods

Literature suggests more materials and methods, which have been experienced successfully at least in research field. The methods or materials under this section have been introduced by modification of current ideas and materials.

Surface treatment- Xu and Chung (2000) reported that the surface treatment of an admixture improves the mechanical properties of concrete, decreases the air void content, improves the workability, and increases the specific heat of cement paste. The authors found that the drying shrinkage is decreased by the use of silane-treated silica fume (Xu & Chung, 2000).

Carbon fibre addition is effective for decreasing the drying shrinkage, as previously reported (Xu & Chung, 2000). The effectiveness is further enhanced by surface treatment of the fibres, although the effect of the fibre surface treatment is small compared to the effect of the fibre addition.

The greater effectiveness of silane treatment compared to the other fibre surface treatments for drying shrinkage reduction is consistent with its greater effectiveness for improving the mechanical properties, decreasing the air void content, and increasing the specific heat (Xu & Chung, 2000).

The increase of the hydrophilic character of fibres and particles after the treatment and the formation of chemical bonds between fibres/particles and cement are believed to be the main reasons for the observed decrease of the drying shrinkage. By adding silane-treated carbon fibres and replacing as-received silica fume by silane-treated silica fume, the shrinkage at 28 days is decreased by 32% (Xu & Chung, 2000).

High performance drying shrinkage reducing admixture- Masanaga et al. (2006) have developed a modified generation of SRAs called NSR-1. By having hydrophobic characteristics, this admixture adsorbs on cement particles and is able to give hydrophobic properties on pore surfaces. As a result, NSR-1 reduces the interfacial tension between pore surfaces and water in these pores, and can reduce drying shrinkage effectively. The NSR-1 showed the same drying shrinkage reducing effect at a dosage of about one-seventh of the addition amount for the conventional DSRA. Besides NSR-1 with hydrophobic and carboxy groups, show higher drying shrinkage reducing effect which is derived from the adsorption of NSR-1 molecules onto cement particles (M. Masanaga, et al., 2006).

2.5 Discussion

In this chapter, the state of the art of the knowledge about shrinkage types and shrinkage mechanisms have been discussed. Furthermore, shrinkage reduction materials and methods have been explained. Different shrinkage mechanisms have been critically reviewed based on their according RH range. Based on these relationships, mechanisms behind shrinkage change by changing the RH of the environment. This transition between mechanisms has been studied in current project, particularly when shrinkage is supposed to reduce by bridging effect of fibres.

In regards to shrinkage reduction materials and methods, literature review revealed that side effects, such as strength reduction, are inevitable consequence of almost all of them. In some expansive agents, even cracking and higher autogenous shrinkage have been observed. These observations unveil the necessity of developing new shrinkage compensating materials with no or limited side effects.

Additionally, the surface treatment method has been reviewed and used as a modification to APP in Chapter 4.

3 Experimental procedures

3.1 Preface

As reviewed in Chapters 1 and 2, shrinkage in restraint concrete can cause shrinkage cracking which will eventually result in water and chemicals ingress in the system. In addition, shrinkage compensation is not usually achieved without compromising other physical or mechanical properties of concrete. Shrinkage compensation is therefore a trade-off of usually between mechanical properties, slump and shrinkage reduction. Furthermore.

The main aim of this research was to develop new shrinkage compensating admixtures, which enhances mechanical properties, or at least minimised compromises. In order to achieve this objective, firstly, current shrinkage compensating materials and methods were studied and assessed critically in Chapter 2. Second phase is to find materials with potential in shrinkage reduction and then investigate their performance. In addition, new shrinkage compensating admixtures can be designed based on new potentials in chemical compositions. As the shrinkage is the main property studied in this research, all admixtures need to be tested for their performance in cement mortars and then other physical and mechanical characteristics.

3.2 Methodology

Number of new admixtures have been chosen or designed to be used and studied in current project. These new admixtures were categorised as chemically active admixtures (expansive admixtures) and microfibres, of which some have been surface treated. SRA has also been used for comparing purposes in Chapter 4. The goal was set to study different mechanisms of shrinkage reduction such as chemical or physical phenomena.

Admixtures in question were added to the OPC mortar and were tested against control (Co) sample. Specimens were stored in lime-saturated water and in drying humidity cabinet for compressive strength test and drying shrinkage test, respectively. Admixture modified specimens and control specimens were then demoulded and cured using the same method in order to be comparable and the results would be repeatable. Flow, fresh density, drying shrinkage, mass loss and compressive strength were the main experiments carried out on all specimens. Based on the admixture and its expected behaviour, some other experiments such as expansion tests or microstructural analysis were also performed on the samples. Size characteristics of the specimens will be described along with test description.

In order to enhance some mechanical and physical effects, some admixtures were modified and then tested again under the same experiments. In the development process of the admixtures, their influence on the durability of cement-based materials was also a key index.

The next step was to investigate the mechanism of each admixture behind its performance in shrinkage compensation/reduction. For this purpose, depending on the expected behaviour, more experiments were chosen and used. Amongst these tests, drying shrinkage in varying RH, expansion in water, lime-saturated water and sulphate solution and microstructural analysis can be mentioned. The results of these experiments were then discussed, in order to provide general explanations for the performance of each admixture.

Coarse aggregates can usually provide more restraint to any volume change in concrete samples (ACI, 2009a) and this results in smaller shrinkage strain in concrete specimens than in mortar specimens. Therefore, laboratory experiments in current research project have been carried out on mortar specimens.

3.3 Raw materials

3.3.1 Main constituents

Table 3. 1 shows the chemical composition of Goliath General Purpose (GP) cement, supplied by Cement Australia was used in all experiments.

Table 3. 1. Chemical composition of Goliath General Purpose cement

Chemical Composition	(%)	Chemical Composition	(%)
CaO	63.98	SO_3	2.65
SiO_2	20.34	MgO	1.48
Al_2O_3	4.15	K_2O	0.77
Fe_2O_3	3.03	TiO_2	0.28
LOI	2.91	Na_2O	0.08

To minimise the effects of extra variables inside the mix, cement binders were not blended with other supplementary cementing materials.

Single washed sand, from Raymond Terrace, NSW, Australia meeting the exact grading requirements of standard specification ASTM C 778-06 (2006) and tested in accordance with set method AS 1141.11.1 (2009) was sourced from Rocla Quarry Products Pty Ltd, NSW, Australia. Prior to use, the fine aggregate was dried to saturated surface dry condition in room temperature to eliminate any excess water. The particle size distribution provided by the supplier is given in Table 3. 2.

Table 3. 2. Particle size distribution of Raymond Terrace single washed sand

Grading	Specification Limits (%)	Percent Passing Sieve (%)
1.18 mm	100	100
600 μm	96-100	96

425 µm	65-75	75
300 µm	20-30	28
150 µm	0-4	1

Drinking grade tap water was used and conditioned at 23 ± 2 °C prior to use in mixing process.

Glenium, a high-range water reducing admixture (HWR), as per AS1478.1 (2000) supplied by BASF, was used as superplasticiser in order to modify the mix design proposed in AS 2350.12 (2006), mainly to maintain constant workability of the mortars. For comparison purposes, all mixes within a set of samples contain the same concentration of HWR, and the flow of mixes with new admixtures and control mix are limited to $\text{Flow}_{\text{mean}}\pm10\%$ or $\text{Flow}_{\text{mean}}\pm15\%$. Glenium is a polycarboxylic-ether based HWR, and is expected to increases the workability of high-performance cementitious materials.

3.3.2 Shrinkage compensating admixture and fibres

The main admixtures and fibres, which were studied in current research, are: Ammonium polyphosphate (APP), surface treated APP (EnAPP), melamine polyphosphate (MePP), melamine, keratin, PE microfiber and wollastonite microfibre.

In order to compare the performance of these new admixtures against a commonly available SRA, a commercial type of SRA, Sika Control PLUS supplied by Sika Australia was selected for use in some mixes in Chapter 4. This type of SRA was supposed to reduce the drying and autogenous shrinkage, when added from 2-4% by weight of cement.

These admixtures and their behaviours will be comprehensively explained in following chapters.

3.4 Sample preparation method

Australian Standards (AS) were used where possible, for preparation of test specimens and the experiments. However, if needed for particular tests and not covered by AS, a few tests and techniques have been adopted from American Society for Testing and Materials (ASTM) as globally recognised testing and material society.

3.4.1 Mortar Mix Proportions

Mortar mix designs were proportioned from standardised raw material fractions listed under Section 6.1 of test method AS 2350.12 (2006). Based on this standard, each batch of three test specimens consists of 450 ±2 g of cement, 1350 ±5 g of sand, and 225 ±1 g of water. The cement-to-water-to-sand ratio was fixed at 1:0.5:3.

The main goal was to find a fixed w/c ratio and a fixed HWR concentration for each set of mixes, of which the flow of every mix would be around the average flow of the set by ±10 to 15%; i.e. to be $\text{Flow}_{\text{mean}}$ ±10% or $\text{Flow}_{\text{mean}}$ ±15%.

Having the mix proposed in AS 2350.12 as reference, the flow test was run to see whether the available Raymond Terrace sand gave enough workability. After doing few trial tests with changing w/c ratio from 0.47-0.53, the addition of HWR seemed clearly to be necessary. Therefore, in this stage several mixes were tested for flow in order to find the optimum concentration of HWR, when w/c ratio was fixed at 0.5. For this reason, the target flow of mixes with and without new admixtures was set to be about 60±10%. Eventually, after several tests with different concentrations of HWR at 23±1ºC and 60-70% RH, the final concentration in control mix and mixes with APP was found to be 1mL. Nevertheless, this concentration was subject to change when testing different additives and fibres.

Throughout each set of tests, which include a control sample, without any shrinkage compensating admixture (SCA), and mixes with SCA, the concentration of HWR was set to be constant. However, the objective was that the flow of mixes with SCA should be equal to of that in control sample with ±10 - 15%.

Another change to proposed mix proportion was subtraction of water used in HWR, which was about 65%, from mixing water. This modification has been applied in calculations and for mixes with 1mL of HWR; the water content is 224.35 g instead of 225 g.

SCAs have been added to mix proportions based on net cement weight. Additionally, all specimens containing SCAs are named and labelled using this concentration. For instance, a mix containing APP by 0.5% of cement weight is named APP 0.5, and for a mix with 450 g cement, there is (0.5% x 450) 2.25 g of APP. For all experimental sets, the control mix is named and labelled as Co.

In this thesis, different SCAs have been studied in different chapters. Therefore, there is a table of mix proportions in those chapters according to each SCA.

3.4.2 Mortar Mixing Procedures

The mechanical mixing of mortar to plastic consistency was conducted in accordance with the prescribed procedures of test method AS 2350.12-2006 (2006). Firstly, the HWR was added to the mixing water and pre-diluted and then the water was poured into the mixing bowl. Glenium addition was thoroughly mixed in water to ensure proper dispersion prior to the commencement of mixing. Prior to adding any PC to water, the mix of Glenium and water was mixed for 30 s on a speed setting of 140 ± 5 rpm using a compliant Hobart mixer.

Figure 3. 1. The Hobart mixer used for this project

Immediately after the first 30 s of mixing, of PC was added to the water, which is being mixed. At 60 s the mixer was stopped and switched to a higher speed setting, i.e. 285 ± 10 rpm. This speed of mixing was continued for 30 s and then the mixer was again stopped and the bowl was removed from the mixer and then covering the bowl for another 90 s. The next task was to put the bowl back in the Hobart mixer and to run the mixer for 60 s at high speed (285 ± 10 rpm). The mix was then tested for flow or cast in the mould. Once flow was measured, the specimen was mixed again for 15 s at high speed.

3.5 Sample preparation for drying shrinkage and compressive strength

Based on AS2350.13 (2006), steel moulds consisting of three horizontal compartments for moulding three prismatic specimens were used. The resultant prismatic specimen for drying shrinkage test were 40 mm×40 mm×145 mm (2350.13, 2006) in size and of that for compressive strength test were 40 mm×40 mm×160 mm in size (2350.11, 2006). Figure 3. 2 and Figure 3. 3 illustrate the compressive strength test moulds and drying shrinkage test moulds based on AS2350.11 and AS2350.13, respectively.

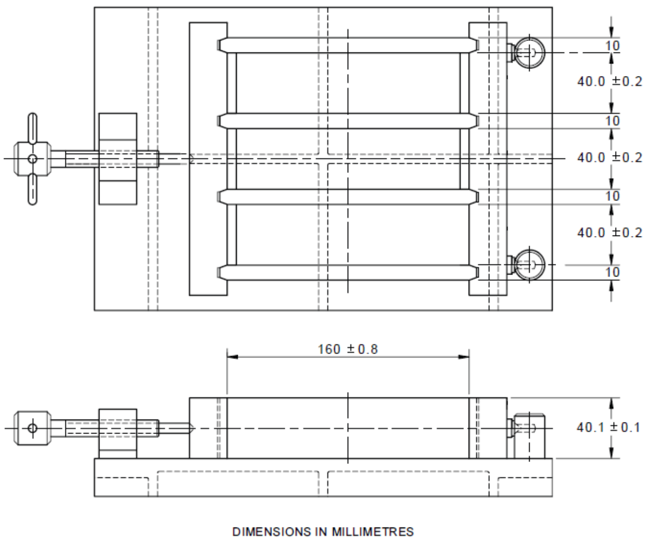
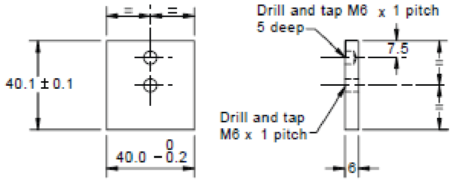


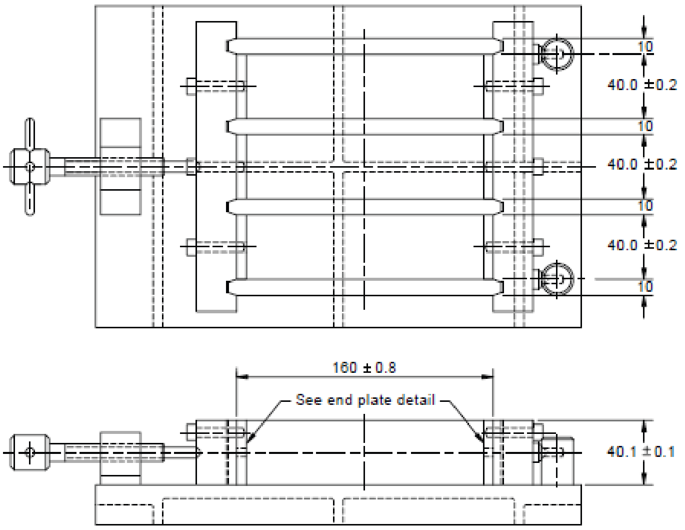
Figure 3. 2. Schematic illustration of compressive strength moulds, AS 2350.11 (2006)

The consolidation method described in AS 2350.12 specifies the use of a vibrating table. This equipment was not available and, thus, an ASTM method of mortar compaction was adopted as a modification for this purpose. The compaction technique listed under Clause 10.4.2 of ASTM C 109 describes hand tamping of mortar specimens by tamping in 2 rounds and each round at right angles to the other one, for each layer of placing (ASTM, 2011). This is also necessary that the compaction pressure should be uniformly applied throughout the prisms. In the modified version, due to the larger size of moulds, two courses of 12 and 18 tamping strokes were applied for each placement layer, instead of 4 and 4, as stated in ASTM C 109.

The mortar specimens for drying shrinkage test and compressive strength tests were prepared, mixed and cast using AS2350.12 and AS2350.13 (2006; 2006), respectively. Since a moist room or curing cabinet for the initial 24 h was unavailable, air-tight zip-lock plastic bags were used for storage of the gang moulds containing the mortar prisms, immediately after casting.



(a) End plate detail



(b) Shrinkage mould

Figure 3. 3. Schematic illustration of drying shrinkage moulds, AS 2350.13 (2006)

At the completion of 24 h moist curing, the mortar prisms were demoulded and labelled. After 24 h, mortar specimens were demoulded and weighed before continuing the curing in lime water for compressive strength test and storage in humidity cabinet for drying shrinkage test processes (2350.12, 2006; 2350.13, 2006). After demoulding, the shrinkage specimens were stored inside the humidity-controlled cabinet at a temperature of 23±2°C and a relative humidity of not less than 50%. In fact, in current research the RH of the humidity cabinet was set at 60%. This was due to that hypothesis that 50% RH is claimed to be a boundary line between different shrinkage mechanisms such as surface tension and disjoining pressure (Kovler & Zhutovsky, 2006).

Figure 3. 4. Adjustable humidity chamber

The length measurements of shrinkage specimens were taken after 7, 14, 21, 28 days following AS2350.13. However, long-term study continued up to for 1-year study for some sets of specimens.

To prevent leaching of CH from mortar and to maintain alkalinity for the curing of compressive strength mortar prisms, lime-saturated water was introduced for ageing mortar prior to testing. These samples were taken for 7, 28 and 56 days studies. Lime-saturated water tub is also prepared in accordance with ASTM C 511 (ASTM, 2009a), by adding 3 g of CH to 1 L of tap water.

3.6 Methods of characterisation

All tests were carried out at 23±1 °C. The RH of mortar lab was mostly ranging from 60-70%. In order to obtain comparable results for the evaluation of the new admixture, four different specimens, including a control specimen, were prepared on the same day and under the same environmental condition.

3.6.1 Flow and wet density of mortar samples

In addition to drying shrinkage and compressive strength measurements of the specimens, a number of physical properties of fresh and hardened state mortars have also been carried out on mortar mixes. The studies mainly include fresh density, based on ASTM C 138 (2009b), flow of mortar, based on AS 2701 (2001), and mass loss of mortars, based on AS2350.13, during storage period.

The workability of fresh hydraulic mortar was determined by measurement of flow following the stipulated procedures of method AS 2701-2001. Flow was determined from the mean reading of four diametrical measurements using a calliper and ruler to an accuracy of 1 mm. The flow can be determined from Equation 3. 1:

$$F\,(\%) = \frac{D_2 - D_1}{D_1} \times 100 \qquad \textbf{Equation 3. 1}$$

where:

F = percent flow

D_1 (mm) = internal base diameter of base of conical flow mould (100 mm)

D_2 (mm) = average diameter of mortar mass after flowing

Figure 3. 5. The flow table

During flow determinations, visual assessments were also carried out for establishing any irregularities in rheological behaviour of the mixes. At the completion of measuring flow, the dispersed mortar contents were returned to the mixing bowl and remixed for an additional 15 s, as specified in test method ASTM C 109/C 109M-08 (2011).

Vessalas (2009) developed a modified test method on the premise of mass per unit volume of freshly mixed concrete using rodding consolidation method described in test method AS 1012.5 (1999) and in test method ASTM C 138/C 138M-09 (2009b). This method was adopted for determining the density of fresh mortar.

Modified changes to equipment listed in Section 4 of test method ASTM C 138/C 138M-09 involved downsizing the capacity of the measure to accommodate mortar. A kitchen bowl scrapper complying with Clause 4.3.2 requirements of test method AS 2350.12-2006 was used for sampling mortar. The volumetric mass of mortar was determined using a steel cylindrical 265 mL measure and 10 mm diametrical rounded rod for tamping. At the completion of 20 times of rodding for each layer, a rubber mallet was used for tapping the measure to ensure closure of voids. With the filled mortar contents, a flat glass cover plate was fitted over the top of the volumetric measure, striking off any excess mortar. By use of the mentioned modified equipment, the procedural steps of Clauses 6.2, 6.3, 6.5, 6.6 and 6.7 of test method ASTM C 138/C 138M-09 were followed for determining volumetric masses.

By combining these measured masses of the filled contents, the wet densities of mortars can be determined from Equation 3. 2:

$$\rho_{wet} = \frac{M_c - M_m}{V_m}$$ **Equation 3. 2**

where:

ρ_{wet} (kg/m^3) = wet density

M_c (kg) = measure filled with cementing mix contents

M_m (kg) = mass of empty measure

V_m (m^3) = volume of measure

The absolute error in wet density determination was taken to be ± 10 kg/m^3 following the criteria stipulated in Section 9 of standard test method ASTM C 138/C 138M-09 and the requirements listed in Section 10 of standard method AS 1012.5 (1999).

3.6.2 Shrinkage measurement

Immediately after demoulding, the initial length of the specimens was measured to the nearest 0.001 mm, using a digital length comparator. Subsequent measurements were also taken after 7, 14, 21, and 28 days of air storage and for some mixes, this was even extended to 56 or 364 days following mixing. The drying shrinkage strain is calculated by Equation 3. 3:

$$\frac{\Delta L}{L} \times 10^6$$

Equation 3. 3

in microstrain, where ΔL is the difference between the initial length measurement taken immediately after demoulding and the length reading at the particular age assessed, and L is the original length of the specimen, which based on AS 2350.13 (2006) is defined as the inner distance between the gauge studs in the mortar specimen.

After each subsequent measurement, the mortar sample was returned to the humidity chamber. In order to minimise the effects of room temperature and RH on accuracy of results, length measurements and mass determinations were carried out in 3 minutes.

Length measurement of samples was also accompanied by specimen mass measurement. By this means, mass change of mortar samples was recorded along with subsequent length measurement.

Figure 3. 6 illustrates a length comparator used for length measurements of mortar specimens. Prior to each measurement of each set of mortars, the length comparator was calibrated using a reference bar.

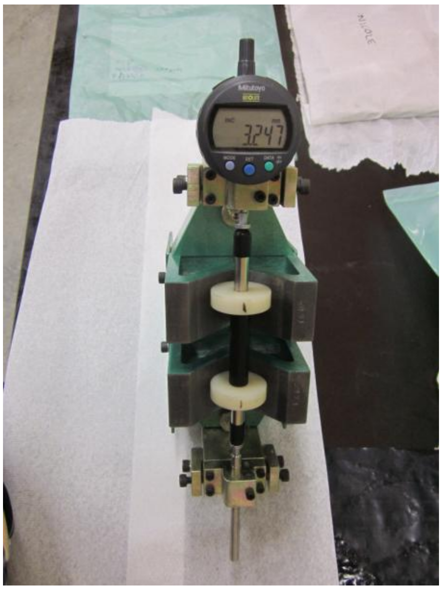


Figure 3. 6. The length comparator used in this project

3.6.3 Compressive strength

A list of physical and mechanical properties of mixes containing new admixtures was also studied. The major contributor to this list is compressive strength measurement of mortar mixes as this is the most important engineering property of cementitious construction materials.

The specimens prepared were stored in their mould in a moist atmosphere for 24 h, then demoulded and placed in lime-saturated water until subsequent strength testing. The testing machine used for the determination of compressive strength met the Grade A requirements of AS 2193 (2005) for the range of loads measured using a rate of loading of 2.4 ± 0.2 kN/s.

Based on AS 2350.12, compressive strength test is defined as the arithmetic mean of the three compressive strength determinations made on a set of three prisms. If one result within the three determinations varies by more than 10% from the mean of the three, all the result shall be discarded and the test shall be repeated.

3.6.4 Behavioural experiments

A number of different experiments were selected in order to assess the performance of each admixture and to study them more comprehensively. The type of these experiments completely depends on the type of admixture and its expected performance in the cement-based matrix. Therefore, the behavioural experiments carried out for APP are different from the behavioural experiments performed for microfibres. For instance for APP investigation, these experiments were carried out:

Expansion in plain water and lime-saturated water- In this experiment the APP modified specimens and control specimens were stored in plain water (tap water) environment and the volume and mass change of each sample were monitored. The mixing, casting and sampling of specimens used in this phase are exactly similar to the drying shrinkage experiment procedure. Therefore, the moulds used here are precisely the ones used for drying shrinkage tests.

In another attempt, similar specimens were prepared and then stored in lime-saturated water (hydrated lime in tap water). Similarly, volume and mass change of all specimens were monitored.

Sulphate solution exposure- This experiment contained of exposing APP modified and control specimens in sulphate saturated water (sodium sulphate in tap water) to monitor their expansion in this particular environment.

Moreover, micro-bridging of microfibres was assessed by:

Exposing the OPC mortars to varying relative humidity- Specimens modified with PE or wollastonite microfibers were stored in humidity cabinet for 8 weeks, during the first 4 weeks the RH was set at 30% and for the next 4 weeks at 65-70%. This experiment was aimed to assess the micro-bridging effect of microfibers by exposing the specimens to very dry and very humid environment.

These tests will be comprehensively introduced in next chapters.

3.7 Plastic shrinkage

In order to investigate cement mortar samples for their early-age shrinkage and cracking behaviour, plastic shrinkage is aimed to be investigated. Since, there is no standard test regarding plastic shrinkage measurement, a modified test method was adopted which will be explained in a separate chapter (Chapter 6) with its results.

3.8 Microstructural analysis

3.8.1 Scanning Electron Microscopy (SEM)

Microstructural phase analysis was carried out in research projects in order to investigate the mechanisms and arrangements behind some shrinkage reducing/compensating admixtures. In the current study, scanning electron microscopy (SEM) and thermal analysis have been used for these purposes.

SEM is a powerful imaging technique capable of producing high-resolution images of a sample's surface morphology (Goldstein, et al., 1992). In essence, SEM employs a high-energy beam of electrons to scan over a small area of a sample surface. This is the interaction of this primary electron beam with the atoms, which make up the sample results in energy loss due to repeated random scattering and absorption. A variety of signals is produced from this interaction; however, the detection from the secondary electrons (SE) are utilised for the production of images. As a result, SE due to their low energy originate within a few nm of the sample's surface, and, hence, images are produced which have excellent topographic contrast and display detail to a maximum of 1 to 5 nm in size.

Microstructural analysis was conducted using a Zeiss Supra 55VP Field Emission Scanning Electron Microscope (FESEM) of UTS, equipped with an in-lens detector. All specimens were carbon coated and placed under vacuum prior to imaging at an accelerating voltage of 20 kV. In order to reduce any charging, a silver dag was employed to provide a conductive path between the sample and the aluminium stub to which the sample was affixed.

3.8.2 Thermal Analysis

Thermal analysis techniques was used to characterise materials by measuring physical and chemical properties as a function of temperature (Haines, 1995), are invaluable for the study of hydration reactions and identifying and quantifying phases formed from the effects of reacting additives. Differential thermal analysis (DTA) monitors the difference in temperature between a substance and a reference material as a function of time, or temperature, whilst the temperature of the two specimens is programmed. The DTA curve is a plot of the difference in temperature between the reference and sample versus the temperature and generally shows a series of peaks, the positions of which are governed by the chemical composition and crystal structure of the substance, and the areas of which are related to the energy involved during the reaction. An endothermic reaction, where energy is absorbed in the form of heat, gives a negative peak, whilst an exothermic reaction, where energy is released in the form of heat, gives a positive peak.

Furthermore, thermogravimetric analysis (TG) may be used to monitor the weight change of a sample in relation to change in temperature. The derivative weight loss (DTG) curves, which are a plot of rate of mass change with temperature, can be used to differentiate the point at which maximum weight loss is most apparent. In addition, decomposition phases can be characterised by TG.

Simultaneous thermal analysis refers to the application of two or more thermal analysis techniques at the same time with DTA-TG being the most frequently used methods. The techniques provide complementary information, allowing for differentiation of endothermic and exothermic events with no associated mass loss (e.g., phase transitions) from those with a mass loss (e.g., dehydration and decarbonation reactions). Reactions taking place in cement paste, between the CH liberated by the hydration of PC and the admixtures added to the mix, may be monitored by the estimation of the proportion of CH present in the cementing system. This method of evaluation allows for the determination of the degree of chemical reactivity applicable to the SCM system under investigation at a given age of maturity.

For testing, a crushed sample of 28-day compressive strength mortar, with the highest result out of 3 in a set, was chosen. This sample was placed in a sealed plastic bag and stored in a freezer (-4 ºC), in order to stop any further hydration reactions. This sample was been prepared for the test by being ground. Then a small portion of the top, middle and bottom layer of pulverised sample was taken in order to get a representative of the mix. Around 50 mg of each mix was utilised in the analysis.

4 Ammonium polyphosphate and other reactive agents

4.1 Preface

This chapter covers a study of those chemical admixtures, which were expected to interfere in and affect cement hydration. From previous chapters, this can be concluded that other shrinkage compensating agents (SCA) such as SRAs and fibres, etc. do not directly contribute to cement paste chemical reactions, except some types of expansive agents.

The admixtures studied in current chapter are derived and redesigned from some particular type of commercial chemical compositions, which was expected to affect shrinkage mechanism and compensate plastic or drying shrinkage by the means of expansion and/or strengthening the cement paste. Chemical design and modifications of these admixtures were gratefully done or guided and supervised by Professor Georgius Adam from the Centre for Built Infrastructure Research, University of Technology, Sydney.

Few numbers of chemical agents have been initially introduced, and then investigated for their performance in shrinkage compensation throughout this chapter. In later stages, more experimental tasks were carried out to further investigate

4.2 Ammonium polyphosphate

Calcium phosphate cement is a well-known binding material in orthopaedic and dental fields (Puri, et al., 2008). Resulting in high compressive strength, calcium phosphate cements have been used as construction material as well as biomaterials (Sturgeon, Allcock, Nair, Laurencin, & Brown, 2009; Watanabe, Tanaka, Sakurai, & Maeda, 2006). Watanabe (2006) has reported that the costly calcium phosphate cement containing silicate sand has enough mechanical strength for construction materials and building materials (Watanabe, et al., 2006).

Phosphate cement-based binders, prepared by mixing MgO powder with $NH_4H_2PO_4$ powder and borax powder, have been used as a concrete repair product due to its rapid hardening, long enough setting time to cast, high early strength and good bond in research projects (Sarkar, 1990; Yang & Wu, 1999).

Bénard et al, (2008) studied cement mortars containing nitrates and phosphates, in order to investigate dimensional stability of these materials for the conditioning of aqueous low-level radioactive wastes generated by nuclear power plants. This was also reported that the mortars containing phosphate or a mixture of phosphates and nitrates exhibit shrinkage at early age, but after a few hours swelling was the predominant behaviour (Bénard, et al., 2008). This transitory shrinkage was attributed to the conversion of these chemicals into hydroxyapatite of a precursor (amorphous calcium phosphate or octacalcium phosphate) readily precipitated in the cement paste after mixing. They also presented that swelling significantly increased with the ionic concentration of the mixing solution. The resultant solution of cement paste is characterized by a high calcium concentration and a high pH. In such conditions, the presence of phosphates is supposed to lead to the formation of hydroxyapatite.

Brown (1999) compared calcium silicates and calcium phosphates hydrations, when the former one forms C-S-H and the latter one forms hydroxyapatite (HAp). Both are introduced to be compounds of variable composition, both incorporate water, and both exhibit high surface areas. Although both are weakly crystalline, HAp is described to be weaker due to small crystallite size.

Calcium phosphates and calcium silicates both are reported to undergo pozzolanic reactions (Martin & Brown, 1993). Calcium phosphate hydration is also illustrated by Martin and Brown (1993) to be:

$$3[4CaO\ .\ P_2O_5] + 3H_2O \rightarrow Ca_{10}(PO_4)_6\,(OH)_2 + 2Ca(OH)_2$$

Additionally, C-S-H and HAp show significant nano-structural differences. HAp contains isolated phosphate tetrahedra while the silica tetrahedra in C-S-H form more extended structures.

This background of calcium phosphate and its hydration led to the idea of the potential of phosphates to be incorporated in cement mortars as shrinkage compensating agent, albeit in a new composition.

In this study ultra high molecular weight ammonium polyphosphate (APP), as a novel inorganic polymer, is evaluated as a shrinkage compensating admixture. This newly designed composition was expected to react in situ with calcium hydroxide (CH) formed during hydration to produce insoluble calcium polyphosphates (CP). This novel agent was prepared and evaluated as fire retarding agent and smoke suppressant at the University of Technology, Sydney (Edye, 2009).

APP is commercially introduced as an inorganic salt of polyphosphoric acid and ammonia containing both chains. Its chemical formula can be presented as $[NH_4\,PO_3]_n$. The properties of APP depend on the number of repeating units in the polymer molecule and to a degree on how often it branches. APP is also used as a food additive and emulsifier, (E number: E545). It is also used as a flame retardant for polyolefins and polyurethanes and as fertilizer.

As a type of fire retardants, commercial APP decomposes to form ammonia and phosphoric acid. The phosphoric acid acts as an acid catalyst in the dehydration of carbon-based poly-alcohols, such as cellulose in wood. The phosphoric acid reacts with alcohol groups to form stable polyphosphate film. The esters decompose to release carbon dioxide and regenerate the phosphoric acid catalyst. The release of non-flammable carbon dioxide helps dilute the air of oxygen and flammable decomposition products of the material that is burning.

Commercially, it can also be used in expanding fireproof material, such as polyurethanes and epoxy resins. It has also been used as the fire retardant of fibre, wood and plastic (Edye, 2009). APP is the main ingredient of expanding retardant thermoplastic due to its high molecular weight and good heat stabilisation.

Similarly in current research, inorganic APP as ultra-high molecular weight is supposed to react with calcium hydroxide produced by cement hydration and form calcium polyphosphate (CP) and volatile amine derivative or ammonia. CP as explained earlier is a type of cementing product expected to be formed in-situ inside the matrix. Therefore, new agent is supposed to enhance the mechanical characteristics of cement-based materials due to the formed binder. On the other hand, the second product of the expected reaction, volatile amine compounds, would be a type of volatile corrosion inhibitor. Thus, this new agent is expected to act as a shrinkage compensating agent which reduces the total shrinkage and at the same time, it is expected to act as a volatile corrosion inhibitor.

Using this admixture, laboratory experiments were carried out using different dosages of APP to assess its efficiency as a shrinkage compensating material and its effect on the physical and mechanical properties of cement mortars.

4.2.1 Experimental results

Table 4. 1 illustrates the mix proportions of mortar samples used for APP investigation.

Table 4. 1. Mix proportions of mortar specimens with and without APP

Mixes / Raw materials	Co	APP0.05	APP 0.1	APP0.2	APP 0.4	APP 0.5	APP 0.6	APP 0.7	APP0.8	APP1.0	SRA4.0
Cement (g)	450	450	450	450	450	450	450	450	450	450	450
Sand (g)	1350	1350	1350	1350	1350	1350	1350	1350	1350	1350	1350
Water (g)	224.35	224.35	224.35	224.35	224.35	224.35	224.35	224.35	224.35	224.35	222.55
HWR (mL)	1	1	1	1	1	1	1	1	1	1	1
APP (g)	0	0.23	0.45	0.90	1.80	2.25	2.70	3.15	3.60	4.50	0
SRA (ml)	0	0	0	0	0	0	0	0	0	0	18

In this range, Co stands for control mix without added APP. APP0.05 to APP1.0 represents mixes with 0.05 to 1.0% of APP concentration. Additionally, SRA4.0 represents a mix without APP, but with 4.0% concentration of a commercial SRA.

4.2.1.1 **Fresh state properties**

Figure 4. 1, demonstrates the workability of fresh mortars based on measurements carried out in accordance with ASTM standards (ASTM, 2007). The flow test was principally performed immediately after 4 minutes of mixing. The sample of mortar used for flow test was then returned to the mortar bowl and the whole mix was remixed for 15 s to be prepared for placing in the moulds.

An increase in workability was observed with 0.1 to 1.0% by weight of cement additions of APP to the mortar mixes. The increase in flow was shown to be directly related to the increase in APP concentration, with the maximum increase in flow dedicated to APP1.0 with 12% rise compared to the Co mix. However, at low concentrations such as 0.05% and high concentrations such as 3.0% of APP, the effect was adverse.

The flow modification of APP might be explained through its anionic nature, before getting involved in any reaction. Anionic admixtures like APP with a chain containing some polar groups can also be used as water-reducing admixtures (Mehta P. K. & M., 2006).

Figure 4. 1 also demonstrates that the commercial SRA has significantly increased the flow of mix, which might easily result in segregation unless a special consideration is taken into account.

Wet density of all mixes was also measured (ASTM, 2009b), no significant difference was observed.

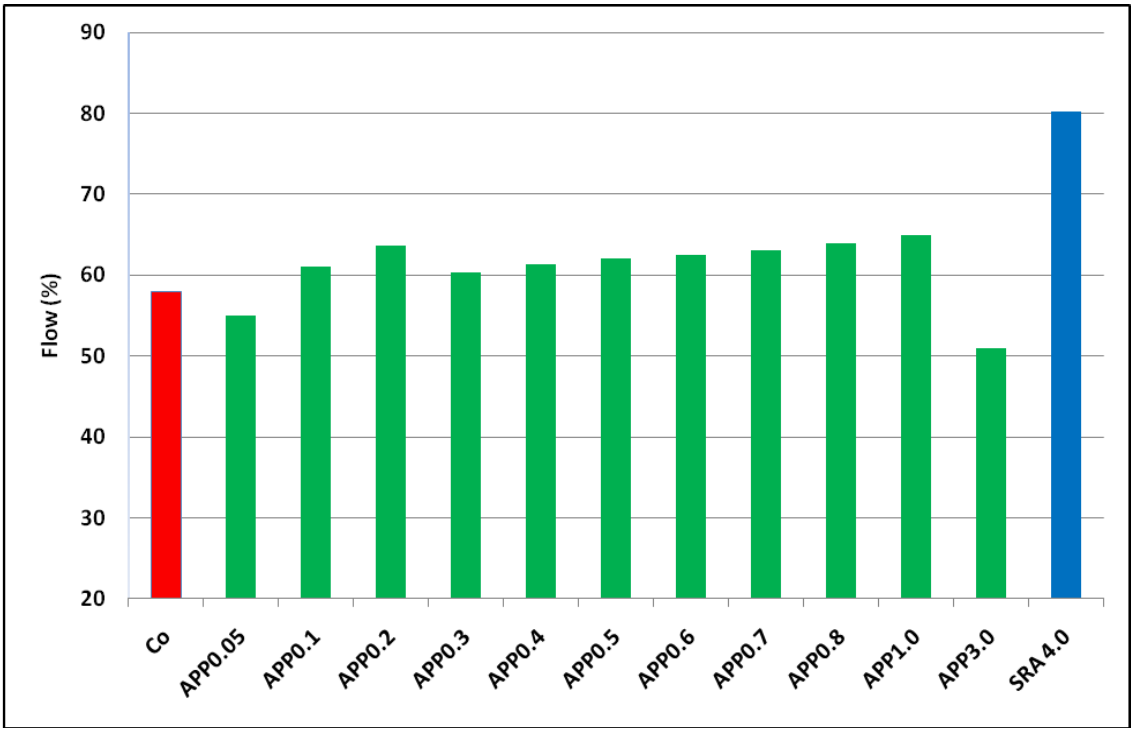


Figure 4. 1. Flow of mixes with and without APP

4.2.1.2 **Drying shrinkage**

Given the limited number of available drying shrinkage moulds, 4 or 6 (in later stages) set of specimens containing different dosages of APP (including 0.0% for Co) could be cast and compared in each single test. In order to have a benchmark for comparison sake in each single test, 1 specimen out of 4 or 6 was always chosen to be the Co. Therefore, it was impossible to test all the APP concentrations in a single test and each set of test was done on a separate day and most likely subject to different RH, temperature, and operator's influence. This might result in different drying strain results for the same mix cast on different days, e.g., Co. For this reason, each set of test was repeated after few weeks to double-check the results and thus, the results of each set were shown in separate graphs. However, in order to avoid redundancy, some of the repeated test results that are not presented in this dissertation.

Figure 4. 2 demonstrates the 56 days drying shrinkage of a set of cement mortars with APP concentration ranging from 0.0 to 0.6% of cement weight. This graph clearly shows that APP modified mortars present reduced drying shrinkage at 28 and 56 days

as important ages for a concrete sample. This decrease was increased by increasing the APP concentration in the mixes.

Figure 4. 2 also illustrates that the 7-day drying shrinkage of APP modified mixes is higher than of that in Co. However, this trend gradually changes in next 7-14 days of storage and drying shrinkage of APP modified specimens drop below the drying shrinkage of control specimens.

This observation suggests that APP modified mixes present higher shrinkage at early ages but lower shrinkage in long-term, compared to Co mixes. This could be due to the delayed reactions of APP in cementitious structure, which in behaviour is similar to delayed ettringite formation (DEF) phenomenon, which provides expansion in cementitious matrix in long-term.

This unique volume change behaviour of APP modified mixes led this study to investigate the expansion characteristics of APP, as the main mechanism behind shrinkage compensation of cement mortars. Therefore, in next sections, the cement mortar samples were subject to different environments to study expansive phenomenon of APP modified mixes against Co samples.

Figure 4. 3 depicts long-term drying strain of APP modified mixes and a SRA modified mix. SRA modified mix has the lowest result of drying shrinkage amongst the other mixes. Next to SRA modified mix, the APP modified mixes have the lower drying shrinkage than Co, with the best result observed for the mix with 1.0 % APP concentration.

Another observation from this test is that all the specimens containing APP were found to have noticeable surface wetness characteristics for first 24 hours and before demoulding. This observation either suggests the water retention in APP modified mixtures, what is only applicable to curing period, or retardation of hardening of cement paste, which seems to be correct. Further increase in APP concentration (greater than 1.0% and up to 3.0%) was also considered, although the specimen was not set even after 24 hours and could not hold the shrinkage pins after demoulding. This observation can also be related to the nature of phosphate agents which are well-known as hydration control agent (Ramachandran & Mailvaganam, 1995). Therefore, the maximum APP concentration used in the study was chosen to be 1.0%.

The results of short-term and long-term drying shrinkage for humidity-controlled storage of specimens with low APP concentrations are shown in Figure 4. 4. According to Figure 4. 4, drying shrinkage was reduced when low concentrations of APP, such as 0.05%, were added into the mix. Maximum reductions of 25% in shrinkage strain after 28 days can be seen in mixes with added APP when compared to the control mix. In reference to long-term behaviour too, Figure 4. 4 can confirm that APP modified mixes still have promising results when compared to the control mix.

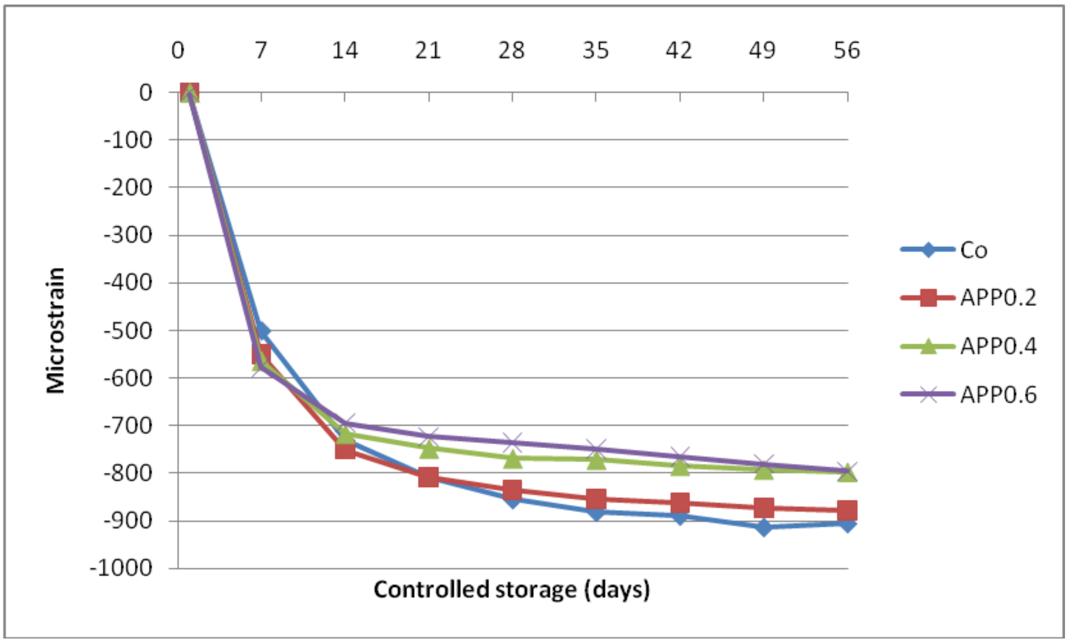


Figure 4. 2. Drying shrinkage of mortar samples

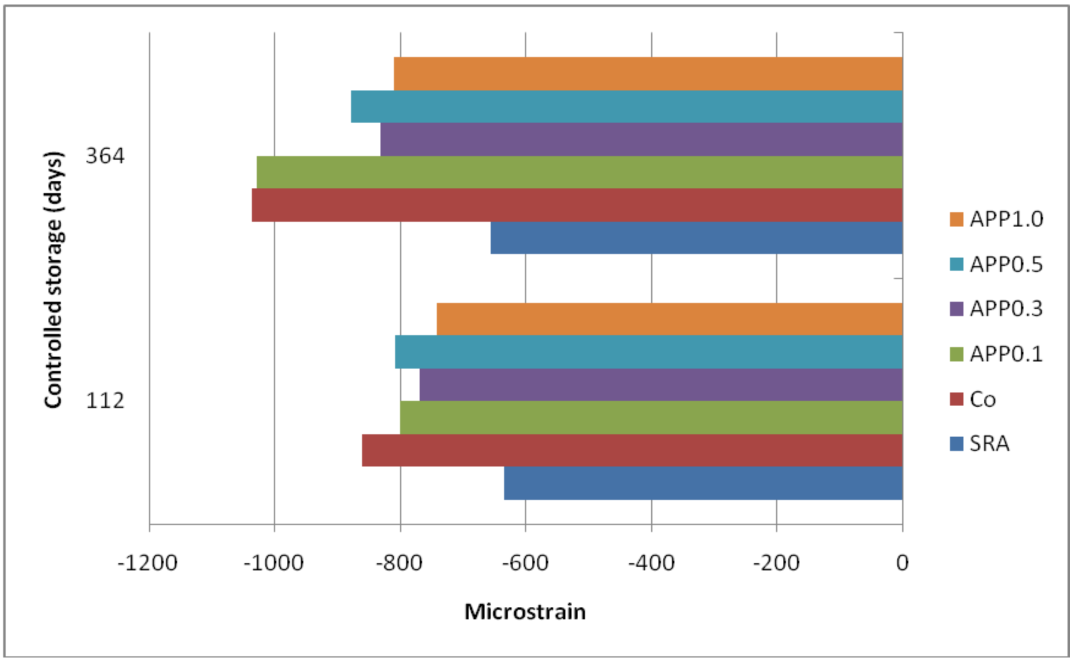


Figure 4. 3. Long-term drying shrinkage of mortar samples

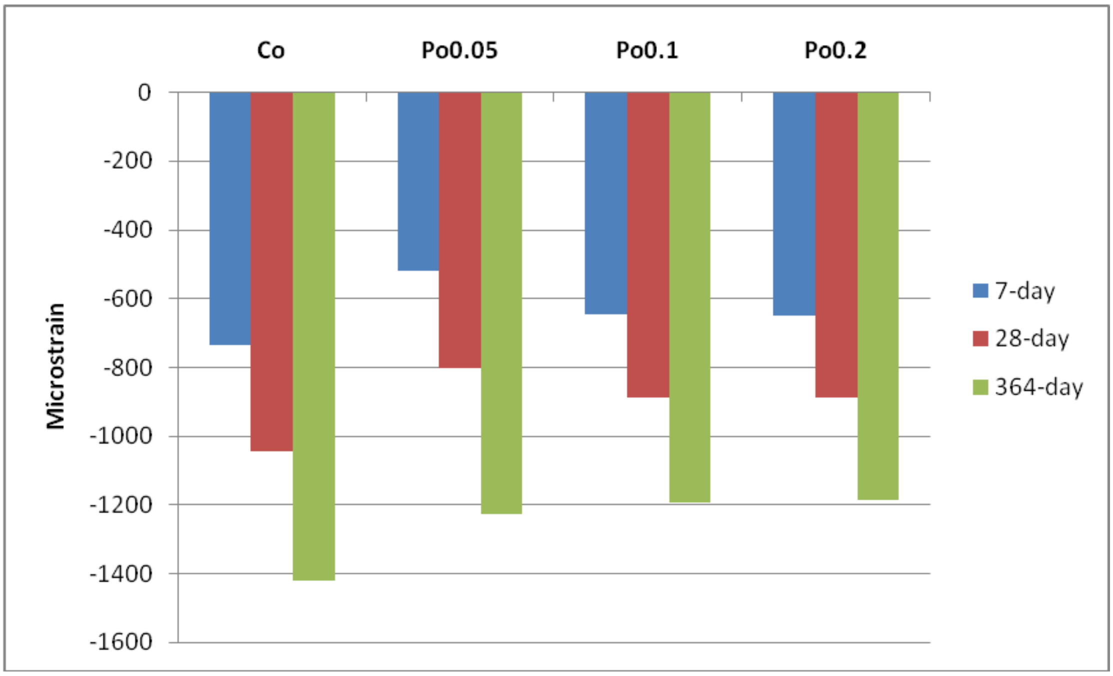


Figure 4. 4. Short-term and long-term drying shrinkage of mortar samples with low concentration of APP

The other noticeable observation was the smell of ammonia during the mixing that became more noticeable at higher concentrations of APP. This observation can support the idea of early reaction of APP with calcium hydroxide present in the mix, which liberates NH_3 as a product.

The given test results in this part are only a representative portion of large number of experiments carried out on APP mixes.

4.2.1.3 **Expansion characteristics**

Despite expansive agents introduced in Chapter 2, there are some other internal phenomena, which produce some amount of expansion in cement-based materials. Amongst all, alkali-aggregate reaction (AAR) occurs between the alkalis present in the cement paste and certain reactive materials in the aggregate (P.K. Mehta & Monteiro, 2006). On the other hand, delayed hydration of crystalline CaO and MgO when present in excessive amounts in Portland cement(ACI, 2009b), can cause expansion and possible cracking, as well as delayed ettringite formation (DEF) which is a case of internal chemical sulphate attack.

Drying shrinkage reduction mechanism of APP has been investigated by different physical and chemical experiments. Since, expansion was one of the theories behind drying shrinkage compensation of APP, two different tests were done on APP modified specimens. In one of these tests, APP modified samples, along with a Co were cured in lime-saturated water after demoulding, and cured under plain water.

Two sets of specimens were cast for each test. These specimens were inserted in the curing tank (lime-saturate water or plain water), immediately after demoulding and initial measurements. One set contains Co1, APP0.2, APP0.4 and APP0.6, and the other set contains Co2, APP0.8, APP1.0 and APP1.2. Co1 and Co2 are identical specimens, which represent the control specimen in this study. Consequently, the set of first 4 specimens were cast at the same time and thus, comparable to each other. Accordingly, the second set of 4 specimens was prepared at the same time and comparable to each other. The temperature of both media was fixed at 22ºC, and within 28 days of experiment, the solutions were not refreshed.

Figure 4. 5 demonstrates volume changes of 2 sets of mixes cured in a lime-saturated water tub. 2 similar sets of specimens were also cast and stored in a plain water tub. Figure 4. 6 depicts the expansive behaviour of cement mortar specimens stored in plain water.

As expected, all the specimens cured under lime-saturated water and plain water were subjected to expansive volume change, due to the ingress of moisture and filling the capillary voids. The volume change observed in APP modified samples was generally greater than the volume changes in Co specimens cured in lime-saturated water. In this regard, APP0.2, APP0.4 and APP0.6 expanded greater than their control mix, Co1. APP0.8, APP1.0 and APP1.2 have been also seen to expand greater than their control mix, Co2, which is related to the amount of lime adsorbed by the specimens.

Within plain water, cement mortars containing low concentrations of APP did not expand as much as their control specimen, Co1. Nevertheless, the specimens with higher concentrations such as 0.8, 1.0 and 1.2 experienced larger volume change than their control specimen, Co2, in plain water.

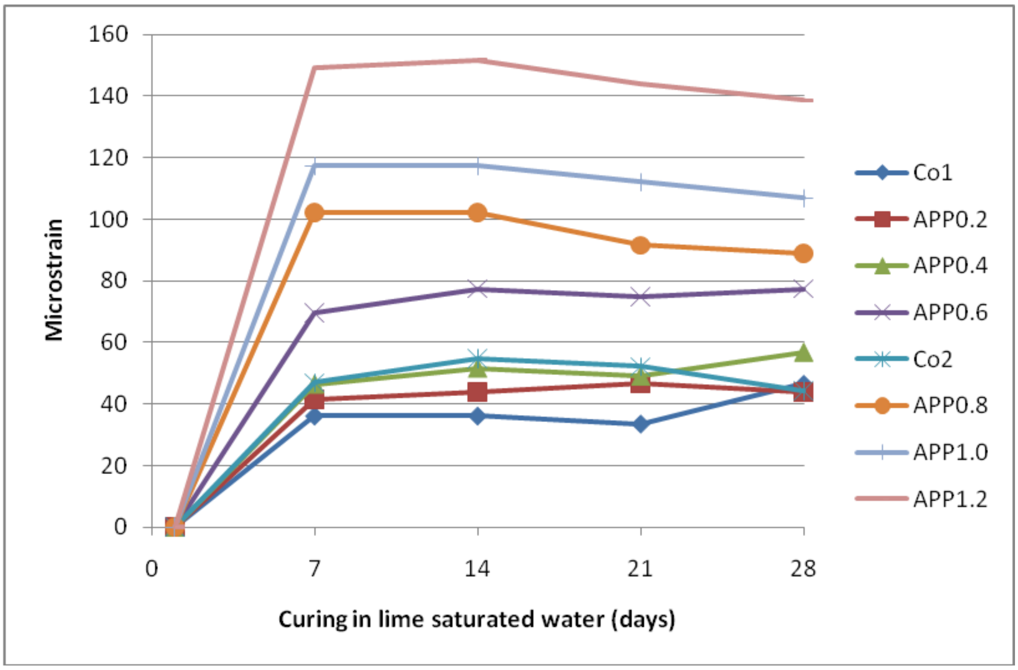


Figure 4. 5. Length change in lime-saturated water

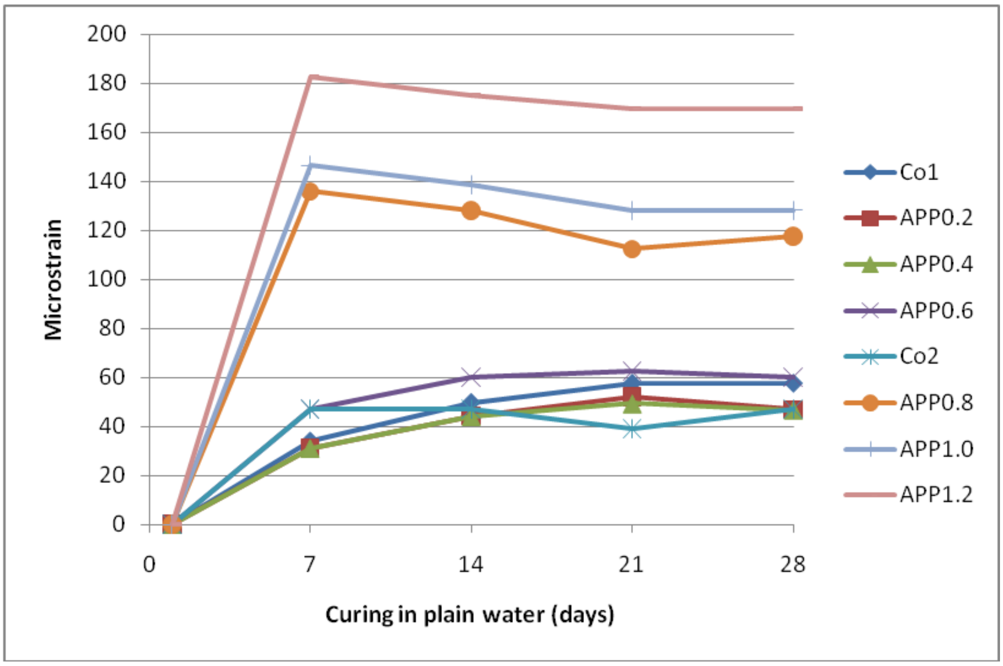


Figure 4. 6. Length change in plain water

Since mixed and cast at different times, Co1 and Co2 specimens did show slightly different end results in each test. However, in each test and set, volume change of APP modified mixes can easily be compared to their according control specimen, i.e. Co1 or Co2.

In general, Figure 4. 5 and Figure 4. 6 suggest that the addition of high concentrations of APP (0.8, 1.0 and 1.2 % cement weight) to cementitious mixtures results in expansion of samples in both media. This observation highlights the phenomenon of expansion capacity of APP in cement mortars. However, the mixes with lower concentrations of APP did not show significant expansive characteristics comparing to control specimens.

Control specimen was supposed to be in balance with lime-saturated environment, in regards to calcium hydroxide (CH) transfer. Whereas, APP mixes were even expected to adsorb CH from the lime-saturated water by osmosis, due to the reduction of CH concentration after reacting with APP. Permanent supply of CH due to the adsorption can help the APP reaction to survive continuously. Therefore, substantial expansion of mixes with high concentrations of APP can be explained.

In contrast, CH produced by cement hydration, was expected to be drained away from control specimens stored in plain water, due to the imbalance of CH in specimen and surrounding medium. However, moisture ingress is still expected to happen and accordingly cause expansion in control specimens as well as APP modified specimens. In APP contained mixes, CH produced from hydration can be assumed to be used for APP reaction and at the same time to be drained away to the plain water with very low lime concentration. This loss of CH from APP modified mixes might be the reason that APP0.2 and APP0.4 expand less than their control specimen. Whereas in APP0.8, APP1.0 and APP1.2, the high concentration of APP causes higher rate of need for CH agents, and thus there will be less amount of CH to leach out. This difference in CH loss and hold resulted in different behaviours of expansions in APP modified mixes.

Expansion characteristics of identical specimens in different environments, i.e. lime-saturated and plain water, were expected to be different, due to dissimilar CH exchange in these media. This hypothesis was studied by casting only 4 specimens, 2 control specimens from the same batch and 2 APP0.2 mortar specimens from another batch. A set containing a Co and an APP0.2 was cured in lime-saturated water and another identical set was cured in plain water. In this case, comparing expansion behaviour of e.g. Co in different media was possible, as both control specimens are from the same mix.

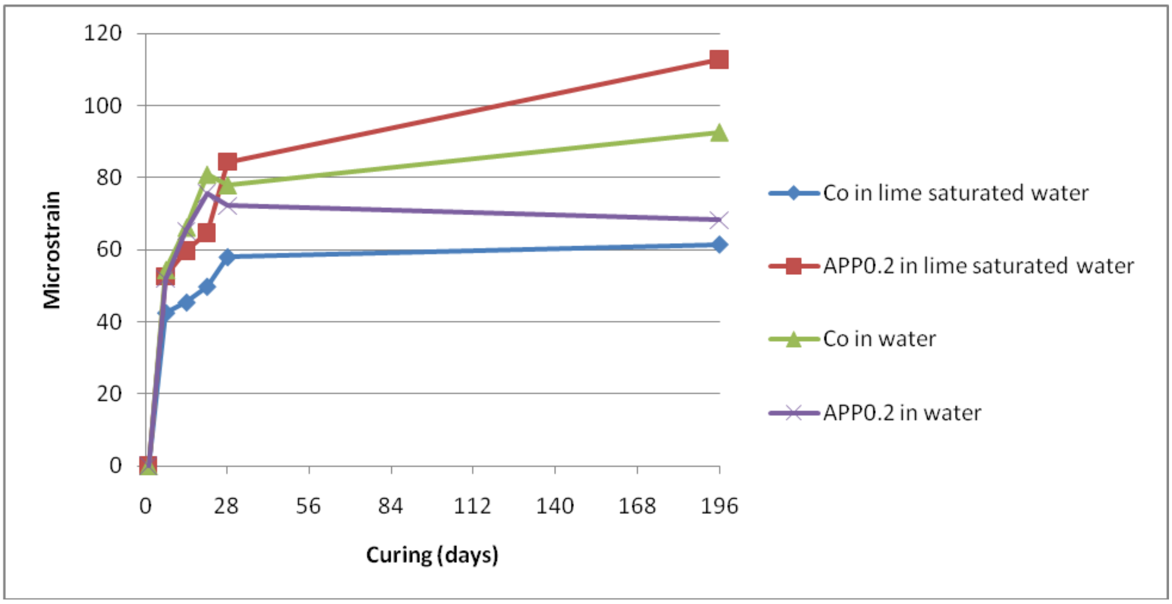


Figure 4. 7. Change of mixes in lime-saturated water curing and water curing conditions for 28 weeks

Figure 4. 7 demonstrates the long term volume change of mixes in both media, where Co expands in higher degrees when cured in plain water than in lime-saturated water; but APP0.2 mix expands more in lime-saturated water than plain water. These observations are in agreement with results of expansion in plain water from Figure 4. 6, which illustrated greater expansion for Co than mortars modified by low concentrations of APP. This expansion can be caused by the concentration gradient forcing more water into the control specimens.

There is no need to mention that the samples in plain water medium have been reached equilibrium in CH concentration after few months.

4.2.1.4 **Compressive strength**

Figure 4. 8 and Figure 4. 9 exemplify the 7-day, 28-day and 180-day compressive strength of mortar specimens. According to these figures, the compressive strength of mortar samples increases generally with increasing addition of APP, and mixes with APP0.8 to APP1.0 in particular showed significant increase in short and long-term.

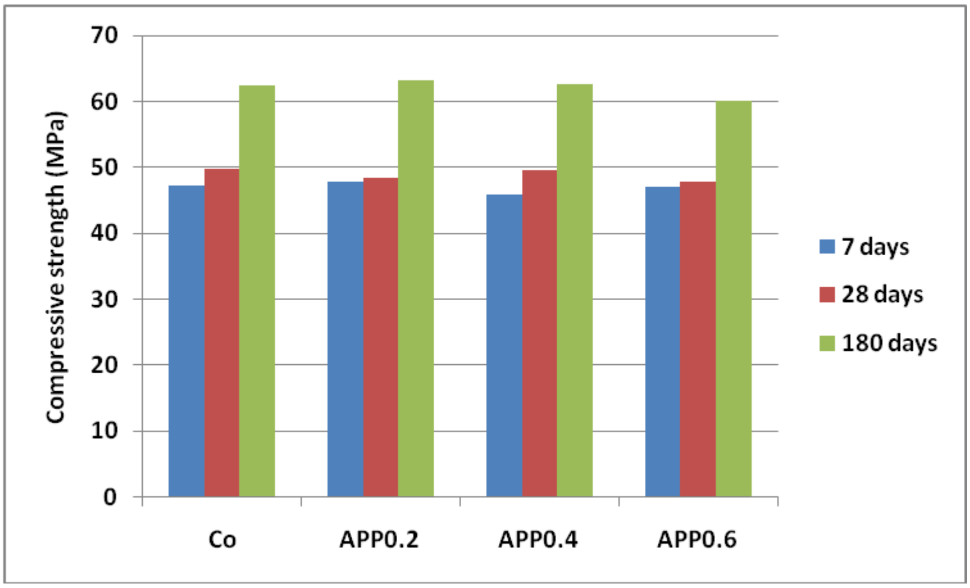


Figure 4. 8. Compressive strength test results for mortar specimens

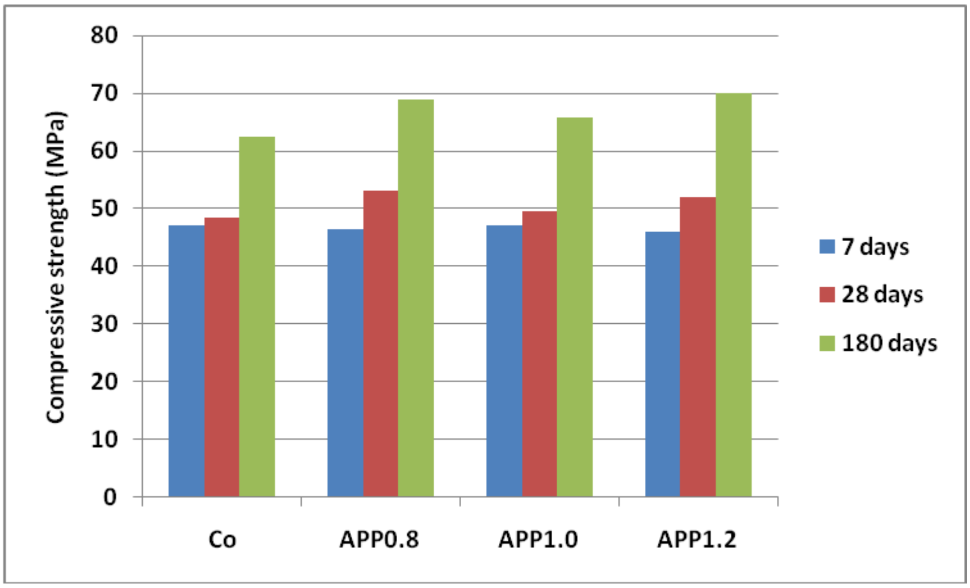


Figure 4. 9. Compressive strength test results for mortar specimens

On the other hand, addition of low concentrations such as 0.2% or 0.4% was found not to increase the compressive strength substantially, and in some cases even to slightly decrease the strength.

In general, it can be concluded that with increasing in APP additions, the compressive strength slightly increases as it can be supported by Figure 4. 10; however, this trend is limited to a certain range of additions, the compressive strength tends to decrease; however, still not lower than of Co. Based on this study, the addition of commercial SRA has decreased the compressive strength when compared to control mix as it was expected from previous studies (J. Brooks & Jiang, 1997).

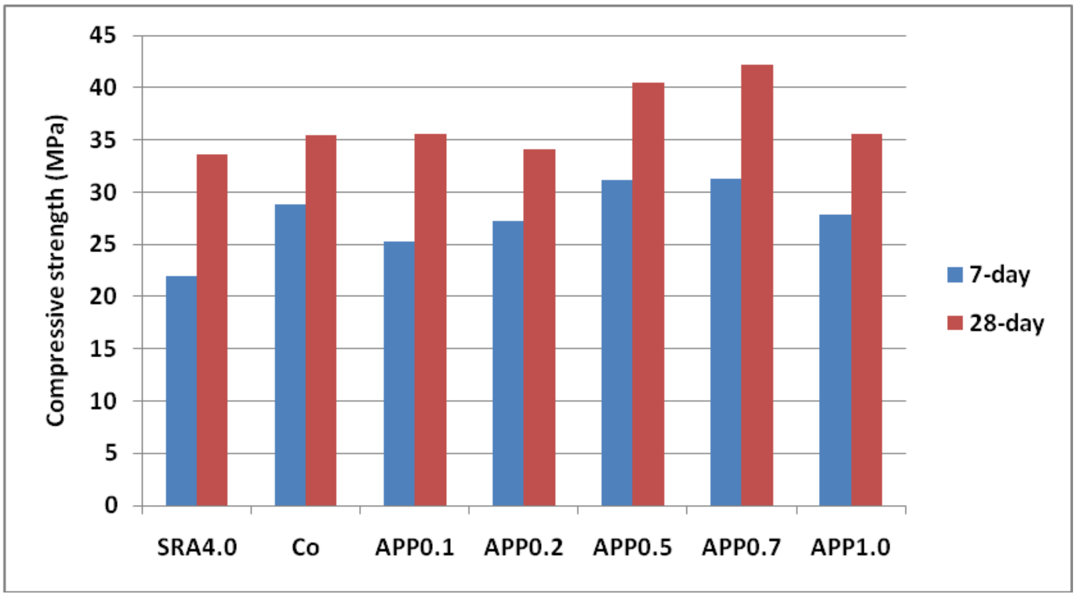


Figure 4. 10. Compressive strength of mortar specimens with and without APP

The high compressive strength obtained in APP modified specimens can be related to the production of calcium polyphosphate and probable magnesium polyphosphate cement inside the paste. Calcium phosphate is a cementitious type material which has been used in dental and orthopaedic applications for years, due to its high mechanical properties (Puri, et al., 2008; Watanabe, et al., 2006).

Calcium polyphosphate is expected to generate a strong structure inside the cement paste, which can also be the reason behind its shrinkage compensation. On the other hand, APP can react with any constituent of MgO present in the mix forming magnesia cement which results in strength modification (Vandeperre, Liska, & Al-Tabbaa, 2008).

4.2.1.5 **Mass loss**

The mass of each drying shrinkage specimen was also measured during each subsequent length measurement. Since the specimens were stored in temperature and humidity controlled chamber (23ºC and 60% RH), it was expected that all specimens would undergo mass loss. Results of percentage mass change after 28 days and 364 days are shown in Figure 4. 11. Based on this figure, the percentage mass change was found to be higher for all additions of APP mortars than mass change of the control mix throughout the experiment.

The increase in the mass loss as a function of APP concentration can be related to the reaction of APP with CH and transferring it to the less stable (volatile) by-product, ammonium hydroxide that can be easily released. However, this mass loss can also be due to greater moisture loss in APP mixes than in Co.

Moisture intake capacity of mixes was also studied by relocating 20 weeks old specimens, which were stored at 50%RH to a new environmentally controlled condition at 80%RH and 23°C and tracking the weight increase of specimens for 4 weeks. The results showed that mixes with 0.5% of APP gained 4.18% weight increase while control mixes gained only 3.63% weight increase. Therefore, it can be concluded that APP mixes can gain and lose moisture in greater degree than control samples do in the certain period of time.

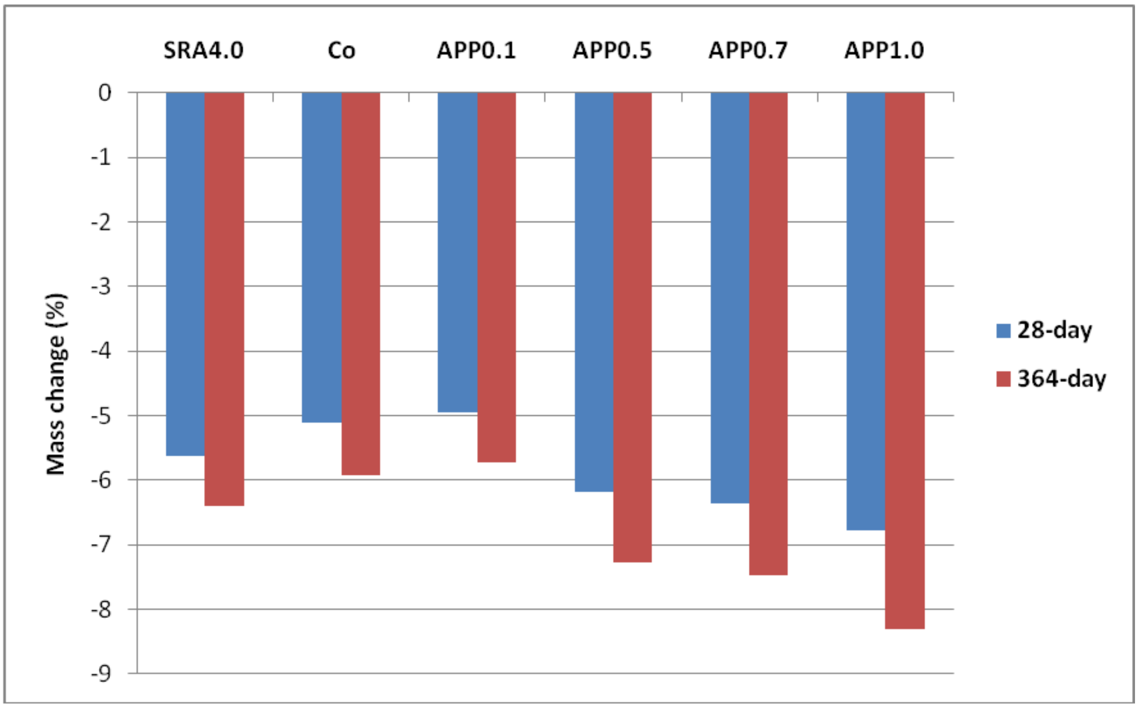


Figure 4. 11. Mass loss after 28 and 364 days

In addition, in terms of chemical structure, losing two hydroxyl groups (molecular weight 34) for each molecule of reacted CH (molecular weight 74) can possibly be another explanation.

Figure 4. 11 also suggests that moisture loss of the mix with commercial SRA is still higher than of that in control mix. Therefore, SRA has no advantage than Co in regards to mass/moisture loss.

4.2.1.6 **Mechanism investigation**

The hypothesis that introduces the reaction between APP and CH as the mechanism behind shrinkage compensation and strength enhancement of mortar samples is studied in this section by the means of chemical reactions and microstructural investigations. Thus, in this section, mortar specimens have been exposed to a few numbers of chemicals during curing and the effects on drying shrinkage and compressive strength have been studied.

Sulphate exposure- Due to the presence of aluminates phases in hydrated Portland cement paste, when a cement paste comes in contact with sulphate ions, whether internally or externally, the alumina-containing hydrates are converted to ettringite, which is known to result in the sulphate-induced expansion in cementitious material (Mehta P. K. & M., 2006). In order to investigate more about the behaviour of APP modified mixtures, two concentrations of APP, 0.2 and 0.4%, were tested along with a control mix. Following AS 2350.14 (2006), these specimens were demoulded after 2 days, at which time they were immersed in lime-saturated water for next 5 days (2006). After 7 days, the specimens were evaluated for their initial length and then stored in a sulphate solution containing 0.352 mol/L of Na_2SO_4 (50g/L). According to this standard, the sodium sulphate solution was refreshed every 2 weeks. The above mentioned samples were mixed and cast in the same way that drying shrinkage samples were mixed and cast.

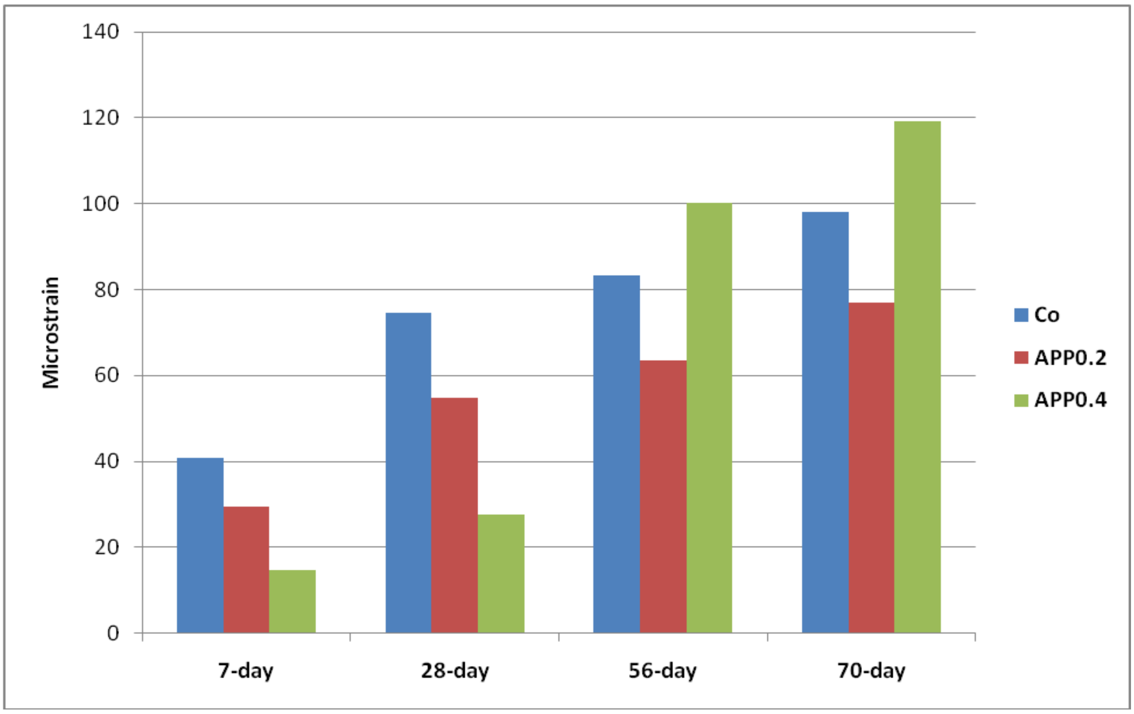


Figure 4. 12. Expansion of mortar samples after exposure to sulphate saturated solution

Figure 4. 12 demonstrates the volume change of mortar specimens after exposure to sulphate saturated medium. Figure 4. 12 suggests, all specimens were subject to continuing expansion due to the sulphate ingress to cementitious samples.

Comparing expansion behaviour of APP0.2 and Co from Figure 4. 12 suggests that APP mixture has less sulphate-induced expansions than control mixture at least during the first 28 days of exposure. Thus, it can be concluded that APP mixtures are more resistant to sulphate invasion and it is possibly due to the shortage of potential reacting CH in APP modified mixtures to be involved in reaction with sulphate ions. Additionally, it can also be concluded that the formed calcium polyphosphate is adequately sulphate resistant. However, long-term results for 56 and 70 days exposure reveal that APP0.4 show significant expansion and change the trend shown in short-term period. This delayed expansion was also seen in drying shrinkage results of APP modified mixes.

Despite the reaction between sulphate ions and CH, gypsum formation (as a result of cation-exchange reactions) is also reported to be capable of causing expansion (P. Kumar Mehta, 1983). In addition, this observation can also be justified by the existence of a rigid network of calcium polyphosphate formed in APP modified cement pastes which can also expand in long-term. This phenomenon was observed in compressive strength enhancement and expansion of APP mixtures in lime-saturated water.

Thermal Analysis- Thermal analysis is a technique, used to characterise materials by measuring physical and chemical properties as a function of temperature (Haines, 1995). Differential thermal analysis (DTA) monitors the difference in temperature between a substance and a reference material as a function of time, or temperature, whilst the temperature of the two specimens is programmed. The DTA curve shows a series of peaks, the positions of which are governed by the chemical composition and crystal structure of the substance, and the areas of which are related to the energy involved during the reaction. An endothermic reaction, where energy is absorbed in the form of heat, gives a negative peak, whilst an exothermic reaction, where energy is released in the form of heat, gives a positive peak.

Thermogravimetric analysis (TGA) monitors the weight change of a sample in relation to change in temperature. The derivative weight loss (DTG) curves, which plot of rate of mass change with temperature, can be used to determine the point at which maximum weight loss is most apparent. Decomposition phases, irrespective of their crystallinity, can be characterised by TGA.

Simultaneous thermal analysis refers to the application of two or more thermal analysis techniques at the same time with DTA-TG being the most frequently used methods.

Chemical reactions, between the CH liberated by the hydration of PC and the APP agent added to some mixes, may be monitored by the estimation of the proportion of CH present in the cementing system.

Thermal analysis was carried out in order to characterise properties of materials as a function of temperature and to gain additional information to the mechanism of reaction of APP that leads to the mentioned results.

After compressive strength tests, a crushed section of a prism, with the highest strength result was picked from the compression test machine. These samples were then stored in a freezer in order to stop their hydration reactions. Then a pulverised sample of about 50 mg was used for thermal analysis. In these experiments, temperature rise was set at 10 ºC per minute and the maximum temperature was fixed at 1000 ºC, as there was no expected agent to be studied beyond that.

Since very low concentration of APP was used in drying shrinkage and compressive strength tests mortar samples, no remarkable change was observed in the thermogravimetric (TGA) analysis results of APP modified mixes such as APP0.4 or APP1.0%, and control samples. Therefore, the tests were repeatedly run with increasing the APP concentration, with no success. As next step, the aggregate was eliminated from both APP mix and Co. Eventually, two slurry samples, without aggregate, of which one was control mixture and the other one a mixture with 10.0% APP concentration, were used. Figure 4. 13 and Figure 4. 14 illustrate the TGA results of Co slurry and APP10.0 slurry, respectively. These slurry specimens were mixed using 450 g of cement, 225 g of water and according percentage of APP. As these samples were supposed to be crushed and pulverised eventually, their size was not important. Thus, the slurry samples were cast in cubic moulds.

The weight change curve on Figure 4. 13 shows that the mass loss of Co sample in second region of differential TGA-DTA curve, around 450ºC, to be about 4.55%, and this change represents the dehydration of CH. While, based on Figure 4. 14 this mass loss is about 2.29% in APP mixture.

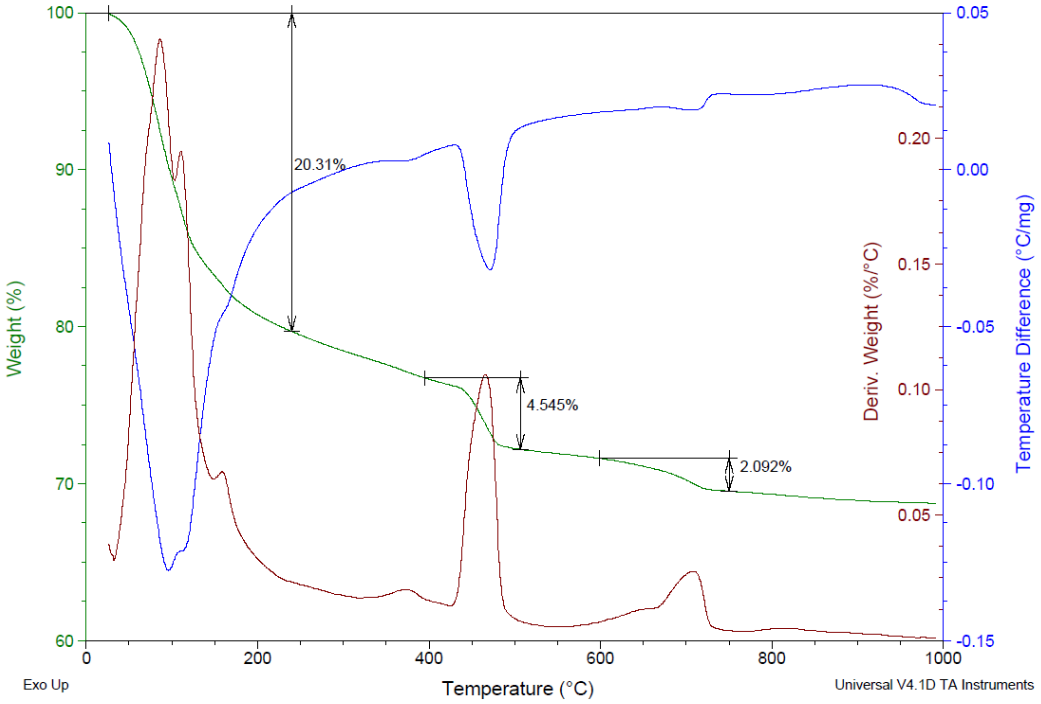


Figure 4. 13. SDT (Simultaneous differential thermal analysis) results of control slurry

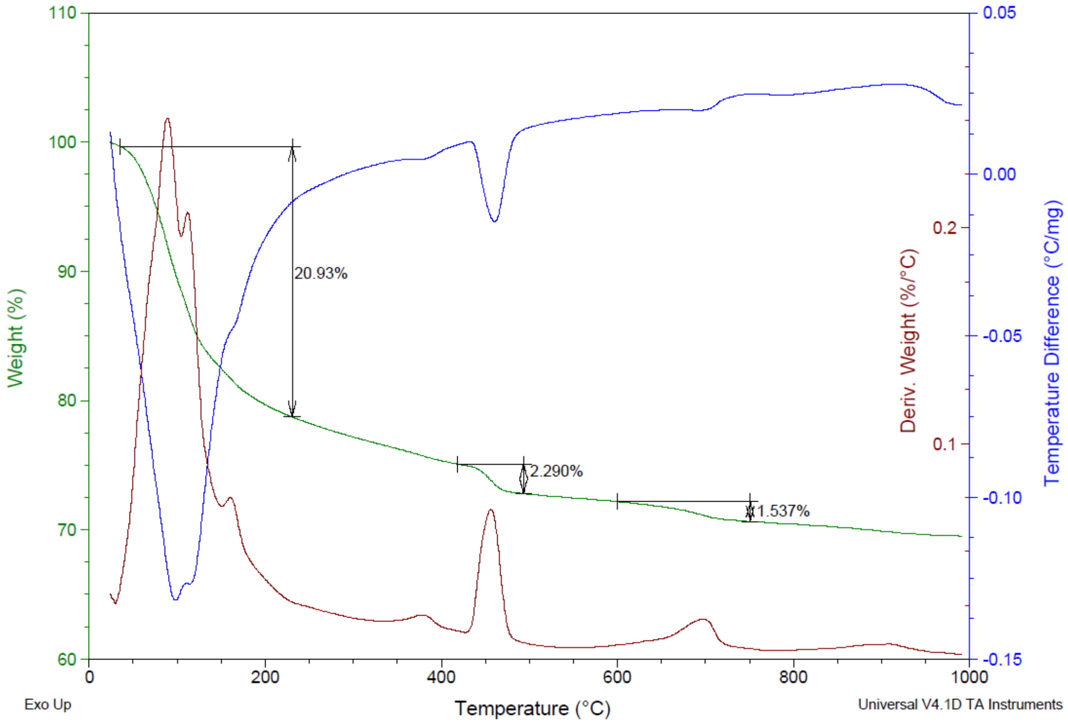


Figure 4. 14. SDT (Simultaneous differential thermal analysis) results of APP10.0 slurry

Figure 4. 13 and Figure 4. 14 generally indicate that the first region below 420 °C corresponds to the free, adsorbed and micro-pore water resulting from the dehydration of C-S-H phases present. These C-S-H phases responsible for strength development have formed from the primary hydration of C_3S and C_2S, depending on age assessed. The second region between 420 to 500 °C is characteristic of the dehydration of CH present and is shown as a mass loss step at 450 °C in the differential TG (DTG) curve, as discussed earlier. In the third region from 500 to 680 °C, the decarbonation of $CaCO_3$ with an asymmetric decomposition peak at circa 630 °C. The results from the third region in Figure 4. 13 and Figure 4. 14 also suggest that the concentration of $CaCO_3$ has been decreased in APP modified mix.

For all thermograms, the thermal decomposition range of 105 to 260 °C associated with the dehydration of identifying C-S-H strengthening phases was obscured due to the loss of adsorbed water masking this region. Consequently, mass loss data in the dehydroxylation and decarbonation regions of thermograms was utilised for determining the activity of APP by studying the degree of consuming CH in the formation of C-S-H strengthening phases.

These results are in agreement with that hypothesis of reactivity of APP with CH, which results in less concentration of CH in APP modified mixtures. This observation verifies the expected mechanism of APP with CH.

4.2.2 Results and discussions

In previous sections a small portion of results from drying shrinkage experiments were presented. The discussed results were selected as a brief narrative of the study of the effect of APP on drying shrinkage. Regarding repeatability of results and in order to consider the error involved in tests, an extensive number of drying shrinkage experiments were conducted and then repeated under the same conditions. Therefore, the presented results are meant to be a proper representative of all results.

Additionally, experiments were carried out using different concentrations of APP, from 0.05% to even 3.0%. Although the shrinkage reduction was not seen in the whole range, but in a vast range of concentrations, drying shrinkage reduction is observed.

Promising results for 0.2-0.8% addition of APP show that a mechanism of shrinkage compensating is actually working inside the matrix. Additionally, small to considerable increase in compressive strength reveals the formation of a new binder or in other words a new strong network as could be expected from the reaction between APP and CH, which produces calcium polyphosphate and NH_4OH, or volatile amine compounds. The latter represents one of the most commercially used corrosion inhibitors known as volatile corrosion inhibitors (Paillere, 1995; Rammelt, Koehler, & Reinhard, 2009). Accordingly, this new multi functional admixture can behave as corrosion inhibitor as well as shrinkage compensating agent.

Additionally, removing the CH formed from hydration, through APP reactions, from concrete and mortar samples can reduce the chance of carbonation reaction and shrinkage, which leads to corrosion of the reinforcements and carbonation shrinkage, respectively.

As mentioned previously, specimens with 3% of APP were unable to hold the preinstalled pins. Even for specimens with 1% of APP, measuring the length change of the mortar samples was difficult as they were too wet even after 24 hours. This observation might be due to retardation in hydration property of APP and therefore water retention that is in agreement with the flow enhancement in APP mixes. However, based on mass loss and gain observations, APP mixes seem to simply lose more water in drying and gain more water during curing, when compared to control mix.

Figure 4. 5 and Figure 4. 6 stated that APP generates expansion in cement mortars, although they also suggest that expansion phenomenon of mixes with new admixture is significantly dependant on their curing conditions. Therefore, it can be concluded that longer curing conditions for concrete elements in construction sites, can enhance the expansion characteristics of APP mixes.

Results from drying shrinkage tests demonstrate that the new inorganic admixture has promising effects on the shrinkage reduction in addition to its effect on enhancing the rheological, physical and mechanical properties of the mixes consisting low dosage range of 0.2-0.8%.

The expansion characteristic of APP can be related to the production of calcium polyphosphate from APP reaction with CH, which as described earlier, in the next stage forms crystalline hydroxyapatite (HAp). This expansion does not occur in early stages and comes to existence after 1-2 weeks.

The late crystallization of the remaining ettringite in a hardened material stored in wet conditions, without any external sulphate supply, can be associated with a global swelling of the material up to about 2% (Brunetaud, Divet, & Damidot, 2008). This type of expansions can also be caused by external sulphate attacks (M. Zhang, Chen, Lv, Wang, & Ye).

Presence of sufficient amounts of reactive components, alkali and moisture are the requirements for the alkali silica reaction (ASR) (Shayan, Diggins, & Ivanusec, 1996; Shayan, Xu, Chirgwin, & Morris, 2010). These phenomena can be the possible explanation of the performance of APP in cement-based materials.

Further investigation using microstructural analytical techniques needs to be carried out in order to derive the fundamental reasons of the shrinkage reduction mechanism of APP.

4.3 Further chemically active admixtures

In current PhD research project, a number of different admixtures were studied, following the study on APP. These admixtures were mostly designed and selected in order to avoid some APP disadvantages, i.e. ammonia odour and moisture loss, and even to enhance its advantages.

Encapsulated version of APP (EnAPP) and Melamine polyphosphate (MePP) were produced in Material laboratory of Faculty of Science, University of Technology Sydney, to overcome these shortcomings of APP.

On the other hand, some more chemicals were investigated for their drying shrinkage reduction potential. From this list, Melamine and Keratin can be named. Melamine did not affect the drying shrinkage results nor did affect the compressive strength. Nevertheless, keratin produced a substantial amount of very early age expansion during mixing and casting, but then suffers from a far large amount of drying shrinkage.

Experimental results are presented under following headings.

4.3.1 Encapsulate polyphosphate

The idea was to prevent ammonia to be instantly released or to be released gradually by encapsulating APP powders with liquid form of a HWR. For this purpose, APP powders were mixed with a liquid form of 1 mL polycarboxylates HWR for 5 minutes and then the solid particles were recovered by drying in oven for 24 hours. The resultant product was then crushed and pulverised. By this means, APP powders were coated by a thin layer of HWR and they were supposed to react with CH very slowly, after its coat is released in water.

The encapsulated APP (EnAPP) powders were generally similar to APP powders but fairly darker in colour.

Contrary to the expectations, EnAPP did not decrease the ammonia odour during mixing significantly, although it delayed the time when the smell is released.

Drying shrinkage was shown to be reduced more significantly than APP concentrations; however, the effect of HWR cannot be compromised as shrinkage reducer (SRA). The compressive strength was also increased by the addition of EnAPP.

Since the mechanism of shrinkage reduction and flow and strength enhancement is not expected to be different from the APP, and EnAPP is APP with a small amount of HWR, there was no need to add similar test results.

4.3.2 Melamine polyphosphate (MePP)

Melamine polyphosphate was the other shrinkage compensating admixture used to evaluate shrinkage efficiency of APP which is simply fulfilled by replacing ammonia with melamine in order to see if the efficiency of the polyphosphate as an expansive agent via forming cellular CPP structures.

In terms of appearance, it is also in white powder form. During mixing and hydration, MePP is supposed to react with CH to form calcium polyphosphate and melamine, the latter has limited solubility in water and completely not volatile. MePP did not generate any ammonia odour during mixing, as was expected.

Figure 4. 15 and Figure 4. 16 show the drying shrinkage behaviour of MePP modified mortar specimens subjected to controlled environment in humidity chamber (23 ºC and 60%RH). Figure 4. 15 illustrates the effects of very low concentrations of MePP which showed some improvements in drying shrinkage. On the other hand, this trend is not reproduced for higher concentrations, based on Figure 4. 16. Although MePP1.0 demonstrates reduced amounts of drying shrinkage after 21 and 28 days comparing to Co. Similar to APP, MePP modified mixes mostly show higher drying shrinkage than control after 7 and 14 days, whereas, after 21 and 28 show less shrinkage than Co.

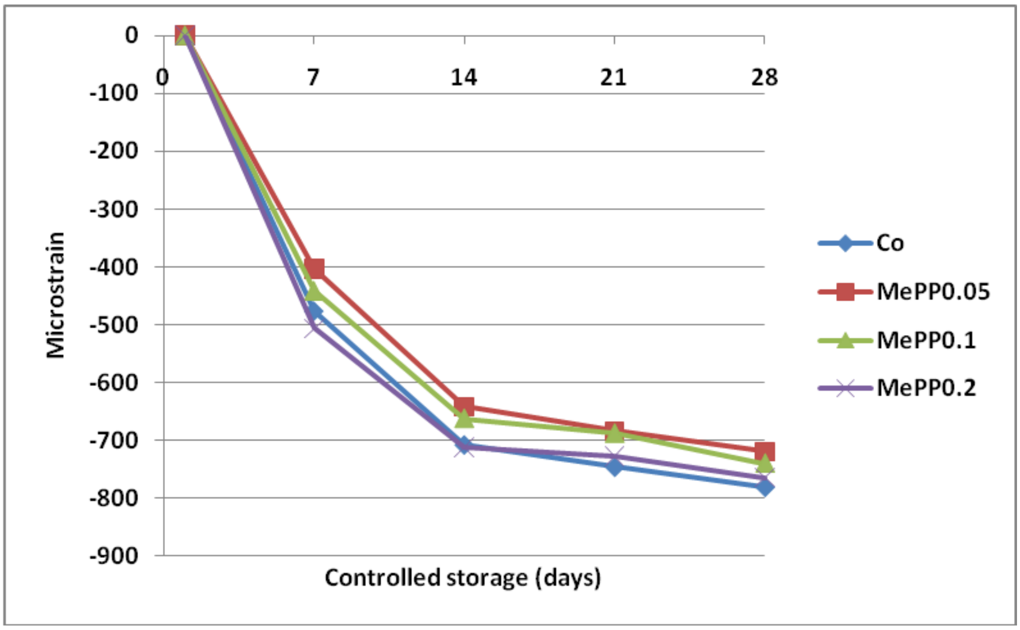


Figure 4. 15. Drying shrinkage of MePP mortar samples

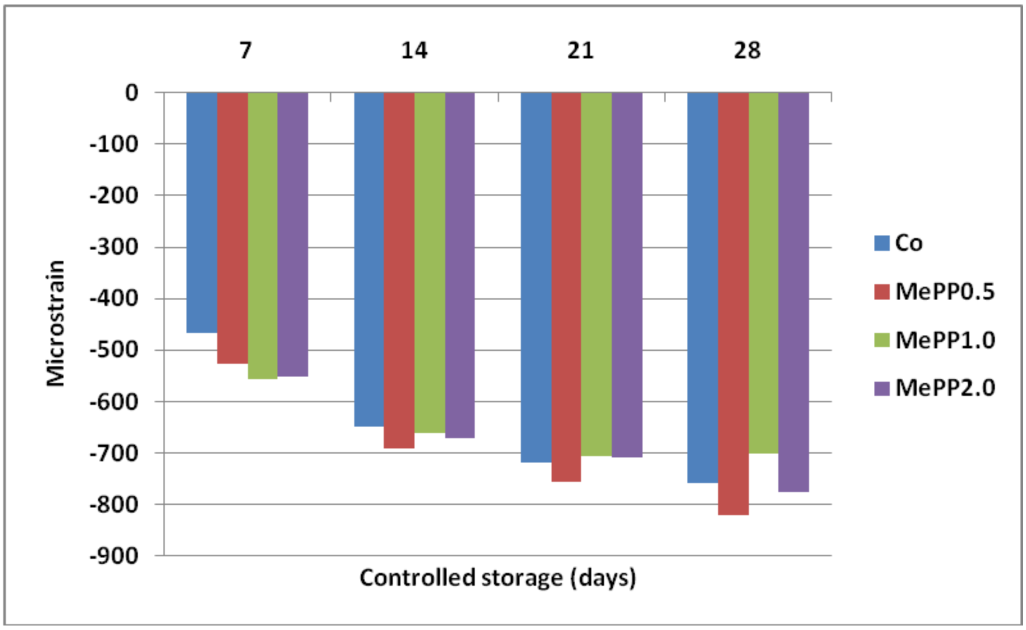


Figure 4. 16. Drying shrinkage of MePP mortar samples

The results of the second set (Co, MePP0.5, MePP1.0 and MePP2.0) were not reproducible and the results shown in Figure 4. 16 are the average of 3 repeated experiments.

Figure 4. 17 provides mass change of mortar specimens with and without MePP over 28 days controlled storage. This figure depicts that rate of mass loss has been reduced for MePP0.05 to MePP0.2 comparing to Co. However, this trend is not the same for higher concentrations of MePP such as 0.5 to 2.0 in which the mass loss/change is substantially higher than Co.

Compressive strength of MePP modified mortar specimens were also tested. Figure 4. 18 points up the 28-day compressive strength of cement mortar samples with and without MePP. Compressive strength is obviously increased by the addition of up to 0.2% of MePP and after that, it starts decreasing.

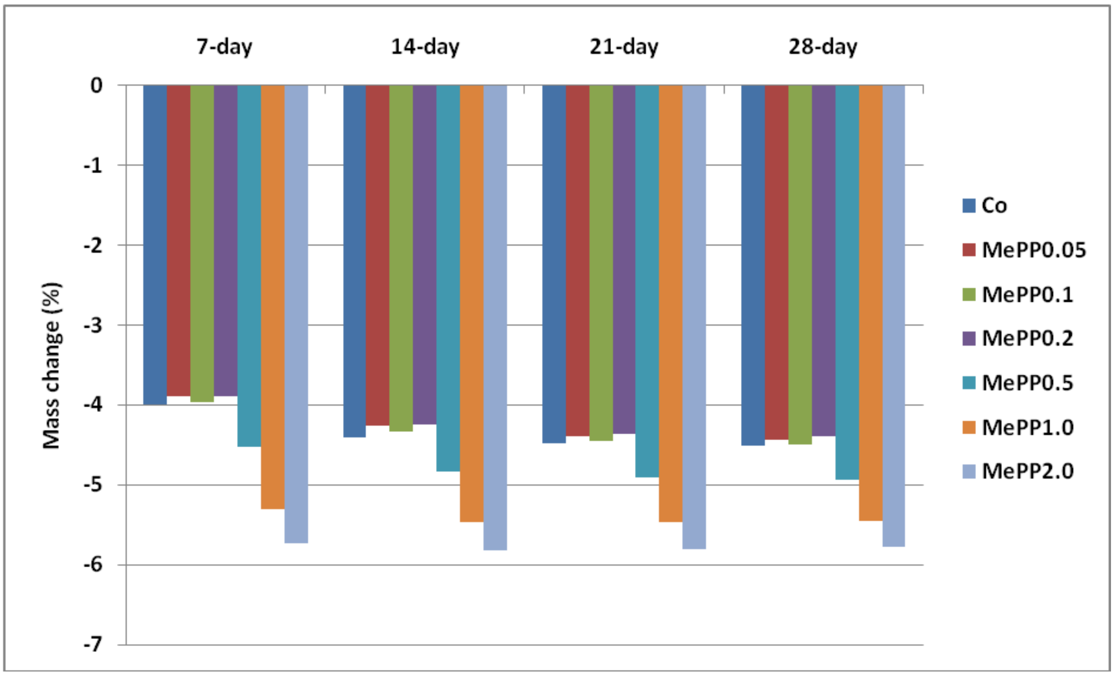


Figure 4. 17. Mass change during controlled storage

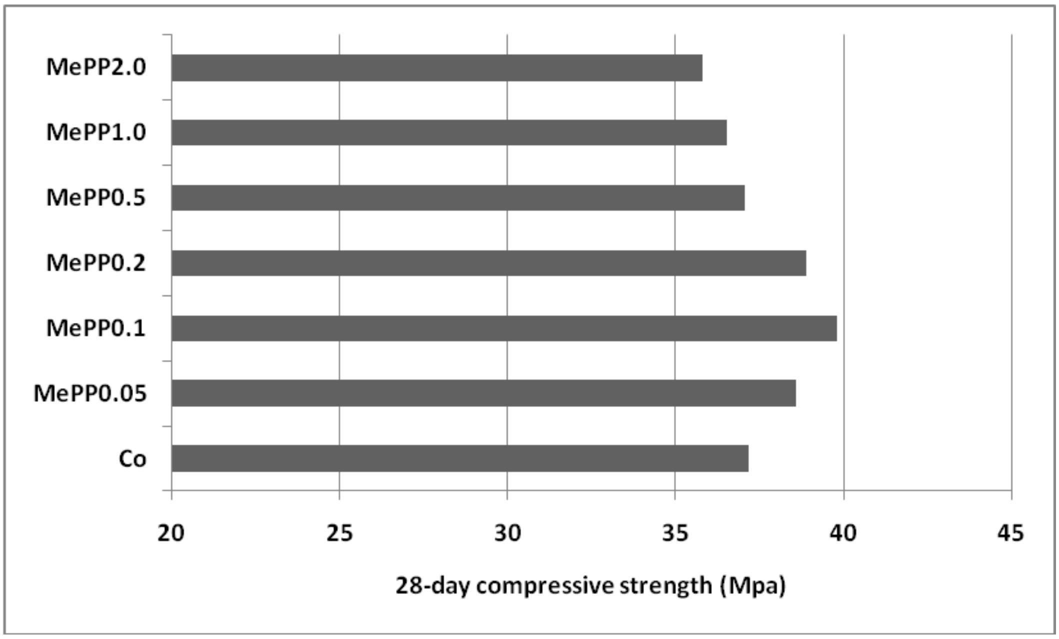


Figure 4. 18. 28-day compressive strength of MePP mortar samples

Very low concentrations of MePP could lessen the drying shrinkage of cement mortar specimens in the same way that APP additions did, possibly due to the hydrophilic nature of melamine due to the formation of strong hydrogen bonding with water despite of its limited water solubility so it might behave as internal curing agent. Both agents when added to cement mortars demonstrate higher drying shrinkage than Co in first couple of weeks and then after 21 or 28 days demonstrate less shrinkage results, which can be related to the higher rate of formation of CH at later stages of curing and consequently higher rate of reaction with polyphosphate. In contrast, unlike APP, these concentrations reduce the mass loss of mortar samples. Therefore, the mechanism behind drying shrinkage reduction of MePP might not be similar to of that in APP.

This can be simply related to the highly polar amino groups of the melamine that can form strong hydrogen bonding between the three amino groups per molecule of melamine and accumulated number of water molecules as represented in the chemical structure. Accordingly, interrupting the capillary channels that enhances the migration of water to surface, which evaporates faster leading to shrinkage and further to hair-cracking.

Melamine, as a separate admixture, was also tested when added to cement before mixing with water. Different concentrations of melamine containing mixes were studied; nevertheless, no significant result was observed to report.

4.3.3 Keratin

For being appraised as an anti-shrinkage admixture, keratin was tested and investigated as an admixture inside cement mortar mixes. Keratin is a member of fibrous structural proteins. In construction industry, it is known as gypsum retarder (Çolak, 2000). Keratin is also being used as foaming agent for production of aerated concrete (Narayanan & Ramamurthy, 2000).

Keratin used in the present study was in light yellow powder form and it was mixed homogenously with cement before adding to the water in mixing bowl.

The important observation during mixing keratin modified mixes comparing to Co was the early age expansion of keratin contained mix. Consequently, the fresh density of mortar samples were reduced up to 24% compared to of that in control mix.

Figure 4. 19 illustrates the drying shrinkage behaviour of mixes with and without keratin. It clearly shows high potential for increasing the drying shrinkage in keratin

contained mixes. Based on foaming capability of keratin, the high drying shrinkage might possibly be due to development of highly porous media.

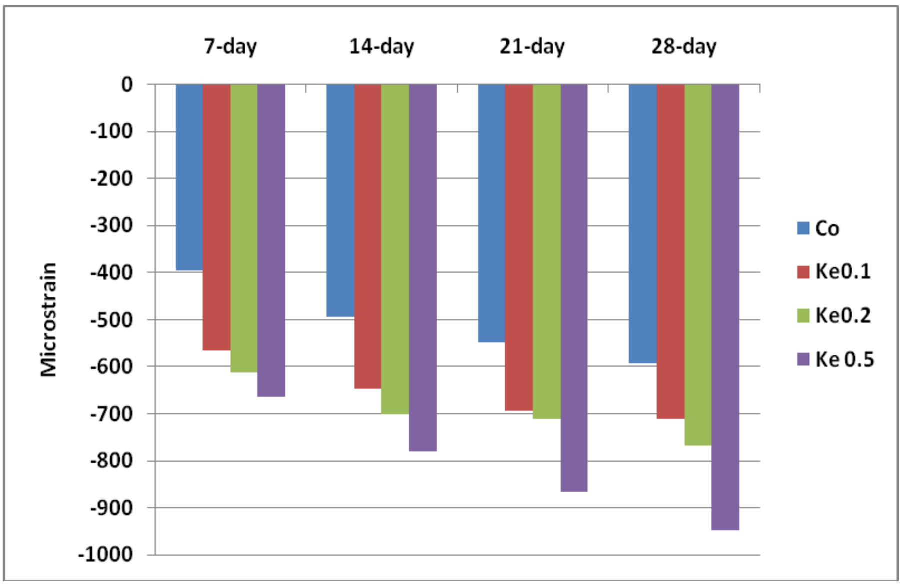


Figure 4. 19. Drying shrinkage of keratin modified cement mortars

In addition a great portion of 28-day shrinkage in keratin mixes has happened in first 7 days of controlled storage, as explained in Figure 4. 20.

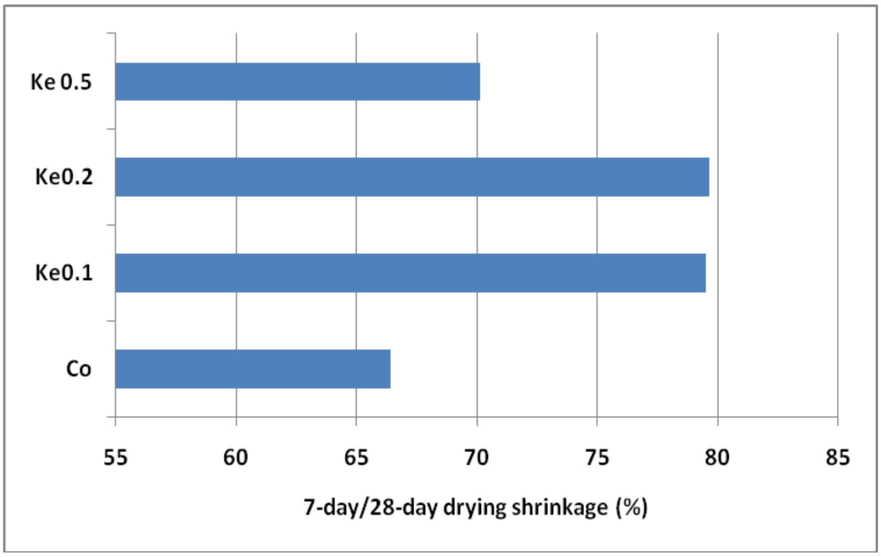


Figure 4. 20. Portion of 7-day drying shrinkage to 28-day drying shrinkage

This shall not be unexpected that keratin containing mixes with their porous structure presented very low compressive strength results. 28-day compressive strength of mixes with and without keratin has been illustrated in Figure 4. 21. Based on these initial results further investigation was needless. Modification of keratin might be useful mainly by controlling the foam-ability of keratin by nano- and micro-encapsulation or by using partially cross-linked keratin.

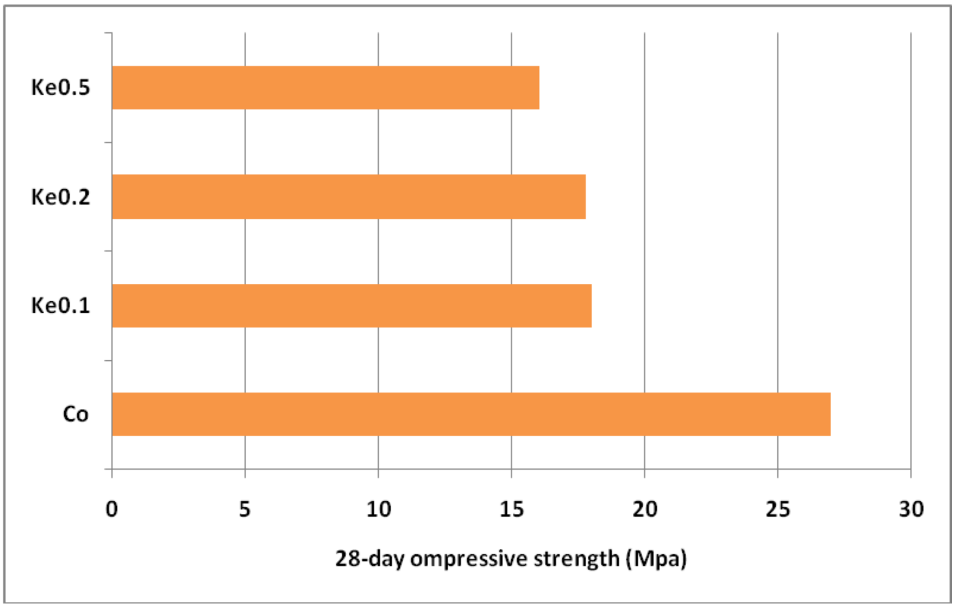


Figure 4. 21. 28-day compressive strength of keratin contained mixes

5 Microfibres in drying shrinkage reduction

5.1 Preface

Fibre-reinforced cementitious composites (FRC) are cement-based composites incorporated mainly with short and discontinuous fibres. Although fibre-reinforced materials have a long history in construction industry, a steady increase in the use of FRC began in the 1960s. The development of FRC mainly attempts to overcome the two major deficiencies of cement-based materials: relatively low tensile strength and a rather low energy consumption capacity or toughness (Z. Li, 2011).

The functions of the fibres in cement-based composites can be classified into two categories: crack control and mechanical and structural property enhancement. In order to control shrinkage cracking, generally small amounts of low modulus and low-strength fibres are added to restrain the early-age shrinkage and to suppress shrinkage cracking (Z. Li, 2011). For mechanical property enhancement, fibre reinforcement has been employed in various concrete structures to improve flexural performance, impact resistance and even to change the failure mode (Z. Li, 2011).

The amount of fibre added can significantly influence the mechanical properties and failure mode of FRC. Based on fibre concentration, fibre-reinforced cementitious composites can be classified into three groups. FRC containing low fibre volume fractions (<1%) utilizes the fibres for reducing shrinkage cracking (P. N. Balaguru & Shah, 1992). FRC with moderate fibre volume fractions (between 1 and 2%) exhibits improved mechanical properties, including modulus of rupture, fracture toughness, and impact resistance. This fibre volume can be used as additional reinforcement in structural members, such as in partial replacement of shear steel stirrups (Batson, Jenkins, & Spatney, 1972; Sharma, 1986), or for crack width control in structural parts (Stang & Aarre, 1992; J. Zhang, Stang, & Li, 2001). More recently, a third class of FRC, generally named high performance FRC (HPFRC), has exhibited strain-hardening behaviour by using high fibre content (Z. Li, 2011).

5.2 Fibres in shrinkage controlling

Fibres are rather known and accepted for their effects on shrinkage cracking resistance, than long-term shrinkage reduction.

Several types of fibres have been introduced to industry thus far. Bentur & Mindess (2007) have listed them as: steel fibres, glass fibres, asbestos fibres, natural fibres and synthetic fibres which contains polypropylene (PP), polyethylene (PE), acrylic, polyester, nylon, carbon, aramid, and polyvinyl alcohol (PVA).

The influence of different classes of fibres in cement-based materials have been thoroughly reviewed and studied from the published literature (S. F. U. Ahmed & Maalej, 2009; Tarek Aly & Sanjayan, 2010; T. Aly, et al., 2008; Banthia & Gupta, 2006; Boghossian & Wegner, 2008; Chen & Chung, 1996; Filho, et al., 2005; Kayali, et al., 1999; Z. Li, 2011; Mesbah & Buyle-Bodin, 1999; Passuello, et al., 2009; Pelisser, Neto, Rovere, & Pinto, 2010a; Pelisser, et al., 2010b; Sivakumar & Santhanam, 2007; P Soroushian & Ravanbakhsh, 1998; Parviz Soroushian, Tlili, Alhozaimy, & Khan, 1993; Sun, Chen, Luo, & Qian, 2001).

In general, there is not many research studies carried out on the effects of fibres and microfibres in drying shrinkage reduction of mortar and concrete. Therefore, fibres are mostly used for prevention of plastic shrinkage cracking. In addition, PE microfibre has never been studied as an admixture to a cement-based matrix. This chapter endeavours to study the effect of microfibres on shrinkage reduction of OPC mortars.

5.2.1 Significance

High modulus fibres usually show high ultimate strength, low strain capacity and small crack width properties, while low modulus fibres have low ultimate strength, high strain capacity and large crack width properties (Shaikh Faiz Uddin Ahmed, Maalej, & Paramasivam, 2007). Polyethylene (PE) can be categorized as low modulus synthetic fibre. However, it can be produced with a relative high modulus fibre. This research deals with PE microfibre. The main advantages of PE fibre are their alkali resistance and low market price, while poor bond to the matrix is mentioned as its disadvantage (Arnon Bentur & Mindess, 2007).

In relevant studies, two different geometries of PE fibres have been used in cement-based composites: 1- short and dispersed, up to 4% by volume; 2- continuous network of fibrillated fibres and about 10% by volume of concrete sample (Arnon Bentur & Mindess, 2007).

Ultimate tensile strain capacity was found to increase with increasing PE fibre contents and beyond a particular fibre content the strain capacity decreased (S. F. U. Ahmed & Maalej, 2009). In addition, hybrid system of steel – PE fibre with the length of 12-13 mm, was shown to have lower ultimate strength but higher deflection capacity at the peak load than the hybrid steel–PVA fibre composites (Shaikh Faiz Uddin Ahmed, et al., 2007). Similar results were reported by Kobayashi & Cho (1981) confirming that the characteristic point of PE fibre reinforced concrete as a structural material, might be its tremendous ductility.

Soroushian et al. (1993) illustrated that both PE pulp and fibre tend to increase the impact resistance, flexural strength and toughness of cementitious materials. Furthermore, positive effects on the compressive strength of cement-based matrices was experienced (Parviz Soroushian, et al., 1993). PE fibres are also found to be weak material in terms of wettability among other types of fibres (Lu, Fu, & Chung, 1998).

In other fields such as composites sciences, there are several studies related to PE fibres. For instance, it was reported that a unidirectional composite of ultra-high-modulus PE fibre and epoxy 618 has poor compressive and flexural properties though its ductility is extremely high (Y. Li, Xian, Choy, Guo, & Zhang, 1999). The researchers modified their composite by adding moderate amount of carbon fibres into the previous composite and gained great improvement in both the compressive and flexural properties.

New PE microfibre- In present research a particular type of PE fibre is examined for its effects on drying shrinkage of cement mortars. This synthetic pulp is hydrophobic fibrillated PE of 0.1 mm length, 0.005 mm diameter, 12 m^2/g of surface area and 0.96 of specific gravity. This specific type of high density polyethylene (HDPE) microfibre is supplied by MINIFIBER, Inc. This type of short fibres is expected to act as dispersed fibres mixed in mortar. PE fibre used in current research with its specific geometry can be categorised as microfibre (N.M.P. Low, Gagnon, & Beaudoin, 1994).

Microfibres due to their size are believed to bridge the micro-cracks which consequently delay the process of macro-cracks formation (Konsta-Gdoutos, Metaxa, & Shah, 2010; Shah, Konsta-Gdoutos, & Metaxa, 2011). On the other hand, decreasing the fibre distance from each other is proved to increase the resistance to the first crack (Y. Akkaya, S. P. Shah, & B. Ankenman, 2001; Betterman, Ouyang, & Shah, 1995). These two phenomena suggest that using microfibres provides remarkable reinforcement for fibre reinforced cementitious composites.

Using microfibre as additive, laboratory experiments were fulfilled using different dosages of additive to evaluate its efficiency as anti-shrinkage additive and its effect on the physical and mechanical characteristics of mortar.

5.2.2 Experiments

PE microfibre with low specific gravity and negative polarity occupy fairly large amount of volume per certain mass. For this reason, PE microfibre is added and then presented as % of cement weight instead of % volume.

Mixing and casting of mixes containing PE microfibre were exactly similar to mixing and casting procedure of chemically active admixtures, except that PE microfibre was added and agitated with sand rather than cement, as its dispersion in cement was difficult due to its hydrophobicity. Demoulding of samples, length measurements and physical properties testing were similar to the procedures which had been performed for chemically active admixtures e.g. APP.

Mortar mix proportions- Cement mortars were prepared using Goliath General Purpose Cement supplied by Cement Australia and Raymond Terrace single washed sand supplied by Rocla Quarry Products Pty Ltd. Glenium, a high-range water reducing (HWR) admixture supplied by BASF, was used as superplasticiser for modification of the mix design proposed in AS 2350.12 (Standards-Australia, 2006) in order to maintain constant workability of the mortars. For comparison purposes, all mixes consist of same concentration of HWR unless stated (mixes with higher concentration of PE microfibre).

Drying shrinkage experiments for microfibres have been in different environmental conditions. First stage of drying shrinkage tests were carried out at constant temperature of 22±1 °C and relative humidity of 60±5 %. In the next stage, new sets of samples were stored at constant temperature of 22±1 °C but in varying RH, i.e. low RH of 30% for 4 weeks and then 65-70% RH for next 4 weeks.

In order to obtain comparable results for the evaluation of the new fibre, a set of either 4 or 6 different mixes, including control mix, were carried out on the same day and under the same environmental ambient. Mortar mix designs, presented in Table 5. 1 were derived and modified from standardized proportions listed under AS 2350.12 (2006). Preparation of mortar mixes was carried out in accordance with the same code.

The PE microfibre was first introduced to sand part of mix, instead of the cement part. Since the microfibre is a hydrophobic material, its dispersion in the mix is difficult (Arnon Bentur & Mindess, 2007). For the aim of having consistent mixes, the whole bag containing sand and microfibre was thoroughly vibrated for about 30 seconds.

5.2.3 Experimental results

All cement mortar mixes are simply named after their concentration of PE microfibre. Therefore, the term Co stands for the control mix without microfibre. Terms such as PE0.01 to PE0.7 stand for mixes with PE microfibres concentration of 0.01% to 0.7% to cement weight, respectively. In addition, PE1.0+SP2 and PE2.0+SP2 stand for mixes with 1.0 and 2.0% of PE microfibre and with 2 mL of HWR, while other mixes contain only 1 mL of HWR. Table 5. 1 illustrates the mix proportion of fibre reinforced cement mortars.

Table 5. 1. Mix proportions of PE microfibre reinforced cement mortars

Mixes / Raw materials	Co	PE0.01	PE0.025	PE0.05	PE0.1	PE0.3	PE0.7	PE1.0	PE1.0+SP2	PE2.0+SP2
Cement (g)	450	450	450	450	450	450	450	450	450	450
Sand (g)	1350	1350	1350	1350	1350	1350	1350	1350	1350	1350
Water(g)	224.35	224.35	224.35	224.35	224.35	224.35	224.35	224.35	224.35	224.35
HWR(ml)	1	1	1	1	1	1	1	1	2	2
Microfibre (g)	0	0.045	0.1125	0.225	0.45	1.35	3.15	4.50	4.50	9.00

5.2.3.1 **Fresh state properties**

The first observation was the comparison between fresh density of control mix and PE0.5 and PE0.7 mix. Following the modified tests method of ASTM C 138/138M (2009b) described in Chapter 3, PE0.5 and PE0.7 showed higher fresh density than that of the control mix by about 2.5% in several trials, although this change is not considerable. In addition, wet density (after 24 hours) of PE microfibre modified cement mortars were seen to be higher than wet density of Co, by less than 1%.

Figure 5. 1 shows the rheology studies of mortars following the measurements carried out on a flow table in accordance with ASTM standards (2007). Although the flow percentages of all samples (except 1% concentration) are in the range of 50±15%, a substantial reduction in workability in the range of 7% to 48% was observed with increasing addition of PE microfibres to the mortar mixes. This possibly can be explained by that addition of more amounts of low specific gravity microfibres to the mortar increases the proportion of dry raw materials used in the mix and the thixotropic properties of the mix; therefore, it decreases the flow of mortars. It can also be the case particularly since the microfibre used is a hydrophobic type. Apparently, low concentrations of PE microfibre did not affect the flow significantly.

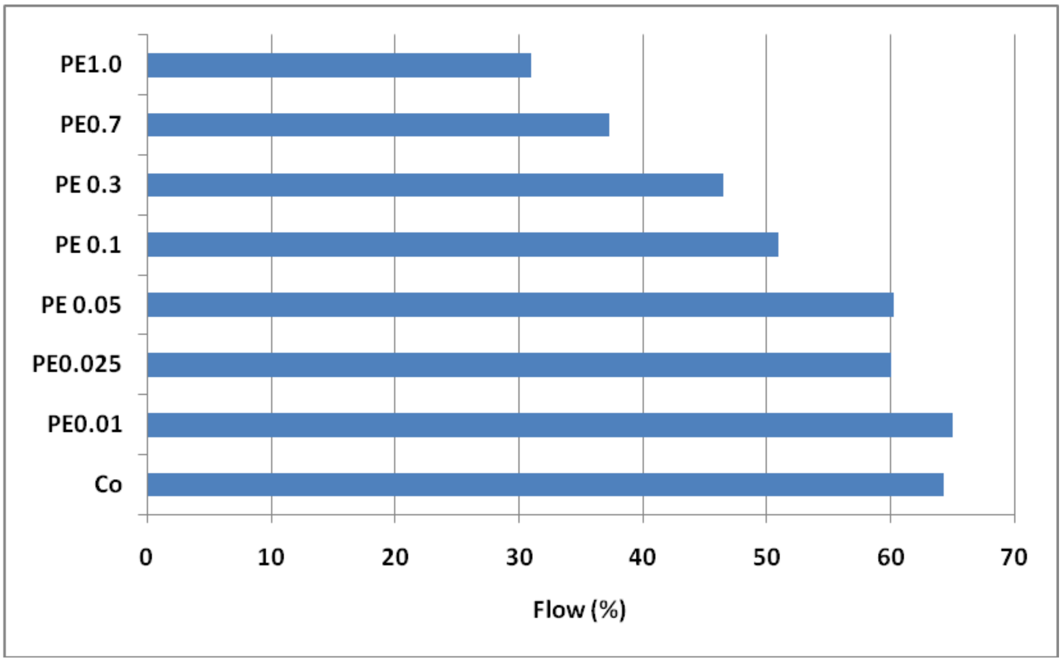


Figure 5. 1. Flow properties of PE microfibre reinforced mixes

Mixing and casting of samples with 1.0% or more concentration of microfibre was difficult, since the produced mix was not workable. They could be made workable by adding more HWR. Thus, for comparing purposes, the effect of higher amount of HWR on shrinkage behaviour of mixes should be considered.

5.2.3.2 **Drying shrinkage**

The results of 28 days drying shrinkage in humidity-controlled storage (60±5% and 23ºC) of specimens are shown in Figure 5. 2 and Figure 5. 3. Drying shrinkage was found to decrease with addition of microfibre. There was a reduction of 25% shrinkage observed after 28 days for the PE0.1 mix. In addition, 36% shrinkage reduction can be seen from the results of PE1.0+SP2; however, the effect of double amount of HWR on drying shrinkage of this specific mix cannot be neglected. Considering the improvements observed in reducing shrinkage, lower concentrations of microfibre additions were thus studied; although, no further improvements in drying shrinkage reduction were observed (Figure 5. 3).

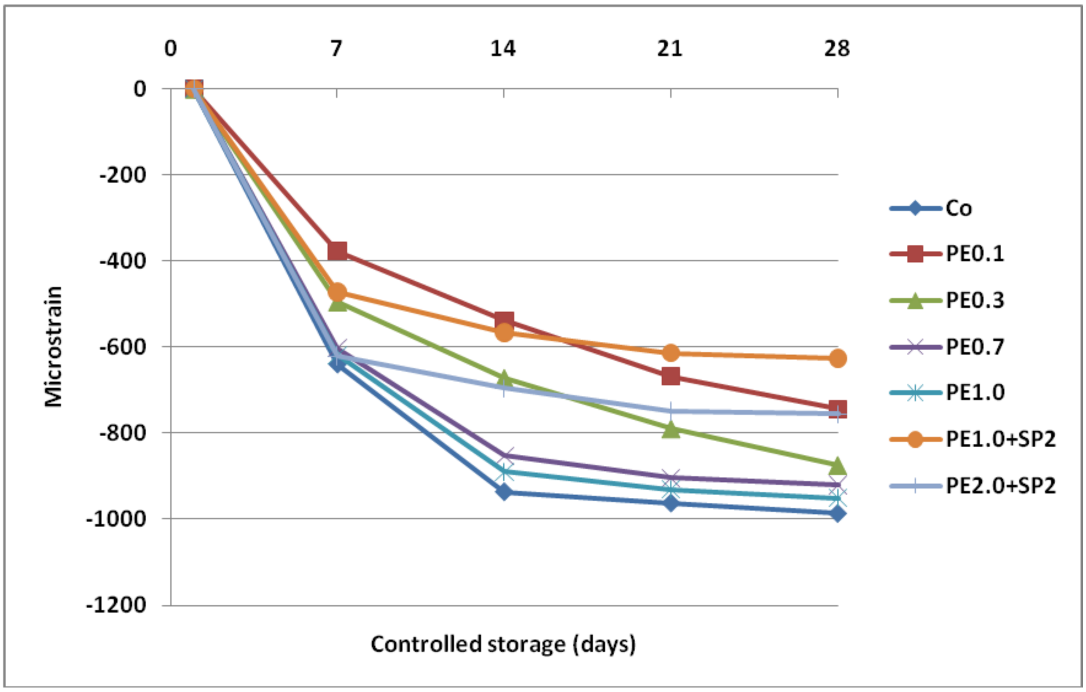


Figure 5. 2. Drying shrinkage in controlled storage

Therefore, it is likely that the 0.1% addition of PE microfibre acts as an optimum addition amount for shrinkage reduction, however; its proper engagement inside the cement paste is crucial.

Figure 5. 3 also suggests that due to very low concentrations of microfibre, fibre particles were not thoroughly dispersed inside the paste and that resulted in irregular results for low microfibre concentrations, e.g. greater shrinkage for PE0.05 than Co. But in general, PE0.1 is presented as the best concentration in terms of drying shrinkage reduction.

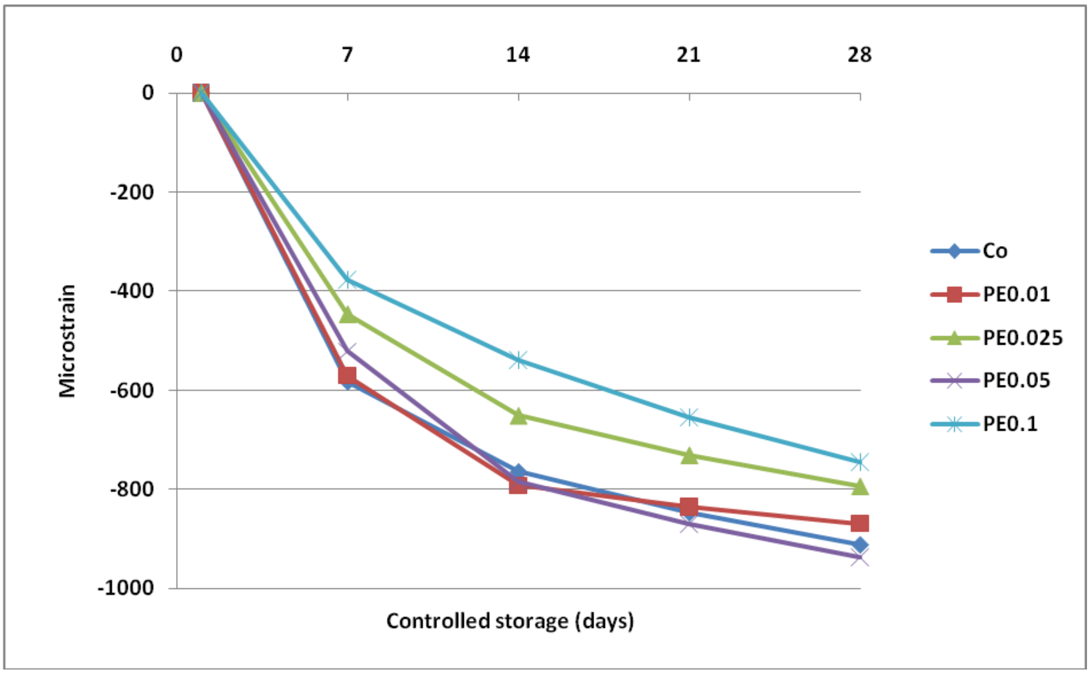


Figure 5. 3. Drying shrinkage in controlled storage

Long-term drying shrinkage of PE fibre reinforced cement mortars have also been studied against the long-term drying shrinkage of Co. In this regard, Figure 5. 4 depicts comprehensive long-term drying shrinkage of these mixes. As was expected, the rate of drying strain gain for all mixes after 28 days of age is lower than that before 28 days. Figure 5. 4 also suggests that 0.1% concentration is the optimum amount in a long-term study, as well.

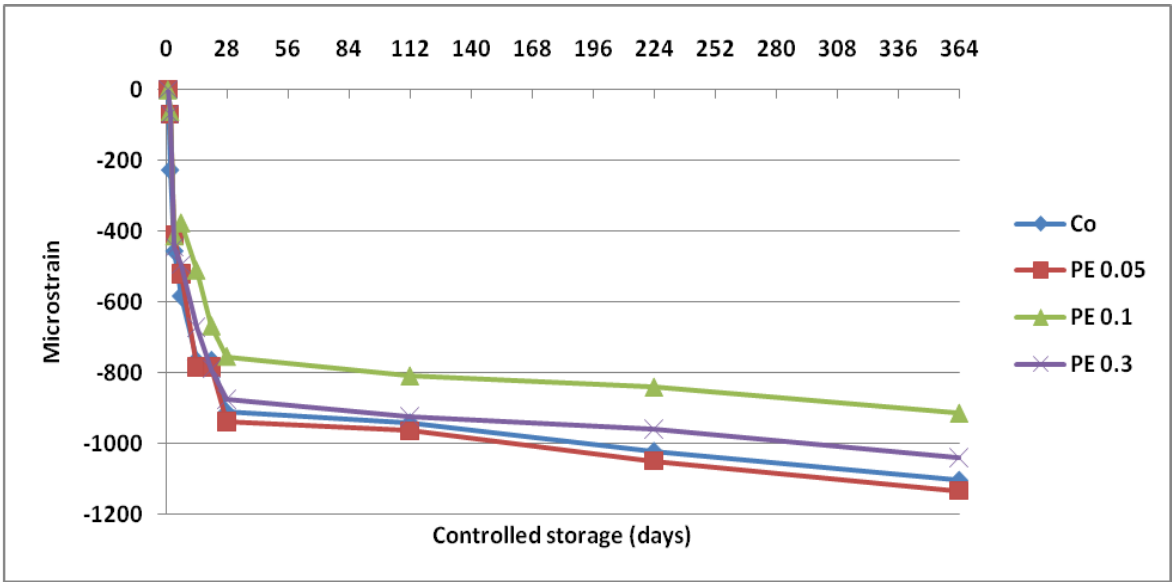


Figure 5. 4. Long-term drying shrinkage of PE microfibre reinforced cement mortars

The drying shrinkage reduction of PE microfibres can be due to blocking the capillary voids of the matrix which results in moisture being trapped and cannot easily be lost. This idea comes from the nature of PE microfibres which makes it hydrophobic. This idea suggests that if a microfibre is placed close to a chain of voids, those voids will be blocked and present water cannot be released easily. The results of mass loss study are also in agreement with this hypothesis. On the other hand the low density of microfibers will suggest that a high portion of existing microfibre is places close to the surface of the mortar, and as there are hydrophobic chains with a segment of the chains anchored in the cement phase and the other part of chain is free which leads to increase the vapour pressure of the water on the surface which leads to decrease the evaporation of water from the surface. This phenomenon is used in several types of concrete curing agents as they are meant to reduce the moisture loss of concrete.

On the other hand, microfibres, as mentioned earlier, are expected to provide reinforcement for microcracks and consequently restraint for shrinkage. In addition, unlike APP, PE microfibres cannot be involved in chemical reactions and affect the shrinkage. Therefore, the possible behaviours are physical interaction between microfibres and the matrix, along with the effect of microfibres transferred to the surface.

To further investigate this hypothesis, another experiment was adopted. In this test, samples with and without PE microfibre were stored in varying environmental condition, i.e. first 4 weeks at 23 ºC and 30% RH and for the next 4 weeks at 23 ºC and 65% RH. 30% RH, as the minimum RH achievable in the chamber, provides an extremely severe condition for samples. Whereas, 65% RH is the maximum RH can be supplied by the chamber and is expected to slow down the rate of drying shrinkage. In addition, the mechanism of drying shrinkage will be different in these two environments.

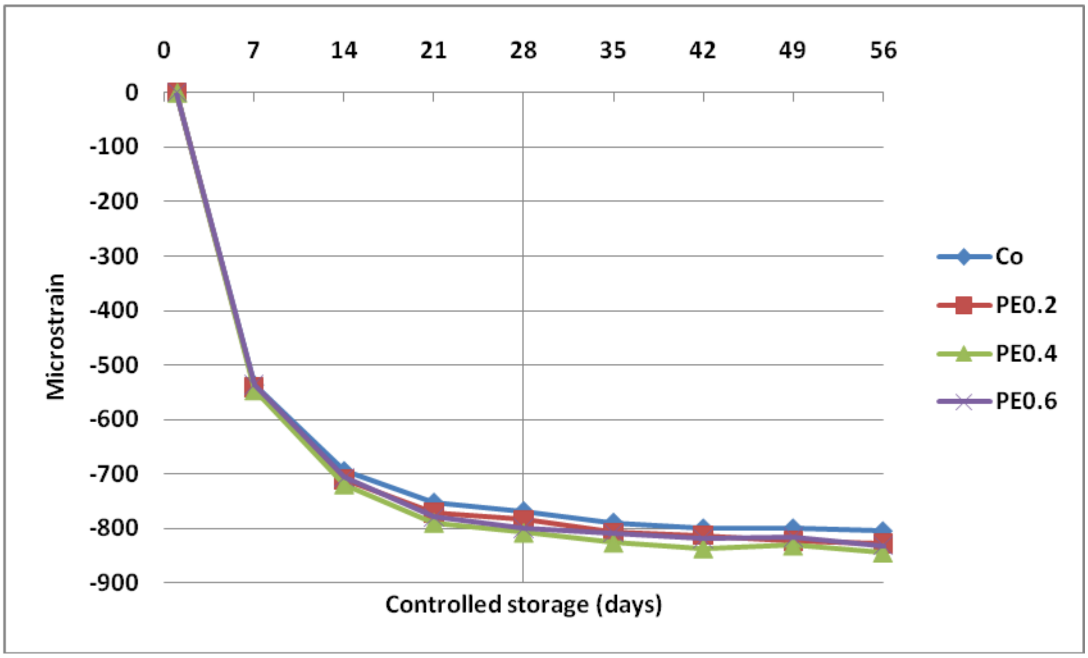


Figure 5. 5. Drying shrinkage of cement mortars stored in varying conditions

Figure 5. 5 illustrates the 56 days results of drying strain, 28 days at 30% and 28 days at 65% RH. Unlike the other experiments carried out at 65% RH, the drying shrinkage has been slightly increased for PE microfibre reinforced specimens. These results might be due to severe environmental conditions occurred during the first 4 weeks.

The other observation is the slow trend of drying shrinkage after changing the environment to a higher RH, as was expected.

5.2.3.3 **Moisture loss**

Similar to APP study, the mass of each sample was also measured after each subsequent length measurement. Results of mass change percentage are shown in Figure 5. 6. As was expected, mass of all mixes was subject to decrease due to moisture loss in a dry environment. From this figure, the mass reduction percentage was found to be lower for all additions of microfibres than the mass loss of control mix. The PE0.1 mix demonstrated the lowest % water loss. These results support the mechanism of water repellence of microfibres within the mix, which is the consequence of PE hydrophobicity.

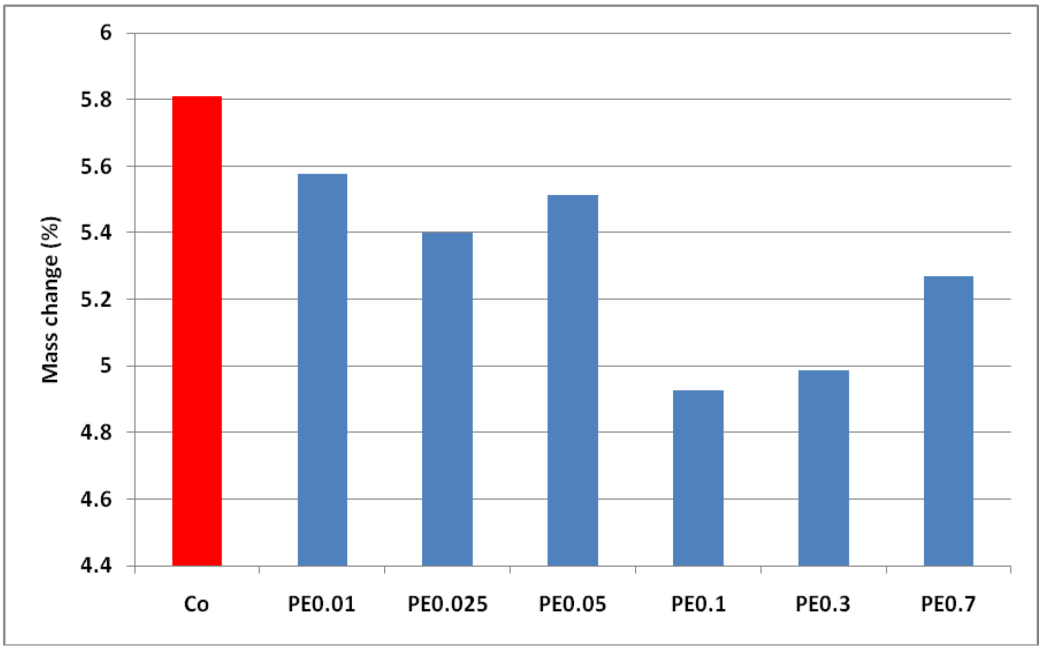


Figure 5. 6. Moisture loss of cement mortars with and without PE microfibre

Unlike APP which showed increase in mass loss, PE microfibre demonstrates decrease in mass loss comparing to Co. This decrease is possibly connected to the decrease in drying shrinkage of PE modified mixes by reduction in moisture evaporation of the sample sealed by hydrophobic PE microfibre.

5.2.3.4 **Compressive strength**

PE microfibre modified specimens observed to have lower compressive strength when compared to the control mix. Figure 5. 7 portrays the 7, 28 and 180-day compressive strength of PE microfibre modified specimens.

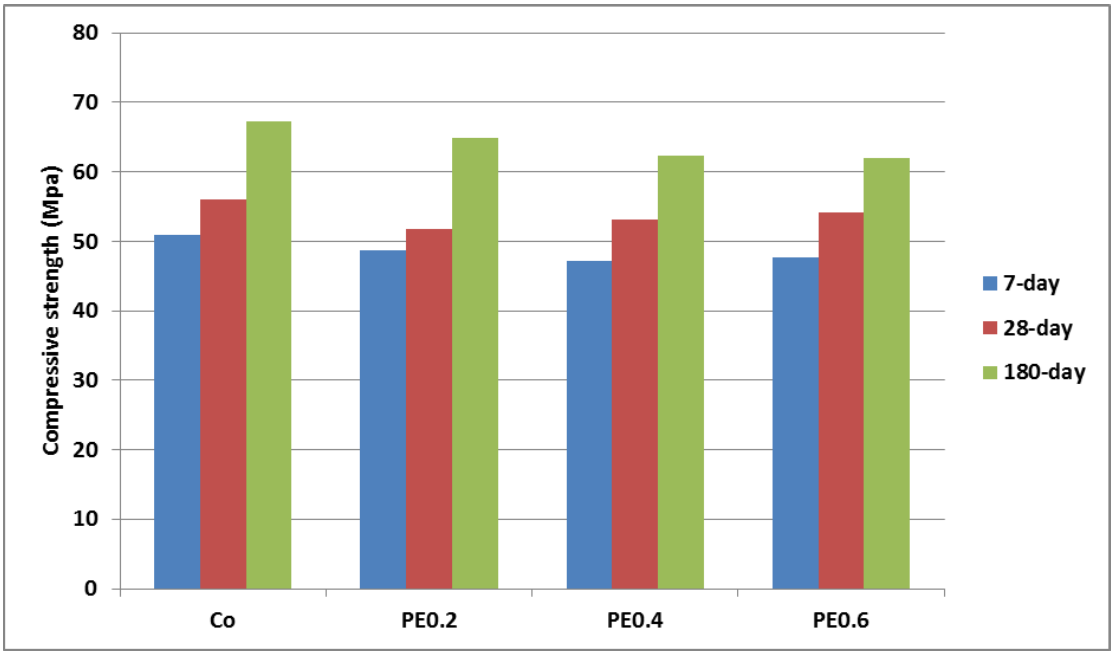


Figure 5. 7. 7, 28 and 180-day compressive strength of OPC mortars with and without PE microfibre

Reduction in compressive strength was an expected phenomenon in reviewed studies (Zheng & Feldman, 1995), and it can possibly be justified by the hydrophobicity of microfibres, which can result in lowering the hydration rate for cement particles around microfibres which suggest investigation of the effect of hydrophilic PE microfibres on the compressive strength and drying shrinkage of mortars.

On the other hand, less mass loss directly means higher water to cement ratio (w/c) in hardened state, which can consequently result in less compressive strength of PE microfibre reinforced samples. Short length of PE microfibre might have been unsuccessful in providing enough interlocking characteristics to cementitious mortars.

5.2.3.5 **Scanning electron microscopy**

Using high-energy beams of electrons and utilising detection from secondary electrons, SEM can provide very high-resolution images of the microstructure and nanostructure of the samples.

At the completion of 28-day compressive strength testing, appropriate representatives of PE microfibre reinforced specimens with 1% by cement weight concentration were stored at -10 °C in order to stop the hydration, until time of SEM examination.

As the typical dimension of fibres is 100 micrometres length by 5 micrometres diameter, the level of magnification was adjusted in this range. Figure 5. 8, Figure 5. 9 and Figure 5. 10 show SEM micrographs of PE1.0 at increasing levels of magnification.

Figure 5. 8. SEM micrograph of PE1.0 mortar after 28 days ageing (x 30)

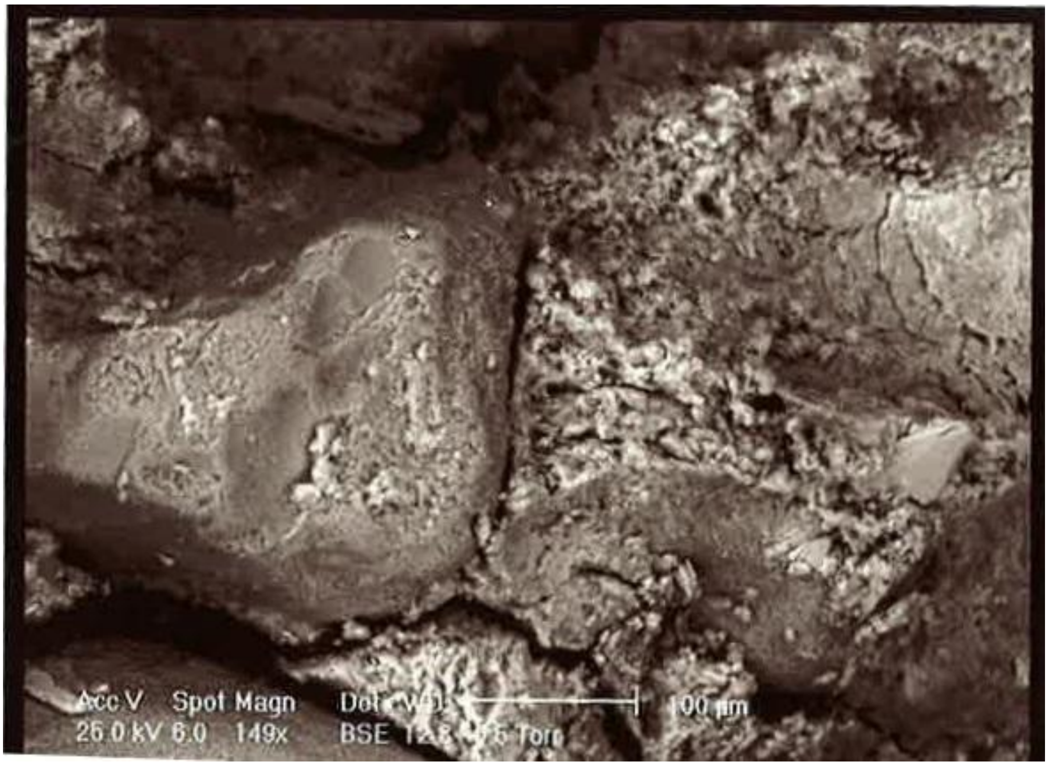


Figure 5. 9. SEM micrograph of PE1.0 mortar after 28 days ageing (x 150)

These micrographs were taken from a thin layer of the specimens, which were carbon coated and placed under vacuum prior to imaging at an accelerating voltage of 20 kV. The magnification of the display was continuously changed in order to find the fibres and their location.

A lengthy experiment was performed; however, only one micrograph was found which illustrates the microfibres. Figure 5. 10 demonstrates a group of fibres bridging adjacent particles. This micrograph can suggest the micro-bridging property of PE microfibres.

Since the concentration of PE microfibres was in a very low range to cement weight (0.1-1.0%), the number and the density of microfibres were rather low and it makes the locating the fibres very difficult.

Figure 5. 10. SEM micrograph of PE1.0 mortar after 28 days ageing (x 300)

5.2.4 Discussion

Although variable results were obtained as function of different concentration of PE microfibres, addition of low concentrations of PE microfibre has well demonstrated reduction in drying shrinkage of OPC mortar specimens. In addition, a direct relationship between shrinkage reduction and specimen moisture loss, indicating the lower the moisture loss, the lower the drying shrinkage, was observed for each mix in Figure 5. 3 and Figure 5. 6.

The measurements of fresh and wet densities, after mixing and after 24 h, respectively, indicated that addition of microfibres to mortar increases the fresh density and wet density of cement mortars compared to the fresh and wet density of control mortar.

Flow was significantly reduced by the addition of PE microfibre, possibly due to the introduction of dry particles into the mix and thixotropic property of PE modified samples.

PE microfibres resulted in a reduction of 7 and 28-day compressive strength of cement mortars. This phenomenon might be due to the effect of hydrophobicity of PE fibres which may have reduced the hydration rate of cement particles in areas around microfibres. The same results were reported by Zheng (1995) and a variety of results were reported by Soroushian et al. (1993).

Based on these observations, the mechanism proposed for shrinkage reduction using PE microfibres can possibly be the interruption of moisture transfer/loss from the capillary structures in the mortar due to the presence of hydrophobic fibres in the cement paste, which results in lessening water transfer from inner layers and pores of the medium to the surface and consequently decreasing moisture loss of sample. Figure 5. 6 supports this mechanism, since the changes in mass of mixes with PE microfibres were less than of that in control samples.

Higher fresh and wet density of PE modified mixes can also support the hypothesis of interruption of moisture transfer/loss by the means of PE microfibre.

A new drying shrinkage reduction method was introduced and assessed in this project. An optimum amount of 0.1% of polyethylene microfibres was found to notably reduce the quantitative amount of drying shrinkage.

5.3 Hybrid systems

There is limited number of combination systems used in experimental shrinkage studies. Mesbah et al. (1999) reported that using cast iron fibres along with PP fibres can significantly contribute to delaying the overall development of cracks. Sivakumar & Santhanam (2007) stated that in hybrid fibre combinations, the steel–polyester combination led to a significant reduction in cracking, compared to plain concrete. Sun et al. (2001) tested concrete with both the expansive agent and hybrid fibres, and found that hybrid fibres of different sizes and types, provided the best results of the shrinkage and permeability resistance.

Thus far, PE microfibre was shown to decrease compressive strength of mortars, whereas, APP addition improved the compressive properties. In addition, APP had shown higher mass loss than control mortar. In contrast, hydrophobic PE microfibre stores water and result in less moisture loss.

This section reports the results of a study of hybrid systems of PE microfibre and APP, when they are added to the mix jointly and comparing them with previous results where PE microfibre and APP were used separately.

5.3.1 Experimental results

The APP admixture was added to cement, while the PE microfibre was added to sand and both well agitated in order to have a consistent mixture of additives.

Table 5. 2 demonstrates the mix proportions of hybrid systems of PE and APP. For instance, term PE0.1+APP0.5 stands for a mix with PE microfibre concentration of 0.1% and APP dosage of 0.5% to cement mass, respectively. Since the mixes with more than 0.5%, optimum dosage of APP were producing considerable amount of ammonia gas and in order to limit the number of combinations, concentration of APP was limited to 0.5%. Additionally, regarding 28-day compressive strength, APP concentration of 0.5% was one of the maximum ones. In addition, mixes with more than 1.0% concentration of PE microfibre was also found to be not workable.

Table 5. 2. Mix proportions of hybrid systems

Raw material	Cement (g)	Sand (g)	Water (g)	HWR (mL)	PE microfibre (g)	APP (g)
Mixes						
Co	450	1350	224.35	1	0	0
PE0.1+APP0.5	450	1350	224.35	1	0.45	2.25
PE0.5+APP0.5	450	1350	224.35	1	2.25	2.25
PE0.5+APP1.0	450	1350	224.35	1	2.25	4.5
PE1.0+APP0.5	450	1350	224.35	1	4.5	2.25

5.3.1.1 **Fresh properties**

Flow table sample of PE1.0+APP0.5 was cracked and broken during flow test since it was dry and not workable. Figure 5. 11 shows the flow of other mortars based on measurements carried out in accordance with ASTM standards (2007). A reduction in workability was observed with increasing additions of PE microfibres and even APP to the mortar mixes. Although for PE0.1+APP0.5 with low concentration of PE microfibre the flow was enhanced significantly.

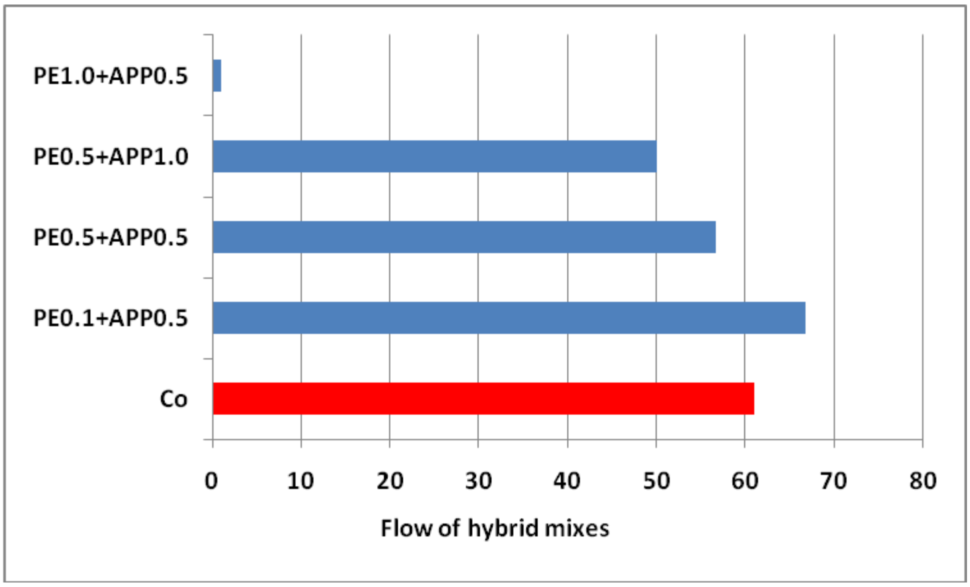


Figure 5. 11. Flow properties of hybrid mixes

5.3.1.2 **Drying shrinkage**

Drying shrinkage behaviour of different samples after 7 and 28 days storage in humidity and temperature-controlled environment (23 ºC and 60% RH) is shown in Figure 5. 12. From Figure 5. 12, drying shrinkage is found to diminish in hybrid mixes by 17-23% which is not far more than each additive when added separately.

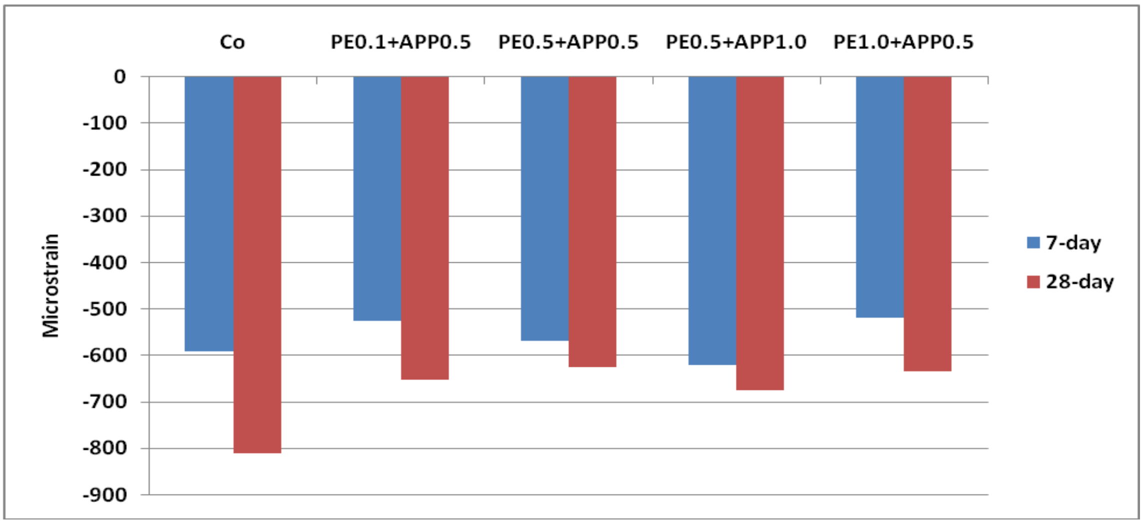


Figure 5. 12. 7 and 28-day drying shrinkage of hybrid mixes

Another remarkable observation is the delayed shrinkage compensation effect of APP which is obvious in lower 28-day drying shrinkage of PE0.5+APP1.0 than of that of Co, while 7-day drying strain of PE0.5+APP1.0 is higher than 7-day of Co.

5.3.1.3 **Compressive strength**

Figure 5. 13 depicts the 28-day compressive strength for the hybrid specimens are either similar to or greater than the Co, indicating improvement in results for PE modified mixes. Compressive strength of hybrid mortars incorporating low addition amounts of microfibres, such as 0.1% was even higher than the compressive strength of control mix due to the produced calcium polyphosphate which comes from APP. But with increasing PE microfibre additions with the same amount of APP, the compressive strength was found to decrease.

Based on this graph, this can be concluded that increasing the APP concentration increased the compressive strength and increase in PE microfibre decreased the compressive strength.

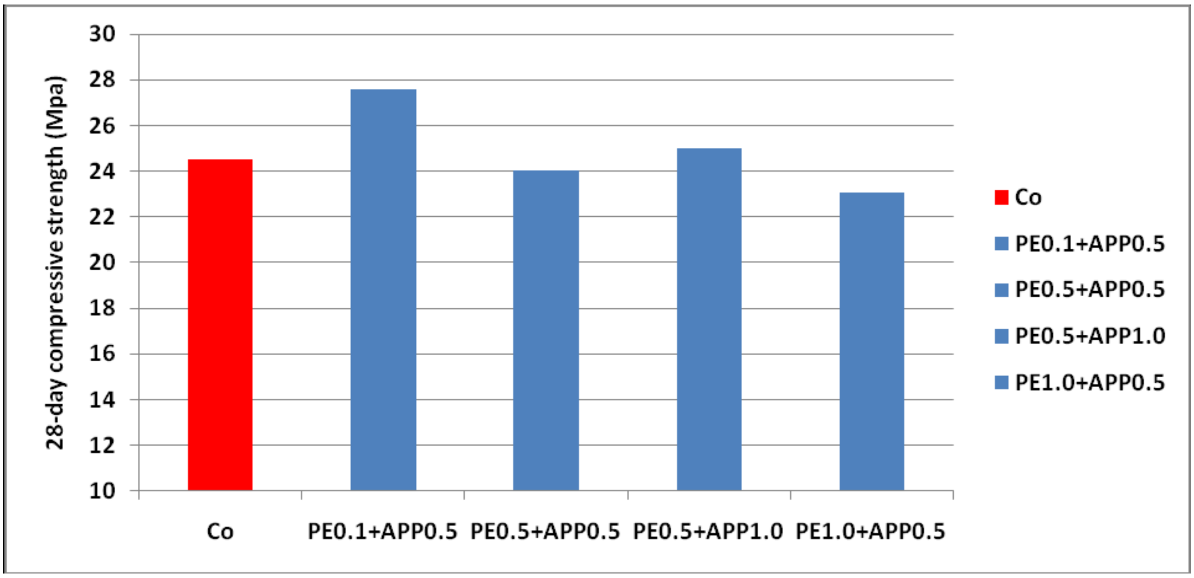


Figure 5. 13. 28-day compressive strength of hybrid mixes

5.3.1.4 **Mass loss**

Change in mass due to moisture loss in drying periods begins immediately after demoulding. This criterion can suggest the predominant mechanism of shrinkage compensating admixtures and also introduces the drying behaviour of mortar samples during storage period, based on collected time dependent data. In general, APP increases the mass loss and PE microfibre decreases it accordingly. Thus, the combination of additives was studies as is it could have some advantageous characteristics.

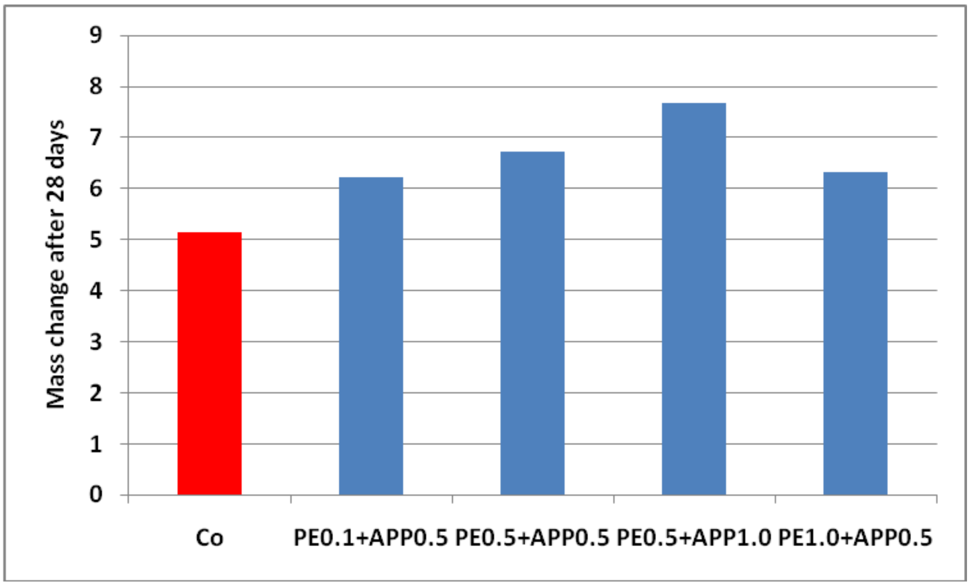


Figure 5. 14. Mass loss of hybrid mixes after 28 days

Results shown in Figure 5. 14 confirm the performance of additives in mass change. In addition, comparing mass loss of PE0.1+APP0.5 and PE0.5+APP0.5 suggests that using PE cannot affect the mass loss in presence of APP and all the hybrid mixes have shown to increase moisture loss. The mix with higher concentration of PE than of APP such as PE1.0+APP0.5 has also shown that the effect of PE on mass change is minor to the effect of APP.

5.3.2 Discussion

The results presented in this section are a combination of results reported previously. Two mixes, PE0.1+APP0.5 and PE0.5+APP0.5 seemed to be the optimum mixes regarding drying shrinkage and mechanical properties.

Addition of 0.1% of PE in addition to 0.5% of APP could reduce drying shrinkage as well as improve the flow and compressive strength of mortar samples. In addition, adding APP has been illustrated to decrease drying shrinkage and modify the compressive strength and flow of PE reinforced mixes. However, in terms of flow, the mix with 1.0% of PE could not be improved with 0.5% of APP agent.

APP had the predominant effect on moisture loss in comparison with PE. It is obvious since all hybrid mixes with the range of 0.1-1.0% of PE had more moisture loss than control mix.

In this study drying shrinkage was reduced in hybrid systems in comparison with mixes where either APP or PE was added separately. However, this reduction is not substantial. On the other hand, flow properties and compressive strength of PE reinforced mortars were improved.

5.4 Wollastonite

Wollastonite is a naturally occurring mineral usually found acicular (needle-shaped) and inert (R. Mathur, Misra, & Goel, 2007). Its micro-fibres have a high elastic modulus of 200 GPa and are also very fine in size and less expensive than steel or carbon micro-fibres (Galea, Hamedanimojarrad, Vessalas, & Thomas, 2012). Fibre dimensions are typically in the range of 0.4-0.6 mm length and 25-150 µm diameter (R. Mathur, et al., 2007).

Wollastonite is calcium inosilicate mineral, $CaSiO_3$ (Renu Mathur, Mishra, & Goel, 2007) which contains small amounts of iron, magnesium and manganese oxides. This natural calcium meta-silicate mineral (13-$CaOSiO_2$) is generally available in the form of acicular particles for commercial applications. The major domestic uses of wollastonite are in plastics, ceramics, metallurgy and paint. Wollastonite is also used in adhesives, joint compounds, rubber, and wallboard applications.

In ceramics, it decreases shrinkage and gas evolution during firing, increases the strength, and reduces cracking, and glaze defects. In plastics, it improves tensile and flexural strength, reduces resin consumption, and improves thermal and dimensional stability at elevated temperatures. Wollastonite is also mined in Australia.

In the experiments explained herein, the wollastonite is added to the mixes as an added microfibre and not for replacement of any component.

Typical properties of wollastonite compared to OPC, has been reported and shown in Table 5. 3 (Ransinchung, Kumar, & Kumar, 2009). This data suggest that the particles used in that research were much finer than cement (approximately 4.5 times smaller in grain size).

Table 5. 3. Physical properties of wollastonite against OPC

Material	Bulk density (g/cm^3)		Specific gravity	Fineness passing 45μm	Mean grain size (μm)
	Dense	Loose			
OPC	1.56	1.16	3.15	89.00	18.0
Wol.	1.02	0.7	2.90	96.80	4.0

Given the dimensions of wollastonite, it can be categorized as microfibre. In this research wollastonite is studied as an additive for its effects on drying shrinkage of cement-based composites. Microfibre when added to mortar and concrete, is supposed to bridge the micro-cracks which delay the process by which the micro-cracks coalesce to form macro-cracks (Shah, et al., 2011). On the other hand, wollastonite forms in needle-like shaped crystals, which can suggest its ability to bridge micro-cracks (Asar, Korkmaz, & Gül, 2010).

It is observed that decreasing the fibre distance increases the resistance to the first crack (Y. Akkaya, S.P. Shah, & B. Ankenman, 2001; Betterman, et al., 1995). For a given volume fraction, the decrease of the fibre distance could be obtained by using microfibres. This has also been reported that small particle size of wollastonite allows it to be mixed homogenously with porcelain powder (Asar, et al., 2010; R. Mathur, et al., 2007).

The wollastonite used for this study was supplied by Namaqua Wollastonite, with composition as shown in Table 5. 4.

Table 5. 4. Chemical composition of wollastonite (examined by XRF)

Constituent	%	Constituent	%
SiO_2	49.8	MgO	0.16
CaO	46.5	K_2O	0.085
LOI	2.58	MnO	0.084
Al_2O_3	0.48	P_2O_5	0.054
Fe_2O_3	0.34	TiO_2	0.03

5.4.1 Wollastonite in application

Wollastonite has already been studied in different research projects. These microfibres are approximately 25-30 µm in the transverse direction and about 0.4 - 0.6mm in length (Norman M. P. Low & Beaudoin, 1992). Thermally treated crushed incinerator bottom ash has significant amount of wollastonite and has been used to produce lightweight concrete (Qiao, Ng, Tyrer, Poon, & Cheeseman, 2008). Furthermore, wollastonite, with and without microsilica, was studied for cement replacement in pavement concrete by Ransinchung et al. (Ransinchung, et al., 2009) since wollastonite improves the properties of admixed concrete in presence of microsilica.

Mathur et al (2007; 2007) investigated the influence of wollastonite on the mechanical properties of concrete and found significant improvements in compressive and flexural strength at 28 and 56 days by incorporating 10% wollastonite as partial replacement of sand and/or total cementitious materials content in concrete mixes. They also reported a reduction in water absorption, drying shrinkage and abrasion loss, and enhanced durability in freeze-thaw and sulphate attack conditions.

The incorporation of wollastonite microfibers in ultra high performance concrete (UHPC) mixtures was reported to have a positive effect on the early-age compressive strength through reinforcing its microstructure (Soliman & Nehdi, 2012). It was also stated that wollastonite microfibers provide passive internal restraint in UHPC, and it results in lower shrinkage strains and delayed onset of cracking (Soliman & Nehdi, 2012).

In non-cement-based materials, Asar et al. (2010) evaluated the effect of wollastonite on firing shrinkage in porcelain ceramics. It was found that an increase in wollastonite addition up to 5% of total porcelain specimen mass resulted in a notable decrease in linear firing shrinkage (approximately 20% reduction). This study also reports that wollastonite is commonly used in ceramics such as wall tiles and sanitary ware, to provide lower shrinkage, improved strength, lower dimensional volumetric change and reduced firing time (Asar, et al., 2010).

The flexural strength characteristics of hydrated cement and cement-silica fume matrices can be maximized by incorporating an optimum amount of natural wollastonite microfibres and silica fume in the composite mixture (Norman M. P.

Low & Beaudoin, 1994). Improvement of the pre-peak and the post-peak load-deflection response by the incorporation of wollastonite microfibres was observed in composite systems (Norman M. P. Low & Beaudoin, 1993). Moreover, Filho et al. (2011) have used wollastonite microfibre to produce an Ultra High Performance Cement Composite.

To date, there appears to be a limited number of publications available on the effect of wollastonite on the shrinkage behaviour of mortars. However, there is some evidence of industry application of wollastonite in mortar and other construction materials, with the assumption that it would provide improved strength and dimensional stability as well as improved durability.

5.4.2 Experiments

In order to obtain a consistent mix, wollastonite microfibre was initially introduced to sand part of mixture. For the aim of having consistent mixes, the whole bag containing sand and microfibre was thoroughly agitated for about 30 seconds.

All cement mortar mixes are simply named after their concentration of wollastonite microfibre. In Table 5. 5, the term –Co” stands for the control mix without wollastonite, while terms such as Wo1.0 or Wo2.0 stand for mixes with wollastonite microfibres concentration of 1.0% or 2.0% to cement weight, respectively.

5.4.3 Test results

Despite drying shrinkage, other physical properties of mixes including the fresh density, flow, mass change of specimens during 28-day ambient storage, 7-day and 28-day compressive strength have also been studied.

Table 5. 5. Mix proportions of mortar specimens

Mixes Raw materials	Co	Wo0.2	Wo0.4	Wo0.6	Wo2.0	Wo4.0	Wo6.0	Wo8.0	Wo10.0	Wo12.0
Cement (g)	450	450	450	450	450	450	450	450	450	450
Sand (g)	1350	1350	1350	1350	1350	1350	1350	1350	1350	1350
Water(g)	224.35	224.35	224.35	224.35	224.35	224.35	224.35	224.35	224.35	224.35
HRWR (ml)	1	1	1	1	1	1	1	1	1	1
Wollast.(g)	0	0.9	1.8	2.7	9	18	27	36	45	54

5.4.3.1 **Fresh state**

The first experiment carried out was mortar fresh density. Based on this test, fresh density of wollastonite mixes increases gradually up to about 1-3 % with increasing wollastonite concentration to 10.0 and 12.0%, comparing to control samples, respectively.

The flow property of mixes with and without wollastonite is presented in Figure 5. 15. It can be concluded that the addition of wollastonite affects the flow reversibly, up to 2.0% addition of wollastonite. However, higher concentrations, i.e. 2-10% additions of wollastonite seem to compensate the drop of flow. The flow of Wo12.0 drops again. But in general, the highest flow still belongs to control mix and all the mixes with wollastonite experience lower flow properties.

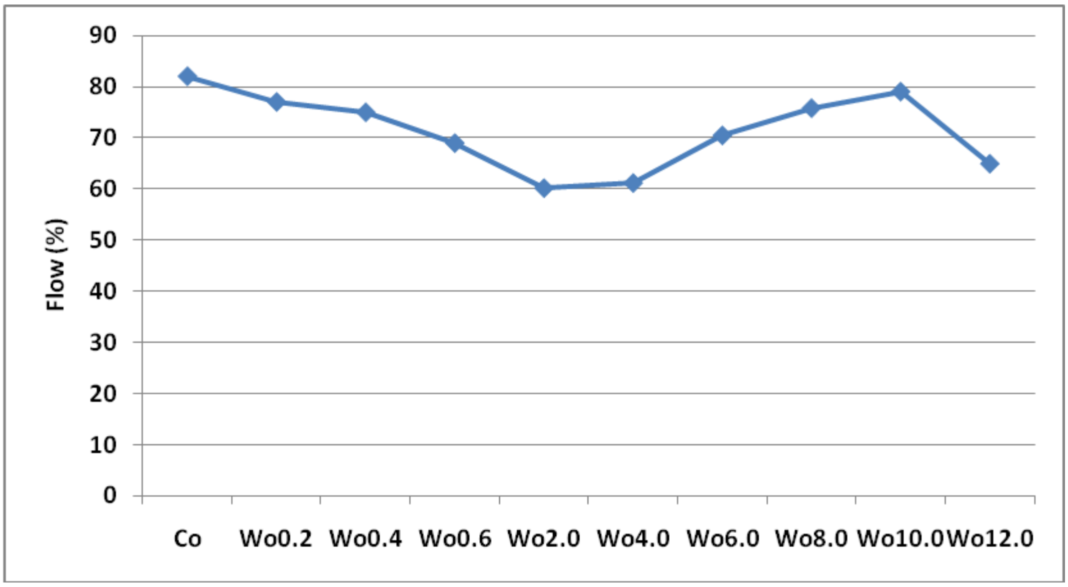


Figure 5. 15. Flow properties of wollastonite reinforced mixes

The decrease in flow might be due to the addition of dry particles to the mix with keeping water content and HWR steady.

5.4.3.2 **Hardened state**

Compressive strength- 7, 28 and 180-day compressive strength of mixes with wollastonite is compared to compressive strength of the control mix in Figure 5. 16. Generally, all mixes with wollastonite addition demonstrate higher compressive strength results comparing to control mix. However, more addition of wollastonite affects the compressive strength boost, adversely.

Similar trends can be seen in both 7 and 28-day compressive strength. Unchanged trend reveals that wollastonite provides reinforcement to the microstructure as soon as the sample has been set.

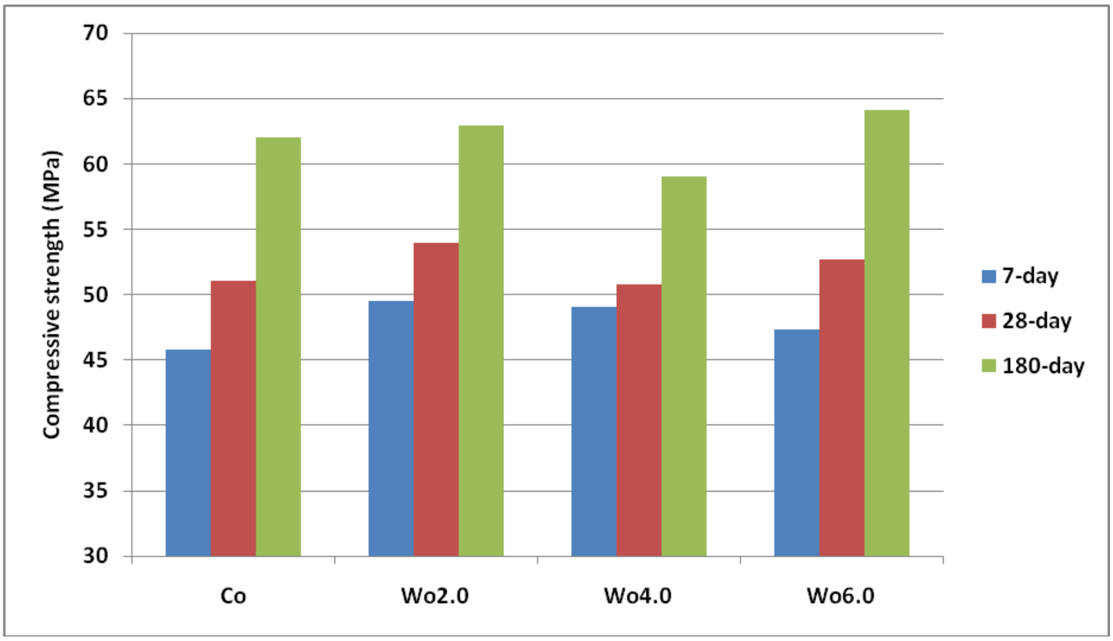


Figure 5. 16. 7, 28 and 180-day compressive strength of wollastonite reinforced mixes

Drying shrinkage- Similar to PE microfibre study, drying shrinkage samples of wollastonite mixes were stored in a controlled environment with 23°C and 60%RH. Another test has also been carried out on varying RH of the environment.

Figure 5. 17 and Figure 5. 18 illustrate the drying strain of mixes with and without wollastonite at constant RH of 60% and constant temperature of 23ºC. It can be seen that lower concentration of wollastonite can decrease the amount of drying strain after 28 and 56 days. However this reduction is insignificant.

On the other hand, higher concentrations of wollastonite show higher degrees of reduction, specifically for Wo2.0 and Wo6.0 mixes. 23% reduction in dying shrinkage unveils the performance of wollastonite in micro-bridging in the microstructure of cement mortars. This phenomenon seems to exist in all mixes, although the concentration and direction of microfibres can influence the performance.

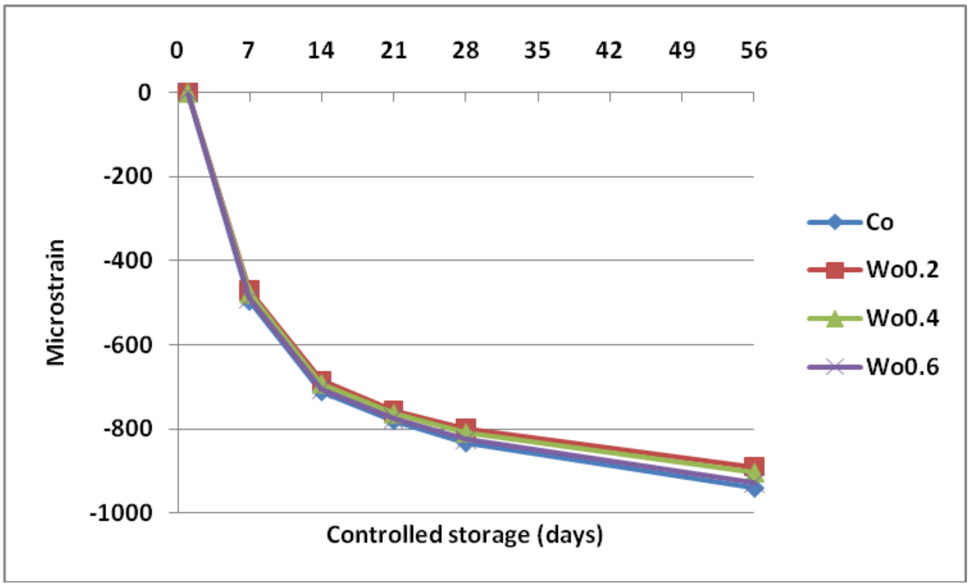


Figure 5. 17. Drying shrinkage of mixes with low concentrations of wollastonite (60% RH constantly)

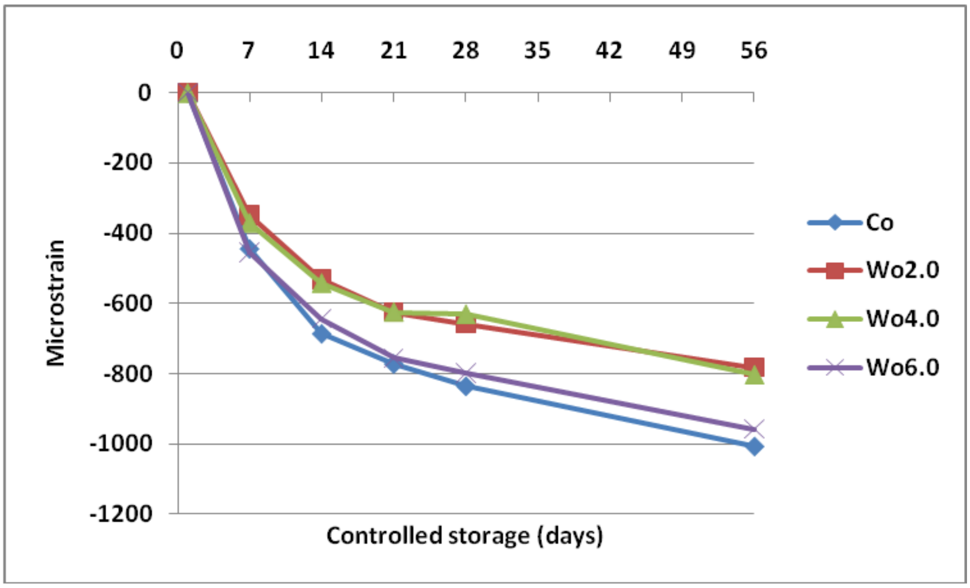


Figure 5. 18. Drying shrinkage of mixes with high concentrations of wollastonite (60% RH constantly)

Figure 5. 19 and Figure 5. 20 illustrate the effects of wollastonite on drying shrinkage properties of cement mortars, in variable environmental conditions. In this case, samples were stored at 30% RH (the minimum that chamber could provide constantly) for first 28 days and then stored at 65-70% for extra 28 days. This condition change was designated to study the efficiency of wollastonite microfibre in

harsh situations, such as 30% RH and then its performance when the predominant shrinkage mechanism will change.

Based on Figure 5. 19, drying shrinkage of mixes with low addition of wollastonite has been reduced comparing to of that in control mix at 28 and 56 days. Nevertheless, higher concentration of wollastonite increases the drying strain.

It is also shown that the drying strain of samples have not been changed significantly between 28 and 56 days, as the RH has been increased after 28 days. Eventually, the shrinkage reduction is not different between 28 days results and 56 days results. The similar trend can also be seen in high concentration of wollastonite in Figure 5. 20.

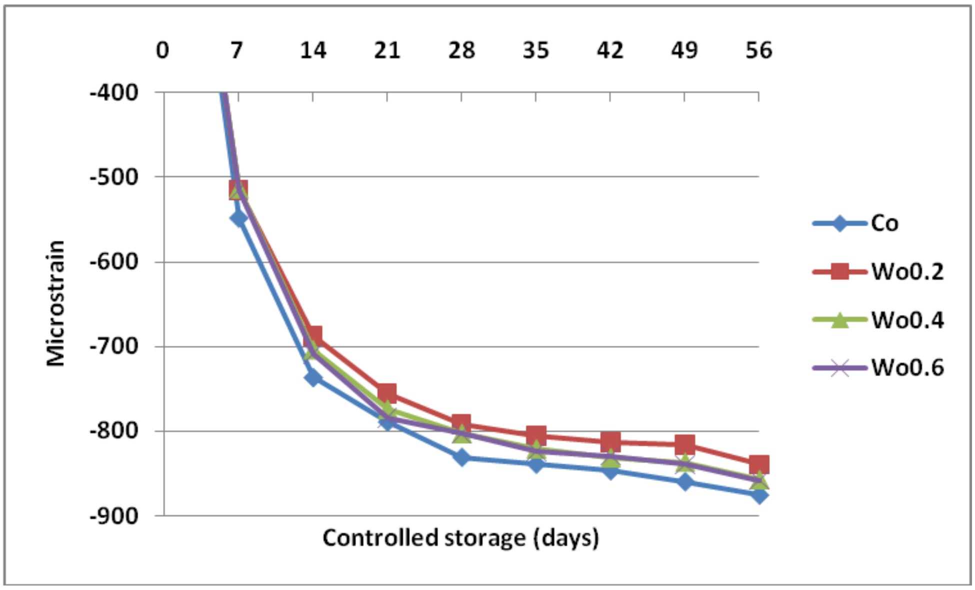


Figure 5. 19. Drying shrinkage of mixes with low concentrations of wollastonite (variable RH)

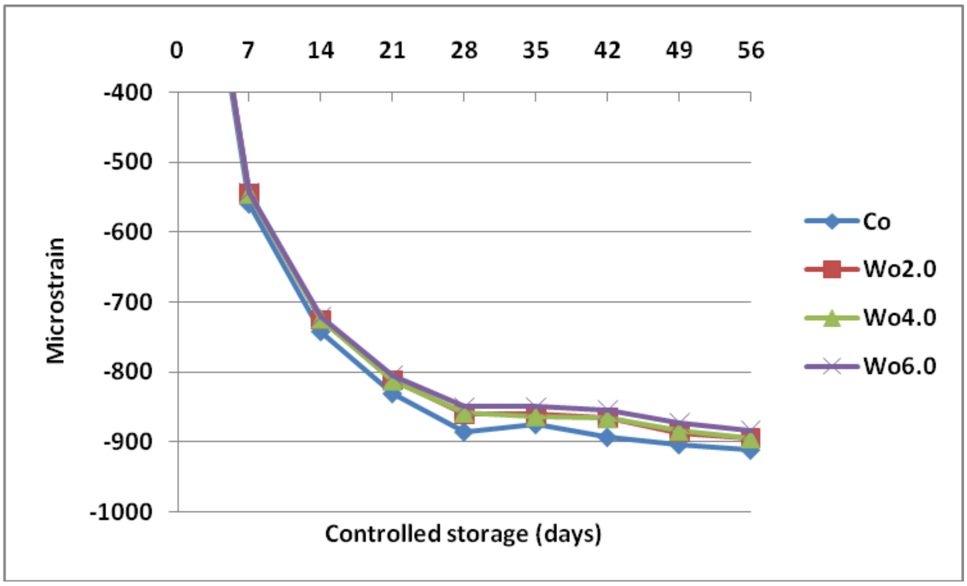


Figure 5. 20. Drying shrinkage of mixes with high concentrations of wollastonite (variable RH)

Similarly, Figure 5. 20 suggests that addition of higher dosages of wollastonite still reduce the drying strain at 28 and 56 days. Unlike, lower concentrations, increasing the concentration of wollastonite decreases the amount of drying strain.

The observed drying shrinkage reduction of wollastonite is not significant. However, this reduction along with compressive strength enhancement reveals the effect of micro-bridging of wollastonite microfibres.

In addition, the micro-bridging effect of wollastonite is still present in varying humidity condition.

Mass loss- Since the mass loss of control and wollastonite samples are due to moisture loss, the mass of each sample was also measured during each subsequent length measurement. Results of mass change percentage after 28 and 56 days of drying are presented in Figure 5. 21 and Figure 5. 22. Referring to these figures, a slight reduction can be observed in mass loss after 28 and 56 days of drying. Nevertheless, there is not a reduction trend in low concentrations of wollastonite shown in Figure 5. 21, as Wo0.4 has lost more moisture, but there can be seen a reduction trend by adding high concentration of wollastonite to cement mortar, as illustrated in Figure 5. 22.

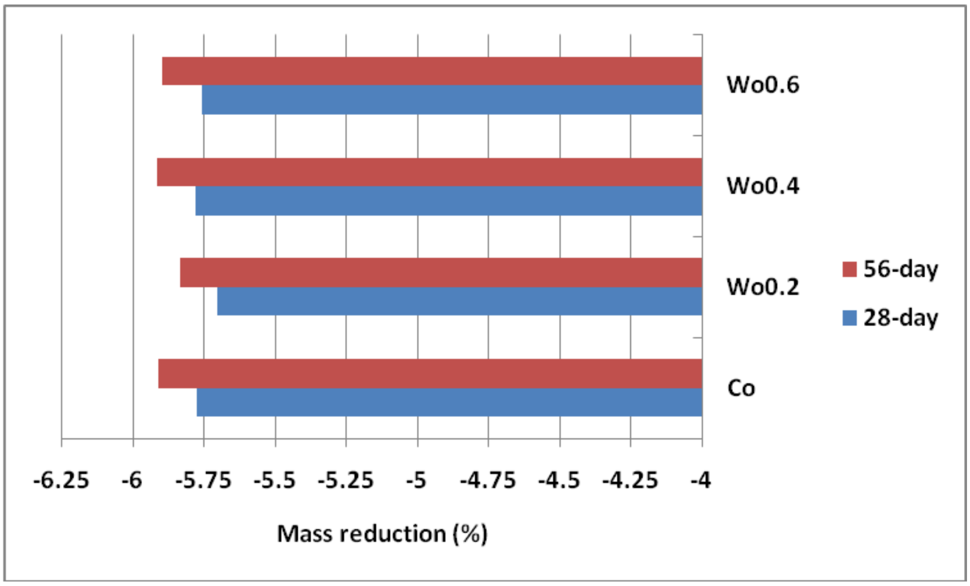


Figure 5. 21. Mass loss of mixes with low concentrations of wollastonite

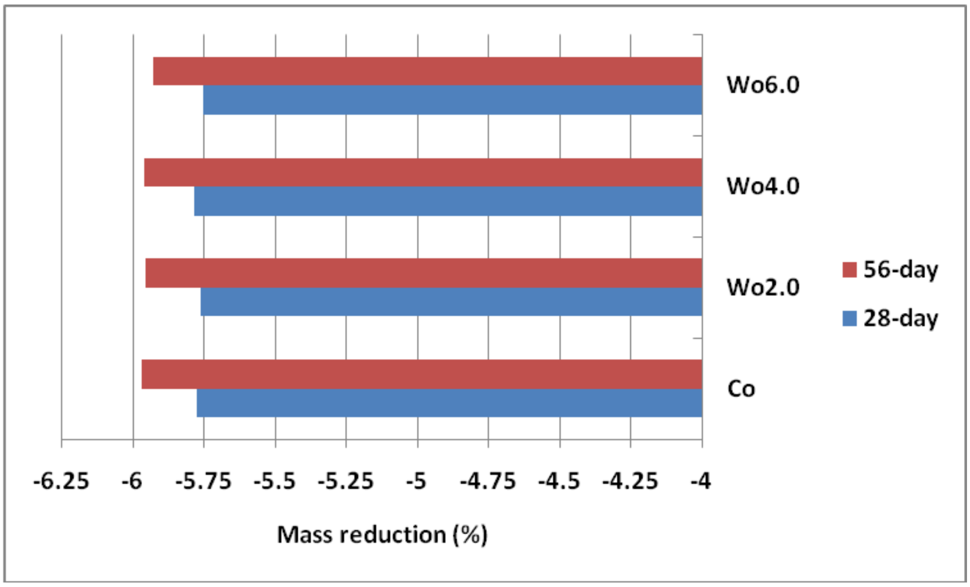


Figure 5. 22. Mass loss of mixes with high concentrations of wollastonite

5.4.4 Discussion

Wollastonite microfibre could enhance the compressive strength and reduce the drying shrinkage of cement mortars. Although unlike PE microfibres, they did not affect the moisture loss significantly. These two observations suggest that the mechanism will only be the micro-bridging effect of wollastonite microfibres within cement matrix. Compressive strength enhancement also agrees with this mechanism.

On the other hand, wollastonite microfibres are hydrophilic whereas PE microfibres are hydrophobic, and this suggests the difference in their shrinkage mechanisms.

6 Plastic shrinkage

6.1 Preface

Plastic shrinkage can be defined as the early volumetric contraction of a system in which water constitutes a continuous phase and the water menisci are located at the surface of the system.

However, depending on the chemical properties of cement, plastic shrinkage cracking may occur even when the surface of the concrete is covered by a plane layer of water (Ravina & Shalon, 1968). The origin of plastic shrinkage and plastic shrinkage induced cracks has been investigated by many researchers during the past five decades; however there is no generally accepted theory in the literature (Radocea, 1994).

Powers (1968) alleged that plastic shrinkage occurs when the rate of evaporation exceeds the rate of bleeding. On the other hand, Wittmann (1976) claimed that plastic shrinkage can be related to the development of capillary pressure in the mixing water. Capillary pressure, in a saturated mixture exposed to drying, depends on the geometry of the spaces between the solid particles near the surface of evaporation and the difference between the amount of evaporated water and the amount of water transferred from inside the mixture to the surface (Radocea, 1994).

Generally, the process of plastic shrinkage involves a mass transfer from the surface to the surroundings by evaporation and a simultaneous mass transfer from inside the concrete to the surface (P.K. Mehta & Monteiro, 2006). It has also been shown that, since water and solid particles can be regarded as incompressible, the amount of water transferred to the surface is equivalent to the total deformation of the sample (A. Radocea, 1992).

6.2 Early volume changes

Early volume contraction of fresh concrete is known as pre-hardening, presetting shrinkage, or plastic shrinkage, since the shrinkage occurs whilst the concrete is still in the plastic state (P.K. Mehta & Monteiro, 2006). As a result of plastic shrinkage, cracks develop over obstructions to uniform settlement, i.e., restraints, reinforcing bars and large aggregate particles.

According to Lura et al. (2007), the driving forces for such cracking are high evaporation rates that lead to the menisci and high tensile stresses, differential settlement, temperature gradients and autogenous shrinkage (Mora-Ruacho, et al., 2009).

Generally, structures or elements having higher surface to volume ratios are prone to rapid drying and such cracking caused by plastic shrinkage, allegedly when the rate of moisture loss from the surface exceeds the rate at which the bleed water is appearing (P.K. Mehta & Monteiro, 2006). Therefore, cracks will develop if the concrete near the surface has become stiff to move but at the same time, is not strong enough yet to withstand the tensile stress caused by the restrained shrinkage.

A variety of causes contribute to plastic shrinkage in concrete: bleeding or sedimentation, absorption of water by subgrade, formwork or aggregate, rapid water loss by evaporation, reduction in the volume of the cement-water system, and bulging or settlement of the formwork. In addition, there are some causes which accelerate plastic shrinkage: high concrete temperature, low RH, and high wind velocity. Plastic shrinkage cracking has been numerously reported in hot weather concreting specially for unprotected elements (P.K. Mehta & Monteiro, 2006).

Review of plastic shrinkage mechanisms: According to Powers (1968) plastic shrinkage is likely to occur when the rate of evaporation exceeds the rate of bleeding. In such a case, a complicated system of water menisci usually forms on the surface of the concrete, and the top most particles are driven downwards by compressive forces. The action of compressive forces on the top most grains may explain a vertical contraction, but not a horizontal contraction or the development of cracks.

Another model of plastic shrinkage reported by Wittman (1976) was the first to show that plastic shrinkage can be related to the development of capillary pressure in the mixing water. In this hypothesis, Wittman mostly concentrated on the maximum capillary pressure, which usually depends on the method of measurement.

It has been reported in the literature (Ravina & Shalon, 1968) that, depending on the chemical composition of the cement used, plastic cracking may occur even when the surface of the concrete is fully covered by a plane layer of water.

According to the Laplace equation, the capillary pressure P is a function of the surface tension of water δ and the mean curvature of the water meniscus R:

$$P = \frac{2\delta}{R}$$

Equation 6. 1

The curve in Figure 6. 1 represents the change of pore-water pressure in a freshly placed cement paste. Immediately after placing, the cement particles are supported entirely by the mixing water, and the hydraulic pressure P_1 at a given depth exceeds the normal hydrostatic pressure P_2 at that depth. This kind of change in water pressure, which describes the settlement of cement grains, is discussed in detail (Adrian Radocea, 1992). During the period t_1 - t_2, when the surface of the paste is covered by a plane layer of water, no change in pore pressure usually takes place. At time t_2, when the surface of the water loses its planeness due to evaporation, the pore-water pressure begins to decrease again.

The attempt to describe the pore structure near the surface by an equivalent pore is motivated by the fact that the pores, communicating with one another, dry as a single pore. This means that a small pore cannot dry faster than a larger one, since the water transport from adjacent larger pores will always supply the smaller ones, which tend to dry faster (Radocea, 1994).

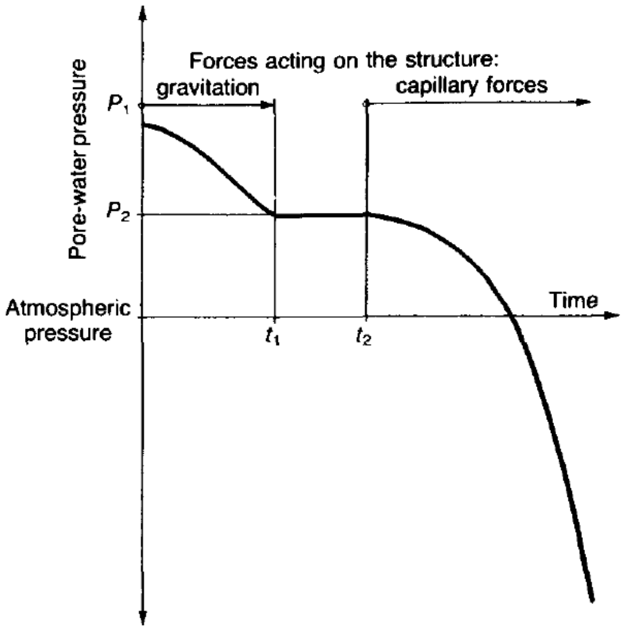


Figure 6. 1. Changes in pore-water pressure in a freshly placed cement paste, courtesy to Radocea (1994)

6.3 Measuring plastic shrinkage

Since the plastic shrinkage happens during early age of the cementitious samples, the volume change, particularly in depth cannot be measured as simply as measuring the drying shrinkage by a length comparator and preinstalled pins.

Instead of using pins and length comparators, Al-Amoudi et al. (2006) and Al-Amoudi et al. (2007) have used linear variable differential transducers (LVDT) installed to aluminium studs embedded in a concrete slab. Mora-Ruacho et al. (2009) have also used LVDT to measure the vertical settlement of a concrete slab. Nevertheless, this type of test is costly and cannot exactly represent the unrestrained early age shrinkage, due to the restraint provided by embedded studs.

The other reviewed approach to study the plastic shrinkage is studying the cracking behaviour of concrete or mortar instead of measuring the actual length change. Therefore, this approach studies the plastic cracking behaviour of restrained samples and compares them in order to assess their cracking resistance. These types of tests are mostly used in research and industry. Carlswärd (2006) has described three main categories of test set-ups which are frequently used to study shrinkage cracking: 1- end-restrained, 2- base restrained and 3- ring tests. Category 2 tests, i.e. overlays cast on a substrate, are clearly the most suitable from the viewpoint that the restraint condition represents the real overlay conditions.

In order to get cracking in samples, ASTM C1579-06 (2006) suggests to store the samples at a fairly low RH, i.e. 30±10% and high temperature, e.g. 36 ± 3ºC as soon as the mixture is set. In order to prepare and maintain such an environment, ASTM C1579-06 proposes a fan box or chamber with de-humidifier and heater. The minimum evaporation rate required by this standard is 1.0 kg/m^2.h from the pan of plain water in the environment (ASTM-C1579, 2006).

Additionally, a steel mould with stress risers is also mentioned in ASTM C1579 (2006) and some other studies (Saliba, Rozière, Grondin, & Loukili, 2011; P Soroushian & Ravanbakhsh, 1998) in order to provide restraint for the sample. The stress risers proposed by ASTM C 1579-06 are illustrated in Figure 6. 2.

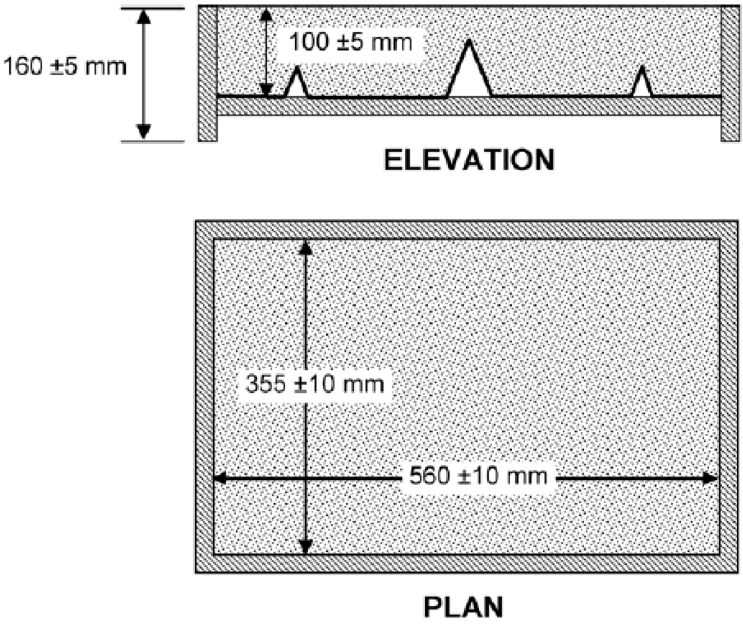


Figure 6. 2. Stress riser arrangement proposed by ASTM C1579-06

On the other hand, Balaguru (1994) arranged different types of restraint using side wire meshes. Pelisser et al. (2010a) have also adopted the same idea by using L-steel brackets to provide restraint to the concrete slab from both end sides.

Alternatively, ASTM-C 1581 (2009) has proposed another test in this regard, which is aimed at determining Age at Cracking by using a steel ring with attached strain gauges (Figure 6. 3).

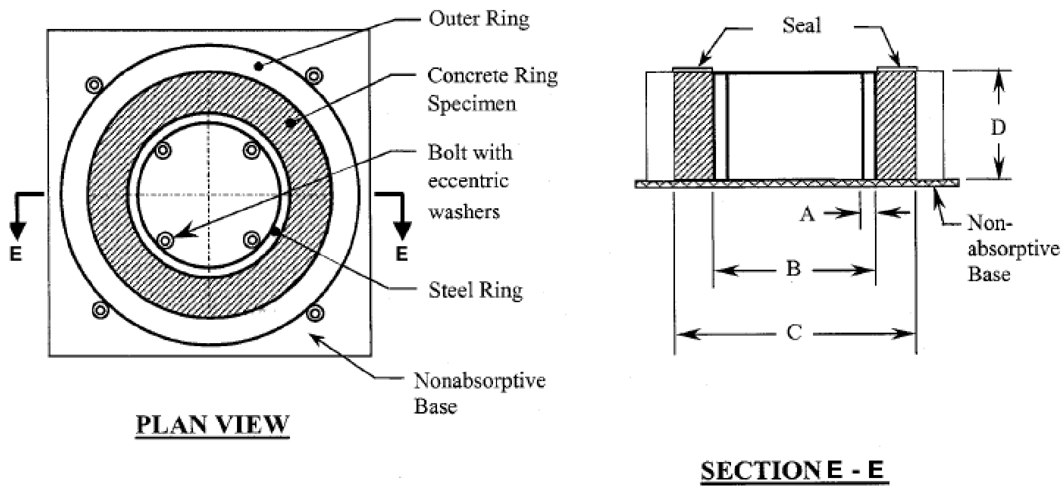


Figure 6. 3. Ring test proposed by ASTM C 1581

The compressive strain developed in the steel ring caused by shrinkage of the restrained mortar or concrete specimen is measured by the strain gauges. Cracking of the test specimen is accompanied by a sudden decrease in the steel ring strain. The age at cracking and the rate of tensile stress development in the test specimen are indicators of the material's resistance to cracking under restrained shrinkage. This test method has also been used, modelled and modified in some other research projects (Eppers, 2011; He, Zhou, & Li, 2004; Kovler, Sikuler, & Bentur, 1993; See, Attiogbe, & Miltenberger, 2003).

Most recently, Carlswärd (2006) studied and modelled a new set-up with End restrained shrinkage test series for overlay samples, in which restraint was obtained by anchoring the ends of thin overlays to a rigid steel beam. This set-up was designed to study plastic cracking of steel fibre reinforced self-compacting concrete overlays.

In all these experiments, providing a proper environmental condition for the cementitious material to crack is essential. Proper environmental conditions include all elements, such as low RH, wind and high temperature which result in an evaporation rate greater than 1.0 kg/m^2.h from a pan of water.

6.4 Significance

In terms of engineering practices, the first concern in shrinkage characteristics of concrete and mortar is plastic shrinkage, whereas, drying shrinkage as the main contributor to total shrinkage happens in long-term. Particularly, in wide elements such as concrete slabs and concrete pavements, this is the early age changes in material which can affect its appearance and then its durability, throughout its life cycle. Not-properly cured concrete elements can be seen to be cracked after few days of placing. Therefore, the most important early age shrinkage type which comes to attention for conventional concrete is plastic shrinkage that results in plastic cracking.

Plastic shrinkage cracking has often been tackled by the incorporation of fibres in concrete (P Soroushian & Ravanbakhsh, 1998), which seize crack opening and, consequently, limit the crack width (Mora-Ruacho, et al., 2009).

In order to further investigate the newly introduced shrinkage compensating materials, their early age behaviour in cement mortars has been tested in this research. Therefore, in this chapter three mixes containing optimum concentrations of APP, PE and wollastonite have been cast and compared to a control mix as they dry immediately after placing.

Experiments: The test method selected for this purpose was the one proposed by ASTM-C1579 (2006). Suggested by the standard a humidity cabinet was used to prepare the RH at 30% and temperature at 25ºC. This environmental condition is prepared and accompanied by constant wind generated by the cabinet's compressor. This situation was tested twice by measuring the evaporation rate from a water pan stored in the cabinet.

Four moulds for restrained plastic shrinkage were built with plywood covered by polyurethane paint in order to have non-absorbent surfaces. Additionally, two short stress risers closer to the both sides and one long stress riser in the middle have been provided for restraining the fresh samples. These stress risers are supposed to induce early age cracking due to plastic shrinkage and/or settlement cracking. Figure 6. 4 shows the schematic of section view of the restrained shrinkage moulds.

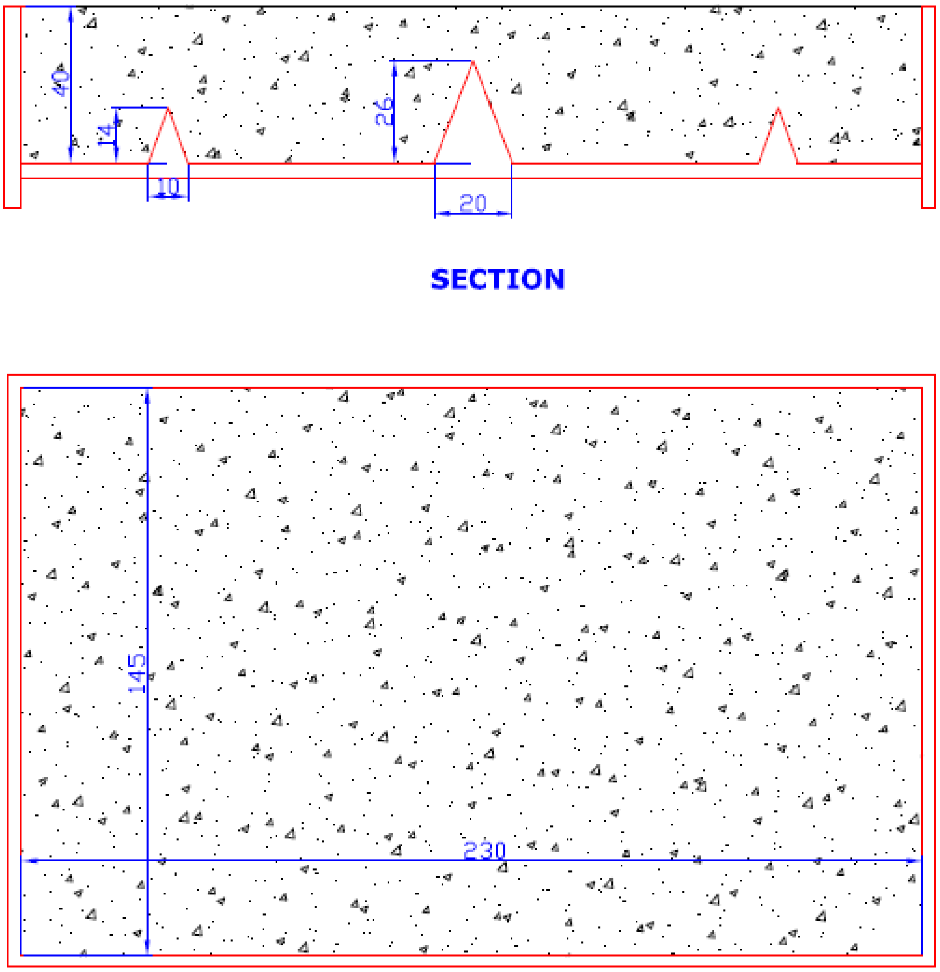


Figure 6. 4. Schematic section view of restrained shrinkage mould

In this experiment Co, APP0.6, PE0.6 and Wo4.0 were studied. The samples were mixed at 23ºC and 76% RH as per instructed in Chapter 3. Then the samples were immediately placed and compacted in the restraining moulds and transferred to humidity chamber immediately.

Crack width has been measured using an on-site crack measure (designed and calibrated to measure minimum of 0.1 mm) and a magnifier.

The experiment were performed by analysing the early age cracks including counting the major cracks, measuring the dimensions and time of first cracking.

6.5 Results

Figure 6. 5 illustrates cracking time for different samples. This graph illustrates the time that first crack occurred in different mixes, while they were stored in the same environmental condition.

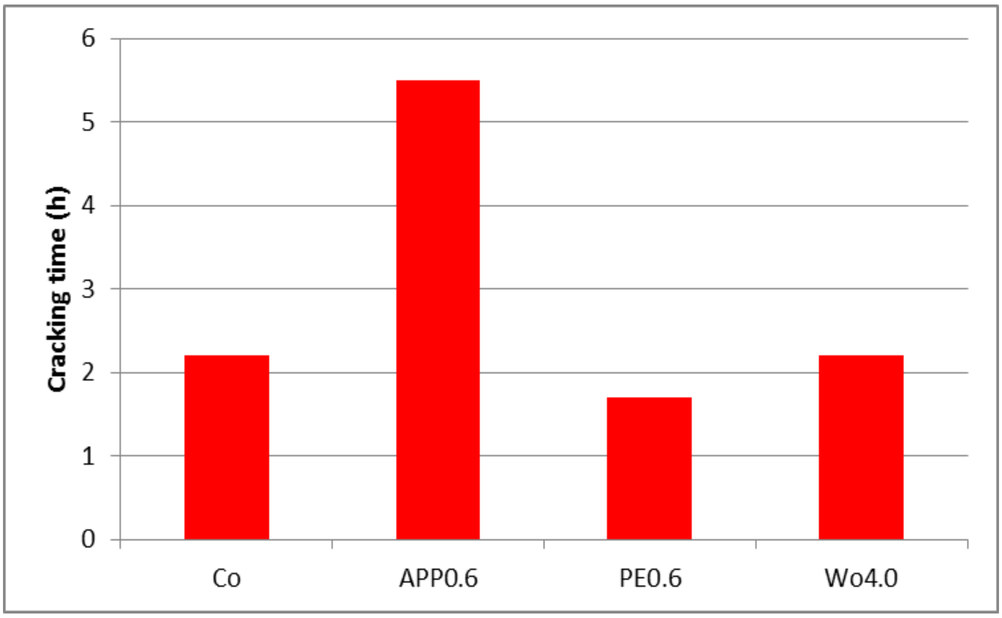


Figure 6. 5. Cracking time of different mixes

This graph clearly shows APP modified mix has the longest crack time and its first crack happened after 5.5 h, whereas the cracking time for Co was slightly longer than 2 h. This observation is in agreement with conclusion of Chapter 4 in regards to stronger structure of APP modifies mixes, which in this case delays the plastic cracking of the mix. This also suggests higher early age tensile strength for APP mixes than Co.

On the other hand, PE0.6 has shorter cracking time than Co, which implies less tensile strength has been developed in the early age for PE0.6. However, early age moisture loss is fewer in PE0.6 than Co, based on Figure 6. 6. Reduction in moisture loss could suggest reduction of plastic shrinkage cracking and longer cracking time for PE0.6, although the results show different outcome.

Wo4.0 showed the cracking behaviour similar to Co. It also demonstrates that wollastonite microfiber could not increase the tensile strength of mixes at early age.

All these additives and agents were shown to reduce the drying shrinkage in short and long-term, nevertheless, they affect plastic shrinkage in differently.

Figure 6. 6 depicts moisture loss (mass loss) of samples in first 6 hours after mixing. As was expected and seen in drying shrinkage tests (Chapters 4 and 5), APP and wollastonite mixes have higher mass loss than Co, whereas, PE mixes have lower moisture loss than Co.

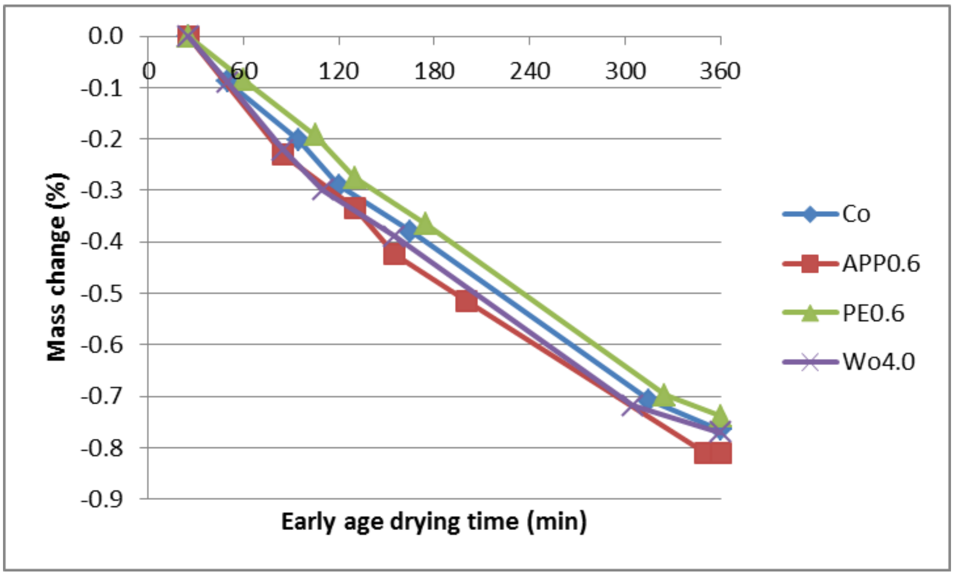


Figure 6. 6. Mass change of mixes in first 6 hours

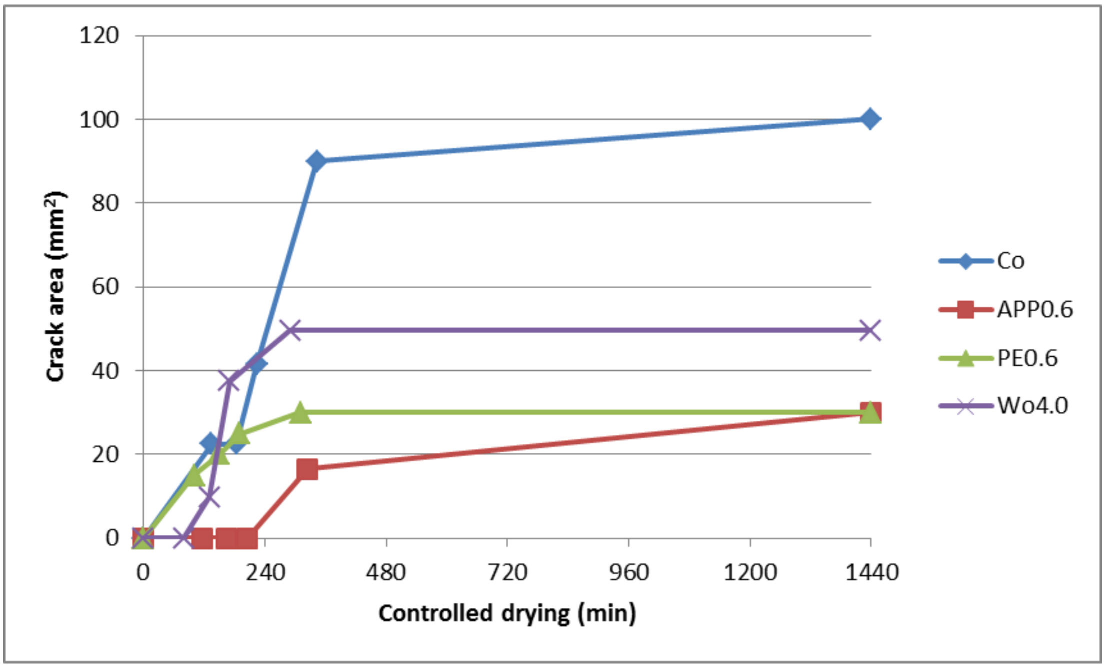


Figure 6. 7. Development of crack area in first 24 hours

Figure 6. 7 illustrates the development of created crack area (length × width) by time for first 24 h. Figure 6. 8 shows the crack area relative to Co's crack area after 24 h, as well as the number of cracks after 24h on secondary axis and values in reverse order. Figure 6. 8 suggests that although cracking time was shorter in PE0.6 than Co, but its crack area is around 30% of Co's crack area. In addition the number of cracks in APP0.6, PE0.6 and Wo4.0 are 1, 1 and 3, respectively, whereas there are 4 cracks on Co.

It can be easily concluded that cracking development and crack area have been significantly decreased by adding either of these additives.

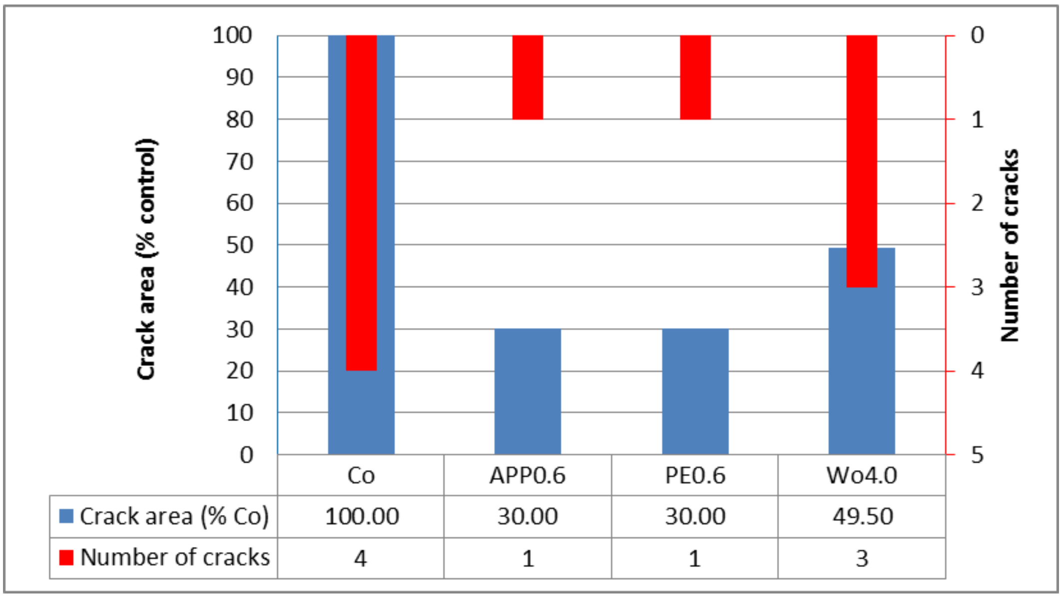


Figure 6. 8. Crack area (% control) and number of cracks

Additionally, Figure 6. 9 demonstrates the maximum crack width of samples. Based on this figure Co has been shown to have the highest crack width and APP0.6 has been shown to have the lowest crack width. This graph implies that the maximum crack width can decrease by the addition of these additives. It also suggests that the samples were more resistant to crack development and propagation than Co, which can also be concluded from the number of cracks for each sample on Figure 6. 8.

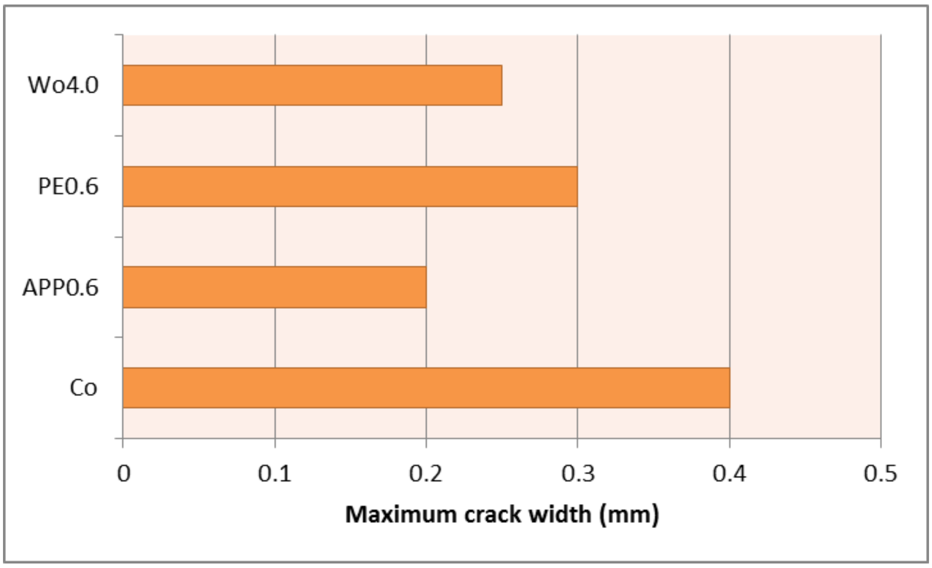


Figure 6. 9. Maximum crack width after 24 hours

Appendix A covers the pictures from this experiment.

6.6 Discussion

These experiments could study different angles of plastic shrinkage by the means of studying early age plastic cracking. The additives used in this chapter were already used in drying shrinkage reduction in Chapters 4 and 5, and in current chapter they were investigated for their behaviour in early age cementitious specimens.

Addition of these additives could considerably decrease maximum crack width, number of cracks and crack area (% Co) in first 24 h of samples, regardless to wether the crack is due to plastic shrinkage or plastic settlement. In regards to cracking time, APP0.6 could stand longer time before cracking than Co, while PE0.6 and Wo4.0 did not show better resistance than Co.

A slab simulated mould with 3 stress risers could make samples crack after few hours and helped investigate the cracking resistance of mortars modified by additives. Being an economical test, it also results in a great number of information.

7 Summary and Conclusions

The principal objectives of this research were to review the current shrinkage compensating admixtures; design new reactions and mechanisms for shrinkage compensating/reducing material; investigate the potential of utilising newly designed agents and additives as shrinkage reducing/compensating agents in cement-based materials; determine other physical and mechanical effects of new agents on cement mortars; investigate the mechanism of agents in shrinkage compensation or reduction; assess aspects of the physical or chemical durability of cement mortars containing novel agents in comparison to control mixtures; and study the effect of novel systems on early age plastic shrinkage cracking. These objectives were met by carrying out a large number of carefully designed and controlled experimental program supported by a combination of analytical testing methods including evaluation of physical and mechanical properties, namely consistencies (through workability and wet density measurements) and compressive strength; through phase analysis using SEM and TG; durability assessment involving sulphate exposure and varying environmental conditions; and performing a simplified early age experiment with sufficient number of results. However, the main goal in this dissertation was to cover as many aspects as possible in early age, short-term and long-term shrinkage studies of admixtures and the main results and conclusions of this thorough study on novel shrinkage compensation mechanisms are summarised below.

Chapter 1 of this dissertation covered an introduction to the subject with introducing shrinkage as a source of concrete deterioration and describing the cement hydration and microstructure of voids and moisture in cement-based materials. Then objectives and significance of the project were explained.

Chapter 2 however tried to explain the shrinkage phenomenon and the state of the art knowledge of shrinkage, based on literature survey. Different classes of shrinkage and their causes were studied and presented in a critical review. In addition, the current understanding of mechanisms of drying shrinkage was discussed.

The influence of relative humidity (RH) as the driving force on the shrinkage mechanism was explained and considered in the experiments, for the first time. The major point in this consideration was that the range 40-50% RH is claimed to be a border line distinguishing capillary tension mechanism or disjoining pressure mechanism with interlayer water or surface energy mechanisms. Therefore, the first conclusion from this chapter was to choose and set a fixed RH for the experiments, at which drying shrinkage is not sensitive. In this case, shrinkage mechanism would not be supposed to transfer from one to another, by slight abrupt changes of RH in humidity chambers. For this purpose, the RH of humidity cabinets was set at 60-65% RH. This range was chosen in a way that removing and placing the samples from and to the cabinet, would not affect the internal RH dramatically. The range 60-65% RH was used in all drying shrinkage experiments, except those in which the RH was intentionally set lower or higher. Despite the effect of RH on drying shrinkage, other influencing factors were also studied.

The effect of high range water reducer (HWR) on the amount of drying strain was a point of controversy in literature. Therefore, the amount of HWR was constant in the mixes which were supposed to be compared to each other. However, in Chapter 5 it was indirectly concluded that the addition of HWR can reduce the drying shrinkage.

The temperature of the environment was also chosen to be steady during the test. On the other hand, the general mix proportion of cement mortars was also fixed in order to avoid different variables in the mix.

Chapter 2 also reviews all the materials, systems and methods used for shrinkage compensation and reduction. It was generally concluded that fibres would not reduce the amount of drying shrinkage and they could only reduce the cracking width and numbers. On the other hand, expansive additives as well as some cement modification solutions were shown to result in cracking, less compressive strength and sometimes even greater drying shrinkage amount.

In addition, shrinkage reducing admixture (SRA) was concluded to reduce substantial portion of compressive strength and to significantly increase the workability of the end product, as it was also seen in Chapter 4 of this dissertation. The general mechanism of existing SRAs has also been introduced in Chapter 2.

Internal curing as one of the latest methods was introduced and described in Chapter 2. In addition, surface treatment as a novel technology was also explained in this chapter but also utilised in Chapter 4 for the treatment of APP in order to produce encapsulated APP.

Chapter 3 endeavoured to establish the research methodology as well as the raw materials for cement mortars. Physical, chemical, mechanical and microstructural experiments were explained in this chapter. The generic mix design used in the experiments was also introduced. Flow table experiment, as one of the initial tests was carried out in order to find the optimum HWR concentration, at which the flow of all samples in a set will be around Flow mean ±10% or 15%. However, early age shrinkage and cracking experiments were left for Chapter 6.

Raw materials and their general characteristics were illustrated in Chapter 3.

Chapter 4 and 5 introduce and study the novel shrinkage compensating/reducing admixtures (SCAs). Firstly, APP was introduced in Chapter 4, as a chemically reactive agent in cement matrix. As thoroughly explained, the performance of phosphate cement and the effects of calcium phosphate on cement-based mixes led this research to study a new composition of phosphates which can also benefit the matrix in more aspects. APP was initially produced as a fire retarding agent at UTS, and then was chosen in this study as an attempt to evaluate the target integral model of using volatile ammonia and calcium polyphosphate as dual-action and multifunctional admixture; shrinkage compensating and volatile corrosion inhibitor

Experimental tests were performed using different low concentrations of APP. Recalling the test results from Chapter 4, APP could enhance the flow of the cement mortars, possibly due to its anionic character, which shares with most water-reducing admixtures. On the other hand, APP modified mixes had shown to be wet even after 24 h of placing, which reveals its hydration retardation characteristic.

Compressive strength was also enhanced, particularly by increasing the APP addition. Unlike the existing SRAs and other expansive agent, APP not only did not reduce the compressive strength, but also in many cases increased it considerably. The produced calcium polyphosphate (CPP) inside the paste is expected to be the cause of strength enhancement, since the calcium phosphate is previously known for its utilisation in dental and orthopaedic applications for years, due to its high mechanical properties. On the other hand, APP can be supposed to react with any constituent of MgO present in the mix forming magnesia cement, which results in strength modification; adding to that, decreasing the calcium hydroxide concentration in the concrete composition will affect remarkably the rate of concrete carbonation.

In general, calcium polyphosphate seems to generate a strong structure inside the cement paste, which can also be the reason behind its shrinkage compensation, as well. This strong structure can be imagined to be like a connected columns and beams of CPP in a 3-dimensional skeleton, similar to a sponge structure. The pictured structure is like a sponge in this sense that absorbs moisture and expands more than the amount that Co samples expand, when exposed to full saturation.

Additionally, this so called structure is expected to be the main resistance to shrinkage of cement-based materials. Sponge structure is not generated immediately after the beginning of the reaction and it needs time, 7-14 days, to be built and resist. This sponge structure can be related to the production of calcium polyphosphate from APP reaction with CH, which as described in Chapter 4, in next stage forms crystalline hydroxyapatite (HAp), which is supposed to be the sponge structure in the matrix. On the other hand, the delayed crystallization of the remaining ettringite in a hardened material stored in wet conditions, without any external sulphate supply, can be associated with a swelling of the material up to about 2%.

Despite CPP, APP also produces ammonium gas and water (NH_3+H_2O), from which ammonia (NH_3) releases immediately and this is obvious from the smell it generates. Gas generation is also known as an expansive mechanism in cementitious grouting materials. However, there is evidence of some dual-action materials, which contain two forms of expansive agents; one agent that produces a gas to counteract shrinkage occurring while the material is still in a plastic state, and another that leads to the formation of a compound that produces expansion in the hardened state.

This explanation seems to be correct for APP, as it generates ammonia gas, as reported in Chapter 4. Ammonia is firstly in the form of ammonium, nevertheless; its H_2O component seemed to be released at higher temperatures (generated by cement hydration) from the ammonia component. Evaporation of H_2O can be concluded from higher early age mass loss resulted in APP modified mixes than Co, where the excess of mass loss can also be due to the evolved ammonia gas.

Additionally, APP as dual-action material produces CPP, which is responsible for expansion in hardened state. This component is explained to have a sponge structure, which compensates shrinkage as soon as it becomes robust enough to constrain drying contraction, whereas at early ages, it has not gained enough strength to resist contraction. This explains the higher drying shrinkage for APP modified mixes than Co specimens during first couple of weeks and then the lower drying shrinkage afterwards.

The sponge structure of CPP hypothesis was also adopted to explain the increase of compressive strength, in this way that vigorous structure of CPP chains results in a stronger cement paste.

Exposure of mixes with and without APP to lime-saturated water could clearly reveal the expansive characteristics of APP, particularly its product, CPP. CH was continually absorbed into APP modified mixes, as the produced CH in specimens were used in APP reaction and the concentration of CH is compensated from the lime-saturated medium. Therefore, constant supply of CH for reactive APP results in steady reaction of APP and CH in APP mixes.

This phenomenon can suggest two justifications for larger expansion in APP mixes: 1- the steady supply of CH and steady reaction of APP cause a stronger cellular structure of CPP; 2- the ingress of CH accompanies by the ingress of moisture combined with CH agents fill the voids and provide expansions. Both phenomena seem to be likely in the system in question. However, in plain water medium, the former justification, in which added amount of APP reacts with formed amount of CH (from the cement hydration) to produce a strong structure of CPP, appears to be applicable, particularly for high concentrations of APP such as 1.0 and 1.2%.

Recalling that CPP contained paste loses and at the same time absorbs the moisture more easily than an ordinary cement paste, can explain the greater results in mass loss of APP modified mixes. Nevertheless, this moisture loss does not end up in greater shrinkage strain, while it is expected in engineering practice.

In further investigation, mixes with and without APP were exposed to a sulphate saturated water (50g/L sulphate, refreshed every 2 weeks) for 10 weeks. Similar to Co, normal cementitious materials expand significantly in this situation, where most likely end up with cracking and adverse effects on durability of restraint samples. However, APP modified mixes were strongly resistant to sulphate induced expansions as detailed in Chapter 4. Surprisingly, APP0.4 expands more dramatically than Co after 56 days which is possibly due to APP induced expansions rather than the effect of sulphate invasion.

Generally, it can be concluded that mixes with low concentrations of APP are more resistant to sulphate invasion and it is possibly due to the shortage of potential reacting CH in APP modified mixtures to be involved in reaction with sulphate ions. Additionally, it can also be concluded that higher concentrations of APP might be resistant to sulphate expansions for short-term but they might expand even more largely in long-term studies. Delay in APP induced expansion was observed earlier in drying shrinkage results of APP modified mixes.

The only microstructural analysis, which was found to be useful for this study, was thermal analysis. However, studying low concentrations of APP against Co did not provide enough information about the differences in chemical compositions of these mixes. Therefore, in first stage, experiments were repeated with elevated concentrations and in next stage; sand portion of mixes was omitted. The goal was to take a pulverised sample of about 50mg of crushed mortars or slurries. Eventually slurry mixes (without sand) with 0 and 10% of APP concentration (% cement weight) were cast, cured in lime-saturated water for 28 days and then crushed in compressive strength machine. The remaining particles were picked and used for thermal experiments.

The results obviously showed the shortage of CH in APP modified sample which reveals the reaction between APP and CH. They also suggest the decrease in $CaCO_3$ concentration in APP modified mix.

Although experiments were carried out using different concentrations of APP, from 0.05% to even 3.0%, the shrinkage reduction was not seen for all concentrations of

APP, but in a vast range of concentrations, drying shrinkage reduction is obviously observed.

Based on the results it can be simply concluded that a mechanism of shrinkage compensating is working inside the matrix. In addition, compressive strength enhancement reveals the formation of a new binder with strong structure, which is expected to be CPP. Rheological enhancement is another aspect seen in APP modified mixes.

The by-product of the reaction between CH and APP is the ammonia agent which represents one of the most commercially used corrosion inhibitors known as volatile corrosion inhibitors. Therefore, this new multi-functional admixture can behave as corrosion inhibitor as well as shrinkage compensating agent. Assessing its corrosion inhibition was outside of the scope of this dissertation.

In addition, removing the CH formed from hydration, through APP reactions, from concrete and mortar samples can reduce the chance of carbonation reaction and carbonation shrinkage, which lead to corrosion of the reinforcements and carbonation shrinkage cracking, respectively.

The APP induced expansion does not occur in early stages and comes to existence after 1-2 weeks. This observation is a witness for some dual-action materials, which contain two forms of expansive agents; for instance, one agent that produces a gas to counteract shrinkage occurring while the material is still in a plastic state and another that leads to the formation of a compound that produces expansion in the hardened state. The former compound can be the ammonia agent and the latter one will be CPP. This dual-action system is being used in cementitious grouts, nowadays.

Chapter 4 continued with a brief description of studies on other chemically active agents, which were derive from APP and its mechanism. In order to mitigate the ammonia odour by preventing it to be released or by slowing down this release, APP powders were encapsulated in a fine layer of superplasticiser. Encapsulated APP (EnAPP) modified mixes could not decrease the ammonia smell during mixing significantly, although it delayed the time when the smell is released. Drying shrinkage was decreased and compressive strength was also increased by the addition of encapsulated APP. Therefore, encapsulation of APP with superplasticiser did not significantly improve the application of APP powders.

The next modification was using Melamine polyphosphate (MePP). Unlike EnAPP, production of MePP needed a chemical reaction. Low concentrations of MePP did reduce the amount of drying shrinkage, whereas higher concentrations were not successful in shrinkage reduction. Similar trend has been seen for mass loss, where mass loss was decreased in lower concentrations and increased for higher concentrations. Again, compressive strength was seen to be enhanced for lower concentrations of MePP, confirming formation of CPP and liberating melamine, which is a known corrosion inhibitor.

All these results suggest that the mechanism of MePP is entirely different to the mechanism of APP, based on different results; however, supports the explained mechanism of APP by forming cellular CPP, which enhanced the compressive strength similarly. This study introduces another shrinkage compensating admixture which still needs to be fully investigated.

Chapter 4 also studies the keratin, which is well-known for its foaming characteristic in aerated concrete production. Keratin generated a significant early age expansion, which was clearly observed during the mixing procedure. In contrast, mixes modified with keratin presented dramatically higher drying strain than Co. Compressive strength was consequently dropped by 34% in keratin modified mixes. This could be expected, considering the high porosity of the samples after mixing.

Chapter 4 ends with supportive results of melamine as not being active as shrinkage compensating admixture.

A general view at the study on chemically reactive agents shows that there is a high potential in designing and modifying this class of SCAs. Further investigation using novel admixtures with newly developed mechanism seems to be highly required. Particularly when designing a SCA with no side effect such as strength loss or change in rheology.

In addition using microstructural analytical techniques in a properly planned manner can provide a large amount of useful information in regards to the effect of agent in the mix. Therefore, in order to derive the fundamental reasons of the shrinkage reduction mechanism of novel SCAs, using microstructural analytical techniques is strongly recommended.

Chapter 5 deals with fibres, which inherently do not involve in chemical reactions with the mix and only interfere physically. The idea in this chapter was to study the effect of some microfibres on the volume change of cement-based materials.

Critical literature review in Chapter 5 disclosed that using fibres has almost never resulted in drying shrinkage reduction; however, it can provide reinforcement against shrinkage cracking. Thus, this chapter aimed to challenge this limitation by studying microfibre-reinforced cement mortars.

On the other hand, literature review revealed that PE and wollastonite microfibres have not been independently investigated in shrinkage studies. Using these fibres in micrometer dimensions was supposed to provide some reinforcement to micro-cracks, which can end up in reduction of macro-cracks, as well.

Chapter 5 firstly introduces and studies PE microfibre. The first observation during the mixing of PE microfibre reinforced sample was its poor workability against Co. The plunge in flow was higher with adding higher concentration of PE. In order to eliminate the effect of HWR on resultant drying shrinkage, addition of more HWR to mixes with high concentration of PE microfibre was out of question.

Drying shrinkage decreased in short term and long term studies in the mixes with PE microfibres comparing to Co, with the optimum concentration of 0.1% cement weight. The reduction was presumably due to the blockage of capillary voids in the cement paste matrix by PE microfibres, which results in moisture being trapped and cannot easily be lost. This idea comes from the hydrophobicity of PE microfibres, which suggests that if a microfibre is placed close to a chain of voids, those voids will be blocked and the moisture within the void cannot be released simply. The results of mass loss studies are also in full agreement with this hypothesis, as the addition of PE microfibre has reduced the amount of moisture lost from the samples.

However, the compressive strength was observed to slump in PE modified cement mortars. Thanks to hydrophobicity of PE microfibres, hydration rate might have been decreased for cement particles placed close to PE microfibres. On the other hand, less mass loss in PE modified mixes directly means higher water to cement ratio (w/c) in hardened state, which consequently results in compressive strength reduction. But in general, this result was in agreement with surveyed literature.

SEM as a part of microstructural analytical experiments could not provide much information as it was unsuccessful in finding a proper structure of a bunch of PE microfibres. In addition, fresh density and wet density (measured after 24 hours curing), were increased in PE microfibre reinforced cement mortars.

Additionally, as the shrinkage reduction of PE microfibre is expected to be a due to physical effect of them, an experiment with varying RH was carried out. Unlike the common experiments performed at 65%, the drying shrinkage was slightly higher than the drying shrinkage of Co, during the severe drying period. This observation might suggest that shrinkage reduction of PE microfibre might not be applicable in severe drying conditions. Therefore, micro-bridging has not been provided by PE microfibre and the reason behind its drying shrinkage reduction might be related to its hydrophobicity and its moisture retention characteristic.

Chapter 5 then continues with the introduction of a hybrid system of APP and PE microfibre when both added to cement mortars. The aim of this system was to enhance the workability and compressive strength of PE modified mixes by adding APP to its mixture.

An improvement in workability was seen in a mix with higher APP addition than PE addition. Even in the mix with 0.5% addition of APP and 0.5% of PE the flow was not significantly different from the flow of Co. On the other hand, 28-day drying shrinkage plunged by 17-23%, which does not suggest any improvement by using both shrinkage compensating agents together. The lack of synergy might be due to their different behaviour as far as moisture trapping in PE microfibre mixes and moisture release in APP modified mixes.

In terms of compressive strength, results clearly depict that APP addition could improve the strength in PE microfibre reinforced mortar. Whereas, in regards to mass loss, all mortar specimens illustrated higher rate of mass loss than Co sample. This can suggest the mechanism of APP is predominantly controlling the volume change of specimens.

This section concludes that PE0.1+APP0.5 and PE0.5+APP0.5 can be known as the optimum mixes regarding drying shrinkage and mechanical properties; however this introduced hybrid system did not enhance drying shrinkage reduction.

Finally, Chapter 5 introduces and studies wollastonite microfibre as a shrinkage compensating agent. Chapter 5 firstly reveals the lack of comprehensive examination on the effects of wollastonite in cementitious products. The surveyed literature review reports some positive effects of wollastonite addition on flexural strength of cementitious specimens. Nevertheless, volume change of the samples with wollastonite was not investigated against the volume change of conventional cementitious materials. Therefore, this section attempts to have a new study on ability of wollastonite to resist volume change in cement-based materials.

Wollastonite was treated and used as microfibre, added to sand part of the mix, and similar to PE microfibre, was expected to physically get involved in shrinkage compensating/reduction of cement mortars. All experiment used for PE microfibre were also used for wollastonite.

The first estimate of the wollastonite concentration was about 2-10% cement weight, based on literature survey and particularly observed enhancement in workability in this range; however, lower concentrations were also investigated.

Compressive strength was slightly improved in wollastonite modified mortar samples after 7, 28 and 180 days, comparing with Co mix.

Drying shrinkage study at constant RH revealed the volume change resistance capacity in wollastonite reinforced mixes, which is in agreement with its compressive strength enhancement. This resistance is expected to be due to micro-bridging of the microfibres which can initiate the resistance to unrestraint length change. Micro-bridging can also assist with holding all paste and aggregate particles together which can result in higher mechanical properties.

Similar to compressive strength results, Wo2.0 to Wo4.0 demonstrate the optimum range for drying shrinkage reduction in cement mortars.

Resistance to drying shrinkage in wollastonite mixes was also seen in the experiment carried out with varying RH. This experiment suggests the efficiency of wollastonite microfibre in shrinkage reduction of mortar samples even in harsh environments (high RH and low RH). However, the trend of shrinkage strain under varying RH was shown to be different from the shrinkage trend under constant RH.

In general, it can be concluded that although the drying shrinkage reduction of wollastonite is not significant, this reduction along with compressive strength enhancement reveals the effect of micro-bridging of wollastonite microfibres in cement pastes. Unlike PE microfibres, this micro-bridging phenomenon might have nothing to do with moisture retention, as the Wo samples had no or a very slight mass loss reduction effect.

Therefore, Chapters 4 and 5 introduced different shrinkage compensating agents from 2 different categories: 1- chemically active admixture, and 2: physically active microfibres. They all result in shrinkage reduction which was the main goal of this dissertation; however, with different mechanisms, as experimental results unveiled.

Chapter 6 reviewed several experiments for plastic shrinkage study and concluded that there is no standard test for plastic shrinkage measurement. Nevertheless, plastic cracking is mainly assessed in laboratory experimentations. Therefore, plastic cracking assessment was studied and reviewed. A simple experiment, which presents a large number of information, was chosen.

This experiment studied different angles of early age plastic shrinkage by the means of studying early age (after casting and for 24 h) plastic cracking. Addition of these additives could considerably decrease maximum crack width, number of cracks and crack area (% Co) in first 24 h of samples. In regards to cracking time, APP modified sample could resist longer time before cracking than Co, while PE microfibre modified sample and wollastonite modified sample did not show better cracking resistance time than Co. In addition, mixes modified by these admixtures ended up having less number of major cracks and smaller sizes of cracks than of them in control specimen.

A slab simulated mould with 3 stress risers could make samples crack after few hours and helped investigate the cracking resistance of mortars modified by additives. Being an economical test, it also results in a great number of information.

Eventually, the current research project was planned to be carried out studying engineering aspects of construction materials as well as the material science of them. Therefore, engineering aspects along with microstructural analysis were adopted. For further investigation, continuing the study of engineering aspects of this research using concrete specimens is recommended as the concrete is the main construction material. The future study can cover other mechanical properties of concrete, most importantly, creep behaviour of concrete using novel shrinkage compensating admixtures.

Appendix A Experimental Results

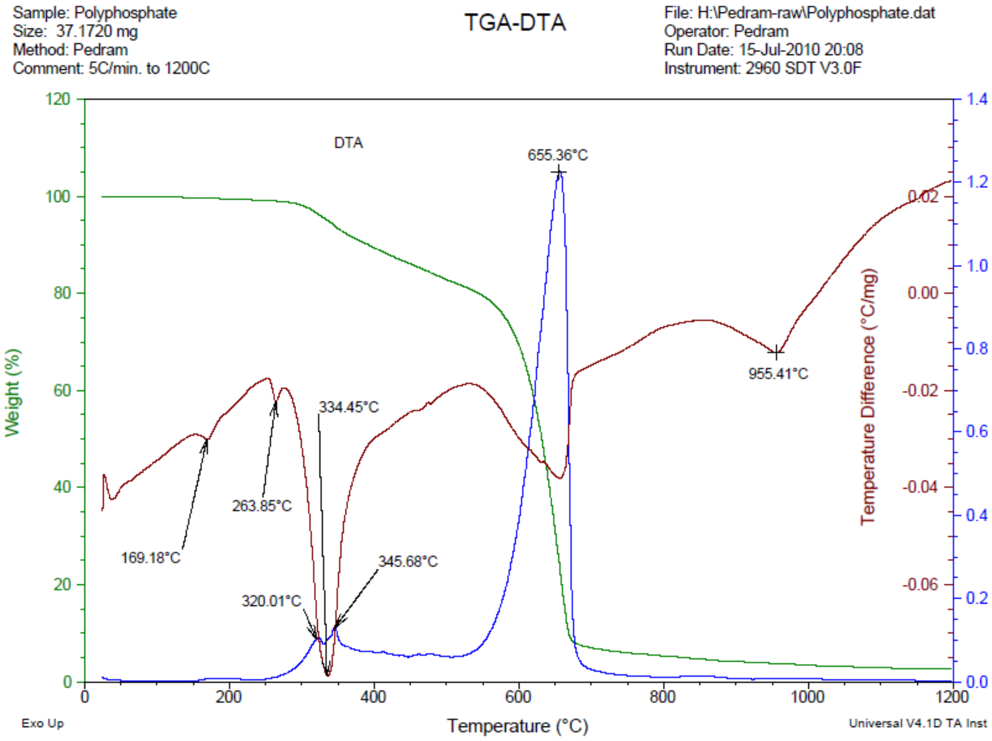


Figure A. 1. DTA of Ammonium polyphosphates (APP)

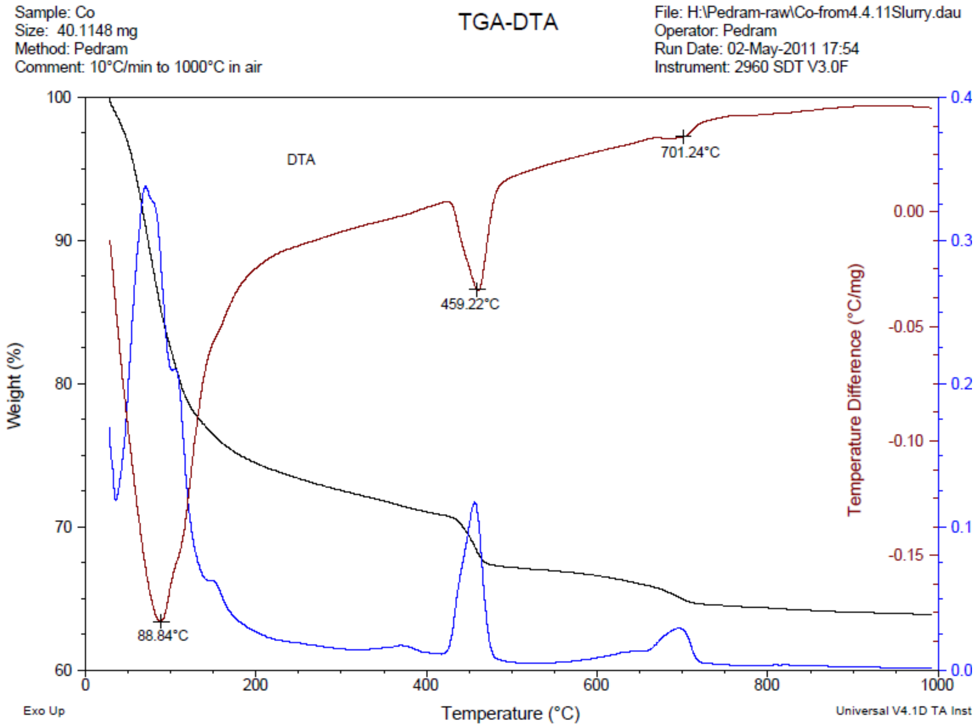


Figure A. 2. DTA of control slurry sample

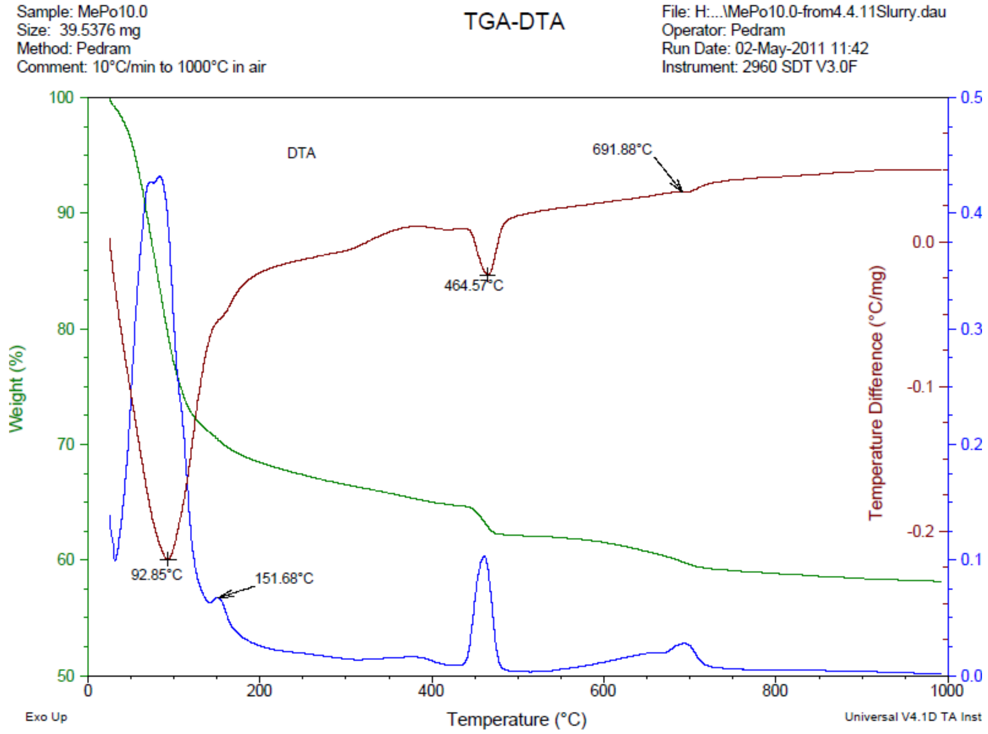


Figure A. 3. DTA of MePP10.0 slurry sample

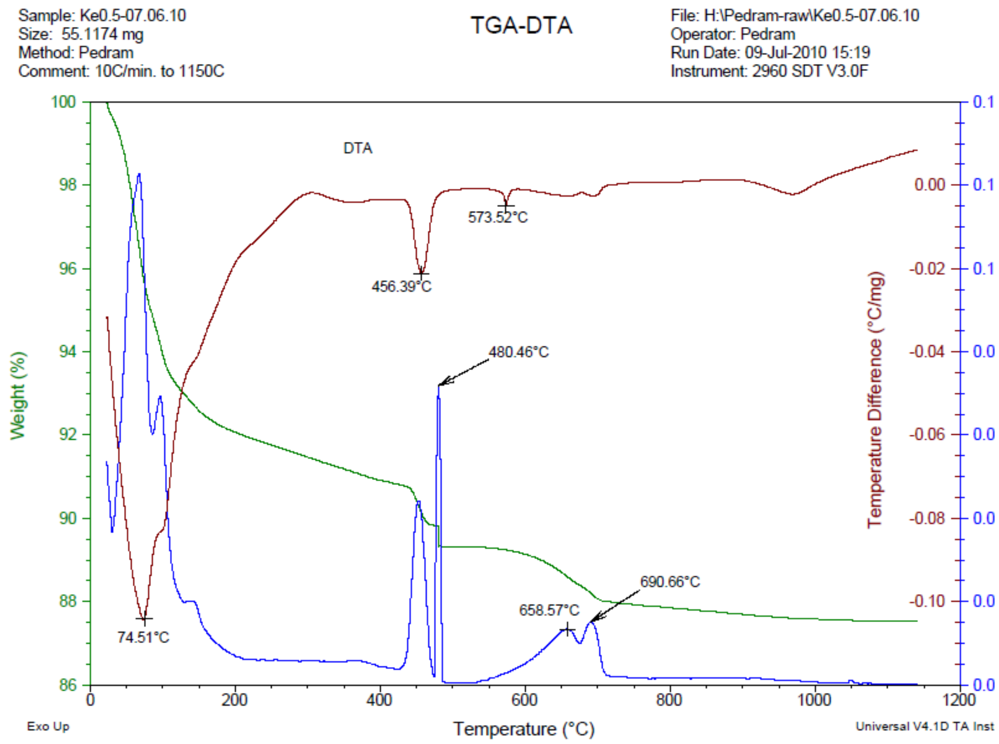


Figure A. 4. DTA of Ke0.5 slurry sample

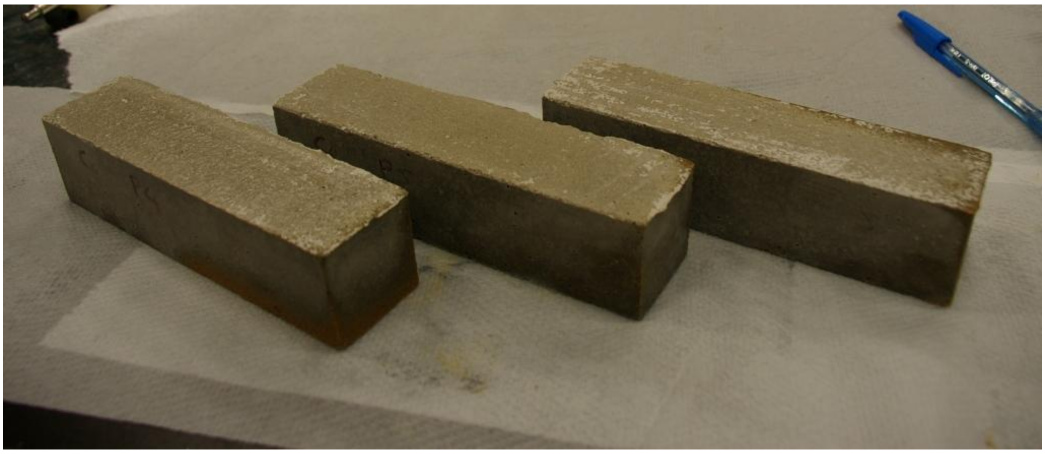


Figure A. 5. After exposure to sulphate solution (control specimens)

Figure A. 6. After exposure to sulphate solution (APP0.6 specimens)

Figure A. 7. Early age cracking of control sample after 24 hours

Figure A. 8. Early age cracking of APP0.6 sample after 24 hours

Figure A. 9. Early age cracking of PE0.6 sample after 24 hours

Figure A. 10. Early age cracking of Wo4.0 sample after 24 hours

Appendix B List of Publications

Author's publications submitted during the candidature of this thesis:

Hamedanimojarrad, P., G, Adam, A. S. Ray, K. Vessalas, P. S. Thomas and S. Nejadi (2010). " A Novel Multi-functional Expansive Additive for Drying Shrinkage Reduction in Mortars." Proceedings of the 21st Australasian Conference on the Mechanics of Structures and Materials, ACMSM 21, Victoria University, Australia.

Hamedanimojarrad, P., G. Adam, A. S. Ray, K. Vessalas and P. S. Thomas (2011). "Development of Shrinkage Resistant Cement-based Materials Using Fibres." Proceedings of the 6th th International Structural Engineering and Construction Conferenceand Conference, Zurich, Switzerland.

Hamedanimojarrad, P., A. Ray, G. Adam, P. S. Thomas and K. Vessalas (2011). "Evaluation of a Hybrid System of Admixture and Fibre for Development of Shrinkage Resistant Cement-based Material." Proceedings of the 9th Symposium on High Performance Concrete; Design, Verification & Utilization, Rotorua, New Zealand.

Hamedanimojarrad, P., G. Adam, A. S. Ray, P. S. Thomas and K. Vessalas (2012). "Development of Shrinkage Resistant Microfibre-Reinforced Cement-Based Composites." Central European Journal of Engineering 2(2): 289-295.

Hamedanimojarrad, P., N. L. Galea, A. S. Ray, G. Adam, K. Vessalas ans P. S. Thomas (2012). "New Mechanism for Drying Shrinkage Compensation in Cementitious Materials." Concrete in Australia 38(3): 33-38.

Galea, N. L., P. Hamedanimojarrad, K. Vessalas and P. S. Thomas (2012). –Assessment of Wollastonite Microfibre on Drying Shrinkage Behaviour of Cement-Based Composites." 22nd ACMSM; Materials to Structures: Advancement through Innovation, Sydney, Australia.

Hamedanimojarrad, P., G. Adam, A. S. Ray and P. S. Thomas (2012 – 2013). –Effects of Ammonium Polyphosphate on Drying Sshrinkage Characteristics of Cement-based Materials." Under Review in Journal of Materials and Structures.

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