Influence of PSMC and other mineral admixtures on the properties of cement mortar.

George Jianzhou. Xu
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INFLUENCE OF PSMC AND OTHER MINERAL ADMIXTURES
ON THE PROPERTIES OF CEMENT MORTAR

by

George Jianzhou Xu

A Dissertation
Submitted to the Faculty of Graduate Studies and Research
through the Engineering Materials Program in Department of Mechanical and Materials
Engineering in Partial Fulfillment of the Requirements for the
Degree of Doctor of Philosophy in Engineering Materials
at University of Windsor

Windsor, Ontario, Canada

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ABSTRACT

PSMC is a waste material produced from pyrolysis of Sheet Molding Compound. The material consists of 35% fibreglass, 55% CaCO₃ and 10% carbon. In this thesis, PSMC and seven other related materials have been investigated for their influences on the overall properties of cement mortar. The materials under investigation in addition to PSMC are the fibreglass part of PSMC (PG), the filler part of PSMC (C+Ca), the ground virgin fibreglass (RG), the virgin CaCO₃ powder, the pyrolysed automotive fluff (PAF). For comparison, one class-F fly ash (FA), and one condensed silica fume (CSF) were also tested. The mortar properties that were studied include workability, strength, drying shrinkage, alkali-silica reactivity, sulphate resistance, freezing-thawing expansion, salt scaling resistance, and wet-dry expansion. The pore structures were also studied using water absorption and water evaporation techniques.

It was found that PSMC increased the compressive strength, mitigated the ASR expansion and improved the sulphate resistance of cement mortar. All these improvements were largely due to the fibreglass content in the PSMC.

Ground fibreglass was found to be a very effective material to improve the properties of cement mortar. It increased the compressive strength, reduced long term drying shrinkage, mitigated the ASR expansion, improved sulphate resistance, decreased the freeze-thaw weight loss and greatly enhanced the salt scaling resistance of cement mortar. The influence of fly ash and condensed silica fume on the properties of cement mortar was found to be similar to that of ground fibreglass.
It was also found that the pore structure of cement mortars was greatly influenced by the mineral admixtures which possess pozzolanic properties. From a statistical analysis, it was concluded that the influence of mineral admixtures on the properties of cement mortar can be explained by their influence on three pore related factors. These factors are the porosity factor, the fine pore factor, and the permeability factor.
Dedicated to my dear wife Suolan and my children Alex, Nancy
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LIST OF ABBREVIATIONS

A = Al₂O₃
ACI = American Concrete Institute
ASR = Alkali Silica Reaction
C = CaO
CH = Ca(OH)₂
C-S-H = Calcium Silicate Hydrates
C₃S = 3CaO·SiO₂
C₂S = 2CaO·SiO₂
C₃A = 3CaO·Al₂O₃
C₆AF = 4CaO·Al₂O₃·Fe₂O₃
C₃AH₆ = 3CaO·Al₂O₃·6H₂O
C₄S₂H₃ = 2CaO·SiO₂·3H₂O
CSA = Canadian Standards Association
CSF = Condensed Silica Fume
EDS = Energy Dispersive Spectrum
F = Fe₂O₃
FA = Fly Ash
H = H₂O
hcp = hydrated cement paste
LOI = Loss on Ignition
M = MgO
NPC = Normal Portland Cement
PAF = Pyrolysed Automotive Fluff
PSMC = Pyrolysed Sheet Molding Compound
PG = Ground Fiberglass from PSMC
RG = Ground Virgin Fiberglass
RH = Relative Humidity
S = SiO₂
SEM = Scanning Electron Microscopy
SMC = Sheet Molding Compound
S = SO₃
SRPC = Sulphate Resistant Portland Cement
Chapter 1

INTRODUCTION

Sheet molding compound (SMC) is glass fibre reinforced, mineral filled, thermoset polymer which is produced in sheet form. Seventy million kilograms of this material were used in the automotive industry alone in North America in 1993. Steady growth in the use of this material in automotive applications is predicted for the future [1-1].

Despite the many advantages of SMC in automotive applications, such as weight reduction, energy/fuel savings, corrosion resistance, flexible formability, lower tooling costs, there is a problem with recycling. The material is traditionally considered non-recyclable. However, due to the efforts of the SMC Automotive Alliance, some potential methods for recycling have been developed[1-2]. Among these methods, a promising option is pyrolysis, where the material is heated to a high temperature in the absence of oxygen and is decomposed into pyro-gas, pyro-oil and residual ash. The gas and oil can be easily recycled for their energy content. The residual ash, which constitutes most of the waste, is left for further disposal. The author has previously investigated the feasibility of utilisation of this residual ash, referred to as PSMC (Pyrolysed Sheet Molding Compound), as an additive to concrete[1-3 to1-12]. It was found that the residual ash, after being finely ground, can not only strengthen concrete, but also inhibit chloride ion diffusivity in concrete[1-13]. The influence of PSMC on other properties of concrete is unknown, and the mechanism by which it influences the properties of concrete is not well-understood. To practically utilise PSMC in concrete, more research is needed.
PSMC consists of essentially 55% CaCO$_3$, 35% of E-glass and 10% of carbon. To study the influence of PSMC on the properties of concrete, it is helpful to know how the individual components of PSMC interact with concrete. However, in practice, it is very difficult to separate all the components of PSMC. It can be best separated into two parts, the fibreglass part (PG) which consists of mostly fibreglass and a small amount of CaCO$_3$ and carbon, and the filler part (C+Ca) which consists mostly of a mixture of carbon and CaCO$_3$ with a small amount of fibreglass. These two components were used as individual additives to concrete in this study. Ground virgin fibreglass and CaCO$_3$, which were originally used to make SMC, were also used as two additional individual additives.

In addition to PSMC, there is another waste material produced in much larger tonnage by the automotive industry called pyrolysed automotive fluff (PAF). This waste is generated by pyrolysis of automotive shredder fluff (also called automotive shredder residual -- ASR). The composition of PAF is complex and varies with different process methods and different sources. However, the major components of PAF are similar to those of PSMC. Finely ground PAF was also used as an individual additive in this study.

Fly ash (FA) and condensed silica fume (CSF) are two well-known mineral admixtures that have been successfully used in concrete for many years. For comparison purposes, these two admixtures were also used in this study.

In summary, eight materials were studied for their influence on the properties of cement mortar. They are PSMC, the fibreglass part of PSMC (PG), the filler part of PSMC (C+Ca), ground virgin fibreglass, virgin CaCO$_3$ powder, PAF, one class-F fly ash and one condensed silica fume. All of these materials will be referred as mineral admixtures in this thesis.
Concrete is the most widely used construction material in the world. Many waste by-products such as fly ash and condensed silica fume have been successfully utilised as mineral admixtures for concrete. There are many reasons for waste utilisation in concrete. These are: (1) economic considerations combined with an awareness of energy and resources conservation[1-14]; (2) ecological concerns about opening of new pits and quarries for the raw materials required for production of portland cement, and concerns about the means of disposal of the industrial waste[1-15]. In addition to the above mentioned reasons, there is another important purpose for adding waste materials to concrete. These materials impart to the concrete special properties that cannot be achieved by the use of portland cement alone. However, there are also problems associated with the use of waste materials in concrete. Despite the tremendous amount of work done in this area, there are still many controversial subjects and disagreement among researchers regarding how mineral admixtures influence the properties of concrete. There is a need for further study in order to fully understand the roles mineral admixtures play and to better utilise them in concrete.

There are two major objectives in this study. The first objective is to investigate the influence of PSMC, its components, and PAF on the properties of cement mortar. The properties studied include workability, strength, drying shrinkage, freezing-thawing durability, salt scaling resistance, alkali-silica reactivity, sulphate resistance and wet-dry durability. The influence on pore structure is also investigated by studying the adsorption, absorption, rate of evaporation and rate of absorption. The second objective is to explore the mechanisms by which these mineral admixtures influence the properties of cement mortar. Statistical techniques were applied to analyse the experimental data and to explain the mechanisms involved in the change of properties in mineral admixtures containing cement mortar.
Chapter 2

LITERATURE REVIEW

The author would like to state that the research on utilisation of PSMC and PAF in concrete is an original work in the field. The literature available for review on this subject exclusively results from the research by the author and co-workers[1-3 to 1-13]. There are other materials which are commonly used as mineral admixtures for concrete such as condensed silica fume and fly ash. For comparison purposes, a review of these latter materials will also be given in this dissertation. It is also assumed that some readers of this dissertation are not familiar with the field of concrete, therefore, a brief review on topics regarding cement chemistry, concrete microstructure, and concrete properties will also be given in this chapter. The purpose of the review on these subjects is to provide background information necessary to understand this thesis. Some of the reviews closely follow the books by Mehta[2-1], Neville[2-2], Lea[2-5] and Dodson[2-4].

2.1. Concrete

Concrete is a composite material made from cement, aggregate and water. When cement and water are mixed together, the mixture is called cement paste. When cement, sand and water are mixed together, the mixture is called cement mortar. When coarse aggregate is also used, the mixture is called concrete. Cement can react with water to form water-insoluble hydrates. In simple terms, these hydrates act as a glue to bind all the aggregate together to form concrete. To study the properties of cement mortar or concrete, it is very important to know the cement chemistry and the microstructure of hydrated cement paste.
2.2. Cement Chemistry

2.2.1. Cement Composition

"Hydraulic cements are defined as cements that not only harden by reacting with water but also form a water-resistant product."[2-1] The major constituents of cement are four compounds which are listed in Table 2.1.

<table>
<thead>
<tr>
<th>Name of compound</th>
<th>Oxide composition</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tricalcium silicate</td>
<td>3CaO·SiO₂</td>
<td>C₃S</td>
</tr>
<tr>
<td>Dicalcium silicate</td>
<td>2CaO·SiO₂</td>
<td>C₂S</td>
</tr>
<tr>
<td>Tricalcium aluminate</td>
<td>3CaO·Al₂O₃</td>
<td>C₃A</td>
</tr>
<tr>
<td>Tetracalcium aluminoferrite</td>
<td>4CaO·Al₂O₃·Fe₂O₃</td>
<td>C₄AF</td>
</tr>
</tbody>
</table>

There are five principal portland cements described in ASTM C 150 [2-3]. These are designated in the US. as type I, II, III, IV, and V. In Canada, they are referred to as type 10, 20, 30, 40, and 50 respectively. The five types of cement have certain behavioural characteristics which lend themselves to a variety of uses. The average chemical composition of the five types of portland cement, expressed in terms of their chemical phases is summarised in Table 2.2.

2.2.2. Hydration of Cement

Cement can react with water to form various hydrates that lead to the development of a structure which causes stiffening, hardening, and finally, strength. The
hydration of the silicate and aluminate phases of portland cement are briefly reviewed in the succeeding sections.

Table 2.2  Average Phase Composition of Portland Cement[2-4]

<table>
<thead>
<tr>
<th>Cement Type</th>
<th>Average Composition (％)</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C₃S</td>
<td>C₂S</td>
</tr>
<tr>
<td>I</td>
<td>55</td>
<td>20</td>
</tr>
<tr>
<td>II</td>
<td>45</td>
<td>30</td>
</tr>
<tr>
<td>III</td>
<td>65</td>
<td>10</td>
</tr>
<tr>
<td>IV</td>
<td>25</td>
<td>50</td>
</tr>
<tr>
<td>V</td>
<td>40</td>
<td>35</td>
</tr>
</tbody>
</table>

2.2.2.1 Hydration of Silicate Phases and the Importance of Ca(OH)₂.

According to Neville[2-2], the rates of hydration of C₃S and C₂S in a pure state differ considerably as shown in Figure 2.1. Hydration of C₃S in portland cement contributes mostly to the early strength of concrete while hydration of C₂S contributes mostly to the latter strength of concrete. If C₃S₂H₃ is considered as the final product of hydration of both C₃S and C₂S, then the reactions of hydration (not as exact stoichiometric equations) can be written as follows[2-2]:
For C₃S:

\[ 2\text{C}_3\text{S} + 6\text{H} \rightarrow \text{C}_3\text{S}_2\text{H}_3 + 3\text{Ca(OH)}_2 \]

The corresponding weights involved are:

\[ 100 + 24 \rightarrow 75 + 49 \]

For C₂S:

\[ 2\text{C}_2\text{S} + 4\text{H} \rightarrow \text{C}_3\text{S}_2\text{H}_3 + \text{Ca(OH)}_2 \]

The corresponding weights are:

\[ 100 + 21 \rightarrow 99 + 22 \]

Thus on a weight basis both silicates require approximately the same amount of water for their hydration, but C₃S produces more than twice as much Ca(OH)₂ as is formed by the hydration of C₂S.

However, if the product of hydration of C₃S is C₃S₂H₃, and that of C₂S is tobermorite (C₅S₆H₅), as suggested by Vance Dodson [2-4], then the quantities of calcium hydroxide produced by same amount of C₃S and C₂S are about the same. Although it is still uncertain what are the exact formulae of the hydration products of C₃S and C₂S, this is not critically important in considering that the products, whatever their true formulae might be, served just as the "glue" to hold the paste, mortar, and concrete
together. However, the quantities of calcium hydroxide produced by hydrating silicates are important in a number of ways. Firstly, \( \text{Ca(OH)}_2 \) can be leached out from concrete structures by alternate wetting and drying. This not only produces a white, unsightly surface stain in concrete referred to as "efflorescence", but also increases the porosity of the concrete structure. Secondly, calcium hydroxide that is not leached out will eventually react with the carbon dioxide in the permeating atmosphere and convert to calcium carbonate. This chemical conversion involves a decrease in the volume of the hardened mass and leads to what is often called "carbonation shrinkage". Thirdly, calcium hydroxide contributes no strength to the cementitious mass, and in the case of concrete can detract from its strength because it tends to deposit in the interfacial zone between the paste and the aggregate and weaken the bond between the two. Fourthly, \( \text{Ca(OH)}_2 \) can react with pozzolans (e.g. silica fume or fly ash) added into concrete to form secondary hydration products (C-S-H). The pozzolanic reaction between \( \text{Ca(OH)}_2 \) and mineral admixtures can positively influence many properties of the concrete. Fifthly, calcium hydroxide is a very important source of (OH\(^-\)) in the pore solution of concrete. The concentration of (OH\(^-\)) in pore solution is very important in controlling corrosion of the reinforcing steel in concrete.

2.2.2.2. Hydration of Aluminate Phases.

The reaction between pure \( \text{C}_3\text{A} \) and water is very violent and leads to immediate stiffening of the paste, known as flash set. The reaction can be written as: [2-2]

\[
\text{C}_3\text{A} + 6\text{H} \rightarrow \text{C}_3\text{AH}_6
\]

When gypsum (\( \text{CaSO}_4 \cdot \text{H}_2\text{O} \)) is added and interground with cement clinker, the reaction of the tricalcium aluminate (\( \text{C}_3\text{A} \)) phase of portland cement takes two steps:[2-4]
Step 1. C₃A first react with water and calcium sulphate forming a compound called ettringite - 3CaO·Al₂O₃·3CaSO₄·32H₂O (C₆A₆S₃H₃₂).

Step 2. The ettringite coating the underlying tricalcium aluminate then reacts with it and additional water to form a low sulphate ettringite - 3CaO·Al₂O₃·CaSO₄·12H₂O (C₃A₆S₃H₁₂).

The final form of calcium aluminate hydrate is probably the cubic crystal C₃AH₆.

Calcium aluminate hydrates contribute little or nothing to the strength of cement except at early ages. When hardened concrete is attacked by sulphate, the hydrates can react with sulphate to form expansive calcium sulphaaluminate and result in a disruption of the hardened paste.

2.3. Water in Concrete

Water, on one hand, is the primary agent to make concrete. On the other hand, water is also the liquid that can cause the destruction of concrete in many ways.

As reviewed in the previous section, cement reacts with water to form hydration products. Theoretically, the amount of water needed for full hydration of cement is about 23 per cent of the weight of anhydrous cement.[2-2]. This part of the water is called chemically combined water or sometimes non-evaporable water (the two are not exactly the same). In practice, much more water is added to cement so as to lubricate the particles and to make the mixture workable. Therefore, in addition to the non-evaporable water, there is extra water left in hardened cement paste. This extra water is sometimes
called evaporable water and it plays an important role affecting many properties of hardened concrete.

2.3.1. Classification of Water in Hydrated Cement Paste

Powers and Brownyard have classified the water in set cement into non-evaporable water (arbitrarily defined as that retained on drying to constant weight) and evaporable water, the latter is the difference between the former value and the amount held in the saturated surface-dry condition[2-5]. The non-evaporable water is usually considered as chemically combined water though the two are not exactly the same. There are different ways to further classify the evaporable water in hydrated cement paste (hcp). On the basis of the degree of difficulty or ease with which it can be removed from the hcp. Mehta[2-1] has classified the evaporable water into capillary water, adsorbed water and interlayer water. Since there is a continuous loss of water from a saturated cement paste as the relative humidity is reduced, the dividing line between the different states of water is not rigid. The following descriptions by Mehta define each type of water in hcp.

Capillary water. This is the water present in voids larger than about 5 nm. The capillary water can be further divided into two categories: (1) the water in large voids (> 50 nm), which may be considered as free water because most of the water in the voids is free of attraction from the pore surface and its removal does not cause any volume change. (2) water held by capillary tension in small capillaries (5 to 50 nm) which on removal may cause shrinkage of the system.

Adsorbed water. Water molecules can be physically adsorbed onto the surface of solids of hcp due to the surface energy of the solid and the hydrogen bond of water. It
has been suggested that up to six molecular layers of water (1.5 nm) can be physically held this way. The water held by the solid surface is referred to as adsorbed water. Removing of adsorbed water in hcp is more difficult than removing of free water, but when drying the hcp to 30% of relative humidity, a major portion of the adsorbed water can be removed. The loss of adsorbed water is mainly responsible for the shrinkage of the hcp on drying.

Interlayer water. This is the water associated with the C-S-H structure. It has been suggested that a mono-molecular water layer between the layers of C-S-H is strongly held by hydrogen bonding. The interlayer water is lost only on strong drying (i.e., below 11 percent relative humidity). The C-S-H structure shrinks considerably when the interlayer water is lost.

The non-evaporable water content in hcp increases progressively as hydration proceeds, but the evaporable water content decreases due to the decrease of porosity during hydration.

When the relative humidity is below 45%, the capillaries are empty and all evaporable water is held by gels as adsorbed water[2-5].

2.4. Voids in Hydrated Cement Paste

There are different classifications of the voids in hydrated cement paste (hcp) as shown in Figure 2.2. Generally, they can be classified into three types: air voids, capillary pores and gel pores. These voids have an important influence on the properties of hcp and consequently on the properties of concrete.
The ways in which Mehta defines the different types of void in hcp are summarised as follows[2-1]:

The first type of voids is air voids. There are two types of air voids in hcp, entrained air bubbles and entrapped air voids. To improve the frost resistance of concrete, entrained air bubbles are purposely introduced into concrete by using of air entraining admixtures. Entrained air voids usually range from 50 to 200 μm [2-1]. Air can also be entrapped in the fresh cement paste during the mixing operation. Entrapped air voids can be as large as 3 mm. Both entrapped and entrained air voids in the hcp are much bigger than the capillary pores. The presence of these voids can reduce the strength and increase the permeability of the concrete.

The second type of voids is capillary voids. Capillary voids represent the space not filled by the solid components of the hcp. The volume and size of capillary pores depend largely on the water to cement ratio of the paste and on the degree of cement hydration. In well hydrated, low water/cement ratio pastes, the size of capillary voids may range from 10 to 50 nm; in high water/cement ratio pastes, at early ages of hydration the capillary voids may be as large as 3 to 5 μm. Capillary voids larger that 50 nm are assumed to be detrimental to strength and impermeability, while voids smaller than 50 nm are assumed to be more important to drying shrinkage and creep.

The third type of voids in hydrated cement paste is the gel pores or the interlayer space in C-S-H. This is the intrinsic porosity associated with the hydrated cement paste and the voids may account for 28 percent of the volume of the solid C-S-H gels. The size of this space may vary from 0.5 to 2.5 nm. This size is too small to have an adverse effect on the strength and impermeability of the hcp.
2.5. Mineral Admixtures

"Mineral admixtures are finely divided siliceous materials which are added to concrete in relatively large amounts"[2-1]. The materials are also referred to as supplementary cementing materials or cementitious materials in some countries including Canada. Currently, there is no single terminology that has been agreed on or accepted on a world-wide basis. Neville[1-15] explained in one article the difficulties of classifying and categorising the different materials involved and proposed some new terminology for world-wide recognition. In this thesis, the term "mineral admixture" will be applied because the materials investigated in this study seems to be more close to the definition of "mineral admixture" than to "supplementary cementing material".

The most often used mineral admixture in the concrete industry is the pozzolan. A pozzolan is defined as "a siliceous or siliceous and aluminous material which in itself possesses little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperature to form compounds possessing cementitious properties."[2-6] The chemical reaction between a pozzolan and Ca(OH)\textsubscript{2} in presence of water is called pozzolanic reaction.

2.5.1. PSMC and PAF as Mineral Admixtures for Concrete

**PSMC (Pyrolysed Sheet Molding Compound).** Sheet molding compound is glass fibre reinforced, mineral filled thermoset plastic. This material has an increased application in automotive industry and appliance industry. Unfortunately, recycling of SMC is difficult. A proposed method for recycling of SMC is by pyrolysis[1-2][2-8].
Chopped pieces of the material are heated to high temperature in the absence of oxygen, transforming the material into pyro-gas, pyro-oil and solid residual. The pyro-gas and pyro-oil can be recycled for their energy content. The solid residual, which comprises about 80% of the mass of the original SMC and which consists of about 35% fibreglass, 55% calcium carbonate and 10% carbon, is left for further disposal. After being finely ground, the solid residual is referred to as PSMC. It has been found by the author that PSMC can increase the strength of cement mortar when used as sand and cement replacement[1-3], but the influence of PSMC on other properties of concrete is unknown. This will be evaluated in this study. A detailed review of the influence of PSMC on the strength of cement mortar will be given in Section 2.6.2.

**PAF (Pyrolysed Automotive Fluff).** This is another waste material generated from recycling used automobiles. In automotive shredder plants, the used automobiles are first disassembled to remove the reusable parts. Then, the whole car is crushed, chopped, and the metal pieces are separated. After passing through a hammer mill, the remainder, commonly called shredder fluff, can then be pyrolysed and transformed into pyro-gas, pyro-oil and residual ash. The oil and gas can be easily recycled for their energy content. The residual ash, that is, the pyrolysed automotive fluff (PAF), is left for further disposal. The composition of PAF is very complex due to the contamination and it varies widely from different sources. The major components of PAF are, however, similar to that of PSMC. PAF is a much more serious waste problem than PSMC because it is produced in very large tonnages.

PSMC and PAF are new waste materials which have not been investigated for possible utilisation in concrete except for the work done at the University of Windsor. However, the major components of PSMC and PAF, which are glass, calcium carbonate, and carbon are not new additives for concrete.
Fibreglass has a chemical composition similar to that of class-C fly ash (Table 2.3). After being finely ground, it is expected that ground fibreglass would be pozzolanic and could be possibly utilised in concrete. It was reported in 1970's that ground glass could be used as a pozzolan for concrete[2-9]. However, no literature on this topic has been found in recent years. On visiting the local municipal recycling centre, the author learned that there was a shortage of recyclable bottle glass, which is the only type collected at curbside in Windsor. Considering the cost of collecting, sorting and storing this type of waste glass, its use as a pozzolan for concrete is probably impractical.

Calcium carbonate, another major component of PSMC, is traditionally considered to be an inert filler for concrete. However, when finely ground, CaCO$_3$ is capable of influencing cement hydration both physically and chemically. In ASTM STP 1064 edited by Klieger and Hooton[2-10], eight papers specifically dealing with the topic of using calcium carbonate as an addition for cement were presented. There was evidence showing that CaCO$_3$ influenced the hydration of the aluminate phase of cement, increased the drying shrinkage of portland cement mortars and increased the "lubricity" of the paste. The influence on sulphate resistance was not significant and the effect on heat of hydration was not consistent. Ramachandran[2-11] found that the addition of CaCO$_3$ accelerated the hydration of the cement. This effect increased with the amount and fineness of the CaCO$_3$. There was evidence of incorporation of CaCO$_3$ into the C-S-H phase[2-12]. CaCO$_3$ also suppresses the formation of the cubic aluminate hydrate in the hydration of C$_3$A. It accelerates the formation of ettringite and its conversion to the monosulfoaluminate phase[2-13][2-14]. In France, CaCO$_3$ is widely used in cement by intergrinding limestone with the cement clinker[2-16]. The Canadian Standard (CSA
CAN3-A5. M83) allows the addition of up to 5% carbonate additions for Type 10 and Type 30 portland cements.

Table 2.3. Chemical Composition and Specific Gravity (S.G.) of Typical Cement, Fly Ash, Silica Fume, Blast Furnace Slag, and E-glass

<table>
<thead>
<tr>
<th>Chemical Component</th>
<th>Type I Cement</th>
<th>Class F Fly Ash</th>
<th>Class C Fly Ash</th>
<th>Silica Fume</th>
<th>Slag</th>
<th>E-glass</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>19.8</td>
<td>43.4</td>
<td>32.5</td>
<td>93.0</td>
<td>36.4</td>
<td>52.56</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>6.1</td>
<td>18.5</td>
<td>21.9</td>
<td>0.4</td>
<td>9.6</td>
<td>12-16</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>2.5</td>
<td>26.9</td>
<td>5.1</td>
<td>0.8</td>
<td>0.7</td>
<td>0-0.8</td>
</tr>
<tr>
<td>CaO</td>
<td>63.7</td>
<td>4.3</td>
<td>27.4</td>
<td>0.6</td>
<td>38.8</td>
<td>16-25</td>
</tr>
<tr>
<td>SO₃</td>
<td>2.2</td>
<td>1.2</td>
<td>2.8</td>
<td>0.3</td>
<td>1.2</td>
<td>-</td>
</tr>
<tr>
<td>MgO</td>
<td>3.5</td>
<td>0.9</td>
<td>4.8</td>
<td>0.6</td>
<td>10.4</td>
<td>0.5</td>
</tr>
<tr>
<td>Alkalies</td>
<td>0.9</td>
<td>0.6</td>
<td>1.1</td>
<td>0.96</td>
<td>0.6</td>
<td>0-2</td>
</tr>
<tr>
<td>LOI*</td>
<td>1.0</td>
<td>3.2</td>
<td>1.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>B₂O₅</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5-10</td>
</tr>
<tr>
<td>S.G.</td>
<td>3.1</td>
<td>2.4</td>
<td>2.6</td>
<td>2.2</td>
<td>2.9</td>
<td>2.55</td>
</tr>
</tbody>
</table>

* LOI is loss on ignition.

Carbon, another component of PSMC, is contained in many waste materials such as fly ash. Due to the very fine particle size and the surface sorptive properties, carbon particles tend to reduce the efficiency of air-entraining admixtures in concrete[2-17]. This raised a concern for the possible influence of fly ash on the freezing-thawing durability of concrete. In many countries, the carbon content in fly ash is limited by the standard specifications to values in the 5 to 12% range[2-18]. However, much research has found that high carbon content does not adversely affect the freezing and thawing resistance of concrete as long as adequate spacing factors are obtained. It was concluded
in a review paper by Berry and Malhotra [2-19] that "the primary effect of fly ash was upon air entrainment agent demand... For same air contents and equal strengths, there are no apparent differences in the freezing and thawing durability of fly-ash and non fly-ash concretes." A study by Hornain et al. [2-18] also indicates that the residual carbon content in fly ash has no detrimental influence on the microstructure and on the mechanical strength development.

2.5.2. Other Mineral Admixtures Commonly Used in Concrete

The most commonly used mineral admixtures in concrete are fly ash and condensed silica fume. For comparison purpose, a partial review of these materials will be given in this section.

**Fly Ash.** Coal is made up of a mixture of carbon, complex organic compounds and inorganic impurities such as clays, quartz, and feldspar. During the combustion of powdered coal in modern power plants, the carbon and organic parts of coal are burned off to generate energy. The mineral impurities in the coal are melted at the high temperature as it passes through the high-temperature zone in the furnace. The fused matter is quickly transported to lower-temperature zones, where it solidifies as spherical particles of glass and fly out as ash. This ash is subsequently collected by electrostatic precipitators and referred to as "fly ash". On the basis of the differences in mineralogical composition and properties, fly ashes can be divided into two categories which differ from each other mainly in calcium content. These are class F fly ash and class C fly ash. One of the major differences between the two types of fly ash is that class F fly ash contains less than 10 percent of analytical CaO while class C fly ash typically contains 15 to 35 percent analytical CaO[2-1]. The vast majority of fly ash used in concrete is class F fly ash which is generally a product of combustion of anthracite and bituminous
coals. In recent years, class C fly ash has come on the market in the United States and Canada[1-14]. This fly ash, produced by burning lignite or sub-bituminous coal, is not only pozzolanic but also cementitious.

**Condensed Silica Fume.** Condensed silica fume, is the by-product of the manufacture of elemental silicon and ferrosilicon alloys in an electric arc furnace. During the process, SiO$_2$ vapours are produced which condense in the low-temperature zone as tiny spherical particles consisting of non-crystalline silica. The silica fume is then collected by a sophisticated dust collecting apparatus from the furnace effluent gases. Condensed silica fume contains between 85 and 98 percent silicon dioxide and consists of extremely fine particles. The average diameter of condensed silica fume is of the order of 0.1 μm and surface area is in the range of 18,000 to 30,000 m$^2$/kg[2-7]. Compared to normal portland cement and typical fly ashes, condensed silica fume samples show particle size distributions that are two orders of magnitude finer. Compared to fly ash and blast furnace slag, condensed silica fume is a relatively new mineral admixture for concrete. However, during the past several years, the benefits of using of silica fume in concrete have been recognised with the result that its price has now escalated substantially. It was considered a waste material not long ago, but the current price of silica fume is one to three times that of the normal portland cement[1-14].

2.6. The Role of Mineral Admixtures on Concrete Properties

2.6.1. Workability

Workability is a general, descriptive term that indicates the effort needed to place, compact, finish and to provide a uniform material. Mehta[2-1] stated that workability is a composite property that contains at least two main components: (1) the consistency that
describes the ease of flow, and (2) the cohesiveness that is seen in the tendency to bleed or segregate.

Workability is one of the key properties that must be satisfied in order to make good concrete. However, due to the composite nature of the property, there is no single measure of it. The slump test is the most universally used test, but it measures only the consistency of concrete. Another laboratory test that gives an indication of the consistency of concrete and its proneness to segregation is called flow test. It is done by measuring the spread of a pile of concrete subjected to jolting. There are other test methods such as Vebe test and the compacting factor test. All these tests can supply some useful information about consistency and cohesiveness of the concrete mixture, but none of them is a direct measurement of workability.

2.6.1.1. Influence of Mineral Admixtures on the Workability of Concrete

The influence of mineral admixtures on workability of fresh concrete is apparent. They tend to affect both consistency and cohesiveness of the concrete.

The specific surface area of condensed silica fume is much larger than that of portland cement. Therefore, the addition of silica fume to concrete increases the water demand in order to maintain the same consistency. Carette et al. [2-20] have shown that the increase in water demand is almost directly proportional to the amount of silica fume added (Figure 2.3). Sellevold et al. [2-21] also showed the relationship between water demand and silica fume content for different cements in Figure 2.4. However, when water reducer or superplasticizer was used together with silica fume, the water demand of the concrete is not increased even at the high silica fume content (Figure 2.4). On the other hand, as stated by Khayat et al. [2-22] in a review paper, condensed silica fume
may not have a significant effect on the water demand of concrete if added to concrete in a small amount (less than 5%).

It has also been reported that silica fume reduced bleeding and segregation of concrete, and consequently, increased the cohesiveness of the concrete[2-21][2-22][2-23][2-24]. The influence of silica fume on bleeding rate of concrete is shown in Figure 2.5[2-7].

Unlike silica fume, the addition of fly ash to concrete generally decreases the water requirement to maintain the same workability as non-fly ash concrete. In the review papers by Malhotra[2-25][2-19], many publications were cited showing the results of water reduction in fly ash concrete. For example, Compton and MacInnis[2-26] reported a 7% water reduction of a concrete made by substituting 30% of cement with an eastern Canadian fly ash while maintaining the same slump as the control concrete. However, there were also cases in which fly ash was found to increase the water demand to maintain the desired slump [2-27][2-28].

2.6.2. Compressive Strength of Concrete

Compressive strength is the most important property of concrete because it is the property generally specified by designers and quality control engineers. On the other hand, strength is related to many other properties of concrete such as density, durability, impermeability, resistance to sulphates, resistance to impact, and resistance to abrasion.

Concrete can be considered as a composite material which consists of two phases: the cement paste and aggregate. The compressive strength of concrete is therefore governed by the strength of the two phases and also by the strength of the
interfaces between them. Once an aggregate is selected for construction, one can do little about its strength. However, there are many things designers can do to improve the strength of cement paste and the strength of the interfacial zone.

For cement paste, there exists a fundamental inverse relationship between porosity and strength. The relationship can be described by the expression[2-1]:

\[ S = S_0 e^{-kp} \quad \text{Eq. 2.1} \]

where \( S \) is the strength of the material which has a given porosity \( p \); \( S_0 \) is the intrinsic strength at zero porosity; and \( k \) is a constant. For hardened cement paste or mortar the porosity can be related to strength, but for concrete, the situation is more complicated due to the presence of the interfacial zone. The transition zone between cement paste and coarse aggregate is usually more porous than cement paste. This transition zone is the major site of micro cracks in concrete.

There are many factors which influence the strength of concrete, but the water/cement ratio is the most important factor because it affects the porosity of both the cement paste and the transition zone between the paste and the coarse aggregate.

2.6.2.1. Influence of PSMC, Fly Ash and Condensed Silica Fume on the Compressive Strength of Cement Mortar

The author has previously studied the influence of PSMC, fly ash and condensed silica fume on compressive strength of cement mortar[1-3]. The mineral admixtures have been used in four different ways: (1) as a partial sand replacement, (2) as a partial cement replacement, (3) as a partial replacement for both sand and cement (for PSMC
only), (4) as a direct addition to mortar (for PSMC only). Some of the mix proportions used are given in Table 2.4.

Table 2.4. Sample proportions for testing the influence of PSMC on the strength of cement mortar

<table>
<thead>
<tr>
<th>Test Group</th>
<th>Cement %</th>
<th>Sand %</th>
<th>Water %</th>
<th>Mortar %</th>
<th>Admixtures %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Partial sand replacement</td>
<td>30</td>
<td>55</td>
<td>15</td>
<td></td>
<td>(Control)</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>50</td>
<td>15</td>
<td></td>
<td>5 PSMC</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>50</td>
<td>15</td>
<td></td>
<td>5 CSF</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>50</td>
<td>15</td>
<td></td>
<td>5 FA</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>50</td>
<td>15</td>
<td></td>
<td>5 SMC</td>
</tr>
<tr>
<td>Partial cement replacement</td>
<td>30</td>
<td>55</td>
<td>15</td>
<td></td>
<td>(Control)</td>
</tr>
<tr>
<td></td>
<td>27</td>
<td>55</td>
<td>15</td>
<td></td>
<td>3 PSMC</td>
</tr>
<tr>
<td></td>
<td>27</td>
<td>55</td>
<td>15</td>
<td></td>
<td>3 CSF</td>
</tr>
<tr>
<td></td>
<td>27</td>
<td>55</td>
<td>15</td>
<td></td>
<td>3 FA</td>
</tr>
<tr>
<td>Replace both cement and sand</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(PSMC)</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>55</td>
<td>15</td>
<td></td>
<td>0</td>
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<td>25</td>
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<td>15</td>
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<td></td>
<td>20</td>
<td>45</td>
<td>15</td>
<td></td>
<td>20</td>
</tr>
<tr>
<td>Direct addition to mortar</td>
<td></td>
<td></td>
<td>2.6*</td>
<td>100</td>
<td>(PSMC)</td>
</tr>
<tr>
<td>(Type 30 cement)</td>
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<td></td>
<td>6.3*</td>
<td>100</td>
<td>0</td>
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<tr>
<td>Direct addition to mortar</td>
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<td></td>
<td></td>
<td>100</td>
<td>(PSMC)</td>
</tr>
<tr>
<td>(Type 10 cement)</td>
<td></td>
<td></td>
<td>3.5*</td>
<td>100</td>
<td>0</td>
</tr>
</tbody>
</table>

Note: * Amount of extra water added to adjust the workability of cement mortar.

It can be seen in Figure 2.6 that when used as 10% sand replacement, PSMC, CSF, and FA all increased the mortar strength at both 7 and 28 days. The strengthening
effects of each of these three admixtures are similar. However, when used as a 10% cement replacement (Figure 2.7), only CSF samples showed increased strength at 28 days. The strength of PSMC and FA samples are lower than that of control mortar. It was also observed that PSMC samples gained 92% of the control samples strength at 28 days which was proportionately higher than at the 7 days age (89%). This implies that the strength loss at early ages due to a reduction in cement content may be compensated for by PSMC at later ages when a substantial part of the pozzolanic reaction is expected to take place. This effect is similar to that of fly ash which, when used as partial cement replacement on a one for one basis, generally reduced the strength of concrete at early ages up to three months and develops higher strength beyond six months. The general form of strength development of fly ash concrete is shown graphically in Figure 2.8[2-25].

PSMC was also investigated as a partial replacement for both cement and sand. An optimisation search method was applied which is illustrated in Figure 2.9. This figure is a ternary diagram, the circles represent different compositions for different strength levels, and the circle on the cement-sand border represents the standard mortar composition. The arrow labelled sand indicated that PSMC is replacing sand; strength increases in this direction. The arrow labelled cement leads to a decrease in strength, but also a potential decrease in cost since PSMC should be less expensive than cement.

The experimental data given in Figure 2.10(a) are 7 day strengths, Figure 2.10(b) are 28 day strengths and Figure 5.7(c) are 100 day strengths. It can be seen in the first two figures that the strength increases with sand replacement but decreases with cement replacement. An interesting finding was that the strength value in point 7 is always higher than that at point 0. At point 7, about 17% of the cement was replaced by PSMC as compared with point 0. Moreover, after 28 days ageing, even the strength at point 8 is
higher than that of point 0. At point 8, about 33% of the cement has been replaced by PSMC. At the age of 100 days the strength at every point is higher than at point 0. The results imply that stronger concrete can be made with PSMC even at early ages.

PSMC was also investigated as a direct addition to cement mortar. In the experimental program, three mix proportions were studied which used 5, 15 and 25% PSMC as a direct addition to the control mortar respectively. Extra water was added to adjust the workability for samples with 15% and 25% PSMC. The results as shown in Figure 2.11 indicated that the strength of mortar samples was influenced by both the PSMC content and the water to cement ratio. It seems that 10% PSMC is the proportion which will give the higher strength while not requiring much extra water to maintain the desired workability.

Fly ash can also be used as a direct addition to concrete without reducing the amount of cement. In this case, fly ash has been found to increase the strength of concrete at all ages due to the increase in total cementitious content of the concrete.

Condensed silica fume can be used in concrete either as a partial cement replacement or as an additive. The strength development of silica fume concrete in both cases is shown in Figure 2.12[2-20] and Figure 2.13[2-30]. It can be seen that when silica fume was used as an additive, the compressive strength of the resulting concrete is higher than the control concrete at all ages. When used as a partial cement replacement, the strength of silica fume concrete is similar to the control at the early ages (1 and 3 days), and is higher at the ages of 7 and 28 days.

Hooton[2-31] studied the compressive strength of concrete with 10%, 15%, and 20% of cement replaced by silica fume. It was found that the strength of silica fume
concrete is higher than that of control mixes even at the 1-day age. At the age of 7 days, the compressive strength of all silica fume mixes was 34 to 57% higher than that of the control, with higher increases as the silica fume contents were increased. However, at the age of 56 days, the silica fume concretes stopped developing strength possibly due to the self-desiccation effects.

It is widely agreed that using silica fume can increase the strength of concrete significantly, but the mechanisms by which this improvement is achieved are still controversial. The proposed mechanisms include: (1) condensed silica fume reduces the total porosity of concrete and densifies the cement paste matrix; (2) condensed silica fume refines the interfacial zone of concrete, thereby improving the bonding between aggregate and cement paste; (3) condensed silica fume can densify the cement paste matrix, refine the interfacial zone, provide more effective packing of the solid phase, and reduce the Ca(OH)_2 content. The improvement on strength is due to the combination of all these effects.

Detwiler et al. [2-32] studied the chemical and physical effects of silica fume on the mechanical behaviour of concrete. They concluded that at early ages up to 7 days, the effect of silica fume on the strength of concrete was primarily a physical pore filling effect. Strength improvement by pozzolanic reaction took place between the ages of 7 and 28 days. Mehta[2-33] found that the strength of concrete is inversely correlated with the volume of large voids (>100 nm) but not the total porosity of the hydrated cement paste. The addition of pozzolanic materials to concrete causes pore refinement, that is, replaces large pores with many small ones[2-34][2-35]. The pore refinement effect by mineral admixtures can lead to strength improvement. Cong et al.[2-36] studied the compressive strength of cement paste, mortar and concrete with silica fume. It was concluded that concrete containing silica fume as a partial replacement for cement
exhibits an increased compressive strength in large part due to the improved strength of its cement paste constituent. However, Rosenberg and Gaidis[2-37] showed theoretically and experimentally that condensed silica fume does not densify the hardened cement paste. They believed that the improvement on concrete strength by silica fume is mainly due to the enhanced bonding between paste and aggregates which is generally the weakest part of concrete. Goldman and Bentur[2-38], Cohen et al.[2-39], Huang et al. [41] also found evidences to support the mechanism of interfacial zone refinement by silica fume.

2.6.3. Absorption and Permeability

2.6.3.1. Definitions

The word absorption, as it is to be used in the present context, actually means absorption capacity, and it is the water required to bring an oven dried sample to a saturated surface dry condition. This value is closely related to the volume of permeable pores in porous materials. The absorption is usually determined by drying the samples to constant weight, then immersing them in water and measuring the weight increase. There are several methods to dry a sample to constant weight: (1) Drying samples in an oven at a temperature of 100 to 110 °C, but this temperature sometimes is considered too high because some combined water can be lost at this temperature[2-5]. (2) Drying samples at a medium high temperature such as 50 or 65 °C, but the time required for drying is much longer[2-5]. (3) Drying at ordinary temperatures over sulphuric acid will result in a smaller loss of water during drying, consequently a smaller absorption on subsequent immersion in water[2-5]. (4) Drying at low temperature using a procedure is known as "D-drying"[2-16]. In this method, the sample is equilibrated under vacuum at -79 °C by continuous evacuation with a rotary pump through a trap cooled in a mixture of solid
CO₂ and ethanol. In the immersion cycle, the penetration of water into the specimen may be assisted by boiling, or by evacuating it before flooding with water.

According to Mehta [2-1], "permeability is defined as the property that governs the rate of flow of a fluid (usually water) into a porous solid. For steady-state flow, the coefficient of permeability (κ) is determined from Darcy's expression:

\[
\frac{dq}{dt} = k \frac{dH \Delta A}{L \eta} \quad Eq. 2.2
\]

where \( dq/dt \) is the rate of fluid flow, \( \eta \) the viscosity of the fluid, \( dH \) the pressure gradient, \( A \) the surface area, and \( L \) the thickness of the solid."

Since permeability determines the relative ease with which water (or other fluids) can move into concrete[2-2], it is therefore an important property with regard to the durability of concrete. For sulphate attack, concrete with low permeability will restrict the movement of sulphate ions into concrete and prevent adverse chemical reactions. Permeability is also important to frost resistance of concrete because it influences the flow of water within concrete due to formation of ice and osmosis. Permeability is critical to alkali-aggregate reaction because it controls the movement of alkali ions and water which are necessary for the reactions and for producing swelling gels. Permeability is also related to fire resistance and steel corrosion resistance.

2.6.3.2. Influence of Mineral Admixtures on Pore Structure and Permeability of Concrete

The influence of mineral admixtures on porosity and on the pore size distribution of hydrated cement paste is a topic of controversy. One reason is that the pore structure of blended cement paste is very complicated. Another is that there is no adequate test method available for this purpose. The results from mercury porosimetry method were
found to be not accurate owing to structural damage that occurs at high intrusion pressures during measurement[2-40][2-41][2-42][2-43]. Day[2-42] studied the alternative methods for measuring the porosity in blended cement pastes including evaporable water content, resaturation porosity, solvent exchange porosity, mercury porosity, and nitrogen sorption. Each of these methods give a partial view of the pore structure of the materials examined, but they all have obvious limitations for testing blended cement paste.

There are published data which show that mineral admixtures reduced total porosity and refined the pore structure of hardened cement paste[2-31][2-34][2-45]. In contradiction to this, other researchers observed that using mineral admixtures did not result in the reduction in the total porosity[2-37][2-46]. This controversy is further complicated from Feldman's results[2-44][2-7]. For the W/(C+SF) = 0.25 mixes, Feldman found that the total porosity of cement paste with 0, 10, and 30% of silica fume are 16.8, 14.43, and 10.08% respectively at 180 days. However, for W/(C+SF) = 0.45 mixes, total porosities of 28.3, 29.8, and 25.3 were observed for 0, 10, and 30% silica fume content at 180 days. In addition, the influence of silica fume on pore structure of paste and mortar is different. The addition of silica fume increases the threshold diameter for mortars but in pastes there is a decrease. The spread of pore volume in the higher pore range was also much greater for mortar than for paste[2-7][2-41][2-44]. Clearly there is no simple answer on how mineral admixtures influence the total porosity of hardened cement paste. It depends on the type of materials used, its content level, age of curing, water cement ratio, and the test method. Figure 2.14 to Figure 2.18 are some results reported by different authors.

The influence of mineral admixtures on permeability of concrete is significant. Several researchers have found that mineral admixtures greatly reduce the permeability
of hydrated cement paste[2-31][2-47][2-48]. Sheetz et al.[2-49], Mehta and Gjov[2-50], and Delage and Aitcin[2-51] also observed that mortars and concretes incorporating silica fume are less permeable. It has been shown that this is due to a decrease in the number of coarse pores of the cement-silica fume paste system, although the total porosity remains nearly the same as neat cement paste. It was also found[2-34] that a paste containing fly ash showed lower permeability even though the porosity and coarser pore content is higher (Figure 2-14). Rosenberg et al. [2-37] also showed experimentally and theoretically that using silica fume does not reduce the porosity but does reduce the permeability of concrete. Hooton[2-31] found that silica fume reduced the total porosity, but he also points out that total porosity is not a good indicator of permeability.

2.6.4. Drying Shrinkage

2.6.4.1. Definitions

When the relative humidity is below 100 %, water in hydrated cement paste begins to escape. Withdrawal of water from hydrated cement paste cause shrinkage. The change in volume of drying hcp is not equal to the volume of water removed. As reviewed in section 2.3, the free water in hcp is held mostly in large cavities (e.g., > 50 nm). Removal of this free water does not cause shrinkage because the free water is not attached to the structure of the hydration products by any physical-chemical bonds. After most of the free water has been lost, then the adsorbed water and the water held in small capillaries will be removed on continued drying. Removing of adsorbed water results in considerable shrinkage.

It has been suggested by Taylor that drying shrinkage is related to the following effects[2-16]: (1) Capillary stress, "Attractive forces exist between the water in a pore
and the solid surfaces; when the liquid evaporates, the tension in the meniscus is transferred to the walls, and the pore tends to shrink... This effect could be important between about 90% and 45% RH. Above 90% it is unlikely to be important because the pores that are being emptied are wide, and the resulting stresses are small, and below about 45%, a stable meniscus cannot form.” (2) Surface free energy. “Due to unsatisfied bonding forces, the surface of a solid particle is under tension, as in a liquid. Adsorbed molecules decreased this tension, and if they are removed, the particle tends to contract... This effect is the greatest when the relative humidity is below about 20%.” (3) Disjoining pressure, attractive forces between two solid surfaces are outweighed by the water molecules between them. This is called a disjoining pressure. The removal of the adsorbed water reduces the disjoining pressure and brings about shrinkage of the system.

2.6.4.2. Influence of Mineral Admixtures on the Drying Shrinkage of Concrete

The influence of mineral admixtures on the drying shrinkage of concrete is also a matter of controversy. According to Mehta’s theory[2-1], the drying shrinkage in concrete is directly associated with water held by small pores in the range 3 to 20 nm. Concretes containing admixtures capable of pore refinement usually show higher drying shrinkage. Pozzolans such as condensed silica fume, fly ash and slag tend to increase the volume of fine pores in the cement hydration product, and therefore may increase the drying shrinkage of concrete. However, Dodson has given a different explanation[2-4]: "The W/C ratio in pozzolanic concretes is generally higher than that of plain concretes in order to attain the desired slump. A good part of that water is prevented by the pozzolanic reaction products from escaping during the course of drying. This results in the creation of fewer empty voids in the concrete which would otherwise be responsible for a good portion of concrete shrinkage.” Based on this explanation, it is believed that pozzolans will reduce the shrinkage of concrete.
In reality, there are sufficient published data supporting both arguments. Rosenberg et al.[2-37] studied the drying shrinkage of two concrete mixes with different cement content and different water cement ratio. It was found that with the addition of silica fume, the drying shrinkage of the concrete is generally reduced (Figure 2.19). Dodson[2-4] evaluated about fifty different pozzolans with respect to their influence on the shrinkage of concrete. The pozzolans were used as 20% (volume) replacement for cement. It was found that the reduction in shrinkage resulting from the use of the pozzolans was to be in the range of 14% to 18%. Mather[2-52] also has data showing that the shrinkage of concrete may be reduced by as much as 25% through the use of pozzolans. Yuan and Cook[2-53] concluded that the replacement of cement by fly ash reduced the drying shrinkage, but the influence is not considered significant (Figure 2.20). Feldman and Huang[2-44] investigated the drying shrinkage of cement paste containing 0, 10 and 30% of silica fume. It was found that at a lower W/C+SF ratio (0.25), no significant difference was observed. At higher W/C+SF ratio (0.45), samples with 30% silica fume showed significantly higher shrinkage than the control mix. Their results are shown in Figure 2.21. Takagi et al.[2-54] studied mortars with W/(C+SF) of 0.55 and sand/cement ratio of 2. Superplasticizer was added to maintain a constant flow. Their results showed a clear increase in drying shrinkage with silica fume content (Figure 2.22). Hooton[2-31] studied the drying shrinkage of four concrete mixes with 0, 10, 15, and 20% of silica fume (as cement replacement). He observed that the differences in shrinkage are minor up to 16 weeks of drying, but at 32 to 64 weeks, all of the silica fume concrete exhibited 10 to 22 percent higher shrinkage than the control concrete. Johansen[55] performed shrinkage measurements on concrete prisms with silica fume content ranging from 0 to 25% and W/(C+SF) ratios from 0.37 to 1.06. It was concluded that for concrete with W/(C+SF) < 0.6, no significant differences in shrinkage existed between the control concrete and condensed silica fume concrete containing up to 10%
silica fume. Concrete containing 25% silica fume with no water reducer showed higher drying shrinkage. Carette and Malhotra[2-20][2-56] have data which indicate that the drying shrinkage of concrete with silica fume is generally comparable to that of control concrete (Figure 2.23)

Despite the controversy from reported data, a report by ACI committee 226[2-24] concluded that the drying shrinkage of silica-fume concrete (after 28 days of moist curing) is generally comparable to that of the control concrete regardless of the water to cementitious materials ratio. Berry and Malhotra[2-19] also stated in a review paper that the use of fly ash in practicable proportions does not significantly influence the drying shrinkage of concrete.

2.6.5. Durability Against Sulphate Attack

Sulphate ions from an outside source can attack concrete by reaction with some of the cement hydrates. As the results, gypsum and calcium sulphaoluminate are formed which have a considerable greater volume than the compounds they replace. This leads to expansion and disruption of the concrete.

2.6.5.1. Chemical Reactions Involved in Sulphate Attack

The sulphate reaction is known to take two forms: (1) sulphate ions react with calcium hydroxide to form gypsum; (2) sulphate ions react with calcium aluminate hydrates to form calcium sulphaoluminate (ettringite). The chemical reaction involved can be written as follows:
(1) Gypsum formation[2-1]:

\[
Na_2SO_4 + Ca(OH)_2 + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O + 2NaOH
\]

(2) Ettringite formation[2-2]:

\[
2(3CaO \cdot Al_2O_3 \cdot 12H_2O + 3(Na_2SO_4 \cdot 10H_2O) \rightarrow 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O + 2Al(OH)_3 + 6NaOH + 17H_2O
\]

2.6.5.2. Testing of Sulphate Resistance

Testing concrete for sulphate resistance can be done in the laboratory by storing the samples in a solution of sodium sulphate or magnesium sulphate. The effect of the exposure can be estimated by the following methods: (1) test the change in strength; (2) test the change in the dynamic modulus of elasticity; (3) measure the expansion of the samples; (4) measure the weight loss; (5) visual assessment.

2.6.5.3. Influence of Mineral Admixtures on Sulphate Resistance

Hooton[2-31] studied the influence of silica fume on the sulphate resistance of cement mortar using the ASTM C 1012 mortar bar expansion method. In that study, silica fume was used to replace 0, 10, and 20% by mass of the normal portland cement (C_3A content was 10.7% ). The W/C ratio was 0.485 for all three mixes and a superplasticizer was used to maintain a constant flow of 110 ± 5. For comparison, a sulphate resistance portland cement (SRPC) mix was cast at W/C ratio of 0.465. One more 10% SF mix was made by adjusting the W/C ratio to 0.535 without using any superplasticizer. All the mortar bars were immersed in a 5 percent Na_2SO_4 solution
when the strengths were about 21 MPa. Expansions of the mortar bars were monitored for up to 1 year. The results are shown in Figure 2.24. It is clearly shown in the figure that with partial replacement of NPC by silica fume, the sulphate resistance of cement mortars was greatly improved. The performance of SF mortars was even better than mortar made with SRPC.

The sulphate resistance of condensed silica fume mortars was also studied by Mather[2-57]. In this study, three cements containing 14.6, 13.1, and 9.4 % C₃A were used. In the experimental design, 30% of the cement was replaced by the same amount of silica fume. The water/cement ratio was 0.485 and sand to cement ratio was 2.75. These mortar bars were immersed in 4% Na₂SO₄ solution for 1 year and the expansions were found to be not significant.

There is one report in which silica fume concrete has been exposed to a real life condition for over 26 years[2-58]. This concrete contains a 15% of silica fume as replacement of normal portland cement. The concrete has shown similar performance to concrete made from sulphate resistant portland cement. The water at the test site contained up to 6 grams of sulphate ion per liter and had a pH of 3.

Dikeou[2-59] studied twelve low calcium fly ashes for their influence on the sulphate resistance of concrete. It was concluded from this research that all of the fly ashes tested greatly improved sulphate resistance of concrete. Part of the data is shown in Figure 2.25. There are also data which showed that replacement of cement with some class-C fly ash can reduce the sulphate resistance of concrete[2-60][2-61]. However, it is general believed that mineral admixtures enhance sulphate resistance and the mechanisms by which mineral admixtures improve sulphate resistance of concrete are: (1) reduction in free lime and reactive alumina due to pozzolanic reaction; (2) reduction
in permeability as a result of pore refinement associated with the pozzolanic reaction; and (3) dilution of the C₃A content of the portland cement[2-7][2-62][2-63].

2.6.6. Alkali-Silica Reaction in Concrete

2.6.6.1. Definition

The hydration of a Portland cement results in a pore solution containing calcium, sodium and potassium hydroxides. Most of the calcium hydroxide produced during hydration is present as a crystalline hydroxide but most of the metal hydroxides are present in the pore solution. If the aggregate used in concrete contains a considerable amount of amorphous silica(te), reaction between the reactive silica(te) and hydroxide will take place. As a result, alkali-silica gel will be produced this can cause the concrete to expand and finally crack. The reaction, known as alkali-silica reaction(ASR), was first recognised as a problem in North America in 1940, in Denmark in the early 1950s, in West Germany in the early 1960s, in the UK in the mid-1970s and in Japan in the early 1980s[2-64].

2.6.6.2. Mechanism of ASR Expansion.

Despite the large amount of work devoted to the study of alkali-silica reactions, the mechanism of the reaction is not well understood. One theory explains the ASR as follows: (1) OH⁻ attacks the reactive aggregate and provokes its dissolution, (2) dissolved silica(te) reacts with alkalis (Na⁺ or K⁺) to form alkali-silica gels, (3a) expansion of concrete is due to the osmotic pressure generated by alkali silica(te) gels which are confined within a semi-permeable membrane of cement paste[2-65]; (3b) the expansion
is a consequence of the formation and subsequent widening of cracks due to mechanical pressure exerted by the reaction products[2-66][2-67]; (3c) the expansion of concrete depends on the type of reaction products, i.e. swelling alkali-silica gel or non-swelling lime-alkali-silica gel. Expansion will occur only when the swelling alkali-silica gel is formed. The Ca\(^{++}\) ion concentration in concrete controls the formation of the type of reaction products[2-68][2-69].

A different theory has been proposed by Chatterji[2-70], the main points of which are delineated as follows: (1) During the reaction, OH\(^{-}\), Na\(^{+}\), K\(^{+}\) and Ca\(^{++}\) ions penetrate reactive grains. The rate of penetration is determined by the size of the ions in solution. (2) More Ca\(^{++}\) ions are left in the liquid phase because their size is larger. (3) During the penetration, some fraction of the silica is set free to migrate away from its original site. (4) The concentration of Ca\(^{++}\) in the environment controls the rate at which dissolved silica diffuses out of the grains. (5) An expansion occurs if more materials penetrate a reactive grain than silica migrates out of the grains. There are many other theories proposed by different researchers (e.g. [2-71][2-72]), but it seems none of these theories is generally accepted.

2.6.6.3. Test Methods for Alkali-Silica Reaction

According to Hobbs[2-64], the alkali-silica reaction is a very slow process. In most cases, it takes more than ten years to manifest itself. This makes it very difficult in practice to test the reaction in the laboratory. In most of the tests, "the reaction has to be accelerated by using an abnormally high cement content, or by adding additional alkalis, or by testing at an abnormally high temperature. The results of these tests, therefore, should be treated with considerable caution for two reasons. Firstly, under such conditions some siliceous constituents may react at a rate significantly faster than they
would do at normal temperatures or more normal alkali concentrations or more normal cement contents. Secondly, the physical effects of the reaction may be different. The tests are only meaningful if the results correlate with the field performance of the aggregates, or, if the results correlate with the performance of concrete of more normal alkali contents tested under controlled conditions at temperatures experienced in practice."

However, for research purposes, people normally choose the method of their preference, all the methods should be able to supply some useful information in certain aspects of ASR if used and interpreted properly.

There are many test methods available to evaluate the ASR. These methods can be divided into four groups. (1) Quick chemical test[2-73]. (2) ASTM mortar bar expansion test[2-74]. (3) Accelerated mortar prism test[2-75][2-76][2-77][2-78]. (4) Concrete prism test[2-79]. The two most widely used tests are the ASTM quick chemical test[2-73] carried out on aggregate and the ASTM mortar-bar expansion test[2-74]. If the aggregate passes the quick chemical test, the aggregate is regarded as innocuous, but if fails the test, a mortar bar expansion test is carried out to check whether the reaction can lead to deleterious expansion.

In recent years, several studies have been carried out to evaluate test methods for assessing the effectiveness of mineral admixtures in suppressing expansion due to alkali-aggregate reaction. Berube and Duchesne[2-80] studied one ground granulated blast furnace slag, two condensed silica fumes, and three pulverised fly ashes using three different test methods. It was concluded that the Concrete Prism Method CAN/CSA-A23.2-14A[2-79] is the procedure most recommended for evaluating the effectiveness of mineral admixtures against ASR. The accelerated mortar bar method ASTM C9-P214 can give results in two weeks and the results are in good agreement with those of the CSA Concrete Prism Method. However, the Pyrex Mortar Bar Method ASTM C441
was found not appropriate for the purpose. Davies and Oberholster[2-81] evaluated the effectiveness of mineral admixtures in preventing the alkali-silica reaction using the NBRI accelerated test method[2-78] and the ASTM mortar bar expansion method (C227)[2-74]. The results were also compared with the field performance of concrete. It is concluded from this research that "the accelerated test can successfully be used to gauge the ability of different mineral admixtures to prevent deleterious expansion due to the alkali-silica reaction, provided the admixture does not contain excessive quantities of active alkaloids".

2.6.6.4. Influence of Mineral Admixtures on ASR

It is well-known that using mineral admixtures can significantly reduce the ASR expansion of concrete. In fact, the use of pozzolanic mineral admixtures seems to be the best solution to counteract the expansion caused by ASR at present. There are many publications which showed the mitigating effect of pozzolans[2-80 to 2-86], and some of these results will be discussed below.

Davies and Oberholster[2-81] studied the influence of several mineral admixtures on alkali-silica reactivity of cement mortar. The results of using silica fume(SF) and fly ash (FA) as cement replacement are shown in Figure 2.26 and Figure 2.27 respectively. It can be seen in the figures that the expansion of mortar and concrete was greatly reduced when using fly ash and condensed silica fume as a partial cement replacement. It can also be seen that regardless of the test method, the more the mineral mixtures used, the more the reduction in ASR expansion. Berube and Duchesne[2-80] evaluated the effectiveness of five mineral admixtures on ASR expansion in the presence of two very alkali-silica reactive aggregates from Canada, a siliceous limestone and a rhyolitic tuff. Some of their results are given in Figure 2.28. It can be seen that, with two exceptions in
the long term, all the mineral admixtures investigated reduced the ASR expansion, but the effectiveness was different depending on the type of the mineral admixture and the amount used.

2.6.6.5. Mechanisms by Which Mineral Admixtures Mitigate ASR Expansion

It is well established that mineral admixtures can reduce the ASR expansion, but the mechanisms by which they accomplish this effect are not well understood. There are many proposed mechanisms which acting alone or in combination. These mechanisms can be briefly summarised as follows[2-70][2-72][2-81][2-87 to 2-91].

(1). As a result of pozzolanic reaction between mineral admixtures and cement hydrates, the permeability of the cement paste is decreased, and consequently the mobility of ions in concrete is reduced.

(2). The improved strength developed by the mineral admixtures provides higher resistance to the expansive stresses produced by ASR.

(3). Mineral admixtures reduce the alkalinity of the pore solution.

(4) Mineral admixtures deplete Ca(OH)$_2$ in the cement paste.

(5) The secondary hydrate produced by pozzolanic reaction entraps alkali ions.

It should be mentioned that there is no general agreement on the mechanisms summarised above at present. Different views are still under debate.

Wang and Gillott[2-71] studied the influence of Ca(OH)$_2$ content on ASR expansion. The results in Figure 2.29 indicated that Ca(OH)$_2$ aggravated the alkali-silica reaction producing increase in expansion. They believed that Ca(OH)$_2$ has two major functions in concrete. Firstly, it acts as a "buffer" to maintain a high pH, and secondly,
Ca++ ions may exchange for alkali ions in silica gel leading to further production of the swelling alkali-silica complex. On the basis of these mechanisms, mineral admixtures capable of pozzolanic reaction will reduce the Ca(OH)$_2$ content in concrete, and therefore reduce the ASR expansion. Chatterji and Taulow[2-70][2-92] proposed a different ASR mechanism from which the same conclusion could be made. That is, the Ca(OH)$_2$ content plays a major role in ASR expansion.

Duchesne and Berube[2-88][2-91] studied the relation between concrete expansion and portlandite depletion. No relationship was observed between these two variables. From the pore solution analysis, they thought the most beneficial effect of a mineral admixture against alkali-silica reaction can be attributed to the depletion of alkali ions in the pore solution down to a safe level. Durand et al.[89] investigated the relationship between pore solution characteristics and ASR expansion. It was found that CSF is capable of incorporating a certain amount of alkali ions into secondary C-S-H, which therefore reduces the concentration of Na$^+$, K$^+$, and OH$^-$ ions in the pore solution (Figure 2.30 and Figure 2.31). As a consequence, the expansions of the mortar bars were reduced. Research by Diamond[2-93] and Nixon et al.[2-94] also suggested that the most beneficial effect of mineral admixtures is the reduction of the alkalinity in the pore solution.

2.6.7. Resistance to Freezing-Thawing

The deterioration of concrete due to freezing-thawing is one of the major problems in North America. Freezing-thawing damage in concrete can take several forms. The most common is cracking, and scaling. There are several mechanisms proposed by Powers and other researchers to describe the frost action in cement paste.
Most of these mechanisms, which have been explained in the book by Cordon[2-95], and in the lecture by Powers[2-96], will be briefly reviewed in the following sections.

2.6.7.1. Hydraulic Pressure Theory

The density of ice is lower than that of liquid water. So when freezing takes place, the volume of ice will be 9% larger than the volume of same amount of water. In a saturated cement paste, when water begins to freeze in a capillary cavity, the increase in volume accompanying the freezing of the water has to be accommodated by either dilation of the cavity, or forcing out the excess water from the cavity, or by both of the effects. During this process, hydraulic pressure is generated. This pressure is capable of causing "fatigue" of the concrete after many repeated freezing-thawing cycles, and can lead finally to the cracking of concrete. The magnitude of the hydraulic pressure depends on the rate of freezing, degree of saturation, permeability of the paste, and the distance from the cavity to the boundary of closest air voids. If there are enough air voids exiting in the cement paste, the excess water expelled from the freezing cavities will be released in these air voids, and the hydraulic pressure will not build up. This explains why air entrainment is necessary in order to produce frost resistant concrete.

2.6.7.2. Osmotic Pressure Theory

When solutions of different concentrations are separated by a permeable barrier, the solvent of the solution has the tendency to move through the permeable barrier toward the solution of greater concentration. The pressure differential caused by this concentration gradient is referred to as osmotic pressure.
Water in hydrated cement paste contains many alkali ions and is actually a solution. When the temperature in concrete is dropped below the freezing point, ice crystals will first form in the larger capillaries. As a result, the concentration of the unfrozen portion of the solution in these capillaries will increase. This creates an osmotic potential which causes water to diffuse from nearby unfrozen pores into the solution in the frozen cavities. The actual pressure in the full capillary cavity at any given instant is the sum of osmotic pressure and the pressure due to hydraulic flow. If the total pressure causes water to diffuse into the larger capillaries, the resulting dilution of the solution in contact with the ice will allow further growth of the body of ice. When the cavity becomes full of ice and solution, any further ice-accretion produces a dilation pressure which can cause the paste to fail. On the other hand, when water is being drawn out of unfrozen capillaries, the paste tends to shrink. The expansion due to ice-accretion in large capillaries and the shrinkage due to loss of water in gel pores tends to offset each other[2-1].

2.6.7.3. Capillary Effect

According to the theory advanced by Litvan[2-97], there are three types of water that are physically held in cement paste. These are the capillary water in small capillaries (10 to 50 nm), the adsorbed water in gel pores, and the interlayer water in the C-S-H structure. The water held by C-S-H (both interlayer and adsorbed in gel pores) in cement paste cannot rearrange itself to form ice at the normal freezing point of water. Generally, the more rigidly a water is held, the lower will be the freezing point. It is estimated that water in gel pores does not freeze above -78 °C[2-1]. When a saturated cement paste is subjected to freezing conditions, only the water in large cavities turns into ice and acquires a low-energy state, the water in gel pores undergoes supercoolling and is in a high-energy state. The difference in entropy of ice and supercooled water forces the
water in gel pores to migrate to the large cavities where it can freeze. This process continues until there is no room to accommodate more ice. Any subsequent tendency for the supercooled water to flow toward the ice-bearing regions would obviously cause internal pressures and expansion of the system.

The capillary effect has also been explained by Hudec [2-98] in a different way. He pointed out that the pore size determines the proportion of the adsorbed vs. 'normal' water held in pore. The smaller pores holding mostly the adsorbed water have a lower vapour pressure; the vapour pressure of the water is proportional to pore radius. Thus, the vapour pressure in very smaller pores will be much lower than in larger pores. If the porous material is fully saturated by immersion, the larger pores contain mostly bulk, normal vapour pressure water, and a vapour pressure potential exists between large and small pores. Because of this difference, higher vapour pressure water is compelled to move towards lower vapour pressure water by osmosis. The pressure in the small pores increases proportionately to the vapour pressure difference. If the osmotic pressure exceeds the tensile strength of the pore walls, a crack develops. The cracks, in turn become the new generation of small pores, advancing the deterioration process.

The hydraulic pressure theory and osmotic pressure theory are now generally accepted by many researchers. However, it seems that there are other causes of expansion of cement pastes exposed to frost action. MacInnis et al. [99] observed the freezing-thawing expansion of cement paste even when benzene, which contracts on freezing, was used as a pore fluid instead of water.
2.6.7.4. De-icing Salt Effects

The effect of de-icing salt on freezing-thawing of concrete is primarily physical rather than chemical. On the positive side, de-icing salt lowers the freezing point of water. So, under normal freezing conditions, the water in concrete undergoes supercooling rather than transforming to ice. This effect could have a negative aspect because when the supercooled water eventually freezes, the formation of ice is more abrupt. De-icing salt has many negative effects on frost resistance. The two most important effects are: (1) de-icing salt increases the degree of saturation of concrete, (2) de-icing salt causes higher osmotic pressure. Overall, the application of de-icing salts is detrimental to the frost resistance of concrete.

2.6.7.5. Surface Scaling Mechanisms

Surface scaling of pavement is one of the most common types of deterioration of concrete. Because of "bleeding", concrete slabs usually have a porous layer immediately beneath a dense surface layer[2-95]. Under freezing conditions, ice crystals can form in the porous layer. As long as there is a sufficient supply of moisture, the ice crystals will continue to grow and eventually lead to surface scaling. Cordon[2-95] explained the effect of de-icing salts on scaling as follows: "De-icing salts not only create additional forces through osmosis, but also provide an additional source of surface moisture in freezing weather by melting the ice and snow. In addition, as snow and ice are melted by de-icing salts, the temperature immediately below the surface is reduced significantly because of the comparatively large heat of fusion of ice. This may cause a damaging temperature drop in the saturated zone immediately beneath the surface, and promoted ice formation in the porous layer." The growth of ice crystals and the osmotic pressure
due to salt concentration gradient are the main reasons of surface scaling in concrete slabs.

2.6.7.6. Influence of Mineral Admixtures on Frost Action

From the discussion of freezing-thawing mechanisms, it can be concluded that frost resistance of concrete is related to several factors, such as air-void systems, strength, permeability and degree of saturation. The effect of mineral admixtures on freezing-thawing durability depends largely on their influence on these factors.

It is well known that the incorporation of mineral admixtures in concrete, such as fly ash and silica fume, generally requires much larger dosages of air entraining agents to obtain the air content and void spacing needed to satisfy the durability of concrete against frost action. In the case of fly ash, the dosages of air-entraining agents can be modified easily as long as the carbon content of the fly ash is known[2-17]. Larson[2-100] studied the use of fly ash in air-entrained concrete, and reviewed the similar work of other researchers. He concluded that "Fly ash has no apparent ill effects on the air voids in hardened concrete. When a proper volume of air is entrained, characteristics of the void system meet generally accepted criteria. ... When valid comparisons are made with equal strengths and air contents, however, there are no apparent differences in the freezing and thawing durability of fly ash and no fly ash concretes." Nasser and Lai[2-101] studied a Saskatchewan lignite fly ash on the resistance of concrete to freezing and thawing. They used fly ash as 20, 35, and 50% replacement of two portland cements (ASTM type I and type V). It was found that concrete containing 20% fly ash gave satisfactory performance as long as its air content and strength were comparable to the control concrete. However, the higher percentages of fly ash (35%, 50%) reduced its resistance to freezing and thawing even though the concretes contained about 6% air.
Carette and Malhotra[2-20][2-102][2-103] did several studies on the freezing and thawing resistance of silica fume concrete using ASTM Standard C666. For one such study, condensed silica fume was used to replace 0 to 30% of portland cement. The W/(C+SF) was maintained at 0.4, and a superplasticizer was used to adjust the loss of slump. For air-entrained samples, the test data are shown in Figure 2.32 and Figure 2.33. It can be seen that for the samples containing up to 15% of condensed silica fume, the freezing-thawing resistance was satisfactory. Samples containing 20 and 30% silica fume showed excessive expansions and low values for relative dynamic modulus even though the air content and spacing factor values were satisfactory. The poor performance of the concretes with high amounts of condensed silica fume was thought to be due to the very dense cement matrix that might have adversely affected the movement of water.

For non-air-entrained concrete, the author concluded that "regardless of the W/(C+SF), and irrespective of the amount of condensed silica fume, the concrete shows very low durability factors and excessive expansion when tested in accordance with ASTM C666 (Procedure A or B)".

Hooton and McGrath[104] studied the freezing-thawing durability of mortar samples containing various amounts of silica fume as cement replacement. It was shown that with 7.5 or 15% cement replacement, condensed silica fume enhanced the freezing-thawing durability of both air-entrained and non air-entrained mortar mixtures. The greatest improvement was found for the samples with a W/(C+SF) ratio of 0.45. The authors attributed the improvement to the reduction of the degree of saturation in the SF mortars due to self-desiccation.

There are also other cases in which non-air-entrained silica fume concrete was found to perform well under freezing-thawing conditions. Sorensen[105] studied both
air-entrained and non-air-entrained concrete containing various amounts of silica fume using a test method which is similar to the ASTM C-672 standard method. He concluded from the research that "Non-air entrained concrete can be produced with 300 kg/m³ cement and 30 kg/m³ microsilica to exhibit outstanding frost resistance at test conditions where a conventional concrete failed completely". Hooton[2-31] investigated four concrete mixes with 0, 10, 15, and 20% of condensed silica fume (as cement replacement). The air content was 0.9, 1.4, 0.8 and 0.9% for hardened concrete with 0, 10, 15, and 20% of silica fume respectively. All the spacing factors were far from acceptable. The tests were conducted using ASTM C666 Procedure A. It was very interesting to find that the control mix failed the usual 60 percent of original dynamic modulus criteria after 58 cycles, while other samples with silica fume performed very well even after 900 cycles of freezing and thawing. The author believed that the excellent performance of SF concrete was due to the self-desiccation effect and the low permeability which prevented the concrete from becoming critically saturated.

Concrete deterioration due to freezing and thawing can take two forms: scaling and internal cracking (expansion), and each of these can occur independently of the other[2-106 to 2-109]. Internal cracking is associated with the air-void spacing factor of concrete, but surface scaling is less dependent on the amount of entrained air. Pigeon et al.[2-107] have data indicating that using silica fume decreased the critical value of the air-void spacing factor. These concretes are therefore more susceptible to internal cracking caused by rapid freeze-thaw cycles in water. On the other hand condensed silica fume reduced the surface scaling of the test specimens under freezing-thawing cycles.
2.6.8. Summary

From all the reviews given in the previous sections, several important points can be summarised as follows:

(1) PSMC was found to be a material possessing pozzolanic properties. When used as an additive to cement mortar, it improved the strength of the cement mortar. To study the feasibility of utilisation of PSMC in concrete, it is important to know how PSMC influences the other properties of cement mortar. In addition, it was not clear how the individual components of PSMC contributed to the strength improvement and how these components will influence the other properties of cement mortar. One of the objectives of this study is to answer these questions.

(2). Condensed silica fume (CSF) and fly ash (FA) are two mineral admixtures that have been widely used in concrete. These two materials have been found to have many beneficial influences on the properties of concrete such as improvement in strength, reduction in ASR and sulphate expansion. There are similarities between PSMC and these two materials, it is therefore beneficial to compare the influences of PSMC on the properties of cement mortar with those of CSF and FA.

(3). The mechanisms by which mineral admixtures (CSF, FA) influence the properties of concrete are not well understood. There are many different viewpoints which are still under debate among researchers, and further research is needed. Comparison of different mineral admixtures on their influence on the properties of cement mortar is helpful to explain the mechanisms involved.
Chapter 3

EXPERIMENTAL DETAILS

3.1. Materials

3.1.1. Sand

In order to study the potential beneficial effect of mineral admixtures on cement mortar, a frost susceptible, shaly sand from the Leamington area of Ontario (Erie Sand and Gravel) was used for this study. The sand is widely used locally and the same sand has been used by several other students at the University of Windsor in their M.A.Sc. thesis projects[3-1][3-2]. Most of the properties of the sand were known before this study, however the sand has never been studied for its alkali-silica reactivity potential. Some of the properties of the sand are listed below:

Lithologic Description[3-2]: "Brown sand, near shore and beach deposit, 16% shale (medium to soft), 10% cherty carbonate, 6% chert, 15% shaly carbonate, 20% carbonate, and 33% silicates."

Sieve analysis of the as received sand is shown in Figure 3.1[3-1]. The actual grading of sand used in this studied was manually graded according to ASTM C 227 specification [2-74] as shown in Table 3.1.

Bulk specific gravity and absorption of the sand were measured according to ASTM C 128-88[3-3], and the results are given in Table 3.2[3-1].
Table 3.1. Grading of the sand according to ASTM C-227

<table>
<thead>
<tr>
<th>Sieve Size</th>
<th>Weight Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Passing</td>
<td>Retained on</td>
</tr>
<tr>
<td>No. 4 (4.75mm)</td>
<td>No. 8 (2.36mm)</td>
</tr>
<tr>
<td>No. 8 (2.36mm)</td>
<td>No. 16 (1.18mm)</td>
</tr>
<tr>
<td>No. 16 (1.18mm)</td>
<td>No. 30 (0.6mm)</td>
</tr>
<tr>
<td>No. 30 (0.6mm)</td>
<td>No. 50 (0.3mm)</td>
</tr>
<tr>
<td>Mo. 50 (0.3mm)</td>
<td>No. 100 (0.15mm)</td>
</tr>
</tbody>
</table>

Table 3.2. Bulk specific gravity, and absorption of the sand [3-1]

<table>
<thead>
<tr>
<th>Sand Lot No.</th>
<th>Bulk Specific Gravity</th>
<th>Absorption (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (unwashed sand)</td>
<td>2.56</td>
<td>3.67</td>
</tr>
<tr>
<td>1 (washed sand)</td>
<td>2.57</td>
<td>2.72</td>
</tr>
<tr>
<td>2 (washed)</td>
<td>2.57</td>
<td>2.95</td>
</tr>
</tbody>
</table>

Sand used in this study was from lot 1 and unwashed. Moisture content of the sand before mix was tested according ASTM C 566-89[3-4]. In program A, wet sand was used (free moisture content is 9.68 %). In program B, air dried sand was used (moisture content 0.67%)

3.1.2. Cement

The cement used in this study was normal portland cement (Type 10) from St. Mary’s Cement Company. The typical composition of the cement is given in Table 3.3.
Table 3.3. Comparison of Chemical Composition and Specific Gravity (S.G.) of Mineral Admixtures and Cement

<table>
<thead>
<tr>
<th>Oxide</th>
<th>CSF</th>
<th>FA</th>
<th>Glass</th>
<th>Cement</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂ %</td>
<td>92.7</td>
<td>46.79</td>
<td>52-56</td>
<td>20</td>
</tr>
<tr>
<td>Al₂O₃ %</td>
<td>0.17</td>
<td>23.99</td>
<td>12-16</td>
<td>6</td>
</tr>
<tr>
<td>CaO %</td>
<td>0.17</td>
<td>3.15</td>
<td>16-25</td>
<td>63</td>
</tr>
<tr>
<td>Fe₂O₃ %</td>
<td>0.29</td>
<td>16.35</td>
<td>0-0.8</td>
<td>3</td>
</tr>
<tr>
<td>MgO %</td>
<td>0.59</td>
<td>0.81</td>
<td>0-5</td>
<td>1.5</td>
</tr>
<tr>
<td>SO₃ %</td>
<td>0.36</td>
<td>1.16</td>
<td>-</td>
<td>2</td>
</tr>
<tr>
<td>Na₂O+K₂O %</td>
<td>1.11</td>
<td>0.61</td>
<td>0-2</td>
<td>1</td>
</tr>
<tr>
<td>B₂O₅ %</td>
<td>-</td>
<td>-</td>
<td>5-10</td>
<td>-</td>
</tr>
<tr>
<td>P₂O₅ %</td>
<td>0.06</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>LOI %</td>
<td>3.24</td>
<td>3.71</td>
<td>-</td>
<td>2</td>
</tr>
<tr>
<td>S.G.</td>
<td>2.22</td>
<td>2.51</td>
<td>2.55</td>
<td>3.1</td>
</tr>
</tbody>
</table>

3.1.3. PSMC, Its Components and other Mineral Admixtures

The abbreviations and descriptions of PSMC and other mineral admixtures used in this study are as follows:

(1) PSMC is finely ground pyrolysed sheet molding composite. Its composition is about 35% glass, 55% CaCO₃, and 10% of carbon. The particle size and distribution of typical PSMC is shown in Figure 3.2. The morphology of PSMC particles is shown in Figure 3.3 to Figure 3.5.

(2) RG is finely ground fibreglass of the type that is used in making sheet molding composites. The chemical composition of the glass is given in Table 3.3.

(3) CaCO₃ is the filler material also of the type used in making sheet molding compound.

(4) PG is finely ground fibreglass separated from PSMC. It consists of mostly glass plus a small amount of calcium carbonate and carbon.
(5) C+Ca is the material left after separating the glass from PSMC and it consists mostly of calcium carbonate and carbon plus a small amount of glass.

(6) PAF is finely ground pyrolysed automotive fluff (also referred to as automotive shredder residue). The composition of PAF varies widely from batch to batch, and the composition of the material used in this study is currently unknown but the major components of PAF are similar to those of PSMC. PAF has never been studied before for possible utilisation in concrete. The reasons for choosing PAF in this study are: (1) to collect preliminary data on this material for use in further study, (2) to compare the effect of this material to that of PSMC, and (3) presently PAF is being sent to landfills in large tonnages.

(7) CSF is a condensed silica fume (or silica fume) from Ontario Hydro. Its chemical composition is given in Table 3.3. The particle size and distribution of a typical condensed silica fume are shown in Figure 3.2. As been review in Chapter 2, silica fume has been studied extensively in recent years for its influence on the properties of concrete. The reasons for choosing CSF in this study are: (1) to compare it with PSMC and other mineral admixtures, (2) to study the influence of a single dosage of CSF on overall properties of cement mortar made with shaly sand.

(8) FA is class F fly ash from Ontario Hydro. Its chemical composition is given in Table 3.3. The particle size and distribution of a typical fly ash are also given in the figure 3.2. The reasons for choosing fly ash in this study are the same as those for choosing CSF.

Among the above listed mineral admixtures, considerable amount of research has been done on fly ash and condensed silica fume. They are well-known materials in concrete industry. PSMC and other related materials are relatively new wastes generated by automotive industry. The research done at the University of Windsor is the first to
explore the feasibility of utilising these materials in concrete. It would be desirable to determine the exact chemical composition and physical properties of PSMC and related materials before using them in concrete. However, PSMC is currently produced only from prototype facilities and its composition varies largely from batch to batch. On the other hand, it is not practicable to do the analysis at the University of Windsor, given the analytical resources available at the time when the research was done.

3.2. Mix Design

There are several methods in proportioning concrete containing mineral admixtures. The most commonly used method is to use mineral admixtures as partial cement replacement; the total amount of cement plus the amount of mineral admixture is equal to the amount of cement in the control mix. However, for low pozzolanic materials such as fly ash and PSMC, the partial cement replacement method resulted in lower early strength of concrete. To overcome this disadvantage, modified replacement methods[2-29] and direct-addition methods[2-30] have also been used in some cases. In the modified replacement method, a given amount of cement is usually replaced with more mineral admixture (by weight) than the amount of cement withheld in an attempt to produce earlier strength development. In the direct-addition method, a certain amount of mineral admixture is added to a reference mix without withholding any cement. In both methods, the workability of the concrete is adjusted by adding extra water or using superplasticizer. In this study, the direct-addition method is used because: (1) it has been found in previous study that when used as a direct addition, PSMC can increase the strength of cement mortar at the age as early as 7 days; (2) the influence of PSMC on the properties of cement mortar can be easily compared with other commonly used mineral admixtures on the same weight basis; (3) the properties of cement mortar with mineral admixtures can be easily compared with the reference mix.

3.2.1. Program A

Previous studies have shown that PSMC increased the 7-day and 28-day strengths of cement mortar when used as a direct additive[1-3][1-8]. However, it is not sure how its components contributed to the strength enhancement. Program A was designed to investigate the influence of the individual components of PSMC, as well as their content,
on the strength of cement mortar. In this program, PSMC was used as a direct additive at the rate of 5%, 10% and 15% to the reference mortar. Each component of PSMC was also used as a direct additive at the corresponding percentages according to their content in PSMC. Recall that the composition of PSMC is about 35% glass, 55% CaCO$_3$ and 10% of carbon, so for the 5% PSMC addition, the percentage of PG will be 1.75% (5% x 35%), and the percentage of corresponding CaCO$_3$ will be 2.75% (5% x 55%) and so on. The detailed mix proportions are shown in Table 3.4.

3.2.2. Program B

Program B was designed to investigate the influence of PSMC and its components on the overall properties of cement mortar, including strength, durability and pore structure. For comparison purposes, a fly ash and a condensed silica fume were also used in this research program. PSMC has been studied before for its influence on the strength of cement mortar[1-3]. It was found that at the water/cement ratio of 0.5, a 10% addition of PSMC seems to be the appropriate amount for the strength improvement and the workability of the cement mortar. From the results in program A, it was also concluded that a 10% addition to cement mortar was a suitable amount for PSMC and its components. For comparison purposes, all other mineral admixtures were also used as 10% additions to cement mortar. This proportion may not be practical for some of the admixtures, but for research purposes, it is valuable to know how this amount of the given mineral admixture influences the overall properties of cement mortar and how these influences are different from that of PSMC.
Table 3.4. Mix design table - Program A

<table>
<thead>
<tr>
<th>Samples @</th>
<th>Mix Proportion (grams per batch for 3 cube samples)</th>
<th>Sand</th>
<th>Cement</th>
<th>Water</th>
<th>Mineral Admixture</th>
<th>Melment L-10</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Reference)</td>
<td></td>
<td>655</td>
<td>238</td>
<td>107</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>b1 (5% PSMC)</td>
<td></td>
<td>655</td>
<td>238</td>
<td>107</td>
<td>50</td>
<td>0</td>
</tr>
<tr>
<td>b2 (10% PSMC)</td>
<td></td>
<td>655</td>
<td>238</td>
<td>107</td>
<td>100</td>
<td>5</td>
</tr>
<tr>
<td>b3 (15% PSMC)</td>
<td></td>
<td>655</td>
<td>238</td>
<td>107</td>
<td>150</td>
<td>7.5</td>
</tr>
<tr>
<td>c1 (1.75% PG)</td>
<td></td>
<td>655</td>
<td>238</td>
<td>107</td>
<td>17.5</td>
<td>0</td>
</tr>
<tr>
<td>c2 (3.5% PG)</td>
<td></td>
<td>655</td>
<td>238</td>
<td>107</td>
<td>35</td>
<td>0</td>
</tr>
<tr>
<td>c3 (5.25% PG)</td>
<td></td>
<td>655</td>
<td>238</td>
<td>107</td>
<td>52.5</td>
<td>0</td>
</tr>
<tr>
<td>d1 (3.25% C+Ca)</td>
<td></td>
<td>655</td>
<td>238</td>
<td>107</td>
<td>32.5</td>
<td>0</td>
</tr>
<tr>
<td>d2 (6.5% C+Ca)</td>
<td></td>
<td>655</td>
<td>238</td>
<td>107</td>
<td>65</td>
<td>0</td>
</tr>
<tr>
<td>d3 (9.75% C+Ca)</td>
<td></td>
<td>655</td>
<td>238</td>
<td>107</td>
<td>97.5</td>
<td>4.5</td>
</tr>
<tr>
<td>e1 (1.75% RG)</td>
<td></td>
<td>655</td>
<td>238</td>
<td>107</td>
<td>17.5</td>
<td>0</td>
</tr>
<tr>
<td>e2 (3.5% RG)</td>
<td></td>
<td>655</td>
<td>238</td>
<td>107</td>
<td>35</td>
<td>0</td>
</tr>
<tr>
<td>e3 (5.25% RG)</td>
<td></td>
<td>655</td>
<td>238</td>
<td>107</td>
<td>52.5</td>
<td>0</td>
</tr>
<tr>
<td>f1 (2.75% CaCO₃)</td>
<td></td>
<td>655</td>
<td>238</td>
<td>107</td>
<td>27.5</td>
<td>0</td>
</tr>
<tr>
<td>f2 (5.5% CaCO₃)</td>
<td></td>
<td>655</td>
<td>238</td>
<td>107</td>
<td>55</td>
<td>0</td>
</tr>
<tr>
<td>f3 (8.25% CaCO₃)</td>
<td></td>
<td>655</td>
<td>238</td>
<td>107</td>
<td>82.5</td>
<td>4</td>
</tr>
</tbody>
</table>

Note: @. The percentages show in the bracket indicate the amount of the admixtures to that of Reference mortar. The values are equal to "mineral / (cement + sand + water) x 100". The effective W/C ratio is equal to 0.716.

In program B, the composition of the reference mortar was 1 part cement to 2.75 parts of sand by mass, and the water to cement ratio by mass was 0.5 for all samples. The samples with admixtures were made by adding 10% of the admixture by mass to the reference mortar during mixing. Melment L-10 superplasticizer was used to adjust the
workability so that all the samples would have the same water to cement ratio and comparable workability. Details of the mix design are shown in Table 3.5

Table 3.5. Mix Design Table - Program B

<table>
<thead>
<tr>
<th>Sample</th>
<th>Admixture</th>
<th>Mix Proportion (g / per batch)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Cement</td>
<td>Sand</td>
</tr>
<tr>
<td>Group</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>Reference</td>
<td>2200</td>
<td>6050</td>
</tr>
<tr>
<td>B</td>
<td>CSF</td>
<td>2200</td>
<td>6050</td>
</tr>
<tr>
<td>C</td>
<td>FA</td>
<td>2200</td>
<td>6050</td>
</tr>
<tr>
<td>D</td>
<td>PSMC</td>
<td>2200</td>
<td>6050</td>
</tr>
<tr>
<td>E</td>
<td>C+Ca</td>
<td>2200</td>
<td>6050</td>
</tr>
<tr>
<td>F</td>
<td>PG</td>
<td>2200</td>
<td>6050</td>
</tr>
<tr>
<td>G</td>
<td>CaCO3</td>
<td>2200</td>
<td>6050</td>
</tr>
<tr>
<td>H</td>
<td>RG</td>
<td>2200</td>
<td>6050</td>
</tr>
<tr>
<td>I</td>
<td>PAF</td>
<td>2200</td>
<td>6050</td>
</tr>
</tbody>
</table>

Note: * 181.5 is the water required to bring sand to saturated surface dry condition.

# RG to mortar ratio is less than 10% (9.3%).

@ The mixture stiffens very fast so that it is difficult to mold the sample even when more superplastisizer was added and the mortar was remixed.
3.3. Sample Preparation

3.3.1. Mortar Mixing Procedures

Mortars were mixed according to ASTM C 305[3-5]. The detail mixing procedure was given in Appendix A-1.

3.3.2. Samples Cast

(1). 50-mm cube specimens were cast using recommended procedures as described in ASTM C 109-88[3-6]. The detailed procedures are given in Appendix A-2. 50 mm cube specimens were used to test strength and absorption.

(2). 2.5 x 2.5 x 21 cm mortar bar specimens were cast using the following procedures: Apply release agent to the molds. Place the mortar in the mold in two approximately equal layers. Compact each layer with the tamper. Work the mortar into the corners and along the surfaces of the mold with the tamper until a homogeneous specimen is obtained. After the top layer has been compacted, strike off the mortar flush with the top of the mold, and smooth the surface with a few strokes of a trowel. Immediately after completion of molding, insert the gage studs in position 1.5 cm away from both ends of the sample. The details of the sample are shown in figure 3.6. Mortar bar specimens were used for testing of drying shrinkage, adsorption, absorption, rate of evaporation, ASR, sulphate resistance, freeze-thaw resistance, scaling resistance, and wet-dry expansion

![Mortar Bar Specimen](image.png)

Figure 3.6. Mortar Bar Specimen
(3). 25 mm cube specimens: After the mortar bar specimens were made, some 25 mm cube specimens were made by sawing the bar specimens. The 25 mm cubes were used for the testing of strength and salt scaling.

3.4. Testing Methods - Program B

3.4.1. Workability

Workability is a composite property that is very difficult to measure directly. In this study, a well-known laboratory test - the flow test was used[3-7][2-2]. The method tests the consistence of concrete and its proneness to segregation. The apparatus used and the test procedures is given in Appendix A-3.

Mineral admixtures have great influence on the workability of concrete as has been reviewed in section 2.6.1. This influence depends largely on the particle size and distribution of the individual mineral admixtures. In this study, a simple test was also used to estimate the water up-take capacity of different mineral admixtures relative to that of cement. Detailed testing procedure is as follows:

(1). Mix 50 g of cement with 25 g of water (w/c ratio = 0.5),
(2). Determine the workability of the mix by hand-feeling and then test the flow of the mix using the flow table with a 3.6 cm diameter ring to hold the paste,
(3). The flow was calculated as \[ \frac{D - 3.6}{3.6} \times 100 \]
(4) Weigh 50 g of one mineral admixture, mix it with certain amount of water so that the workability of the mix feels the same as the cement paste with 0.5 w/c ratio. Then do a flow test on the mix.

(5) Test each mineral admixture as in step 4.

3.4.2. Compressive strength

The compressive strength of mortar was tested according to ASTM C 109-88[3-6]. The detailed procedures were given in Appendix A-4.

3.4.3. Pore structure

Pore structure has significant influences on the properties of hardened concrete, but the pore related parameters are usually difficult to measure. For plain portland cement paste, the mercury intrusion porosimetry (MIP) has been widely used to study the pore size and distribution. In this technique, mercury is forced under pressure into the dried and evacuated pores. The volume of intrusion and the pressure required for the intrusion are related to the pore size and the corresponding pore volume. In this way a pore size distribution can be determined. However, for blended cement paste (cement blended with mineral admixtures), the MIP method was found not accurate[2-40 to 2-43]. The explanation lies on the sophisticated pore structure of blended cement paste which could be damaged at high intrusion pressures during measurement. In this study, several simple tests were applied to investigate some pore related properties of cement mortar. The purpose was to see how PSMC and other individual mineral admixtures influence these pore related properties and how these influences are correlated to other properties of cement mortar.
(a). Adsorption test

The introduction of water vapour to a dry, porous material initially causes the formation of an adsorbed film of water on the interior pore surface. The amount of water adsorbed by the solid surface is proportional to the specific surface area of the solid. Based on this principle, the specific surface of the internal pores can be calculated from the amount of adsorbed water using the BET (Brunauer, Emmett and Teller) equation[2-5]. However, it was not the intention of this study to obtain the precise internal surface area of the cement mortar. The adsorption test was used to compare the relative internal surface area and fine pore content of different samples.

The adsorption tests were carried out according to the following procedures:

(1). Dry the samples in an oven at the temperature of 65 °C for 24 hours.
(2). Let the samples cool down in a desiccator over silica gel for 24 hours.
(3). Measure the initial length and weight of the samples and then place them into a container where the relative humidity was maintained at about 60% at 22 °C.
(4). Measure the length and weight of each sample after four days. Then return the samples to another container where the relative humidity was maintained at 80%.
(5). Measure the length and weight of each sample four and eight days.
(6). Calculate the adsorption and linear expansion as follows:

\[ Ad = \frac{W - W_0}{W_0} \times 100 \]
\[ Exp = \frac{L - L_0}{L_0} \times 100 \]
where:

\[ Ad = \text{adsorption of the samples, } \% \]
\[ Exp = \text{linear expansion associated with adsorption, } \% \]
\[ W, L = \text{weight and length of the samples after adsorption,} \]
\[ Wo, Lo = \text{weight and length of the samples before adsorption.} \]

(b) Absorption

The water absorption of concrete is determined by measuring the increase in weight of an oven-dried sample after immersion in water for a certain period of time. The amount of water absorbed depends primarily on the abundance and continuity of the pores in the sample. The value of absorption can be considered as an indication of effective porosity and is a rough indicator of pore volume, but not pore size[3-8]. In this study, the absorption test procedures followed the ASTM C 642-90 standard method[3-9]. It was thought that the initial moisture content of the samples has significant influence on the absorption results. To compare the effect of initial moisture content on the absorption of cement mortar, two drying temperatures were chosen which are 110 °C and 65 °C. If the samples are dried at 110 °C, the values of absorption obtained are closely related to the total volume of permeable pores, though a small amount of chemically combined water can also be removed at this drying condition[1-5]. Drying at 65 °C for 24 hours can not remove all the evaporable water in the samples and the absorption data obtained are more representative for the large pore content.

Samples after adsorption test were used for absorption study. The detailed procedures described in ASTM C 642 - 90 are summarised in Appendix A-5.
(c). Interval evaporation

Evaporation of water from saturated samples at different drying conditions is related to the pore structure of cement mortar. Water in large capillaries acts as bulk water, and is easy to remove by drying. On the other hand, adsorbed water is firmly held by the surface of pores and is difficult to remove by drying. It is therefore useful to study the amount of water evaporated from mortar samples at different drying conditions. The results are expected to supply some information related to the pore structure. For this purpose, an interval evaporation method was designed which is described as follows:

1. Dry the samples at 65 °C for 24 hours.
2. Immerse the samples in water for more than 3 days followed by boiling the samples for 6 hours.
3. Cool the samples in water for 24 hours and measure the weight of samples, designate this weight as $W_0$.
4. Dry the samples according to the conditions given in the Table 3.6.
5. Measure the weight of the samples after each drying interval, designate these weights as $W_i$.
6. Calculate the cumulative evaporation of water from the samples as follows:

\[
\text{Evaporation} = \frac{W_0 - W_i}{W_0} \times 100
\]
Table 3.6. Interval Evaporation Method, Drying Conditions

<table>
<thead>
<tr>
<th>Drying Intervals</th>
<th>Drying Temperature (°C)</th>
<th>Drying Time (hours)</th>
<th>Cumulative Drying Time (hours)</th>
<th>Cumulative Evaporation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1</td>
<td>23</td>
<td>24</td>
<td>24</td>
<td>Measured and Calculated</td>
</tr>
<tr>
<td>D2</td>
<td>65</td>
<td>24</td>
<td>48</td>
<td></td>
</tr>
<tr>
<td>D3</td>
<td>105</td>
<td>24</td>
<td>72</td>
<td></td>
</tr>
<tr>
<td>D4</td>
<td>105</td>
<td>24</td>
<td>96</td>
<td></td>
</tr>
<tr>
<td>D5</td>
<td>105</td>
<td>24</td>
<td>120</td>
<td></td>
</tr>
<tr>
<td>D6</td>
<td>105</td>
<td>24</td>
<td>144</td>
<td></td>
</tr>
</tbody>
</table>

(d) Rate of absorption

When mortar samples are in contact with or partially immersed in water, the samples will absorb water due to both "humidity gradient" and the force of "capillary suction". The rate of water up-take by the mortar samples is strongly related to their pore structure. However, there is no standard method available for testing the rate of absorption. In this study, a method initially developed by Hudec[3-10] for testing the rate of absorption of different rock samples was slightly modified and used to test the absorption rate of different mortar samples. The principles behind the method and the data interpretation were discussed in detail by Hudec[3-10]. The following is a brief summary of the test procedures and the test set-up (Figure 3.7):

1. Dry the samples in an oven at the temperature of 110 °C for 48 hours, then cool the samples in air for 24 hours.

2. Suspend one end of the sample under a balance with a wire, the other end of
the sample is hung over a container but not in contact with the bottom of the container. (Fig. 3.7).

(3). Carefully add water to the container until 1 cm of the sample is immersed in water.

(4). Read the weight of the sample from the balance immediately after 1 cm of the sample is immersed. Record this value as a reference (A)

(5). Record the readings of the balance every 5 minutes for 1 hour, designate these values as Bₜ.

(6). Calculate the absorption at each interval as follows:

\[
\text{Abs} = \frac{B_t - A}{A} \times 100
\]

(7). Plot the absorption verses the time of immersion.

(8). Calculate the absorption rate as follows:

\[
\text{Absorate} = \frac{\text{Abs}_{50} - \text{Abs}_{20}}{50 - 20}
\]

where:

Absₜ₅₀ and Abs₂₀ are absorptions at 50 minutes and 20 minutes respectively.

3.4.4. Drying shrinkage

Testing of the drying shrinkage followed the ASTM C 596[3-11] and C 157[3-12]. The procedures are summarised in Appendix A-6
3.4.5. Wet-dry expansion

Wet-dry cycling is a common weathering phenomenon which is capable of causing deterioration of concrete. There are however, no standard test methods available to study the wet-dry resistance of concrete. In this study, simple procedures were applied to test the expansion of cement mortar due to wet-dry cycling. The test procedures are described as follows:

(1). After demolding, moisture cure the samples for 27 days followed by 1 year storage in air (the relative humidity can fluctuate between 10% to 60%).
(2). Immerse the samples in tap water for 24 hours, then measure the initial length and weight of the samples.
(3). Oven dry the samples at a temperature of 65 °C for 24 hours, then return the samples to the water tank and keep immersed for 24 hours,
(4). Measure the length and weight, and repeat the wet-dry process for 14 cycles.
(5). The wet-dry expansion is calculated as following

\[ dL = \frac{L_i - L_o}{L_o} \times 100 \]

where:

\[ dL = \text{Wet-dry expansion after } i \text{ cycles, } \% \]

\[ L_i = \text{length after } i \text{ wet-dry cycles,} \]

\[ L_o = \text{Initial length before wet-dry cycles.} \]
3.4.6. Frost Resistance

(a). Freezing-thawing expansion and freezing-thawing weight loss

The most widely used method in testing freezing-thawing durability of concrete is the ASTM C 666 standard method [3-13]. There are two procedures in this method: procedure A - rapid freezing and thawing in water, and procedure B - rapid freezing in air and thawing in water. The test method used in this study is similar to procedure A in regard to the freezing and thawing media (i.e. in water). Samples used were 2.5 x 2.5 x 21 cm mortar bars. The linear expansion and weight loss of the samples were measured during the test. The detailed procedure is described as follows:

1. After curing in lime water for 13 days (i.e. at the age of 14 days), take the samples out of lime water and place them in plastic containers. Fill the containers with tap water and make sure the water level is about 1 cm above the top surface of the samples.

2. Measure the initial length and weight of the samples after immersion in water for 12 hours, then return the samples into the containers.

3. Place the containers with the samples immersed in water into a walk-in freezer for 10 hours (the temperature is controlled to -18 ± 2 °C).

4. Take the containers out of the freezer and thaw at room temperature for 14 hours, measure the length of the samples. Then return the samples to the freezer again.

5. Repeat the freezing-thawing cycles and make frequent measurements on the length and weight of the samples during the 100 freezing - thawing cycles.

6. Calculate the linear expansion and weight loss as following:
\[ dL = \frac{L_i - L_o}{L_o} \times 100 \]

\[ dW = \frac{W_i - W_o}{W_o} \times 100 \]

where:

dL = linear expansion of the sample after i cycles of freezing-thawing,

dW = weight loss (scaling) of the samples after i cycles of freezing-thawing,

L_i, W_i = length and weight of the sample after i cycles of freezing-thawing,

L_o, W_o = length and weight of the sample before freezing-thawing.

(b). Salt scaling resistance

The most widely used method to test the surface scaling resistance of concrete is the ASTM C 672 standard method[3-14]. The test requires large block concrete samples for testing. This was not practical in this study due to the large number of samples involved and the amount of materials required. To use smaller mortar samples, a new method was developed which is similar to the one used by McCann [3-1][3-15] in a similar study. In this method, 2.5 cm cube samples were used and the samples were totally immersed in 3% NaCl solution during freezing-thawing cycling. The results obtained from this method may not be comparable with those from ASTM C 672. However, for comparison purposes, the data obtained may be used as an indication of both surface and overall salt scaling resistance of cement mortar. The experimental procedure is summarised as follows:
(1). After curing the mortar bar samples in lime water for 27 days (i.e. at the age of 28 days), make 25 mm small cube samples by saw cutting the mortar bar, and put the cubes in a container that is filled with 3% NaCl solution.

(2). Measure the initial weight of the cube samples after immersion in salt water for 24 hours.

(3). Put the container with the samples immersed in salt water into a walk-in freezer for 10 hours. The temperature inside the freezer is controlled at -18 ± 2 °C.

(4). Thaw the samples at room temperature (about 22 °C) for 14 hours. Measure the weight of each sample and then return them to the container.

(5). Repeat the freezing-thawing cycle 100 times or until the cubes were totally disintegrated.

(6). Calculate the weight loss of the samples as follows:

\[ dW = \frac{W_i - W_0}{W_0} \times 100 \]

where:

- \( dW \) = weight loss (scaling) of the samples after \( i \) cycles of freezing-thawing,
- \( W_i \) = weight of the sample after \( i \) cycles of freezing-thawing,
- \( W_0 \) = initial weight of the sample before freezing-thawing.
3.4.7. Alkali-silica reaction

(a). Accelerated mortar bar expansion test

There are many test methods dealing with alkali-silica reaction[2-73][2-74][2-79][3-16 to 3-22]. Among them the accelerated mortar bar method, such as the MTO LS-620[3-18], and South Africa NBRI[3-21], is a very convenient and widely used method. The most important feature of the accelerated mortar bar method is that a fairly reliable result can be obtained in a relatively short time (normally within a month). Comparative evaluation of test methods for assessing the effectiveness of mineral admixtures in suppressing expansion due to alkali-aggregate reactions have been reported by Berube et al. and Davies et al.[2-80, 2-81]. They concluded that the accelerated mortar bar method yields results in good agreement with those of the CSA Concrete Prism Method[3-21]. It was suggested by them that the accelerated mortar bar method may give a good indication of the effectiveness of pozzolans in reducing expansion in concrete due to ASR.

The method used in this study is similar to other accelerated mortar bar methods and consists of the following steps:

(1). After demolding, cure the samples in hot water (80 °C) for 24 hours,
(2). Measure the initial length of the samples immediately after curing,
(3). Place the samples in 1 N NaOH solution and maintain the temperature at 80 °C,
(4). Measure the length of the samples every three days for the first 4 measurements and then every week for a total of eight weeks (Prolonged measuring period was suggested in the MTO method[3-18]).
(5). Calculate the ASR expansion as follows:

\[ \text{Exp} = \frac{L_i - L_o}{L_o} \times 100 \]

where:

\( \text{Exp} \) = expansion caused by ASR, %,

\( L_i, L_o \) = length of the sample after \( i \) days of reaction and length before reaction.

(b) Optical microscopy study

After being subjected to the accelerated mortar bar expansion test, cubes were cut from each bar and the cross-section was polished. A binocular optical microscope was used to observe the morphology of the samples. Photomicrographs were taken for evidence of reaction in the samples.

(c). Analysis of the reactivity of sand particles

(c-1). To identify the reactive components of the sand particles, the sand particles were separated as follows:

Sample 1: Shale particles only,
Sample 2: Non-shale particles,
Sample 3: Sand as received which consist of a mixture of shale and non shale particles.

Samples of each of the 3 sand samples above were immersed in 1 N NaOH solution and were held at 80 °C for 2 weeks. The solution and the sand particles were visually examined after the test for any changes that occurred during the test.
(c-2). Shale particles in different solutions

The sand sample comprised of shale only was put into each of the following solutions and maintained at 80 °C for 2 weeks. The solutions and shale particles were visually inspected for any changes after the test.

Solution 1: Tap water,
Solution 2: Saturated lime water,
Solution 3: 3% NaCl solution,
Solution 4: 1N NaOH solution,
Solution 5: Mixture of solution 2 and solution 3 in a half-half ratio.

(c-3). Analysing the composition change of shale particles after reaction

Shale particles retained in No. 8 sieve were immersed in 1 N NaOH solution and kept at 80 °C for 15 days. The samples of sand before and after reaction were ground to a fine power and their composition was determined using the EDS method on a scanning electron microscope.

(d). SEM and EDS study of the substance extracted from the reacted solutions after ASR test and to identify the ASR gel in mortar samples

Selected solutions of reaction were condensed by heating at 110 °C to evaporate all the water. The solid substance remaining after evaporation was studied by using the SEM and EDS methods. Four solutions were selected for analysis:
(1) the solution which had been reacted with shale particles for 2 weeks,
(2) the solution that had been reacted with reference mortar samples for 2 months,
(3) the solution that had been reacted with mortar samples containing silica
    fume for 2 months,
(4) the solution that had been reacted with mortar samples containing
    ground fibreglass for 2 months.

SEM study was also conducted on reference mortar and the mortars with CSF,
PSMC and RG to identify the possible ASR gels.

(e). Interval evaporation method

Interval evaporation method as described in section 3.4.3 (c) was used to study
the samples that have been used for ASR test and the samples not subjected to ASR test.

3.4.8. Sulphate Resistance

The mortar bar expansion method was used in this study. The experimental work
was conducted according to ASTM C 1012-89[3-23]. The detail procedures are
summarised in Appendix A-7.

3.4.9. Evaporable Water Content (Program A)

The cube samples used in Program A were cured in lime water. At the time of
strength testing, the samples were at moisture state (Saturated Surface Dry). After the
strength test, the samples were immediately weighed (the weight was recorded as \( W_0 \))
and then dried in an oven at the temperature of 65 °C. After drying for 24 hours, the
samples were weighed again (the weight was recorded as $W_{65}$) and then returned to the oven to dry for another 48 hours at the temperature of 110 °C. The weight of the samples at the end of drying were also recorded (referred to as $W_{110}$). The amount of evaporable water removed from the samples during the first period of drying (65 °C for 24 hours) was referred to as Evap65 which was calculated using the following equation:

$$\text{Evap65} = \frac{W_0 - W_{65}}{W_0} \times 100$$

The total evaporable water was referred to as Evap110 which was calculated using a similar equation.

$$\text{Evap110} = \frac{W_0 - W_{110}}{W_0} \times 100$$
Chapter 4

RESULTS AND DISCUSSION - PROGRAM A

Program A was designed for two purposes: (1) to investigate the influence of different dosages of PSMC addition on the compressive strength of cement mortar; (2) to investigate the influence of the individual components of PSMC on the compressive strength of cement mortar. Discussions on the significance of the influence by mineral admixtures on the properties of cement mortar are based on the results of the Student's t Test. The concepts and procedures of the Student's t Test are summarised in Appendix B.

4.1. Influence of PSMC on the Compressive Strength of Cement Mortar

The compressive strengths of cement mortars with different percentages of PSMC additions are shown in Figure 4.1. It can be seen from the figure that both the 7-day strength and the 28-day strength of cement mortar were increased with the addition of PSMC. Mortar samples with 5% PSMC showed a great improvement in strength as compared with the reference. When the amount of PSMC was increased from 5% to 15%, the 7-day strength of mortar samples increased slightly. It is also observed that at the age of 28 days, the strength of mortars with 10% of PSMC was slightly lower than the strength of mortar with 5% PSMC. This is believed to be due to the scatter of the experimental data.

It can also be seen from Figure 4.1 that the strength increase by PSMC at the age of 7 days was higher than the increase at the age of 28 days. This might be explained by the physical and chemical effect of PSMC particles on the strength development of cement mortar. Physically, PSMC can fill the space between cement particles as well as the space between sand particles. This "void filling effect" provided more effective packing of the
solid phase of cement mortar which resulted in an improvement on the strength at early ages. Also, when PSMC particles are evenly dispersed within cement mortar, they may act as nucleation sites for the cement hydrates. As a result, the cement hydration process was accelerated and the hydrated grains were refined. The "grain refinement effect" was also cited by other authors as one of the mechanisms explaining the strength improvement by mineral admixtures[2-87]. Chemically, the pozzolanic component of PSMC (glass) can react with the Ca(OH)$_2$ produced from cement hydration to form secondary C-S-H hydrates. The reduction in Ca(OH)$_2$ content and increase in C-S-H hydrates resulted in strength improvement. It was found in the previous work by the author that the pozzolanic reaction of PSMC took place mostly after the age of 28 days[1-3]. So, at the age of 7 days, the strength improvement was mainly due to the physical effect of PSMC. At the age of 28 days, this physical effect diminished after the cement was well hydrated. During that time, only limited pozzolanic reaction has taken place and would not be expected to significantly increase the strength of cement mortar. This explains the relatively lower improvement in strength by PSMC at the age of 28 days. The physical effect of mineral admixtures on the early strength was also observed by other researchers[2-32]. The higher 7-day strength of cement mortar with PSMC may also relate to the water to solids ratio of the mixture. Recall from the experimental design that the water to cement ratio in Program A was kept constant for all the samples, so the water to solids ratio was decreased with the increase of PSMC additions.

4.2. Influence of PSMC on the Evaporable Water Content of Mortar Samples

The influence of PSMC on the evaporable water content is shown in Figure 4.2. It can be seen from the figure that the Evap65 (water evaporated from saturated mortar samples after drying at 65 °C for 24 hours) decreases with the increase of PSMC content at both 7 days and 28 days. This is in good agreement with the strength results. That is,
the lower the Evap65, the higher the strength. Since the Evap65 is the water evaporated during the first period of drying, the values of Evap65 indicated the free water content which could be related to the large pore content of cement mortars. Evap65 is also related to the tortuosity of cement mortar. Clearly, PSMC has reduced the large pore content which resulted in the strength increase. PSMC also reduced slightly the values of Evap110 - the total porosity of cement mortar, but the influence was not as significant as on the values of Evap65.

4.3. Influence of the PG on Compressive Strength and Evaporable Water Content of Cement Mortar

PG consists mostly of ground fibreglass and a small amount of carbon and calcium carbonate. The percentage of glass in PSMC is about 35% which is the pozzolanic portion of PSMC. The PG was used as an addition to cement mortar at 1.75, 3.5, and 5.25% corresponding to the 5, 10, and 15% of PSMC addition. The compressive strength of these PG samples is given in Figure 4.3.

It can be seen from Figure 4.3 that the compressive strength of cement mortar at 7 days was increased slightly with the addition of PG. The general trend is that the more the PG content, the higher the strength. It was also noticed that the strength improvement by PG at 7 days was not as large as the improvement by PSMC. One reason was that the PG additions were smaller than the PSMC. A second factor was that the PG had a larger particle size compared to that of PSMC (the particle size of all mineral admixtures will be discussed in more detail in the next chapter). These two factors have an effect on the strength of cement mortar. At the age of 28 days, the strength of mortar samples with 1.75% of PG was lower than that of the reference mortar. However, the strength of mortar samples with 3.5% and 5.25% of PG was higher than that of reference mortar, and
the increase in strength for these two compositions at 28 days was proportionally higher than that at 7 days. The results shown in Figure 4.3 indicated that the physical effect of PG particles on strength was not significant. The improvement on strength by PG at 28 days was mainly due to the chemical effect, that is, the pozzolanic reaction with Ca(OH)$_2$. From the results of Student's t Test (Table B1), it was found that the strengths of cement mortar with various amount of PG (from 1.75 to 5.25%) were not significantly different from that of controls. The data also suggested that a higher percentage of PG should be used in order to achieve significant improvement in the strength of cement mortar.

The influence of PG on the evaporable water content of cement mortar is shown in Figure 4.4. At 7 days, the values of both Evap65 and Evap110 were not reduced by the addition of PG as compared with that of reference samples. However, for the PG mortars, the values of Evap65 and Evap110 decreased with an increase of PG content. At the age of 28 days, mortar samples with 3.5% and 5.25% PG showed lower value of Evap65 as compared with the reference mortar while samples with 1.75% PG showed a higher value. This result is in agreement with the strength of the mortar samples at 28 days. PG was also found to has increased the total porosity of the cement mortar (higher Evap110 values) and the change in Evap110 did not seem to be related to the amount of PG added.

4.4. Influence of C+CaCO$_3$ on Compressive Strength and Evaporable Water Content of Cement Mortar.

C+Ca refers to the material remaining after separating the glass portion from PSMC. It is essentially a mixture of carbon and calcium carbonate with a small amount of glass. C+Ca was added to cement mortar at the ratio of 3.25%, 6.5%, and 9.75% corresponding to the 5%, 10%, and 15% for PSMC.
The compressive strength of cement mortar containing various amounts of C+Ca is given in Figure 4.5. Clearly, the 7-day strengths of cement mortar were significantly improved with the addition of C+Ca and the improvement increases with the increasing amount of C+Ca. At the age of 28 days, 6.5% C+Ca showed the highest strength among all samples, but the improvement in strength by C+Ca at various additions was not considered significant (Table B1). C+Ca is the inert portion of PSMC with a finer particle size than the glass portion. It was expected that the main effect of the material on the strength of cement mortar would be mainly physical in nature. The improvement in 7-day's strength was obviously due to the above mentioned "voids filling effect" and the "grain refinement effect". These effects diminish as the cement hydration proceeds. At the age of 28 days, the physical effects became insignificant.

Figure 4.6 shows the influence of C+Ca addition on the evaporable water content of cement mortar. In agreement with the increased strength at 7 days, the large pore content of cement mortar (as indicated by the value of Evap65) decreased with the increasing amounts of C+Ca addition. At the age of 28 days, the values of Evap65 did not seem to be influenced very much by the addition of C+Ca.

4.5. Influence of the RG on Compressive Strength and Evaporable Water Content of Cement Mortar

RG refers to the ground raw fibreglass, that is the virgin fibreglass which is normally used in making Sheet Molding Compound. The RG was added into cement mortar at the same ratio as that of PG (1.75, 3.5, and 5.25%).
Figure 4.7 shows the results of compressive strength of mortar samples with various amounts of RG addition. It can be seen from the figure that the strength of samples with 1.75 and 3.5% RG was slightly lower than that of reference mortar at the age of 7 days and was much lower at the age of 28 days. However, when the amount of RG was increased to 5.25%, both 7-day and 28-day strengths of the cement mortar were increased. From the results of Student's t Test (Table B1), it was found that the strengths of cement mortar with various amount of RG (from 1.75 to 5.25%) were not significantly different from that of controls. The data also suggested that a higher percentage of RG should be used in order to achieve significant improvement in the strength of cement mortar.

After studying the influence of RG on the evaporable water content of cement mortar (Figure 4.8), it was found that the values of both Evap65 and Evap110 were increased with the addition of 1.75% of RG at 7 and 28 days. This indicated that the porosity of the cement mortar with 1.75% of RG was increased at 7 days. The porosity was however decreased with the increased amount of the RG addition. Although the values of Evap65 for mortar samples with 3.5% RG were lower than that of controls at the age of both 7 days and 28 days, the strength for this composition was not increased at the age of 7 days and even decreased at the age of 28 days. This may indicate that 3.5% RG addition did not reduce the large pore content of cement mortar but made the pore system more tortuous. The samples with 5.25% RG showed decreased value of Evap65 at both 7 and 28 days and this corresponds to the strength increase for the samples of this composition.
4.6. Influence of CaCO₃ on Compressive Strength and the Evaporable Water Content of Cement Mortar

As mentioned previously, PSMC can be most easily separated into two parts, the first part consists of mostly fibreglass and the second part consists of a mixture of carbon and CaCO₃. Since it was almost impossible to further separate carbon from calcium carbonate, the mixture was used as one component referred to as C+Ca. However, to understand the role CaCO₃ played, the virgin CaCO₃ which is normally used as a filler for making Sheet Molding Compound (SMC), was also used in this study as a single mineral admixture. CaCO₃ was used at the ratio of 2.75, 5.5, and 8.25% in Program A corresponding to the ratio of 5, 10 and 15% for PSMC.

The compressive strength of cement mortar with 0 to 8.25% of CaCO₃ is shown in Figure 4.9. It can be observed from the figure that at 7 days, the strength of mortar samples increased with increasing amounts of CaCO₃ addition. The strength improvement at early ages by the addition of CaCO₃ is believed due to the "physical effect". At the age of 28 days, it was found that only the samples with 8.25% of CaCO₃ showed higher strength than that of controls while samples with 2.75 and 5.5% of CaCO₃ showed lower strength than that of controls. However, from the Student t Test, it was found that the influence of CaCO₃ on the strength of cement mortar was not significant.

Figure 4.10 shows the influence of CaCO₃ on the evaporable water content of cement mortar. It was found that the Evap65 was not decreased by CaCO₃ at the ages of both 7 and 28 days. This is not in agreement with the results of strength at 7 days.
4.7. Influence of the Amount of Mineral Admixtures on the Compressive Strength of Cement Mortar

It has been discussed in the previous sections that the influence of PSMC and its components on the strength of cement mortar depend not only on the chemical and physical nature of the individual materials, but also on the amount of the materials added to the cement mortar. To study the relation between the strength and the amount of the admixture used, the relative strength (the ratio of the strength of a given cement mortar to the strength of the reference samples) was plotted against the amount of the admixtures used regardless of the type of the materials. The results are shown in Figures 4.11 and 4.12 for 7-day's and 28-day's strengths respectively. For simplicity, PSMC and its components will be referred to as "mineral admixtures" in the following discussion.

It can be seen from Figure 4.11 that the relative strength of cement mortar at 7 days increases with an increase in the amount of mineral admixtures used. Because mineral admixtures contribute to 7-days strength mainly by the "physical effect", the amount of mineral admixture used was more important than its chemical reactivity. From the general trend of the curve in Figure 4.11, it seems that at the point of 10% mineral admixture, the curve becomes flat and further increase in the amount of mineral admixture does not result in much increase in strength.

The data shown in Figure 4.12 are more scattered than the data shown in Figure 4.11. At the age of 28 days, the physical effect of mineral admixtures on the strength of cement mortar was less important and the pozzolanic reactivity of the materials starts to play a role. Because of the difference in chemical reactivity of the mineral admixtures, the same amount of addition of different admixtures resulted in different degrees of strength improvement. This is believed to be the reason for the scattered data in Figure 4.12. It is
also observed in Figure 4.12 that when used in a small amount, mineral admixtures did not improve the 28-day strength of cement mortar. For the RG and PG samples, significant improvement in strength took place only when the amount used was larger than 5%. Despite the scatter of the data in Figure 4.12, the general trend is that the higher the mineral admixture content, the greater the strength improvement.

4.8. Summary

1. PSMC increased the strength of cement mortar when used as a direct addition at the rate of 5, 10 and 15%. Compared with the reference mortar, the strength of mortar samples with 5% of PSMC addition showed higher strength at both 7 and 28 days. When the amount of PSMC was increased from 5 to 15%, the strength was further increased but the improvement was not significant. Previous research showed that PSMC contributed significantly to strength gain of cement mortar after the age of 28 days[1-3]. It is expected that the strength of cement mortar would be further improved at later ages and the improvement would increase with increasing amounts of PSMC.

2. There are two mechanisms by which PSMC improved the strength of cement mortar. Physically, PSMC particles filled in the voids between sand particles and the space between cement particles. This void filling effect provided more efficient packing of the solid phase in cement mortar and consequently improved its strength. In addition, due to the small particle size of PSMC, it acted as nucleation sites for cement hydrates. This not only accelerated the cement hydration process, but also refined the grains of cement hydrates. Chemically, PSMC reacted with Ca(OH)₂ to form secondary C-S-H hydrates which further refined the pore structures of cement mortar and led to a strength increase.
3. The strength improvement on 7-day's strength was mainly due to the physical effect of PSMC. The physical effect was mainly contributed by the inert portion of PSMC, that is the carbon and calcium carbonate. The strength improvement at 28 days was mainly due to the pozzolanic effect of PSMC. This effect was contributed by the glass portion contained in PSMC.

4. The strength improvement at 7 days obtained by the use of mineral admixtures was strongly correlated with the amount of mineral admixtures used. A direct addition of 10% seems to be the optimum amount which maximised the physical effect of the mineral admixtures on strength. The strength improvement at 28 days depended not only on the amount of mineral admixtures used, but also on the pozzolanic reactivity of the materials. For RG and PG to be effective at both 7 and 28 days, a minimum of 5% should be used.

5. The values of $\phi_{0.5}$ are indications of the large pore content and the tortuosity of the pore system in cement mortar. These values correlated well with the strength of cement mortar.
Chapter 5

RESULTS AND DISCUSSION - PROGRAM B

There are two major objectives in program B: (1) to investigate the influence of PSMC on overall properties of cement mortar including workability, pore structure, strength, drying shrinkage and durability; (2) to compare PSMC and seven other mineral admixtures for their influence on the overall properties of cement mortar when used as a 10% addition to cement mortar. The properties of mortar samples with different mineral admixtures were compared with the properties of reference mortar using the Student's t test. The statistical concepts and procedures of the Student's t test are given in Appendix B. The t values calculated for all the samples with different mineral admixtures are given in Table B2.

5.1. Influence of PSMC and other Mineral Admixtures on the Workability of Cement Mortar

5.1.1. Estimation of the relative surface area of mineral admixtures

The water take-up capacity of all the mineral admixtures (see section 3.4.1) is shown in Table 5.1. It can be seen from the table that the water take-up capacity of all mineral admixtures relative to cement can be ranked as follows:

Silica Fume > PAF > C+CaCO₃ >Cement > PSMC > Fly Ash > RG > PG > CaCO₃
Table 5.1. Comparison of Water Take up Capacity of all Admixtures and Cement

<table>
<thead>
<tr>
<th>Materials</th>
<th>Water (g / per 50g of solid material)</th>
<th>Flow (%)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement</td>
<td>25.38</td>
<td>114</td>
<td>as reference</td>
</tr>
<tr>
<td>Silica Fume</td>
<td>45.60</td>
<td>106</td>
<td>takes up more water</td>
</tr>
<tr>
<td>PAF</td>
<td>25.40</td>
<td>108</td>
<td>takes up more water</td>
</tr>
<tr>
<td>C+CaCO₃</td>
<td>25.00</td>
<td>108</td>
<td>takes up more water</td>
</tr>
<tr>
<td>PSMC</td>
<td>25.00</td>
<td>133</td>
<td>takes up less water</td>
</tr>
<tr>
<td>Fly Ash</td>
<td>25.00</td>
<td>150</td>
<td>takes up less water</td>
</tr>
<tr>
<td>RG</td>
<td>21.50</td>
<td>117</td>
<td>takes up less water</td>
</tr>
<tr>
<td>PG</td>
<td>21.30</td>
<td>128</td>
<td>takes up less water</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>22.12</td>
<td>144</td>
<td>takes up less water</td>
</tr>
</tbody>
</table>

The water take-up capacity is a rough indication of two parameters, the relative surface area (i.e. the particle size and distribution) and the properties of the surface (i.e., the affinity to water). As indicated in section 2.5.2, condensed silica fume is a much finer material than fly ash and portland cement. It is not surprising that CSF takes up much more water than the rest of the mineral admixtures. The particle size distribution of PSMC is similar to that of typical fly ash and portland cement as has been shown in Figure 3.1. So, the water take up capacities of these materials are comparable. The particle size distributions of RG, PG, PAF, CaCO₃ and C+Ca are unknown, but their relative surface area can be estimated from their water take-up capacity. On the basis of this rough estimation, it is believed that the relative surface area of PAF and C+Ca is larger than that of cement while the relative surface area of RG, PG, and CaCO₃ is smaller than that of cement. The data of water take up capacities were useful in determining the amount of superplasticizer needed for each mineral admixture when used as a direct addition to cement mortar.
5.1.2. Workability of the Freshly Mixed Mortar with and without Mineral Admixtures

The flow of freshly mixed mortars was tested using a procedure described in Appendix A-3. The results are given in Table 5.2. It can be seen that the flow numbers of the mortars with condensed silica fume or PG are lower than those of reference mortars. The flow of the rest of the mortar mixes is comparable. During the test, it was also found that most the mixes had a comparable workability except the mortar with PG. Although the flow of silica fume mortar was lower, its workability was still good. However, mortar with PG behaved differently. This mortar mix became stiff within a minute after stopping the mixer. When more superplasticizer was added and remixing was carried out, the mortar regained its workability. However, the mortar stiffened again when the mixer was stopped. This stiffening phenomenon was not observed in program A experiments in which PG was used in a smaller amount and no superplasticizer was added. It was thought that PG particles interacted with the superplasticizer and made it ineffective. Because of the lower consistency of this mix, the samples of this composition were cast with much more effort. These samples may contain more entrapped air bubbles due to the difficulty in compacting them.

Table 5.2. Flow of Mortars with Different Admixtures

<table>
<thead>
<tr>
<th>Mortar Type</th>
<th>Superplasticizer (g / per 10 Kg mortar)</th>
<th>Flow (%)</th>
<th>Workability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference Mortar</td>
<td>0</td>
<td>105</td>
<td>good</td>
</tr>
<tr>
<td>Mortar with CSF</td>
<td>142</td>
<td>60</td>
<td>good</td>
</tr>
<tr>
<td>Mortar with FA</td>
<td>50</td>
<td>90</td>
<td>good</td>
</tr>
<tr>
<td>Mortar with PSMC</td>
<td>52</td>
<td>85</td>
<td>good</td>
</tr>
<tr>
<td>Mortar with C+Ca</td>
<td>50</td>
<td>90</td>
<td>good</td>
</tr>
<tr>
<td>Mortar with PG</td>
<td>52 + 25</td>
<td>30</td>
<td>poor</td>
</tr>
<tr>
<td>Mortar with CaCO₃</td>
<td>50</td>
<td>90</td>
<td>good</td>
</tr>
<tr>
<td>Mortar with RG</td>
<td>50</td>
<td>105</td>
<td>good</td>
</tr>
<tr>
<td>Mortar with PAF</td>
<td>70</td>
<td>100</td>
<td>good</td>
</tr>
</tbody>
</table>
5.1.3. Summary

Except for condensed silica fume, the particle size of the mineral admixtures used in this study were similar to that of cement. When used as 10% addition to cement mortar, the loss in workability of mortar can be made up by using a small amount of superplasticizer. The use of mineral admixtures together with superplasticizer generally improved the workability of the mortar mixtures.

5.2. Influence of PSMC and other Mineral Admixtures on the Pore Structure of Cement Mortar

5.2.1 Influences of PSMC and other Mineral Admixtures on the Adsorption of Cement Mortar

The influence of mineral admixtures on the adsorption of cement mortar at 80% relative humidity is shown in Figure 5.1. It can be seen in the figure that the adsorption of mortar samples with PSMC, its components and FA were comparable with that of the reference mortars. The samples with CSF and PAF showed increased water adsorption compared with the reference mortar. Because adsorption is an indication of internal surface area, it is thought that CSF and PAF have increased the internal surface of mortar samples. For CSF, this may result from the pore refinement effect by which large pores have been transformed into finer ones. For PAF, the explanation is different. It was observed that PAF has caused an abnormal expansion of mortar samples during the first day of curing in their moulds. Micro cracks and some unusual air voids were found in these samples (Figure 5.2) and this may explain the increased internal surface area in PAF mortar samples. The major components of PAF are glass, calcium carbonate and
carbon. None of these materials is expected to cause expansion of cement mortar. However, PAF also contained some minor components which may induce this abnormal expansion of cement mortar. A research group at the University of Detroit Mercy studied the utilisation of automotive shredder residues (referred to as ASR in the automotive industry) in composite applications. They reported that automotive shredder residues contained a small amount of various metals [5-1][5-2][5-3]. These metals included copper, lead, zinc and possibly aluminium. The metals were contained in all five automotive shredder residues studied by this group. It is very likely that PAF used in this study also contained these metals. If this was the case, then the expansion of the mortar samples can be explained by the way in which gas concrete is made. In making gas concrete, powder aluminium or zinc and their alloys are commonly used. The reaction of these active powders with hydroxide of calcium or alkalis liberates hydrogen, which forms the bubbles and results in the expansion of the mortar system [2-2]. By closely examining the microstructure in Figure 5.2, it is believed that the unusual air voids could have been generated by the liberated gas (hydrogen). PAF is a newly developed waste material, its exact composition is very complicated and varies widely from different sources [5-2]. The motives for selecting PAF in this study were to compare with PSMC and to generate preliminary data on this material for possible utilisation in concrete. It is however not the intention of this study to investigate PAF in great detail. The expansion caused by PAF is certainly worth investigation in further studies. If the "gas liberating assumption" proved to be true and predictable, then there is a potential to utilise PAF in making aerated concrete.
5.2.2. Influences of PSMC and other Mineral Admixtures on the Water Absorption of Cement Mortar

During the absorption test, water flows into mortar samples and replaces air. However, not all of the air can be replaced by water during this test since some air bubbles get blocked in. Boiling can replace these air bubbles with water vapour which then draws in water during the subsequent cooling period. Mortar samples gain full saturation after boiling.

Figure 5.3 shows the influence of PSMC and other admixtures on the absorption of cement mortar initially dried at 110 °C (the absorption values will be referred to as Absor110 in later discussions). It can be seen that the absorption of most of the mortar samples is comparable except for PAF and CSF samples. For PAF samples, the absorption before boiling is slightly higher than that of references, but the difference is not considered significant. However, the absorption after boiling is much higher for PAF samples than for the rest of the samples. The increase in absorption of PAF samples by boiling indicated that a lot of air bubbles were blocked in during the absorption test. This is in good agreement with the "gas liberating assumption" described in the previous section (Section 5.2.1). That is, gas bubbles were generated in PAF samples due to the reaction between calcium hydroxide and some metal powders contained in PAF. The gas has occupied all the voids created in the samples and the voids were not filled with water during immersion. The additional absorption by boiling could be an indication of the volume of the pores generated by the gas in PAF samples. Boiling also increased the absorption of the rest of the samples and the increases were proportionally higher for CSF and RG samples (Figure 5.4). For CSF samples, the absorption is higher than that of references. This indicated that CSF did not reduce the total porosity of the cement mortar.
The volume of permeable pores in mortar samples was calculated using the method described in Appendix A-5. The results are given in Figure 5.5. As can be seen, the volume of permeable pores in cement mortar was not greatly influenced by using different mineral admixtures except for the PAF samples.

The results from the absorption test were influenced by the initial moisture content of the mortar samples. Figure 5.6 shows the results obtained from the samples initially dried at 65 °C. In this method, the saturated samples were first dried in air at room temperature for 24 hours followed by drying at 65 °C for another 24 hours before the absorption test. Then, the dried samples were immersed into water for 72 hours followed by boiling for 6 hours. The absorption was calculated from the weight differences between saturated samples (72 hours immersion and 5 hours boiling) and dry samples (65 °C for 24 hours). The absorption values obtained from this method will be referred to as Absor65-I in later discussions and these values are given in Figure 5.6.

Comparing with the results shown in Figure 5.3, it was found that the values of Absor65-I were lower than those of Absor110. This is not surprising because drying at 65 °C for 24 hours could not remove all the evaporable water in mortar samples. What is interesting is that most of the mortar samples with mineral admixtures shown a decrease in absorption as compared with reference mortar. This is different from what was observed in Figure 5.3 in which the absorption of all the samples (except PAF) was comparable (In fact the absorption of CSF was even a little higher than the other samples). It was mentioned in the experiment design that drying the samples at 65 °C for 24 hours was not expected to drive out all the evaporable water. Instead, only a portion of the evaporable water would be removed at this dry condition. The proportion of evaporable water removed was different for individual samples depending on their pore structure. If the samples contain more free water, that is more large pores, then the proportion of the evaporable water removed at 65 °C would be higher. On the other
hand, if the samples contain more fine pores, or if the pore structure is more tortuous, then the proportion of the evaporable water removed would be lower. For the reasons discussed above, it was thought that the values of Absor65-I could be considered as a reference to compare the large pore content and the tortuosity of the pore structure of different mortar samples. On the basis of this principle and the results in Figure 5.6 and Figure 5.3, it is thought that except for CaCO₃, all other mineral admixtures have influenced the pore structure of cement mortar. The lower values of Absor65-I for CSF, FA, PG, PSMC, C+Ca and RG samples indicate that these mineral admixtures have reduced the large pore content or have made the pore structure more tortuous in the mortar samples. The effect was greater for high pozzolanic materials such as CSF, FA and RG. Filler material such as CaCO₃ did not seem to influence the pore structure of cement mortar.

In another experimental procedure, mortar samples were first air dried for about a year followed by drying at 65 °C for 24 hours. After measuring the dry weight, the samples were then immersed in water for 72 hours followed by boiling for 6 hours. The absorption data obtained from this method are given in Figure 5.7. It can be seen in the figure that only CSF and RG samples showed absorption (Absor65-II) lower than that of reference samples. Again, the initial moisture content of the samples before the absorption test played an important role. Clearly the rate of water evaporation from different mortar samples was related to their pore structure. This topic will be discussed further in the following section.

5.2.3. Influence of PSMC and other Mineral Admixtures on the Evaporation of Water from Mortar Samples

To study the characteristics of water evaporation from saturated mortar samples, an interval evaporation method was used. The detailed procedure is given in section
3.4.3 (c). The cumulative water evaporation from mortar samples after each drying interval is given in Figure 5.8. If the values of evaporation after the final drying interval (110 °C for 96 hours) are considered as the total evaporable water contents for all samples, then the cumulative percentages of total evaporable water removed from mortar samples after each drying interval can be calculated and the results are given in Figure 5.9. It can be observed from Figure 5.8 and Figure 5.9 that the ease with which water has been removed from mortar samples was different. The figures show that it is relatively easier to remove water from reference mortar and the mortar with PAF than from mortars with other mineral admixtures. At the same drying condition, a much smaller amount of water was removed from the mortars with CSF and RG addition than from the reference mortar. To further investigate this phenomenon, the evaporation of water from mortar samples during each drying interval was expressed as the percentage of their total evaporable water content. The calculated results are given in Table 5.3.

Table 5.3. Percentage of Total Evaporable Water Removed during each Drying Interval

<table>
<thead>
<tr>
<th>Samples</th>
<th>Water Evaporation from each Drying Interval (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Interval 1</td>
</tr>
<tr>
<td></td>
<td>(D1)</td>
</tr>
<tr>
<td>Reference</td>
<td>34.7</td>
</tr>
<tr>
<td>CSF</td>
<td>21.4</td>
</tr>
<tr>
<td>FA</td>
<td>27.0</td>
</tr>
<tr>
<td>PSMC</td>
<td>34.6</td>
</tr>
<tr>
<td>C+Ca</td>
<td>31.6</td>
</tr>
<tr>
<td>PG</td>
<td>25.8</td>
</tr>
<tr>
<td>CaCO$_3$</td>
<td>33.1</td>
</tr>
<tr>
<td>RG</td>
<td>23.2</td>
</tr>
<tr>
<td>PAF</td>
<td>39.6</td>
</tr>
</tbody>
</table>
The water removed during the first two drying intervals is shown in Figure 5.10. It can be seen in the figure that during the mild drying condition (air dry or drying at 65 °C), the evaporation of water from the reference mortar was higher than from the others (except for PAF). PAF samples showed the highest evaporation, probably due to its higher porosity or its more open pore structure. The evaporation behaviour of the samples with CaCO$_3$ was similar to that of the reference samples. This implies that CaCO$_3$ did not have much influence on the pore structure of cement mortar. CSF and RG samples showed the least evaporation indicating that these two mineral admixtures have greatly influenced the pore structure of mortar samples. They might have refined the pores, or have made the pores more tortuous. The evaporation of mortar samples with FA or PG was also lower than the reference, but was not as low as that of CSF or RG samples. This implies that both FA and PG also changed the pore structure of cement mortar but the influence was not as significant as that by CSF or RG. Compared with the reference, the evaporation of PSMC and C+Ca samples was also lower. This indicates that these two materials also influenced the pore structure cement mortar, but the influence was not as significant as that by CSF, FA, RG and PG. It was also noticed that the pozzolanic reactive nature of the mineral admixtures played an important role in influencing the pore structure of cement mortar. From highly pozzolanic materials down to inert filler, the ability to influence the pore structure of cement mortar diminishes.

Figure 5.11 shows the amount of water removed during the third drying interval, that is, drying at 110 °C for 24 hours. A considerable amount of the evaporable water of the samples with CSF, FA, PG, or RG was removed during this period of strong drying. For the reference samples and the samples with CaCO$_3$ or PAF, almost all their remaining evaporable water was driven out during this drying interval.
Figure 5.12 shows the remaining portion of the total evaporable water in all the samples after the third drying interval. This portion of water was all driven out from the samples during the last three drying intervals. It can be seen that the pozzolanic mineral admixtures have increased the amount of this portion of water. These values are strongly related to the fine pore content and the tortuosity of the pore system in the mortar samples.

5.2.4. Influence of PSMC and other Mineral Admixtures on the Rate of Absorption of Cement Mortar

Absorption of water is a very fast process when mortar samples are totally immersed in water. As shown in Figure 5.13, all samples achieved approximately their maximum absorption within 7 hours after been totally immersed into water. Prolonged immersion did not increase their absorption significantly.

The rate of absorption, or more precisely, the rate of water intake by mortar samples was measured by the method described in section 3.4.3 (d). In Figure 5.14, the water intake of mortar samples was plotted against time of partial immersion. It can be seen from the figure that during the first 20 minutes, the rate of absorption was not constant for all samples. It was decreasing gradually. Between 20 minutes and 50 minutes, the absorption curve was approximately a straight line for all the samples. This implies that during this period, the rate of absorption was steady. The slopes of these straight lines (referred to as the rate of absorption) were then calculated, and the results are given in Figure 5.15. It can be observed from this figure that the reference samples showed the highest rate of absorption. All the mineral admixtures reduced this rate to different degrees. The absorption rate is an indication of the relative ease with which mortar samples can be saturated with water. Therefore, it is thought that all the mineral
admixtures have increased the discontinuity or tortuosity of the pore system in mortar samples. The highly reactive pozzolanic materials were found more effective than the less pozzolanic material for this effect.

5.2.5. Summary

The main results and interpretations from the preceding work are:

1. The influence of PSMC and other mineral admixtures on the total absorption (total volume of permeable pores) of cement mortar was not significant. Among all the materials studied, only PAF increased the total porosity of cement mortar. This increase in porosity is believed due to the "gas liberating reaction" of some metals contained in PAF with calcium hydroxide and alkalis from the cement hydration.

2. The ease with which water evaporates from the mortar samples and the ease with which water intake by mortar samples was decreased by most of the mineral admixtures investigated in this study. These results indicate that mineral admixtures have refined the pores in cement mortar, or have made the pore system more tortuous. The effectiveness of mineral admixtures in changing the pore structure of cement mortar varied according to their pozzolanic reactivity. Highly reactive materials such as CSF and RG were very effective, and the inert filler such as calcium carbonate had little effect. PSMC is a mixture of both reactive material (glass) and inert filler (carbon and calcium carbonate). It did have some influence on the pore structure of mortar samples, but the influence was not as significant as that by highly pozzolanic materials such as CSF and RG.

3. CSF and ground fibreglass are very effective in changing the pore structure of mortar samples. However, the changes they made appear to be different. Considering
the data of adsorption in which the value for CSF samples was higher than that of reference and the value for RG samples was lower, it is thought that CSF was more effective in refining the pore system while ground fibreglass might be more effective in increasing the tortuosity of the pore system.

4. Results from the interval evaporation test showed that the amount of water evaporated from mortar samples during each drying interval was related to their pore structures. The values from this test may be used as an indication for the content of pores of different size ranges. If this assumption were to be confirmed by a Mercury Intrusion Porosimetry (MIP) study, then the interval evaporation method could be very useful to study the size and tortuosity of the pores in cement mortar.

5.3. Influence of PSMC and other Mineral Admixtures on Compressive Strength of Cement Mortar

The development of strength in mortar samples with different mineral admixtures is shown in Figure 5.16 and Figure 5.17. The main results are as follows: (1) condensed silica fume (CSF) and ground fibre-glass (RG) produce a significant improvement on the mortar strength at all ages; (2) PSMC, C+Ca, and fly ash showed moderate improvement in the mortar strength; (3) the influence of CaCO₃ on mortar strength was negligible; (4) PAF greatly decreased the mortar strength and PG samples also showed a slight decrease in mortar strength. (5) The strength of the reference mortar at the age of 250 days was surprisingly lower than the strength at 100 days. To explain these results, it is useful to rethink the mechanisms by which mineral admixtures influence the strength of cement mortar as previously discussed in Chapter 2 and Chapter 4. Although there are different views on the "strength enhancement mechanisms" by mineral admixtures, the following two points are generally agreed upon among most of the researchers: (1) Mineral
admixtures that possess pozzolanic properties can react with Ca(OH)\textsubscript{2} to form secondary C-S-H gels, and therefore refine the pore system in cement mortar. Moreover, the reaction reduces the localised concentration of Ca(OH)\textsubscript{2} crystals in the interfacial zone, and consequently improves the bonding between aggregate and cement paste. (2) Mineral admixtures that have a small particle size can fill the voids between sand particles, and therefore provide more efficient packing of the aggregate particles, consequently improving the strength of cement mortar. Clearly improvement of mortar strength by CSF, RG, FA, PSMC was related to their chemical and physical properties. Highly reactive materials were more effective than less reactive materials. Inert fillers such as CaCO\textsubscript{3} were not effective. There were however two exceptional cases in which PG and PAF reduced the strength of cement mortar, although they are also possess pozzolanic properties. The explanations are: (1) Due to the "gas liberating reaction", PAF generated many air voids in the mortar samples and considerably increased their porosity. This has caused a strength decrease. (2) For samples with PG, it was found that the superplasticizer was not effective in maintaining the workability of the mortar mixture. The samples of this composition were not been compacted properly. This might be the reason for the strength decrease. The strength of reference mortar at 240 days was surprisingly lower and may be attributed to an experimental error.

Figure 5.18 shows the relative strength (as a percentage of the reference mortar) of all the mortar samples with different admixtures at the age of 7 days, 28 days and 100 days. It can be seen from the figure that the strength of samples with condensed silica fume and ground fibreglass is much higher than that of reference mortars at all ages. The maximum improvement in relative strength was obtained at the age of 28 days. These results indicate that highly pozzolanic materials can react with Ca(OH)\textsubscript{2} at very early stages of cement hydration. At the age of 28 days, most of the pozzolanic reaction has taken place.
For low pozzolanic materials such as fly ash and PSMC, the relative strength was a minimum at the age of 28 days. This means that during the early days of curing, the strength improvement was mainly due to the physical filling of voids. The contribution to strength by pozzolanic reaction occurred mostly after 28 days ageing. For inert fillers such as CaCO₃, the strength improvements decrease with an increase of curing age. This indicates that inert fillers increase the strength only by void filling and this effect is not significant after cement was well cured.

In summary, mineral admixtures which possess pozzolanic properties increased the strength of cement mortar at all ages when used as a direct addition. The mechanism of the strength improvement was believed due to both pozzolanic reaction and physical void filling effect. PSMC increased the strength of cement mortar, especially after the age of 28 days. Non-pozzolanic mineral admixtures increased the strength of cement mortar at early ages, and this increase was believed due to the void filling effect only. Their influence on well-cured concrete was not significant.

5.4. Influence of PSMC and other Mineral Admixtures on Drying Shrinkage of Cement Mortar

5.4.1. Influence of Mineral Admixtures on Drying Shrinkage of Cement Mortar

Figure 5.19 shows the drying shrinkage of mortar samples during the first 28 days of the curing period. During this period, the relative humidity was controlled at about 80%. It was found that with the exception of CSF samples which show less shrinkage than those of the reference mortars, all other samples had higher drying shrinkage than the reference mortars. PG samples show the highest shrinkage. After 28 days, all the samples were dried in air at room temperature. The fluctuation in the relative humidity
during the experiment is given in Figure 5.20 and the results of shrinkage are shown in Figure 5.21. It can be seen in this figure that after reducing the relative humidity from 80% to about 25%, the drying shrinkage of mortar samples increased rapidly to their maximum value. Then the shrinkage changes slightly with the change of relative humidity. It can also be seen that samples with ground fibreglass, CaCO₃, and fly ash show lower shrinkage than that of the reference mortars, samples with CSF, PSMC and C+CaCO₃ showed similar shrinkage to that of the reference mortars. Mortar samples with PAF and with PG had higher shrinkage than that of the reference mortars.

As has been reviewed in Chapter 2, the drying shrinkage of cement mortar usually results from loss of adsorbed water. The magnitude of the shrinkage in an unrestrained paste is approximately equal to the loss of a water layer one molecule thick from the surface of all the gel particles [2-2]. Therefore, the larger the specific surface of the hydration products, the greater the drying shrinkage. In other words, the more the adsorbed water content, the more the drying shrinkage. Mineral admixtures on one hand accelerated the hydration process by acting as the nucleation sites for hydration products[2-87]. On the other hand, the admixtures reacted with Ca(OH)₂ to produce secondary C-S-H hydrates. Both of the effects would increase the content of hydration products and therefore increase the internal surface area of cement mortar. As a consequence, samples containing mineral admixture would show higher drying shrinkage. The result shown in Figure 5.19 appears to support this for most of the samples. However, there is another aspect to consider. By pozzolanic reaction and the void filling effect, mineral admixtures generally increased the tortuosity of the pore system in cement mortar. Because of this, the rate of water evaporation from samples with mineral admixtures would be lower than that of the references. This means that under the same drying condition, the portion of the adsorbed water been removed from the samples with mineral admixtures would be lower. This effect will tend to reduce the
drying shrinkage of cement mortar. CSF is a very pozzolanic material, the discontinuous pore system in CSF samples could be well formed at early ages of curing. As a consequence of the lower rate of water evaporation, the drying shrinkage of CSF samples was lower before the age of 28 days as compared with other samples (Figure 5.19).

Corresponding to Figure 5.21, the drying weight loss of mortar samples when dried in air for a period of 240 days is given in Figure 5.22. For RG and CSF samples, the weight loss was similar during the entire drying period, but the drying shrinkage of CSF samples was higher than that of RG samples. This is another indication that the pores in CSF samples were finer than the pores in RG samples although the tortuosity of the pores in both samples was similar. For CaCO₃ samples, the water loss during the drying period was slightly higher than that of references, but the shrinkage was lower. This indicates that the pores in CaCO₃ samples were coarser and more continuous. Due to the unique pore system of PAF samples as discussed before, it showed the highest water loss and highest drying shrinkage. The drying shrinkage of mortar samples with PG was also very high, but the increased shrinkage occurred mainly during the first 28 days of curing. Comparing the drying shrinkage and drying weight loss of FA samples with that of the RG samples, it was found that the drying shrinkage of FA samples was similar to that of RG samples though the amount of water loss was higher. This may indicate that the pores in FA samples were coarser than the ones in RG samples.

5.4.2. Relationship between Drying Shrinkage and Drying Weight Loss

The correlation between drying weight loss and drying shrinkage for all the samples is presented in Figure 2.23 (a) to (c). A more or less linear relationship seems to exist between these two variables. In Figure 2.23(a), it can be seen that at the
beginning of the drying period (<1% water loss), the same amount of water loss resulted in approximately the same amount of shrinkage for RG, CSF, and FA samples as compared to the reference. After the water loss was greater than 1%, then the same amount of water loss resulted in a higher value of shrinkage for RG, CSF, and FA samples as compared to the reference samples. This is an indication that the pores in the samples with these mineral admixtures were finer than that in reference samples. The correlation line of FA samples fell in between the line of reference and the line of RG and CSF (both of which almost coincide). It is therefore thought that the pores in FA samples were finer than those of the references but were coarser than those in CSF and RG samples.

In Figure 5.23(b), the correlation lines almost coincide for all samples in the range of 0 to 3.5% drying weight loss. This implied that the pores from which the water has been removed in all the samples were approximately the same size for this range. Beyond the 3.5% point, the same amount of water loss resulted in a slightly higher shrinkage for PSMC and C+Ca samples than those for the reference and CaCO$_3$ samples. This is in agreement with the previous discussions that the pore structure for CaCO$_3$ samples was similar to that of references, while the pore structure in PSMC and C+Ca samples have been slightly refined.

Figure 5.23(c) shows the correlation of water loss and shrinkage for the samples with PAF and PG. It can be seen that the shrinkage of PAF samples was higher than that of reference samples for the same amount of water loss beyond the 2% weight loss point. For PG samples, the trend was the same as for that of PAF samples, but the initial drying shrinkage (28 day's shrinkage) of PG samples was higher.
5.4.3. Reversible and Irreversible Drying Shrinkage

After the drying shrinkage test, re-saturating the samples can cause recovery of a certain portion of the total shrinkage. This phenomenon is shown in Figure 5.24. In this Figure, the 28 days drying shrinkage (28 DS), 227 days air drying shrinkage (Air227 DS) as well as oven drying shrinkage (65°C dry, 110°C dry) are shown. The irreversible shrinkage was obtained by re-saturating the samples (3 days water absorption followed by boiling for 6 hours) after drying in an oven at 65°C for 24 hours. Figure 5.25 showed the influence of admixtures on the maximum shrinkage (shrinkage after all the evaporable water was removed by oven drying) and the irreversible shrinkage (the shrinkage that can not be recovered from re-saturation) as well as the 28 days drying shrinkage of mortar samples. It was clear from the figure that the adsorbed water content alone can not explain the drying shrinkage of the mortar samples. As discussed in section 5.2, the total porosity of most of the mortar samples was approximately the same (except for the PAF samples). The adsorbed water content in the samples with RG, CSF and FA was higher due to their pozzolanic reactivity and their pore refinement effect. However, the results shown in Figure 5.25 did not indicate that these samples give higher shrinkage even when all the adsorbed water was removed. On the contrary, samples with RG, FA showed reduced drying shrinkage as compared with the reference samples. It was also observed in this figure that PAF and PG increased both the maximum and the irreversible shrinkage of mortar samples, while RG and FA decreased these shrinkages. In Figure 5.26, the shrinkage of mortar samples was calculated using the 28 day length as reference. It can be seen that FA, RG, and CaCO₃ samples showed less shrinkage than that of references, while other samples showed an increase in drying shrinkage. However, from the Student's t Test (Table B-2), it is concluded that the influence of
mineral admixtures on drying shrinkage of cement mortar was not significant (except for PAF which increased the drying shrinkage).

5.4.4. Summary

From the above results and discussion, it can be concluded that:

1. Except for CSF, all other mineral admixtures increased the 28-day drying shrinkage of mortar samples as compared to that of the references. RG and FA reduced the total drying shrinkage and the irreversible drying shrinkage of mortar samples after drying in air for 227 days, but PG and PAF increased these two shrinkages. However, the results from the Student's t Test indicated that the influence of mineral admixtures on the drying shrinkages of cement mortar was not significant.

2. The drying shrinkage of cement mortar is related to its adsorbed water content and the tortuosity of the pore system. Removing of water from finer pores resulted in more shrinkage than removing water from larger pores. However, the content of adsorbed water alone can not explain the drying shrinkage behaviour of cement mortars. The drying shrinkage of mortar samples with RG or FA was lower even when all the adsorbed water had been removed.

3. For each mortar sample, there is a correlation between the drying weight loss and the drying shrinkage. Using mineral admixtures slightly changes this correlation. That is, the same amount of water loss resulted in a slightly different amount of increase in shrinkage for samples with different mineral admixtures. This is another indication of the change in pore structures of cement mortar by the addition of mineral admixtures.
5.5. Influence of PSMC and other Mineral Admixtures on Wet-Dry Expansion of Cement Mortar

The influence of mineral admixtures on wet-dry expansion is shown in Figure 2.27. It can be seen that CSF samples showed a much higher wet-dry expansion than all other samples. Compared with the reference, the RG samples also showed higher expansion but the values were much lower than those of CSF samples. PAF and CaCO₃ reduced slightly this expansion while PSMC and all other samples did not seem to have a noticeable influence on the wet-dry expansion. It seems that repeated wetting and drying has a great influence on mortars with fine pore structures. Figure 5.28 shows the weight change of saturated samples as a result of wet-dry cycling. It can be seen that there was a continuous increase in the water intake during the wet dry cycling. For CSF and RG samples, this occurs from the first wet-dry cycle. For all other samples, an increase in water intake was also observed after several wet-dry cycles. The explanation is that when mortar samples were dried at a higher temperature, some pores in the mortar samples collapsed and new cracks were generated. During the wetting cycles, the newly created cracks took up water, resulting in a higher absorption. The repeated wet-dry cycling inevitably resulted in expansion of the mortar samples. It is thought that samples with fine and tortuous structures were prone to wet-dry damage while samples with coarse and continuous pore structure were more resistant to wet-dry cycling.

In summary, CSF significantly increased the wet-dry expansion of mortar samples because of the fine pore structure. The influence of PSMC and other mineral admixtures on the wet-dry expansion of cement mortar was not significant.
5.6. Influence of PSMC and other Mineral Admixtures on Frost Resistance of Cement Mortar

5.6.1. Influence of Mineral Admixtures on Freezing-Thawing Expansion

Figure 5.29 and Figure 5.30 show the influence of mineral admixtures on the length change of mortar samples during freezing and thawing cycling. According to the expansion results, the admixtures can be classified into three groups. The first group includes FA, PAF, CaCO$_3$, and RG. In the presence of these admixtures, mortar samples undergo contraction rather than expansion. The second group includes CSF, PSMC, and C+Ca. The expansion of samples with these admixtures was slightly higher but still comparable with that of reference mortars. The third group is PG alone. The expansion of PG samples was higher than that of reference mortars. There are several theories to explain the freezing-thawing expansion. The details of each theory have been reviewed in Chapter 2. According to Litvan [2-67], there is moisture transportation within the concrete when it experiences freezing-thawing cycling. When freezing takes place, ice is first formed in the larger pores and water in smaller pores undergoes super-cooling. Due to the different energy between ice and super-cooled water, the small pore water tends to migrate to larger pores where freezing can take place. Freezing of water in larger pores results in expansion but removal of water from the smaller pores may cause shrinkage. The net effect on a sample is the combination of these two opposite tendencies. On the basis of this explanation, the samples which had undergone contraction when subjected to freezing-thawing cycling were not likely to have been critically saturated. This may be true for PAF samples because the samples contained many "gas bubbles" which were not filled with water. RG samples might also have contained some "air bubbles" as was shown in the figure 5.4 that boiling increased the water absorption of the RG samples considerably. It is however, difficult to explain the samples with FA and CaCO$_3$, which
showed contraction under freezing-thawing cycles. There seems no reason for these two samples to achieve lower saturation than the reference. It was also observed that all samples began to scale after 20 freezing-thawing cycles. The scaling of the samples was more of a problem than expansion and this will be discussed in the next section. The results from the Student's t Test also indicated that the influence of mineral admixtures on the freezing-thawing expansion was not significant.

5.6.2. Influence of Mineral Admixtures on Freezing Thawing Weight Loss of Cement Mortar

It was observed that during the freezing and thawing test, scaling took place at about 20 freezing-thawing cycles. The weight loss of mortar samples was then recorded and used as an indication of scaling resistance. The values should be distinct from the standard surface scaling test because the weight loss included the scaling from all parts of the samples, not just the top surface. The data of freezing and thawing weight loss of mortar samples is plotted in Figure 5.31. It is clearly seen that with the addition of CSF or RG, the scaling resistance of mortar samples was improved significantly. However, with the addition of C+Ca, the scaling resistance of mortar samples was significantly reduced. The influence of PSMC and other mineral admixtures on scaling resistance of mortar samples was not significant. The mechanisms by which concrete scaling takes place are very complicated and are not well-understood. There are however, many factors which influence the scaling resistance of concrete. The quality of the aggregate is a very important factor, but this is not a major concern in this study because all the samples used the same sand. The strength of mortar samples is another important factor considering that higher strength will resist higher dilation pressure generated by freezing-thawing cycles. In fact, the freezing-thawing weight loss in this study was found to be inversely correlated with the strength of the cement mortar (Figure 5.32). The pore
structure of cement mortar is a critical factor in freezing-thawing resistance because on one hand it determines the degree of saturation in mortar samples, and on the other hand, it influences the ease with which water moves within the samples during the freezing-thawing cycles. In addition to the higher strength, the improved scaling resistance by CSF, RG, and FA may also result from their refinement on pore structures which then prevented the sand particles from becoming critically saturated. Scaling and expansion are two forms of freezing-thawing damage to concrete. However, scaling and expansion can occur independent of each other[2-106 to 2-109]. Results in this study also showed that there was no correlation between freezing-thawing weight loss and freezing-thawing expansion (Figure 5.33).

5.6.3. Influence of Mineral Admixtures on Salt Scaling Resistance of Cement Mortar

The salt scaling resistance of mortar samples was tested by immersing the 2.5 cm cube samples into 3% salt water during freezing-thawing cycling. The results are shown in Figure 5.34. It was found that CSF and ground fibreglass (RG) improved the salt scaling resistance significantly. After 20 freeze-thaw cycles, the reference mortar lost about 80% of its weight due to scaling, but the mortar with CSF lost less than 5% and the RG mortar less than 10% of their weight. Mortar with CaCO₃ lost 100% of its weight (totally disintegrated due to scaling), and the mortar with C+Ca lost about 90% of its weight. The scaling resistance of mortar samples with PSMC, PAF, or PG was similar to that of the reference samples. Fly ash also improved the salt scaling resistance of mortar samples but the improvement is not as significant as that of CSF or RG. Figure 5.35 shows that after 50 freeze-thaw cycles, most samples have totally broken down due to scaling. However, the samples with CSF or RG can stand 100 freeze-thaw cycles without significant scaling. The mechanisms by which mineral admixtures influence salt scaling resistance are similar to the ones discussed in the previous section on freeze-thaw
weight loss, but scaling was more severe in a salt solution than in tap water. The explanations are: (1) mortar samples gain a higher degree of saturation in salt solution than in tap water; (2) salt generates osmotic pressure in mortar samples due to the concentration difference between different size pores. The relationship between salt scaling and freeze-thaw weight loss is shown in Figure 5.36.

5.6.4. Summary

1. The influences of PSMC and other mineral admixtures on freeze-thaw expansion of cement mortar were very complicated. Some admixtures caused expansion while others caused contraction. However, these influences are not considered significant from the Student's t test. It is also observed in this study that scaling was the major damage of mortar samples made with shaly sand under freezing-thawing conditions. So, freezing-thawing expansion results are not considered as important as the F-T weight loss in this study.

2. The influence of mineral admixtures on freeze-thaw weight loss depends on their influence on the pore structure and on the strength of mortar samples. CSF and ground fibreglass greatly improved the scaling resistance of mortar samples. This appears to be due to largely their improvement on the strength of cement mortar. The freeze-thaw weight loss of the PSMC samples was comparable with that of the reference mortars.

3. Freezing-thawing in salt solution aggravated the scaling weight loss of all mortar samples, but the influence seems more severe on the samples with the CaCO₃ addition. The shaly sand used in this study was well-known to be very vulnerable to salt
scaling. However, with the addition of CSF or ground fibreglass, the salt scaling resistance of these cement mortars are very much improved.

5.7. Influence of PSMC and other Mineral Admixtures on Alkali-Silica Reaction of Cement Mortar

5.7.1 Effectiveness of PSMC and other Mineral Admixtures in Reducing ASR Expansion

The influence of PSMC and other mineral admixtures on ASR expansion is shown in Figure 5.37. It should be mentioned that for the accelerated test, an expansion in excess of 0.1% at 12 days is considered to be deleterious. This criterion is thought to be equivalent to 0.05% at 1 year in the ASTM C227 method[2-78][2-80]. The main purpose of this study, however, was to compare the relative effectiveness of different mineral admixtures in mitigating the ASR expansion. Therefore, the absolute value of expansion is less important. The following facts are revealed in Figure 5.37:

(a) All the samples with admixtures show less expansion than that of reference mortars. Based on the expansion of mortar samples, the mineral admixtures can be divided into two groups: The first group includes CaCO₃ and C+CaCO₃. samples with these mineral admixtures showed less expansion than those of reference samples. The second group includes all the other mineral admixtures. The expansion of mortar samples in this group was significantly decreased.

(b) The effectiveness of PSMC and PAF in controlling ASR expansion is comparable to that of CSF and FA. However the glass is the most important component in PSMC and PAF contributing to the effect. In descending order, the glass content of the admixtures related to pyrolyzed products are RG (100%) >
PG > PAF > PSMC > C+Ca > CaCO$_3$ (0%). The effectiveness in controlling ASR expansion, as shown in Figure 5.37, gives exactly the same ranking.

(c) Of all the admixtures tested, ground fibreglass is the most effective material in mitigating ASR expansion although the SiO$_2$ content of the glass is much less than that of CSF.

5.7.2. Evidence of ASR Using Optical Microscopy

From the microscopic study, it was found that all the samples show some evidence of reaction around shale particles (reaction rim and cracking of the sand particles) (Figure 5.38), but the degree of reaction was different. For the reference sample and the sample with inert filler (calcium carbonate), the reaction was much more severe than the other admixture samples. This is in agreement with the expansion results in which the reference and CaCO$_3$ samples show greater expansion than those of the other admixture samples. For the samples with ground fibreglass (RG) and CSF, the evidence of reaction was confined merely to a few small particles close to the exterior surface of the samples. There was no sign of reaction in the centre portion of the sample. It was also observed that the reaction took place only around shale particles. Shale is not widely used as aggregate for concrete because of its poor physical properties. In this study, shale was found to be alkali-silica reactive when using a rapid mortar bar expansion method.

5.7.3 Response of Different Components of Sand to ASR

The information from visual observations of different sand samples after soaking in hot NaOH solution is summarised in Table 5.4.
Table 5.4. Observation of Changes after ASR Testing on Different Sand Samples

<table>
<thead>
<tr>
<th>Sand Samples</th>
<th>Colour of Solution After Test</th>
<th>State of Sand After Test</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Shale Only</td>
<td>Dark Brown</td>
<td>Soft, Muddy</td>
</tr>
<tr>
<td>2. Non-Shale</td>
<td>Clear</td>
<td>Hard, Strong</td>
</tr>
<tr>
<td>3. Sand as Received</td>
<td>Brown</td>
<td>Only Shale Particles Soft</td>
</tr>
</tbody>
</table>

From the results listed in Table 5.4 and the evidence from microscopic studies, it is concluded that shale is the only reactive component of the sand used. The reaction was able to cause the shale particles to crack and to totally break down. There are two possibilities for the colour change involved in the reaction. First, the colour change may be associated with the iron oxide component in the shale particles. Second, the change in colour of the solution could also be caused by the organic content in the shale particles. This topic will be further discussed in the following sections.

5.7.4. Response of Shale Particles to Different Solutions

Shale particles have been observed for reactivity in different solutions by immersing them in those solutions and heating to 80 °C. It can be seen from the Table 5.5 that only the NaOH solution reacted significantly with the shale particles. On the basis that the NaOH solution changed colour very soon after contact with shale, it is thought that the colour change may not be associated with alkali-silica reaction but rather with the organic content of shale. It is not uncommon for shale to contain some organic components. Under normal conditions, this organic matter is retained by the shale particle and would not affect the cement hydration process. However, after having been exposed to a strong alkali solution, the organic matter can be dissolved as has been found
in this study. To confirm that the organic matter contained in the shale was not normally harmful to the properties of cement mortar, a standard method (ASTM C 40)[5-4] was used to test the sand. In this method, a sample of sand was immersed in 3% NaOH solution for 24 hours. The colour of the solution was then compared with a reference standard colour solution freshly made from potassium dichromate and sulphuric acid. It is stated in the ASTM C 40 that "If the colour of the supernatant liquid of the sand sample is darker than that of the reference standard colour, the sand under test shall be considered to possibly contain injurious amount of organic compounds, and further tests should be made before approving the sand for using in concrete." The sand used in this study passed this test, its colour was lighter than the standard solution.

Table 5.5. Changes after Shale Was Immersed in Different Solutions at 80 °C

<table>
<thead>
<tr>
<th>Solutions (two weeks immersion except NaOH)</th>
<th>Colour change of the Solution After Reaction</th>
<th>State of Shale Particle After Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Tap Water</td>
<td>none</td>
<td>no change</td>
</tr>
<tr>
<td>2. Lime Water</td>
<td>slightly brown</td>
<td>no change</td>
</tr>
<tr>
<td>3. 3% NaCl</td>
<td>none</td>
<td>no change</td>
</tr>
<tr>
<td>4. 1N NaOH (1 day)</td>
<td>light brown</td>
<td>no change</td>
</tr>
<tr>
<td>4. 1N NaOH (15 day)</td>
<td>dark brown</td>
<td>soft and muddy</td>
</tr>
<tr>
<td>5. 3% NaCl + 1N Ca(OH)₂</td>
<td>slightly brown</td>
<td>no change</td>
</tr>
</tbody>
</table>

5.7.5. Composition Change of Shale Particles after Reaction

Figure 5.39 shows the composition of the shale before and after reaction with different solutions. In the figure, URS represents unreacted shale; RS represents shale after reaction with NaOH for 15 days; PRS represents shale reacted with NaOH for 1 day; and RSCa represents shale reacted with Ca(OH)₂ for 15 days. It can be seen from the bar chart that the composition of unreacted shale consists of mostly SiO₂ and Al₂O₃.
with a small amount of K₂O, CaO and FeO. However, the composition was changed after reaction with NaOH for 15 days. The SiO₂ content has dropped from 61% to 51%, and Na₂O content has increased from 0 to 9%. It is clear that during the reaction, Na⁺ ions have penetrated into shale particles while some Si ions have been dissolved and were leached out. It can also be seen in the figure that the composition of shale was not changed after sitting in Ca(OH)₂ for 15 days. This indicates that shale is only alkali-silica reactive in a strong alkali environment.

5.7.6. Chemical Composition of the Solid Substances Extracted from the Reacted Solutions and the ASR Gels found in the Mortar Samples

Table 5.6 lists the chemical composition of the solid substances extracted from four solutions after reaction for 15 days in hot 1N NaOH. S1 and S2 are two typical

<table>
<thead>
<tr>
<th>Composition %</th>
<th>Parent Solution Which Has Been Reacted With</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Shale</td>
</tr>
<tr>
<td>Na₂O</td>
<td>48.24</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>5.68</td>
</tr>
<tr>
<td>SiO₂</td>
<td>43.80</td>
</tr>
<tr>
<td>SO₃</td>
<td>2.28</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.00</td>
</tr>
<tr>
<td>CaO</td>
<td>0.00</td>
</tr>
<tr>
<td>FeO</td>
<td>0.00</td>
</tr>
</tbody>
</table>

products found in the solution that has been reacted with shale particles only. It is clearly seen that both products are silica rich. As studied by SEM photography, it is found that the product S1 is essentially a mixture of NaOH crystals and silica rich substances (Figure 5.40). Product S2 is a mixture of some aluminium rich crystals and silica rich
crystals (Figure 5.41). The solid substance extracted from the solution in which reference mortars were immersed during the ASR test had a similar composition to the substance extracted from the solution in which CSF samples were immersed during the ASR test (Table 5.6). However, their morphology seems different (Figure 5.42 and Figure 5.43). It should be mentioned that the compositions of reaction products shown in Table 5.6 and the morphology shown in SEM photos were not only the products leached out from the samples during ASR test, but a mixture of NaOH and the leached-out products. It can also be seen from Table 5.6 that the chemical composition of the substance found in the solution which reacted with RG samples contained little reaction product since about 90% of the substance is NaOH that is from the 1N NaOH solution. Figure 5.44 confirmed that the substance found in the solution is mostly NaOH crystals. This indicates that the silica rich products were not formed in the samples with RG or that these products, if produced, were not leached out.

To identify the alkali-silica gel, mortar samples were fractured after the ASR expansion test. Small pieces of the fractured surfaces were used for SEM and EDS study. It was found that some white substance was deposited in the pore bottoms of the reference mortar. From the SEM microscopy (Figure 5.45) and the analysis of the EDS spectrum (Figure 5.46), it is thought that the white substance found in the pore bottom was very likely an alkali-silica gel. Similar product was also observed in CSF samples but was not found in RG samples.

5.7.7. Amount of Evaporable Water in Mortar Samples as Influenced by ASR

Evaporation of water from mortar samples is closely related to the pore structure of the mortar. Measurements of the evaporable water content in samples after ASR testing compared with samples not subjected to the ASR test are given in Figure 5.47 and
Figure 5.48. In these two figures, the ordinate is the cumulative evaporation of water from mortar samples, the abscissa is the drying conditions (D). (The drying conditions are: D1 - air drying at room temperature for 24 hours; D2 - drying at 65 °C for 24 hours; D3 - drying at 110 °C for 24 hours; D4 - drying at 110 °C for 48 hours; D5 - drying at 110 °C for 72; D6 - drying at 110 °C for 96 hours). The evaporation curves in Figure 5.47 show that for mild drying conditions (D1, D2), about the same amount of water was removed from AR and non-AR samples. But under elevated drying temperature conditions, more water was removed from AR samples than from non-AR samples, and the amount of total evaporable water was higher for the samples that had undergone the ASR test. The samples with the above mentioned characteristics include the reference mortar and the mortar with inert fillers. Except for the CSF specimens, these samples showed higher expansion as indicated in Figure 5.37.

The evaporation curves shown in Figure 5.48 are quite different from those shown in Figure 5.47. Under mild drying conditions, less water was evaporated from the AR samples. At elevated temperature drying conditions, more water came out from the AR samples than from the non-AR samples. The amount of total evaporable water was slightly higher for the samples that experienced the ASR. The samples in this group have one thing in common: they contain admixtures which consist wholly or partly of ground fibreglass. The exception is fly ash, which has however, a composition similar to that of glass.

As the results show in Figure 5.47 and Figure 5.48, the total evaporable water content in AR samples is higher than in non-AR samples, and the additional amount of evaporable water comes mostly from the adsorbed water. It is thought that this additional amount of water could be the water adsorbed by alkali-silica gel or by the micro cracks generated by the ASR. Therefore, the difference in total evaporable water
between AR and non-AR samples, (designated as the amount of additional evaporable water - AEW) may serve as an indication of the amount of alkali-silica gel produced by the alkali-silica reaction. The relationship between AEW and ASR expansion is given in Figure 5.49. As can be seen, if the AEW is less than 1.4%, the expansion of the samples is negligible. This means that ASR did generate some alkali-silica gel in these samples, but the amount of the gel was not enough to cause significant expansion. When the AEW is over 1.4%, then the ASR expansion increased rapidly with the increase of AEW. (samples with CSF are an exception).

5.7.8. Pozzolanic Reaction and Alkali-Silica Reaction

The pozzolanic reaction is expressed by many researchers as the following [2-72] [5-5] [5-6] [5-7]:

\[
\text{SiO}_2 (s) + \text{Ca}^{++} (aq) + 2\text{OH}^- (aq) \rightarrow \text{xCaO.SiO}_2.y\text{H}_2\text{O (CSH)}
\]

The alkali-silica reaction can be expressed as following [2-72]:

\[
\text{SiO}_2 + 2\text{Na}^+(K^+) + 2\text{OH}^- \rightarrow \text{Na}_2(K_2)\text{SiO}_3.\text{H}_2\text{O}
\]

There are similarities between these two reactions. It is possible that in the first reaction some alkali metal ions can be incorporated into secondary CSH hydrates, and it is also possible that lime-alkali-silica gel will form in the second reaction when some Ca\(^{++}\) ions are incorporated. Therefore, the products from both reactions could form part of a spectrum of compositions. It has been suggested that reaction products of different chemical composition (from low viscosity gel to CSH) may be observed in the same concrete[2-72]. But secondary CSH hydrates can improve the properties of concrete.
while expansive alkali-silica gel will damage the concrete if produced in a large quantity. In the presence of mineral admixtures and under a strong alkali environment, both pozzolanic and alkali-silica reactions can take place simultaneously. However, when admixtures are present, the alkali-silica reaction is not only between the alkali and the aggregate but also between the alkali and the mineral admixtures. Therefore, the gel produced can be distributed evenly within the concrete and can be accommodated by the concrete. In addition, not all the gels produced are expansive. One important consequence of the pozzolanic reaction and the alkali-silica reaction is that both of them will reduce the alkali content in the concrete. Another consequence is that both of them will reduce the permeability of concrete, which will further reduce the free movement of alkali ions. These two consequences will reduce or prevent the potential reaction between alkalis and aggregate.

5.7.9. Effectiveness of CSF and Ground Fibreglass in Mitigating ASR

Many researchers have found that CSF is the most effective material to control ASR[5-8][2-81] but others have questioned the long term effectiveness of CSF[2-88]. In this study, it was found that ground fibreglass is more effective than CSF. As shown in Table 5.6, alkali-silica gel (low viscosity) was found in CSF samples as well as in the reference mortar, but no gel was found in glass containing samples. The AEW values in Figure 5.49 suggests that there was a considerable amount of gel produced in the CSF samples, but little in the glass bearing samples. Possible explanations are as follows:

(1). The optimum amount of admixtures to control ASR differs for every admixture. In this study, all the admixtures were used in the same amount, which may not be the optimum for all of them.
(2). The chemical compositions of CSF and fibreglass are different (Table 3.3). CSF contains mostly SiO₂. Under strong alkali conditions and at high temperatures, both pozzolanic and alkali-silica reactions are expected to take place in samples with CSF. Ground fibreglass contains not only SiO₂ but also Al₂O₃ and CaO. The presence of Al₂O₃ and CaO lowers the solubility and the rate of dissolution of silica glasses[2-72]. Once dissolved, alumina reacts instantaneously with lime[5-9]. Thus the pozzolanic reaction may dominate in the samples with ground fibreglass.

(3). The products of the pozzolanic reaction (secondary CSH) can incorporate alkali metal ions into their structure and reduce the alkalinity of the pore solution. At the same time, the secondary CSH hydrates fill the adjacent pores and reduce the permeability of concrete, consequently reducing the free movement of alkali ions. When there is a continuous supply of alkali from an outside source (as the case of accelerated mortar bar method), the latter effect is more important because it will slow down (if not stop) the supply of alkalis to concrete. The formation of alkali-silica reaction products in a small amount may also reduce the alkalinity of the pore solution and the permeability of concrete. But some of these reaction products are expansive. There is a limit to the amount that the concrete will accommodate without expanding, even when they are distributed evenly. Ideally, the alkali reaction will not result in expansive products. This appears to be the case when using ground fibreglass in which alkali-silica gel was not found. In CSF samples, the amount of alkali-silica gel produced is relatively high, but the expansion of the mortar samples is not as large (Figure 5.49). It is thought that the higher strengths of CSF samples resist the expansion pressure by the gels.
5.7.10. Effectiveness of CaCO$_3$ and the "Dilution Effect".

When CaCO$_3$ is added to concrete mixture in finely ground form, it may influence the hydration process of cement and consequently the composition of hydration products[2-12]. However, many researchers believe that CaCO$_3$ is chemically inert in concrete, and the influence of CaCO$_3$ on concrete properties is mainly physical[2-32][2-81]. With regard to ASR, the results shown in Figure 5.37 indicate that the expansion of mortar samples with CaCO$_3$ was reduced, though not as much as that of samples with other pozzolans. Since the solubility of CaCO$_3$ is very low under a strong alkali environment, it is thought that the reduced expansion by CaCO$_3$ is mainly due to the "dilution effect". That is, the addition of 10% mineral admixture to the mortar reduced the unit concentration of reactive aggregate and alkalis in the mortar samples, and therefore the ASR expansion was reduced.

5.7.11. Summary

1. Among the mineral admixtures investigated in this study, ground fibreglass was the most effective in controlling ASR expansion. The effectiveness of PSMC and PAF was comparable to that of fly ash and condensed silica fume. However, the effective component of PSMC and PAF in controlling ASR was the finely ground fibreglass. Inert fillers contained in PSMC and PAF such as carbon and calcium carbonate were not effective in controlling ASR in concrete. The lower expansion caused by these inert fillers is believed to be mainly due to the "dilution effect".

2. In the presence of pozzolanic mineral admixtures, and under a strong alkali condition, both the pozzolanic reaction and alkali silica reaction can simultaneously take place. These reactions consumed alkali ions and reduced the permeability of cement
mortar. The overall effect was to reduce the possibility of detrimental reactions between the alkali ions and the aggregate.

3. Sand containing shale in the finer sizes has occasionally found acceptable for using in concrete. This research showed that due to alkali reactivity, deterioration of concrete containing shale is to be expected unless mitigating measures are taken.

5.8. Influence of PSMC and other Mineral Admixtures on Sulphate Resistance of Cement Mortar

The influence of admixtures on sulphate resistance is given in Figure 5.50. It can be seen in the figure that CSF, fly ash and ground fibreglass are very effective in reducing the sulphate expansion. PSMC and PG are also effective but not as effective as CSF, FA and RG. With the addition of PAF, the sulphate expansion is increased. The expansion of the samples with CaCO₃ is comparable with that of reference mortar.

Sulphate attack on concrete comprises three processes:

(1) Sulphate ion diffusion into concrete mass. This is governed by the porosity and pore-size distribution in the cementitious matrix.

(2) Chemical reaction between the sulphate solution and the compounds of portland cement paste resulting in considerable expansion. The reactions involve C₃A hydrates and CH to form ettringite and gypsum respectively.

(3) Cracking of the cementitious matrix giving an increase in concrete damage.
The improvement in sulphate resistance by mineral admixtures was due to their influence on the pore structure and the Ca(OH)$_2$ content of cement mortar. As discussed in the previous sections, most mineral admixtures used in this study have refined the pore structure and increased the tortuosity of the pore system in the cement mortar. This has certainly reduced the rate at which sulphate ions penetrate into the cement mortar. In addition, pozzolanic mineral admixtures reacted with Ca(OH)$_2$ to form secondary C-S-H hydrates. As a result, the amount of Ca(OH)$_2$ available for sulph
5.9. Statistical Analysis

It is not the intention of the author to discuss the concepts of statistical analysis in
great detail in this thesis. However, to help the readers to understand this section, some
statistical concepts and terminology will be summarised at the beginning of each relevant
topic. These introductory materials closely follow the SPSS-X Statistics Guide by Marija

5.9.1. Extraction of Original Data for Analysis

As has been shown and discussed in the previous sections, eight major properties
of cement mortar involving more than 30 parameters (variables) have been investigated.
To study the interrelationship among these variables and to gain an understanding of the
experimental data, a statistical analysis is needed. As the first step, representative
experimental data have been extracted and summarised in Table 5.7. The meaning of each
variable is listed below.

(a). Pore structure related variables

<table>
<thead>
<tr>
<th>Adsor</th>
<th>Adsorption, which is an indication of the internal surface of the cement mortar.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absor10</td>
<td>Absorption of mortar samples after drying at 110 °C. The values are closely related to the total porosity of the cement mortar.</td>
</tr>
<tr>
<td>Absor65</td>
<td>Absorption of mortar samples after drying at 65 °C. The values are related to the large pore content of the cement mortar.</td>
</tr>
<tr>
<td>Variables</td>
<td>Reference</td>
</tr>
<tr>
<td>------------</td>
<td>-----------</td>
</tr>
<tr>
<td>Adsor</td>
<td>2.01</td>
</tr>
<tr>
<td>Absor65</td>
<td>8.45</td>
</tr>
<tr>
<td>Evap1</td>
<td>78.80</td>
</tr>
<tr>
<td>Evap2</td>
<td>18.56</td>
</tr>
<tr>
<td>Evap3</td>
<td>2.64</td>
</tr>
<tr>
<td>Absorate</td>
<td>1.15</td>
</tr>
<tr>
<td>Stren7</td>
<td>27.80</td>
</tr>
<tr>
<td>Stren28</td>
<td>36.10</td>
</tr>
<tr>
<td>Stren100</td>
<td>45.70</td>
</tr>
<tr>
<td>Shrink28</td>
<td>0.02</td>
</tr>
<tr>
<td>Shrinkma</td>
<td>0.18</td>
</tr>
<tr>
<td>Shrinkir</td>
<td>0.08</td>
</tr>
<tr>
<td>Wdexp</td>
<td>0.07</td>
</tr>
<tr>
<td>Wdwgain</td>
<td>8.59</td>
</tr>
<tr>
<td>Ftwloss</td>
<td>7.99</td>
</tr>
<tr>
<td>Saltscale</td>
<td>71.39</td>
</tr>
<tr>
<td>Arexp14</td>
<td>0.26</td>
</tr>
<tr>
<td>Arexp56</td>
<td>0.48</td>
</tr>
<tr>
<td>AEW</td>
<td>2.33</td>
</tr>
<tr>
<td>Sulexp66</td>
<td>0.26</td>
</tr>
</tbody>
</table>
Table 5.7(b). Standardized Data for Statistic Analysis (Z Scores)

<table>
<thead>
<tr>
<th>Variables</th>
<th>Reference</th>
<th>CSF</th>
<th>FA</th>
<th>PSMC</th>
<th>C+Ca</th>
<th>PG</th>
<th>CaCO₃</th>
<th>RG</th>
<th>PAF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsor</td>
<td>-0.39</td>
<td>1.82</td>
<td>0.01</td>
<td>-0.80</td>
<td>-0.88</td>
<td>0.20</td>
<td>-0.34</td>
<td>-1.01</td>
<td>1.39</td>
</tr>
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Evap1  Evaporation of water during the first two drying intervals. These values are related to the large pore content and the tortuosity of the cement mortar.
Evap2  Evaporation of water during the third drying interval.
Evap3  Evaporation of water during the last three drying intervals. The values are related to the finer pore content and the tortuosity of the cement mortar.
Absorate  Absorption rate of mortar samples after partial immersion in water. The values are related to the tortuosity of the pore structure of the cement mortar.

(b). Strength variables

Stren7  Compressive strength at the age of 7 days
Stren28  Compressive strength at the age of 28 days
Stren100  Compressive strength at the age of 100 days

(c). Shrinkage variables

Shrink28  Drying shrinkage of the mortar samples at the age of 28 days.
Shrinkma  Maximum shrinkage of the mortar samples after removing all the evaporable water by drying.
Shrinkir  Irreversible shrinkage of the mortar samples after re-wetting.

(d). Durability variables

Wdexp  Expansion of mortar samples caused by alternating wet-dry cycles.
Wdwgain  Weight increase of mortar samples caused by alternating wet-dry cycles.
Ftwloss  Weight loss of mortar samples caused by freezing-thawing cycles in water.
Saltscal  Weight loss of mortar samples caused by freezing-thawing cycles in 3% salt solution.
Arexp14  Expansion of mortar bars at 14 days when tested in the hot NaOH solution.
Arexp56  Expansion of mortar bars at 56 days when tested in the hot NaOH solution.
AEW     Additional evaporable water caused by ASR in the mortar samples
Sulexp66  Expansion of mortar samples after immersing in a sulphate solution for 66 weeks.

5.9.2. Correlation Analysis

5.9.2.1. Related terminology and statistical concepts

The simplest relationship between two variables is a linear equation of the form $Y = a + bX$. In practice, the experiment data rarely falls exactly along this line, but they are somewhat associated with it. It is always useful to quantify the strength of the association by calculating a summary index. One commonly used measure is the Pearson correlation coefficient, denoted by $r$, and defined as[5-10]:

$$r = \frac{\sum_{i=1}^{N}(X_i - \bar{X})(Y_i - \bar{Y})}{(N-1)S_xS_y}$$

Eq. 5.1

where $X_i$ and $Y_i$ are the individual $X$ and $Y$ values respectively, $\bar{X}$ and $\bar{Y}$ are the average values of the variables $X$ and $Y$, $N$ is the number of cases and $S_x$ and $S_y$ are the standard deviations of the two variables. The absolute value of $r$ indicates the strength of the linear relationship. The largest possible absolute value is 1, which occurs when all points fall
exactly on the line of the form $Y = a + bX$. The sign of $r$ (positive or negative) matches the sign of the slope of the best fit line.

In statistical analysis, it is often desirable to describe the relative position of an observation within a distribution. One way of doing this is to calculate its standard score of the observation. This score, sometimes called the $Z$ score\[5-11\], indicates how far above or below the mean an observation falls, in the units of standard deviations. The value is calculated by finding the difference between the value of a particular observation $X_i$ and the mean of the distribution, and then dividing this difference by the standard deviation $S$:

$$Z_i = \frac{X_i - \overline{X}}{S} \quad \text{Eq. B.2}$$

The mean of $Z$ scores is 0, and the standard deviation is 1.

5.9.2.2. Results and discussions on the correlation among variables

There are 21 parameters (variables) that have been extracted from the experimental data for analysis. These variables are listed in Table 5.7. The correlation coefficient of the data matrix was calculated and the results are given in Table 5.8. It can be seen from the table that many variables are correlated with each other. Some of these strongly correlated variables will be discussed below.

Absor65 is strongly correlated with strength parameters. The relationship is shown in Figure 5.51. However, the correlation between Absor110 and strength is not
Table 5.8. Pearson Correlation Coefficient

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<td>-0.62</td>
<td>0.95**</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stren7</td>
<td>-0.67*</td>
<td>-0.41</td>
<td>-0.68*</td>
<td>-0.65</td>
<td>0.91**</td>
<td>0.95**</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulexp66</td>
<td>0.74*</td>
<td>0.23</td>
<td>0.54</td>
<td>0.43</td>
<td>-0.71*</td>
<td>-0.68*</td>
<td>-0.78*</td>
<td>1.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wdexp</td>
<td>-0.75*</td>
<td>-0.65</td>
<td>-0.17</td>
<td>-0.17</td>
<td>0.67*</td>
<td>0.81**</td>
<td>0.76*</td>
<td>-0.56</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td>Wdwgain</td>
<td>-0.84**</td>
<td>-0.53</td>
<td>-0.07</td>
<td>-0.09</td>
<td>0.53</td>
<td>0.72*</td>
<td>0.67*</td>
<td>-0.55</td>
<td>0.96**</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Note:  ** --- 0.01 significance level (two tailed)
       * --- 0.05 significance level (two tailed)
strong (Figure 5.52). As has been discussed in the previous sections, Absor65 is a parameter related to the large pore content of the cement mortar, while Absor110 is more associated with the total porosity of cement mortar. The results in Figure 5.51 and Figure 5.52 indicate that the strength is more depend on the large pore content of the cement mortar but not on its total porosity. This is in agreement with the results by Mehta[2-33] in which the strength was found to be inversely correlated to the volume of large pores (>100 nm) of the hydrated cement paste.

Absor65 was also found to correlate with the maximum drying shrinkage (Shrinkma) and the irreversible drying shrinkage (Shrinkir) of the cement mortar. This is shown in Figure 5.53. It is generally believed that removing of adsorbed water from small pores results in shrinkage. Data shown in Figure 5.53 indicate that the irreversible shrinkage is more related to the large pore content and the tortuosity of the cement mortar.

Freezing-thawing weight loss (Ftwloss) and salt scaling weight loss (Saltscal) were found to correlate with the strength of mortar samples(Figure 5.54, Figure 5.55). This is not surprising since the higher the strength, the more it will resist the pressures generated during the F-T cycles.

In addition to strength, Ftwloss and Saltscal were also found to be correlated with Evap1 and Evap2 (Figure 5.56, Figure 5.57). Evap1 is the percentage of evaporable water removed during the first two drying intervals. These values represent the large pore content and inversely the tortuosity of the cement paste. Evap3 is the percentage of evaporable water removed during the last three drying intervals. These values represent the small pore content and inversely the tortuosity of the cement paste. Data in Figure 5.56 and 5.57 indicated that freezing-thawing weight loss (Ftwloss) and salt scaling weight
loss (Saltscal) were related to the pore structure of the cement mortar. The greater the large pore content (or the more the permeability), the greater the F-T weight loss. It is therefore thought that a denser and less permeable structure of cement paste could reduce the scaling of the cement mortar made with frost susceptible shaly sand.

Table 5.8 also shows that ASR expansion is strongly correlated to the absorption rate (Figure 5.58). Since the absorption rate indicates the ease with which water can penetrate into cement mortar, it is therefore thought that ASR expansion is strongly associated with the permeability of cement mortar. Because the alkali was supplied from an outside source in accelerated mortar bar method, so, if the permeability of mortar is low, then the alkali ions will find it difficult to move into the mortar sample. This will mitigate the ASR.

Sulphate expansion (Sulexp66) is not only correlated to the strength but also to evaporation characteristics of the cement mortar (Figure 5.59, 5.60). It is positively correlated with the large pore content (as indicated by Evap1) and inversely correlated with the fine pore content (as indicated by Evap 2 and Evap3). The data suggest that pore structure is very important to control sulphate expansion.

5.9.3. Factor Analysis

5.9.3.1. Concepts of factor analysis

Factor analysis is a statistical technique used to identify a relatively small number of factors that can be used to represent relationships among sets of many interrelated variables. The basic assumption of factor analysis is that underlying dimensions, or factors, can be used to explain complex phenomena. Observed correlation between
variables results from their sharing these factors. The goal of factor analysis is to identify
the not-directly observable factors based on a set of observable variables.

The mathematical model for factor analysis is somewhat similar to a multiple
regression equation. Each variable is expressed as a linear combination of factors that are
not actually observed. For example, variable1 might be expressed as:

\[
\text{variable1} = aF_1 + bF_2 + cF_3 + \ldots + U_i
\]

Eq. 5.3

where \(F_1, F_2, F_3\) ... are the common factors, the \(U\) is the unique factor.

The factors are inferred from the observed variables and can be estimated as linear
combinations of them. The general expression for the estimate of the \(j\)th factor \(F_j\) is

\[
F_j = \sum_{i=1}^{p} W_{ij} X_i = W_{j1} X_1 + W_{j2} X_2 + \ldots + W_{jp} X_p
\]

Eq. 5.4.[5-10]

The \(W_i\)'s are known as factor score coefficients, \(X_i\) is the standardised value of the \(i\)th
variable for the case, and \(p\) is the number of variables.

5.9.3.2. Analysis procedures and results

Factor analysis usually consist of the following procedures:

1. Calculate the correlation coefficient among all variables.
2. Extract factors necessary to represent the data.
3. Transform the factors to make them more interpretable.
4. Compute the factor scores for each case.
The correlation matrix for the 21 property variables has already been given in Table 5.8. Since one of the goals of factor analysis is to obtain "factors" that help explain the correlation, the variables must be related to each other for the factor model to be appropriate. If the correlation between variables are small, it is unlikely that they share common factors.

The goal of the factor extraction step is to determine the factors. In this study, the factors are extracted using principal components analysis[5-10]. That is linear combinations of the observed variables are formed. The first principal component is the combination that accounts for the largest amount of variance in the sample. The second principal component accounts for the next largest amount of variance and is uncorrelated with the first. Successive components explain progressively smaller portions of the total sample variance, and all are uncorrelated with each other.

It is possible to compute as many principal components as there are variables. If all principal components are used, each variable can be exactly represented by them, but nothing has been gained since there are as many factors (principal components) as variables. When all factors are included in the solution, all of the variance of each variable is accounted for, and there is no need for a unique factor in the model. The proportion of variance accounted for by the common factors, or the communality of a variable, is 1 for all the variables.

To decide how many factors are needed to represent the data, it is helpful to examine the percentage of total variance explained by each. For simplicity, all variables and factors are expressed in standardised form with a mean of 0 and standard deviation of 1. The total variance is the sum of the variance of each variable. Since there are 21
variables and each is standardised to have a variance of 1, the total variance is 21 in this study.

Table 5.9 contains the initial statistics for each factor extracted. The total variance explained by each factor is listed in the column labelled EIGENVALUE. The next column contains the percentage of the total variance attributable to each factor. For example, the linear combination formed by factor 1 has a variance of 10.75, which is 51.2% of the total variance of 21. The last column, the cumulative percentage, indicates the percentage of variance attributable to that factor and those that precede it in the table.

Table 5.9. Factors Extracted from the Analysis and the Variance Attributable to Each Factor

<table>
<thead>
<tr>
<th>Factor</th>
<th>Eigenvalue</th>
<th>Pct of Var</th>
<th>Cum Pct</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10.75</td>
<td>51.2</td>
<td>51.2</td>
</tr>
<tr>
<td>2</td>
<td>4.79</td>
<td>22.8</td>
<td>74.0</td>
</tr>
<tr>
<td>3</td>
<td>3.07</td>
<td>14.6</td>
<td>88.6</td>
</tr>
<tr>
<td>4</td>
<td>0.96</td>
<td>4.6</td>
<td>93.2</td>
</tr>
<tr>
<td>5</td>
<td>0.51</td>
<td>2.4</td>
<td>95.6</td>
</tr>
<tr>
<td>6</td>
<td>0.41</td>
<td>2.0</td>
<td>97.6</td>
</tr>
<tr>
<td>7</td>
<td>0.35</td>
<td>1.7</td>
<td>99.3</td>
</tr>
<tr>
<td>8</td>
<td>0.16</td>
<td>0.7</td>
<td>100.0</td>
</tr>
</tbody>
</table>

Table 5.9 shows that 88.6% of the total variance are attributable to the first three factors. Therefore, a model with three factors may be adequate to represent the data.

Table 5.10 contains the coefficients that relate the variables to the three factors. Each variable can be expressed by the three factors as:
Variable 1 = a₁F₁ + b₁F₂ + c₁F₃

where a₁, b₁, c₁ are coefficient between variable 1 and three factors F₁, F₂, and F₃ respectively.

Table 5.10. Coefficient Matrix Related the 21 Variables to the Three Factors

<table>
<thead>
<tr>
<th>Variables</th>
<th>Factor 1</th>
<th>Factor 2</th>
<th>Factor 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absor65</td>
<td>0.942</td>
<td>-0.248</td>
<td>-0.012</td>
</tr>
<tr>
<td>Absor110</td>
<td>0.931</td>
<td>0.112</td>
<td>-0.260</td>
</tr>
<tr>
<td>Shrinkir</td>
<td>0.924</td>
<td>-0.116</td>
<td>0.010</td>
</tr>
<tr>
<td>Shrinkma</td>
<td>0.865</td>
<td>-0.141</td>
<td>-0.033</td>
</tr>
<tr>
<td>Stren100</td>
<td>-0.722</td>
<td>0.592</td>
<td>-0.056</td>
</tr>
<tr>
<td>Evap2</td>
<td>-0.700</td>
<td>0.369</td>
<td>-0.414</td>
</tr>
<tr>
<td>Stren7</td>
<td>-0.691</td>
<td>0.639</td>
<td>-0.188</td>
</tr>
<tr>
<td>Evapl</td>
<td>0.658</td>
<td>-0.533</td>
<td>0.499</td>
</tr>
<tr>
<td>Adsor</td>
<td>0.649</td>
<td>0.623</td>
<td>-0.147</td>
</tr>
<tr>
<td>Stren28</td>
<td>-0.608</td>
<td>0.746</td>
<td>-0.083</td>
</tr>
<tr>
<td>Evap3</td>
<td>-0.500</td>
<td>0.639</td>
<td>-0.518</td>
</tr>
<tr>
<td>Sulexp66</td>
<td>0.573</td>
<td>-0.462</td>
<td>0.580</td>
</tr>
<tr>
<td>Wdexp</td>
<td>-0.118</td>
<td>0.965</td>
<td>-0.056</td>
</tr>
<tr>
<td>Wdwgain</td>
<td>0.028</td>
<td>0.948</td>
<td>-0.245</td>
</tr>
<tr>
<td>Saltscal</td>
<td>0.206</td>
<td>-0.773</td>
<td>0.516</td>
</tr>
<tr>
<td>Shrink28</td>
<td>0.108</td>
<td>-0.765</td>
<td>-0.381</td>
</tr>
<tr>
<td>Ftwloss</td>
<td>0.484</td>
<td>-0.668</td>
<td>0.245</td>
</tr>
<tr>
<td>Arexp14</td>
<td>-0.049</td>
<td>-0.046</td>
<td>0.975</td>
</tr>
<tr>
<td>Arexp56</td>
<td>-0.007</td>
<td>-0.172</td>
<td>0.963</td>
</tr>
<tr>
<td>AEW</td>
<td>-0.063</td>
<td>0.177</td>
<td>0.948</td>
</tr>
<tr>
<td>Absorate</td>
<td>-0.042</td>
<td>-0.198</td>
<td>0.873</td>
</tr>
</tbody>
</table>
5.9.3.3. Interpretation of Factors

Factor 1, The Porosity Factor

Factor 1 is believed to be the porosity factor. As can be seen in Table 5.10, factor 1 is strongly correlated with absorption and drying shrinkage of cement mortar. It is expected that as the porosity of the material increases, its absorption and drying shrinkage will also increase. This factor is also inversely correlated with strength. This is in agreement with the strength-porosity relationship (section 2.6.2.1). That is, the more porous the material, the lower the strength. Factor 1 is also correlated with the evaporation and adsorption. Both of the properties are related to the porosity of cement mortar.

Factor 2, The Fine Pore Factor

Factor 2 is associated with the wet-dry expansion (Wdexp) and wet-dry weight gain (Wdwdgain). Both of them are related to the fine pore structure of the cement mortar. This topic has been discussed in section 5.5. Factor 2 is also found to be inversely correlated with the F-T weight loss (Ftwloss) and the salt scaling weight loss (Saltscal). It seems that cement paste with a finer pore structure will be more resistant to scaling under freezing-thawing cycling.

Factor 3, The Permeability Factor

Factor 3 is associated with absorption rate (Absorate) which is a measure of the ease with which water can penetrate into the cement mortar. Factor 3 is also correlated
with ASR expansion and additional evaporable water (AEW). It has been mentioned in section 5.7 that when using the accelerated mortar bar method to test ASR expansion, the alkalis are supplied mainly from an outside source. The permeability of cement mortar is therefore very important in its influence on the results of this ASR expansion test.

5.9.3.4. Influence of Mineral Admixture on the Observed Factors.

One of the goals of factor analysis is to reduce a large number of variables to a smaller number of factors. It is desirable to estimate factor scores for each case. Recall from Section 5.9.3.1, factor scores can be estimated as a linear combination of the original variables using the equation 5.4. That is, for case \( k \), the score for the \( j \)th factor is estimated as:

\[
F_{jk} = \sum_{i=1}^{P} W_{ji} X_{ik}
\]

where \( X_{ik} \) is the standardised value of the \( i \)th variable for case \( k \) and \( W_{ji} \) is the factor score coefficient for the \( j \)th factor and the \( i \)th variable. The standardised values of all the variables for all the cases were given in Table 5.7(b). The methods for estimating factor score coefficients are a matter of mathematical derivation which were discussed in detail by Tucker [5-12] and Harman [5-13]. In this study, a commercial computer program (SPSS) was used to calculate the factor scores for different cases. The final results are given in Table 5.11. The value is standardised so that all factors have a mean of 0 and a standard deviation of 1.
Table 5.11. Factor Scores for all Cases

<table>
<thead>
<tr>
<th></th>
<th>Factor 1</th>
<th>Factor 2</th>
<th>Factor 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference</td>
<td>-0.05</td>
<td>0.10</td>
<td>1.91</td>
</tr>
<tr>
<td>CSF</td>
<td>0.11</td>
<td>2.55</td>
<td>-0.01</td>
</tr>
<tr>
<td>FA</td>
<td>-0.69</td>
<td>-0.17</td>
<td>-0.54</td>
</tr>
<tr>
<td>PSMC</td>
<td>-0.04</td>
<td>-0.33</td>
<td>0.00</td>
</tr>
<tr>
<td>C+Ca</td>
<td>-0.33</td>
<td>-0.62</td>
<td>0.57</td>
</tr>
<tr>
<td>PG</td>
<td>-0.03</td>
<td>-0.74</td>
<td>-0.79</td>
</tr>
<tr>
<td>CaCO3</td>
<td>-0.25</td>
<td>-0.60</td>
<td>0.89</td>
</tr>
<tr>
<td>RG</td>
<td>-1.16</td>
<td>-0.09</td>
<td>-1.4</td>
</tr>
<tr>
<td>PAF</td>
<td>2.45</td>
<td>-0.28</td>
<td>-0.62</td>
</tr>
</tbody>
</table>

Figure 5.61 shows the influence of mineral admixtures on the scores for factor 1. Since factor 1 is interpreted as the porosity factor, only PAF has significantly increased the porosity of cement mortar. RG and FA have slightly decreased the porosity factor, but the influence is not significant. PSMC and other mineral admixtures do not seem to have any influence on this factor.

Figure 5.62 shows the influence of mineral admixtures on the scores of factor 2. It can be seen that, only CSF increased the scores considerably while PSMC and other mineral admixtures did not show much influence on the score of this factor. Since factor 2 was interpreted as the fine pore factor, it is therefore thought that CSF is caused by far the most significant effect on pore refinement.

Figure 5.63 shows the influence of mineral admixtures on the score of factor 3. It can be seen in the figure that all the mineral admixtures have greatly reduced the score of factor 2 compared with reference. Since factor 2 was interpreted as the permeability factor, therefore, the results indicate that all admixtures have significantly reduced the
permeability of mortar samples compared to the reference mortar. Ground fibreglass seems to be the most effective material to reduce the permeability.

5.9.4. Cluster Analysis

Cluster analysis classifies cases into categories. The goal of cluster analysis is to identify homogeneous groups or clusters.

In cluster analysis, cases are grouped on the basis of their "nearness". There are many different definitions of distance and similarity. A commonly used index is the squared Euclidean distance, which is the sum of the squared differences over all of the variables.

\[
\text{Euclidean distances } = \sqrt{\sum_i (X_i - Y_i)^2} \quad \text{Eq. 5.6 [5-10]}
\]

where \(X_i\) is the ith variable of case \(X\), and \(Y_i\) is the ith variable of case \(Y\).

The dissimilarity among all groups of samples is shown in Table 5.12. The larger the coefficient, the greater the dissimilarity.

The similarity between all groups can also be illustrated by Figure 5.64. In this figure, all the groups gradually join together according to the distance among them. Samples with closest distance will be joined together in the first step, the next closest one being joined in the following step and so on. It can be seen in the figure that PSMC, C+CaCO\(_3\) and CaCO\(_3\) samples were classified into the same category. When added to cement mortar, these materials did not make significant changes to the properties as
compared to the reference sample. Fly ash and ground fibreglass were classified into a same group. There are many similarities between these two materials. When added to cement mortar, they improved many properties of the cement mortar. Condensed silica fume and pyrolysed automotive fluff (PAF) are unique materials that have great influence on the properties of cement mortar.

Table 5.12 Squared Euclidean Dissimilarity Coefficient Matrix

<table>
<thead>
<tr>
<th></th>
<th>Reference</th>
<th>CSF</th>
<th>FA</th>
<th>PSMC</th>
<th>C+Ca</th>
<th>PG</th>
<th>CaCO₃</th>
<th>RG</th>
</tr>
</thead>
<tbody>
<tr>
<td>CSF</td>
<td>77.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FA</td>
<td>37.2</td>
<td>38.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PSMC</td>
<td>21.9</td>
<td>53.8</td>
<td>13.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C+Ca</td>
<td>15.0</td>
<td>67.6</td>
<td>19.0</td>
<td>7.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PG</td>
<td>39.6</td>
<td>62.0</td>
<td>15.5</td>
<td>10.6</td>
<td>16.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaCO₃</td>
<td>8.7</td>
<td>74.7</td>
<td>22.4</td>
<td>11.9</td>
<td>5.1</td>
<td>20.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RG</td>
<td>75.7</td>
<td>34.7</td>
<td>15.1</td>
<td>36.2</td>
<td>47.1</td>
<td>37.2</td>
<td>54.5</td>
<td></td>
</tr>
<tr>
<td>PAF</td>
<td>66.9</td>
<td>123.8</td>
<td>72.6</td>
<td>45.8</td>
<td>54.0</td>
<td>45.9</td>
<td>52.1</td>
<td>111.5</td>
</tr>
</tbody>
</table>

5.9.5. Summary

1. Among all the properties studied, many of them were found to be correlated with each other. On the basis of these correlations, three important factors were extracted to represent all the properties tested in this study. These three factors were interpreted as the porosity factor, the fine pore factor and the permeability factor. The three factor model explained 88.6% of the total variance for all samples.

2. The influences of mineral admixtures on the score of the three factors depended on their individual properties. Although all the admixtures effectively reduced the
permeability of concrete, ground fibreglass was most effective among them. Condensed silica fume was very effective in refining the pore structure of cement mortar, the others had much less influence on this property. PAF increased the total porosity of cement mortar considerably, while RG and FA slightly decreased the porosity. PSMC and all other mineral admixtures did not show a significant influence on the total porosity of cement mortar.

3. All the mineral admixtures could be classified into four groups according to their influence on the properties of concrete. PSMC and its individual components were classified into the first group. Although this group of materials showed influence on certain properties of cement mortar, the overall influence was not considered significant. The second group included ground fibreglass and fly ash. These materials improved many properties of concrete. Condensed silica fume and pyrolysed automotive fluff made up the third and fourth group respectively. The influence of condensed silica fume on the properties of concrete was significant, and most of these influences lead to the improvement on the properties of cement mortar. Although PAF also had significant influence on the properties of cement mortar, most of these influences are detrimental due to the increased porosity and microcracks in the PAF samples.
Chapter 6

CONCLUSIONS

On the basis of the results and discussions given in Chapter 4 and Chapter 5, the following conclusions can be made:

1. When used as a direct addition, PSMC increased the compressive strength of cement mortar at all ages. The strength improvement at early ages was mainly due to the "physical void filling effect", and the strength improvement at later ages was mainly due to the "pozzolanic reactivity" of PSMC. The inert portion of PSMC, that is the carbon and calcium carbonate, contributed mostly to the "physical voids filling effect", while the glass portion contributed the pozzolanic reactivity.

2. In addition to strength, PSMC also mitigated the ASR expansion and improved the sulphate resistance of cement mortar. All these improvements were largely due to the pozzolanic reactivity which was contributed by the fibreglass portion of PSMC. The influence of PSMC on other properties such as frost resistance, wet-dry expansion, and drying shrinkage of cement mortar was not significant.

3. In view of the conclusions 1 and 2, it is feasible to utilise PSMC as a mineral admixture for concrete. Although from the points of material availability, uniformity and from the points of economic and technical advantages to concrete industry, there is still a distance to go to utilise PSMC in concrete in a practical way. However, from the viewpoint of waste disposal, it is certainly worthwhile to further study the use of PSMC as a mineral admixture for concrete.
4. Mineral admixtures which possess pozzolanic reactivity can change the pore structure of cement mortar. The main influences were (1) to refine the pore structure (transform large pores into small ones), (2) to make the pore system more tortuous and therefore reduced the permeability of cement mortar. CSF is a very effective material to refine the pore structure of cement mortar. Ground fibreglass and FA are effective materials to increase the tortuosity of cement mortar though the pore refinement effect of these two materials is not as great as that of CSF. The influence of inert fillers on the pore structure of cement mortar was not significant.

5. Most mineral admixtures do not have significant influence on the long term drying shrinkage of cement mortar even though some of them showed higher shrinkage at the age of 28 days. For mortar samples containing fly ash and the samples containing ground fibreglass, the long term drying shrinkage and the irreversible drying shrinkage were lower as compared to that of references.

6. Mortar samples with CSF and RG showed higher wet-dry expansion than that of reference mortars. Other mineral admixtures did not seem to have a significant influence on this property. It seems that the samples with a more sophisticated pore structure were more susceptible to wet-dry damage.

7. Cement mortar made with shaly sand was prone to scaling under freezing-thawing cycling. The scaling of mortar samples was aggravated when freezing and thawing took place in a salt solution. However, the scaling resistance of mortar samples was significantly improved by the addition of CSF and RG. The improvement was partially due to the increase in mortar strength by CSF and RG. It also seemed that a denser structure of hydrated cement paste was more resistant to scaling under F-T cycles.
8. All the mineral admixtures investigated in this study reduced the ASR expansion of cement mortar. Among them, ground fibreglass was the most effective in controlling ASR expansion. The effectiveness of PSMC and PAF was comparable to that of fly ash and condensed silica fume. However, the effective component of PSMC and PAF in controlling ASR was the finely ground fibreglass. Inert fillers contained in PSMC and PAF such as carbon and calcium carbonate were not effective in controlling ASR in concrete. The lower expansion caused by these inert fillers is believed to be mainly due to the "dilution effect". The mechanism by which mineral admixtures reduce the ASR expansion is believed to be the pozzolanic reaction which reduced the permeability of cement mortar. In addition, the reaction products entrapped alkali ions and prevented them from reacting with the aggregate. It was also found in this study that shale particles were alkali silica reactive. Shale is known to cause deterioration of concrete due to its poor physical properties. Results from this research indicated that the deterioration of concrete containing shale may also be partly due to its alkali reactivity.

9. CSF, FA and ground fibreglass improved the sulphate resistance of cement mortar significantly. The effect of PSMC and PG on sulphate resistance was moderate. Inert fillers such as CaCO\textsubscript{3} did not have much influence on sulphate resistance. PAF increased the porosity of cement mortar and consequently, decreased its sulphate resistance. The influence of mineral admixtures on sulphate resistance of cement mortar largely depended on their influence on the pore structure and the Ca(OH)\textsubscript{2} content.

10. From the statistical analysis, three factors were extracted to represent the experimental data from this study. These factors were interpreted as the porosity factor, the fine pore factor and the permeability factor. The influences of mineral admixtures on the score of the three factors depended on their individual properties. Although all the admixtures effectively reduced the permeability factor of concrete, ground fibreglass was
most effective among them. Condensed silica fume significantly increased the fine pore factor indicating that it was very effective in refining the pore structure of cement mortar; the others did not seem to have much influence on this property. PAF increased the score of the porosity factor while RG and FA slightly decreased it. PSMC and all other mineral admixtures did not show significant influence on the porosity factor.

11. From the cluster analysis, all the mineral admixtures could be classified into four groups according to their influence on the properties of concrete. PSMC and its individual components were classified into the first group. This group of materials showed improvement on certain properties of cement mortar, but the overall influence was not considered significant. The second group included ground fibreglass and fly ash. There are similarities between these two materials. They improved many properties of concrete. Condensed silica fume and pyrolysed automotive fluff individually made up the third and fourth group respectively. The influence of condensed silica fume on the properties of concrete was significant, and most of these influences lead to the improvement on the properties of cement mortar. Although PAF also had significant influence on the properties of cement mortar, most of these influences were detrimental due to the increased porosity and microcracks in the PAF samples.
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Mehta's Classification

<table>
<thead>
<tr>
<th>gel pore</th>
<th>capillary voids</th>
<th>entrained air bubbles</th>
<th>entrapped air voids</th>
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Powers Classification

<table>
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<th>capillary pores</th>
<th>air voids</th>
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IUPAC

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<tr>
<th>micro</th>
<th>meso</th>
<th>macro</th>
<th>air voids</th>
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D3 - drying at 110 °C for 24 hours,
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A-1. Mortar mix procedure

The mix procedure of mortar was done according to ASTM C 305[3-5] as follows:

(1). Place the dry paddle and the dry bowl in the mixing position in the mixer.
(2). Place all the mixing water and superplastisizer in the bowl.
(3). Add the cement to the water; then start the mixer and mix at the slow speed for 30 seconds.
(4). Stop the mixer, add the entire quantity of sand and the mineral admixture, mix at slow speed for 30 seconds.
(5). Change to medium speed and mix for 30 seconds.
(6). Stop the mixer and let the mortar stand for 1.5 min. During this interval, quickly scrape down into the batch any mortar that may have collected on the side of the bowl.
(7). Finish by mixing for 1 min. at medium speed.
(8). In any case requiring a remixing interval, scrape any mortar adhering to the side of the bowl with the scraper into the batch prior to remixing.

A-2. Procedures used to cast 50 mm cube samples

The 50 mm cube samples were cast using recommended procedures which was described below[3-6]:

Start molding the specimens within a total elapsed time of not more than 2 min and 30 s after completion of the original mixing of the mortar batch. Place a layer of
mortar about 15 mm (approximately one half of the depth of the mold) in all of the cube compartments. Tamp the mortar in each cube compartment 32 times in about 10 seconds in 4 rounds. When the tamping of the first layer in all of the cube compartments is completed, fill the compartments with the remaining mortar and then tamp as specified for the first layer. On completion of the tamping, the tops of all cubes should extend slightly above the tops of the molds. Bring in the mortar that has been forced out onto the tops of the molds with a trowel and smooth off the cubes by drawing the flat side of the trowel once across the top of each cube at right angles to the length of the mold. The samples with their molds is then covered with plastic film for 24 hours before demolding. After demolding, the samples is cured in saturated lime water. The 50-mm cube specimens were used for strength testing.

A-3. Flow Test[3-7][2-2]

Apparatus:

The flow table consists essentially of a brass-top table, 762 mm in diameter, mounted so that it can be jolted by a drop of 13 mm. A mold in the shape of a frustum of a cone, much more squat than the slump cone, is used for hold fresh mortar sample.

Test Procedure:

(1) Wipe the flow-table clean and dry, and place the flow mold at the centre.
(2) Place a layer of mortar about 25 mm in thickness in the mold and tamp 20 times with the tamper. Then fill the mold with mortar and tamp as specified for the first layer.
(3) Cut off the mortar to a plane surface, flush with the top of the mold, by drawing the straight edge of a trowel with a sawing motion across the top of the mold.
(4) Wipe the table top clean and dry. Lift the mold away from the mortar. Immediately jolt (drop) the table 25 times in 15 seconds.

(5) Measure the average diameter of the spread mortar.

(6) Calculate the flow as the percentage increase in the average diameter of the spread mortar (D in inches) over the original diameter of the base (10 in).

\[
\text{Flow} = \frac{D - 10}{10} \times 100
\]

A-4. Compressive strength test

The compressive strength of mortar was tested according to ASTM C 109 - 88[3-6]. The test consists of following procedures:

(1). Remove the samples from the storage tank at the specific date of curing, wipe each specimen to a surface-dry condition, and remove any loose sand grains or incrustations from the faces that will be in contact with the bearing blocks of the testing machine.

(2). Carefully place the specimen in the testing machine below the centre of the upper bearing block, make sure the spherically seated block is free to tilt.

(3) Apply load at such a rate that the maximum load will be reached in not less than 20 nor more than 80 seconds from start of loading. Make no adjustment in the controls of the testing machine while a specimen is yielding before failure.

(4) Record the total maximum load indicated by the testing machine, and calculate the compressive strength.

(5) In determining the compressive strength, do not consider specimens that are manifestly faulty, or that give strengths differing by more than 10% from the average value of all test specimens made from the same sample and tested at the same period.
A-5. Absorption test

Absorption was tested according to ASTM C642-90[3-9]. The detail procedures are as follows:

(1) Dry the samples in an oven at a temperature of 110 °C, weigh the samples every 24 hours until the difference between any two successive weights is less than 0.5% of the lowest weight obtained. Designate this last weight A.

(2) Immerse the dried samples in water at approximately 21 °C for not less than 48 h, weigh the samples and until two successive weightings of the surface-dried sample at intervals of 24 h show an increase in weight of less than 0.5% of the heavier weight. Designate the final weight after immersion B.

(3) Boil the samples in water for 5 hours and allow them to cool by natural loss of heat for not less than 14 hours to a temperature of 20 to 25 °C. Remove the surface moisture and weigh the specimen. Designate this weight C.

(4) Suspend the specimen, after immersion and boiling, by a wire and weigh in water. Designate this weight D.

(5) By using the weights determined in accordance with the procedures described above, make the following calculations:

Absorption after immersion, \( \% = \frac{(B - A)}{A} \times 100 \)

Absorption after boiling, \( \% = \frac{(C - A)}{A} \times 100 \)

Bulk specific gravity, \( \% = \frac{A}{(C - D)} \times 100 = g1 \)
Apparent specific gravity, \( \% = \frac{A}{(A - D)} \times 100 = g_2 \)

Volume of permeable pore space (voids), \( \% = \frac{(g_2 - g_1)}{g_2} \times 100 \)

or \( \% = \frac{(C - A)}{(C - D)} \times 100 \)

where:

\( A \) = mass of oven-dried sample in air, (grams)

\( B \) = mass of surface-dry sample in air after immersion,

\( C \) = mass of surface-dry sample in air after immersion and boiling,

\( D \) = mass of sample in water after immersion and boiling,

\( g_1 \) = bulk specific gravity, dry,

\( g_2 \) = apparent specific gravity.

A-6. Drying shrinkage test

Testing of the drying shrinkage followed the ASTM C 596[3-11] and C 157[3-12].

The procedures are summarised as follows:

1. After curing the specimens in lime water for 48 hours, remove the specimens from the curing tank, wipe off the surface water and immediately obtain a length comparator reading for each specimen. Designate this length as \( L_0 \).

2. Put the specimens in containers where the relative humidity is kept at 80 ± 2 %.

3. Measure the length of each specimen after 4, 11, 18, and 25 days of storage at the relative humidity of 80 %. Designate these readings as \( L_r \).

4. At the age of 30 days, take the specimens out of the container and immediately obtain a length and weight reading. Designate these readings as \( L_{30} \) and \( W_{30} \). Then, place the samples in a room with uncontrolled environment.
(5). Record the length and weight of each specimen for 200 days with frequent measurement at the beginning and fewer measurements when the change in length and weight becomes minimal. During the testing period, record the room temperature and relative humidity.

(6). Calculate the linear shrinkage and water loss of each specimen at each age of air drying as following:

\[
\text{Shrinkage} = \frac{L_0 - L_i}{L_0} \times 100
\]

\[
\text{Water loss} = \frac{W_{30} - W_i}{W_{30}} \times 100
\]

A-7. Test for sulphate resistance

Sulphate resistance of cement mortar was tested according to ASTM C 1012 - 89 [3-23]. The procedure is summarised as follows:

(1). Prepare the sulphate solution so that every liter of solution contains 50 g of \( \text{Na}_2\text{SO}_4 \) and the pH value of the solution is within 6.0 to 8.0.

(2). After demolding, the samples were cured in lime water until the strength of the samples reaches 20 MPa. (the samples were cured for 7 days in lime water in this study).

(3). At the age of 7 days, take the samples out of the lime water and obtain an initial length reading \( (L_o) \) for each sample. Then immerse the samples in the previously prepared sulphate solution.

(4). Measure the length of samples at 1, 2, 3, 4, 8, 13, and 15 weeks and then every month after the bars are placed in the sulphate solution. When the expansion is changing
rapidly at any period in the test, the interval between readings should be adjusted so that it is short enough to permit observing and reporting the behaviour of the bars.

(5). Use previously prepared 0.5 M H₂SO₄ solution to adjust the pH value of the sulphate solution to approximately 7 after every measurement.

(6). Calculate the length change at any age as follows

\[ dL = \frac{L_i - L_o}{L_o} \times 100 \]

where:

- \( dL \) = Change in length at \( x \) age, \( \% \),
- \( L_i \) = Gage length at the age of \( i \),
- \( L_o \) = Initial gage length.
Appendix B

Statistical Concepts and Terminology Related to the Student's t Test - the Mean Comparison

The materials briefly reviewed here closely follow the book by Mason and Lind[5-11]. Interested readers should consult the source for more detailed information.

1. Related Terminology

Hypothesis is "a statement about the value of a population parameter"

Hypothesis testing is "a procedure based on sample evidence and probability theory used to determine whether the hypothesis is a reasonable statement and should not be rejected, or is unreasonable and should be rejected."

Null hypothesis is "a tentative assumption made about the value of a population parameter. Usually, it is a statement that the population parameter has a specific value."

Alternate Hypothesis is "a statement that will be accepted if our sample data provide us with ample evidence that the null hypothesis is false."

Level of significance is "the risk we assume of rejecting the null hypothesis when it is actually true."

Critical value is "a number that is the dividing point between the region of acceptance and the region of rejection"
2. Procedures used to compare the means of different mortar samples

One of the objectives of this study is to compare the influence of eight different mineral admixtures on the properties of cement mortar. It is therefore desirable to know whether the influences by these mineral admixtures are significant or not. Mean comparison is one of the statistical methods which can be used for this purpose.

There are four steps in this mean comparing procedure:

Step 1. The Null Hypothesis

The null hypothesis is that there is no difference between the mean property of the control mortar (e.g. compressive strength) and that of the mortars with mineral admixtures. The alternative hypothesis is that there is a significant difference between the properties of the control mortar and that of the mortars with mineral admixtures. Symbolically:

\[ H_0 : \mu_1 = \mu_2 \]
\[ H_1 : \mu_1 \neq \mu_2 \]

Step 2. The Level of Significance

The 0.05 level of significance has been chosen in this study. This is to say that the probability of committing an error (the probability of rejecting the null hypothesis \( H_0 \), when it is actually true) is 0.05.

Step 3. The Statistical Test

In this study, three samples were used for testing each property of a mortar. Because the number of the samples is small, the student's t test is more appropriate than the z test.
The formula for calculate t is:

\[
t = \frac{\bar{X}_1 - \bar{X}_2}{\sqrt{\left(\frac{n_1 - 1}{n_1} S_1^2 + \frac{n_2 - 1}{n_2} S_2^2\right)\left(\frac{1}{n_1} + \frac{1}{n_2}\right)}}
\]

\[5.11\]

with \( n_1 + n_2 - 2 \) degrees of freedom, where:

\( \bar{X}_1 \) is the arithmetic mean of the property of the control mortar.

\( \bar{X}_2 \) is the arithmetic mean of the property of the mortars with different mineral admixtures.

\( n_1 \) is the number of samples of the control mortar tested for each property.

\( n_2 \) is the number of samples of the mortar with mineral admixtures.

\( S_1^2 \) is the variance of the samples of the control mortar.

\( S_2^2 \) is the variance of the samples of the mortars with mineral admixtures.

\[
S_1^2 = \frac{\sum X_1^2 - (\sum X_1)^2}{n_1 - 1}
\]

\[
S_2^2 = \frac{\sum X_2^2 - (\sum X_2)^2}{n_2 - 1}
\]

The calculated t values for selected properties are given in Table B-1 and Table B-2.

Step 4. The Judgement Criteria

For the 0.05 level of significance, and 4 degrees of freedom (\( n_1 + n_2 - 2 = 3 + 3 - 2 = 4 \)), the critical value of t was found to be 2.776 [5.11 Appendix F]. So, if the calculated t values fall within the region between plus
and minus 2.776, the null hypothesis is accepted. It will be concluded that the influence of mineral admixtures on the properties of cement mortar is not significant. If the computed absolute t values are greater than 2.776, it will be then concluded that the mineral admixtures have significantly influence the properties of cement mortar.
Table B1. Results from the Student's t Test (Program A)

<table>
<thead>
<tr>
<th>Sample Composition</th>
<th>Strength 28day</th>
<th>Strength 7day</th>
<th>Absor110 28day</th>
<th>Absor65 28day</th>
<th>Absor110 7day</th>
<th>Absor65-7day</th>
</tr>
</thead>
<tbody>
<tr>
<td>b1. 5% PSMC</td>
<td>-1.18</td>
<td>-2.54</td>
<td>0.47</td>
<td>2.31</td>
<td>-0.14</td>
<td>3.14</td>
</tr>
<tr>
<td>b2. 10% PSMC</td>
<td>-0.94</td>
<td>-2.58</td>
<td>-1.17</td>
<td>2.08</td>
<td>0.27</td>
<td>4.85</td>
</tr>
<tr>
<td>b3. 15% PSMC</td>
<td>-1.79</td>
<td>-3.48</td>
<td>1.83</td>
<td>3.48</td>
<td>1.81</td>
<td>10.19</td>
</tr>
<tr>
<td>c1. 1.75% PG</td>
<td>0.55</td>
<td>-0.65</td>
<td>-4.98</td>
<td>-2.53</td>
<td>-2.13</td>
<td>-2.31</td>
</tr>
<tr>
<td>c2. 3.5% PG</td>
<td>-0.64</td>
<td>-0.37</td>
<td>-4.88</td>
<td>0.70</td>
<td>-1.93</td>
<td>-0.99</td>
</tr>
<tr>
<td>c3. 5.25% PG</td>
<td>-1.07</td>
<td>-1.25</td>
<td>-2.59</td>
<td>2.00</td>
<td>-1.11</td>
<td>1.22</td>
</tr>
<tr>
<td>d1. 3.25% C+Ca</td>
<td>-0.31</td>
<td>-2.05</td>
<td>-4.90</td>
<td>0.17</td>
<td>-2.08</td>
<td>0.71</td>
</tr>
<tr>
<td>d2. 6.5% C+Ca</td>
<td>-0.63</td>
<td>-2.89</td>
<td>-6.27</td>
<td>0.73</td>
<td>-0.94</td>
<td>4.38</td>
</tr>
<tr>
<td>d3. 9.75% C+Ca</td>
<td>-0.20</td>
<td>-4.28</td>
<td>-8.02</td>
<td>-0.44</td>
<td>-0.69</td>
<td>5.60</td>
</tr>
<tr>
<td>e1. 1.75% RG</td>
<td>1.36</td>
<td>0.56</td>
<td>-6.45</td>
<td>-1.28</td>
<td>-2.34</td>
<td>-2.01</td>
</tr>
<tr>
<td>e2. 3.5% RG</td>
<td>1.13</td>
<td>0.15</td>
<td>-6.71</td>
<td>0.88</td>
<td>-1.40</td>
<td>5.26</td>
</tr>
<tr>
<td>e3. 5.25% RG</td>
<td>-0.65</td>
<td>-2.65</td>
<td>-8.29</td>
<td>3.04</td>
<td>-1.11</td>
<td>13.92</td>
</tr>
<tr>
<td>f1. 2.75% CaCO₃</td>
<td>0.57</td>
<td>-1.40</td>
<td>-10.46</td>
<td>-3.44</td>
<td>-1.96</td>
<td>-1.70</td>
</tr>
<tr>
<td>f2. 5.5% CaCO₃</td>
<td>0.63</td>
<td>-1.96</td>
<td>-9.19</td>
<td>-3.82</td>
<td>-1.88</td>
<td>-1.53</td>
</tr>
<tr>
<td>f3. 8.25% CaCO₃</td>
<td>-0.31</td>
<td>-1.89</td>
<td>-4.00</td>
<td>-1.80</td>
<td>-0.64</td>
<td>1.01</td>
</tr>
</tbody>
</table>

Note: The critical t value is 2.776 at 0.05 level of significance.
Table B2. Results from the Student's t Test (Program B)

<table>
<thead>
<tr>
<th>Properties</th>
<th>Reference Figure</th>
<th>CSF</th>
<th>FA</th>
<th>PSMC</th>
<th>C+Ca</th>
<th>PG</th>
<th>CaCO3</th>
<th>RG</th>
<th>PAF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption</td>
<td>fig.5-1</td>
<td>-5.10</td>
<td>-0.92</td>
<td>1.06</td>
<td>1.36</td>
<td>-1.16</td>
<td>-0.17</td>
<td>2.02</td>
<td>-4.99</td>
</tr>
<tr>
<td>Absorption (110 °C dry)</td>
<td>fig.5-3</td>
<td>-5.18</td>
<td>1.64</td>
<td>0.61</td>
<td>1.55</td>
<td>-1.34</td>
<td>1.90</td>
<td>0.00</td>
<td>-30.24</td>
</tr>
<tr>
<td>Absorption (65 °C dry)</td>
<td>fig.5-6</td>
<td>38.50</td>
<td>16.13</td>
<td>15.62</td>
<td>25.67</td>
<td>20.11</td>
<td>7.50</td>
<td>32.81</td>
<td>-50.74</td>
</tr>
<tr>
<td>Absorption (65 °C dry)</td>
<td>fig.5-7</td>
<td>7.53</td>
<td>3.83</td>
<td>1.73</td>
<td>3.07</td>
<td>3.33</td>
<td>0.08</td>
<td>10.92</td>
<td>-28.68</td>
</tr>
<tr>
<td>Sulphate Exp.(66 weeks)</td>
<td>fig.5-50</td>
<td>7.92</td>
<td>8.19</td>
<td>5.54</td>
<td>1.07</td>
<td>5.31</td>
<td>-0.61</td>
<td>7.90</td>
<td>-1.49</td>
</tr>
<tr>
<td>AR Expansion (56 days)</td>
<td>fig.5-37</td>
<td>6.43</td>
<td>6.44</td>
<td>5.84</td>
<td>3.40</td>
<td>6.42</td>
<td>2.32</td>
<td>7.77</td>
<td>6.29</td>
</tr>
<tr>
<td>AR Expansion (14 days)</td>
<td>fig.5-37</td>
<td>8.17</td>
<td>8.45</td>
<td>8.77</td>
<td>5.93</td>
<td>7.07</td>
<td>4.95</td>
<td>11.88</td>
<td>8.97</td>
</tr>
<tr>
<td>Salt Scaling (15 cycles)</td>
<td>fig.5-34</td>
<td>29.23</td>
<td>7.30</td>
<td>1.77</td>
<td>-6.92</td>
<td>0.24</td>
<td>-9.22</td>
<td>26.48</td>
<td>2.35</td>
</tr>
<tr>
<td>F-Tw. loss(100 cycles)</td>
<td>fig.5-31</td>
<td>5.54</td>
<td>1.40</td>
<td>-0.13</td>
<td>-7.82</td>
<td>-1.76</td>
<td>-1.05</td>
<td>4.33</td>
<td>-2.76</td>
</tr>
<tr>
<td>F-T Exp. (65 cycles)</td>
<td>fig.5-29</td>
<td>-2.17</td>
<td>1.24</td>
<td>-0.32</td>
<td>-1.17</td>
<td>-1.91</td>
<td>1.39</td>
<td>0.78</td>
<td>1.47</td>
</tr>
<tr>
<td>Wet-Dry w. gain</td>
<td>fig.5-28</td>
<td>-2.03</td>
<td>0.61</td>
<td>1.13</td>
<td>0.63</td>
<td>1.20</td>
<td>0.95</td>
<td>-0.90</td>
<td>2.51</td>
</tr>
<tr>
<td>Wet-Dry Exp.(14 cycles)</td>
<td>fig.5-27</td>
<td>-11.47</td>
<td>0.59</td>
<td>0.44</td>
<td>0.31</td>
<td>0.54</td>
<td>1.65</td>
<td>-1.46</td>
<td>1.88</td>
</tr>
<tr>
<td>Shrinkage (irreversible)</td>
<td>fig.5-25</td>
<td>0.48</td>
<td>1.44</td>
<td>-0.62</td>
<td>0.11</td>
<td>-2.11</td>
<td>-0.41</td>
<td>1.54</td>
<td>-3.32</td>
</tr>
<tr>
<td>Shrinkage (maximum)</td>
<td>fig.5-25</td>
<td>-0.30</td>
<td>1.70</td>
<td>-1.20</td>
<td>0.17</td>
<td>-2.20</td>
<td>0.13</td>
<td>1.50</td>
<td>-5.57</td>
</tr>
<tr>
<td>Shrinkage (28 days)</td>
<td>fig.5-25</td>
<td>0.40</td>
<td>-0.21</td>
<td>-0.44</td>
<td>0.07</td>
<td>-1.15</td>
<td>-0.78</td>
<td>-0.62</td>
<td>-0.76</td>
</tr>
<tr>
<td>Strength (240 days)</td>
<td>fig.5-17</td>
<td>-3.90</td>
<td>-1.89</td>
<td>-3.13</td>
<td>-2.99</td>
<td>-0.14</td>
<td>-0.57</td>
<td>-6.18</td>
<td>2.52</td>
</tr>
<tr>
<td>Strength (100 days)</td>
<td>fig.5-17</td>
<td>-3.43</td>
<td>-0.56</td>
<td>-1.57</td>
<td>-1.06</td>
<td>1.53</td>
<td>0.35</td>
<td>-3.37</td>
<td>4.05</td>
</tr>
<tr>
<td>Strength (28 days)</td>
<td>fig.5-17</td>
<td>-21.34</td>
<td>0.05</td>
<td>-0.66</td>
<td>-0.32</td>
<td>2.11</td>
<td>-0.16</td>
<td>-10.05</td>
<td>8.48</td>
</tr>
<tr>
<td>Strength (7 daysa)</td>
<td>fig.5-17</td>
<td>-5.08</td>
<td>-1.74</td>
<td>-0.71</td>
<td>-1.84</td>
<td>-0.41</td>
<td>-1.07</td>
<td>-3.16</td>
<td>2.48</td>
</tr>
<tr>
<td>Evap. (interval 1&amp;2)</td>
<td>fig.5-10</td>
<td>29.46</td>
<td>15.16</td>
<td>5.89</td>
<td>6.07</td>
<td>14.08</td>
<td>0.32</td>
<td>27.55</td>
<td>-10.22</td>
</tr>
<tr>
<td>Evap. (interval 4-6)</td>
<td>fig.5-12</td>
<td>-38.99</td>
<td>-20.51</td>
<td>-3.05</td>
<td>-2.59</td>
<td>-12.56</td>
<td>1.49</td>
<td>-68.24</td>
<td>9.77</td>
</tr>
</tbody>
</table>

Note: Critical t value is 2.776 at 0.05 level of significance
SIGNIFICANT CONTRIBUTIONS OF THIS RESEARCH

From the viewpoint of waste recycling:

* This research is an original work to investigate the feasibility of utilisation of PSMC in concrete. The results have indicated that using the waste solid residuals of pyrolysis as a concrete admixture is an alternative method to solving the waste problem of fibreglass reinforced plastics.

* For the first time, PAF has been studied for use in concrete as a mineral admixture. Though the results show some negative effects on the properties of cement mortar, the data are useful as reference for further research on this topic.

From the viewpoint of concrete technology:

* This research studied the influence of a broad variety of mineral admixtures on the properties of cement mortar. Through comparison with each other, the mechanisms by which mineral admixtures influence the properties of cement mortar has been well explained.

* This research studied the influence of mineral admixtures on the overall properties of cement mortar including pore structure, strength, durability and drying shrinkage.

* This research explained the mechanisms by which PSMC influences the properties of cement mortar.
* The ease with which water is evaporated from mortar samples was found to be closed related to the pozzolanity of the mineral admixtures used. This property was also found to be correlated with many other properties of cement mortar.

* Ground fibreglass has been found to be a very effective additive to improve the properties of cement mortar.

* This research is the first to find shaly sand to be alkali-silica reactive, and also that the ASR expansion can be significantly reduced by using pozzolanic materials such as ground fibreglass and CSF.
RECOMMENDATIONS FOR FURTHER WORK

The following recommendations are made for further research on this topic:

1. Study the influence of different percentage of PSMC and other mineral admixtures (more mix proportions) on the overall properties of cement mortar.

2. Study the influence of PSMC on the properties of cement mortar when used as partial cement replacement

3. Investigate the influence of PSMC on the properties of concrete

4. Study the composition of PAF and the abnormal expansive reaction with cement

5. More studies on using ground fibreglass in concrete.

PREVIOUS PUBLICATIONS ON THIS TOPIC BY THE AUTHOR


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