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Calcium Sulfoaluminate Cement as Binder for Structural Concrete

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ABSTRACT

The use of calcium sulfoaluminate (CSA) cement as a concrete material can save energy by 25% and reduce CO_2 emissions by 40%. The potential of using ggbs, pfa, bottom ash, pyrite ash and other by-product and waste materials to produce the CSA cement can result in further environmental benefits.

The research undertaken in this investigation aimed to explore the potential of CSA cement as the main binding material for structural grade concrete, identify the limitation of this material in this context and suggest possible applications for the resulting concrete. The experimental study covered a number of variables, anhydrite content, OPC and lime inclusion, water/cement ratio and curing regimes. The investigation encompassed the preparation of CSA cement in the laboratory and the use of a commercially produced CSA. The systems investigated included paste specimens prepared with laboratory produced CSA and commercially manufactured CSA and concrete specimens prepared with the commercially manufactured CSA cement. The investigation in paste included hydration product identification using X-ray diffractometry and scanning electron microscopy, expansion and compressive strength development. Setting time of CSA cement paste was determined using samples made with the commercially manufactured CSA cement. The properties of fresh and hardened concrete investigated were setting time, workability using both slump test and Tattersall's two-point test, expansion, compressive strength, indirect tensile strength, flexural strength, oxygen permeability, water absorption and rapid chloride permeability.

The research carried out in this investigation on CSA cement paste established that ettringite was the main product of hydration. The hydration reaction occurred at a fast rate, with hydration being almost complete within a week after casting. Formation of ettringite as a result of CSA and anhydrite hydration did not cause expansion but in the presence of calcium hydroxide in the system, resulted in expansion. In systems where expansion was evident after long-term water storage, it is suggested that this had resulted from the ettringite imbibing water and expanding. This expansion was found to be controlled by the presence of internal constraints, such as unhydrous particles or aggregates (in the case of concrete). The use of low water/cement ratio and the resulting low water absorption can further reduce such expansion.

Concrete workability was improved in CSA cement and anhydrite systems over that of control OPC concrete resulting in lower water demand. The use of OPC as cement replacement in CSA concrete adversely affected the workability and accelerated the initial setting time. The compressive and flexural strength of concrete made with CSA cement and anhydrite were considerably superior to those of control OPC concrete but, in general, were comparable with respect to their indirect tensile strengths. However, compressive strength was found to degrade by 10-20% with prolonged water storage and the OPC, as cement replacement, did not contribute significantly to strength. The need for water for CSA cement hydration was generally higher than the mixing water required for workability. As a consequence, CSA concrete is expected to have lower capillary porosity than OPC concrete. This fact was manifested in the lower water absorption value found for CSA concrete. High oxygen permeability found for CSA concrete and the inconclusive results of the rapid chloride permeability test suggest that further research into the durability performance and durability related properties is required. The high early-age flexural strength of CSA concrete is an advantage for applications in rigid pavements and pre-stressed concrete. The low pH of CSA concrete is another advantage when glass or vegetal fibres are used. The concrete, however, needs to be of low permeability to safeguard against steel corrosion.

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List of Abbreviations

ASTM = American Society for Testing and Materials
ABC = Activated Belite Cement
BS = British Standard
CSA = Calcium Sulfoaluminate
CSH = Calcium Silicate Hydrate
DoH = Degree of Hydration
DTA = Differential Thermal Analysis
FAC =Ferroaluminate Cement
LSF = Lime Saturation Factor
OPC = Ordinary Portland Cement
PC = Portland Cement
XRD =X-Ray Diffraction
SEM = Scanning Electron Microscopy
TEM = Transmission Electron Microscopy
SAB = Sulfoaluminate Belite
SAC = Sulfoaluminate Cement
pfa = pulverised fuel ash
ggbfs = granulated blastfurnace slag
w/cm = water/cementitious

List of Chemical Notations

Compounds:	Notation	
	Chemistry	Cement
Oxides:		
Calcium dioxide (Lime)	CaO	C
Silicon oxide	SiO_2	S
Alumina oxide	Al_2O_3	A
Iron oxide	Fe_2O_3	F
Sodium oxide	Na_2O	N
Sylfur oxide	SO_3	$\overline{S}$
Water	H_2O	H
Carbon dioxide	CO_2	$\overline{C}$
Cement Compounds:		
Tricalcium silicate (alite)	$3CaO.SiO_2$	C_3S
Dicalcium silicate (belite)	$2CaO.SiO_2$	C_2S
Tricalcium aluminate	$3CaO. Al_2O_3$	C_3A
Tetracalcium aluminoferrite	$4CaO.Al_2O_3.Fe_2O_3$	C_4AF
Calcium aluminate	$3CaO. Al_2O_3$	CA
Calcium sulfoaluminate (Klein's compound)	$4CaO.Al_2O_3.3SO_3$	$C_4A_3\overline{S}$
Anhydrite	$CaSO_4$	$C\overline{S}$
Gypsum	$CaSO4.2H_2O$	$C\overline{S}H_2$
Gehlenite	$2CaO.Al_2O_3.SiO_2$	C_2AS
Hydration Products:		
Calcium Silicate Hydrate	$3CaO.2SiO_2.H_2O$	CSH
Calcium Hydroxide (Porlandite)	$Ca(OH)_2$	CH
Ettringite (AFt)	$6CaO.Al_2O_3.3SO_3.32H_2O$	$C_6A\overline{S}_3H_{32}$
Monosulfate (Afm)	$4CaO.Al_2O_3.SO_3.10H_2O$	$C_4A\overline{S}H_{10}$
Aluminate Hydroxide (Gibbsite)	$Al(OH)_3$	AH_3
U-phase	$4CaO.0.9Al_2O_3.1.1SO_3.0.5Na_2O\ 16H_2O$	$C_4A_{0.9}\overline{S}_{1.1}N_{\cdot 0.5}H_{10}$
Stratlingite	$2CaO.Al2O_3.SiO_2.8H_2O$	C_2ASH_8

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I

INTRODUCTION

1.1 Background

The increasing concern of global warming effects on living creatures on this planet has become a serious issue leading to the efforts aimed at reducing carbon dioxide (CO_2) emissions to the atmosphere. In the concrete industry, in spite of the significantly high emission of CO_2 from the production of Portland cement, this cement is still predominantly used as the binding material in concrete. This coupled with the high energy consumed to produce Portland cement, alternative binding materials are needed to be found as a part of integrated efforts in saving the world.

The use of cement replacement materials such as: pulverised fuel ash, microsilica, meta-kaolin and ground granulated blastfurnace slag (ggbfs) in order to reduce the use of Portland cement has been widely accepted. Considerable research has been carried out on properties of concrete containing these materials which have increased the confidence of users to apply them not only as cement replacement materials but also as a part of binder systems in concrete matrix. The reduction of 10%-40% of cement can be expected by using the cement replacement materials (Lawrence , 1998).

Further reduction in the use of Portland cement as the binding material in concrete could be by developing calcium sulfoaluminate (CSA) based cement. Lower content of $CaCO_3$ needed to produce CSA based cement compared to that needed to produce Portland cement significantly reduces the emission of CO_2 into the atmosphere. As the sintering temperature of CSA based cement is about 1300^0C while PC is sintered at 1450^0C, the energy required to produce the CSA based cement is lower than the energy required to produce Portland cement. Beside, using waste materials to produce the CSA based cement: such as: ggbfs, bottom ash, pulverised fuel ash, pyrite ash, limekiln bag house dust and scrubber sludge can result in further benefits (Arjunan, et al, 1999).

Based on the potential of CSA cement that could be exploited to reduce the demand on OPC, the properties of concrete made from CSA based cement are examined based on theory developed from the existing literature review and the experimental works on paste and concrete made from CSA cement. Some research has been done on CSA based cement and its derivatives. Unfortunately, most of the published research is focused on the hydration characteristics of cement paste. In order to bring this invaluable cement into practice especially as a structural concrete material, further comprehensive research on properties of concrete made with CSA based cement and the possibility of incorporating OPC in this system is absolutely required.

1.2 Ettringite as a Binder in Concrete

In OPC concrete, ettringite is found in small amounts as a product of tricalcium aluminate (C_3A) and gypsum reaction. It is commonly associated with sulfate attack as the conversion from monosulfate to ettringite in the presence of external sulfate from causing expansion. Purposely, ettringite has been introduced into the OPC matrix as a result of reaction between calcium sulfoaluminate (CSA), also known as Klein's compound ($C_4A_3\overline{S}$), calcium sulfate ($C\overline{S}$) and calcium hydroxide (CH). The use of CSA in concrete is intended to produce an initial expansion in OPC concrete to compensate the drying shrinkage of OPC concrete. Later, CSA was also used in higher content in OPC concrete to produce self-stressing concrete.

The formation of ettringite follows the equation:

$$C_4A_3\bar{S} + 8C\bar{S} + 6CH + 90H \rightarrow 3C_6A\bar{S}_3H_{32} \qquad (1.1)$$

CH is introduced into the system by the OPC hydration and sometimes in small content, CH is intentionally interground into Klein's compound. The proportion of $C_4A_3\bar{S}$ and gypsum or anhydrite used depends on the expansion degree required (Taylor, 1997).

Further development using CSA cement was the use of ettringite as a main binder in concrete (Zang, et al, 1999). CSA cement and anhydrite with or without the presence of OPC as cement replacement forms ettringite crystals. The difference in nature between ettringite crystals and CSA gel is expected to result in different characteristics of concrete.

Considering the following equations of hydration:

$$2(C_3S) + 6H = C_3S_2H_3 + 3CH \ldots\ldots (1.2)$$

$$C_4A_3\bar{S} + 2C\bar{S} + 38H = C_6A\bar{S}_3H_{32} + 2AH_3 \ldots\ldots (1.3)$$

Equation (1.2) is the approximate reaction of CSH formation from alite and equations (1.1) and (1.3) are the reactions of ettringite formation. Stoichiometrically, the water/cement ratio required for equation (1.2) is 0.24, while for equations (1.1) and (1.3) it is 0.76 and 0.78, respectively. It is clearly seen that the formation of etrringite is more water demanding than that of CSH-gel.

In practice, the water/cementitious ratio used in OPC is much higher than 0.24 unless a superplasticiser is used. The remaining water forms the pore system which later plays a great role in determining the properties of OPC concrete. In most cases, where more mixing water was available in the system than that required for hydration, there is still some unhydrated C_3S to be found in old concrete, acting as nucleus for hydrated particles. If by any chance, the unhydrated part of C_3S comes into contact with water, further reaction will occur and increase of strength, without significant change of volume can be expected. This is not the case in the reaction of CSA based cement. As the water required for hydration is much higher that that for OPC, in practice, the water demand for workability is mostly lower than the water required for hydration. It means that most of the mixing water is used for hydration. It is expected that the pore system in CSA concrete is fundamentally different to that in OPC concrete. Which in turn, results in different characteristics in both type of concrete.

Expansion is expected to be the main problem in developing CSA cement as a structural concrete material. The expansion of ettringite is closely related to the mechanism of ettringite formation, the amount of ettringite in the concrete, and the ingress of water to the concrete. Based on these factors, the content of anhydrite used, w/cm ratio, and the content of OPC are the important parameters considered in this research.

The experimental investigation of calcium sulfoaluminate based cement developed in this research is expected to result in the optimum water and anhydrite content required for producing concrete fulfilling the requirements for structural applications in terms of workability, setting times, expansion, strength and durability

1.3 Objective and Scope of Research

The objective of the research is to to characterise the hydration products and to examine the properties of CSA based cement, and the properties of concrete made with CSA based cement to establish the potential of CSA cement to produce structural grade concrete

The investigation will be focused on:

a hydration processes & development of microstructure
b properties of fresh concrete; setting time and workability
c properties of hardened concrete; volume stability, strength development, deformation characteristics and durability of concrete.

The variables used in the research are:

a. water/cementitious ratio from 0.30 to 070,
b. variation in anhydrite contents
c incorporating OPC
d response of concrete to superplasticiser
e curing regimes: water curing, sealing as cast, storing at room temperature (20 ± 1) ^{0}C, water curing after sealing for 28 days.

1.4 Thesis Outline

The thesis is organised into 9 chapters as follows:

Chapter1 covers the introduction, including the background of the research, ettringite as a binder in concrete and objectives and scope of the research.

Chapter 2 covers the literature review related to the CSA cement concrete. Previous work carried out by researchers on CSA cement as a concrete material are reviewed in order to build up a better understanding of the material. The production process of CSA and its variations, the properties of ettringite as the reaction product and the properties of paste and concrete made from CSA are briefly discussed.

Chapter 3 contains materials used in this investigation and the experimental design. The properties of materials used, design for paste made from laboratory produced CSA and commercially manufactured CSA cement and design for concrete made from commercially manufactured CSA cement are presented. The test methods for the investigation are also included.,

Chapter 4 presents the synthesis of CSA cement in the laboratory. The composition of raw material, production process, the quality of CSA product and the control of the production repeatability were the main concerns discussed in this chapter.

Chapter 5 covers the properties of paste made with the laboratory produced CSA cement. Properties of paste discussed including hydration, expansion and compressive strength of paste with variation of w/c ratio, anhydrite content and curing regimes.

Chapter 6 presents the effect of OPC inclusion on properties of paste made with CSA cement produced in the laboratory. The effect of different contents of OPC replacement on hydration, expansion and compressive strength are discussed.

Chapter 7 contains the properties of paste made with commercially manufactured CSA cement. Properties of paste discussed include setting time, hydration, expansion and compressive strength of paste with variable anhydrite content and curing regimes. The effects of OPC inclusion on properties of paste are also discussed.

Chapter 8 presents the properties of concrete using commercially manufactured CSA cement. The properties of concrete included the properties of fresh concrete such as: setting times and workability and the properties of hardened concrete such as: expansion, compressive strength, indirect tensile strength, flexural strength, oxygen permeability, absorption value and chloride permeability.

Chapter 9 contains conclusions of the research including the main findings of the research, applications of the research and recommendations for future research.

II

LITERATURE REVIEW

2.1 General

It has been generally accepted that Portland cement (PC) is a heavily energy consuming product. The energy required to produce PC is nearly 3000 $kJkg^{-1}$ of cement with two-thirds being required to dry the raw feed and carry out the chemical reactions and one-third being consumed in energy losses through radiation etc. The calculated energy requirement to form PC clinker depends upon the Lime Saturation Factor (LSF), and increases from 1570 to 1800 $kJkg^{-1}$ as the LSF is increased from 80 to 100 % (Lawrence, 1998).

As producing PC generally uses carbon-based fuels as the source of energy, it consequently releases a huge amount of CO_2 into the atmosphere. De-carbonation of limestone as a main material of PC further adds to the amount of CO_2 released into the atmosphere. The total emission of CO_2 for every kg of cement is 0.98 kg, consisting of 0.53 kg from the de-carbonation of calcite, 0.33 kg from the burning process and 0.12 kg from the electrical power. In effect, for every ton of PC produced, an equal amount of CO_2 is released into the atmosphere. Cement production worldwide is greater than 1 ton per head of population, hence the industry releases more than 1 ton of CO_2 into the atmosphere for every man, woman and child alive today. (Sharp, et al, 1999)

Since more than half of CO_2 released in the manufacture of PC is from the de-carbonation of calcite, a change in cement composition could bring a major reduction in the release of CO_2. It can be done by partial replacement of PC by industrial waste material or natural minerals to produce blended or composite cement or by manufacturing low alite or even alite-free containing cement. (Sharp, et al, 1999).

Calcium sulfoaluminate based cement is considered as low energy cement and therefore more environmentally friendly than PC. The total lime requirement to produce such cement is about 50 wt% as against about 65 wt% for Portland cement. The cement can be synthesized at a lower temperature of 1200^0C, rather than the 1400^0C to 1500^0C for PC. The existence of a significant amount of sulfates will result in different hydration reactions and products compared to Portland cement. The possibility of using waste materials such as: fly ash, blastfurnace slag, belitic waste, phosphogypsum, bag house dust, scrubber sludge is a further advantage of calcium sulfoaluminate based cement in saving the environment. (Arjunan, et al, 1999).

2.2 Clinker

2.2.1 Alite (C_3S)

Basically OPC is made up of four major component oxides in the system Ca-Si-Al-Fe or in cement notation C-S-A-F. The average lime requirement is about 65% wt.%. The potential mineralogical phases of OPC are alite (C_3S), belite (β-C_2S), tri-calcium aluminate (C_3A), tetracalcium aluminoferrite (C_4AF) and other mineral components. In modern PC clinker, alite or tricalcium silicate (C_3S), as the principal constituent of PC, provides 50 –70 % of the total weight of cement (Neville, 1998). C_3S is a combination of three moles of lime and one mole of silica, and forms at a temperature of about 1450^0C. This compound can be thought of as the back bone of Portland cement, because its hydration products, along with the hydration of C_3A to a much lower degree, are responsible for developing the high early strength of concrete.

As alite in Portland cement is responsible for consuming high energy and releasing high CO_2 into the atmosphere, any effort taken to replace part or the whole of alite in cement clinker with other binding materials will significantly save energy and reduce the emission of CO_2 into the atmosphere.

2.2.2 Belite (β-C_2S)

Belite is produced along with other Portland cement constituent compounds at 1450^{0}C. Basically, belite may be produced at lower temperature and therefore involves lower energy consumption. This is evident when the enthalpy of formation of both C_3S and C_2S from calcium carbonate and silica is compared. The values, calculated on the basis of thermodynamic data, are as follows: ~ 1810 kJ/kg of C_3S and ~ 1350 kJ/kg of C_2S. So the difference is about 460 kJ/kg (Kurdowski, et al, 1997).

$$3C\overline{C} + S \rightarrow C_3S + 3\overline{C}$$

$$2C\overline{C} + S \rightarrow C_2S + 2\overline{C}$$

There is a large reduction in CO_2 released into the atmosphere when alite is replaced by belite, as shown by the equation above.

The reduction in alite content of the fired clinker and corresponding increase in the belite content result in a reduced LSF, which in turn leads directly to a reduction in the amount of energy consumed and in the amount of carbon dioxide evolved. As belite hydrates relatively slowly, the enhancement of reactivity or incorporation of an additional reactive phase is necessary. The former route leads to activated belite cements (ABC) and the latter route to (among others) sulfoaluminate-belite (SAB) cements (Sharp, 1999).

The activation of belite may be enhanced by rapid quenching of the clinker to stabilise a high temperature polymorph, incorporation of ions in solid solution within the crystal structure, again to stabilise a more reactive polymorph, or by addition of small amount of ordinary Portland cement clinker to the low energy clinker to provide some alite to accelerate the belite hydration.

Experimentally, Kurdowski, et al, (1996) activated C_2S by combining low temperature synthesis and activators. C_2S was produced by calcining C-S-H, previously synthesised from pure analytical reagent (AR) materials of calcium hydroxide and amorphous silica. The activators used were 5% of $CaSO_4.0.5H_2O$, 3% of K_2SO_4, 3 and 6% of Na_2SO_4 and 5 and 10% of $BaSO_4$. Calcination temperatures were 800^0C and 900^0C over the course of one hour. The samples with barium sulfate addition were also burned at 1000^0C. The burned sample was quickly cooled in the air. From their work it was found that there was no difference in phase composition between material burnt at 800^0C and 900^0C, where βC_2S is the major phase in all samples and in the majority of samples small quantities of α' and γ phases were also found. Samples burnt at lower temperature had higher specific surface and then gave higher heat of hydration. The highest heat of hydration was produced by samples with $BaSO_4$ burnt at 800^0C, while the addition of gypsum gave rather negative influence, shown by low heat of hydration. At lower temperature, gypsum remained as anhydrite after burning at 900^0C.

Lu and Su, (1996) examined the effect of different sintering conditions on the reactivity of β-C_2S. They found that under rapid sintering (800^0C/min. with sintering temperature 1400^0C and length of temperature conservation of 20 minutes), β-C_2S has a finer crystal size, higher internal micro-stress, larger specific surface of pores, and thus a higher rate of hydration compared to the one produced by normal sintering (25^0C/minute with sintering temperature 1400^0C and length of temperature conservation of 720 minutes). Increasing length of temperature conservation decreased the activity of β-C_2S as it encouraged formation of larger crystal size and smaller inner micro-stress.

2.2.3 Klein's Compound

Calcium sulfoaluminate, $C_4A_3\overline{S}$ is commonly known as Klein's compound after the American Inventor. The compound has been used since 1968 in expansive cements based on its addition to PC. Cement clinker may be produced in the CaO-Al_2O_3-SiO_2-Fe_2O_3-SO_3 system with $C_4A_3\overline{S}$, C_2S, C_4AF and $C\overline{S}$ as the major phases formed. The compound is readily formed at temperatures above 1200^0C and is stable up to about 1400^0C. (Ohsawa, et al, 1999). The ferrite phase in the system hydrates more readily in sulfoaluminate cement than in ordinary Portland cement, presumably because of its formation at a lower temperature (Sharp, et al, 1999).

Ali et al (1994) in their experiment produced calcium sulfoaluminate cement from molar mixes of the oxides of calcium aluminium and sulfur derived from synthetic pure chemical and commercial grade natural minerals, such as limestone, bauxite and gypsum. The formation of $C_4A_3\overline{S}$ in the temperature range of 1100-1325^0C occurs by solid state reaction between constituent oxides as well as through intermediate calcium aluminate phases. The degree of formation of the calcium sulfoaluminate phase is comparatively higher from pure chemicals. This is due to the increased solid state reaction between oxides. The formation obeys the rate law equation $1-(1-x)^{1/3}=Kt$ where x is the fraction of $C_4A_3\overline{S}$ formed at time t. The activation energy of the formation was about 90 kcal $mole^{-1}$. An X ray diffraction study of partially fired mixes of lime, alumina and sulfur bearing materials indicates substantial amount of the $C_4A_3\overline{S}$ phase at 1100^0C if chemical grade raw materials are used. The formation of $C_4A_3\overline{S}$ is completed at 1350^0C when re-fired for one hour.

2.2.4 Calcium Sulfoaluminate Belite

The existence of sulfate in cement raw materials will result in calcium sulfoaluminate belite (SAB) cement. SAB cement may be synthesized from raw meals containing natural minerals and industrial by-products such as fly ash, red mud and blastfurnace slag at a temperature of 1200-1300^{0}C. The clinkerization temperature of belite is the same as for calcium sulfoaluminate but lower than those of PC. The total theoretical heat requirement for sulfoaluminate belite cement is 1337 kJ/kg compared to 1756 kJ/kg for PC. The fired SAB clinker is easy to grind. In comparison, the energy consumption for grinding PC is 40 – 50 kWh/t and for grinding SAB cement is 20-30 kWh/t, and emission of CO_2, calculated on the content of limestone in the raw meal, is 0.5 t/t for PC but only 0.2-0.3 ton/ton for SAB (Janotka, Krajci, 1999).

A reduction in limestone utilisation of about 40% and energy saving of 25% appear to be possible in cement with high $C_4A_3\bar{S}$ content. Low lime content of raw material will result in a clinker that can be ground more easily. (Sharp, et al,1999). The Chinese cement clinkers contain a content of $C_4A_3\bar{S}$ ranging from 35 to 70 mass percent, and substantial amounts of belite and ferrite phases. The production process is similar to that for PC, a dry process rotary kiln with pre-heater commonly being employed, using a burning temperature between 1250 and 1350^{0}C. The ultimate phase composition formed above 1300^{0}C comprises $C_4A_3\bar{S}$, $\alpha'C_2S$, the ferrite phase and $C\bar{S}$ (Sharp, 1999).

Sulfoaluminate cement (SAC) and ferroaluminate cement (FAC), i.e. calcium sulfoaluminate belite cement developed in China, are made by burning mixtures of limestone, bauxite (or iron-rich bauxite) and gypsum of appropriate composition, ultimately to a moderate temperature (1300-1350^{0}C) to obtain a clinker having as its major mineral component $C_4A_3\bar{S}$, C_2S, and an Al-rich ferrite (Zang et al. 1999).

In the CaO-Al_2O_3-SiO_2-Fe_2O_3-SO_3 system, Sahu and Majling (1993) identified eighteen equilibrium phase assemblages, each containing five phases relevant to belite clinkers (See table: 2.1). Later, work carried out by Majling et al. (1994), different compositions of limestones, fly ash and gypsum as raw material were sintered at 1200^0C for half an hour. C_2S, $C_4A_3\overline{S}$ and $C\overline{S}$ are always found as major phases in all compositions. The existence of C, C_4AF, C_2F and C_2AS were dependent upon the amount of limestone and fly ash in the compositions.

Majling et al. (1999) stated that fly ash is a suitable raw material source for the production of calcium sulfoaluminate based cements. They used different kinds of fly ash along with limestone and gypsum to produce sulfoaluminate cement consisting of C_2S, $C_4A_3\overline{S}$ and C_4AF phases. The content of each phase is within the following limits: C_2S, 60.7-83.4 wt %; $C_4A_3\overline{S}$, 4.2-27.2 wt % and C_4AF 2.6-30.5 wt%. Fly ash with low SiO_2/Al_2O_3 or $SiO_2/(Al_2O_3 + Fe_2O_3)$ ratios produces clinkers with the preferred proportions of the mineral phases.

Arjunan et al. (1999) produced calcium sulfoaluminate cement from a lime kiln bag house dust, a low-calcium fly ash, and a scrubber sludge. The clinkering temperature to produce calcium sulfoaluminate ($4CaO.3Al_2O_3.SO_3$) and di-calcium silicate ($2CaO.SiO_2$) was at 1250^0C, if nodulized raw meal was used, and at 1175^0C if powdered raw material was used for clinker preparation, compared to the ~ 1500^0C sintering temperature required for Portland cement. The fired clinkers were relatively soft and friable and were easy to grind. Depending on the composition of raw material, the main phases of the clinkers were β-C_2S, $C_4A_3\overline{S}$ C_4AF, $C\overline{S}$ and free CaO.

Table 2.1: Phases Assemblages in the System C-S-A-F-$\bar{S}$ Relevant to Sulfoaluminate Belite Clinkers. (Sahu and Majling, 1993)

Assemblance	Phase
1	$C_2S - C - C_3A - C_4AF - C_4A_3\bar{S}$
2	$C_2S - C - C_2F - C_4AF - C\bar{S}$
3	$C_2S - C - C_4AF - C_4A_3\bar{S} - C\bar{S}$
4	$C_2S - C_3S_2 - F - C_2AS - C_4A_3\bar{S}$
5	$C_2S - C_3A - C_{12}A_7 - C_4AF - C_4A_3\bar{S}$
6	$C_2S - C_{12}A_7 - CA - C_4AF - C_4A_3\bar{S}$
7	$C_2S - CA - CF - CF_2 - C_4A_3\bar{S}$
8	$C_2S - CA - CF - C_4AF - C_4A_3\bar{S}$
9	$C_2S - CA - CF_2 - C_2AS - C_4A_3\bar{S}$
10	$C_2S - C_2F - CF - C_4AF - C_4A_3\bar{S}$
11	$C_2S - C_2F - CF - C_4A_3\bar{S} - CS\bar{S}$
12	$C_2S - C_2F - C_4AF - C_4A_3\bar{S} - C\bar{S}$
13	$C_2S - CF - CF_2 - C_4A_3\bar{S} - C\bar{S}$
14	$C_2S - CF_2 - F - C_2AS - C_4A_3\bar{S}$
15	$C_2S - CF_2 - F - C_2AS - C\bar{S}$
16	$C_2S - CF_2 - F - C_4A_3\bar{S} - C\bar{S}$
17	$C_2S - CF_2 - C_2AS - C_4A_3\bar{S} - C\bar{S}$
18	$C_2S - F - C_2AS - C_4A_3\bar{S} - C\bar{S}$

In the CaO-SiO_2-Al_2O_3-Fe_2O_3-SO_3-CaF_2 systems, Knofel et al. (1994) synthesised three kinds of quick cements from different clinkers. One of them was comprised of $C_4A_3\bar{S}$, C_2S, $C_2(AF)$ which can be classified as calcium sulfoaluminate cement. The existence of SO_3 and CaF_2 in the system accelerated the binding of lime. It can be noticed that alite has already been formed at 1100^{0}C and the content of free lime could be reduced to about 1 ma.-% already between 1300^{0}C and 1350^{0}C. At the same time, for these temperatures the main clinker phases alite, $C_{11}A_7 \cdot CaF_2$, $C_4A_3\bar{S}$ and belite can be determined. In system $CaO-SiO_2-Al_2O_3-Fe_2O_3-SO_3-CaF_2$ the burning temperature for clinkers is distinctly lower than for normal Portland cement clinker (roughly around 100^0C-200^0C).

Overall, the real phase composition of calcium sulfoaluminate belite cement will, however, be markedly related to the burnability of raw meals used for their production, the presence of impurities, mineralizers, fluxing agents, etc (Majling, et al, 1999).

2.3 Hydration of Calcium Sulfoaluminate Based Cement

The hydration of the $C_4A_3\overline{S}$ phase follows a very rapid hydration reaction, leading to the formation of needle-like ettringite. The reaction may follow the equation:

$$Ca_4Al_6(SO_4)O_{12} + 2CaSO_4 + 38H_2O = Ca_3Al_2O_63CaSO_432H_2O + 4\ Al(OH)_3$$

Or in cement chemist's short-hand notation:

$$C_4A_3\overline{S} + 2C\overline{S} + 38H = C_6A\overline{S}_3H_{32} + 2AH_3 \text{ ....}(2.1)$$

A higher yield of ettringite may be obtained when lime is present:

$$C_4A_3\overline{S} + 8C\overline{S} + 6CH + 90H = 3C_6A\overline{S}_3H_{32} \text{ ....}(2.2)$$

The reaction proceeds via a through solution mechanism. Calcium, sulfate and aluminate ions enter the solution, which rapidly becomes saturated with respect to ettringite. This phase crystallises as needles, which can be up to

150 µm in length, depending upon the lime concentration in solution (Sharp, 1999).

In the case where less gypsum is available in the composition, the reaction may follow the equation:

$4C_4A_3\overline{S} + 8C\overline{S}H_2 + 24CH + 74H = 3C_6A\overline{S}_3H_{32} + 3C_4A_3\overline{S} + 18CH$........(2.3)

$3C_6A\overline{S}_3H_{32} + 3C_4A_3\overline{S} + 18CH + (12x\text{-}114)H = 12C_4A\overline{S}H_x$ ....(2.4)

as shown by Hanic et al. (1989) where in their experiment, the molar ratio of $C_4A_3\overline{S}$, $C\overline{S}$ and CH was 1:2:6. By using XRD and thermal methods, it was found that the formation of hydration product in the mixture was a two-step reaction. The reaction product in the first step was ettringite, while monosulfoaluminate hydrate, $C_4A\overline{S}H_x$, was formed in the second step of the hydration reaction.

Ettringite formation involves a solution-precipitation process. The crystals of ettringite form in situ in pore solution with high hydroxyl ion concentration, and form both in situ and in bulk solution under conditions of low hydroxyl ion concentration (Deng and Tang, 1994)

The paste hydration products of calcium sulfoaluminate belite cement consist mainly of ettringite, mono-calcium sulfoaluminate hydrate (AFm), alumina gel and ferrite gel. The hydration will still take place in subzero temperatures (Zang and Wang, 1999). By using CA, C_3A, $C_4A_3\overline{S}$,AFm and C_4AF, Odler and Colan-Subauste (1999) found that a rapid ettringite formation took place in the paste made with CA, $C_4A_3\overline{S}$ and AFm. The reaction was distinctly slower in the paste made with C_3A, and even slower in that made with C_4AF. Pastes cured under water generally hydrated slightly faster than those cured in humid air and the hydration process of specimens cured in dry air virtually stopped within a few days due to loss of significant free water under this condition.

According to Sahu and Majling (1993) the presence of a certain amount of free lime plays an important role in accelerating the formation of ettringite. The reaction will follow the scheme (2.1 and 2.2). As C_2S is a slow hydrating phase and the required amount of free lime is not available immediately in the system, further hydration process follows reaction steps (2.5) and (2.6) :

$C_2S + H \rightarrow CSH + CH$ .... (2.5)

$3CH + AH_3 + 3C\overline{S} + 28H \rightarrow C_6A\overline{S}_3H_{32}$ ....(2.6)

The presence of free lime, which raises the pH value of the liquid phase to > 10.7, promotes the formation kinetics of ettringite in a relatively saturated lime condition.

Clark and Brown (1999) found that the rate of ettringite formation was retarded in sodium hydroxide solution. An increased sulfate content in the system enhances ettringite formation and suppresses U-phase ($4CaO.0.9Al_2O_3.1.1SO_3.0.5Na_2O.16H_2O$) formation. Ettringite forms at high sulfate levels; when the sulfate/aluminate ratio decreases, in the presence of Na(OH), U phase formation becomes favourable. Once ettringite is formed, it does not convert to the U-phase.

The hydration of a commercial Chinese sulfoaluminate cement was examined by Andac and Glasser (1999) by using XRD, TEM-EDTA and DTA. After 1 day, the main hydration product was ettringite together with some AFm. After 3-7 days, the main hydration products were AFm and C_2ASH_8 but ettringite was still present. The content of AFm and C_2ASH_8 increased with increasing duration of curing, but the content of ettringite remained nearly constant and was progressively diluted by other hydrates. After 45 days, according to the X-ray and TEM-EDXA results, the principal crystalline phases were C_2ASH_8 and two AFm-type phases, one of which was low in sulfate and the other high in sulfate, as well as ettringite. Also two different non-crystalline phases were observed. One was sulfur-free or very nearly free, ~ 3.95 wt% S ion, CSH-gel and the other was CSH-gel but with a characteristically higher sulfur content, ~ 20.81 wt%. After 60 days, un-reacted cement clinker components were still identified by XRD.

Knofel and Wang (1994) found that from the CaO-SiO_2-Al_2O_3-Fe_2O_3-SO_3-CaF_2 system, clinker with phases $C_4A\bar{S}$, C_2S, $C_2(A.F)$ produced AFt, AFm and $AlF_3{\cdot}3H$ after 2 hours of hydration. After 1 day C_4AH_{13}, CH and C_2ASH_8 were found. The same products were also found after 28 days.

Long et al. (1995) suggested that the formation of ettringite might be through solid reaction where needle-shaped ettringite crystals grow from the surface of grains and link the grains together. The mode of hydration might begin with the dissolution of calcium aluminate into water and reaction with solid phase of $CaSO_4.2H_2O$ to form ettringite on the surface of gypsum. Once, calcium aluminates come into contact with water, hydrated calcium aluminate phases form rapidly on the surface grains. These newly formed hydrated calcium aluminates, which have high reactivity, react with gypsum to form ettringite by ions diffusing. These ettringite crystals are formed close to the surface of gypsum.

2.4 Stability of Ettringite

The stability of ettringite is a very important factor to be considered. The properties of decomposition products will directly affect the binding characteristics of ettringite as a binding material in the concrete matrix. Finely ground ettringite is stable up to 60^0C in a solution with pH value around 11. It gradually dissociates with time. It converts to the low sulfate form after one hour boiling which decomposes further to gypsum after 14 days. Gypsum appears first when the pH of the solution is lowered to 9 and the aluminium concentration clearly decreases. The ettringite grain size plays a great role in maintaining the stability of ettringite as greater grain size of ettringite will hinder the sulfate splitting and will retard the decomposition process to monosulfate (Ghorab, et al, 1985)

The solubility product of ettringite was found to be 1.98×10^{-37} in pure water, 1.11×10^{-40} in the presence of alite with a mole ratio of 10, and insoluble in the presence of saturated lime solution as well as in an excess amount of monocarboaluminate hydrate. The ettringite phase reacts with calcium silicate hydrates with the weakening of its X-ray diffraction intensity; at the boiling temperature of water the tobermorite phase forms, in the presence of lime or monocarboaluminate hydrate, the hydrogarnet phase appears beside the mono-phase solid solution. (Ghorab, et al, 1998)

At pressure 150 up to 900 kPa ettringite in the presence of its saturated aqueous solution is thermally stable at temperatures lower than 107 to 111^0C, respectively. The decomposition products are $3CaO.Al_2O_3.CaSO_4.12H_2O$ and predominantly $CaSO_4$. The thermal dissociation of monosulfate under the same conditions is $3CaO.Al_2O_3.CaSO_4.10H_2O(s)$, $3CaO.Al_2O_3.6H_2O(s)$, $CaSO_4(s)$ and $H_2O(g)$. The $3CaO.Al_2O_3.CaSO_4.10H_2O$ thermal dissociation equilibrium temperatures reach values from 150^0C to 177^0C at the pressure of water vapour from 100 kPa to 900 kPa, respectively (Nerad, et al, 1994).

2.5 Properties of Fresh Concrete Made with CSA-Based Cement

As a new type of cement, only a few data are available concerning the properties of fresh concrete made with CSA-cement. Basically, rapid formation of ettringite will cause a very fast setting time. The working time of fresh concrete is therefore very limited. In China, the initial setting time between 2-10 hours may be adjusted by using special admixtures. Concrete with w/cm as low as 0.24 - 0.35 can still have adequate workability by using a special retarding superplasticizer (Zang, et al, 1999). Unfortunately, the composition of special admixtures and the special retarding-superplasticizer are not specified in the report.

By using laboratory calcium sulphoaluminate cement, Lan and Glasser (1996) found that the initial and final setting times of cement were I h 10 min and 2 h respectively. In the commercially manufactured calcium sulfoaluminate cement produced in UK, the initial setting was 2 h and 30 m. Unfortunately, in both types of cement, there was no indication of the $CaSO_4$ content and the phases used.

Work, done by Janotka and Krajci (1999) shows that incorporation of Portland cement improved the setting characteristics of SAB cement. If the initial and final setting time of SAB alone are 10-20 minutes and 20-30 minutes respectively, the use of 85% SAB and 15% PC increases the initial setting times to 90 minutes and final setting time to 120 minutes.

Addition of a so called retarding agent does not cause any appreciable slowing of setting. Simultaneous addition of a retarding agent and Portland cement, however, could delay the initial and final setting by about 15 minutes each. Delaying setting times depends on the basicity of the pore solution. It is dependent on the amount of added retarder as well as on the phases present in the cement (Knofel and Wang, 1994).

2.6 Properties of Hardened Concrete Made with CSA-Cement

2.6.1 Microstructure

SEM studies by Sahu and Majling (1993) on 7 day old hydrated CSA belite cement show that the formation of ettringite was found throughout the whole matrix of the cement paste, but more intense formation could be found in the voids. Also formation of gel could be seen

SEM studies by Arjunan et al. (1999) on hydrated calcium sulfoaluminate cement made from proportioning lime bag house dust, low-calcium fly ash and scrubber sludge showed the presence of sponge-like sulfoaluminate phases in the whole matrix and needle-like ettringite phases in the voids after 1 day of hydration. After 28 days, small amounts of calcium hydroxide and calcium silicate hydrate were observed, indicating that hydration of β-C_2S was taking place. $C_4A_3\overline{S}$ was completely hydrated much before 28 days.

2.6.2 Porosity

Porosity measurements carried out by Sahu and Majling (1993) show that at early age, the porosity of CSA cement mortar is comparatively lower than the porosity of PC mortar and at 28 days the total pore volume is almost the same in both types of cement. Maximum sized pores are filled in the first day in the case of sulfoaluminate belite cement but such a condition is achieved between 1 and 3 days in the case of PC. This phenomenon can be explained by the fact that about 40 wt.% of the original phases of sulfoaluminate cement take part in the formation of ettringite. Moreover this reaction to form ettringite is rapid and is almost over within one day.

However, Janotka and Krajci (1999) show that the water absorption capacity of mortar made with SAB is higher than that of mortar made with PC. The increase in the PC portion reduces the water absorption capacity.

The pore size distribution in mortar made with calcium sulfoaluminate cement showed greater differences for different conditions of storage. After 28 days stored in water, the greatest amount of pores can be found in the size range of 1.9-3.0 nm, up to 180 days the pore size between 1.9-10 nm increased, in particular for smaller pores 1.9-3 nm, but the pore size larger than 10 nm decreased very distinctly. In the case of samples stored in CO_2-rich atmosphere, as carbonation progresses the volume of capillary pores increases (particularly the pores with radii between 30-250nm) and the volume of gel pores (between 1.9-3 nm) decreases. CO_2 does react with the hydration product; as a result of these changes the volume of bigger pores (capillary pores) increases and that of smaller pores (gel pores) decreases (Knofel and Wang, 1994).

2.6.3 Volume Stability

Expansion is still a major concern in calcium sulfoaluminate-based cement. The causes of expansion in calcium sulfoaluminate cement are an intensive argument among researchers. The expansion results from forces exerted by the growth of ettringite crystals (Taylor, 1997). Metha and Hu (1978) stated that the expansion associated with ettringite formation was insignificant compared to the expansion, which occurred when ettringite was exposed to liquid water. Since the crystals formed in a basic environment should have a negative surface charge, it was a combination of high surface area and a negatively charged surface, which were responsible for ettringite's attraction of a large amount of water.

The formation of ettringite in calcium sulfoaluminate based cement may cause expansion and cracking of hardened concrete. If ettringite or monosulfate form while the concrete is still in a plastic state, the surrounding paste will simply accommodate this volumetric change. However, if ettringite forms after the concrete has set the ettringite formation causes expansion leading to cracking and thus structural damage. Ettringite expansion is always affected by many factors, such as the kinetics of ettringite formation, the matrix strength of cement paste and its development. The expansive force results from crystallisation pressure as well as swelling pressure converted from the reduction of chemical potentials in the reaction of ettringite formation. Expansion is closely related to the distribution of ettringite crystals in the cement pastes. If confined in the vicinity of the surface of aluminium-bearing grains, ettringite may cause a large expansion. If scattered both in the surface zone of aluminate phases and in the bulk pore solution, ettringite formation will result in a little or no expansion. Ettringite formed under the condition of a solution unsaturated with lime, such as that in sulfoaluminate cement paste, can produce expansion, and the presence of alkalies further promote the expansion of ettringite. The higher the content of alkali added, the larger is the expansion. This is because the addition of alkali increases the concentration of $(OH)^-$ ions in the pore solution of the paste and the latter may increase the expansion of ettringite. (Deng and Tang, 1994)

A comparison of the expansion taking place in humid air and water cured samples revealed that at equal levels the expansion was greater in the water. Thus it appears that the enhanced water uptake under these conditions stimulates the expansions of hardened paste. In this case swelling phenomena were involved in the expansion process. But results obtained on the test specimens cured in dry air revealed that an uptake of water is not essential for expansion to take place (Odler and Colan-Subauste, 1999).

Length change measurements carried out by Janotka and Krajci (1999), showed that the dimensional behaviour of mortar specimens is significantly dependent on the moisture content in air. PC mortar has a distinct expansion under moist air cure, and a distinct shrinkage under dry air cure while SAB cement mortar even has a slight shrinkage in moist air, and less intensive shrinkage in dry air. The evidence of the shrinkage compensation properties of SAB cement was shown by the fact that the difference in 90 day values of length changes between moist and dry air cure for PC mortar is about 0.06%, whereas for SAB cement mortar it is only about 0.025%. It also showed that a shrinkage of 85%PC/15% SAB cement mortar is markedly higher than that of PC mortar under dry air cure. By contrast, the mortar made with the 85 % SAB cement+15% PC showed less expansion in moist air and slightly less shrinkage under dry air cure. One can deduce that mortars made with SAB cement and its blend with 15% PC have decreased dilatation between 100 and 60% moist air at 20^0C, opposite the behaviour of PC mortar (see fig. 2.1).

The use of slag or limestone as an interground additive may control an excessive expansion caused by calcium sulfoaluminate belite cement (Knofel and Wang, 1994).

2.6.4 Strength Development of Concrete Made with CSA-Based Cement

Strength development of concrete made with CSA-based cement at early age is faster than that made with PC. The existence of belite in the cement matrix is expected to provide the long-term strength development. Concrete made with ferroaluminate cement in China has much faster early strength development and steadily increases in strength at later ages. At w/cm 0.3, the strength of 70 and 91 MPa at age of 3 and 28 days respectively were achieved (Zang, et al, 1999).

With cement : sand = 1 : 2 and w/cm = 0.5 and 0.4, Sahu and Majling (1993) found that compressive strength development of mortar made with CSA cement containing free lime was higher than the compressive strength of mortar made with CSA cement without free lime. Free lime up to 10 % has no harmful effect. However, cement containing more than 10 % free lime showed high early strength but later on, strength decreased due to unwanted expansion. The strength of mortar containing 10 wt.% free lime at 3 days and 28 days are 17.7 , 36.3 MPa (w/cm=0.5) and 20 and 50 MPa (w/cm= 0.4) respectively. Without free lime, the strength of mortar at 3 days and 28 days was 9.6 and 19.5 MPa (w/cm=0.5) respectively.

Arjunan et al. (1999) found that the compressive strength of calcium sulfoaluminate belite cement paste was lower than the compressive strength of Portland cement paste at all ages. But the comparison was made based on paste of calcium sulfoaluminate belite with w/cm=0.4 and paste of Portland cement with w/cm=0.3. It was also stated that the contribution of calcium sulfoaluminates to strength development was only during the first early stages. In later ages, strength development depends mostly on CSH formation.

By combining SAB produced in Slovakia and Romania with Portland cement, Jonatka and Krajci (1999) found that the flexural and compressive strength of mortar are considerably influenced by curing conditions and the portion of Portland cement in matrix. The strength of SAB concrete is lower than those of PC concrete at the same w/cm ratio used. Increasing the content of PC in the matrix increases the strength of the mortar (See table: 2.2). The strength of mortar made with SAB produced in Slovakia and Romania is lower than those of either the Chinese or British product. This is probably because the SAB manufactured in Slovakia and Romania was manufactured at a clinkering temperature of 1250^0C, which is lower than the temperature of 1300-1350 and 1400^0C used in China and Britain respectively. At w/cm=0.5 and cement/sand=1/3, compressive strengths of mortar made with SAB and Portland cement were 22.1 and 51.3 MPa respectively. Compressive strengths of mortar made with a combination of SAB and Portland cement at

15 %, 30%, 55% and 85% of PC replaced by SAB are 43.5, 44.5, 45.7, and 35.5 MPa respectively.

Table 2.2: Strength Characteristics of Tested Mortar (Janotka and Krajci, 1999)

Mortar with	90 day curing condition	Strength (MPa)	
		Flexural	Compressive
100 % PC	Wet Dry	10.3 6.1	51.3 24.2
85 % PC + 15 % SAB	Wet Dry	8.6 4.7	43.5 17.2
70 % PC + 30 % SAB	Wet Dry	8.3 5.2	44.5 19.5
55 % PC + 45 % SAB	Wet Dry	8.4 3.7	45.7 13.7
15 % PC + 85 % SAB	Wet Dry	7.3 3.1	35.5 16.1
100 % SAB	Wet Dry	5.9 3.1	22.1 16.1

Work done by Knofel and Wang (1994) shows that by adding 20% - 50% slag and limestone as interground additives into calcium sulfoaluminate belite cement, compressive strengths of 7-28 MPa at 2 hours and 45-64 MPa at 28 days were reached. Higher amounts of added blastfurnace slag and limestone powder (20-50%) do not have negative influence on the strength development. Blastfurnace slag as an interground additive does improve the later strength development. Strength development is similar for cement cured at 20^0C and 5^0C.

2.6.5 Durability of Concrete made with CSA cement

Concrete made with CSA-based cement in China has been reported to show excellent resistance to sulfate attack, brine attack and re-crystallization damage. Freeze-thaw and carbonation resistance is also satisfactory. The concrete has also shown good resistance to alkali-aggregate reactivity (AAR). Results from accelerated tests of mortar and concrete containing highly active quartz glass and dolomite aggregates from Kingston, Canada, show that potential AAR expansion can be effectively restrained (Zang, et al, 1999).

Janotka and Krajci (1999) suggested that as the pH value of SAB cement (pH=11.12) is lower than the pH value of Portland cement (pH=12.56), the sensitivity of steel to corrosion in an SAB composite cement increases. By using a pH meter, OP113 and Potentiastat OH 405 at polarisation rate of 30 mV/min, they found that in SAB cement mortar, the breakdown potential value is only 210 mV and the steel is not completely passivated but occurs in the non stable state. This is confirmed by the relatively low pH value (11.32) of SAB mortar extract 11.32, while the γ-Fe_2O_3 protective oxide film on the steel surface starts to deteriorate below pH 11.7. Below pH 11.0 the protective film degradation proceeds on the steel surface, and the γ-Fe_2O_3 film is completely destroyed at a pH value of about 9.5. Based on their experience where the conductivity value of 2.0 mS/cm in mortar extracts equate to the transition of steel between passive and active corrosion regimes, 15% of PC in the blend is sufficient to secure passivation of steel in the mortar specimens.

However, research done by Andac and Glasser (1999) on a commercial Chinese calcium sulfoaluminate cement found that the pH of the pore solution was high enough to prevent the γ-Fe_2O_3 protective oxide film from dissociating. At the first day of curing they found the pH of the pore solution was 13.1 and after 60 days, the pH reduced to 12.9. The high pore fluid pH was effectively maintained by the alkalis. Alkali released from hydrating clinker occurred rapidly at early ages. The effect of added gypsum on the pore fluid chemistry was believed to be slight, at least over the range of composition in which gypsum reacts completely.

2.7 Conclusions of Literature Review

1. As an environmentally friendly cement, calcium sulfoaluminate based cement requires lower energy to produce and gives lower emissions of CO_2 into the atmosphere when compared to Portland cement. The possibility of using waste material is another advantage of calcium sulfoaluminate based cement in reducing the impact of environmental pollution.

2. Even if calcium sulfoaluminate and belite have been formed at lower temperatures than Portland cement, it is necessary to use a sintering temperature not less than 1300^0C in order to reduce the free CaO content and to produce a more reactive product.

3. The main hydration product of calcium sulfoaluminate based cement is ettringite. The hydration of calcium sulfoaluminate to form ettringite may proceed through topochemical diffusion processes on the surfaces of solid phases or by crystallisation from supersaturated solutions or by combination of both mechanisms. The hydration of calcium sulfoaluminate cement mostly occurs at an early age. The presence of calcium hydroxide enhances the hydration process. In CSA–belite cement, long-term hydration of unhydrated CSA might be expected following the production of calcium hydroxide produced by the hydration of belite. The conversion of ettringite into monosulfoaluminate hydrate might occur in the case of less gypsum being available.

4. The finely ground ettringite is stable up to 60^{0}C. It will convert to the low sulfate form after 1 hour and then decompose to gypsum after 14 hours. The ettringite might react with calcium silicate hydrates. At temperature of boiling water the tobermorite phase forms. In the presence of lime or monocarboaluminate hydrate, the hydrogarnet phase appears beside the monophase solid solution.

5. Basically, the setting times of calcium sulfoaluminate cement are very short. The addition of Portland cement into the mix significantly increases the setting times. Retarding agents commonly used in Portland cement do not affect the setting times unless Portland cement is incorporated into the mix. In China, the setting times of CSA cement can be arranged between 2 and 10 hours.

6. At the early stages, the porosity of CSA-cement mortar is comparatively lower than the porosity of Portland cement and after 28 days the total pore volume is almost the same in both type of cement. Curing conditions influence the distribution of pore size.

7. Ettringite expansion is affected by the kinetics of ettringite formation, swelling due to uptake of water, matrix strength of the concrete and its development. Solutions unsaturated with lime and the presence of alkalies promote the expansion of ettringite.

8. Early strength development of CSA cement is faster than that of Portland cement. The presence of belite contributes to the ultimate strength development. CSA-based cement sintered at temperatures lower than 1300^{0}C results in lower compressive strength than that produced at temperatures of 1300^{0}C or more. The addition of $Ca(OH)_2$ to CSA-based cement will increase the strength. CSA-based cement can develop strength at sub-zero temperatures at the same rate as at 20^{0}C.

9. In some respects, concrete made with CSA cement may have better durability than concrete made with Portland cement. Excellent resistance to sulfate attack, brine attack and re-crystallization damage, freeze and thaw and carbonation have been claimed by various authors. But the relatively low pH of concrete made with CSA may cause a problem in protecting reinforcing steels. The addition of Portland cement into the concrete matrix may increase the pH up to the level that can prevent the protective oxide film of reinforcing steel to disintegrate.

III

MATERIAL AND EXPERIMENTAL DESIGN

3.1 Materials Used for Experimental Work

3.1.1 Binding Materials

3.1.1.1 Calcium Sulfoaluminate Cement

Two types of calcium sulfoaluminate (CSA) cement were used throughout the experimental work. Nearly pure CSA cement synthesised in the laboratory from AR raw materials was used for assessing the properties of the paste. Because of the limited amount of pure CSA cement that can be produced in the laboratory, this type of cement was mainly used to examine the hydration process, compressive strength and stability of paste samples. It is expected that the study of pure CSA cement will build up more a comprehensive understanding of the properties of ettringite formed under various conditions. Production of CSA cement in the laboratory is discussed in Chapter IV.

The second cement investigated was a commercially manufactured CSA cement produced in the UK. This is available in large amounts and was used to assess the properties of paste and of fresh and hardened concrete. The data obtained from the investigation of nearly pure CSA were adopted to optimise the advantages of CSA as a binding material in concrete. The properties of the commercially manufactured CSA cement are given in table 7.1.

3.1.1.2 Anhydrite

Calcium sulphate ($CaSO_4$) as the other compound required beside CSA cement to form ettringite was used in form of anhydrite. There is no special reason in using anhydrite instead of other phases of calcium sulphate, notably gypsum, except the availability consideration. In some research work, it is not uncommon to use gypsum as an ingredient to form ettringite and the results have been as successful and effective as the use of anhydrite in studying the properties of ettringite as a binding material (see Chapter II).

3.1.1.3 Calcium Hydroxide

Analytical reagent (AR) calcium hydroxide was used to examine the effect of this material on the formation of ettringite and on its properties. The use of calcium hydroxide as an ingredient in the formation of ettringite was only applied in a limited number of paste samples.

3.1.1.4 Portland Cement

Ordinary Portland cement (OPC) was introduced into the matrix in pastes and concretes. The purpose of using OPC in the system is to examine the effect of it on the properties of the pastes and concretes. The presence of CSH and ettringite might be expected to affect the properties of the system. And also further reaction of CH as a product of OPC hydration with unhydrated CSA cement and anhydrite would certainly increase the amount of ettringite ($C_6A\bar{S}_3H_{32}$) in the system (equation 1.1, Chapter 1).

3.1.2. Aggregates

For concrete mixes, medium sized river sand was used as the fine aggregate. The coarse aggregates were rounded river gravel with a combination of 30% 10 mm maximum size and 70% 20 mm maximum size. The properties of the fine and coarse aggregates are given in table 3.1

Table 3.1: Properties of Aggregates

Test	Sand	Coarse Aggregates 10 mm	Coarse Aggregates 20mm
Sieve Analysis:			
% Passing			
No. of Sieve			
4.75	98		
2.36	86		
1.18	76		
600	62		
300	20		
150	6		
75	0		
Fine Modulus	2.51		
Specific Gravity:			
Saturated Surface Dry	2.59	2.58	2.60
Dry	2.58	2.55	2.59
Apparent	2.62	2.63	2.63
Water Absorption (%)	0.59	1.12	0.58

3.1.3 Water

Tap water was used as the mixing water for paste and concrete. Considering that the water is potable, it should be suitable in fulfilling the requirement of water for paste and concrete.

3.1.4 Superplasticiser

Poly carboxylate based superplasticizer was used to produce a low water/ cement ratio concrete at a reasonable workability. As a practically new generation of superplasticizer compared to melamine or napthalane based superplasticizer, its compatibility with calcium sulphoaluminate cement was carefully monitored in the experiments.

3.2 Experimental Design

3.2.1 Design of Paste Mixes Made with CSA Cement Synthesised in Laboratory

As only a limited amount of calcium sulfoaluminate cement can be synthesised in the laboratory at any one time, the experimental work using this cement focused on the properties of the cement paste. Based on the use of binding material, the mixes were designed as below:

3.2.1.1 Calcium Sulfoaluminate Cement With Different Contents of Anhydrite and Different w/cm Ratio

Three different contents of anhydrite were applied in the experimental work. The highest content was determined by the stoichiometric reaction calculated as follows:

Equation Reaction:

$4CaO.3Al_2O_3.SO_3+2(CaO.SO_3)+35H_2O=6CaO.Al_2O_3.3SO_3.32H_20+2Al_2O_3.3H_2O$

Relative Masses of Atoms:

Ca =	40.08	O=	15.999
Al=	26.98	S=	32.064
C=	12.011	H=	1.008

CaO=	56.079 g/mole	SO_3=	80.061 g/mole
Al_2O_3=	101.957 g/mole	H_2O=	18.015 g/mole

Table 3.2: Reaction Products

Reaction Products	Chemicals Equations	Relative Masses of Molecules	1 g
I Ettringite	$6CaO.Al_2O_3.3SO_3.32H_2O$	1255.094 g/mole	0.000797 mole
II Gibsite	$2Al_2O_3.3H_2O$	257.959 g/mole	0.003877 mole

And for 1 g ettringite, the substances required, therefore, are:

4CaO.3Al2O3.SO3 = 0.486g
2(CaO.SO3) = 0.217 g
38 H2O = 0.545 g

For the stoichiometric condition
Anhydrite/Klein's compound = 0.446
Anhydrite/(Klein's compound + Anhydrite) = 0.309
Water/Klein's compound = 1.122
Water/(Klein's compound + Anhydrite) = 0.776

The proportions derived from the above calculation were used as a starting point for further development on the variation of water and anhydrite contents. Designations and compositions of mixes, involving the use of 3 w/cm ratios and 3 different contents of anhydrite, are given in table: 3.3

Table 3.3: Designations and Composition of Mixes for Calcium Sulfoaluminate Paste

Designation	w/cm	Anhydrite Content (%)
A11	0.78	31
A12	0.50	31
A13	0.30	31
A21	0.78	22.5
A22	0.50	22.5
A23	0.30	22.5
A31	0.78	15
A32	0.50	15
A33	0.30	15

3.2.1.2 Incorporation of Calcium Hydroxide into the CSA Cement and Anhydrite System

The design is based on the chemical equation:

$4CaO.3Al_2O_3.SO_3+8(CaO.SO_3.)+6Ca(OH)_2+90H_2O=3(6CaO.Al_2O_3.3SO_3.32H_20)$

Relative Masses of Atoms

Ca = 40.08 O =15.999 C=12.011

Al = 26.98 S = 32.064 H = 1.008

Relative Masses of Molecules:

CaO = 56.079 g/mole; SO_3 = 80.061g/mole

Al_2O_3 = 101.957 g/mole; H_2O =18.015 g/mole

Table 3.4: Weight of substances for 1 g of ettringite:

Elements	Weight (g)
4CaO.3Al2O3.SO3	0.162
8(CaO.SO3)	0.289
6(CaOH)2	0.118
90H2O	0.431

Based on the weight of substances in Table 3.4, the proportion of substances was calculated and presented in Table 3.5.

Table 3.5: Proportions of Substances

Proportion	Ratio
Anhydrite/Klein's compound	1.78
Anhydrite/(Klein's compound+Anhydrite)	0.64
Anhydrite/(Klein's compound+Anhydrite+CH)	0.51
CH/(Klein's compound + Anhydrite+CH)	0.21
Water/Klein's compound	2.66
Water/(Klein's compound + Anhydrite+CH)	0.76

3.2.1.3 Incorporation of Ordinary Portland Cement (OPC) into CSA Cement + Anhydrite System

OPC was included into the mix at a water/cementitious ratio 0.5 at different contents of anhydrite. The content of OPC was 25% of total binder and the proportion of anhydrite was 40%, 30% and 20%. The designations and compositions of the materials are given in table: 3.6

Table 3.6: Designation and Compositions of Mixes containing CSA + Anhydrite + OPC

Designation	w/cm	OPC (%)	Anhydrite (%)	CSA
C1	0.50	25	30	45
C2	0.50	25	22.5	52.5
C3	0.50	25	15	60

3.2.2 Design of Concrete

An OPC concrete with w/cm ratio=0.50 and a reasonable workability indicated by a slump between 100-125 mm was designed as a reference mix (REF-0.5 in table 3.7). For CSA concrete mixes, the OPC was replaced by CSA cement and anhydrite at the same level of w/cm ratio, water content and weight of binding materials. The difference in density between OPC on the one hand and CSA cement and anhydrite on the other hand was corrected by adjusting the content of sand based on the absolute volume method. The anhydrite contents used were 15 and 25% of the total binder (RF15-0.5 and RF25-05 respectively in Table 3.7).

CSA cement and anhydrite concrete containing Portland cement was designed by inclusion of Portland cement with a content of 25% of the total binders into mixes with 15 and 25% anhydrite contents RC15-0.5 and RC25-05 respectively in Table 3.7).

The details of mixes with water/cement ratio = 0.50 and their designations are given in table: 3.7.

Table 3.7: CSA Cement Concrete Mixes with wcm Ratio = 0.50

Material	Weight/M^3 of Concrete				
	Ref-0.5	RF15-0.5	RF25-0.5	RC15-0.5	RC25-0.5
Water	166.00	166.00	166.00	166.00	166.00
Anhydrite		49.80	83.00	37.35	62.25
CSA Cement		282.20	249.00	211.65	186.75
PC	332.00			83.00	83.00
Sand	743.19	701.74	704.44	735.99	714.13
C. Agg. (20 mm)	767.37	767.37	767.37	767.37	767.37
C. Agg. (10 mm)	328.94	328.94	328.94	328.94	328.94
Total Weight/M^3	2337.50	2296.05	2298.75	2330.30	2308.44

Mixes with different w/cm ratios were designed to investigate their effects on the properties of the concrete. The variations of w/cm ratio used were 0.70, 0.60, 0.50, 0.40, and 0.30. The same water content as for reference mix 0.5 was applied to the other mixes. And again, the differences in cementitious material contents were corrected by adjusting the content of sand based on the absolute volume method.

In order to avoid excessive cement content, a lower water content was applied to the mix with w/cm ratio of 0.30. Polycarboxylate based superplasticiser was used to maintain a reasonable workability. The details of the compositions and designations of OPC concrete mixes as references with different w/cm ratios are given in table 3.8 and for commercially manufactured CSA concrete mixes are given in table 3.9.

Table 3.8: Reference OPC Concrete Mixes with Different w/cm Ratios

Material	Weight of Material/M^3 of Concrete Kg)				
	REF-0.7	REF-0.6	REF-0.5	REF-0.4	REF-0.3
w/cm Ratio	0.7	0.6	0.5	0.4	0.3
Water	166.00	166.00	166.00	166.00	135.00
PC	237.14	276.67	332.00	415.00	450.00
Super-plasticizer					3.38
Sand	821.19	788.69	743.19	674.95	720.60
Coarse Aggregate (20 mm)	767.37	767.37	767.37	767.37	771.49
Coarse Aggregate (10 mm)	328.94	328.94	328.94	328.94	330.70
Total Weight/M^3	2320.64	2327.66	2337.50	2352.25	2411.16

Table 3.9: CSA Cement Concrete Mixes with Different w/cm Ratio

Material	Weight of Material/m^3 of Concrete (Kg)				
	RF25-0.7	**RF25-0.6**	**RF25-0.5**	**RF25-0.4**	**RF25-0.3**
w/cm Ratio	0.7	0.6	0.5	0.4	0.3
Water	166.00	166.00	166.00	166.00	135.00
Anhydrite	59.29	69.17	83.00	105.87	112.50
CSA Cement	177.86	207.50	249.00	317.61	337.50
Super-plasticizer					1.80
Sand	793.50	756.39	698.07	704.44	668.08
Coarse Aggregate (20 mm)	767.37	767.37	767.37	767.37	771.49
Coarse Aggregate (10 mm)	328.94	328.94	328.94	328.94	330.70
Total Weight/m^3	2292.96	2295.37	1594.31	2298.75	2357.07

3.3 Experimental Work and Investigations

3.3.1 General

The experimental work was divided into 2 steps. The first step was carried out to investigate the properties of paste made from CSA synthesised in the laboratory. The second step involved the investigation of the properties of CSA concrete made with commercially manufactured CSA cement. The later work was developed based on the results of the first step. The overall experimental work and the investigation are summarised in Fig: 3.1

3.3.2 Investigation of The Properties of Paste Made from Calcium Sulfoaluminate Cement Synthesised in The Laboratory

The investigation of the properties of calcium sulfoaluminate cement synthesised in the laboratory covered:

- Hydration process
- Expansion
- Compressive Strength Development
- Porosity
- Microstructure

Because of the limited amount of sample that could be prepared in the laboratory, the experiment was performed on a paste sample.

3.3.2.1 Hydration Process

The hydration process was principally monitored using X-ray diffraction (XRD) analysis. The X-ray diffraction equipment used was a Philips 1730 diffractometer using CuK_α radiation at 50 kV and 30 mA. Samples used for XRD analysis were prepared from crushed cement paste samples left over after compressive strength testing. The samples was ground into finely divided powder passing 45 um sieve. A copper sample holder was used. A front loaded technique was applied. The hydration development was measured after 6 hours, 1 day, 3 days, 7 days, 28 days, 3 months and six months. Additionally, Scanning Electron Microscopy (SEM) was used to examine microstructure of selected samples.

3.3.2.2 Expansion

The development of expansion was investigated on hardened paste samples with dimensions 20 x 20 x 120 mm using a set of length change equipment at the age of the paste: 6 hours, 1 day, 3 days, 7 days, 28 days, 3 months, and 6 months. Some of the samples were cured in water and in air, and some of them were, firstly, cured in air and then after a certain age when contraction had stopped, the curing was continued in water. The weight change of samples was also monitored during the period that the length change testing was carried out.

3.3.2.3 Compressive Strength

Compressive strength tests were conducted on paste samples with dimensions 20 x 20 x 20 mm. The ages and curing conditions of the samples were the same as those in the expansion tests.

3.3.3 Properties of Concrete Made with Commercially Manufactured CSA Cement

Based on the fact that the properties of concrete are influenced by the characteristics of the binding materials, the aggregates and any interaction between them, research carried out on cement paste alone could not sufficiently represent all the properties of concrete. Especially for a new type of cement such as CSA based cement, it must essentially fulfil some specific criteria of fresh concrete and hardened concrete properties before the cement can be used confidently as a structural concrete material.

The experimental work done by using cement synthesised in the laboratory, therefore, was followed up by an investigation into the properties of concrete made with manufactured CSA cement, and on the effects of incorporating admixtures and Portland cement on the performance of the concrete.

3.3.3.1 Investigations of Fresh Concrete

3.3.3.1.1 Setting Time

Initial and final setting times of paste made with manufactured CSA cement were tested by using a Vicat apparatus, according to ASTM C 191-92. The contents of synthetic anhydrite and OPC were varied. The effect of addition of the superplasticiser on the setting time was also examined.

Stiffening times of different concrete mixes were measured with a Proctor probe, according to BS 5075 : Part 1 : 1982 (British Standard, 1982). The samples were mortar specimens sieved out of the concrete, using a 5 mm sieve.

3.3.3.1.2 Workability of Concrete

The effects of different mixes on the workability of the concrete were accessed by using the slump test according to BS 1881 : Part 102 : 1983 (British Standard, 1983) and Tatersall's two-point test. Loss of slump was also investigated (Tattersall, 1991).

3.3.3.1.3 Other Investigations

For every mix, the density of the fresh concrete, the air content, bleeding and segregation were investigated visually and experimentally.

3.3.3.2 Investigations of Hardened Concrete

3.3.3.2.1 Strength of Concrete

The strengths of different mixes were investigated at different levels of curing (water curing, seal curing, air curing, and air curing followed by water curing). Strength development of concrete was monitored at 1 day, 3 days, 7 days, 28 days and 6 months.

a Compressive Strength

The compressive strength of concrete samples was tested according to BS 1881 : Part 116 : 1983 (British Standard, 1983), by using concrete cubes with dimensions 100 x 100 x 100 mm.

b Indirect Tensile Strength

Indirect tensile strength of different concrete mixes was tested according to BS 1881:Part 117: 1983 (British Standard, 1983), by using concrete cylinders with dimensions diameter 100 mm and height 200 mm.

c Flexural Strength

The flexural strength of different concrete mixes was tested according to BS 1881 : Part 118 : 1983 (British Standard, 1983), by using the third point loading test on concrete prisms dimensions 100 x 100 x 300 mm. The test was carried out at selected ages of the concrete.

3.3.3.2.2 Length Change and Weight Change of Concrete

The length change of different concrete mixes at different ages and curing conditions was tested according to ASTM C 1293 (1995), by using concrete prisms with dimensions 75 x 75 x 254 mm. The weight changes were monitored by using the same samples used for length change investigations at the same ages. The weights were measured on a balance accurate to ± 0.1 g.

3.3.3.2.3 Durability Related Parameters

a Oxygen Permeability

The oxygen permeability of different concrete mixes at different ages and curing conditions was measured by using the modified Cement and Concrete Association Cell and the Leeds Cell (Cabrera and Lynsdale, 1988) on cylinder samples with size diameter 100 mm and height 50 mm.

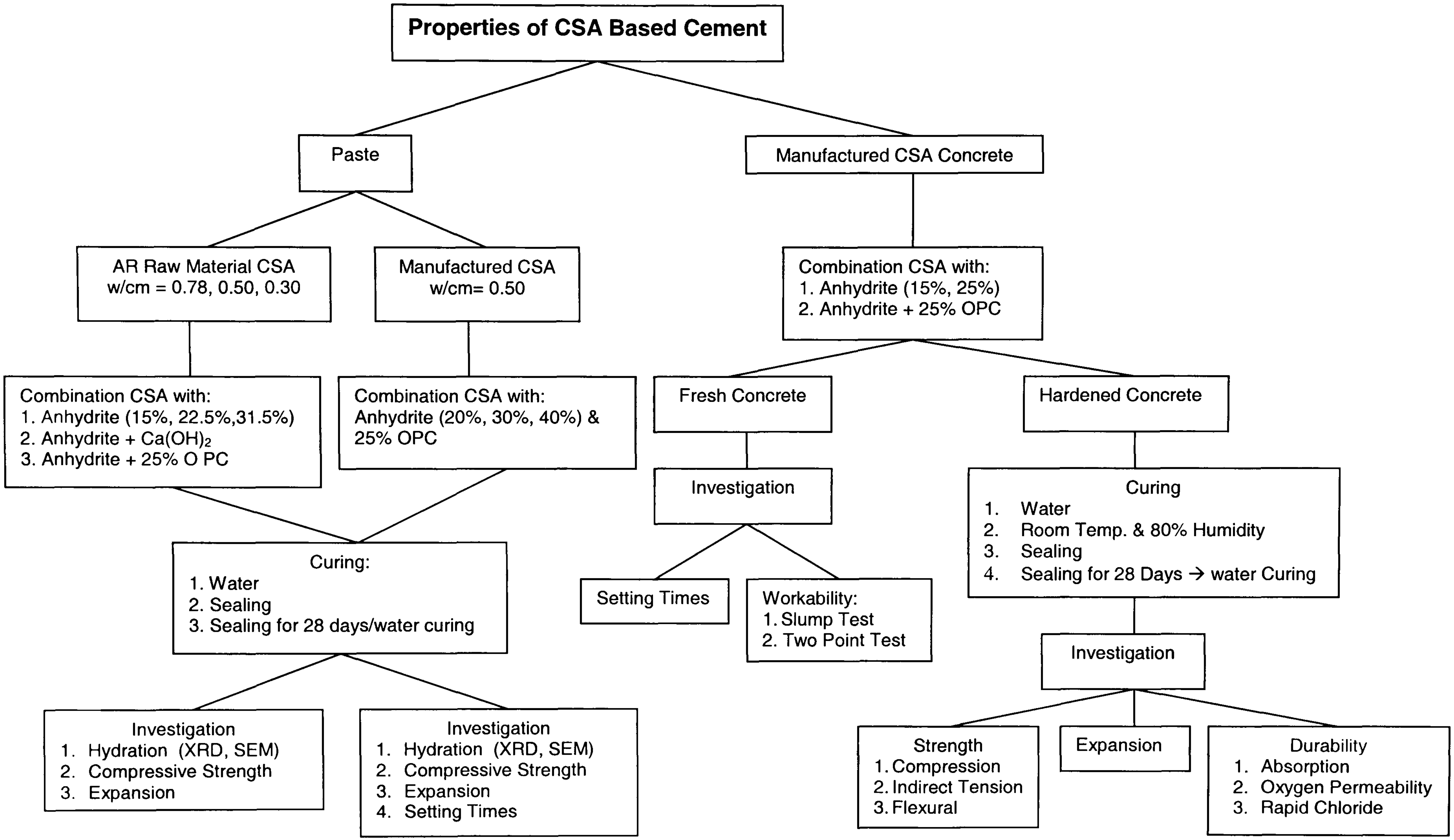
b Porosity

The porosity of different concrete mixes at different ages and curing conditions was determined on the same sample used for determination of oxygen permeability. The porosity of the sample was assessed by measuring the volume of the sample and the volume of water contained in the sample at saturated surface dry condition. In order to optimise the absorption of water into the dry concrete samples, the dry concrete samples were held under vacuum for 24 hours before being immersed into de-ionised water. A further 24 hours vacuum process was applied after the samples were immersed.

c Rapid Chloride Permeability

The rapid chloride permeability of different concrete mixes at different ages and curing conditions was assessed according to the modified ASSHTO T277 test (AASTHO, 1993). The samples used for the oxygen permeability and porosity tests were also used for the rapid chloride permeability test.

Fig. 3.1: Summary of Research



IV

SYNTHESIS OF KLEIN'S COMPOUND (CSA CEMENT) IN THE LABORATORY

4.1 Material

As the purpose of synthesising Klein's compound ($C_4A_3\bar{S}$) in the laboratory is to obtain the compound as pure as possible, the raw materials used were analytical reagent (AR) $CaCO_3$, $Al(OH)_3$ and $CaSO_4$. Their crystalline form ensures that the raw materials can be identified by X-ray diffraction (XRD) analysis in order to monitor their purity. Peak identification for a given material issued by JCPDS-International Centre for Diffraction Data was used as comparison. Two Theta angles from 5 to 55^0 were scanned at a scan speed of 2^0/min. An XRD graph of each material and a table of d-spacing and 2θ angles for the 3 strongest lines of each material are given in fig. 4.1a-c and table 4.1, respectively.

Table 4.1: XRD data for $CaCO_3$, $Al(OH)_3$ and $CaSO_4$

Material	d-spacing (Å)		Relative Intensity (%)		2θ (^{0})
	Found	JCPDS	Found	JCPDS	Found
$CaCO_3$	3.029 2.282 2.092	3.030 2.284 2.094	100 5 3	100 27 18	29.47 39.46 43.20
$Al(OH)_3$	4.819 4.350 2.379	4.82 4.34 2.37	100 35 19	100 40 20	18.40 20.40 37.78
$CaSO_4$	3.494 2.847 2.326	3.499 2.849 2.328	100 11 8	100 35 20	25.47 31.40 38.68

The purity of each raw material can be confirmed from the XRD results. $CaCO_3$ $Al(OH)_3$, and $CaSO_4$ are confirmed by three strongest lines with d spacings of (3.029 Å, 2.282 Å and 2.092 Å), (4.819 Å , 4.350 Å , 2.379 Å) and (3.494 Å , 2.847 Å , 2.326 Å), respectively. The anhydrite samples was free from the presence of any gypsum which would have been readily identified in Fig. 4.1.c.

4.2 Proportion of Raw Materials

The proportions of $CaCO_3$, $Al(OH)_3$ and $CaSO_4$ were calculated based on the stoichiometric reaction as follows:

$3CaCO_3 + 6Al(OH)_3 + CaSO_4 = 4CaO.3Al_2O_3.SO_3 + 9H_2O + 3CO_2$ ......(4.1)

The RAM of each element is Ca = 40.08, Al=26.98, S=32.064, C=12.011, H=1.008 and O=15.999, hence the calculated RMM of each material is:

$CaCO_3$ = 100.088 g/mole
$Al(OH)_3$ = 78.001 g/mole
$CaSO_4$ = 136.14 g/mole

and RMM of $4CaO.3Al_2O_3.SO_3$ is 610.248 g/mole.

To produce I g of Klein's compound, therefore, the required amounts of raw material are as follows:

$CaCO_3$ = 3 x 100.088 / 610.248 = 0.4920 g.
$Al(OH)_3$ = 6 x 78.001 / 610.248 = 0.7669 g.
$CaSO_4$ = 1 x 136.14 / 610.248 = 0.2231 g.

4.3 Sample Preparation

4.3.1 Procedures

Because of the limited volume capacity of the furnace that can be used for a single sintering process, a raw mix was prepared to produce 1000 g of Klein's compound for each production. The weights of raw materials required were:

$CaCO_3$ = 1000 * 0.4920 = 492.04 g
$Al(OH)_3$ = 1000 * 0.7669 = 766.91 g
$CaSO_4$ = 1000 * 0.2231 = 223.09 g

Each sample was weighed using a Unimatic CL41 balance to an accuracy of ± 0.0005 g.

The raw material was thoroughly mixed in a porcelain ball mill with tap water (water/solid = 0.5) and alumina balls as ball media for 4 hours. The sample was then drained and dried in an oven at 110^0C. The dried sample was reground to produce a finely divided powder.

The mixing process is one of the most critical parts in producing Klein's compound, as the reaction of the raw material is extremely dependent on the distribution of the constitutive materials in the mix.

4.3.2 Monitoring Loss of Sample during Preparation

Loss of sample during preparation was monitored by weighing the sample before and after the preparation process. From 10 mixes, it was found that the average weight loss was 2.5 %, with a standard deviation of 0.45% and a coefficient of variation of 18.18% (see table 4.2). At this stage of the process, loss of sample is considered fairly high. But it was not unexpected because some loss of wet sample occurs when moved from ball mill to container, some of the sample is inevitably left in the container after the drying process and, some loss of sample during the grinding and sieving processes in unavoidable.

Table 4.2: Monitoring weight of sample before and after preparation

Weight (G)		% Loss	Notes
Initial weight	After Mixing And Drying		
1482.04	1440.98	2.77	
1482.04	1445.58	2.46	Standard Deviation = 0.45 %
1482.04	1436.98	3.04	
1482.04	1454.92	1.83	Coefficient Variation = 18.18 %
1482.04	1451.80	2.04	
1482.04	1454.77	1.84	
1482.04	1444.84	2.51	
1482.04	1446.17	2.42	
1482.04	1438.17	2.96	
1482.04	1435.80	3.12	
Total	14450.01	24.99	
Average	1445.00	2.50	

4.4 Sintering

4.4.1 Firing Process

The prepared powder samples were stored in alumina containers and then were fired in a Lenton Electrical Furnace at a maximum temperature of 1300^{0}C. The heating rate was 5^{0}C/min, the fastest rate of temperature increase that the furnace could sustain. The samples were held at 1300^{0}C for 3 hours and then cooled in air at a cooling rate of 5^{0}C/minute. The maximum temperature and duration of firing were chosen to minimise the content of free-CaO and to obtain Klein's compound.

The sintered sample was ground by using a ball mill with alumina balls as ball media for 4 hours and sieved to pass 45 μm mesh.

4.4.2 Characterisation of Sintered Products

4.4.2.1 Loss of Sample in Sintering Process

The calculated reduction of sample is 32.5% after the sintering process. The loss of sample consists of evolved H_2O and CO_2 (equation 4.1) and missing material in the handling process. In practice, the sample was weighed before sintering and just after the cooling process. Therefore the loss of sample due to grinding and sieving after the sintering process was not considered. It was found that from 10 burnt samples the average loss of sample was 32.07% with standard deviation and coefficient of variation being 0.48% and 1.50%, respectively (See Table 4.3). These figures explain that the handling process of sintering was highly reliable. The sintered loss of sample was almost the same as the calculated loss of sample indicating that the purity of Klein's compound produced is reasonably good.

Table 4.3: Monitoring weight of sample before and after firing process

Weight (G)		% Loss	Notes
Before Firing	After Firing		
1440.98	966.90	32.9	
1445.58	977.21	32.4	Standard Deviation = 0.48 %
1436.98	975.71	32.1	
1454.92	987.89	32.1	Coefficient Variation = 1.50 %
1451.80	995.94	31.4	
1454.77	993.61	31.7	Calculated Loss of Samples=32.5%
1444.84	979.60	32.2	(Based on equation 1-3)
1446.17	979.06	32.3	
1438.17	989.46	31.2	
1435.80	970.60	32.4	
Total	9815.97	320.7	
Average	981.60	32.07	

4.4.2.2 XRD Investigation

The phases of the fired samples were assessed by XRD. The graph of XRD and table of d-spacing and 2θ angles are given in figure 4.2 and table 4.4, respectively.

Table 4.4: XRD of phases in the fired sample

Phases	d-spacing Å	Relative Intensity (%)	($^0 2\theta$)
$C_4A_3\overline{S}$	3.750	100	23.71
	2.653	29	33.76
	2.165	21	41.68
CA	2.966	7	30.10
	2.517	2	35.64
	2.416	2	37.18

Klein's compound ($C_4A_3\overline{S}$) was the dominant phase in the sample. It is obvious from its three strongest lines at d-spacing (3.750 Å , 2.653 Å , 2.165 Å). Some CA was also detected, represented by d-spacing (2.966 Å , 2.517 Å , 2.416 Å). It is shown by the peaks labelled CA in Fig. 4.2.

A semi-quantitative approach was also carried out to monitor the purity of the Klein's compound produced in each individual firing. The counts under the highest XRD peak area of Klein's compound were calculated. From 10 preparations, it was found that the average of the counts was 21983.5 with a standard deviation and coefficient variation of 258 and 1.2% respectively (See table 4.5). This relatively low standard deviation and coefficient of variation confirmed the homogeneity and repeatability of the Klein's compound production.

Table 4.5: Calculation of counts under the highest peak area

Counts under Highest Peak Area	Notes
22134	
22157	Average = 21983.5
21791	Standard Deviation = 258
21469	Coefficient of Variation = 1.18%
22132	
21947	
21648	
22306	
21997	
22254	

Fig. 4.1.a: XRD of CaCO3

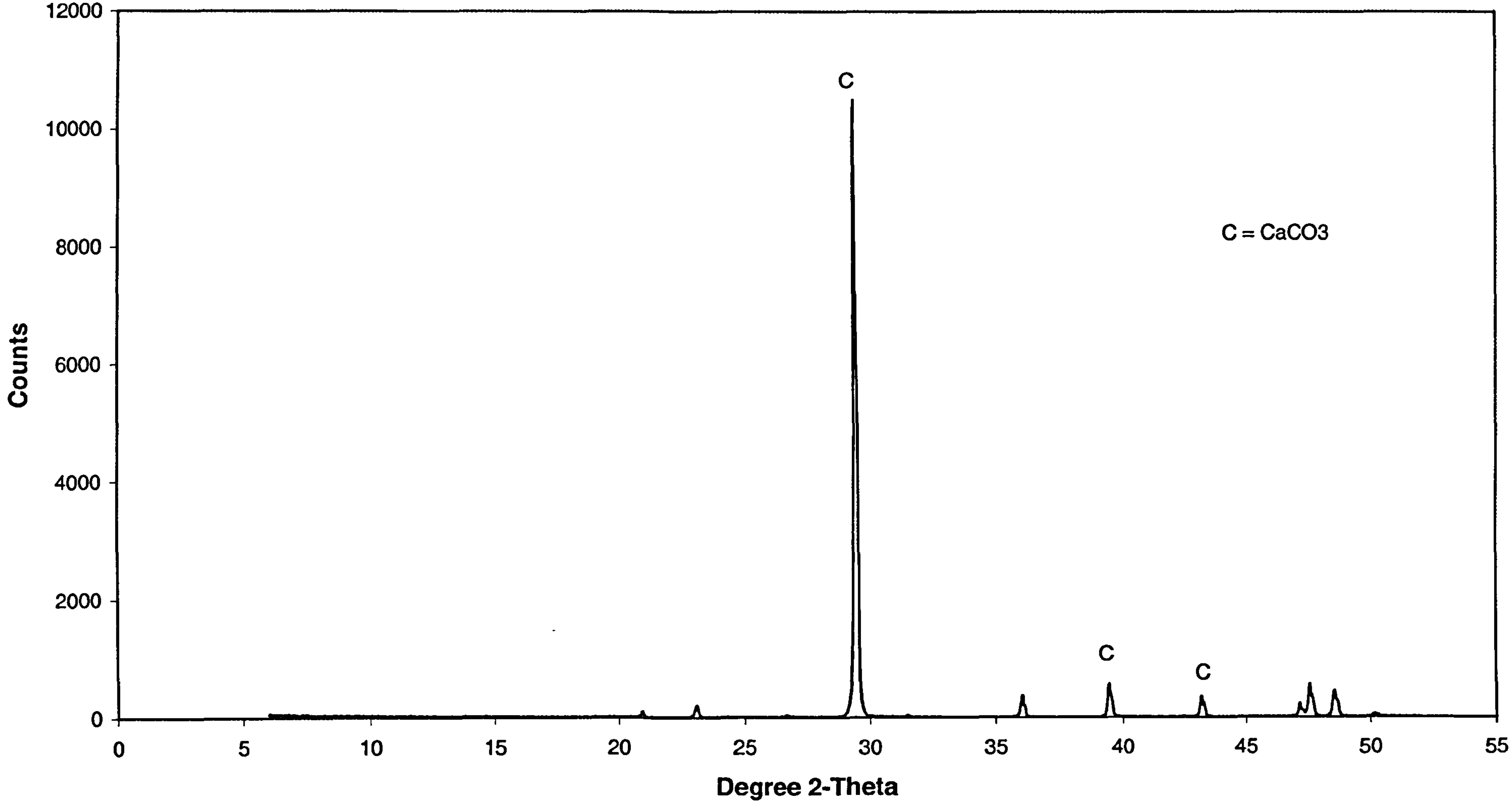


Fig. 4.1.b: XRD of $Al(OH)_3$

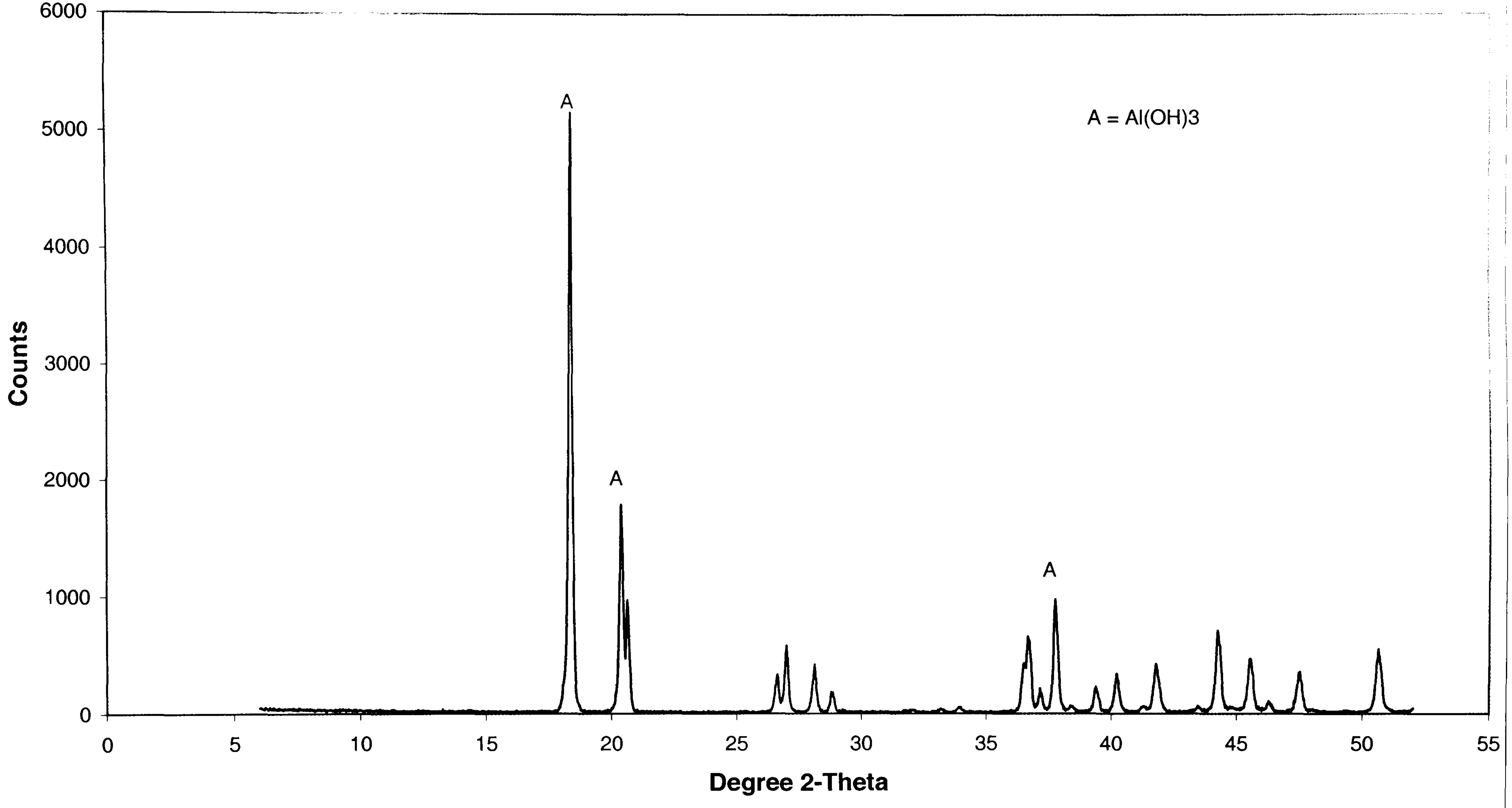


Fig. 4.1.c: XRD of CaSO4

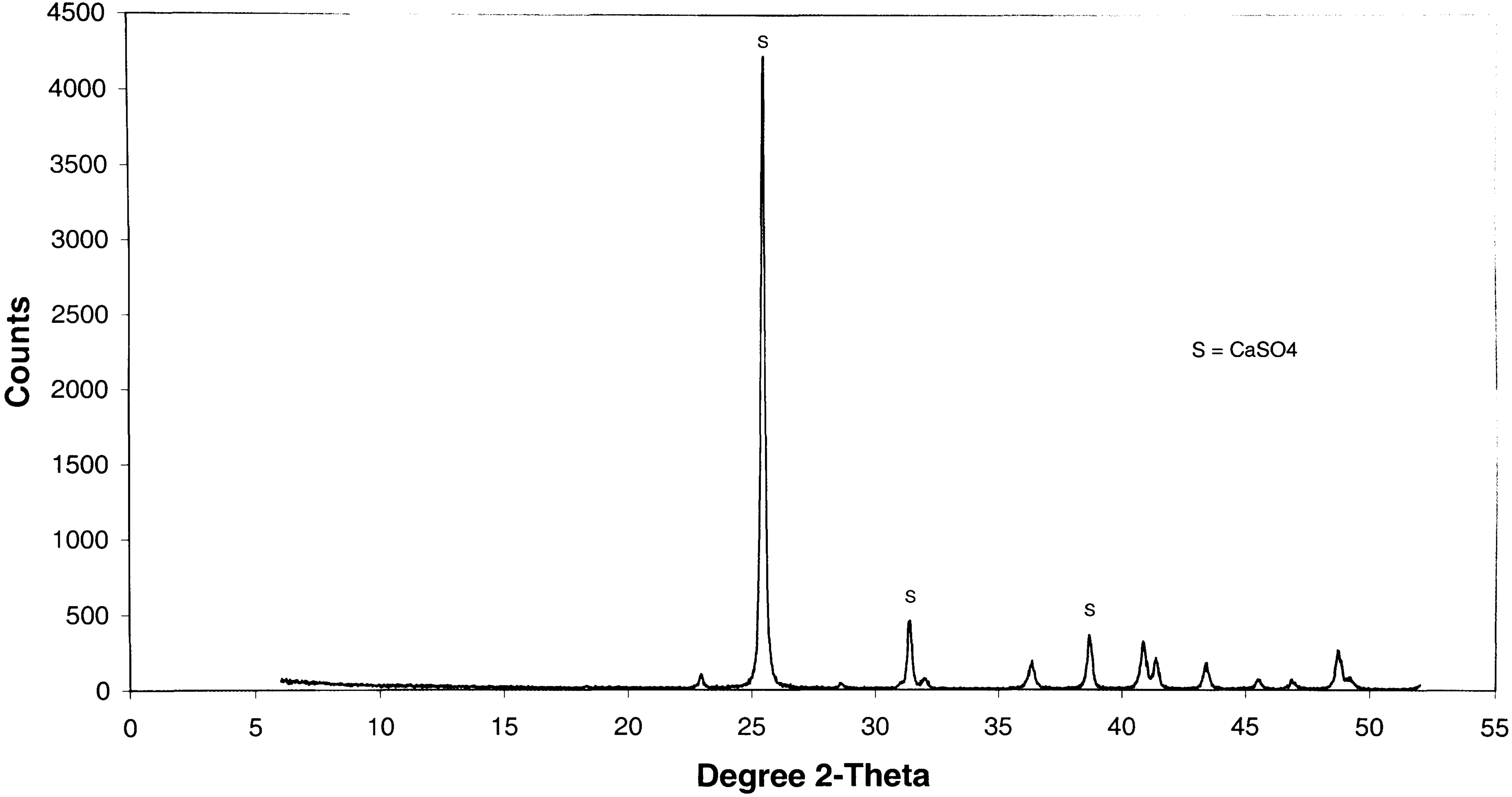
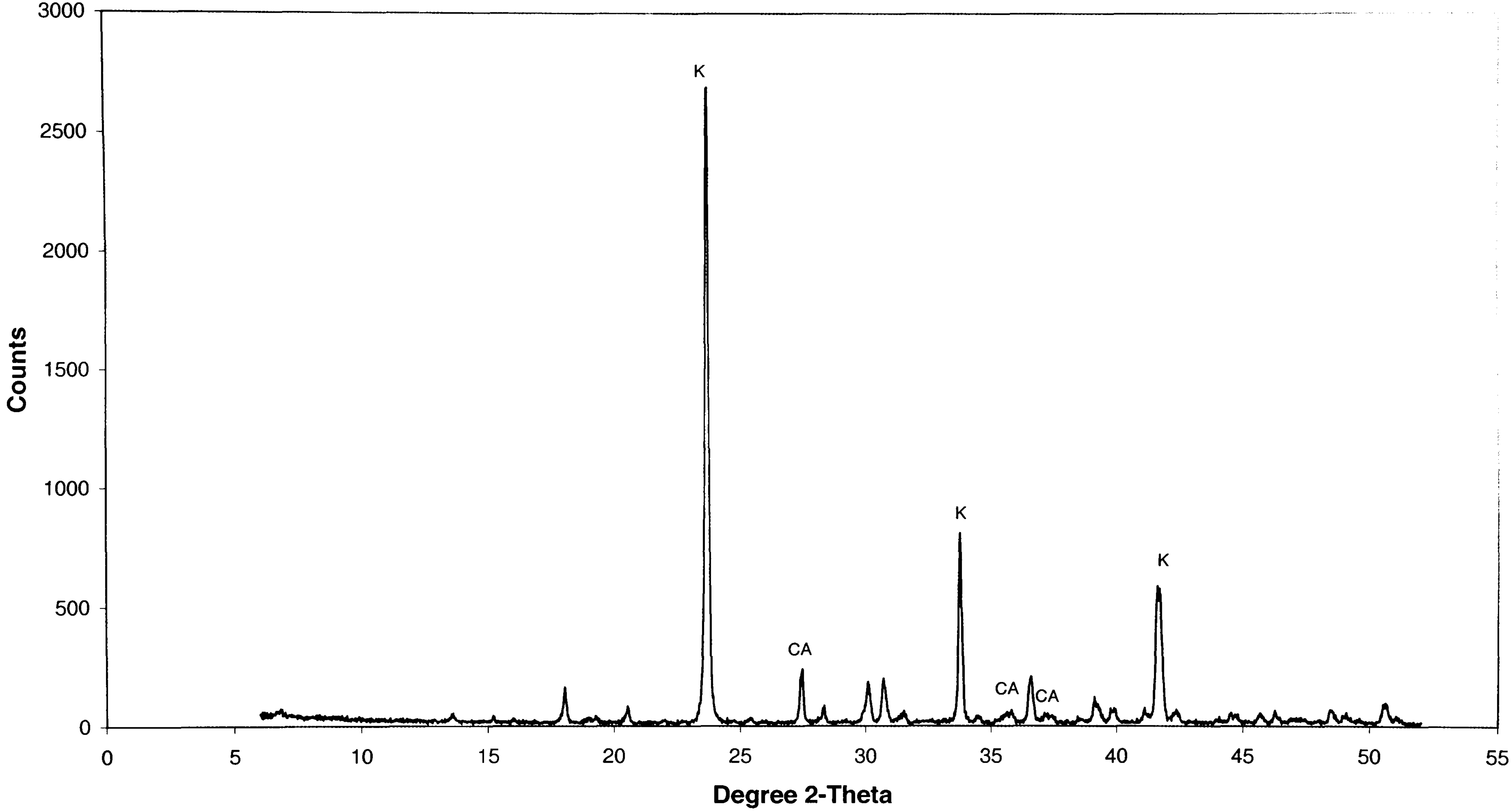


Fig. 4.2: XRD of Klein's Compound Made in Laboratory



V

PROPERTIES OF PASTE MADE WITH CSA CEMENT SYNTHESISED IN LABORATORY

5.1 Introduction

The properties of a cement paste made with laboratory synthesised CSA cement have been examined. The hydration process, dimensional stability and development of compressive strength of samples are included. The discussion will focus on the effect of different water/cementitious material (w/cm) ratio, different anhydrite contents, and different curing regimes on the properties of CSA cement paste.

In the experiments, w/cm ratios used in were 0.78 (derived from the stoichiometric equation), 0.5 and 0.3, while anhydrite contents were 31% (derived from the stoichiometric equation), 22.5% and 15%. Curing regimes applied to the samples were water curing, sealed as cast curing, water curing after sealing as cast for 28 days.

5.2 Hydration Process

5.2.1 General

The hydration of CSA cement and anhydrite is expected to follow the equation:

$$4CaO.3Al_2O_3.SO_3 + 2(CaO.SO_3) + 38H_2O=6CaO.Al_2O_3.3SO_3.32H_2O + 2Al_2O_3.3H_2O\ldots(5.1)$$

or in cement chemist's notation:

$$C_4A_3\bar{S} + 2C\bar{S} + 38H = C_6A\bar{S}_3H_{32} + 2AH_3$$

From equation 5.1, the requirement to produce a perfect reaction is w/cm ratio of 0.78 and an anhydrite content of 31% by mass of solid reactant. It is clearly seen that the hydration of CSA cement and anhydrite is much more water demanding than the hydration of C_3S in PC where the water requirement is about 23% of total solid. This high water demand plays a major part in influencing the hydration performance of CSA if used as the main substance in CSA based cement. It was expected that variation in anhydrite content would be an important factor in the hydration of CSA cement. The possibility of excess or lack of anhydrite in the system is expected to influence the hydration products.

Hydration of CSA paste was monitored using XRD and SEM. XRD was mostly used to study the hydration development, the degree of hydration (DoH) that can be reached at different w/cm ratios, different anhydrite contents and different curing conditions at any given age of the paste. SEM was applied on selected samples to look at the topographical images of ettringite formed under different conditions.

5.2.2 Curing Regimes

In order to investigate the effects of different water movement in the samples on hydration process and also the effects of $CaSO_4$ on samples, four curing conditions were applied to the samples. These involved:

- Sealing the samples directly after demolding by using cling film
- Curing the samples in water
- Sealing the samples for 28 days after demolding followed by curing in water
- Sealing the samples for 28 days after demolding followed by immersion in saturated $CaSO_4$ solution

The samples were maintained in the curing conditions until the tests were carried out at the ages of 1, 3, 7, 14, 28, 91 and 182 days.

5.2.3 Monitoring The Hydration Process Using XRD Method

5.2.3.1 Sample Preparation

Samples used for XRD analysis were prepared from crushed samples after compressive strength tests had been carried out. During the period from when the samples were taken from the compressive strength test until the XRD analysis was carried out, the samples were immersed in acetone to avoid further hydration. The crushed paste was ground into finely divided powder just before XRD analysis. 2θ Angles from 5^0 to 50^0 were scanned at a scan speed of 2^0/min. XRD patterns were obtained for each sample.

5.2.3.2 Hydration Products

An XRD pattern of a typical hydration product of CSA cement is shown in Fig. 5.1, based on the stoichiometric composition according to equation 5.1. Mix A10 consisted of CSA cement and anhydrite without the addition of water, and mix A11 was a sample sealed and cured for 28 days at room temperature (20 ± 1^0C). The XRD results were compared by peak identification issued by JCPDS-International Centre for Diffraction Data. It can be seen that ettringite was, as expected, the main hydration product. It is shown in graph A11 by the peaks marked as E. $Al(OH)_3$, as the expected second reaction product, could not be identified by the XRD test, perhaps because the material was amorphous in nature, i.e. alumina gel.

A considerable amount of anhydrous CSA is still clearly seen by the presence of peaks notified by K in mix A11. In fact the w/cm given by the stoichiometric composition was not sufficient to dissolve all the contributing materials into the solution. Unfortunately, the anhydrous anhydrite could not be traced as its peaks overlapped with peaks due to the growing ettringite. It is shown at peaks notified with E/A in Fig. 5.1. The presence of monosulfate and gypsum were not evident.

5.2.3.3 Semi-Quantitative Approach to Monitor The Hydration Process

In order to build up a better understanding of the hydration process of CSA cement, a semi-quantitative approach using the XRD results was carried out. The approach was firstly to determine the amount of ettringite that could be produced relative to the amount of CSA cement consumed. The preference to follow CSA instead of anhydrite was based on the coincidence of many the 2θ values between anhydrite and ettringite. The correlation between counts under the area of the strongest peak of ettringite at $2\theta = 9.14^0$ and of CSA at $2\theta = 23.74^0$ was made based on the mixes A1 (anhydrite content of 31%) at different w/cm ratios, different curing conditions and different ages.

As shown in Fig. 5.2, a linear relationship was found between the ettringite formed and the CSA consumed, given by the formula:

$$Y = -1.0866\,X + 9362.2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5.2)$$

where X is the intensity of the ettringite formed and Y is that for the CSA consumed. With $R^2 = 0.9747$, it can be said that there is a strong and fairly accurate correlation between ettringite formed and CSA consumed. At $Y = 0$, therefore, the value of X will give the maximum counts of ettringite that can be produced at the stoichiometric composition. This value, later on, is assumed to represent 100% DoH that could be achieved by a stoichiometric composition of CSA cement and anhydrite. The DoH of other mixes containing pure CSA cement with different w/cm ratio, anhydrite contents and curing conditions have been calculated based on the ratio of each count relative to the counts of 100% hydration.

The approach is suitable to measure the DoH of the samples, but it is not accurate to be used as a measure of the ettringite content in the samples. The reason for this is that the XRD analysis was carried out on solid powders with almost the same fineness at the same volume provided by the sample holder. In the samples, however, the content of solids and voids is different relative to the w/cm ratio and the anhydrite content. At a given anhydrite content, for example, a mix with a lower w/cm ratio would contain a higher amount of solid and lower amount of voids than one with a higher w/cm ratio.

5.2.3.4 Hydration Development of CSA Paste Based on Semi Quantitative Approach

5.2.3.4.1 Samples Sealed Directly After Demolding

Because the reaction between Klein's compound and anhydrite to form ettringite mainly occurred via a through solution mechanism, the water needed to dissolve the anhydrous particles into solution plays the most important part in the hydration process of CSA cement and anhydrite. For samples sealed and cured at room temperature, as there was no water movement in and out of the samples, the hydration of the sealed samples was totally dependent on the ability of the mixing water to dissolve the reacting particles.

The hydration development of samples with this condition is given in Fig. 5.4. From the figures, it can be clearly seen that the hydration process of CSA cement and anhydrite occurred rapidly once the particles were dissolved into the mixing water. The ultimate DoH was achieved at 7 days of curing period and beyond that age no further hydration took place. Generally, at any given anhydrite content, the ultimate DoH decreased with reduction of the w/cm ratio.

The limitation of the mixing water used to dissolve the reacting particles was most pronounced in the mix with a high anhydrite content. In samples containing 31% anhydrite (Fig. 5.4.a), not even a water content as high as that at the w/cm ratio derived from the stoichiometric equation was able to completely hydrate the reacting particles. The ultimate DoH was more or less the same as the mix with 22.5% anhydrite content at the same level of w/cm ratio (Fig. 5.4.b). The lower ultimate DoH of mix containing 15% anhydrite at the same level of w/cm ratio (Fig. 5.4.c) shows that the level DoH was controlled by the completely dissolving anhydrite particles. At 31% and 22.5% anhydrite and 0.78 w/cm, the DoH reached ~ 60%. At 15% anhydrite and 0.78 w/cm the DoH reached ~ 45%. So for maximum hydration under sealed curing, a certain amount of anhydrite is needed in the mix and this amount lies somewhere between 15 and 22.5%.

At w/cm=0.50, it seems that the ability of mixing water to hydrate the anhydrite particles is at approximately 15% of anhydrite content. The lowest DoH was produced by mixes at w/cm=0.30. As a rule of thumb, the anhydrous particles act as a filler, the amount of which depends upon w/cm ratio and anhydrite content.

5.2.2.4.2 Samples Cured in Water Directly After Demolding

As the level of pore water should be maintained to dissolve the anhydrous particles, the replacement of water consumed during earlier hydration is needed later on. The loss of water may also be caused by its incorporation into the ettringite formed. For these reasons curing the samples as soon as possible in water after demolding was thought to be necessary to follow the progress of the hydration process of CSA cement. Hydration development was monitored on pastes at the ages of 1, 3, 7, 14, 28, 91 and 182 days. The results are given in Fig. 5.5.

Generally, about half of the ultimate hydration has taken place after only 3 days of casting. In the mix containing 31% of anhydrite content, at w/cm=0.78, 50%. Hydration of the anhydrous particles continued at a rapid rate until 7 days of curing (Fig.5.5.a). A high content of interconnected voids because of the high w/cm ratio allowed the water from outside to ingress into the system. The penetrated water accelerated the formation of ettringite and then promoted the formation of open cracks in the samples (see Fig. 5.3). The cracks that started to develop in the samples were responsible for the fast development of DoH, because they became channels for water to ingress into the samples. After 7 days, the rate of hydration reduced as the availability of anhydrous particles decreased. The increase of the DoH from 91 days to 182 days of curing, as shown by XRD results, was most likely due to the leaching out of $Al(OH)_3$ into curing water. This was clearly seen in the curing water. It caused the XRD analysis to indicate more ettringite in the sample.

This crack induced hydration process was also clearly seen in the mix containing 31% anhydrite, at w/cm=0.50 (Fig.5.5.a). Naturally, with the lower w/cm ratio at the same anhydrite content, the mix would contain more solid particles and it would, therefore, leave more anhydrous particles at the early stages, hence the interconnected voids created were less than those at w/cm=0.78. Once open cracks had developed, the hydration continued at a fairly high rate. Further hydration caused more open cracks to be formed (see Fig. 5.3). The increase of open cracks in the samples encouraged the development of hydration, which continued until 92 days of curing. The rate of hydration subsequently slowed down with reduction in the amount of available anhydrous particles.

In the paste at w/cm=0.3 with the same 31% anhydrite (Fig. 5.5.a), the DoH was rapid up to 7 days of curing. A very low void content and then a more impermeable paste would allow only a limited amount of water to penetrate into the system to maintain the hydration. This condition would therefore allow a high proportion of particles to remain anhydrous. As no open cracks developed in the samples (see Fig. 5.3), only slow hydration development was observed up to 182 days of curing period.

Generally, a reduction of the anhydrite content in a mix would leave less anhydrous anhydrite available after a few days of hydration. It would cause only limited hydration activity at later ages. In mixes containing 22.5% of anhydrite (Fig. 5.5.b), at w/cm=0.78, the combination of high interconnected voids and the formation of open cracks was sufficient enough to allow the hydration to continue until 28 days. Then, after almost all of the anhydrite had been consumed, no further hydration took place. At this level of anhydrite, the ettringite formed in samples with w/cm=0.50, but was not able to cause open cracks. Therefore, the hydration was limited by the penetration of water into the system only through the pore system, which was relatively less permeable than the paste at w/cm=0.78 at the same content of anhydrite. The low permeability of samples with w/cm =0.3 was a constraint to the development of the hydration of CSA paste at this level of anhydrite content.

Reducing the anhydrite content to 15% significantly reduced the amount of ettringite formed, and hence the level of expansion, so that no open cracks developed. The hydration development in the sample containing 15% of anhydrite mostly relied on the ability of water to penetrate into the system. At the earlier ages up to 7 days of curing the hydration development of samples with w/cm=0.78 and w/cm=0.50 progressed at almost the same rate. At w/cm=0.30 the main formation of ettringite ended after 3 days of hydration. As the mixing water at w/cm=0.78 and 0.50 was able to dissolve the anhydrite, at this level of anhydrite content, there was much less difference in hydration development between samples cured in water and those sealed.

From Fig. 5.4 and Fig. 5.5, it is clearly seen that at w/cm=0.30, the effect of curing on the hydration development was not so pronounced. The low permeability of samples dictated the development of hydration in both samples cured in water or sealed directly after demolding.

5.2.3.5 Effect of w/cm Ratio on the Hydration of CSA Cement Paste

5.2.3.5.1 Calculated Relationship Between w/cm Ratio and the DoH of CSA Cement Paste

The relationships between w/cm ratio and the DoH of CSA cement paste at different levels of anhydrite content were observed along with the calculated DoH based on the chemical equation of hydration of CSA cement and anhydrite as a comparison (see Fig. 5.6 and 5.7). The calculated DoH was determined based on the assumption, that depending upon the composition, either water or anhydrite was fully consumed in the reaction process. The amount of ettringite formed at the stoichiometric composition was taken as 100% DoH and the amount of ettringite formed at lower contents of anhydrite and/or lower w/cm ratio could be related to it.

In any mix in which the content of the anhydrite was less than the stoichiometric composition of 31%, the maximum amount of ettringite formed was calculated at the optimum w/cm ratio that caused all the anhydrite to be consumed in the hydration process. Therefore the calculated curve ascends from lower w/cm ratio to reach that level of w/cm ratio and then descends when the w/cm ratio is beyond that optimum value, as shown in Fig. 5.6 and 5.7.

5.2.3.5.2 Relationship Between w/cm Ratio and DoH of CSA Cement Paste Sealed Directly After Demolding and Cured at Room Temperature

The main factor affecting the relationship between w/cm ratio and DoH of cement paste sealed and cured at room temperature is the ability of the mixing water to dissolve the reacting particles into solution. The results of this investigation are presented in Fig. 5.6.

The DoHs of all samples sealed directly after demolding and containing 22.5% and 31% anhydrite were lower than the calculated DoH. At the same curing condition, the DoH of samples containing 15% anhydrite passed the calculated DoHs at w/cm 0.78 after 91 days of curing (See Fig. 5.6). The results confirmed that at 0.78 w/cm, there was a certain amount of anhydrite, between 15% and 22.5%, allowed all the anhydrite to be consumed in the hydration of samples under sealed curing conditions.

The DoH of samples containing 31% anhydrite content were as expected always below that calculated at any given w/cm ratio and age (Fig. 5.6.a). At this level of anhydrite content, the difference between calculated and observed DOH at w/cm=0.78 was slightly higher than the mix with lower w/cm ratio.

For the mix with an anhydrite content of 22.5% (Fig. 5.6.b), at w/cm=0.78, the DoH was close to the calculated DoH, but at w/cm=0.5 and w/cm=0.3, the DoHs were considerably below the calculated DoH. For the mix with anhydrite content of 15% (Fig. 5.6.c), the DoH was even higher than the calculated hydration at w/cm=0.78, whereas the observed DoH was lower at the reduced w/cm ratio.

5.2.3.5.3 Relationship Between w/cm Ratio and DoH of CSA Cement Paste Cured in Water

Besides the different amount of the mixing water provided by different w/cm ratios, the different pore structures created by the different w/cm ratios are another important factor affecting the relationship between w/cm ratio and DoH of CSA cement paste. Higher w/cm ratios result in a more permeable paste where curing water can more easily penetrate into the pore system. The relationship between w/cm ratio and DoH of CSA paste continuously cured in water is given in Fig. 5.7.

The DoHs of samples cured in water was lower than the calculated DoHs at w/cm =0.3 at all anhydrite contents. The inability of water to penetrate the samples due to their lower permeability at lower w/cm is the reason that the DoH was not fully developed. The DoH of samples containing 31% anhydrite content passes the calculated DoH at 0.50 w/cm. It is possible as the calculated DoH at this stage was based on the amount of ettringite formed when all the available water was consumed during the hydration and anhydrous particles were still available. In fact in the experiment, with the open crack formation in the samples further hydration took place. At w/cm=0.78, the DoHs of samples containing 15% and 22.5% reached the optimum calculated DoH, since the ease with which water penetrated into the system caused all the anhydrite to be consumed during the hydration process (See Fig. 5.7).

In samples containing 31% of anhydrite content (Fig. 5.7.a), at 3 days of curing, the DoH increases almost linearly with the increase of w/cm ratio. At later ages, the formation of ettringite in w/cm 0.50 and 0.78 was faster and the DoH for those w/cm ratios passed the calculated values. This was possible because the open crack formation allowed the ingress of water into the system. Evidently, DoH values higher than 100% at 91 and 182 days of curing for mix with w/cm=0.78 were not real figures. This was because the leaching out of $Al(OH)_3$ from the system during the curing period caused the ettringite content to appear higher. At w/cm=0.50, the DoH of the paste at 91 and 182 days of curing was higher than that calculated. It is absolutely reasonable because reducing the w/cm ratio means increasing the solid content in the system. The existence of open cracks optimises the hydration of the particles.

In pastes containing 22.5% of anhydrite (Fig. 5.7.b), only samples with w/cm=0.78 passed the calculated DoH level or even the maximum DoH. In this state, anhydrous CSA particles will serve as a filler among the ettringite crystals formed. At lower w/cm ratio, the amount of ettringite produced was not sufficient to cause the formation of open cracks. As a consequence, the water ingress in to the paste was limited by the pore system and it left anhydrous particles surrounded by ettringite.

Mixes containing 15% anhydrite (Fig. 5.7.c) provided a better relationship between w/cm ratio and the DoH of CSA cement paste cured in water. As there were no open cracks formed, the hydration merely depended on the initial mixing water and the permeability of the samples due to the pore structure created by mixing water at a given w/cm. At w/cm ratio=0.78, all of the anhydrite was used up in the hydration process. The DoH reached the maximum calculated value at the age of 91 days after curing. At w/cm=0.50, the DoH almost achieved the calculated DoH at the same ages of curing. A lower level than the calculated hydration was found in samples with w/cm=0.3.

At w/cm=0.3, the DoH of all mixes with different anhydrite contents was lower than that calculated at any age of samples. At this level a great deal of the anhydrous CSA and anhydrite was surrounded by the ettringite formed.

5.2.3.5.4 Effect of Water Curing after Sealing for 28 Days on Hydration of CSA Cement Paste

The hydration of CSA cement and anhydrite samples sealed directly after demolding was discontinued after a few days, but some samples were then immersed into the water to encourage further hydration of anhydrous particles left in the paste system. As a certain DoH had previously developed in the samples, when they were sealed for 28 days, this initial ettringite formation before immersing them into water was, to some extent, expected to affect the progress of further hydration in respect to the penetration ability of water into the samples.

Fig. 5.8 shows the results of the effect of additional water curing on the hydration of the CSA cement paste containing 31% of anhydrite. The graph provides a comparison between the hydration of samples continuously cured in water and the samples cured in water after being sealed for the first 28 days. The greatest difference in DoH between samples cured in water and samples first sealed for 28 days was found in samples containing 31% anhydrite content and w/cm=0.78. This difference was because the amount of water in the sealed samples was not sufficient to dissolve the particles into solution, as there was no replenishment from water curing. In addition to this, a fairly high amount of ettringite was formed initially and consumed the remainder of the pore water. Once the sealed samples were immersed into water, the hydration quickly restarted. The highly permeable samples and the open crack formation due to expansion accelerated the hydration to equal the DoH of samples continuously cured in water after 56 of immersion and steadily continued at the same rate up to 182 days where complete hydration was achieved (Fig. 5.8.a).

At w/cm=0.50, the difference in DoH at 28 days between samples continuously cured in water and samples cured in water after sealing for 28 days was reduced. The lower w/cm ratio reduced the void content of the samples. The hydration development of the samples continuously cured in water was then more dominated by the water penetrating through the open cracks that developed with time than the water ingress through the pore system. When the initially sealed samples were immersed into the water, the expansion of samples started to create the open cracks through which the water easily penetrated into the samples to continue the hydration process. The DoH of samples continuously cured in water was passed after 56 days of immersion and they remained constant until 182 days. Both samples approached a DoH of 100% (Fig. 5.8.b).

At w/cm=0.30, the difference in DoH between samples cured in water and samples sealed for 28 days was relatively low. At this level of w/cm ratio, the development of hydration was controlled by the limitation of water movement due to reduced permeability of the paste. Immersion of previously sealed samples into the water allowed continuation of the hydration process at only a very slow rate. After 182 days of curing, the DoH in both systems only reached about 40% (Fig. 5.8.c).

The effect of curing in water after samples were sealed for 28 days on the hydration of CSA paste containing 22.5% of anhydrite is shown in Fig. 5.9. At w/cm=0.78, reducing the anhydrite content from 31% to 22.5% essentially reduced the difference of DoH between samples sealed for 28 days and samples directly cured in water. This was because a lesser amount of the anhydrous anhydrite was available in the samples after being sealed for 28 days. Immersion of the sealed samples into water hydrated the remainder of the anhydrous particles at a fast rate as the samples also formed open cracks. The DoH of samples continuously cured in water was equalled after 56 days of immersion and was passed at the age of 182 days, when the DoH was over 90% (Fig. 5.9.a).

At this level of anhydrite content, lowering the w/cm ratio to 0.50 caused the continuation of hydration of samples first sealed after immersion at a slower rate as the hydration relied on the water ingress through the pore system because no open cracks developed (Fig. 5.9.b). At w/cm=0.30, the effect of the additional curing was similar to the mix containing 31% anhydrite at the same level of w/cm (Fig. 5.9.c)

In the paste containing 15% anhydrite and w/cm=0.78, most of the anhydrite had been used up in the reaction with the mixing water. Therefore, the differences between samples sealed and stored at room temperature and samples continuously cured in water were very small (Fig. 5.10.a). Only a limited amount of anhydrous anhydrite remained after the samples were sealed for 28 days. At the age of 91 days, the amount of ettringite formed for both conditions had been equalled and then the progress of reaction was almost the same. At w/cm=0.50, the DoH of samples cured in water after sealing for 28 days was constantly slightly lower than that obtained for the continuously water cured samples after 91 days. But the DoH of samples cured in water after sealing for 28 days passed the DoH of samples continuously cured in water at the age of 182 days (Fig. 5.10.b). At w/cm=0.30, the lower DoH of samples sealed for 28 days was not recovered by immersion into water. The very low permeability of these samples inhibited the dissolution of anhydrous particles into the pore system. The DoH of these samples was always below the DoH of samples continuously cured in water (Fig. 5.10.c).

5.2.3.6 Effect of Immersing Samples in $CaSO_4$

The experimental results of the effect of immersing samples into saturated $CaSO_4$ solution are shown in Fig. 5.11, 5.12 and 5.13. As the concentration of $CaSO_4$ in solution was very low, the effect on DoH of immersing previously sealed samples into $CaSO_4$ solution should not be so significant. The main problem with the immersion of samples into $CaSO_4$ solution was their instability. The readily available $CaSO_4$ in the solution directly reacted with the CSA particles at the surface. The hydration initiated from the surface damaged the samples containing 31% anhydrite at w/cm=0.78 and 0.50 (Fig. 5.11a and b) and the samples containing 22.5% at w/cm=0.78 (Fig. 5.12.a) between 56 and 154 days of immersion.

After 56 days of immersion in the saturated $CaSO_4$ solution, the hydration development of samples containing 31% of anhydrite and w/cm=0.78 (Fig. 5.11.a) was slightly slower than that of samples continuously cured in water for the same curing period. This is probably because the degraded surface was continuously leached out into solution, while the reaction of the inner part was not as fast as the reaction at the surface. Tests for samples after 154 days of immersion could not be conducted, as all samples had totally degraded. This was also the case for the samples with w/cm=0.50 at the same level of anhydrite content (Fig. 5.11.b). The mix with w/cm=0.30 at this level of w/cm ratio did not suffer serious degradation as the samples were more impermeable and hence less penetrated by solution. In fact, a slightly higher hydration development after 2 months of immersion was observed, and even the same DoH after 6 months of curing (Fig. 5.11.c)

Degradation initiated from the surface was also observed in samples containing 22.5% anhydrite at w/cm=0.78 (Fig. 5.12.a). The DoH at 56 days of immersion in $CaSO_4$ solution was slightly higher than the DoH of the same samples continuously cured in water. Less damage in the sample at the time of testing meant that more representative samples could be tested. With the same content of anhydrite, reducing w/cm ratio to 0.50 reduced the damage so much that the test at 154 days of immersion could be conducted. The hydration development of the samples followed a similar pattern as samples continuously cured in water (Fig 5.12.b). At w/cm=0.30, again more impermeable samples could withstand the damage caused by immersion in the $CaSO_4$. A lower DoH at the age of 6 months was found (Fig. 5.12.c).

At an anhydrite content of 15% (Fig. 5.13), all samples at any w/cm ratio successfully avoided total degradation due to immersion in $CaSO_4$ solution. Even if the anhydrous anhydrite was very low before the immersion, while the content of hydrated CSA was relatively high, the hydration development seems to be similar to the samples cured in water. This was found especially in sample with w/cm=0.78 (Fig. 5.13.a). In the sample with w/cm=0.50 (Fig. 5.13.b), the DoH increased steadily, but at 92 days of curing it was still lower than the DoH in the samples continuously cured in water. After 182 days of curing, however, the DoH was slightly higher than that in the samples cured in water. In samples with w/cm=0.3, the hydration developed very slowly and the level was always lower than the level of samples cured in water (Fig. 5.13.c).

5.2.4 Examination of Hydration Using SEM

5.2.4.1 Sample Preparation

Selected samples consisting of hydrated paste containing 22.5% anhydrite with w/cm=0.78, 0.50 and 0.30 were examined by SEM. The choice of samples with that particular anhydrite content was based on the fact that the paste represented the average condition between high and low content of anhydrite. Before the testing was conducted, the samples were continuously cured in water for 182 days. The samples were dried at room temperature and then placed in vacuum. The samples were gold coated before the tests were carried out.

5.2.4.2 SEM Results

The examination was conducted on the surface of fractured samples by applying secondary electron imaging to produce topographical images of samples. The SEM results are given in Fig. 5.14.a and b for the sample with w/cm=0.78, Fig. 5.15.a and b for the sample with w/cm=0.50 and Fig. 5.16.a and b for the sample with w/cm=0.30. Magnifications of 1500 and 6000 were used on each sample to provide a view of the general microstructure and a more detailed view of microstructure of an interesting area of the surface.

The image shown in Fig. 5.14.a was of a randomly distributed needle-like ettringite produced by the mix at w/cm=0.78. This high w/cm ratio provided a considerable void space in which hydration could take place and it resulted in ettringite needles with large size and a microstructure containing a great amount of pores (Fig. 5.14.b).

Reducing the w/cm ratio to 0.50 resulted in an increase in the solid content in the paste. This restricted the space available for the ettringite to form. It resulted in more compact ettringite as shown in Fig. 5.15.a. Long needle-like ettringite crystals were also found in the areas where more space was available. This was mostly in cracked areas where water could easily penetrate into the system. Such a region is shown in Fig. 5.15.b.

Even more compact and massive ettringite was observed in the sample with w/cm=0.3 (Fig.5.16.a). Very limited void space was available, hence the formation of ettringite was constrained and the small crystals surrounded the anhydrous particles. The cracks found between the crystals (Fig. 5.16.b) were probably caused by self desiccation as the water from outside could not penetrate in to the paste system.

5.3 Expansion of CSA Paste.

5.3.1 General

The mechanism of ettringite expansion has long been a debate among research workers (Mehta and Hu, 1978, F Deng and Tang, 1994; Janotka and Krajci, 1999; Knofel and Wang, 1994; Odler and Colan-Subauste, 1999), who were involved in this topic. It is still not established whether the expansion is due to water absorptive characteristics of ettringite or the repulsive action of intermeshing crystals as they are formed. The expansion of CSA paste in this research was monitored using change of length and change of weight of samples at different levels of anhydrite content, w/cm ratio, ages of hydration and curing conditions.

5.3.2 Length Change Development of CSA Paste

5.3.2.1 Samples Sealed Directly After Demolding

Changes in length of CSA pastes with time at different anhydrite contents and w/cm ratios for samples sealed directly after demolding are given in Fig. 5.17. Sealed samples caused contraction that was proportional to the w/cm ratio. The contraction was higher with increasing w/cm ratio. In fact, even under sealed conditions, the formation of ettringite did not cease until 7 days (see Fig. 5.4 and Fig. 5.6), but during this time the samples underwent much of the observed contraction. This finding establishes that the formation of ettringite due to reaction of CSA cement and anhydrite does not cause expansion. On the contrary, the formation of ettringite caused a reduction in volume compared to that of the reactants. Expansion due to crystal repulsion during the formation of ettringite was not observed during the hydration of a mixture of CSA cement and anhydrite.

For sealed samples at w/cm = 0.50 and w/cm = 0.30, regardless of the anhydrite content, the contraction developed was mainly only found in the first

7 days of sealing and was subsequently almost constant up to 28 days. The contraction of the samples with w/cm=0.30 was below 0.1%, and the contraction of the samples with w/cm=0.50 was below 0.2%. The difference might be because the amount of ettringite formed increased at the higher w/cm ratio.

For samples with w/cm=0.78, the extent of the contraction increased with increasing time and with reduction of anhydrite content up to a maximum of 0.8% after 28 days. This was most likely due to loss of water during testing when the samples were uncovered and exposed to the ambient conditions. The high void content caused the samples to be unable to retain the pore water in the system, whereas the lower void content in samples with lower w/cm ratio was able to maintain the pore water in the system.

5.3.2.2 Samples Continuously Cured in Water Directly After Demolding

As shown in Fig. 5.18.a, CSA paste with the stoichiometric composition incorporating 31% anhydrite and continuously cured in water experienced expansions that developed with the age of paste. The magnitude of expansion was proportional to w/cm ratio. With w/cm=0.78, excessive expansion up to 8% was developed at earlier ages and continued up to 42 days, then continued more slowly at later ages. The magnitude of expansion at early ages was initiated by absorption of water by ettringite through the interconnected voids as a consequence of using a high w/cm ratio. The open crack system that developed due to the initial expansion accelerated the expansion. The open cracks became apparent as early as 3 days after curing, and then the cracks could accommodate the ingress of water to the system to form more ettringite and hence further expansion (see Fig. 5.3). This level of expansion and associated crack development render the paste unsuitable for practical applications.

Reducing the w/cm ratio to 0.5 at this anhydrite content meant an increase in the solid content, potentially forming more ettringite. Because of less interconnected void spaces, the expansion at earlier ages was slower, but after 14 days of curing, probably because the initiation of open crack formation accelerated the formation of ettringite and hence expansion. The magnitude of expansion was even higher than the mix with w/cm=0.78 after 28 days, when the samples have been so badly damaged that no further measurements could be conducted (See Fig. 5.3).

At the lower w/cm ratio of 0.30, the very impermeable microstructure produced and the lower ettringite content resulted in virtually no expansion during initial curing. Expansion started to develop at a very low after about 28 days of curing. The rate of expansion increased with time of curing. After 91 days of curing, the samples had broken into 2 pieces. As the expansion developed from the surface, the differential expansion between the inner part and the outer part caused the tension in the outer samples. The breaking of samples into two pieces occurred when the stress developed was in excess of the tensile strength of the pastes. During the curing period an open crack system was not able to develop (see Fig. 5.3). The expansion of samples of 0.5% at the fracture was much lower than the expansions observed for samples made at higher w/cm ratios, whose value was around 8% (Fig. 5.18.a).

Reduction of the anhydrite content caused an increase in the amount of anhydrous CSA present. This material could then act as a filler for the ettringite formed and could restrain the expansion of the paste. In the mix containing 22.5% anhydrite (Fig 5.18.b), at w/cm=0.78, the expansion developed rapidly at earlier ages and continued to increase at later ages. Open cracks also developed at this composition. The expansion at 182 days was approximately 25% lower than that of the samples with anhydrite content of 31% as shown in Fig. 5.18 a and b. Reduction of w/cm ratio to 0.50 at the same level of anhydrite content was followed by a slower rate of expansion. It was caused by the reduction of the formation of open cracks as a result of less ettringite formed. In the mix with this anhydrite content, at w/cm=0.30, the expansion continuously developed but at a much slower rate. The expansion of the samples after 182 days of curing was much lower than the values of the expansion of samples with higher w/cm ratio at the same level of the anhydrite content (Fig. 5.18.b).

The use of 15% anhydrite in the paste reduced the expansion even further (Fig. 5.18.c). The formation of less ettringite and the presence of more anhydrous CSA particles were responsible for this reduction. The expansion increased with the increase in w/cm ratio at all times. The sample with w/cm ratio 0.30 had broken after only 56 days of curing. It seems that the samples with low w/cm ratio are prone to break under the condition of water curing. As the samples could only be penetrated by water with difficulty, the expansion in the outer layers caused a differential stress distribution across the samples, leading to fracture.

It is clear that the expansion associated with the reaction of CSA cement and anhydrite was not due to interlocking crystals of ettringite but was caused by the water absorptive characteristics of ettringite. Therefore, the expansion depends predominantly on the permeability of the sample, the amount of ettringite in the sample and the amount of filler, which has a major role as a constraint to the development of expansion.

5.3.2.3 Samples Cured in Water After Sealing For 28 Days

The immersion of samples that had been cured for 28 days in a sealed state into water caused them to expand (see Fig. 5.19). In the mixes containing 31% anhydrite content, the extent of expansion of samples occurred was as great as that of samples cured in water directly after demolding. The samples with w/cm=0.50 expanded at a faster rate than the samples with w/cm=0.78. Even prior to the immersion, the DoH of samples with w/cm=0.50 had been high enough, but the anhydrous particles which potentially turned into ettringite when in contact with water were still present at significantly high levels. When the samples were immersed in water, the expansion in samples with w/cm=0.78 was mostly caused by water absorption of the existing ettringite, with a small part contributed by the formation of new ettringite during water curing. For samples with w/cm=0.5, the expansion was initiated by water absorption of the existing ettringite and enhanced by the newly formed ettringite as the anhydrous particles hydrated to form more ettringite in the presence of water curing. The expansion induced cracks were observed in samples at both w/cm ratios. The excessive expansion in samples with w/cm=0.50 damaged the samples after 28 days of immersion.

At w/cm=0.3, a small expansion of the samples was detected after 14 days of immersion and continuously developed at a very slow rate for 182 days of curing. The sample was still intact up to this age. Sealed curing for 28 days had lead to a build up in sample strength. This made the samples robust enough to withstand the subsequent expansion produced during water curing. And also, during immersion, formation of open cracks was not observed.

In mixes containing 22.5% anhydrite (Fig. 5.19.b), the expansion of samples cured in water after 28 days of sealing was significantly lower than the expansion of samples cured in water directly after demolding. It was also found that the samples with w/cm=0.50 expanded at a faster rate and to a greater extent than the samples with w/cm=0.78. It seems that the initial strength developed during the time that the samples were sealed was higher than the stress induced by expansion. During immersion therefore the samples were relatively free from open crack formation. The lower ettringite content in samples with w/cm=0.78 caused the expansion to be lower than the samples with w/cm=0.50. The high void content in samples at 0.78 w/cm provided the void space for expanded ettringite to occupy leading to reduced sample expansion. Negligible expansion occurred in the sample with w/cm=0.30 (Fig.5.19.b).

Very low expansion was the case for all three samples containing 15% anhydrite (Fig.5.19.c) It was much lower than the expansion of samples continuously cured in water. And again the initial conditions built up during the times that the samples were sealed, was responsible for reduction of expansion in the paste containing 15% anhydrite. For the samples with w/cm=0.78, the expansion was even lower than the initial contraction, so that up to 182 days overall the samples still underwent slight contraction.

5.3.3 Weight Change Development of CSA Paste

The samples used for tests of weight change were the same samples used for the tests of length change. The tests were carried out directly after the tests of length change had taken place

5.3.3.1 Samples Sealed Directly After Demolding

The experimental results for the weight changes observed for samples sealed directly after demolding are presented in Fig. 5.20. Basically, weight change development of samples occurred due to the water movement in to the samples. It was supposed that no water movement occurred during the times the samples were sealed directly after demolding, so that consequently no weight changes should have occurred in these samples, but this was not the case for the CSA samples. In most cases, the samples with w/cm=0.50 and 0.30 increased in weight, except that at the early ages the samples with w/cm=0.78 exhibited a reduction in weight.

It seems that movement of water occurred during the times that testing was carried out when the samples were uncovered and exposed to the ambient conditions. The low void content of the samples made with w/cm=0.50 and 0.30 was able to retain the existing pore water or even absorb water from the humidity. The high void content of the samples made with w/cm=0.78, on the other hand, allowed release of the some water during testing.

5.3.3.2 Samples Continuously Cured in Water Directly After Demolding

The weight change of CSA pastes cured in water is given in Fig. 5.21. For samples directly cured in water after demolding, the paste made with an anhydrite content of 31% and w/cm=0.78 created a considerable amount of voids, which in turn resulted in a large increase in weight (> 20%) at early ages due to the ingress of water (Fig. 5.21.a). The water was absorbed as replacement for the water consumed during the hydration process and also because of absorption by the ettringite formed. The increase in weight occurred continuously at a slower rate up to the age of 56 days. The absorption of water by ettringite was responsible for the weight gain observed at this stage as the hydration process was almost complete. This development took place up to 182 days of curing at a very slow rate. It seems that the ettringite finally achieved the saturation point where the absorption only occurred at a very low rate.

With the same anhydrite content, reduction of w/cm ratio to 0.50 resulted in two stages of weight change development. After 3 days, the increase of weight was almost at the same level as the mix with w/cm=0.78. The increase of weight was mostly due to the replacement of water consumed during the earlier hydration. As the porosity of the samples was lower with thee reduced w/cm ratio, the absorption of water by ettringite occurred at a slower rate up to 7 days of curing, and then the rate steadily increased as the formation of an open crack network developed. This condition continued until the samples were badly damaged at the age of 28 days (Fig.5.20.a)

At 31% of anhydrite content, the samples with w/cm=0.30 also showed the same level of weight change development after 3 days of curing. For the same reason, the increase in weight was due to water absorption experienced by the sample in order to replace the water consumed in the hydration process at earlier ages. As the samples were more impermeable, further increase in weight occurred at a very low rate until the samples broke at the age of 92 days.

Using 22.5% of anhydrite in the paste did not result in any significant difference in weight change development of samples with w/cm=0.78 directly cured in water after demolding (Fig. 5.21.b). The gain in weight after 182 days of curing was slightly lower than that of the samples with anhydrite content=31% at the same w/cm ratio and curing conditions. Reduction in the amount of ettringite formed as the anhydrite content reduced is thought to be the reason for the slightly lower weight gain in these samples. Samples with w/cm=0.50 gave approximately the same weight gain after 28 days of curing but beyond that age, the weight change was either increased at a very slow rate or not at all.

Samples from the mix containing an anhydrite content of 15% with w/cm=0.78 and w/cm=0.50 gained weight up to 12% after the first 3 days after curing (Fig. 5.21.c). The samples with w/cm=0.78 then developed a greater gain in weight than samples with w/cm=0.50, but the trend of the gain in weight for the two w/cm ratios was similar. At w/cm=0.30, the weight change of samples with anhydrite content 15% was almost exactly of the same pattern and amount as those of the mixes with anhydrite content of 22.5% at the same level of w/cm ratio. The samples with 15% of anhydrite content had broken after 56 days (Fig. 5.21.c).

5.3.3.3 Samples Cured in Water After 28 Days of Sealing

The results of the investigation of the weight change of samples cured in water after 28 days of sealing are given in Fig. 5.22. Samples containing 31% anhydrite at w/cm=0.78 and 0.50 gained in weight at almost the same rate as that for the samples continuously cured in water. The samples with w/cm=0.30, the gain in weight due to water immersion was slightly lower than the gain in weight of samples continuously cured in water at the same level of w/cm ratios (Fig. 5.22.a).

Twenty eight days of sealing before the immersion into water improved the weight change pattern of samples with 22.5% of anhydrite at any level of w/cm ratio, when compared to the weight change development of samples with 31% of anhydrite at the same level of w/cm ratio (Fig. 5.22.b).

At 15% anhydrite content, seven days after immersion in water, samples with w/cm=0.50 and 0.78 sharply increased in weight and then their weight change were almost constant up to 182 days. Samples with w/cm=0.30 gained in weight in the same pattern as samples with 22.5% anhydrite at the same level of w/cm ratio (Fig. 5.22.c).

5.3.4 Effect of Immersion of CSA Paste in $CaSO_4$ Solution

5.3.4.1 Effect of immersion in $CaSO_4$ Solution on Length Change Development

The effect of immersion in saturated $CaSO_4$ solution on length change development is presented in Fig. 5.23. The samples with anhydrite content of 31% and at w/cm=0.50 and 0.78 expanded at almost the same rate as samples cured in water after sealing for 28 days (compare Fig. 5.19.a & Fig. 5.23.a). Further measurement of length change could not be recorded as the samples were badly damaged. It seems that the expansion was closely related to the absorption of water by ettringite, while the presence of $CaSO_4$ in solution accelerated the damage to samples by eroding them from the external surface. The length change development of the samples with w/cm=0.30 at this level of anhydrite content was not seriously affected by the $CaSO_4$ solution (Fig. 5.23.a).

In the mix with anhydrite content=22.5% (Fig, 5.23.b), the effect of $CaSO_4$ solution was more noticeable in samples with w/cm=0.78. The combination of high capability in absorbing water and the gradation from the surface caused a development of open cracks at a rapid rate. This caused the high rate of length change and the early damage to the samples. Lowering the w/cm ratio down to 0.50 reduced the effect of $CaSO_4$ solution and length change was merely a factor of absorbing water by the ettringite. In samples with w/cm=0.30, the effect of $CaSO_4$ solution was negligible.

Reducing the anhydrite content to 15% caused no effect from $CaSO_4$ solution on the length change of samples. The length change of samples in this condition was almost as low as that of samples cured in water after 28 days sealed (Fig. 5.23.c)

5.3.4.2 Effect of immersion in $CaSO_4$ Solution on Weight Change Development

Up to 72 days, samples containing 31% anhydrite (Fig. 5.24.a) possessed the similar pattern of weight change development as the samples at the same composition cured in water after sealing for 28 days. After 72 days, samples with w/cm=0.78 and 0.50 underwent significant damage and therefore no further weight change development could be recorded. However, samples with w/cm=0.30 continuously gained weight with curing time. The gain in weight was more determined by the absorptive characteristics of the samples than the effect of the existence of $CaSO_4$ in solution, while the existence of $CaSO_4$ in solution accelerated the damage to the samples.

At 22.5% anhydrite content (Fig. 5.24.b), a difference was found in samples with w/cm=0.78. The outer parts of the samples were more badly cracked because of the reaction of anhydrous CSA particles with $CaSO_4$ from solution and this provided extra space, which was filled with water to continue the hydration to form more ettringite. Rapid increase in weight with time was followed by damage to the samples at 56 days of immersion. However, mixes with lower w/cm ratio were not seriously affected by the $CaSO_4$ solution.

The same also occurred in the case of mixes containing 15% of anhydrite (Fig.5.24.c). While samples with w/cm=0.30 and 0.50 behaved in a similar manner to that when they were cured in water after sealing for 28 days, the samples with w/cm=0.78 followed the same path until 91 days but then started to be eroded and lost a large amount of weight. The reaction of anhydrous CSA particles in the outer part encouraged the erosion process of the samples.

5.4 Compressive Strength of CSA Cement Paste

5.4.1 General

The compressive strength of CSA cement paste was essencially established by the strength of interlocking ettringite crystals, the strength of bonding between the crystals and the crystal/void ratio in the samples. Therefore, factors such as: the anhydrite content, w/cm ratio and the curing conditions play a major role in determining the build up of strength of CSA cement paste. The effect of each factor and its interaction on the strength of CSA paste is discussed in the following sections.

5.4.2 Compressive Strength Development of CSA Paste

5.4.2.1 Samples Cured in Water Directly After Demolding

The compressive strength development of samples cured in water directly after demolding is given in Fig. 5.25. While the continuation of ettringite formation is determined by the presence of water, the absorption characteristics of ettringite and consequent expansion certainly controlled the observed strength of the CSA paste. This can be clearly seen from the data for high w/cm ratio and high content of anhydrite. In the mix containing 31% of anhydrite with w/cm=0.78 (Fig.5.25.a), the strength developed up to 3 days of curing and then declined due to growing damage to the sample with continuation of curing. The same trend was also found in the mix with the same anhydrite content but at w/cm=0.50 (Fig. 5.25.a). As the lower w/cm ratio produced paste with low void content, the strength development of paste was higher up to 3 days of curing. On the other hand, increasing its solid content potentially produces more ettringite in the paste causing growing damage and consequent loss of strength at much faster rate. As a consequence, the decrease of compressive strength after 3 days of curing was also higher. The test carried out at 91 and 182 days indicated that the samples were very weak. At w/cm=0.3 (Fig. 5.25.a), the strength of the paste was mostly controlled by the low void content. Even with the low amount of ettringite formed, it was sufficient to develop high strength in the paste after only 7 days of curing. The compressive strength of the mix at this age reached 120 MPa. As the low void content in the paste effectively blocked the ingress of water, no further development of strength was observed after 4 days of curing. The self desiccation activity and absorption of pore water by the ettringite caused some reduction in strength up to 28 days curing period but then the sample attained a stable strength of about 100 MPa up to 182 days of curing.

Reducing the anhydrite content to 22.5% was not sufficient to reduce the effect of sample damage on the reduction of strength development in the paste with w/cm=0.78. The samples with this anhydrite content and w/cm ratio never developed much compressive strength (Fig. 5.25.b). High void content and the amount of ettringite formed were enough to produce the same level of damage in samples as those samples with an anhydrite content 31% at the same w/cm ratio. But at the w/cm=0.50 (Fig. 5.25.b), high strength development up to 3 days of curing was followed by a slight reduction from 7 days to 14 days of curing and subsequently the strength development was stable up to 182 days of curing. Reduction of void space and the amount of ettringite formed were the reasons for the stability of the strength development of samples at this level of anhydrite content and w/cm ratio. Contrary to the mix containing 31% anhydrite, at w/cm=0.3 the mix containing 22.5% anhydrite had high strength development at 7 days, which decreased up to 14 days of curing and then was stable up to 28 days. Subsequently the strength decreased continuously up to 182 days (Fig 5.25.b). The decrease of the compressive strength with time in samples with the low w/cm ratio was suspected to be due to expansion of the surface.

In the paste containing 15% of anhydrite (Fig. 5.25.c), the paste with w/cm=0.78 showed the slowest decrease after 7 days onwards. The strength development of paste with w/cm=0.50 was as stable as the mix containing 22.5% anhydrite at 182 days. However, in the mix at w/cm=0.30 mix, high strength development up to 7 days of curing was also followed by a strength decrease as found in samples containing 22.5% of anhydrite at the same level of w/cm ratio.

It seems that the compressive strength of samples with a high content of anhydrite possessed greater stability in their long term development at low w/cm ratio, whereas the compressive strength in samples with a lower content of anhydrite was more stable in their long term development at higher w/cm ratio. As the compressive strength stability was closely related to the expansion characteristics of the samples, the use of the anhydrite content of the pastes made with only CSA cement and 31% anhydrite, the stoichiometric composition, was not suitable at w/cm=0.78 and w/cm=0.50. Reducing the anhydrite content at this level of w/cm increases the availability of anhydrous particles which is extremely important in constraining the expansion.

5.4.2.2 Samples Sealed Directly after Demolding

Because of the effect of water in damaging the ettringite based paste, especially in samples with high w/cm ratio and high anhydrite content, the compressive strength development of samples sealed directly after demolding represented the true contribution of the ettringite formed to the compressive strength development because the samples were still intact at the compressive strength was carried out.

Fig. 5.26 presents the compressive strength development of samples sealed after demolding. The mix containing 31% anhydrite content (Fig. 5.26.a) with w/cm=0.78 developed compressive strength at a similar rate as the same mix cured in water. This development continued at a much slower rate up to 14 days and then was stable until 182 days. the strength achieved approached

40 MPa. Lowering the w/cm ratio to 0.50, the high compressive strength development in the first 7 days was followed by a slower development up to 14 days, subsequently decreased slightly to 28 days. The strength achieved approached 80 MPa. This was probably because of formation of induced micro-cracks as the void water was used for further dissolution of solid particles. Re-healing of micro-cracks due to formation of new ettringite brought about a further increase in the strength up to 92 days, followed by a small reduction in strength up to 182 days. There was no indication that self-desiccation had occurred in the samples with w/cm=0.30 and hence these achieved very high strength, in excess of 100 MPa (Fig. 5.26a)

For the mixes containing 22.5% anhydrite (Fig. 5.26.b), those with w/cm=0.78 and 0.50 developed compressive strength in the same pattern as the mixes containing 31% anhydrite at the same level of w/cm ratio, but lower strength was achieved. The reduction of strength after 7 days was observed again in samples with w/cm=0.30. Reduction of anhydrite content at this level of w/cm ratio caused the significant amount of water still available in the void system to be used to hydrate the anhydrous particles. As a result, a fairly stable strength development ensued, leading to compressive strength in excess 80 MPa.

Reducing the anhydrite content to 15% (Fig. 5.26.c) did not significantly change the pattern of strength development of the samples. The noticeable difference was seen in the w/cm=0.3 samples, where after decrease of strength from 7 days to 28 days, it was followed with stable strength up to 92 days and then a slow decrease up to 182 days. There is no clear reason for this occurrence, but in fact the hydration development also showed a similar decrease. The ultimate compressive strength was again in excess of 80 MPa.

5.4.2.3 Samples Cured in Water After Sealing for 28 Days

The main difference between samples continuously cured in water after demolding and the samples cured in water after sealing for 28 days was that the latter had developed a certain DoH and therefore a certain strength before being immersed into the curing water. To some extent, this initial strength development influenced the subsequent behaviour of the samples when they were immersed in the water.

Compressive strength development of samples cured in water after sealing for 28 days is given in Fig. 5.27. In samples containing 31% anhydrite (Fig. 5.27.a), at w/cm=0.78 and 0.50, the initial strength was not sufficient to restrain the development of stress due to expansion, and then the open cracks that occurred severely reduced the compressive strength of the samples at the age of 92 and 182 days. At w/cm=0.30, the low void content prevented the ease of water movement which was found in the mixes with higher w/cm ratio levels. Further hydration was mostly initiated from the outer layer of the paste. This reaction slightly increased the strength up to 92 day of curing but further hydration beyond that age seemed to create micro-cracks in the paste, which in turn caused reduction in strength at 182 days. Because of this the samples had slightly lower compressive strength than the same paste cured continuously in water, but it was still above 90 MPa.

Expansion imposed damage was also observed in the samples containing 22.5% anhydrite at w/cm=0.78 and w/cm=0.50 (Fig. 5.27.b), resulting in drop in strength. The reduction of strength was not as high as the samples containing 31% anhydrite at the same w/cm ratios. At w/cm=0.30 a small reduction in compressive strength after 92 days curing period was followed by an increase in strength at 182 days. The compressive strength after 182 days was in excess of 100 MPa.

In the mix containing 15% anhydrite (Fig. 5.27.c), an increase in strength up to 92 days was followed by decline beyond that age up to 182 days of curing for samples with w/cm=0.78 and w/cm=0.50. The strength development of the mix with w/cm=0.30 had the same trend as the mix containing 22.50% anhydrite at the same w/cm ratio, and gave a final compressive strength of above 80 MPa.

5.4.3 Relationship Between Compressive Strength and W/CM Ratio of CSA Paste.

5.4.3.1 Samples Continuously Cured in Water Directly After Demolding

Apart from controlling hydration activities, the main role of w/cm ratio of the paste was in determining the amount and structure of the void space present in the system, which in turn predominantly contributed to the compressive strength of the paste. It has been well known in PC paste systems that the strength of the paste increases with reduction in the w/cm ratio. This rule was not necessarily followed in the case of CSA paste, as expansion imposed damage could be experienced by samples and could completely change the condition of the paste.

The relationship between compressive strength and w/cm ratio for samples continuously cured in water after various curing periods is given in Fig. 5.28. After 3 days of curing, when the samples were still intact, except for the mix containing 31% of anhydrite, the relationships of the strength of paste and w/cm ratio comply with the expected rule. The exception occurred in the mix at w/cm=0.30 which was lower than the strength of paste at w/cm=0.5. Slow hydration process due to lack of water in the system of the mix with w/cm=0.3 was the reason for this condition. But once the hydration process was developed the paste gained the strength as shown in 28 days of curing. The drop of strength of mix with w/cm=0.50 at this level of anhydrite content was due the damage of samples caused by the expansion.

The pattern of the compressive strength and w/cm ratio relationship changed with the progress of curing relative to the extent of damage in samples. The sensitivity of small samples used in the experiment might lead to misinterpretation of the observations. Roughly, all mixes with w/cm=0.3 and/or containing anhydrite content 15% gave the most stable compressive strengths.

5.4.3.2 Samples Sealed Directly after Demolding

The relationship between compressive strength and w/cm ratio for samples sealed directly after demolding is given in Fig. 5.29. As physically, all the samples were tested while in a good condition, the sealed samples are more representative of the relationship between w/cm ratio and the strength of paste. In all cases, the strength of paste followed the rule of the relationship with w/cm ratio as found in OPC paste. Mixes containing 31% of anhydrite produced higher strength at all periods of curing, especially at low w/cm.

At high w/cm ratio, the difference in strength due to the difference of anhydrite content was relatively close as the strength of paste was mainly dominated by the high void content of the paste. On reducing the w/cm ratio the difference in strength became more pronounced, so that at w/cm=0.30 the highest strength of paste was produced by the mixes containing the highest anhydrite content, particularly at longer ages, as shown in Fig. 5.29.c and d.

5.4.4 Effect of Immersing Samples in $CaSO_4$ Solution on Compressive Strength of CSA Paste.

The pattern of the effect of immersing samples in $CaSO_4$ solution on compressive strength was essencially the same as the effect of samples cured in water after sealing for 28 days (Fig.5.30) In mixes containing 31% of anhydrite, the strength of samples with high w/cm ratio reduced with time of immersion, while the mixes with low w/cm ratio gained strength up to 91 days but decreased when the samples were cured up to 182 days.

Irregularity in the pattern of the compressive strength development was also influenced by the magnitude of the damage to the samples. It seems that the mix containing 22.5% anhydrite with w/cm=0.30 showed the best performance under immersion in $CaSO_4$.

5.5 Conclusion

1. Ettringite is the main hydration product of the reaction between CSA and anhydrite. The formation of ettringite in a mix containing CSA paste and anhydrite is strongly influenced by the anhydrite content, w/cm ratio and curing conditions. The DoH increases with increase in the anhydrite content and the w/cm ratio.

2. The hydration process of CSA paste and anhydrite occurred at a rapid rate and most of the hydration was completed in 7 days. The continuation of hydration in sealed paste samples occurred at a very slow rate. The higher hydration rate in paste samples cured in water is mostly due to the ingress of water through the cracks induced by expansion.

3. Under sealed curing conditions, the samples exhibited shrinkage even at ages when ettringite was still forming. This confirms that ettringite formation from the reaction between CSA and anhydrite does not cause expansion. The degree of shrinkage increased with the increase in w/cm ratio and with reduction in anhydrite content.

4. Expansion occurred if the paste was cured in water. The degree of expansion increased with increase in w/cm ratio and anhydrite content. Regardless of the anhydrite content, samples with 0.30 w/cm produced distinctly lower expansion. Regardless of w/cm, the samples containing 15% anhydrite also produced low expansion comparable with the expansion produced by samples with 0.30 w/cm at any anhydrite content. The promotion of cracks initiated by expansion caused excessive expansion in samples with high w/cm and high anhydrite content.

5. CSA pastes develop compressive strength at a very rapid rate at early ages. Under sealed conditions, the compressive strength develops at a constant rate after 7 days. The compressive strength

increases with decrease in w/cm ratio, but a change in anhydrite content does not produce a consistent pattern with respect to compressive strength development.

6 The compressive strength of pastes cured in water or immersed in $CaSO_4$ was influenced by the degree of damage caused by expansion. The small sample size used in experimental works possibly influenced the results achieved. Samples containing 15% anhydrite and samples with w/cm=0.3 showed better compressive strength performance.

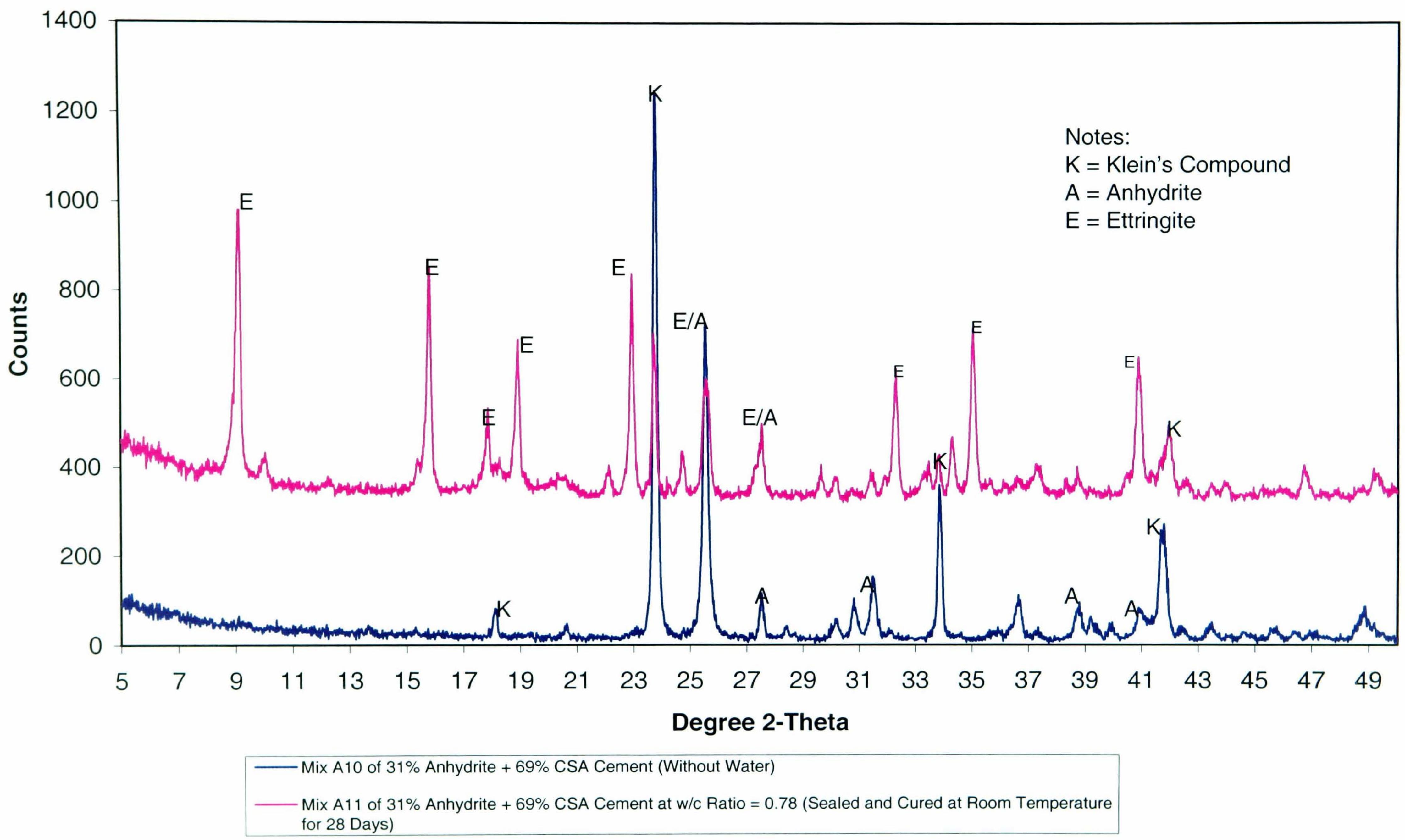
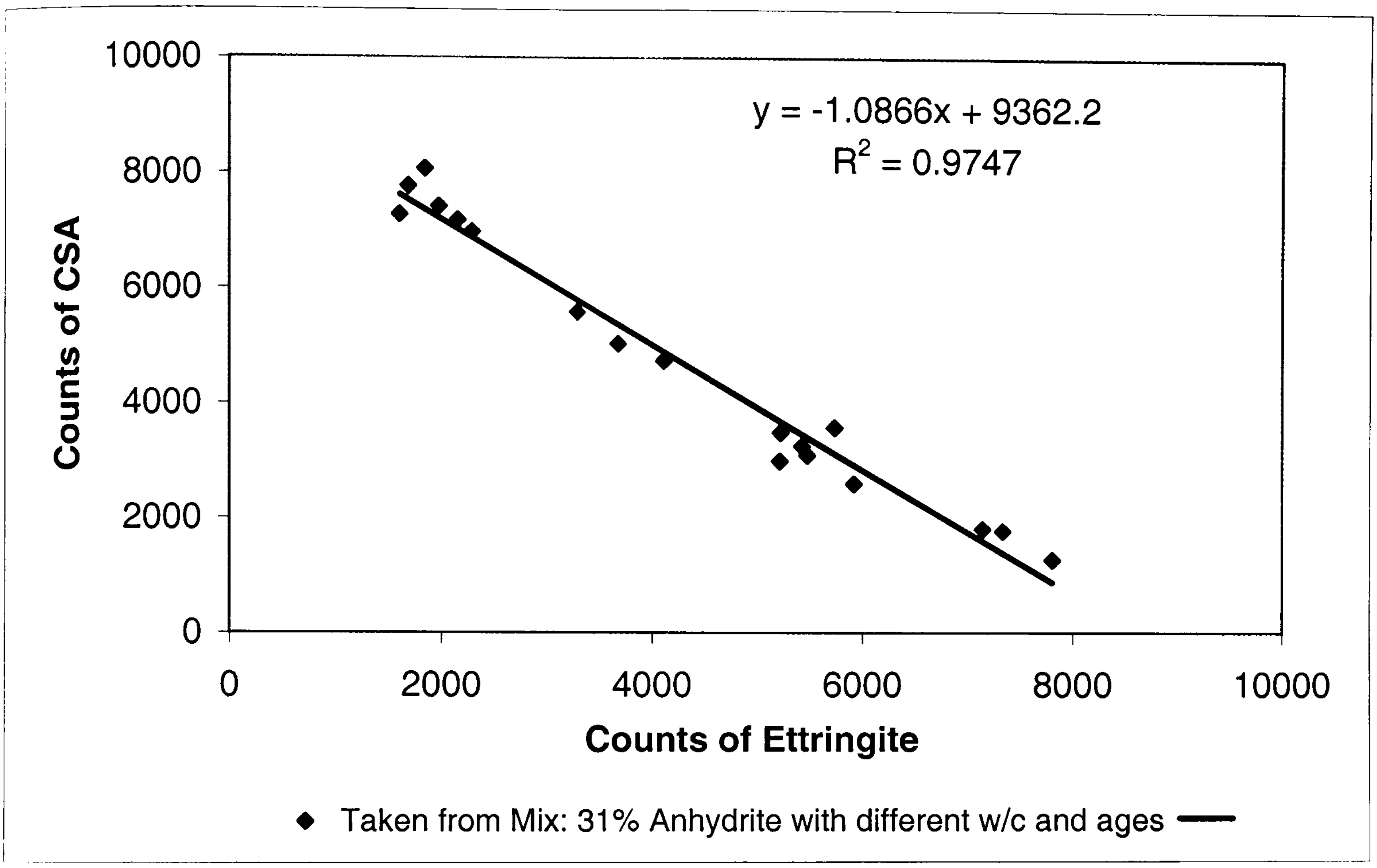


Fig.: 5.1 Typical Hydration Product of CSA Cement

Fig. 5.2: Relationship Between Formed Ettringite & Anhydrous CSA Based on Counts under Highest Peak Area of XRD



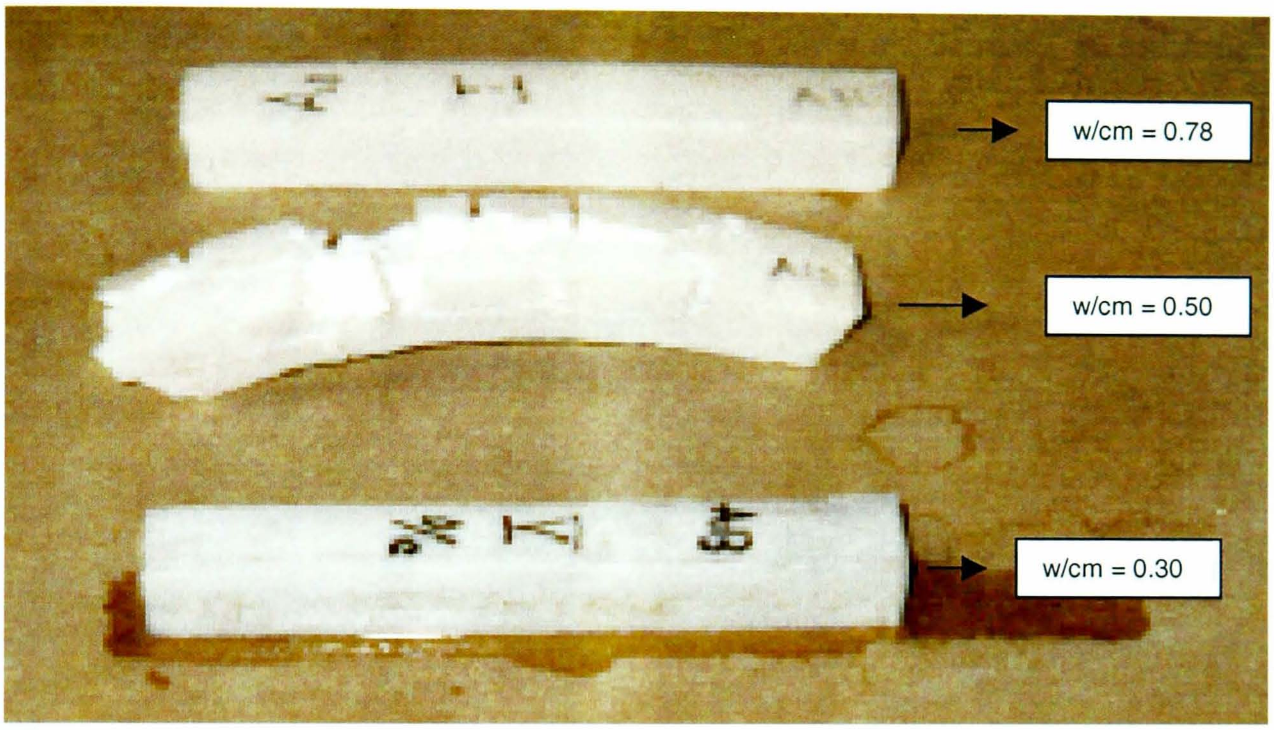


Fig 5.3: The pattern of expansive induced deterioration of CSA paste containing 31% of anhydrite and different w/cm ratio. The samples were cured in the water fo 28 days. No crack appeared in samples with 0.30, heavy cracks in samples with w/cm = 0.50, cracks also appeared in samples 0.78 (not seen in the Figure).

Fig. 5.4: Hydration Development of CSA Cement Paste Based on XRD Analysis
(Sealed and Cured at Room Temperature)

Fig. 5.4.a: 31% Anhydrite (Sealed Curing)

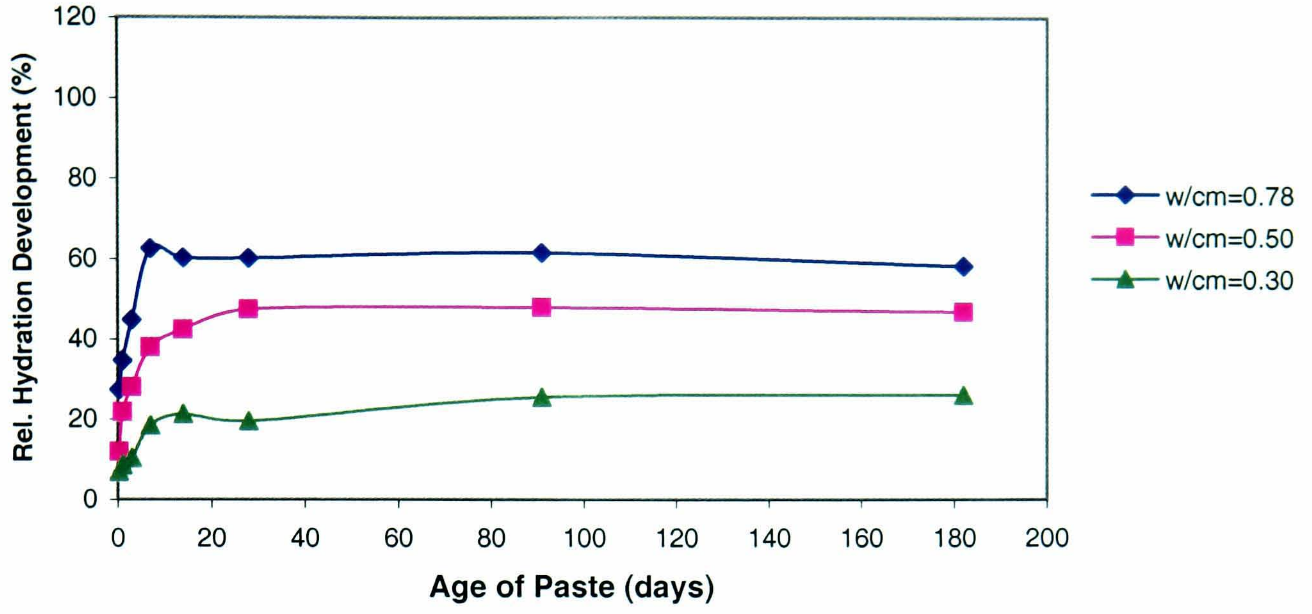


Fig. 5.4.b: 22.5% Anhydrite (Sealed Curing)

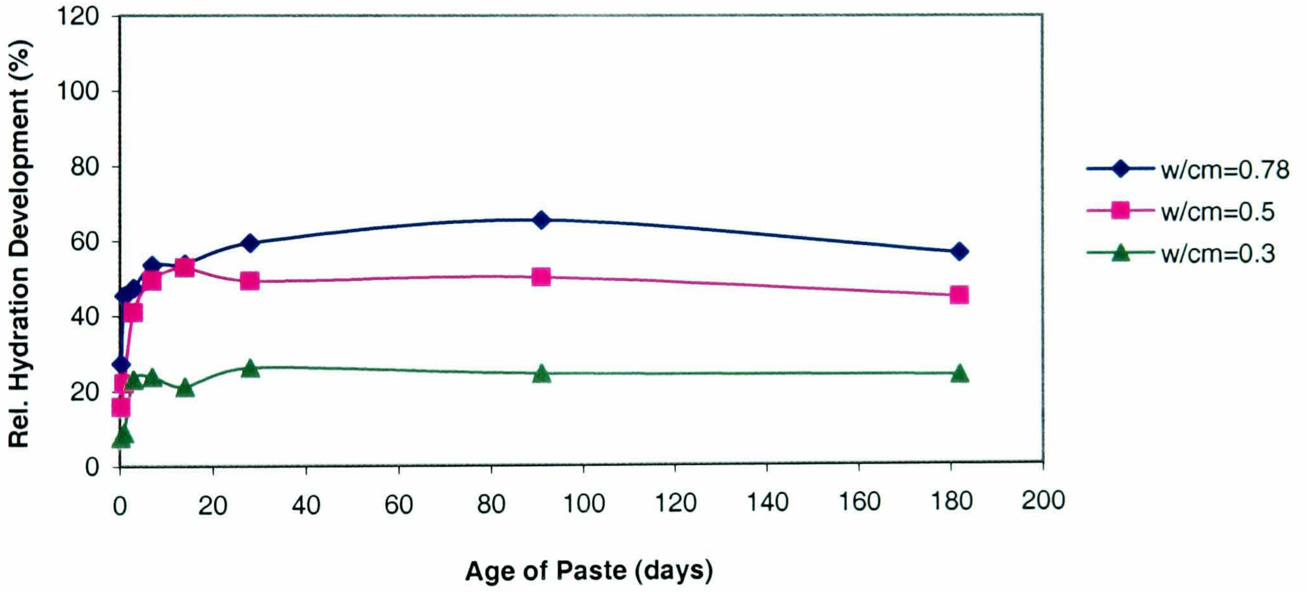


Fig. 5.4.c: 15% Anhydrite (Sealed Curing)

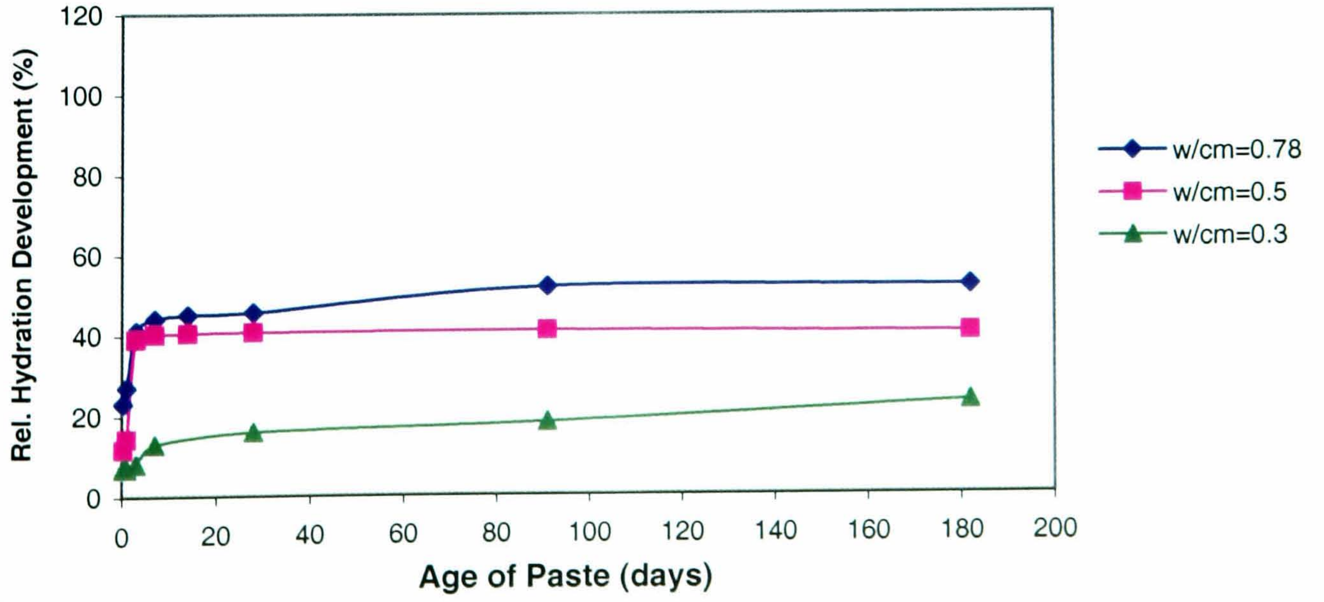


Fig. 5.5: Hydration Development of CSA Cement Paste Based on XRD Analysis (Water Curing)

Fig. 5.5.a: 31% Anhydrite (Water Curing)

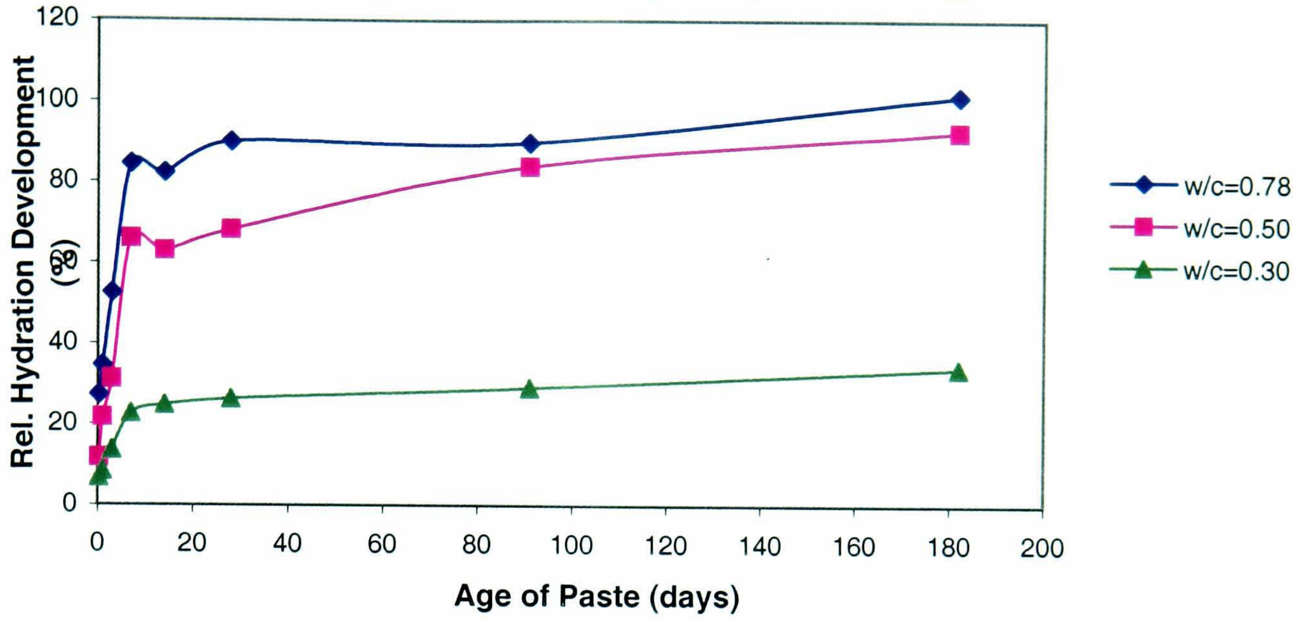


Fig. 5.5.b: 22.5% Anhydrite (Water Curing)

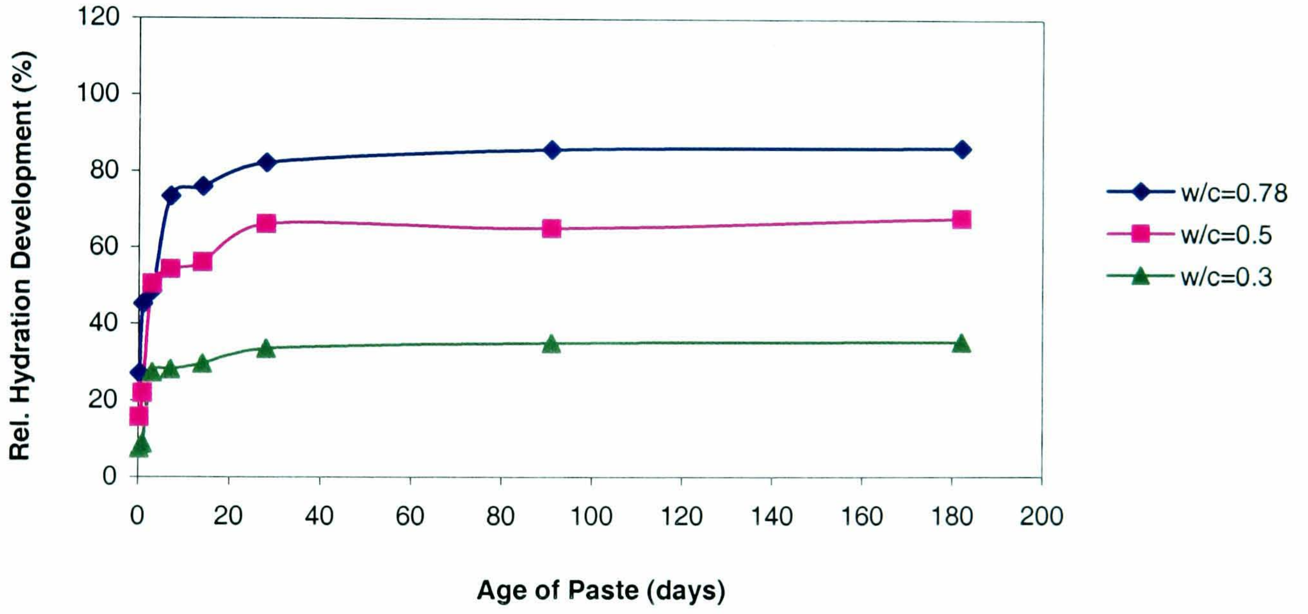


Fig. 5.5.c 15% Anhydrite (Water Curing)

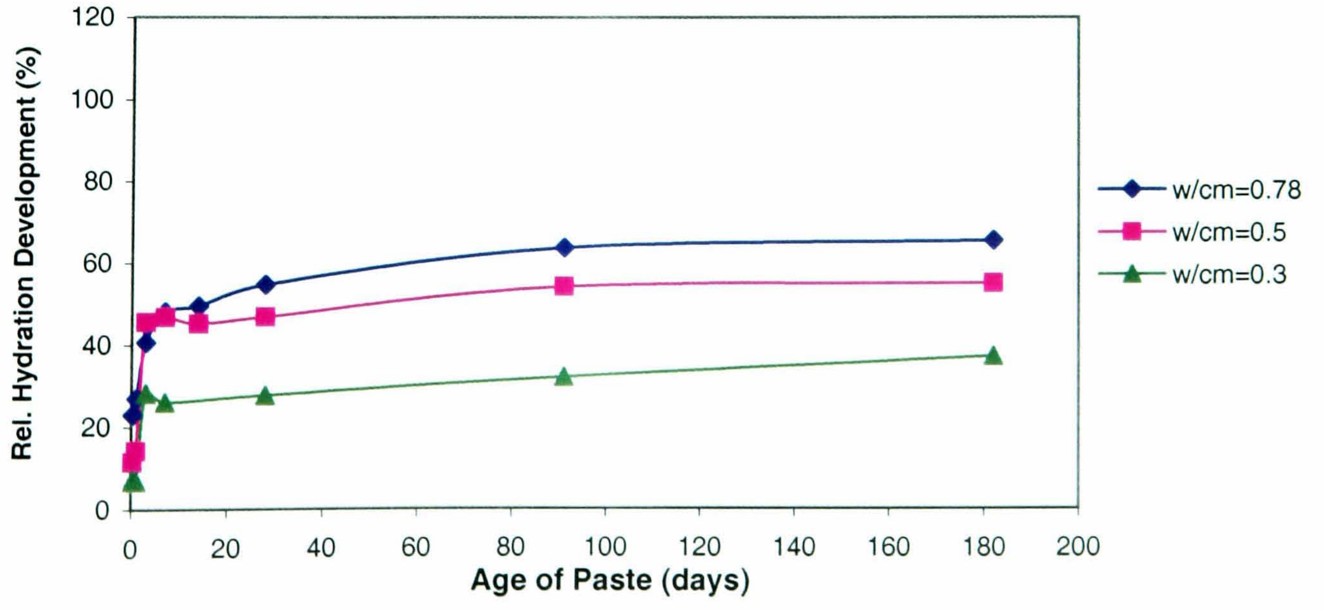


Fig. 5.6: Effect of w/cm on Hydration of CSA Cement Paste (Sealed and Cured at Room Temperature)

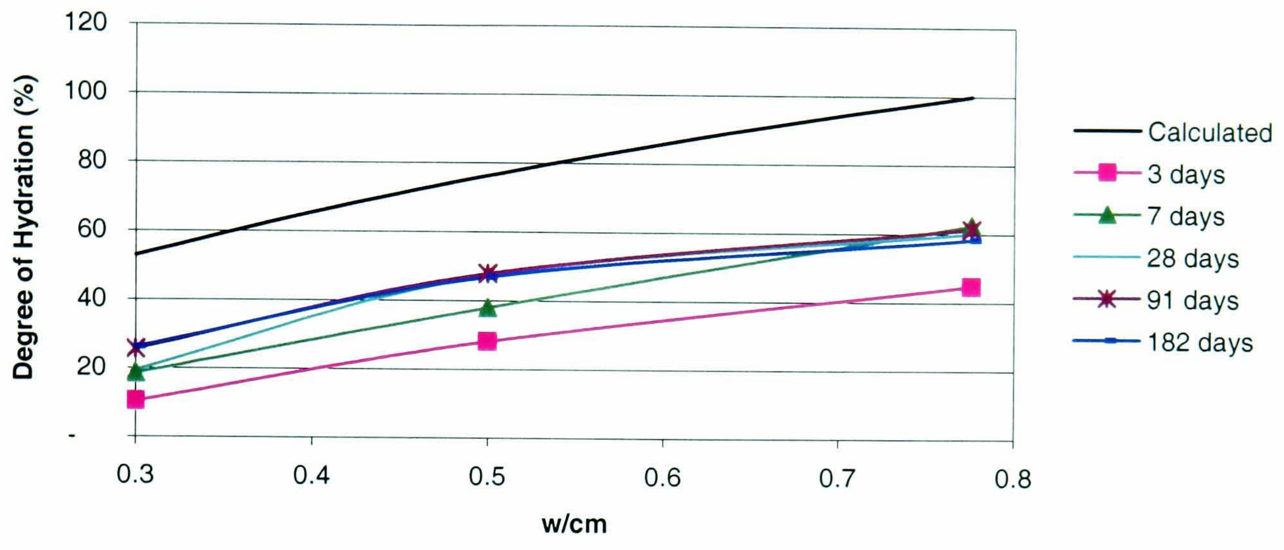


Fig. 5.6.a: 31% Anhydrite (Sealed Curing)

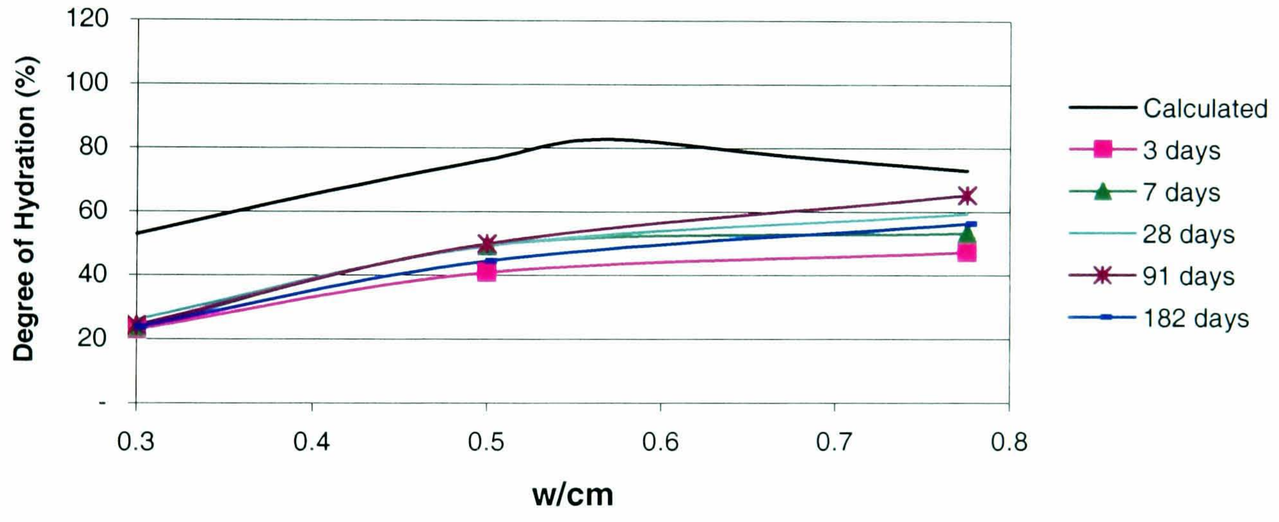


Fig. 5.6.b: 22.5% Anhydrite (Sealed Curing)

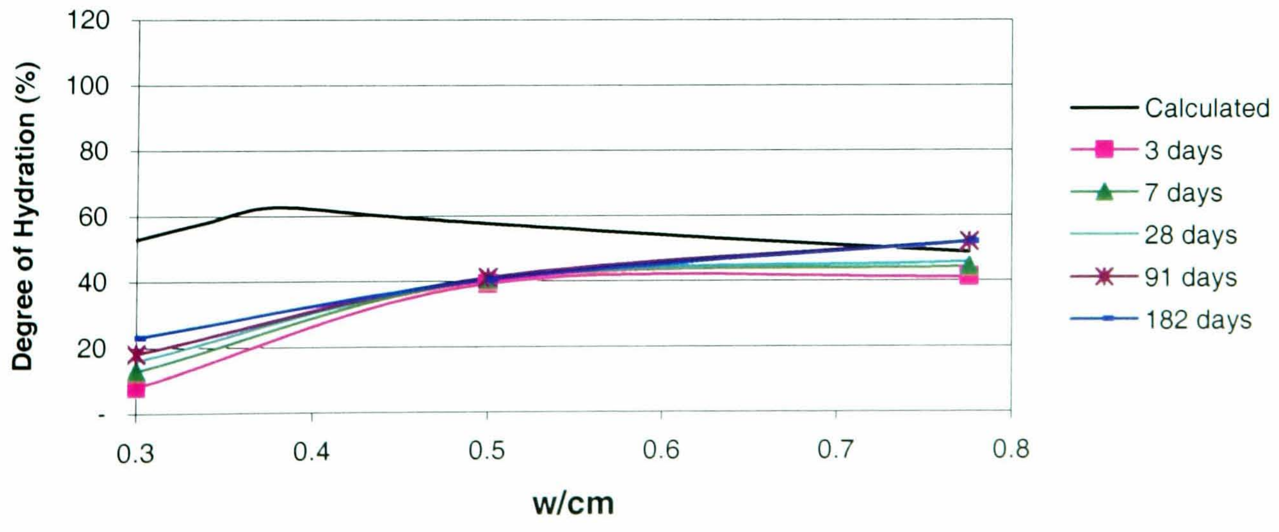


Fig. 5.6.c: 15% Anhydrite (Sealed Curing)

Fig. 5.7: Effect of w/cm on Hydration of CSA Cement Paste (Water Curing)

Fig. 5.7.a: 31% Anhydrite Content (Water Curing)

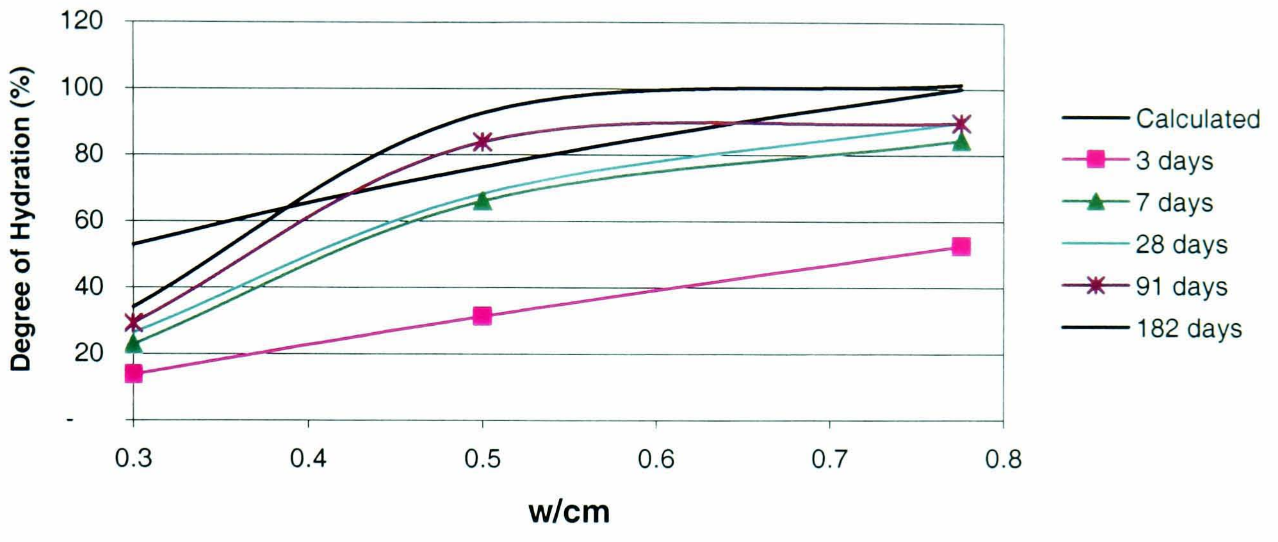


Fig. 5.7.b: 22.5% Anhydrite Content (Water Curing)

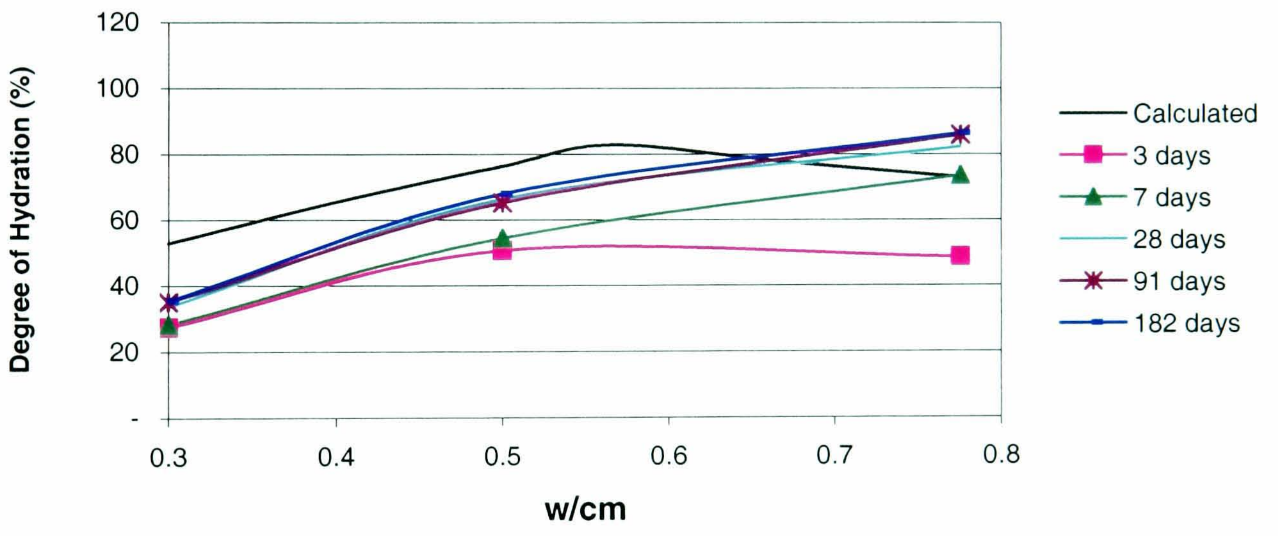


Fig.5.7.c: 15% Anhydrite (Water Curing)

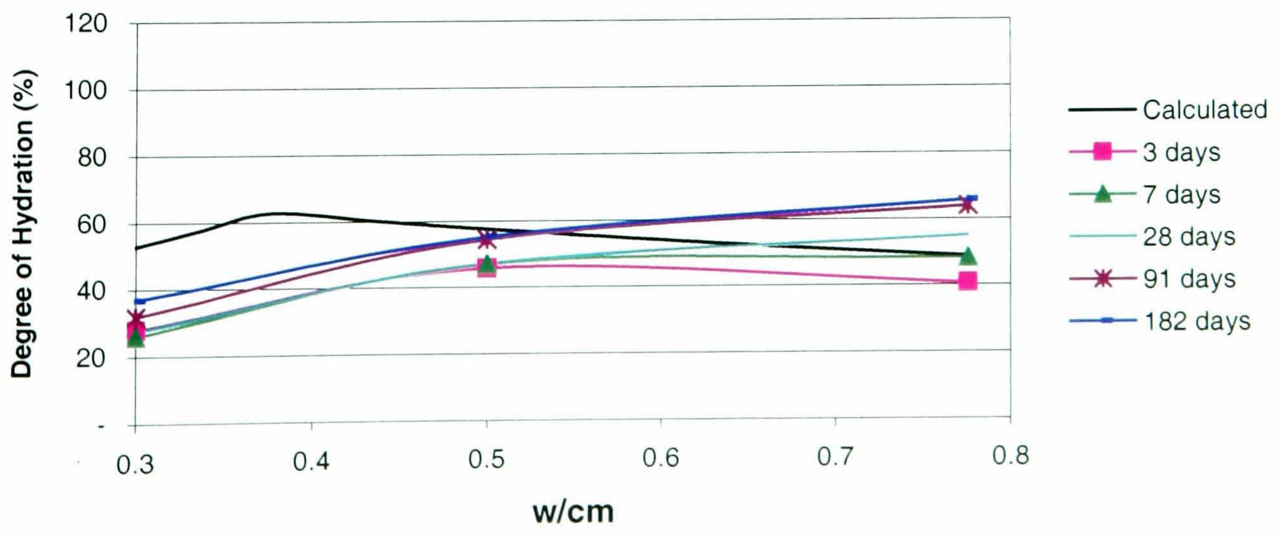


Fig. 5.8: Effect of Water Curing after Sealing For 28 Days on Hydration of CSA Cement Paste Containing 31% Anhydrite

Fig. 5.8.a: 31%of Anhydrite and w/cm=0.78

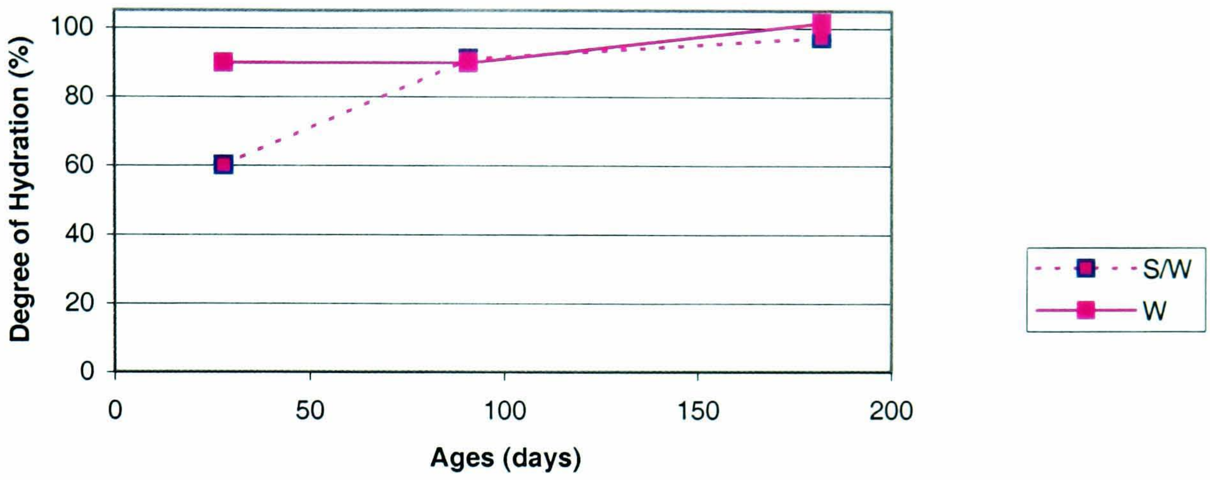


Fig. 5.8.b: 31%of Anhydrite and w/cm=0.50

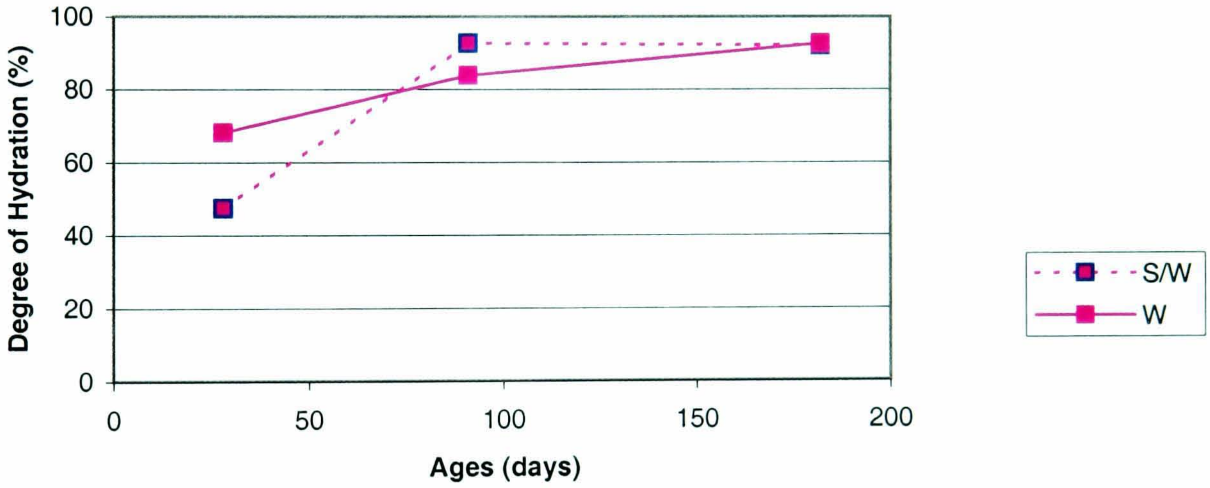
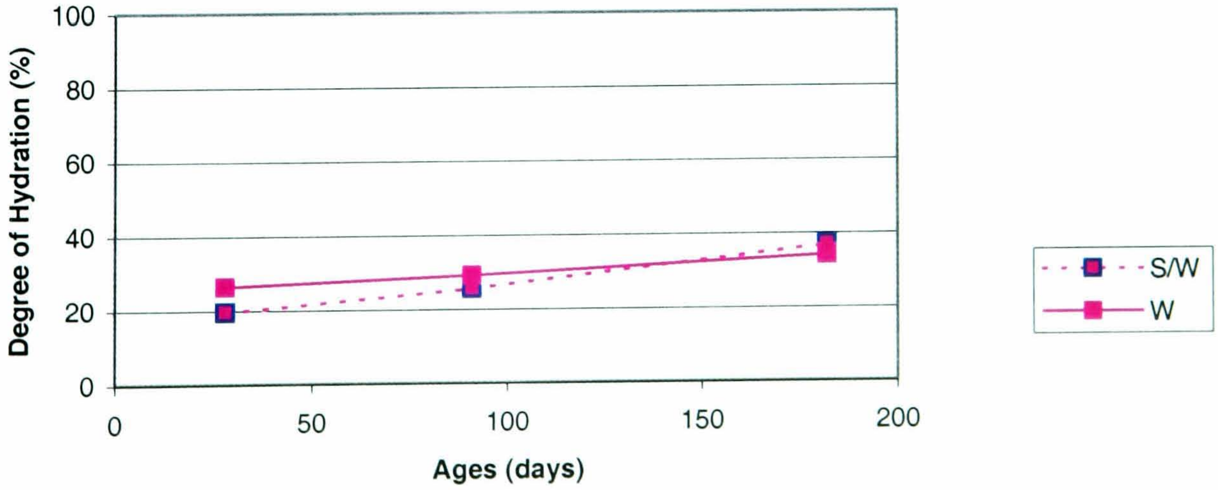


Fig. 5.8.c :31%of Anhydrite and w/cm=0.30



S/W = Water curing after sealing for 28 days
W = Water curing

Fig. 5.9: Effect of Water Curing after Sealing For 28 Days on Hydration of CSA Cement Paste Containing 22.5% Anhydrite

Fig. 5.9.a: 22.5% of Anhydrite and w/cm=0.78

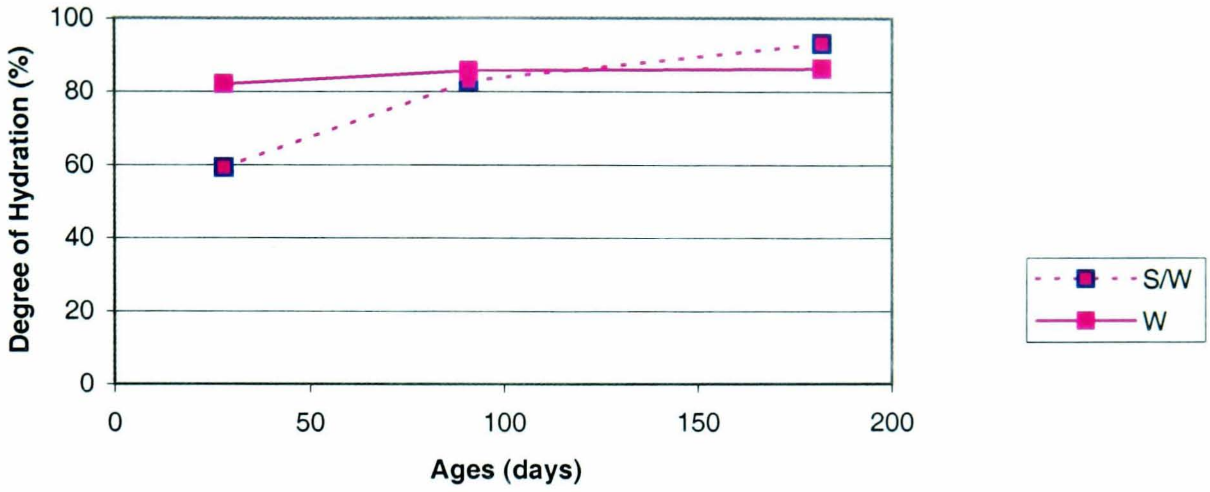


Fig. 5.9.b: 22.5%of Anhydrite and w/cm=0.50

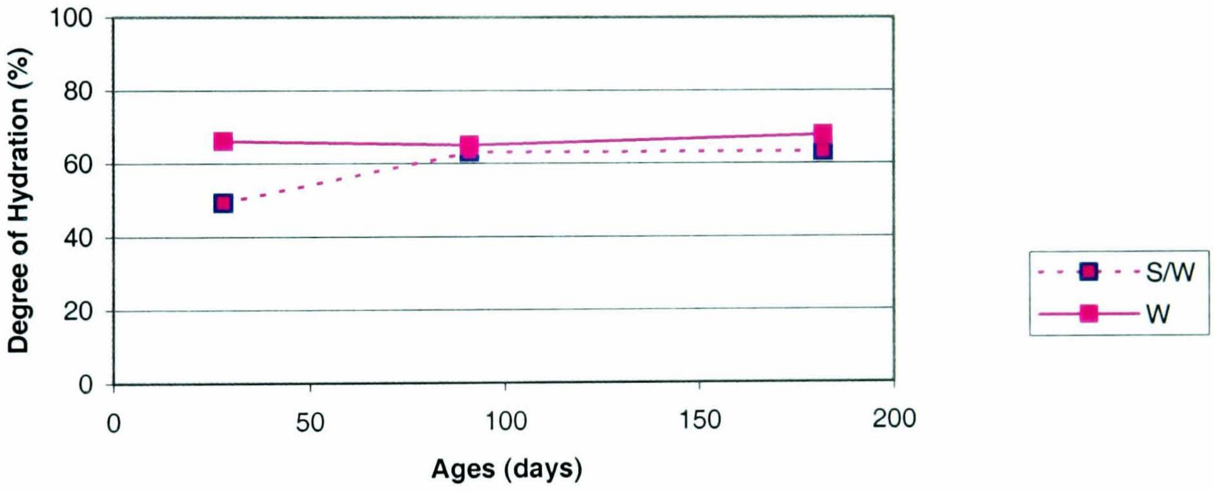
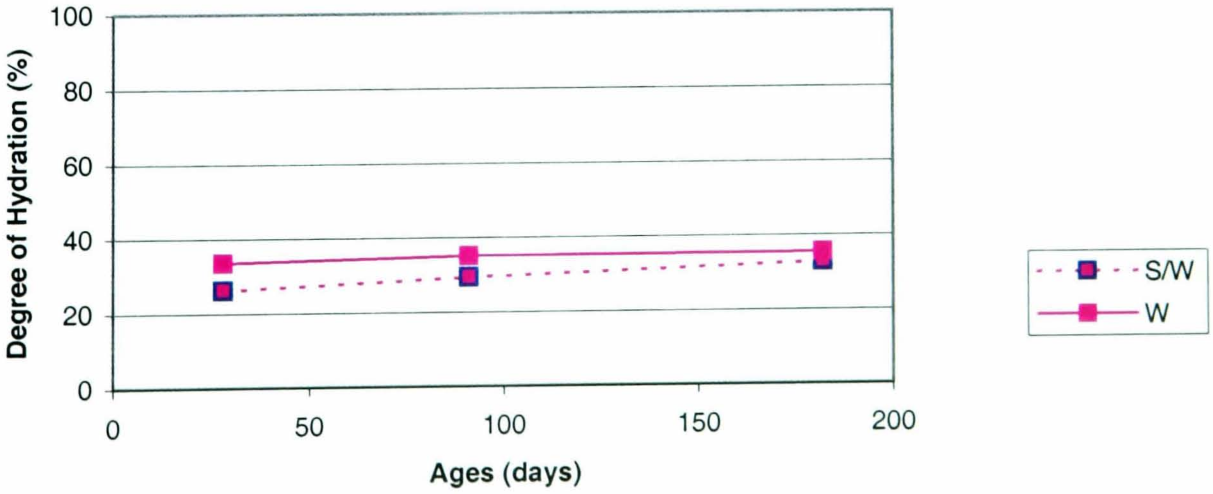


Fig. 5.9.c: 22.5% of Anhydrite and w/cm=0.30



S/W = Water curing after sealing for 28 days

W = Water curing

Fig. 5.10: Effect of Water Curing after Sealing For 28 Days on Hydration of CSA Cement Paste Containing 15% Anhydrite

Fig. 5.10.a: 15% of Anhydrite and w/cm=0.78

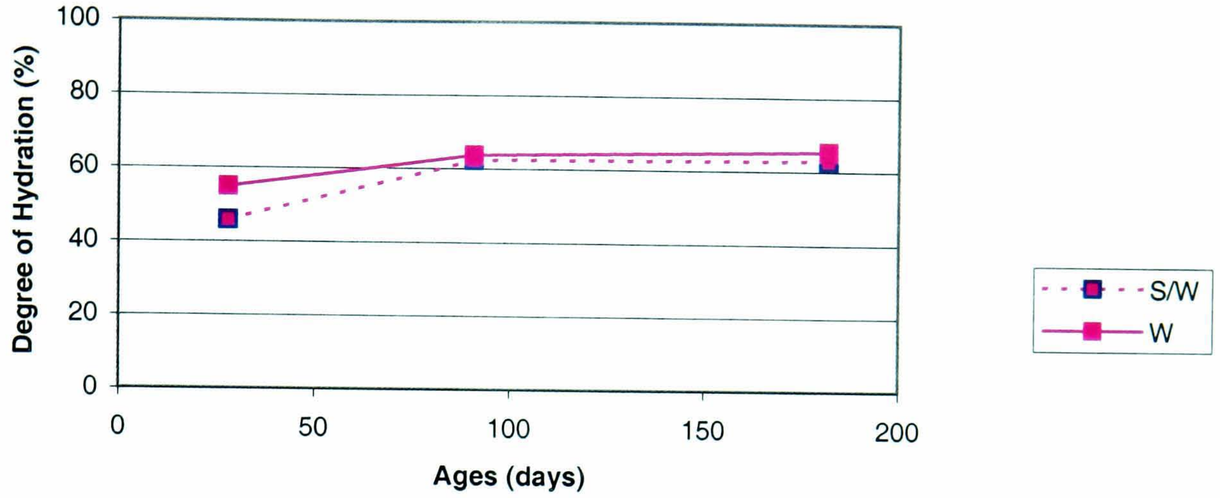


Fig. 5.10.b: 15% of Anhydrite and w/cm=0.50

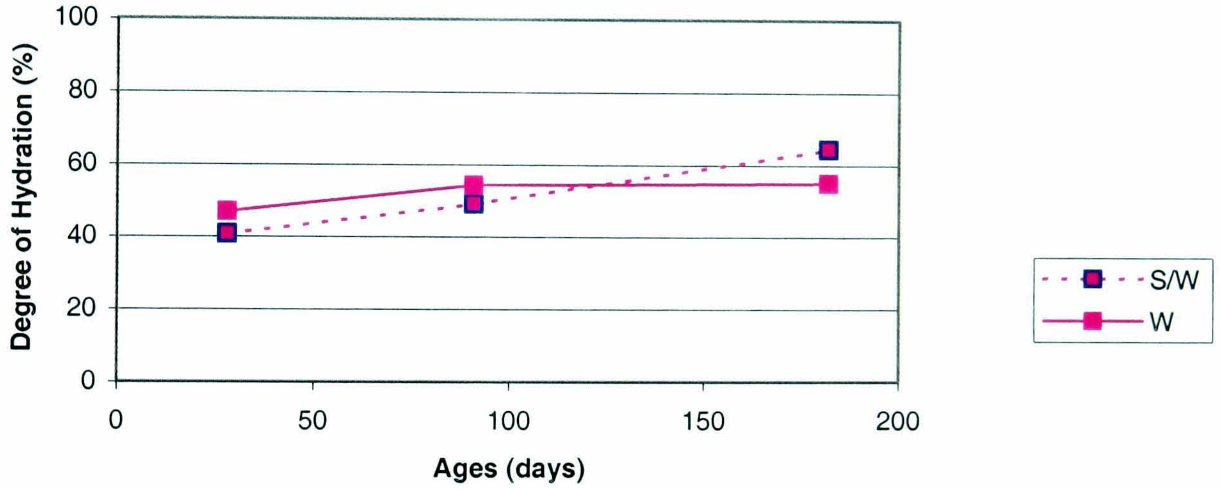
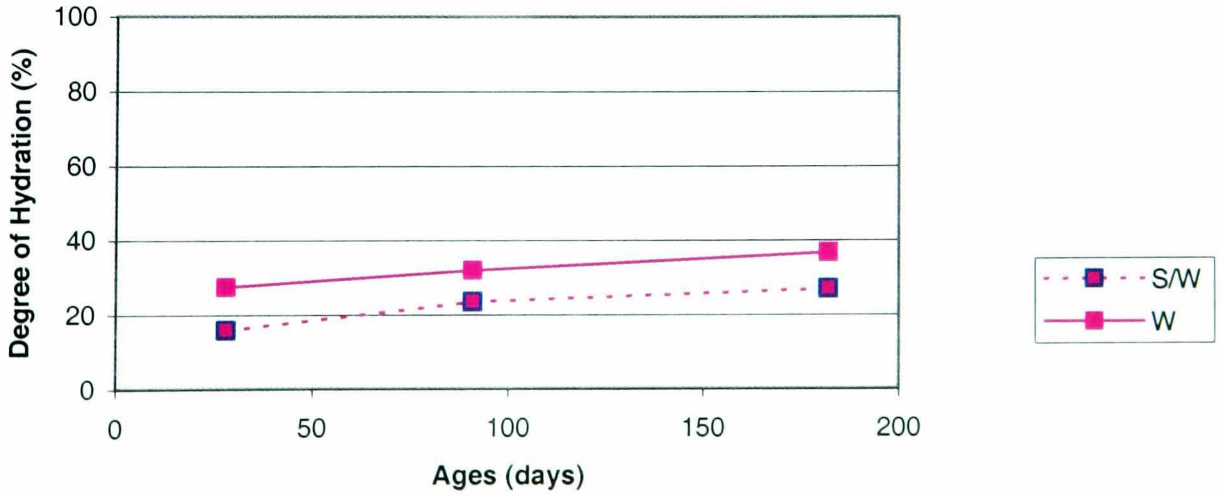


Fig. 5.10.c: 15% of Anhydrite and w/cm=0.30



S/W = Water curing after sealing for 28 days
W = Water curing

Fig. 5.11: Effect on Hydration of Samples Containing 31% Anhydrite Immersed in Saturated CaSO4 Solution

Fig. 5.11.a: 31% of Anhydrite and w/cm=0.78

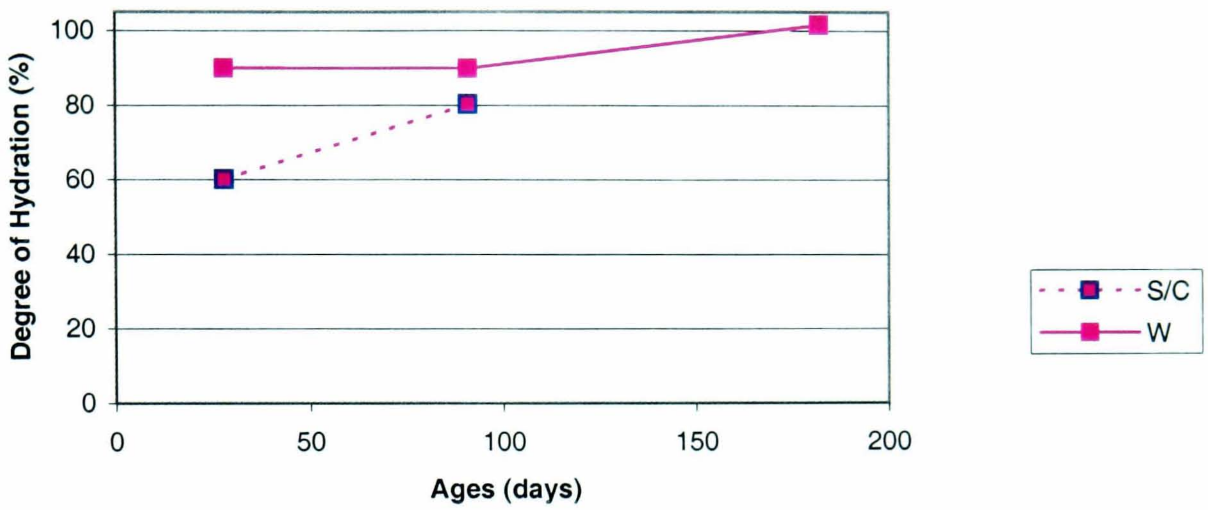


Fig. 5.11.b: 31% of Anhydrite and w/cm=0.50

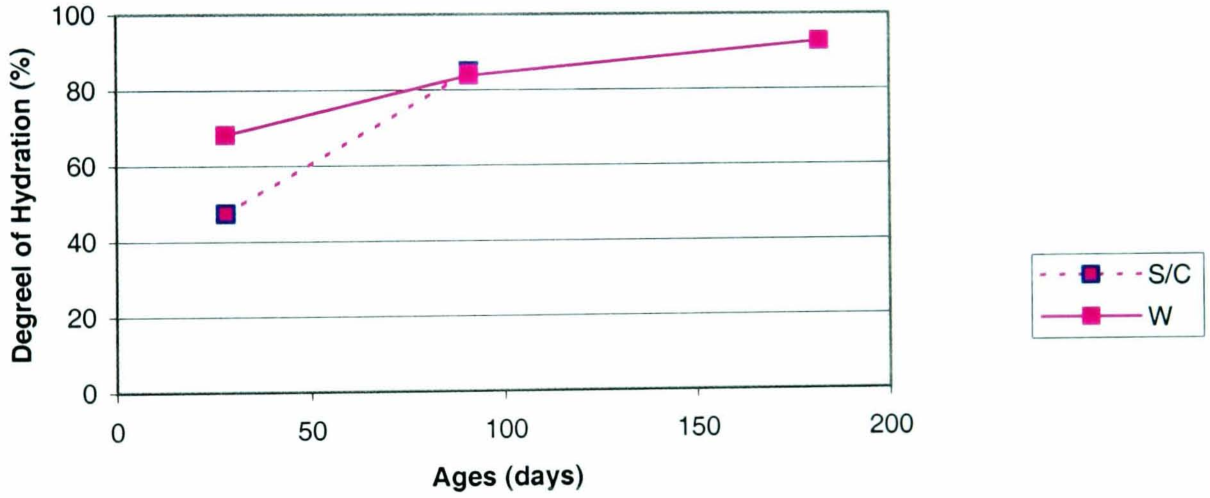
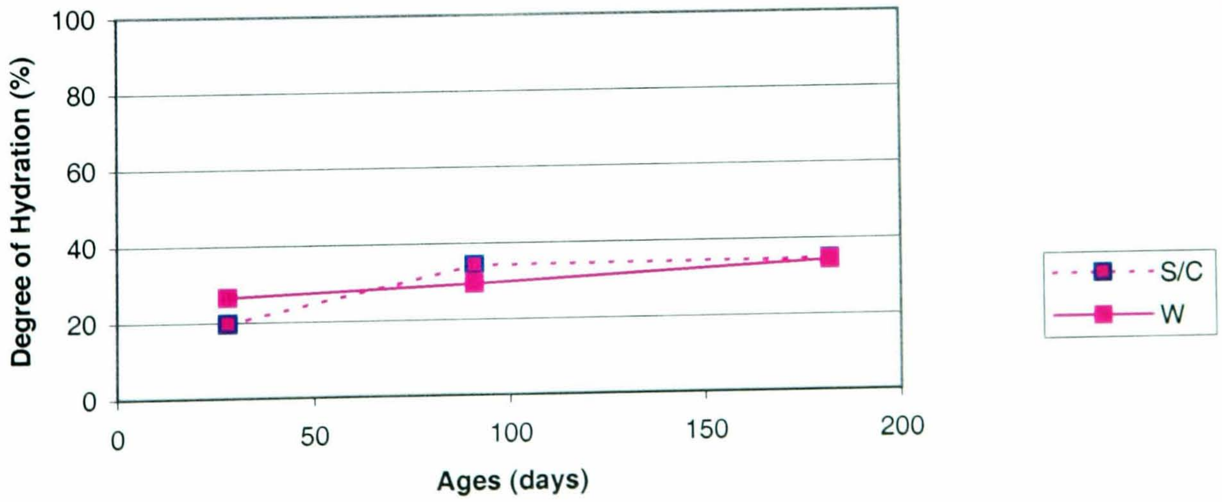


Fig. 5.11.c: 31% of Anhydrite and w/cm=0.30



S/C = Storage in saturated $CaSO_4$ solution after sealing for 28 days
W = Water curing

Fig. 5.12: Effect on Hydration of Samples Containing 22.5% Anhydrite Immersed in Saturated CaSO4 Solution

Fig. 5.12.a: 22.5% of Anhydrite and w/cm=0.78

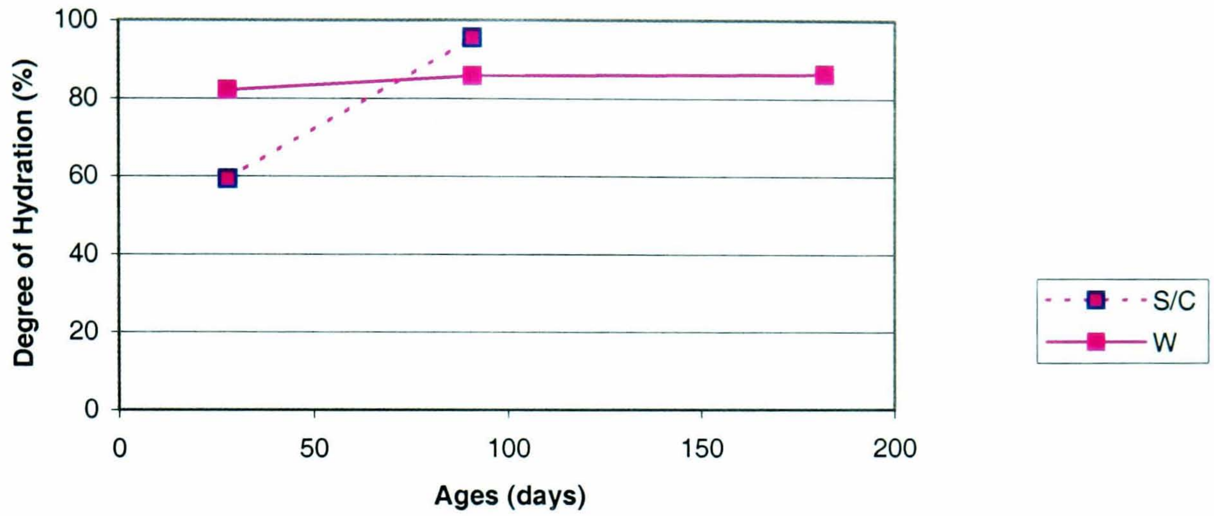


Fig. 5.12.b: 22.5% of Anhydrite and w/cm=0.50

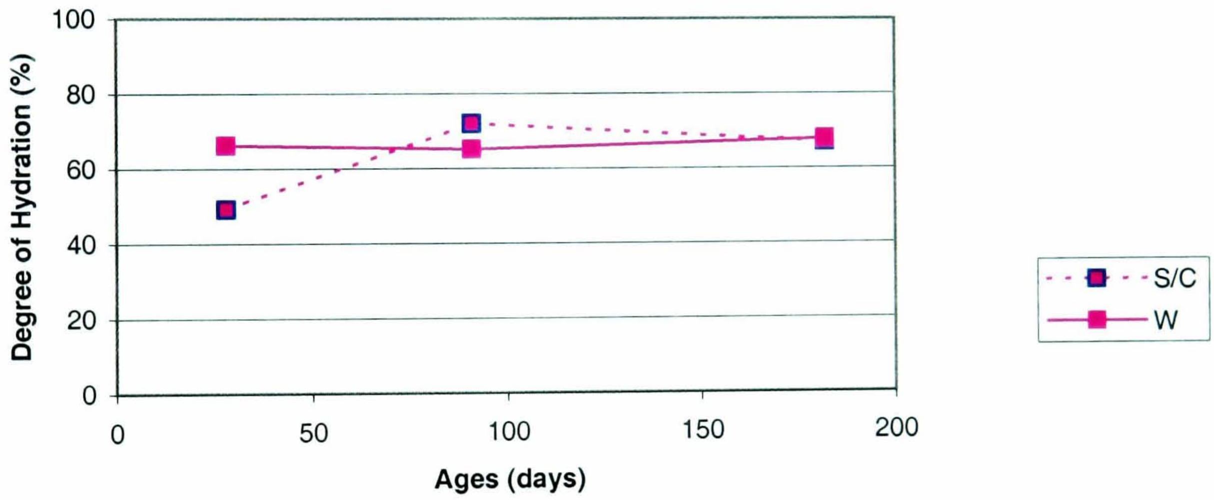
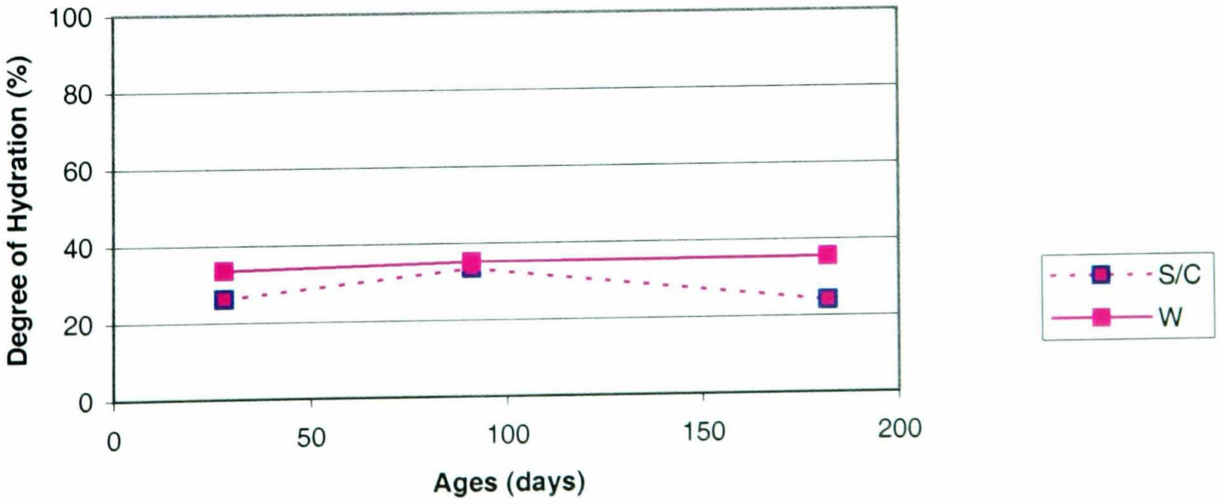


Fig. 5.12.c: 22.5% of Anhydrite and w/cm=0.30



S/C = Storage in saturated $CaSO_4$ solution after sealing for 28 days

W = Water curing

Fig. 5.13: Effect on Hydration of Samples Containing 15% Anhydrite Immersed in Saturated CaSO4 Solution

Fig. 5.13.a: 15% of Anhydrite and w/cm=0.78

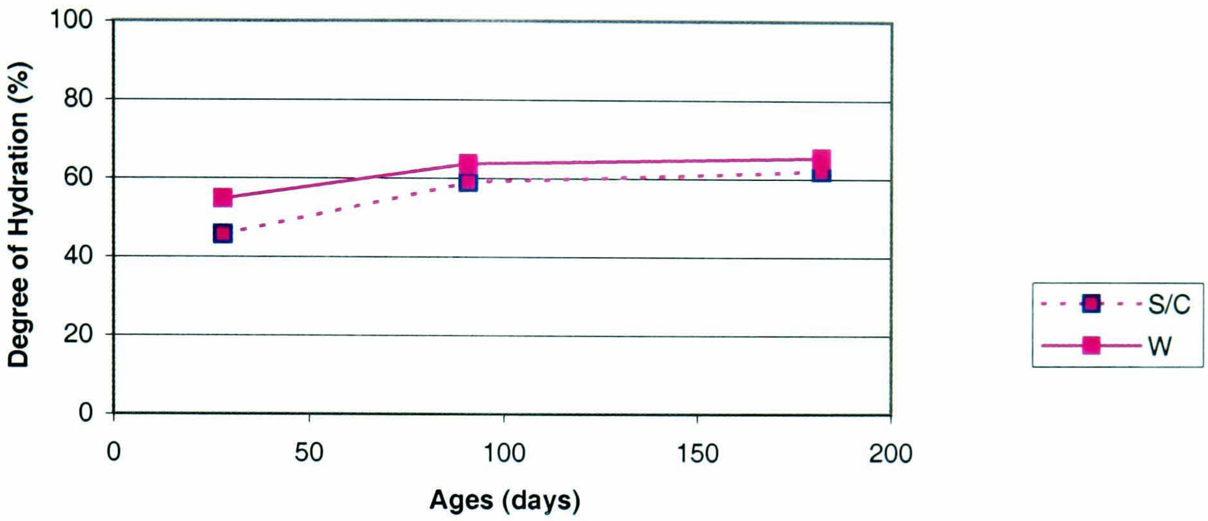


Fig. 5.13.b: 15% of Anhydrite and w/cm=0.50

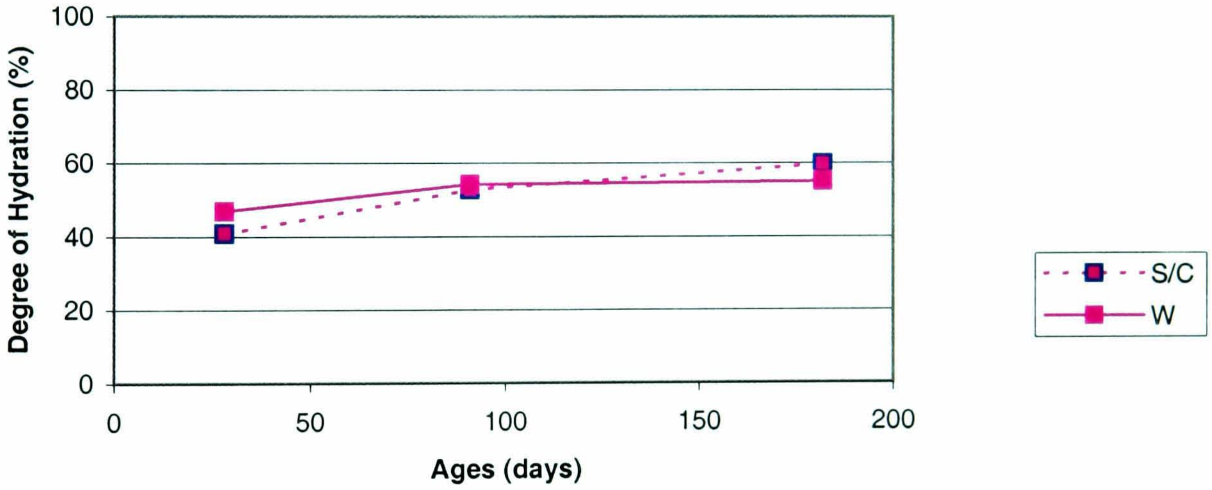
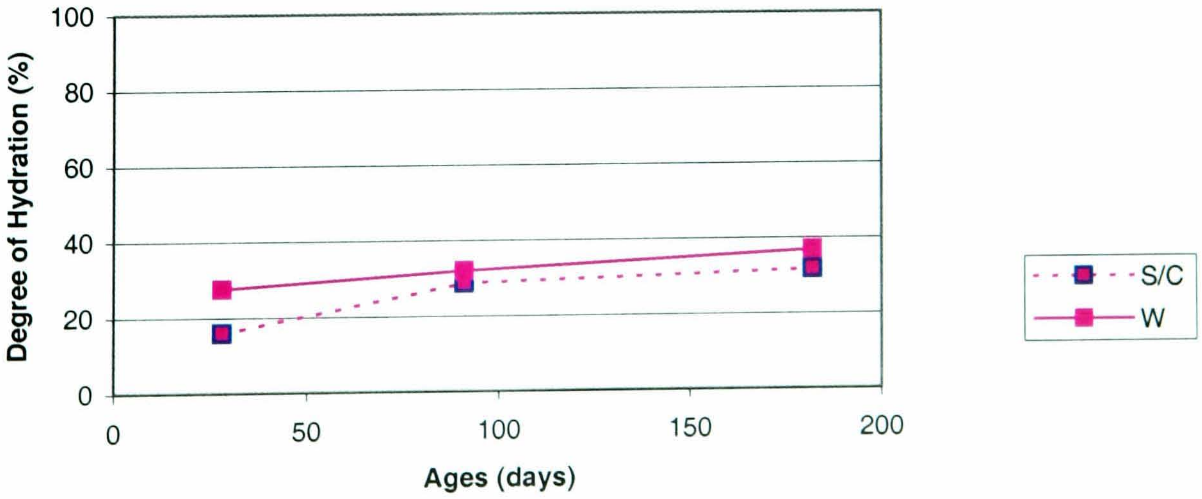


Fig. 5.13.c: 15% of Anhydrite and w/cm=0.30



S/C = Storage in saturated CaSO4 solution after sealing for 28 days

W = Water curing

Fig. 5.14: SEM of Mix Containing 22.5% Anhydrite and w/cm=0.78 (Cured in Water for 6 month)

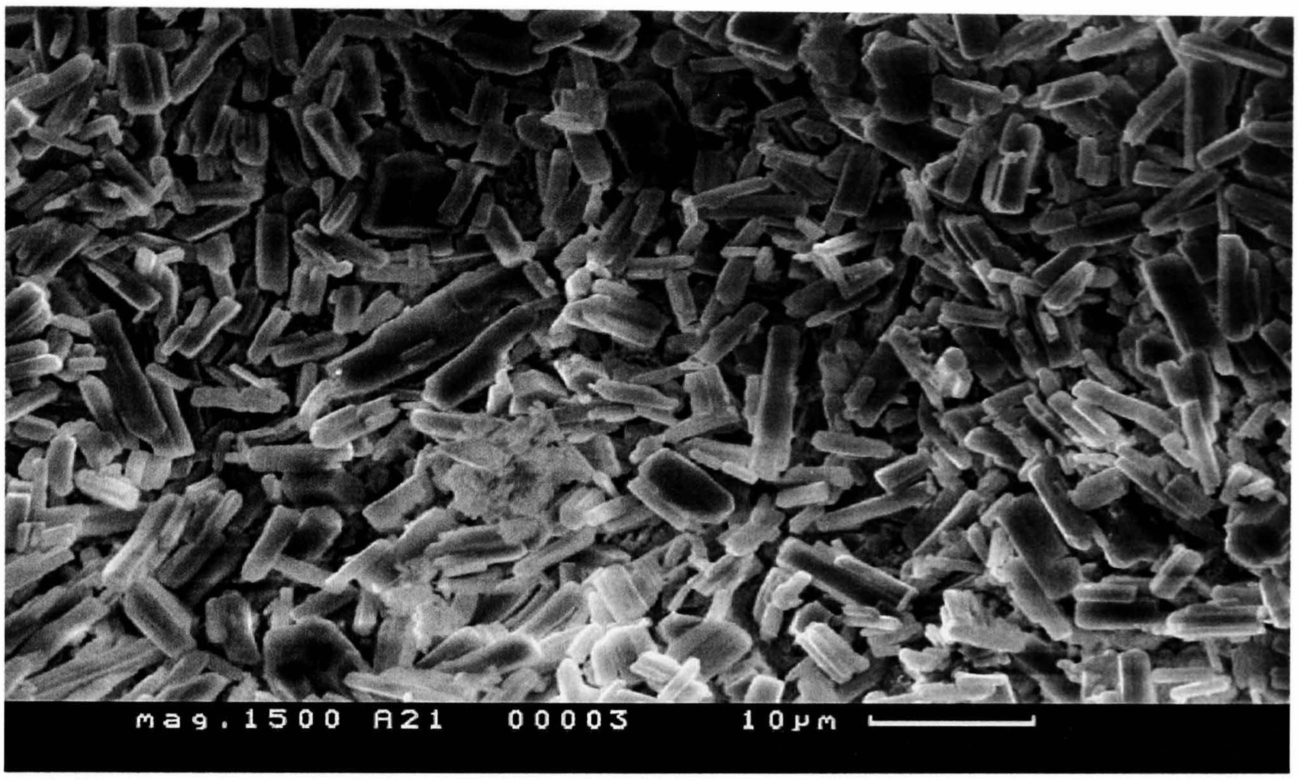


Fig. 5.14.a Magnification of 1500

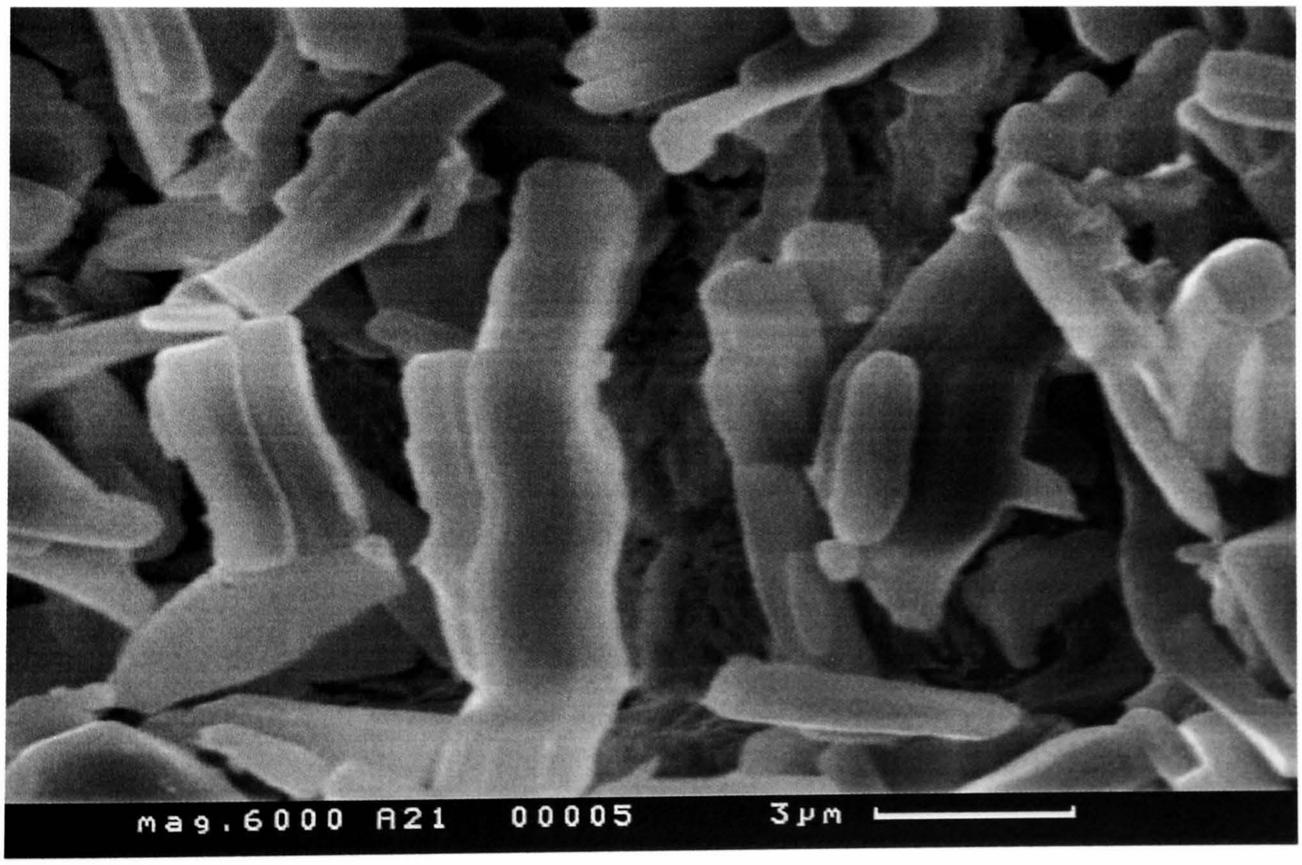


Fig. 5.14.b Magnification of 6000

Fig. 5.15: SEM of Mix Containing 22.5% Anhydrite and w/c=0.50 (Cured in Water for 6 months)

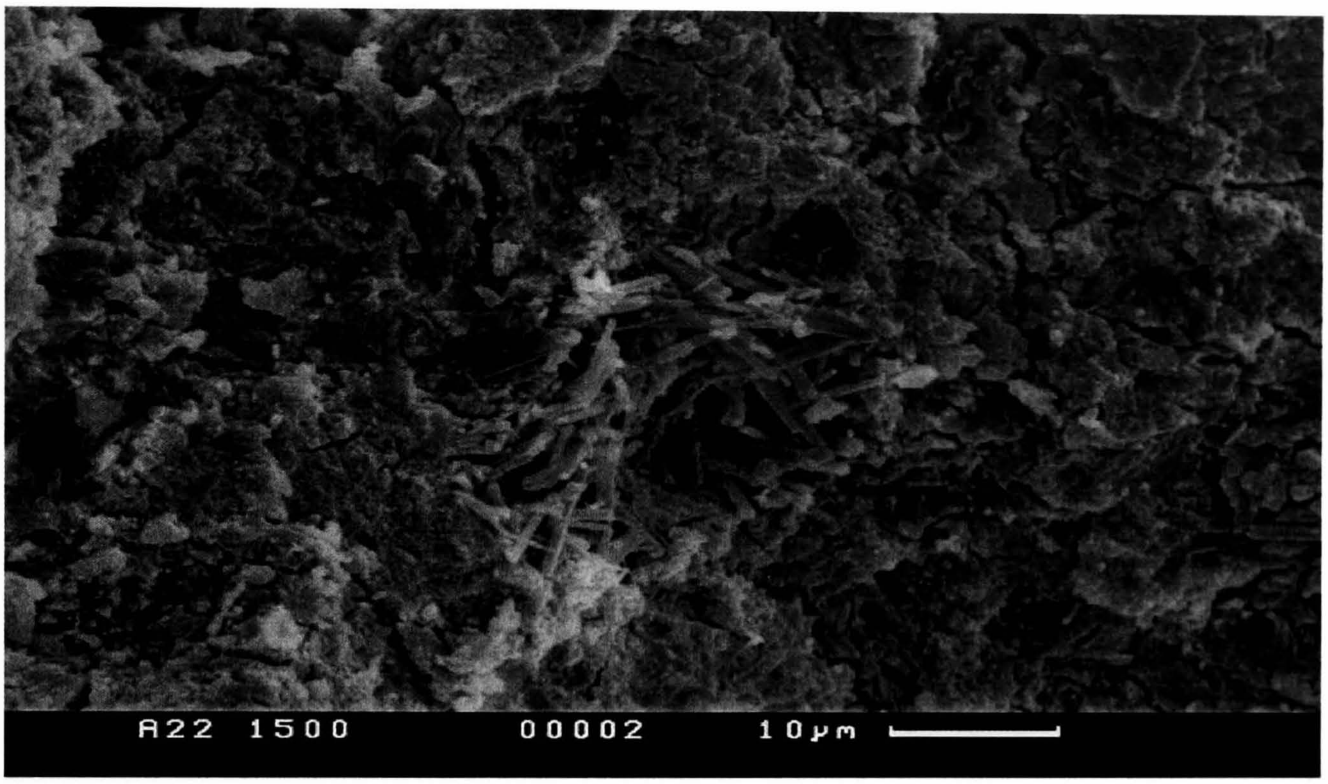


Fig. 5.15.a Magnification of 1500

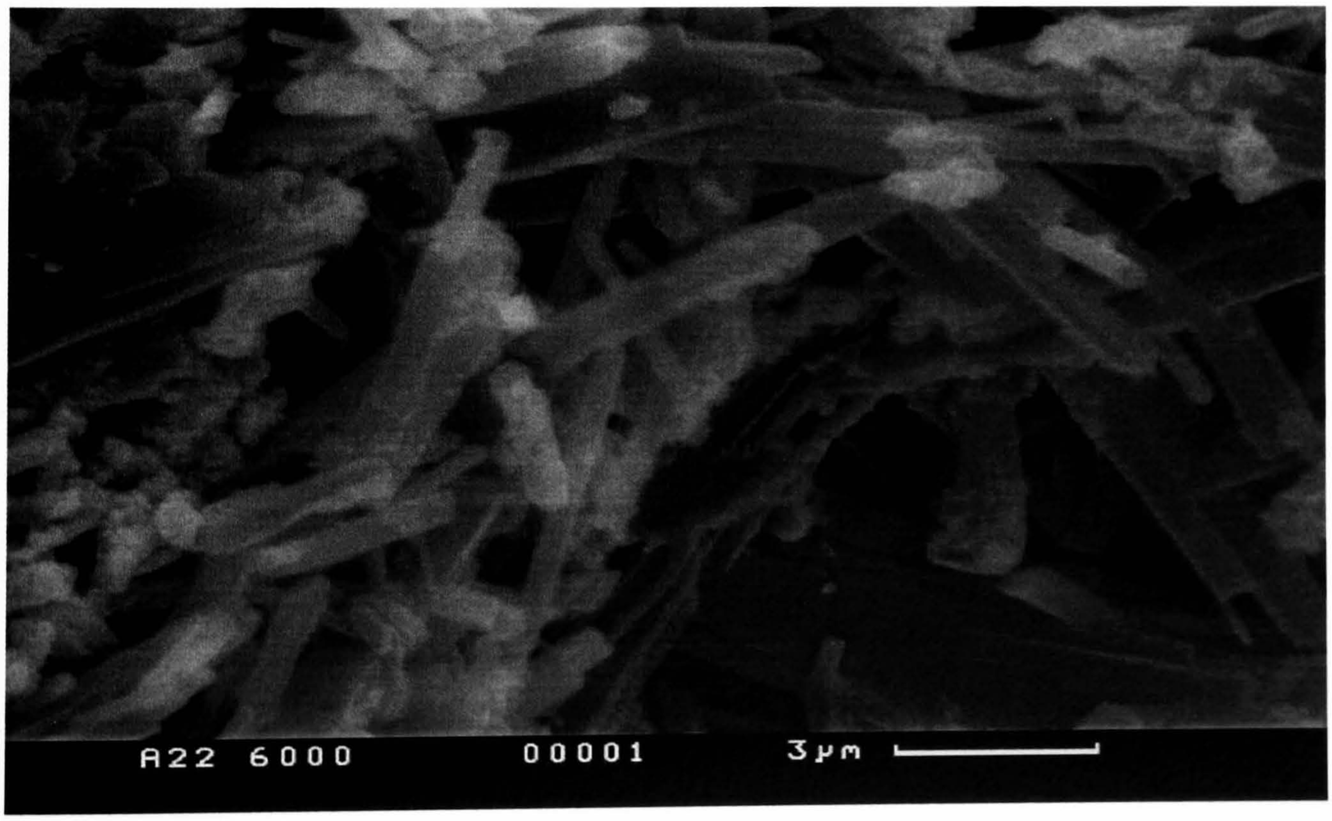


Fig. 5.15.b Magnification of 6000

Fig. 5.16: SEM of Mix Containing 22.5% Anhydrite and w/c=0.30 (Cured in Water for 6 month)

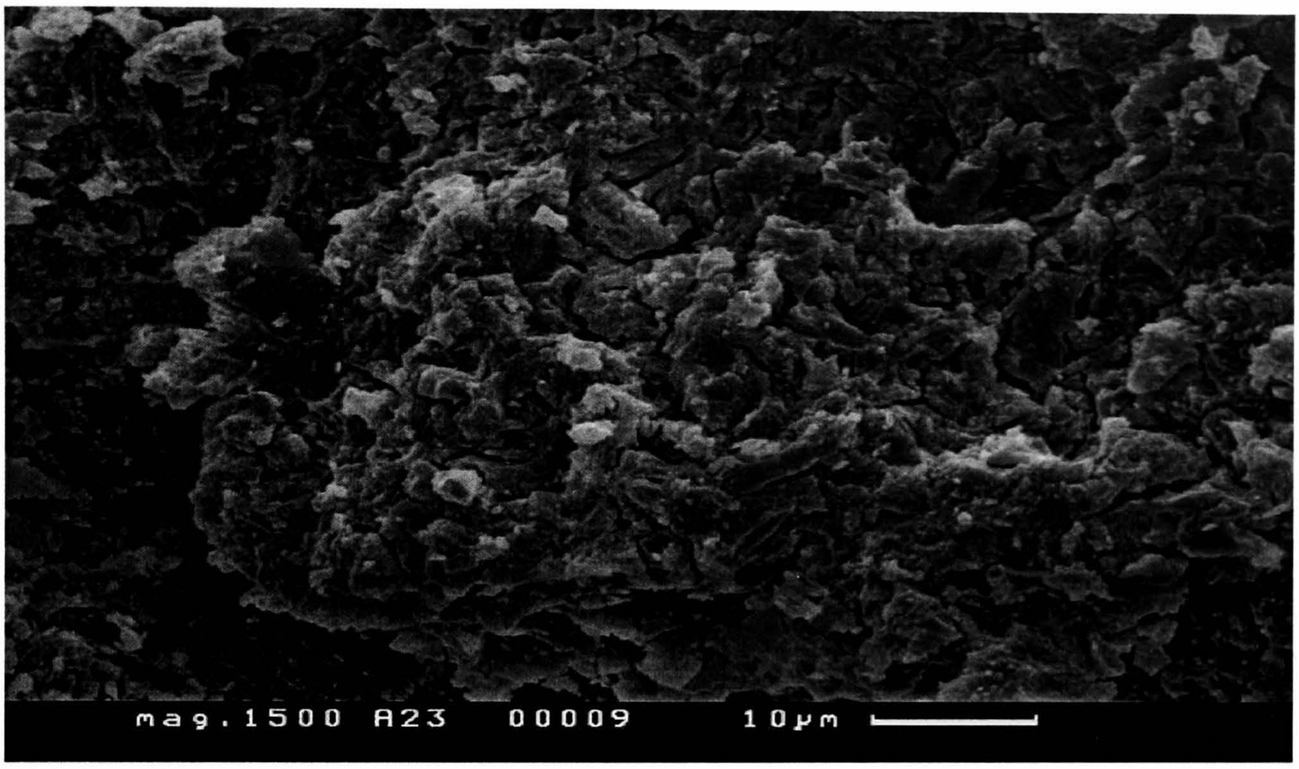


Fig. 5.16.a Magnification of 1500

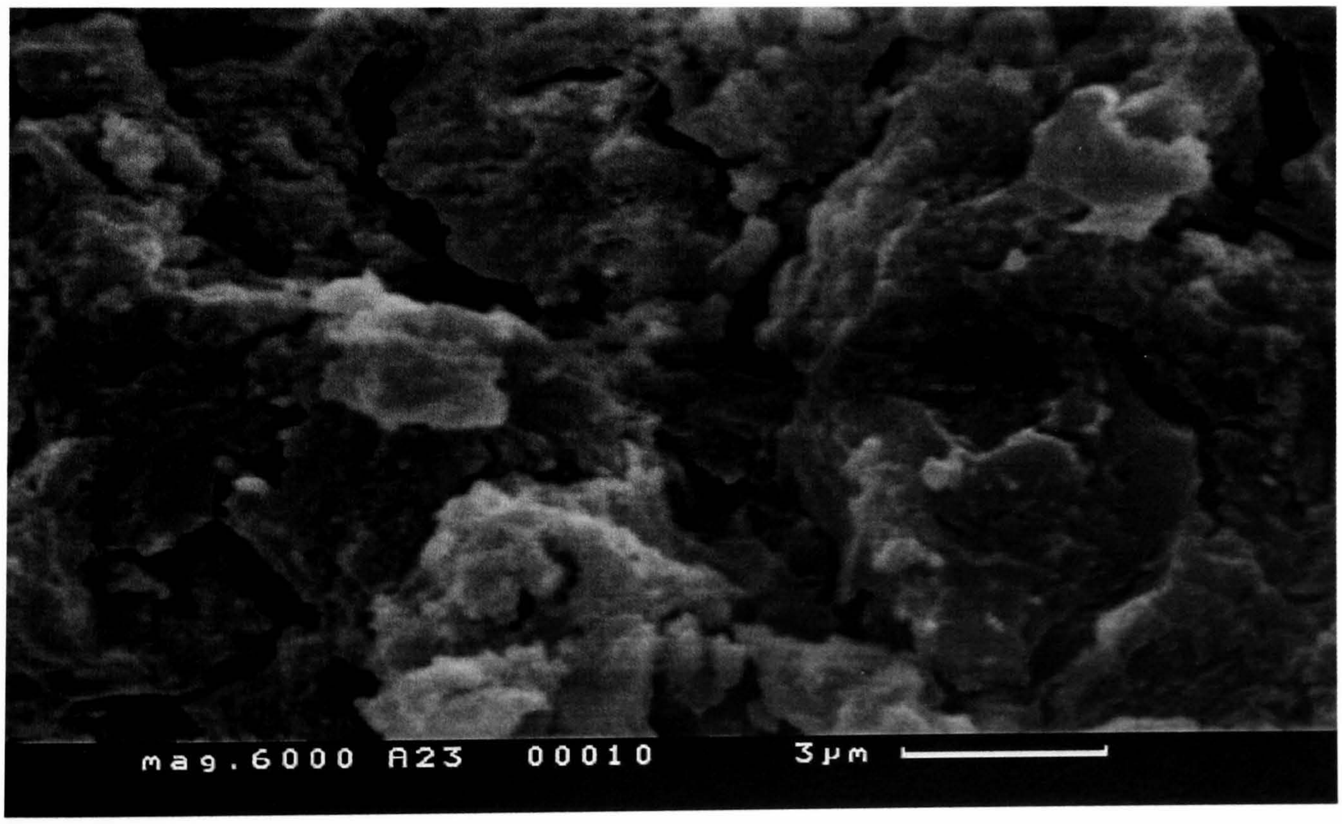


Fig. 5.16.b Magnification of 6000

Fig. 5.17: Length Change Development of CSA Paste Sealed and Cured at Room Temperature

Fig. 5.17.a: 31% Anhydrite Content (Sealed Curing)

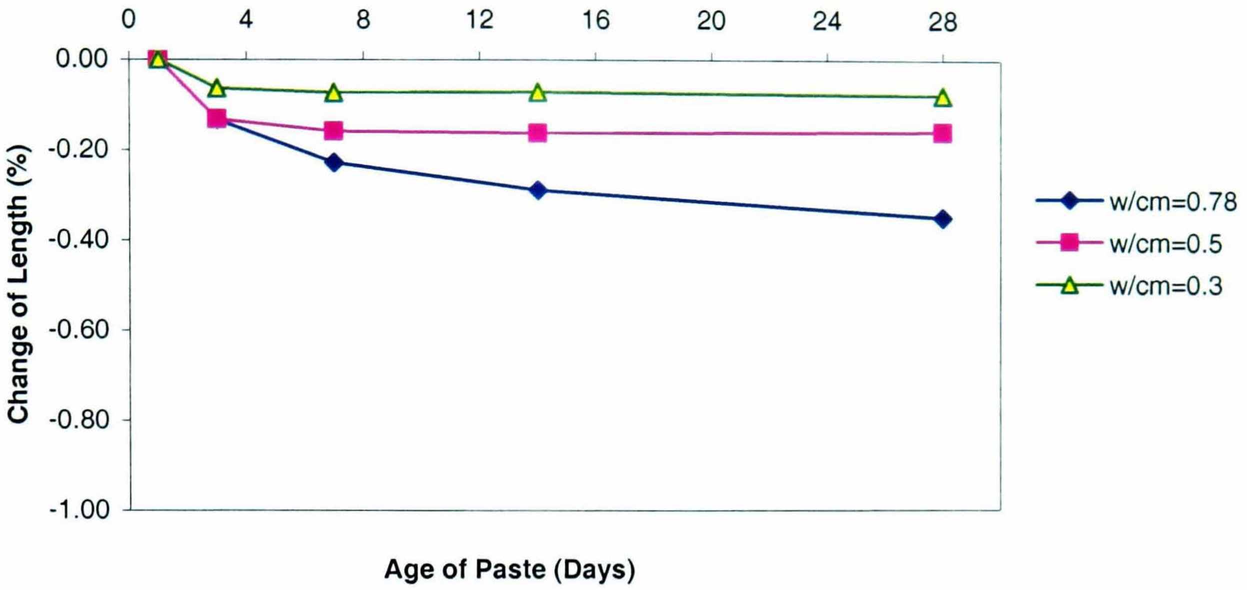


Fig. 5.17.c: 22.5% Anhydrite Content (Sealed Curing)

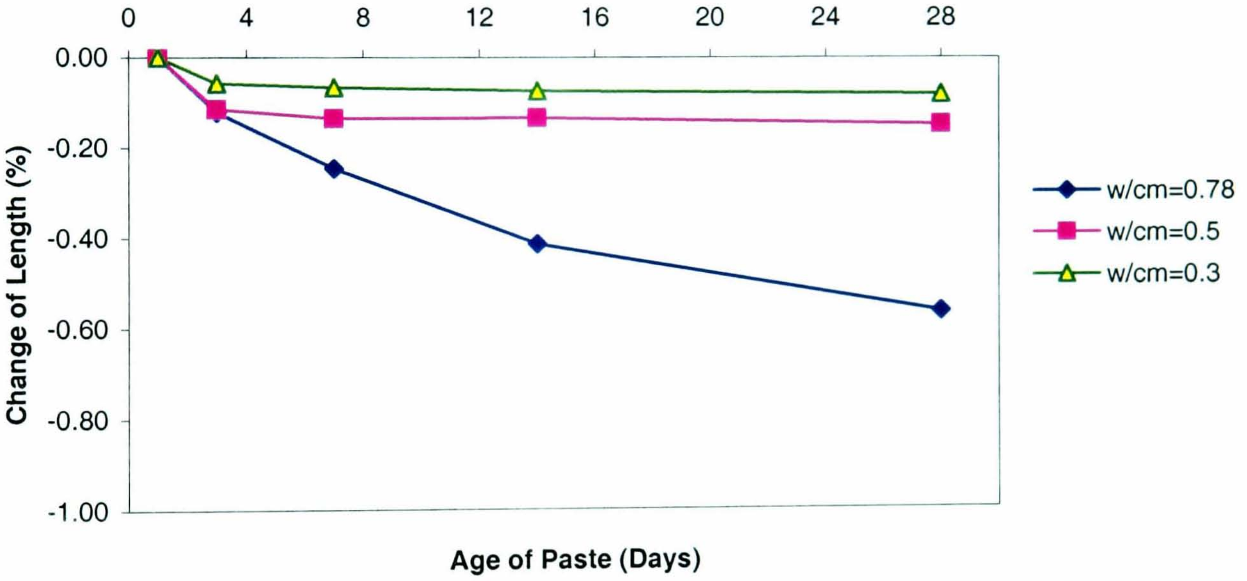


Fig. 5.17.c: 15% Anhydrite Content (Sealed Curing)

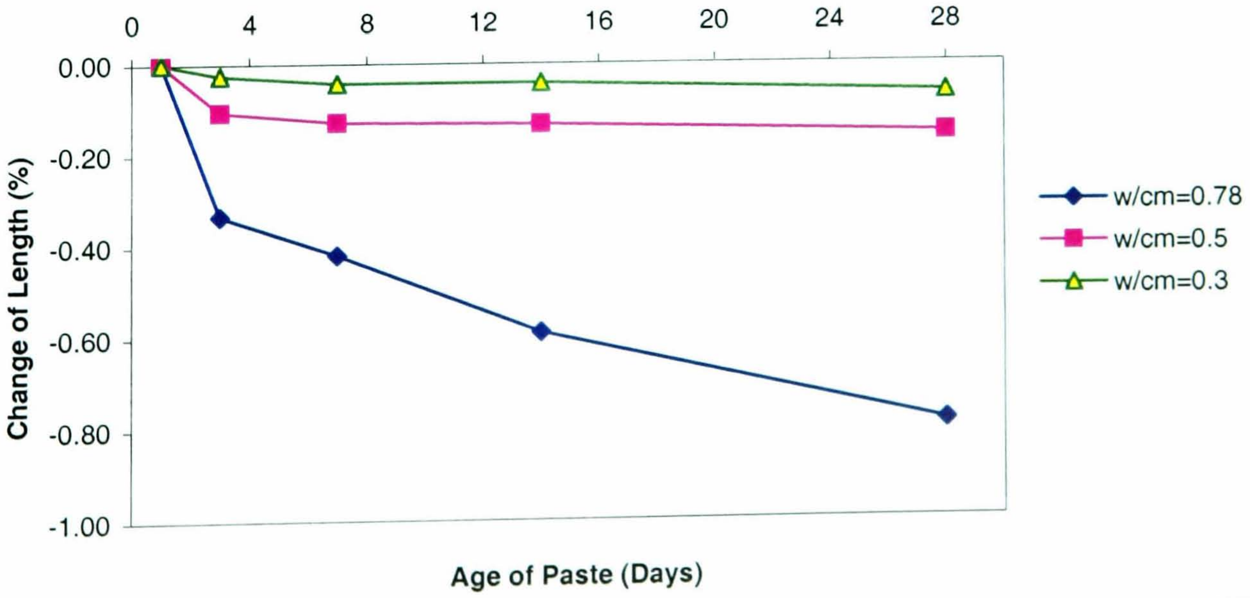


Fig. 5.18: Length Change Development of CSA Paste Cured in Water Directly After Demolding

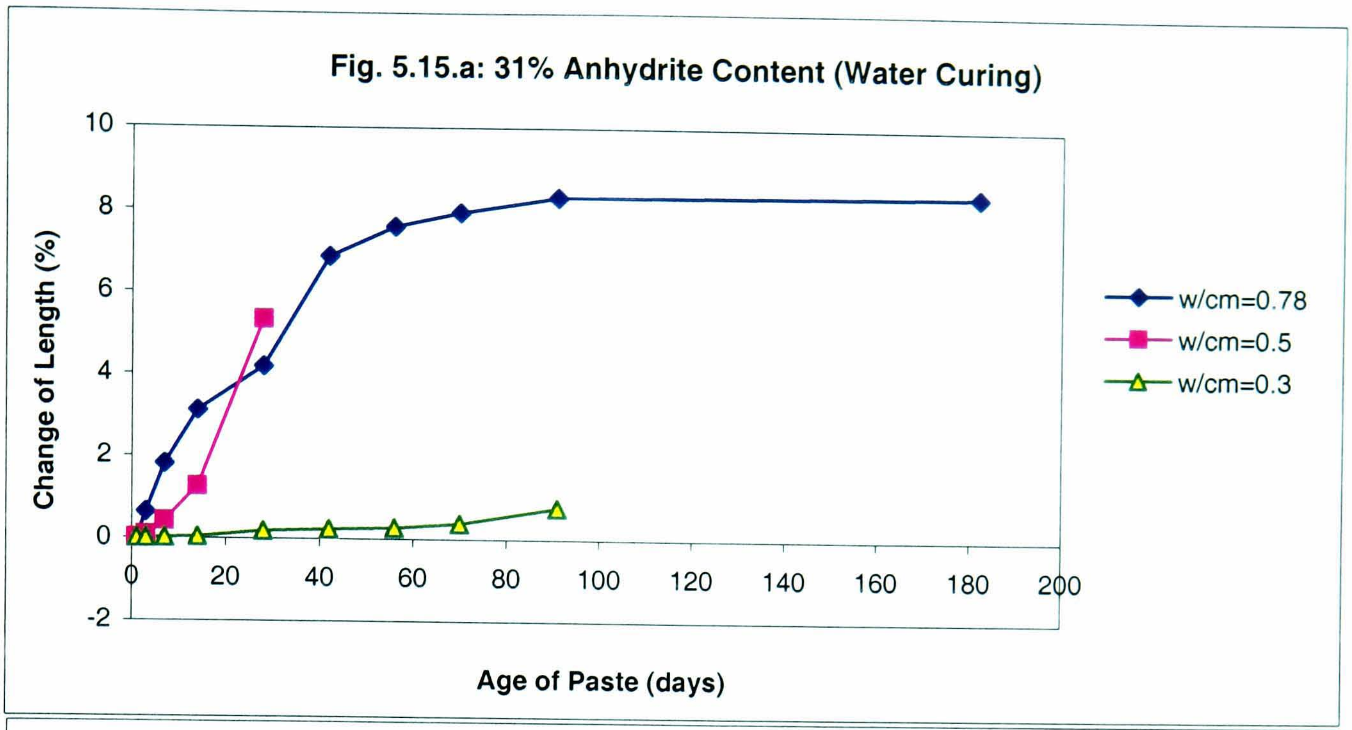


Fig. 5.15.a: 31% Anhydrite Content (Water Curing)

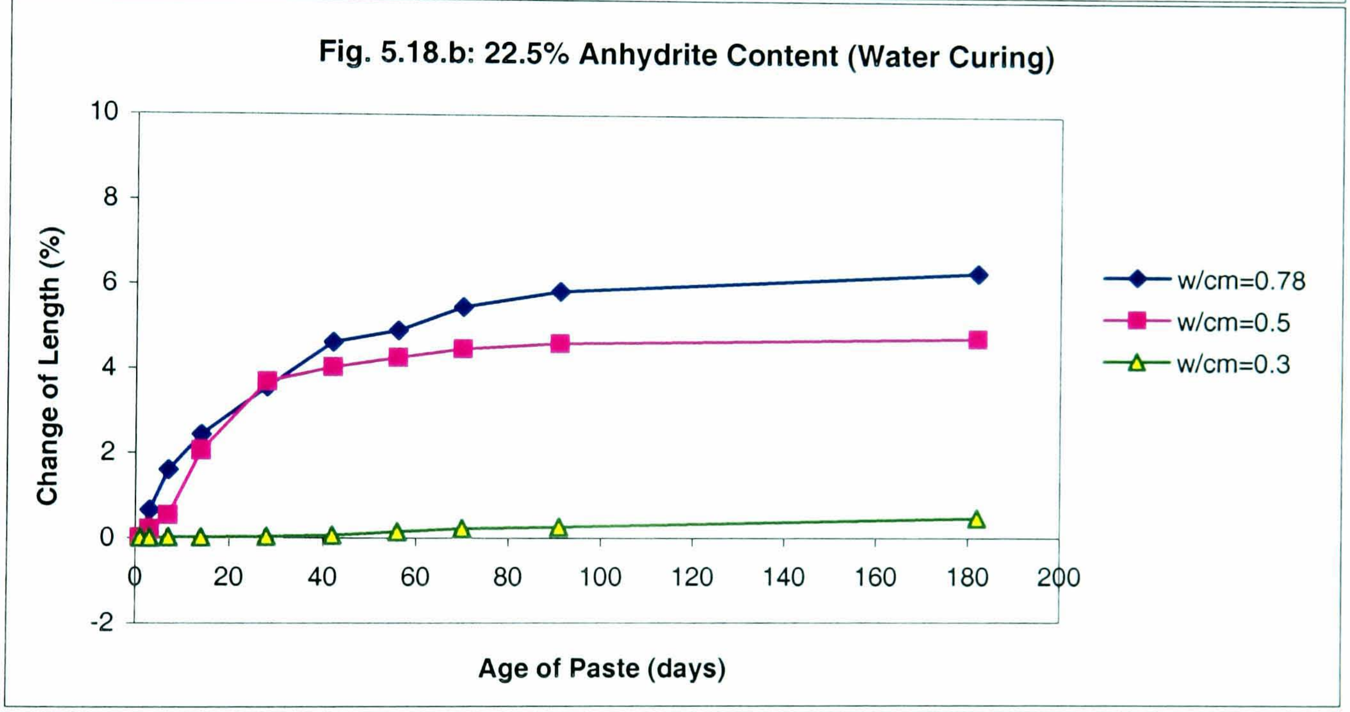


Fig. 5.18.b: 22.5% Anhydrite Content (Water Curing)

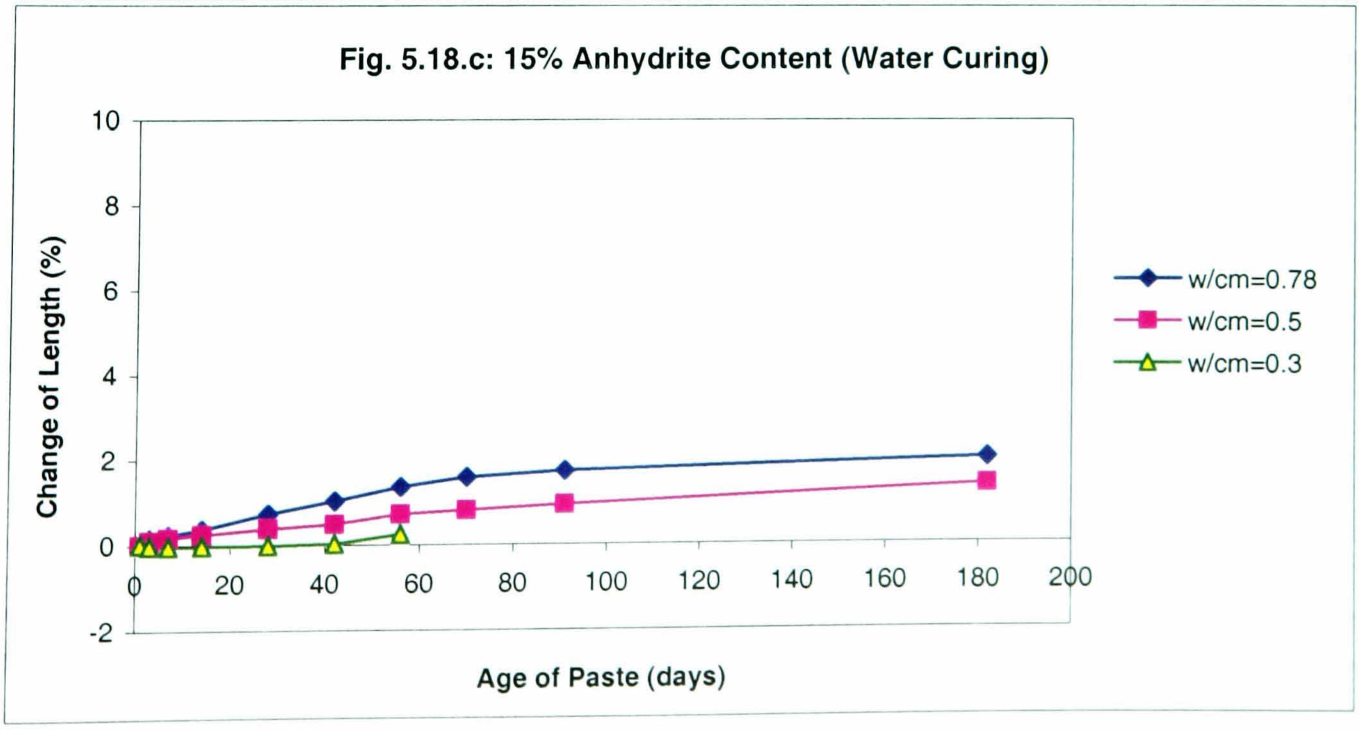


Fig. 5.18.c: 15% Anhydrite Content (Water Curing)

Fig. 5.19: Length Change Development of CSA Paste Cured in Water After Sealing for 28 Days

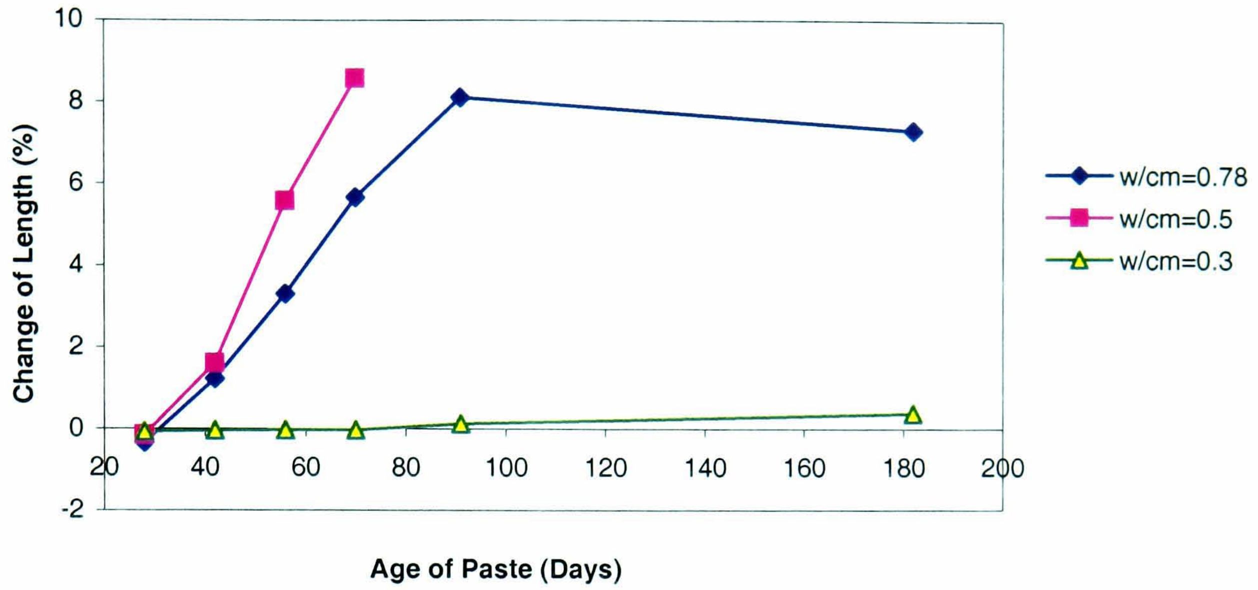


Fig. 5.19.a: 31% Anhydrite Content (Sealed/Water Curing)

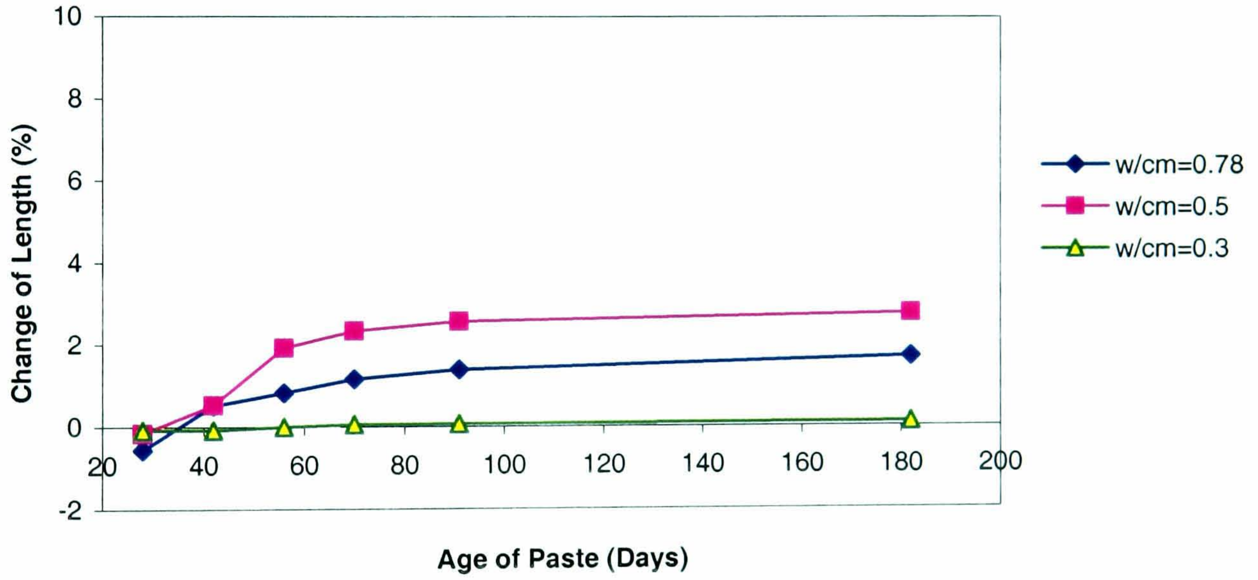


Fig. 5.19.b: 22.5% Anhydrite Content (Sealed/Water Curing)

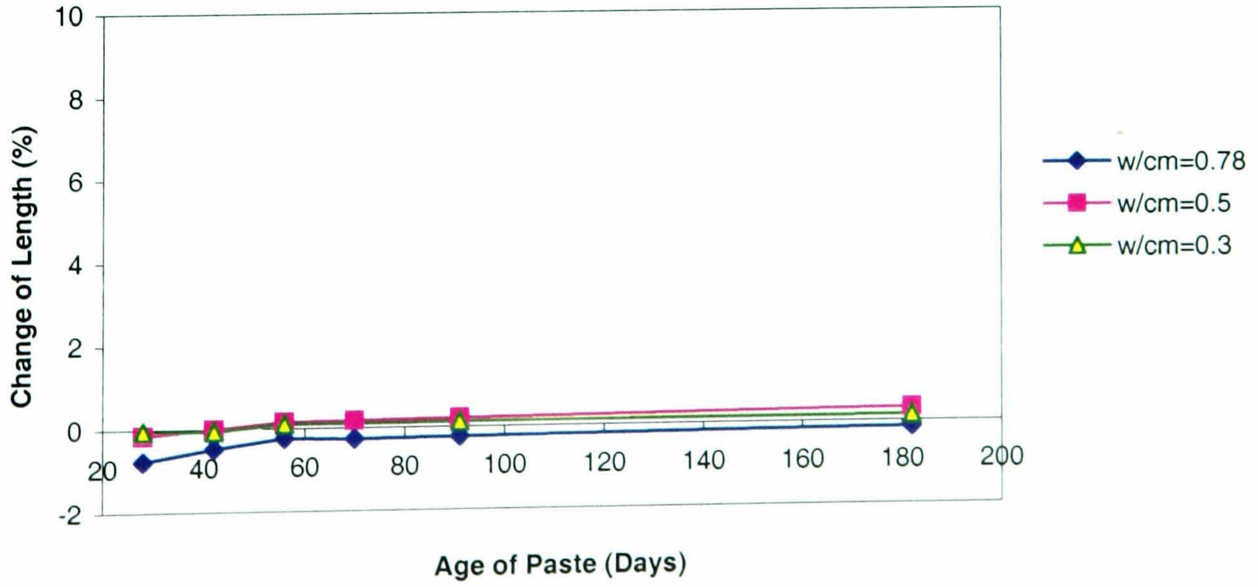


Fig. 5.19.c: 15% Anhydrite Content (Sealed/Water Curing)

Fig. 5.20: Weight Change Development of CSA Paste Sealed and Cured at Room Temperature for 28 Days

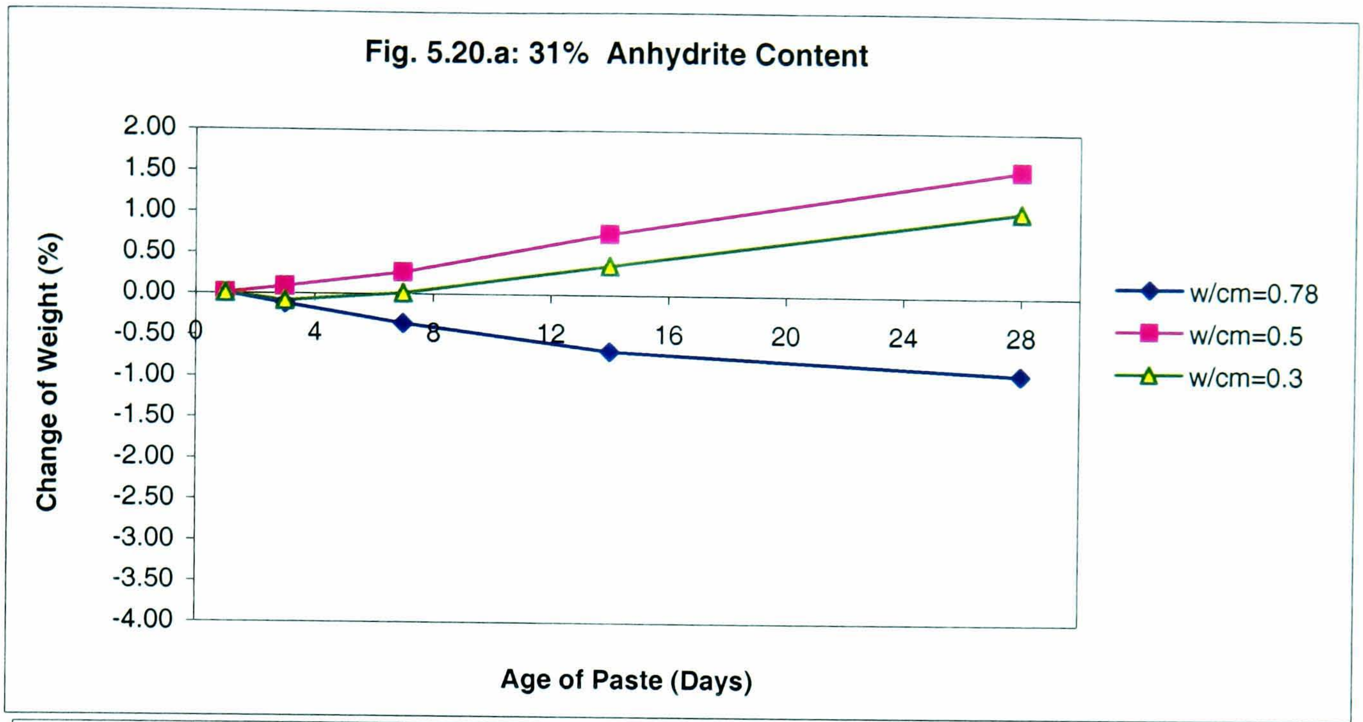


Fig. 5.20.a: 31% Anhydrite Content

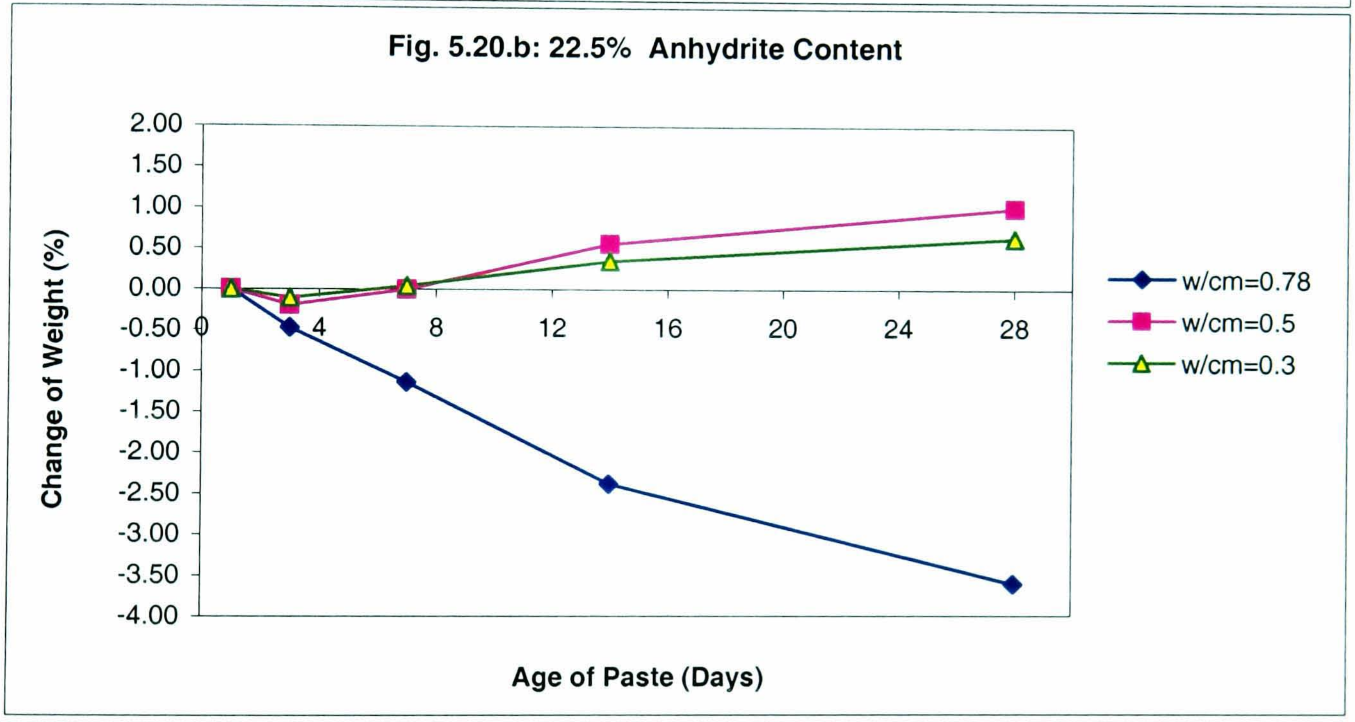


Fig. 5.20.b: 22.5% Anhydrite Content

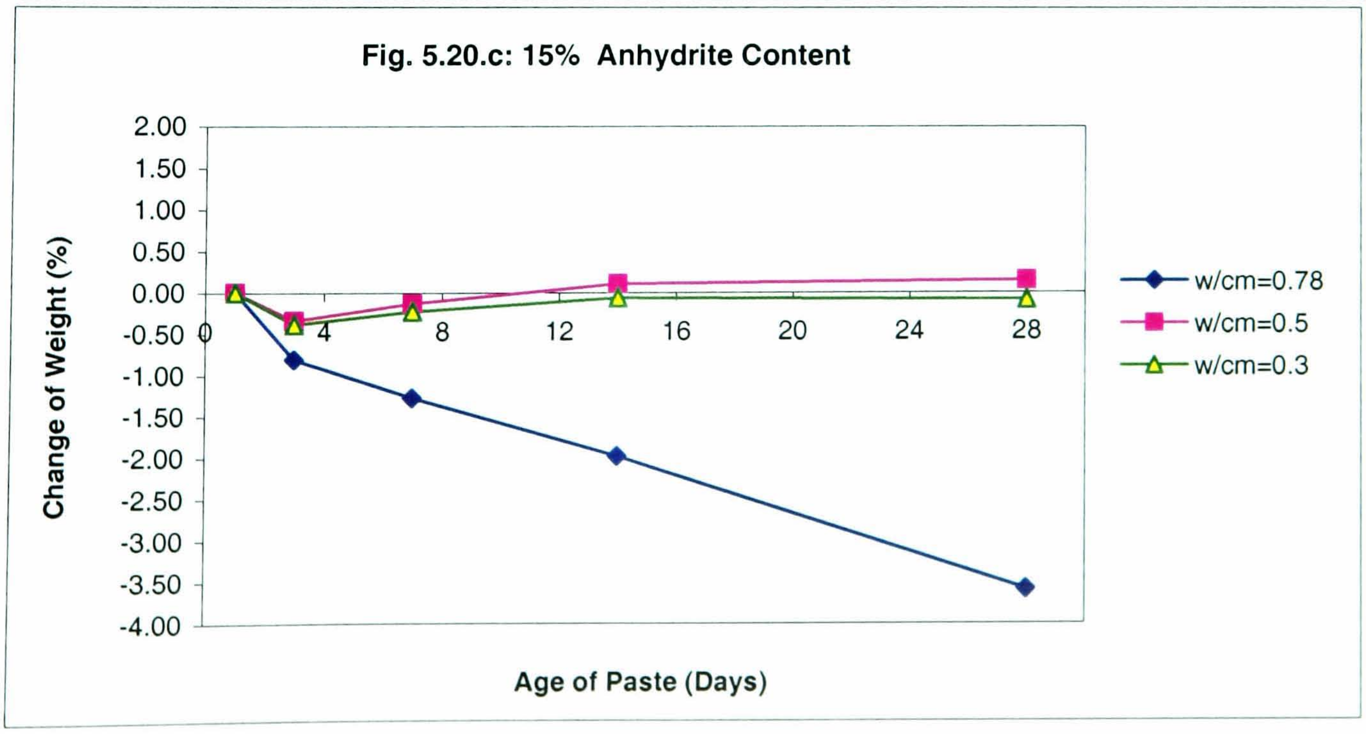


Fig. 5.20.c: 15% Anhydrite Content

Fig. 5.21: Weight Change Development of CSA Paste Cured in Water Directly After Demolding

Fig. 5.21.a: 31% Anhydrite Content

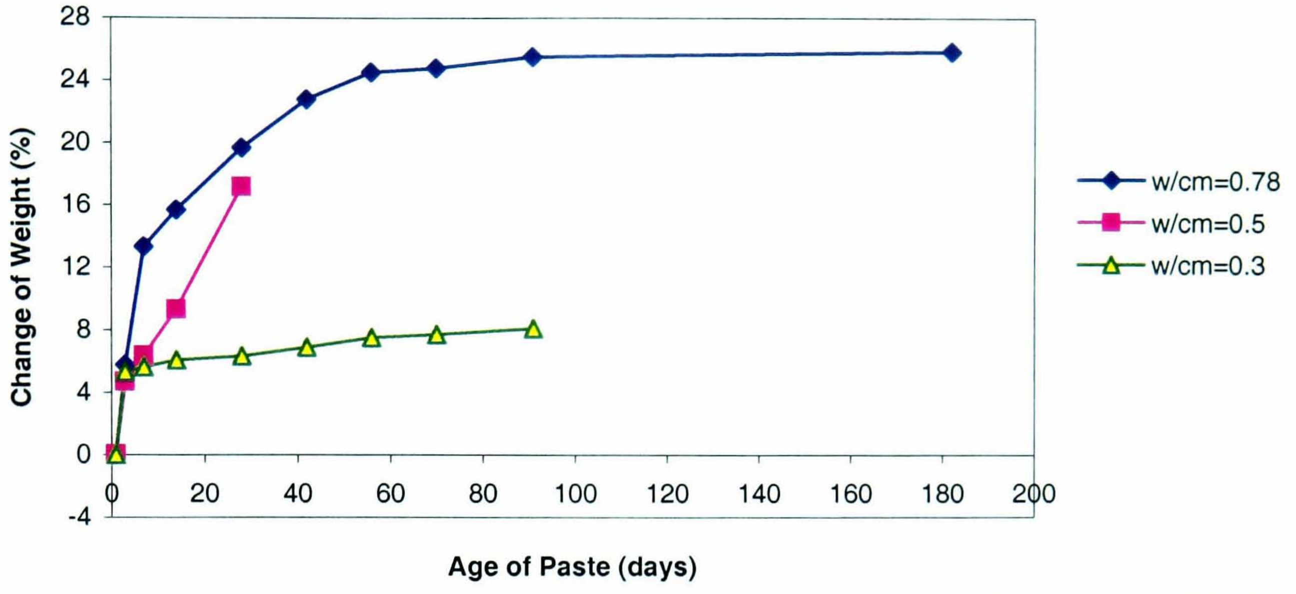


Fig. 5.21.b: 22.5% Anhydrite Content

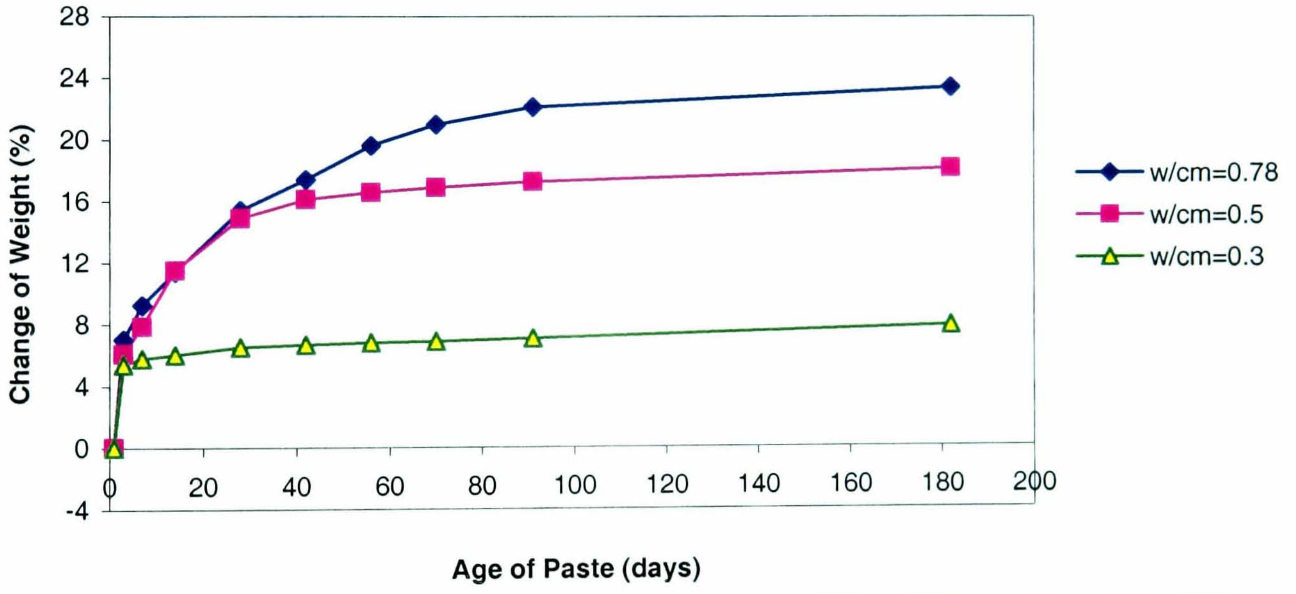


Fig. 5.21.c: 15% Anhydrite Content

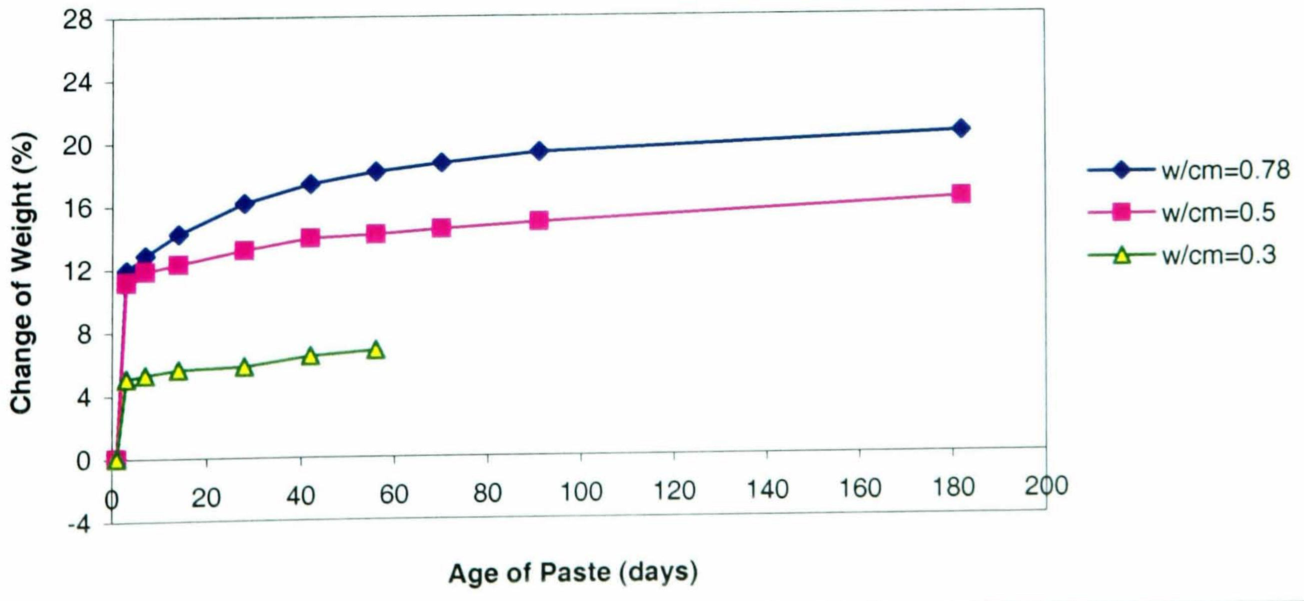


Fig. 5.22: Weight Change Development of CSA Paste Cured in Water After Sealing for 28 Days

Fig. 5.22.a: 31% Anhydrite Content (Sealed/Water Curing)

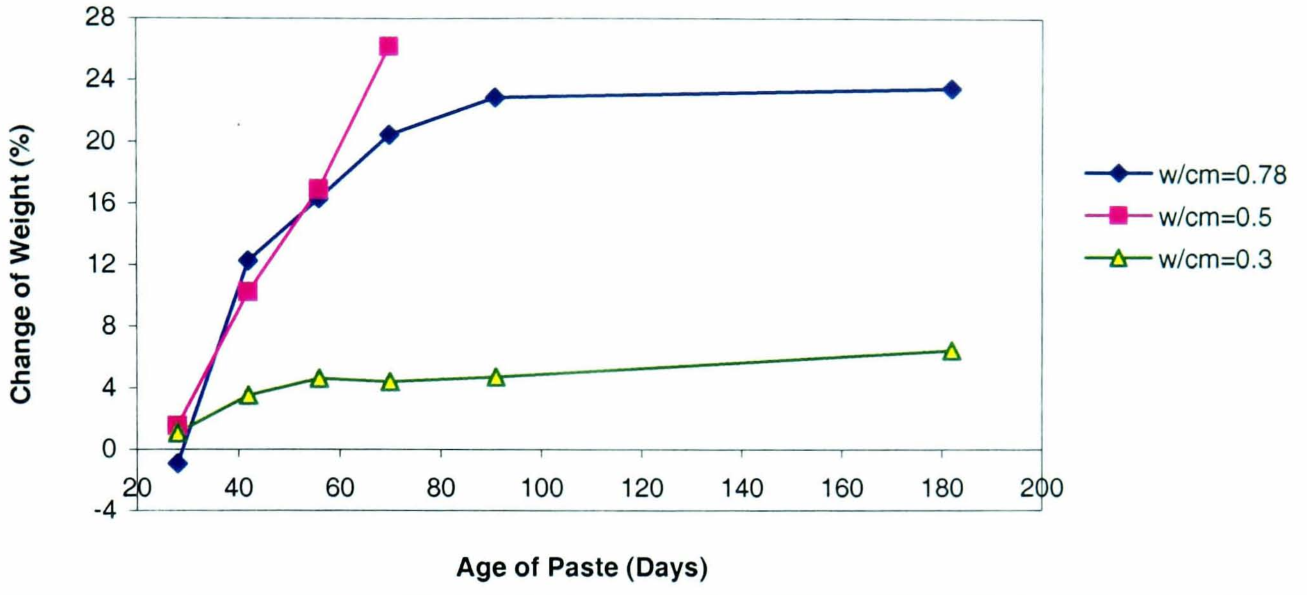


Fig. 5.22.b: 22.5% Anhydrite Content (Sealed/Water Curing)

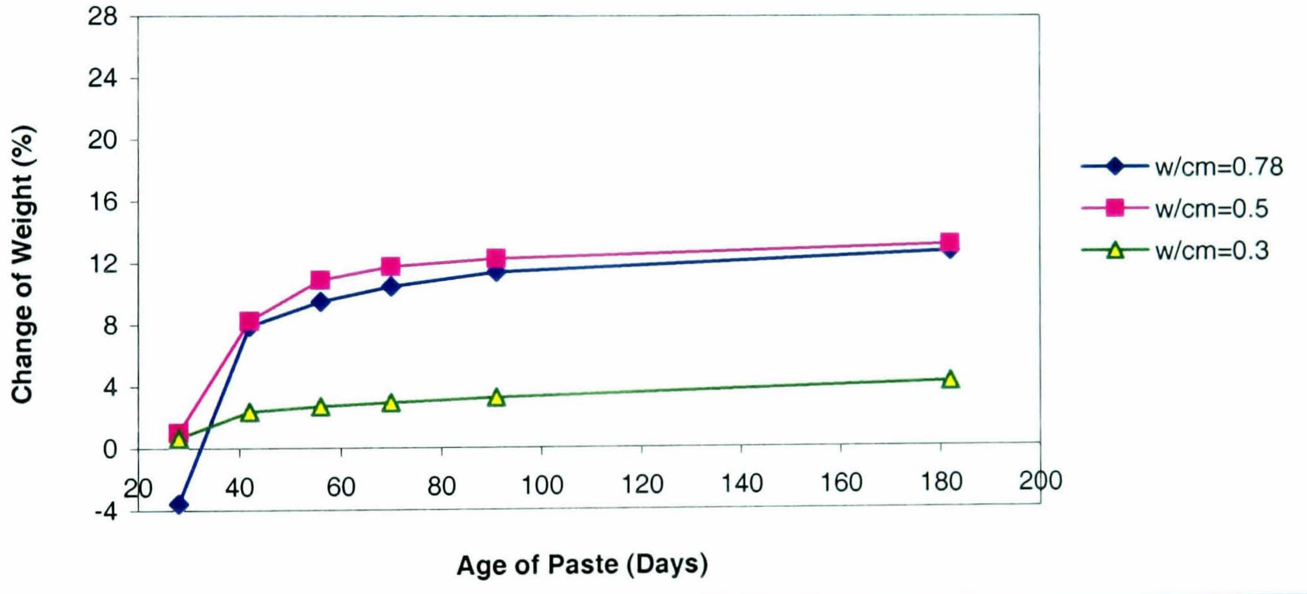


Fig. 5.22.c: 15% Anhydrite Content (Sealed/Water Curing)

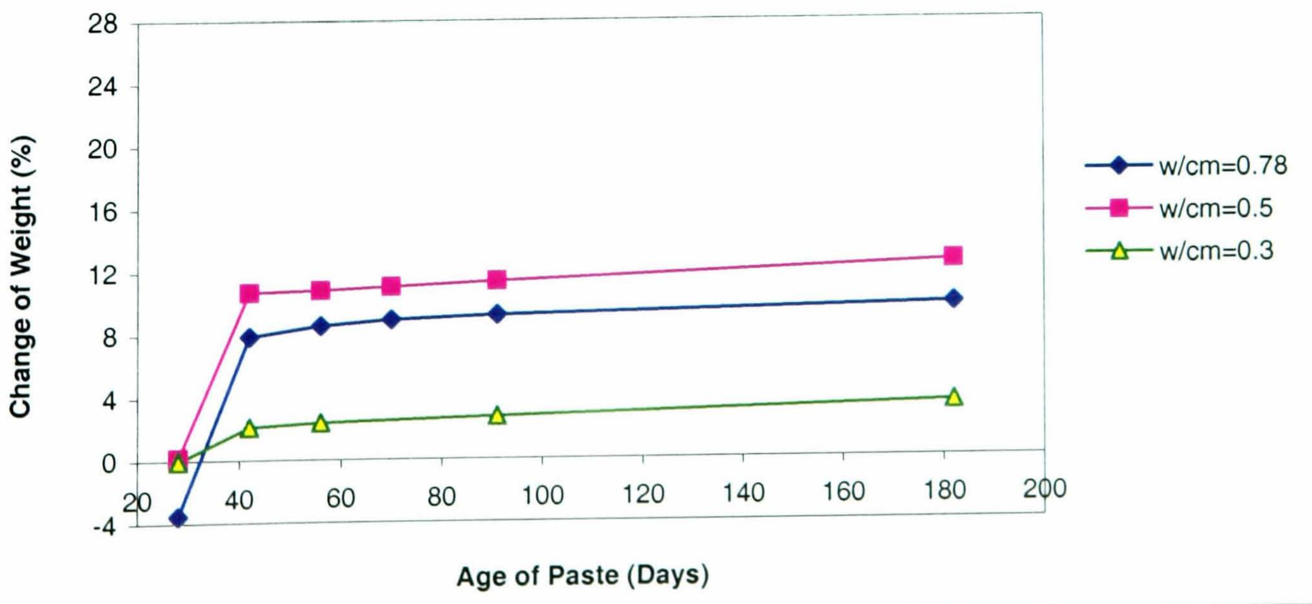


Fig. 5.23: Length Change Development of CSA Paste Immersed in CaSO4 Solution

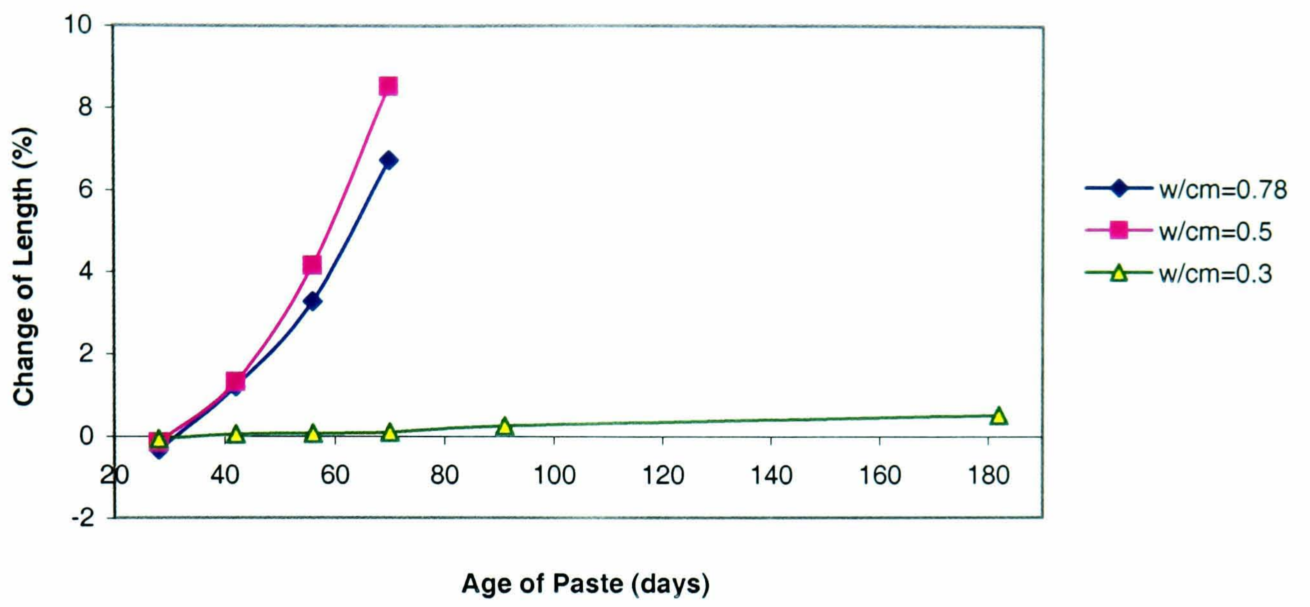


Fig.5.23.a: 31% Anhydrite

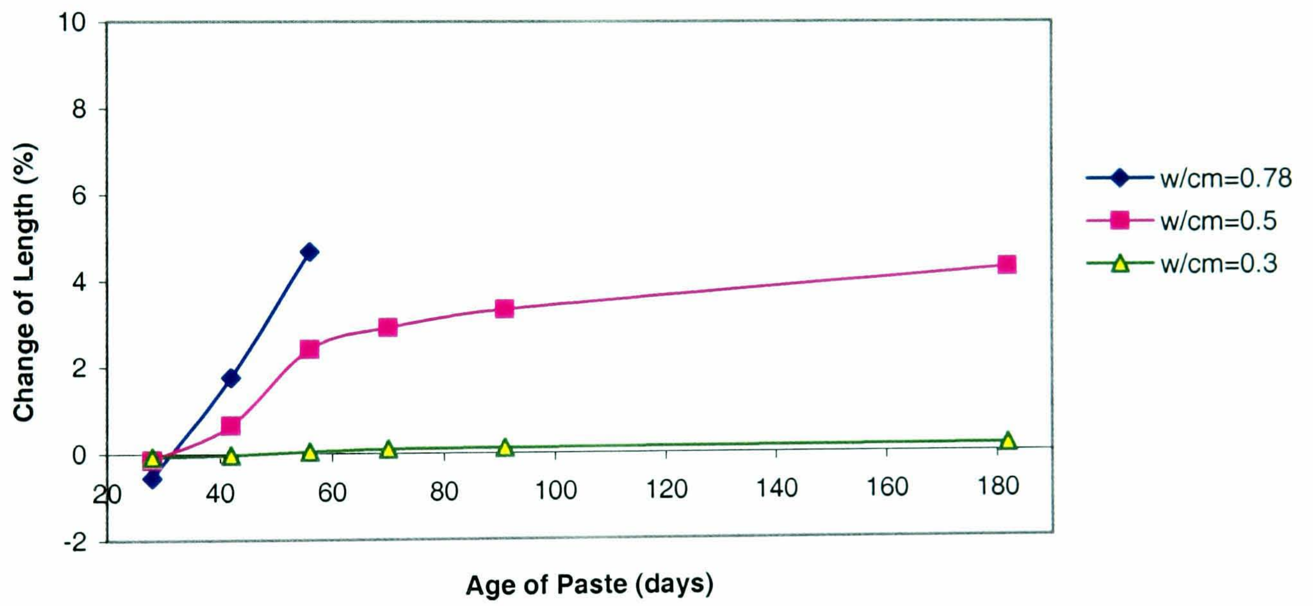


Fig. 5.23.b: 22.5% Anhydrite

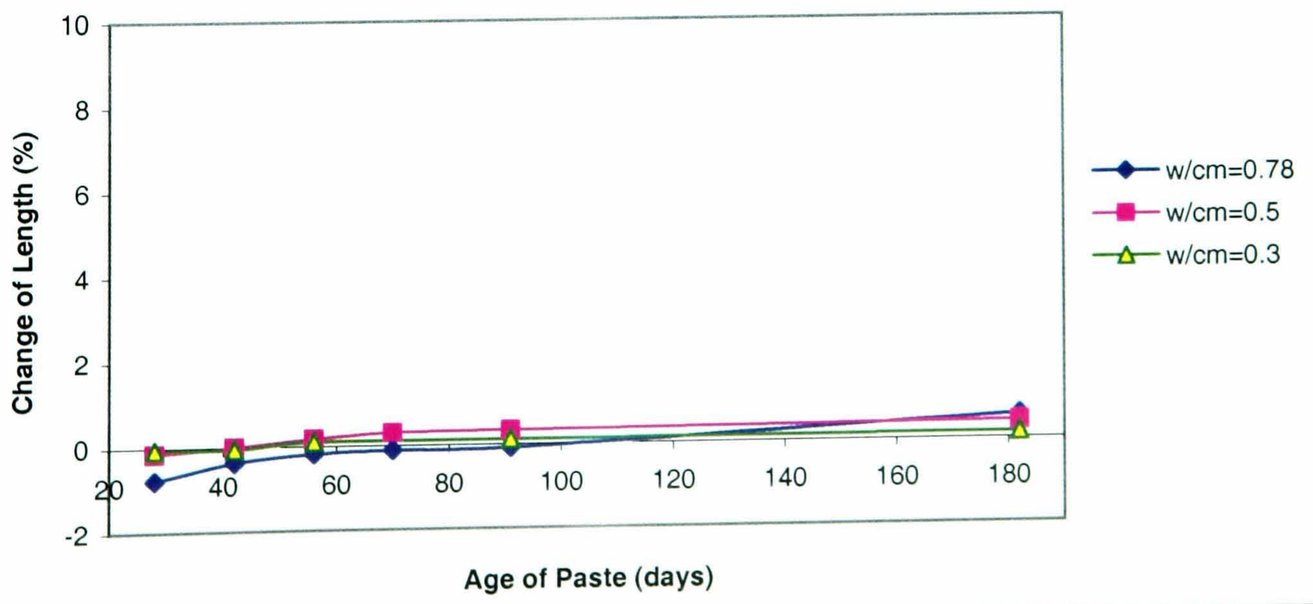


Fig. 5.23.c: 15% Anhydrite

Fig. 5.24: Weight Change Development of CSA Paste Immersed in CaSO4 Solution

Fig. 5.24.a: 31% Anhydrite Content

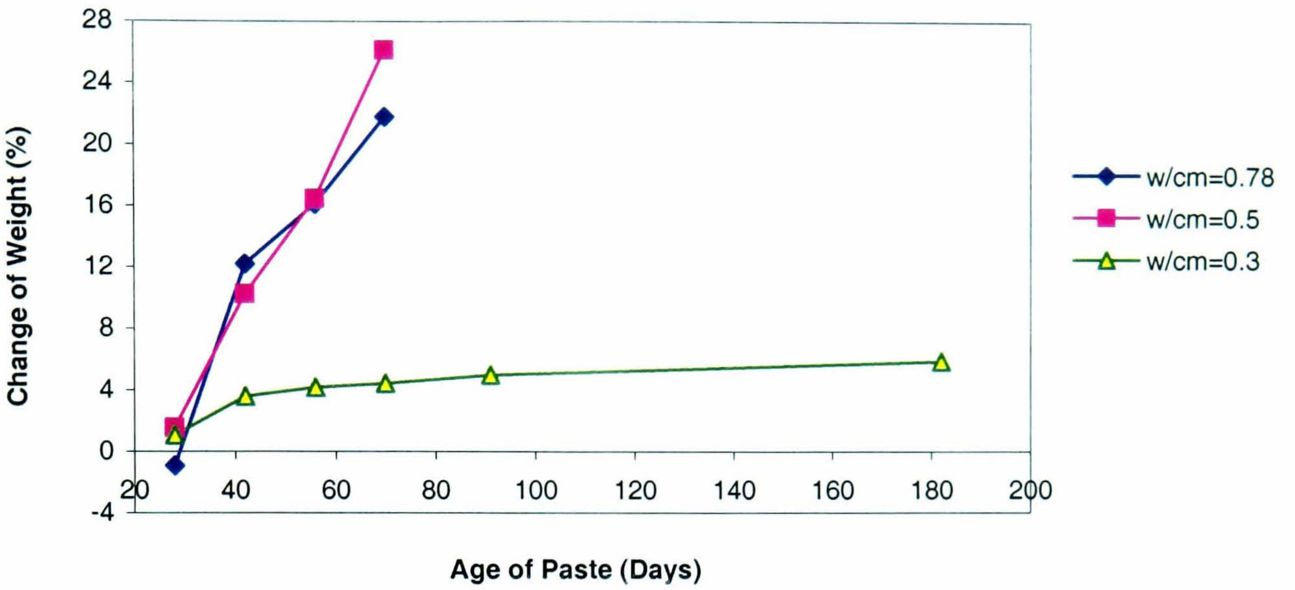


Fig. 5.23.b: 22.5% Anhydrite Content

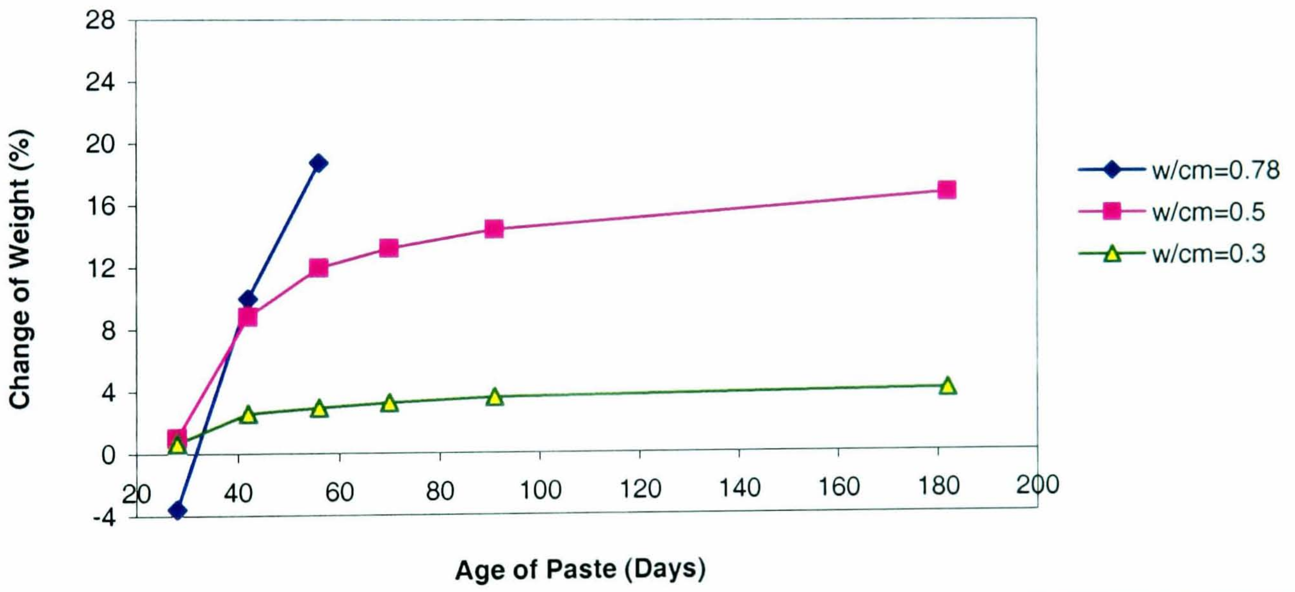


Fig. 5.24.c: 15% Anhydrite Content

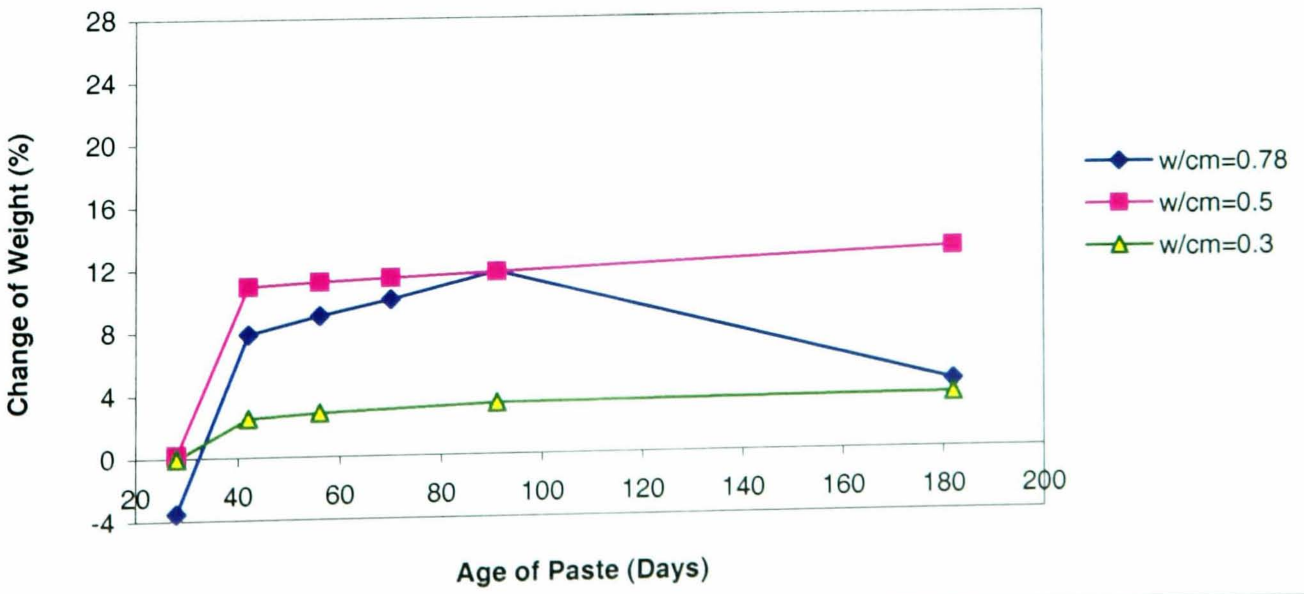


Fig. 5.25: Compressive Strength Development of CSA Paste Cured in Water directly After Demolding

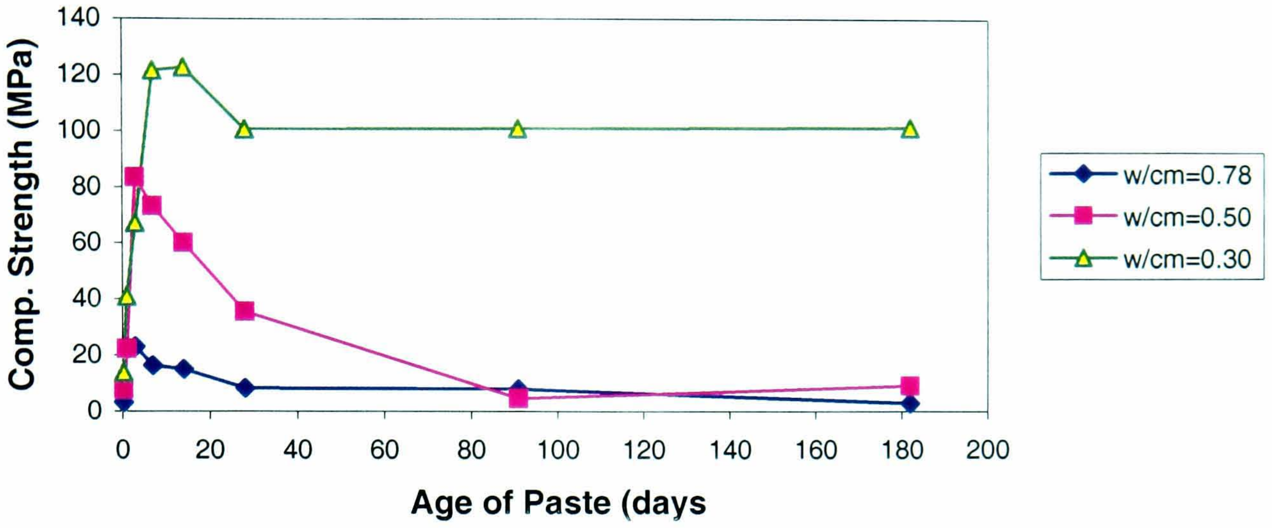


Fig. 5.25.a: 31 % Anhydrite Content

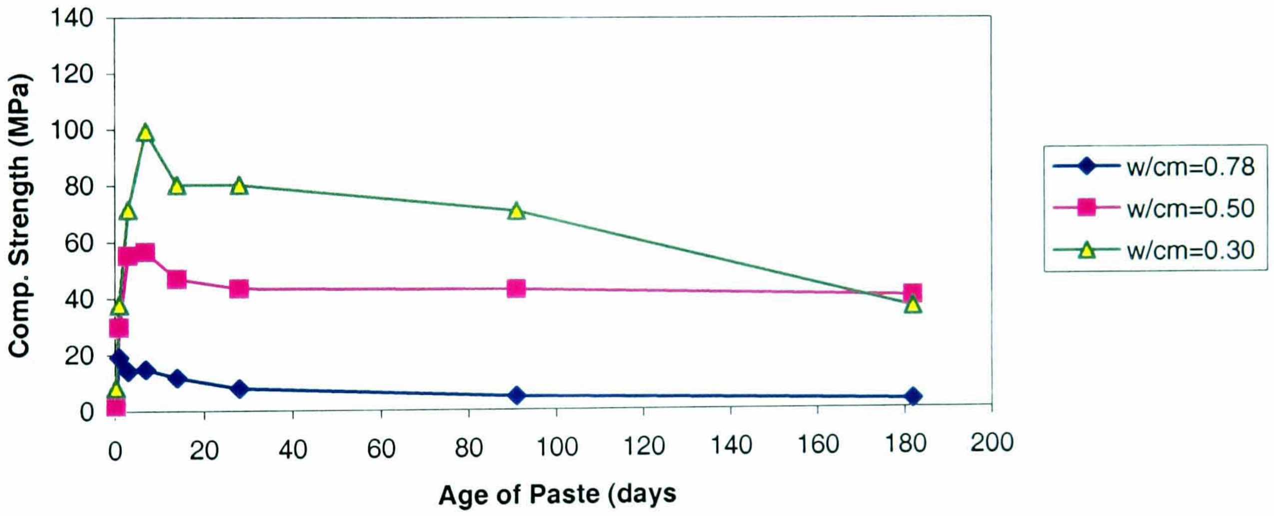


Fig. 5.25.b: 22.5 % Anhydrite Content

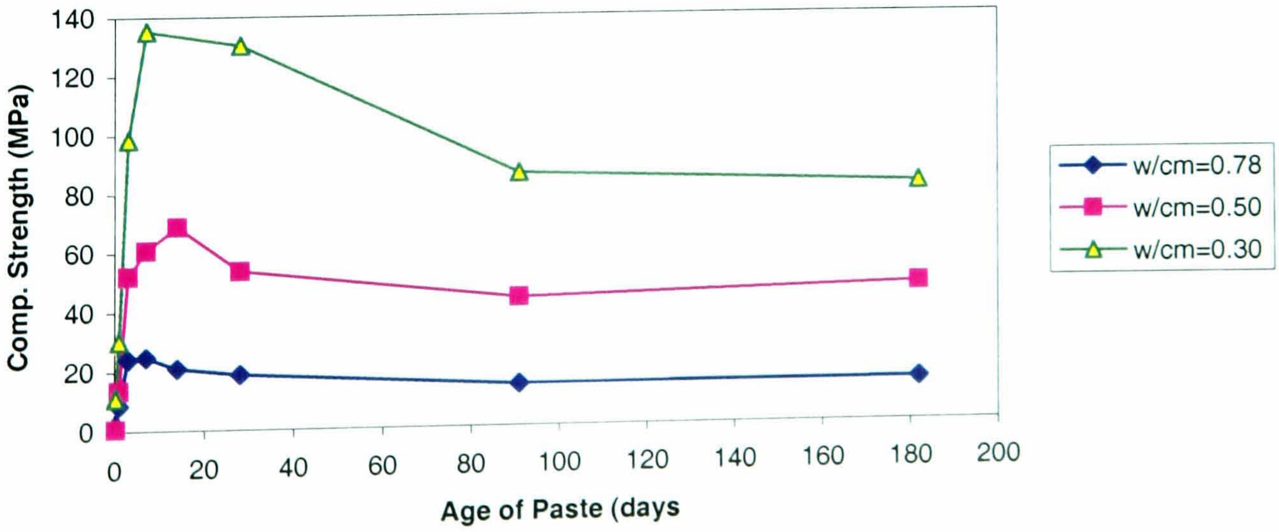


Fig. 5.25.c: 15 % Anhydrite Content

Fig. 5.26: Compressive Strength Development of CSA Paste Sealed and Cured in Room Temperature

Fig. 5.26.a: 31 % Anhydrite Content

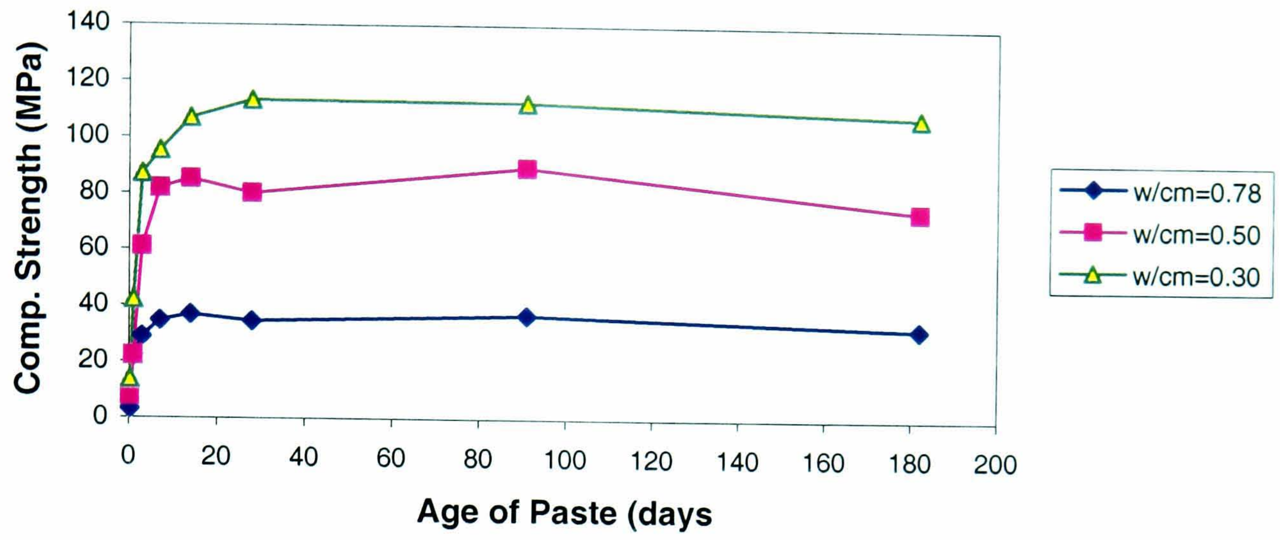


Fig. 5.26.a: 22.5 % Anhydrite Content

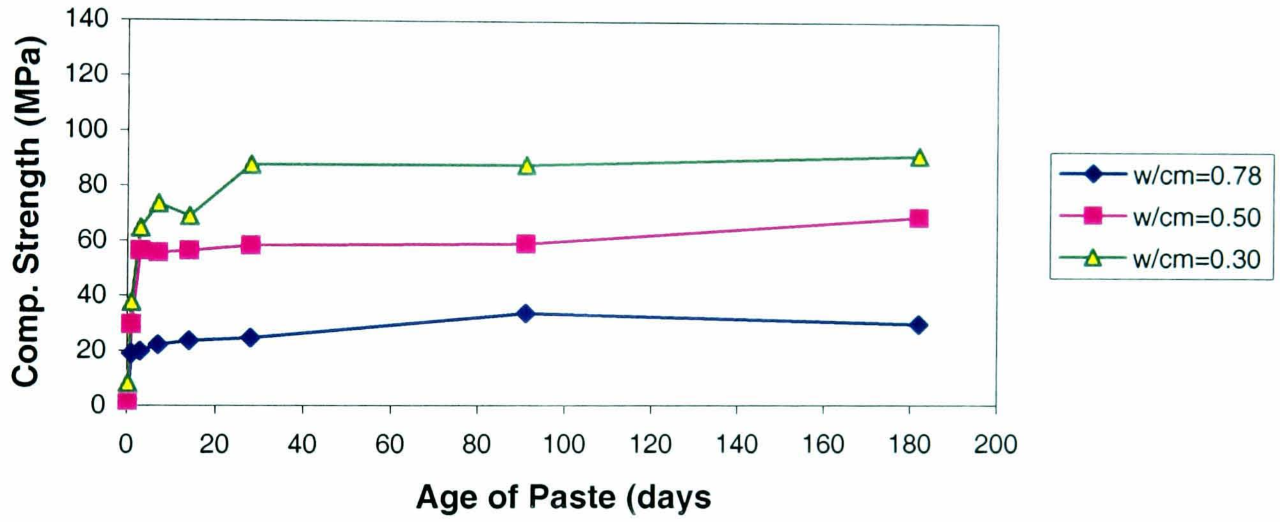


Fig. 5.26.a: 15 % Anhydrite Content

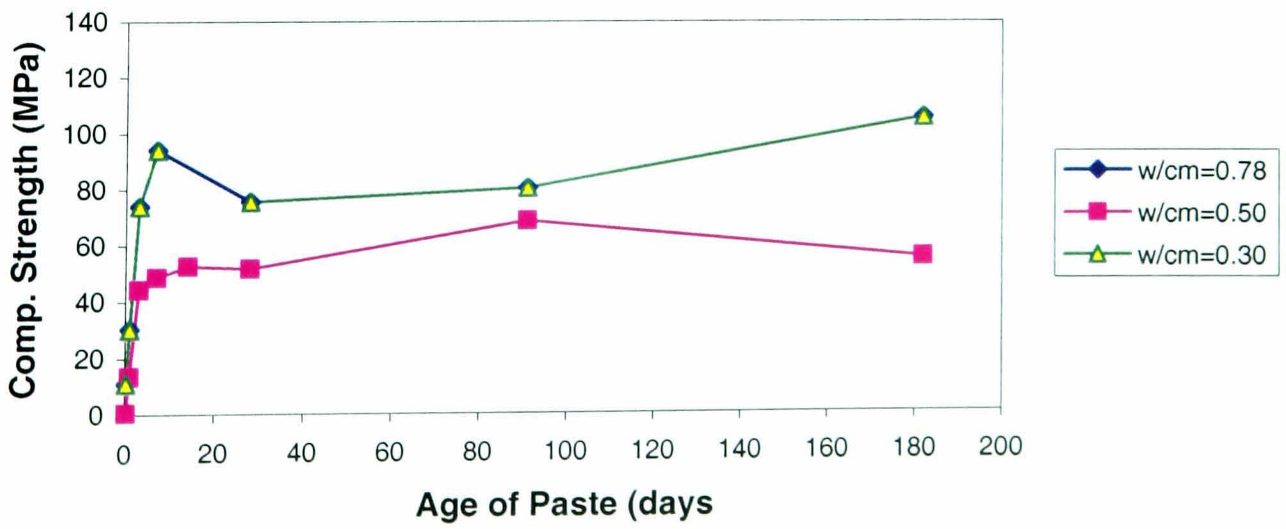


Fig. 5.27: Effect of Water Curing after Sealing for 28 Days on Compressive Strength of CSA Cement Paste

Fig. 5.27.a: 31% Anhydrite

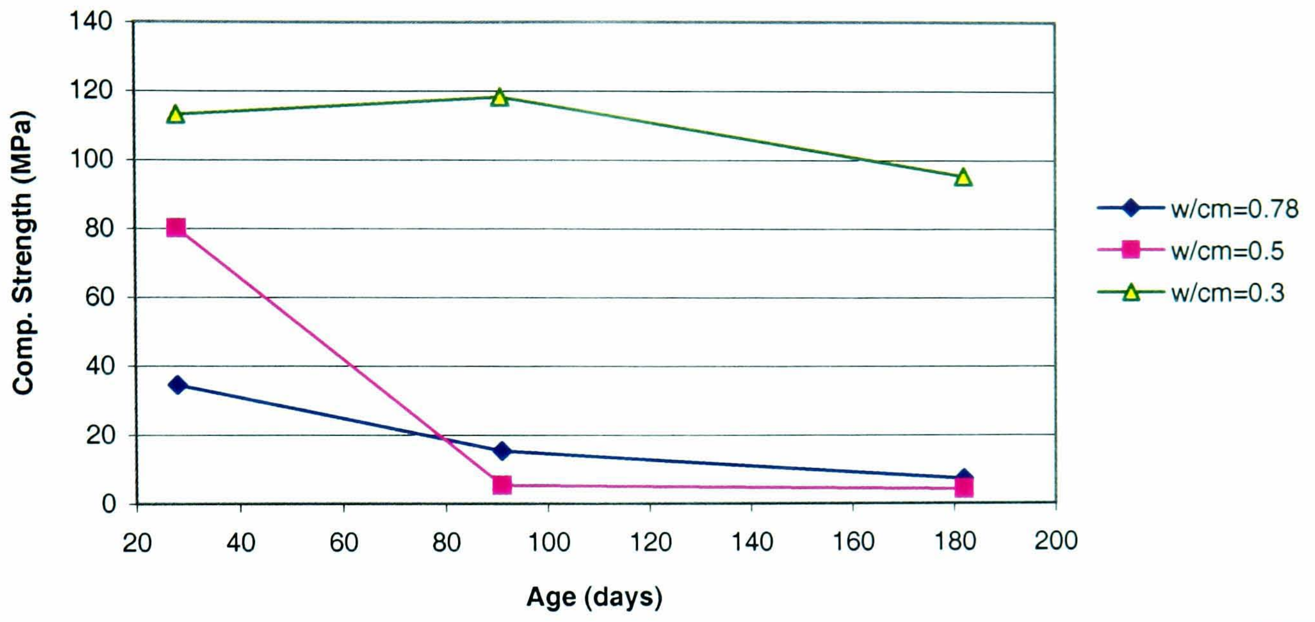


Fig. 5.27.b: 22.5% Anhydrite

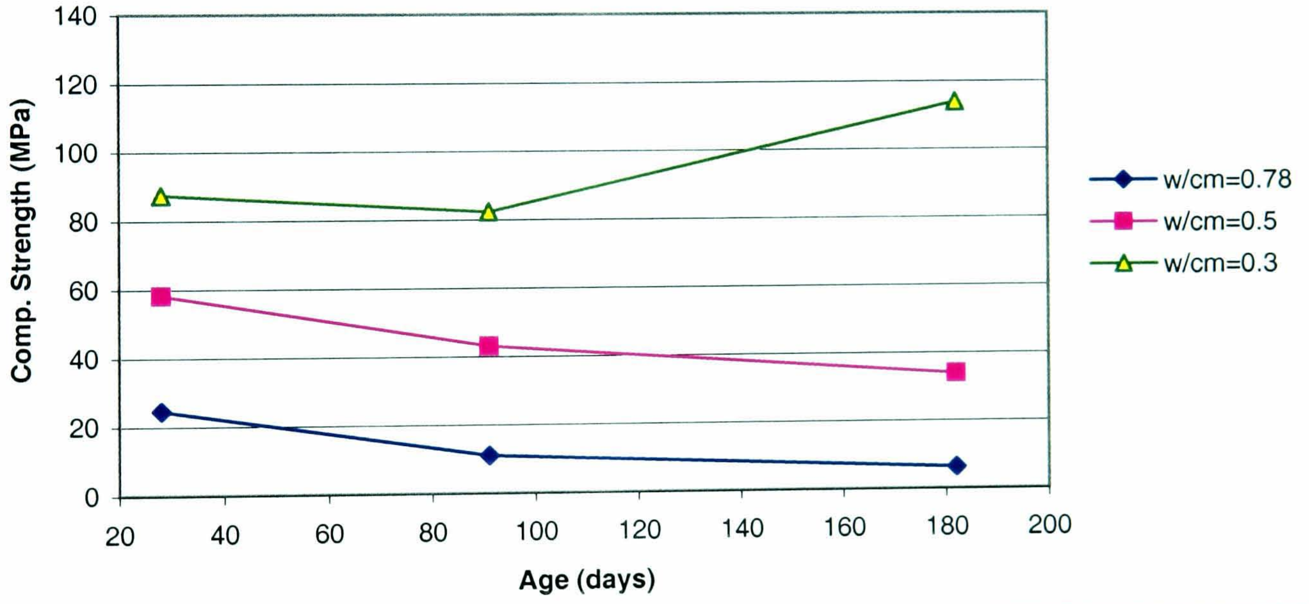


Fig. 5.27.c: 15% Anhydrite

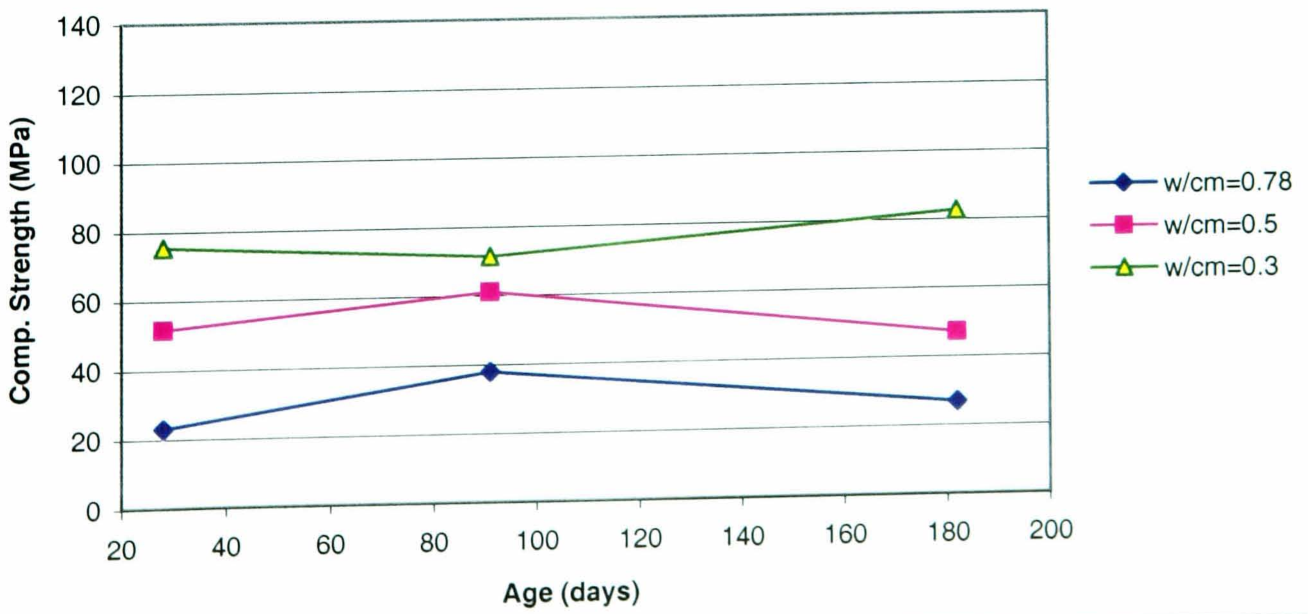


Fig. 5.28: Relationship Between Compressive Strength and w/cm Ratio at Different Anhydrite Content (Water Curing)

Fig. 5.27.a: 3 Days of Paste (Water Curing)

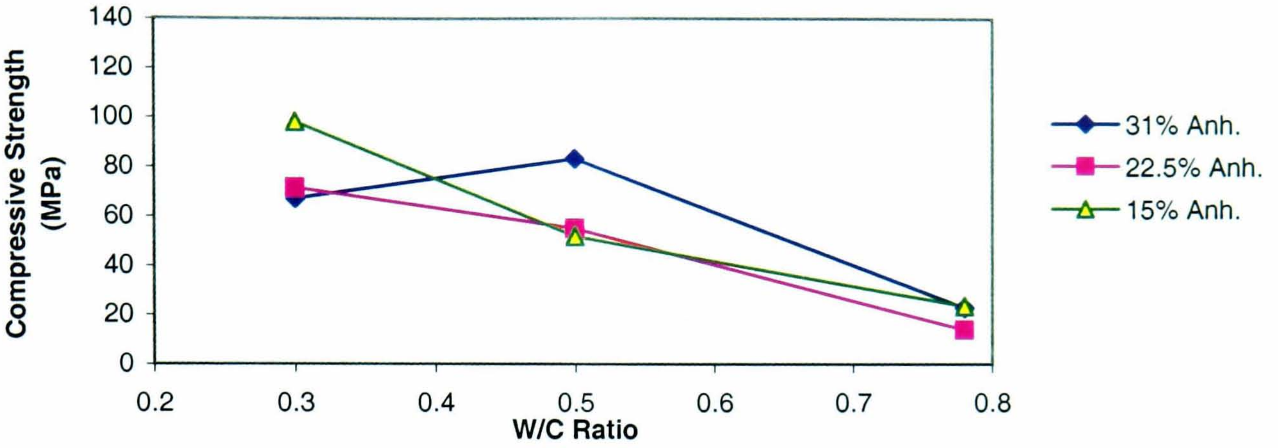


Fig. 5.28.b: 28 Days of Paste (Water Curing)

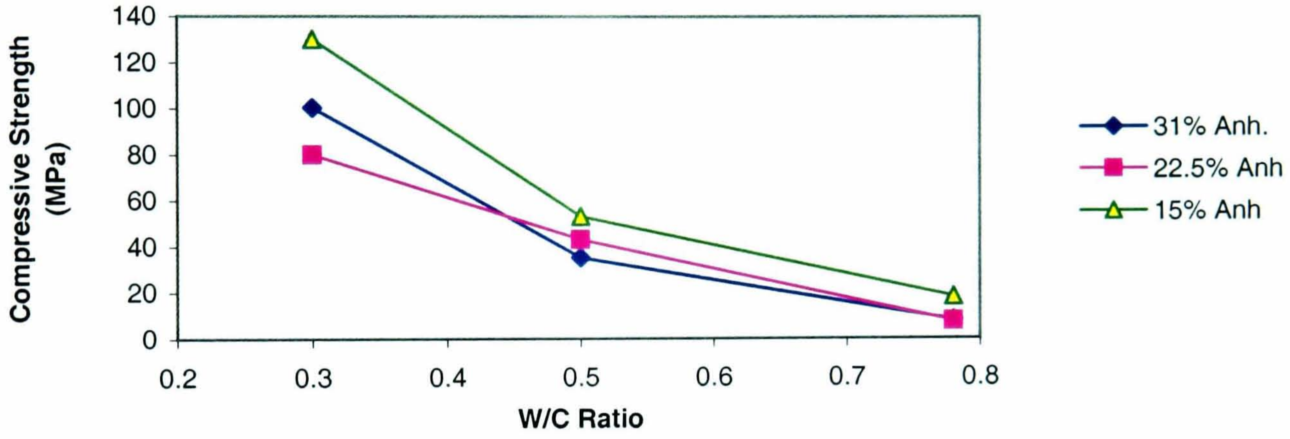


Fig. 5.28.c: 91 Days of Paste (Water Curing)

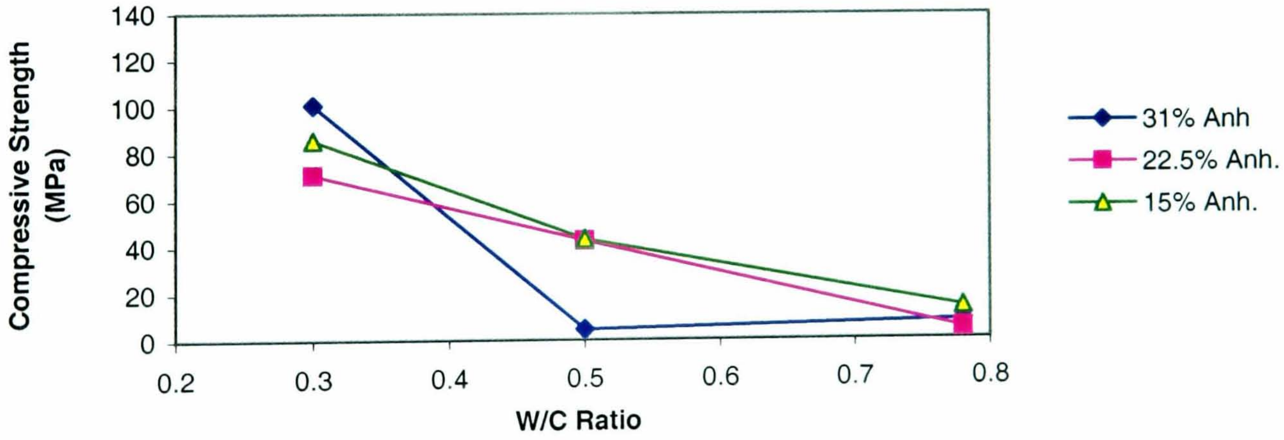


Fig. 5.26.d: 182 Days of Paste (Water Curing)

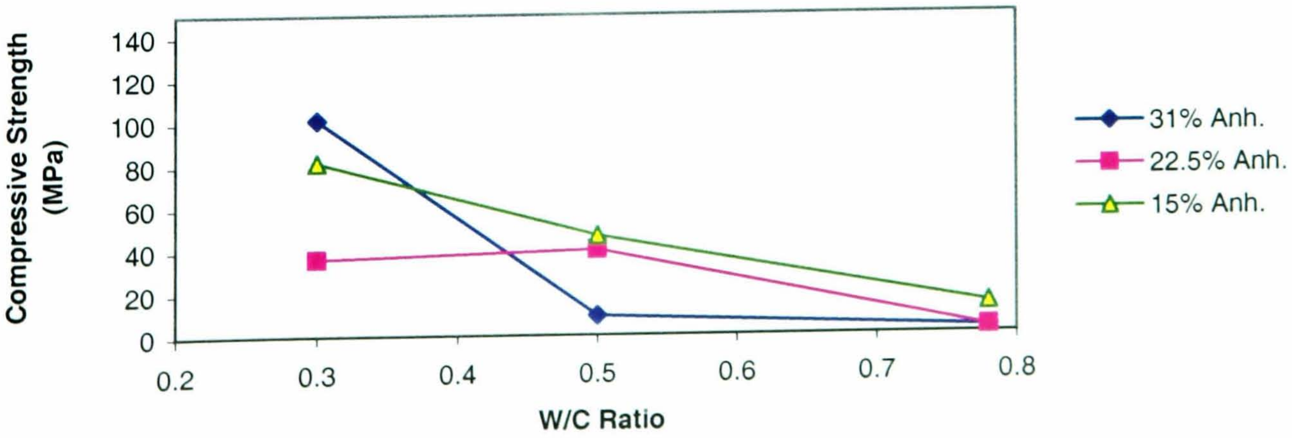


Fig. 5.29: Relationship Between Compressive Strength and w/cm Ratio at Different Anhydrite Content (Sealed Curing)

Fig. 5.29.a: 3 Days of Paste (Sealed Curing)

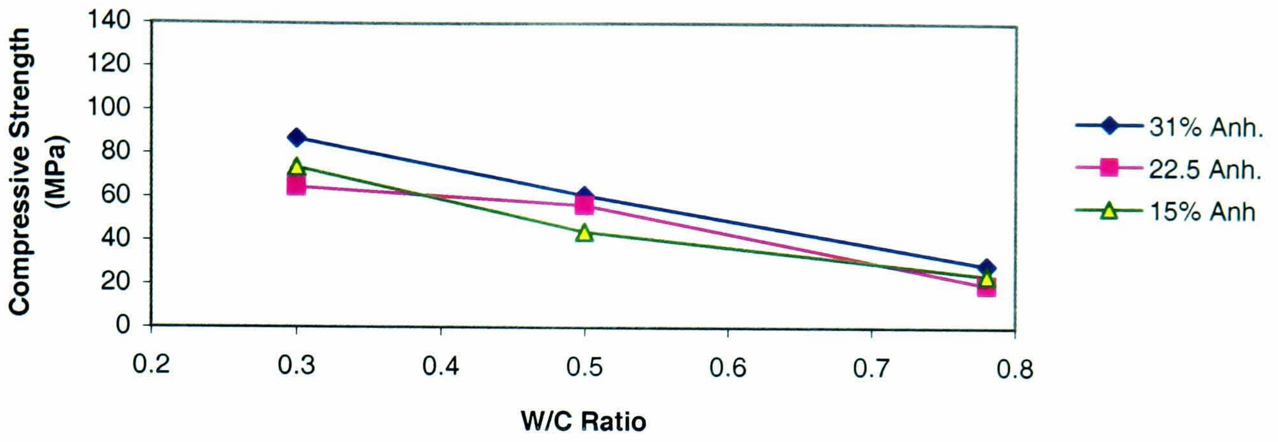


Fig. 5.29.b: 28 Days of Paste (Sealed Curing)

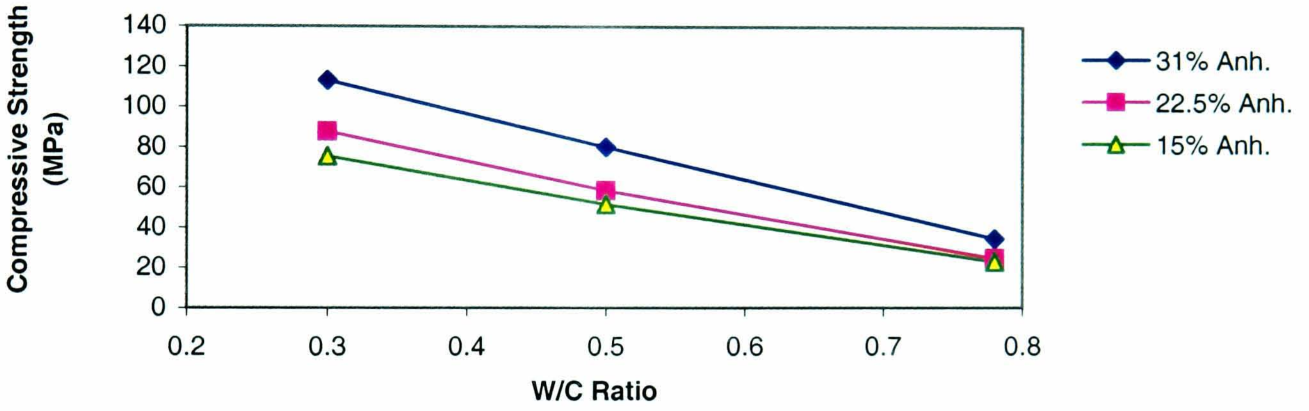


Fig. 5.29.c: 91 Days of Paste (Sealed)

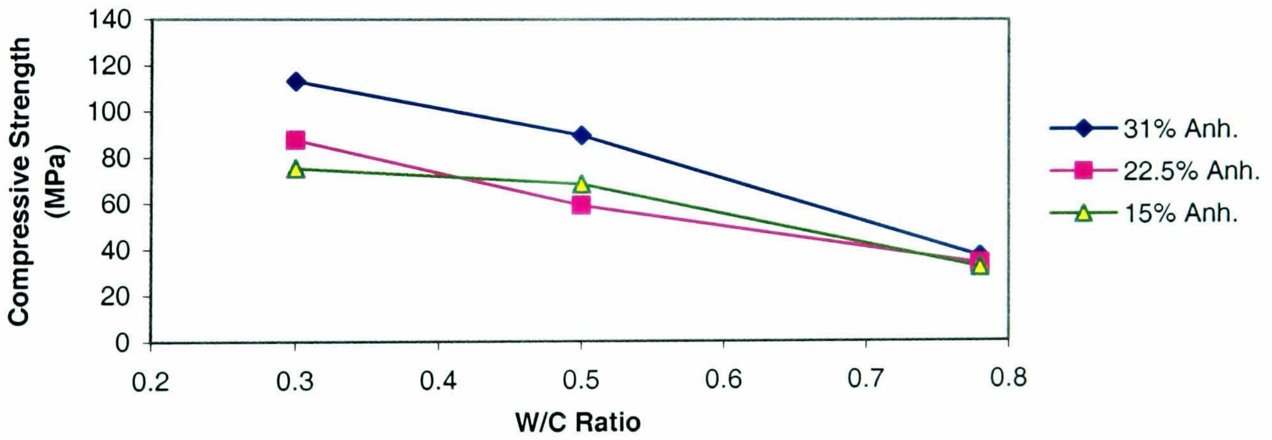


Fig. 5.27.d: 182 Days of Paste (Sealed Curing)

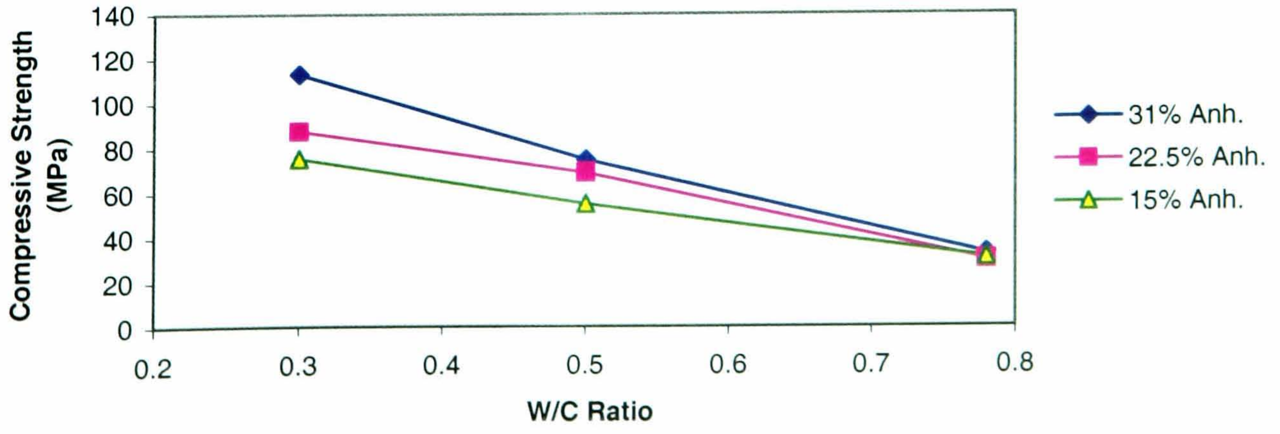


Fig. 5.30: Effect of Immersing in CaSO4 Solution on Compressive Strength of CSA Cement Paste

Fig. 5.30.a: 31% Anhydrite

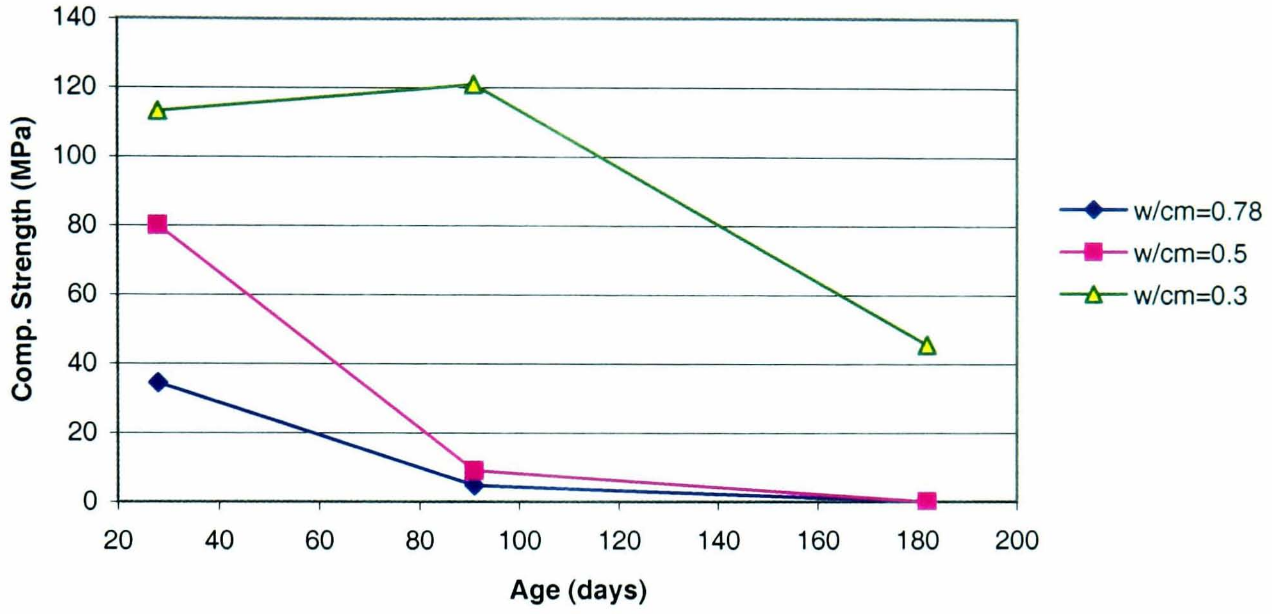


Fig. 5.30.b: 22.5% Anhydrite

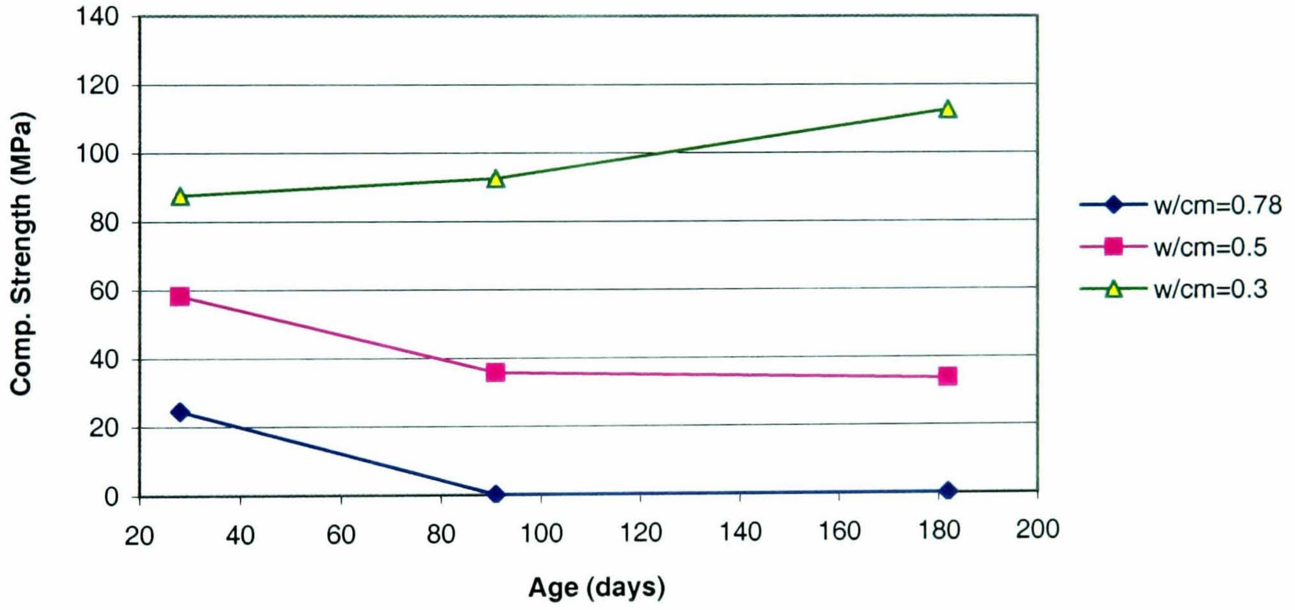
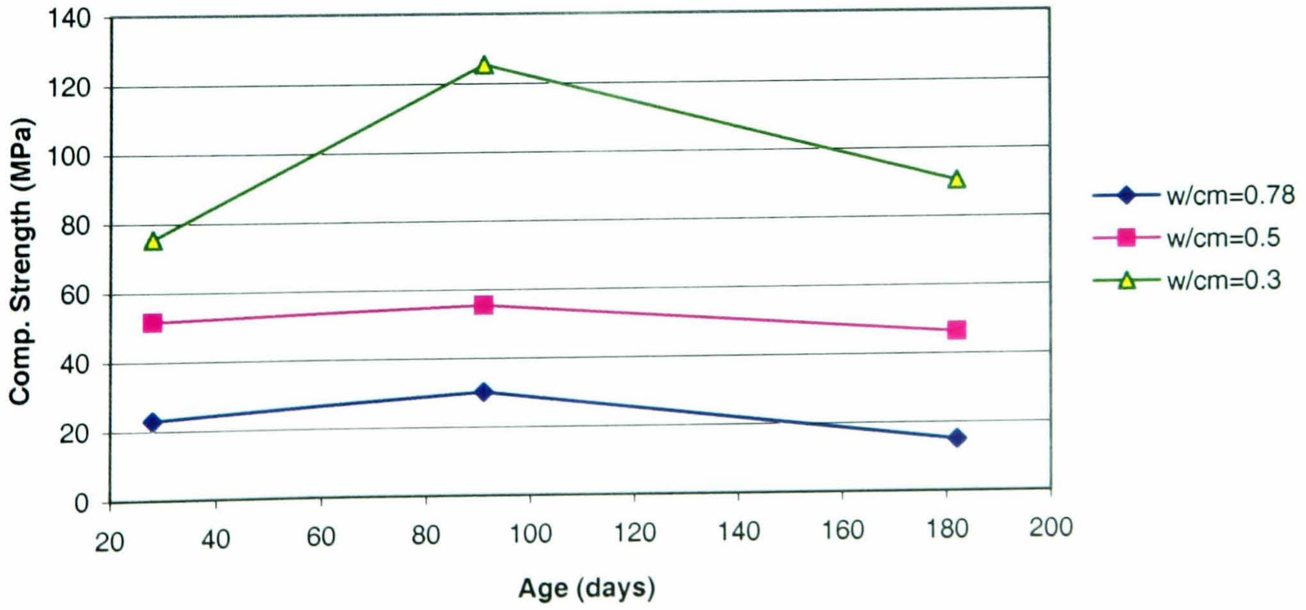


Fig. 5.30.c: 15% Anhydrite



VI

EFFECT OF OPC INCLUSION ON PROPERTIES OF PASTE MADE WITH CSA CEMENT SYNTHESISED IN LABORATORY

6.1 Introduction

The use of CSA based cement in concrete as an OPC replacement has been a common practice in producing expansive concrete or shrinkage compensating concrete. The presence of calcium hydroxide in the CSA and $CaSO_4$ system causes the repulsive action during the formation of ettringite (Taylor, 1997), which is responsible for the expected expansion. The content of CSA and $CaSO_4$ in the cement matrix depends on the expansion required with the OPC still being the main cementitious material.

In this research, instead of producing expansive paste with OPC as a main binder, CSA based cement was developed to be the main binding material. The effect of replacement of CSA based cement by OPC on the properties of the paste will be discussed. Twenty five percent of CSA based cement was replaced with OPC at different $CaSO_4$ contents and at w/c ratio = 0.50. The incorporation of OPC into CSA cement paste is expected to affect the properties of the paste in several ways. The presence of CSH-gel in the system filling the ettringite crystal skeleton may improve the performance of paste. The reaction of CH (as a product of OPC hydration), with CSA and anhydrite may produce further ettringite in the system.

Based on these assumptions, the effect of OPC inclusion on properties of CSA paste was examined. The examination covered the hydration process, stability of the samples and their compressive strength. The discussion is focused on the effect of different anhydrite contents and different curing regimes on the properties of CSA cement paste at w/c=0.50.

In order to build up a better understanding about the effect of the presence of CH on CSA paste, the experimental work was initiated by examining the properties of a mix containing CSA + anhydrite + CH.

6.2 Properties of Paste Made With CSA, Anhydrite and CH at Stoichiometric Composition.

6.2.1 Mix Composition.

The mix composition was based on the stoichiometric composition derived from the following reaction equation:

$$4CaO.3Al_2O_3.SO_3 + 8(CaO.SO_3.) + 6Ca(OH)_2 + 90H_2O = 3(6CaO.Al_2O_3.SO_3.32H_2O)\ldots(6.1)$$

or in cement chemist's notation:

$$C_4A_3\bar{S} + 8C\bar{S} + 6CH + 90H = 3C_6A\bar{S}_3H_{32}$$

From the equation, the composition of the mix was calculated as CSA = 28%, anhydrite=51%, and CH = 21% with w/c=0.76.

The reaction between CSA and anhydrite without addition of CH is given by equation (5.1). From equation (5.1), the composition was CSA = 69% and anhydrite 31% with w/c=0.78, which means that for the same amount of CSA, the presence of CH potentially may produce three times as much ettringite.

6.2.2 Stability of Samples

In contrast with the mix containing CSA and anhydrite only, the mix containing CSA + anhydrite + CH at the stoichiometric composition resulted in a very poor paste. One day after demolding, samples sealed as cast had expanded by up to almost twice the initial volume (see Fig. 6.1). Samples cured in water had completely dissolved only a few moments after their immersion. As a result, the test of length change and weight change on the sample, as a quantitative indicator for volume stability could not be carried out. Reducing the CH content to 5% caused acceleration in the setting time of the paste. The paste had set at a rate such that the casting could not be carried out properly.

6.2.3 Hydration Products

6.2.3.1 XRD Analysis

From the XRD results from the samples sealed as cast for 14 days, it was found that the products of the mix containing CSA + Anhydrite + CH were basically similar to the product of the mix containing CSA + Anhydrite only (See Fig. 6.2). Ettringite was the main product of reaction along with anhydrous particles such as: CSA and anhydrite. The CH peaks, which should exist at the angles of 17.97, 34.05, and 47.07 were not traceable. It seems that the CH particles had significantly reduced during the hydration process while the growth of ettringite as the reaction product overlapped the positions of the CH peaks.

6.2.3.2 SEM

The image produced from SEM (See Fig.6.3) showed that extremely porous crystalline structures were produced by the mix. The pores were believed to have formed as a result of repulsive action during crystals formation because the presence of CH in the system, which then produced the expansion in the paste. This is in accordance with the expansion theory in ettringite formation (Taylor, 1997).

6.2.4 Compressive Strength

As a consequence of the highly porous samples produced by the mix, a very low compressive strength resulted. At 14 days, the samples sealed as cast only produced a compressive strength as low as 2.50 MPa.

6.3 The effect of OPC Incorporation on Properties of CSA Paste

6.3.1 Mix Composition

Throughout the experimental work, 25% of OPC replacement was applied to the mixes. The content of 20%, 30% and 40% anhydrite was used. The use of 40% anhydrite was aimed at observing the effect of an excessive anhydrite content in the mix. As shown in the equation (6.1), the presence of CH required more anhydrite in the mix. In this case, CH was expected to be provided by the hydration of OPC.

6.3.2 Hydration Products

6.3.2.1 XRD Test

From XRD analysis (Fig. 6.4), it is difficult to distinguish between the reaction products of CSA paste with and without OPC. Ettringite and Klein's compound were the crystalline phases identified. Anhydrite and CH peaks were overlapped by the peaks due to ettringite. The XRD could not monitor the phase of CSH-gel phase because it is amorphous.

6.3.2.2 SEM

The SEM images of the CSA mix containing 25% OPC and 30% anhydrite are given in Fig. 6.5. The micrographs were obtained from samples after 6 months curing in water. A compact crystalline ettringite was seen among the CSH gel phase. In the pore area, where sufficient space was available, the long needlelike crystals of ettringite appeared.

6.4 Expansion of CSA Paste Containing OPC

6.4.1 General

As shown in the previous Chapter, a reduction in the anhydrite content in the CSA mix could reduce the expansion of CSA paste. The anhydrous particles would act as a constraint in the system. Replacing 25% of CSA and anhydrite with OPC was expected to reduce the expansion with the presence of CSH-gel as a constraint. On the other hand, the presence of CH as a second product of C_3S hydration was suspected to enhance the expansion when ettringite formed.

The two contradictory factors were assumed to dictate the expansion characteristics of CSA paste containing OPC in respect to different anhydrite contents and different curing conditions. Three curing conditions were applied to the samples. These were water curing, sealed after demolding, and water curing after sealing for 28 days.

6.4.2 Length Change Development of CSA Paste Containing OPC

6.4.2.1 Samples Sealed Directly After Demolding

Length development of CSA paste containing OPC at different anhydrite contents and at w/c ratio = 0.50 for samples sealed directly after demolding are given in Fig. 6.6.a. Similar to the CSA paste without OPC, CSA paste with OPC sealed after demolding experienced a small contraction relative to the content of anhydrite. The contraction of paste was higher with reduction in anhydrite content. The major part of the contraction occurred at early ages of paste hydration and the development continued slowly beyond 3 days.

The expansion as shown by the mix according to equation (6.1) was not the case even in the mix containing 40% of anhydrite. Inadequate availability of water in the mix was probably responsible for reducing the expansion in the paste. As w/c=0.50 was far below the required water to hydrate the particles, the initial formation of ettringite followed the equation (5.1). The CH as second product of OPC hydration could not react with the anhydrous CSA and anhydrite because there was not sufficient water available in the mix.

Overall, the contraction of CSA paste containing 25% OPC was lower than that produced by CSA without OPC at the same w/c ratio.

6.4.2.2 Samples Continuously Cured in Water Directly After Demolding

Length change development of samples cured in water is presented in Fig. 6.6.b. The expansion of paste containing 40% of anhydrite could not be monitored because the samples were badly damaged due to excessive expansion just after one day of immersion. With the intrusion of the curing water into the system, a considerable amount of the anhydrous anhydrite reacted with the anhydrous CSA and CH produced by OPC hydration to form ettringite in accordance with equation (6.1). The reaction caused HIGH expansion, which led to the expansion induced cracks. These cracks accelerated further expansion up to and beyond the limit that the length change equipment could measure.

Lowering the anhydrite content to 30% drastically reduced the expansion of the samples. Lack of availability of anhydrous anhydrite led the reaction mostly to follow the reaction equation (5.1), as the formation of ettringite from equation (6.1) demanded a high amount of anhydrite. The expansion was mainly caused by the water absorption of the ettringite formed. The presence of CSH-gel and reduction of particles with the potential to form ettringite reduced the expansion, which was much lower than the mix without OPC containing 31% anhydrite at the same level w/c ratio. In the mix without OPC containing 31% anhydrite, the expansion after 21 days reached 6% and after that the samples were badly damaged, whereas the mix containing 25% OPC and 30% anhydrite produced only around 1% expansion after 28 days. The encouraging factor was that the expansion stopped increasing after the samples were cured up to 91 days. It shows that the presence of 25% OPC in the system gives more volume stability to the samples.

The use of 20% anhydrite in the mix with 25% OPC caused even lower expansion in the samples. Only 0.2% expansion after 91 days was monitored. It is much less than the expansion of CSA without OPC containing 15% anhydrite at the same level of w/c ratio where the expansion at the same age was around 0.6%.

6.4.2.3 Samples Cured in Water After Sealing for 28 Days

The expansion of samples immersed in water after being sealed for 28 days is given in Fig. 6.6.c. Twenty-eight days of seal curing developed higher strengths in the samples due to further formation of CSH gel and ettringite. Immersion of these samples into the water at this stage significantly reduced the expansion. However, in samples with an anhydrite content of 40%, the expansion still produced adequate stress that led to open cracks in the samples and then created further expansion. An expansion as high as 2.6% resulted at the first reading, when the paste was immersed after 28 days. This amount should have been reached at the earlier days of immersion, as the expansion seemed to be dominated by formation of ettringite through equation (6.1). This value was still much lower than the expansion of CSA paste without OPC containing 31% anhydrite at the same w/c ratio, where the expansion was around 8% after 28 days of immersion. The further increase of length change up to 91 days was relatively insignificant.

The reduction in the length change was more pronounced in samples containing 30% and 20% anhydrite. The length change was as low as 0.1% for samples containing 20% anhydrite and around 0.6% for samples containing 30% anhydrite, which shows that the replacement of CSA and anhydrite with 25% OPC successfully controlled the expansion of paste made with CSA based cement. Furthermore, these results demonstrate that to avoid excessive expansion in CSA-OPC composite cement, it is necessary to avoid high levels of anhydrite as seemingly required by the stoichiometry of the reaction.

6.4.3 Weight Change Development of CSA Paste

6.4.3.1 Samples Sealed Directly After Demolding

The weight change development of samples sealed directly after demolding was shown in Fig. 6.7.a. Based on the fact that the change of weight in samples was mainly due to the movement of pore water in the system, the change of weight in samples sealed directly after demolding was extremely influenced by the quality of sealing and the absorption characteristic of samples against ambient humidity during the testing period. As the weight change test was carried out after the length change test, where the samples were exposed to ambient conditions, it is thought that some of the pore water of samples evaporated into air. All samples experienced loss of weight after 3 days of sealing. At this stage the evaporation of pore water to the surface was higher than the water used for continuation of hydration. The elevation of temperature during early hydration enhanced the evaporation.

Beyond 3 days, samples containing 30% and 40% anhydrite gradually gained weight. The weight gain reached 0.3% after being sealed for 28 days. Relatively high amounts of initial ettringite formation could retain pore water in the system, while absorption of water took place when the samples were exposed to ambient conditions during testing was carried out. On the other hand, less ettringite formation in the samples containing 20% of anhydrite caused evaporation of pore water, so that and the loss of weight was therefore the case for the samples containing 20% anhydrite. The loss of weight reached 1.9% after 28 days.

The amount of initial ettringite formation was an important factor influencing weight change in samples sealed directly after demolding. Replacing 25% of the particles contributing to ettringite formation with OPC significantly reduced the amount of initial ettringite formation. After 28 days, the gain in weight of samples with OPC containing 30% and 40% anhydrite was less than the gain of weight in samples without OPC containing 31% anhydrite at the same level of w/c ratio. Even samples without OPC containing 15% anhydrite at w/c ratio = 0.50 still gained weight at 28 days, while samples with 25% OPC containing 20% anhydrite underwent loss of weight (see Fig. 5.20 & Fig 6.7a).

6.4.3.2 Samples Cured in Water Directly After Demolding

The development of the length change of samples immersed directly after demolding is given in Fig. 6.7.b. Samples containing 40% anhydrite underwent excessive expansion induced cracks after only one day of curing in water. The samples, therefore, could not be tested. The gain in weight in samples containing 20% and 30% anhydrite mainly took place in the first 3 days. For samples containing 20% anhydrite, the gain in weight more or less stopped after 3 days, while for samples containing 30% anhydrite the process continued at a slower rate until 7 days of curing.

Considering that samples containing 30% anhydrite gained more weight than samples containing 20% anhydrite, it shows that the samples possessing higher ettringite were more absorptive. The replacement of 25% of particles contributing to ettringite formation with OPC reduced the gain of weight up to half of the gain of weight of samples without OPC and increased the stability of samples as shown by stopping the gain of weight after 7 days of curing (see: Fig. 5.21 and Fig. 6.7.b).

6.4.3.3 Samples Cured in Water After 28 Days of Sealing

The subsequent length development of samples cured in water after 28 days of sealing is given in Fig. 6.7.c. Enough strength developed in the samples during the sealing period to reduce the intensity of cracks in samples containing 40% anhydrite. The length change and then the weight change investigations therefore could be carried out. After 28 days of sealing, the samples showed the highest gain in weight compared to the samples containing 20% and 30% of anhydrite. The two latter samples produced lower gain in weight than the samples directly cured in water after demolding (See Fig. 6.7.b & 6.7.c).

As a consequence of reducing the expansion due to initial seal curing for 28 days, the samples with 25% OPC produced a lower gain in weight than the samples without OPC. The weight gains of samples containing 25% OPC were between 6% and 12%.

6.4.4 Effect of Immersion in $CaSO_4$ Solution

The investigation of the length change and weight change development of samples immersed in a saturated solution of $CaSO_4$ is presented in Fig. 6.8.a and 6.8.b, respectively. Immersing samples in a saturated solution of $CaSO_4$ did not give a significant difference compared to the samples cured in water (see Fig 6.6.c, 6.7c, 6.8.a and 6.8.b). Either change of length or change of weight produced almost similar results. Only samples containing 40% anhydrite produced a slightly higher change of length and change of weight than the samples at the same anhydrite content cured in water. This is because the sulfate solution, which had penetrated through the open cracks into the system, had also increased the formation of ettringite.

6.5 Compressive Strength of CSA Cement Paste Containing OPC

6.5.1 General

Besides the strength of interlocking ettringite crystals, the strength of bonding between the crystals and the crystal/void ratio in samples, the compressive strength of CSA cement paste containing OPC was also influenced by the interaction of ettringite and CSH - gel. The effect of inclusion of 25% OPC as replacement for CSA cement and anhydrite is discussed in the following sections.

6.5.2 Compressive Strength of Samples Cured in Water Directly After Demolding

The compressive strength of samples containing 40% anhydrite could not be monitored because the samples had excessively expanded after the first day of immersion (See Fig. 6.9). The testing results of compressive strength development of samples containing 20% and 30% anhydrite are given in Fig. 6.9.a. Similar to the pastes without OPC, the compressive strength of CSA paste with OPC also mainly developed at early ages of curing. The compressive strength produced by samples containing 30% anhydrite was distinctively higher than that produced by samples containing only 20% anhydrite. More ettringite could be formed at higher anhydrite contents and this was responsible for the higher strength produced. After 180 days, the samples with 20% anhydrite had reached a compressive strength in excess of 50 MPa, whereas that with 30% anhydrite was in excess of 60 MPa.

Apparently, the compressive strength of CSA paste without OPC containing 31 and 22.5% anhydrite at the same w/c ratio was slightly higher than the compressive strength of CSA paste with OPC (Fig. 5.25.a, 5.25.b & 6.10a). This is an indication that the ettringite based paste possesses a higher strength than the OPC based paste. Whereas the compressive strength of CSA paste without OPC containing 31% anhydrite drastically reduced with time of curing (related to open crack formation) and the compressive strength of CSA paste without OPC containing 22.5% anhydrite was constant at the later ages, the compressive strength of paste with OPC continuously increased with time at a slow rate. The continuation of C_3S hydration and later C_2S hydration made it possible to develop the compressive strength of the paste at the later ages.

6.5.3 Compressive Strength of Samples Sealed Directly after Demolding

The compressive strength of samples sealed as cast after demolding is given in Fig. 6.9.b. Because the samples could be maintained intact throughout the curing period in this curing condition, the three different anhydrite contents of the samples could be well monitored. The amount of ettringite in the samples was a dominant factor in contributing to the compressive strength. Samples containing 30% and 40% anhydrite produced almost the same compressive strength with the ultimate compressive strength around 80 MPa at 91 days of curing, while samples containing 20% anhydrite only reached half of that amount. All three samples continued to gain strength slowly between 91 and 180 days, presumably due to the continuing hydration of alite and belite on the OPC.

Interestingly, the ultimate compressive strength of the samples containing 30% of anhydrite in this curing condition was higher than that cured in water. It seems that the samples cured in water, to some extent, underwent the formation of micro-cracks when the expansion took place that influenced the development of the compressive strength (see Fig. 6.9. a and Fig. 6.9.b).

On the other hand, the compressive strength of the samples containing 20% anhydrite and sealed as cast was almost the same as that cured in water. More controllable expansion due to reduced ettringite formation in the system led to greater stability in samples in terms of compressive strength.

6.5.4 Compressive Strength of Samples Cured in Water After Sealing for 28 Days

The compressive strength of samples cured in water after sealing for 28 days is presented in Fig. 6.9.c. Except for samples containing 40% anhydrite where the strength reduced drastically due to the expansion induced cracks, the samples containing 20% and 30% anhydrite largely retained their strength after 63 days of immersion in water. The samples containing 20% anhydrite even constantly developed the compressive strength after 63 days of immersion in water.

Compared to the samples without OPC containing 31% and 22.5% anhydrite, where water curing considerably reduced the compressive strength, the presence of OPC in the system clearly gave the advantage in retaining the compressive strength in the long term. As the stability of compressive strength in CSA paste was dictated by the extent of expansion in the samples, the presence of CSA-gel and the anhydrous particles acting as a constraint in controlling expansion contributed to the stability of the compressive strength in CSA paste with OPC.

6.5.5 Effect of Immersing Samples in $CaSO_4$ Solution on Compressive Strength of CSA Paste Containing OPC.

The pattern of the effect of immersing samples in $CaSO_4$ solution on compressive strength of paste was essencially the same as the effect of samples cured in water after 28 days sealed as cast. Samples containing 40% of anhydrite also developed expansion induced cracking leading to a drop in compressive strength after 63 days of immersion. The samples containing 20% and 30% anhydrite developed a very gradual build up in compressive strength.

6.6 Conclusions

1 The presence of CH in the CSA and anhydrite cement system at stoichiometric composition did not change the product of hydration. Ettringite was still the main product. The repulsive action of crystal growth during the formation caused an excessive expansion in the samples, which in turn produced a porous and very weak sample.

2 The incorporation of OPC into the CSA cement and anhydrite system also caused excessive expansion in samples containing 40% anhydrite when cured in water. Sufficient anhydrous anhydrite and CSA available after moulding for 1 day, the presence of CH from OPC hydration and ingress water into the systems enhanced a further reaction to follow equation 1.1 (Chapter1). On the other hand, the samples containing 20% and 30% anhydrite produced more controllable expansion under the same curing conditions. At those levels of anhydrite contents, the reaction mostly followed equation 1.3 (Chapter 1). The reduction of ettringite formation due to OPC replacement and the presence of CSH-gel and anhydrous particles acting as a constraint against the expansion were thought also to be responsible for the reduced expansion in samples containing 20% and 30% anhydrite.

3 As a consequence, the compressive strength of samples containing 40% anhydrite directly cured in water could not be monitored, while the samples cured in water after sealing for 28 days underwent a drop in compressive strength. The samples containing 20% and 30% of anhydrite could maintain their long-term compressive strength.

4 At comparable anhydrite contents, samples incorporating OPC produced a lower compressive strength than that those without OPC. This is an indication that ettringite based cement potentially produces higher strength than OPC.

5 There was no significant effect on either the expansion or the compressive strength due to the immersion of samples in saturated $CaSO_4$ solution.

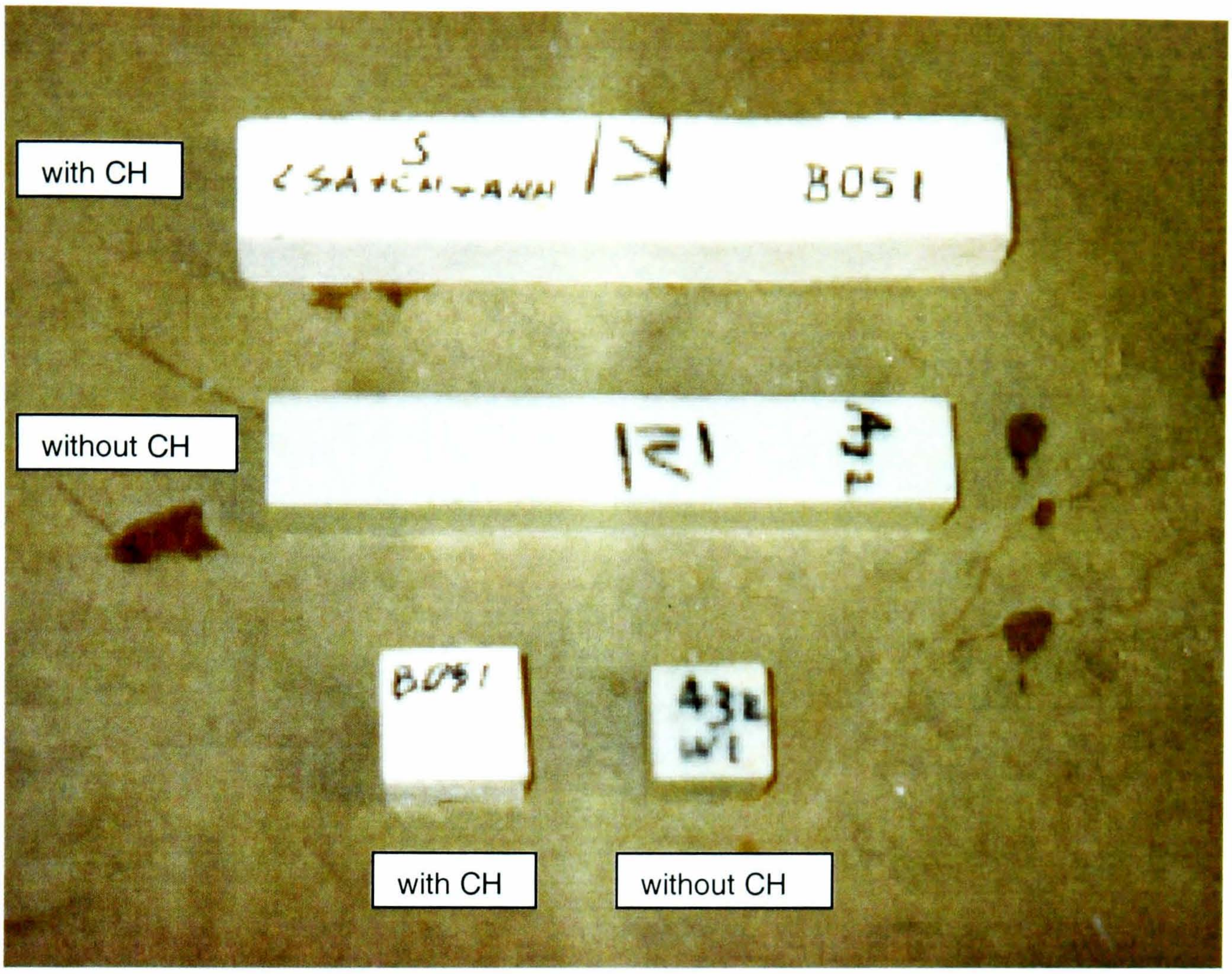


Fig. 6.1: The Comparison between Samples of CSA Mix with CH at Stoichiometric Composition and Mix without CH at 31% anhydrite and w/cm=0.50. All samples were seal cured.

Fig. 6.2: Comparison of XRD Peaks Between CSA Mix without and with CH

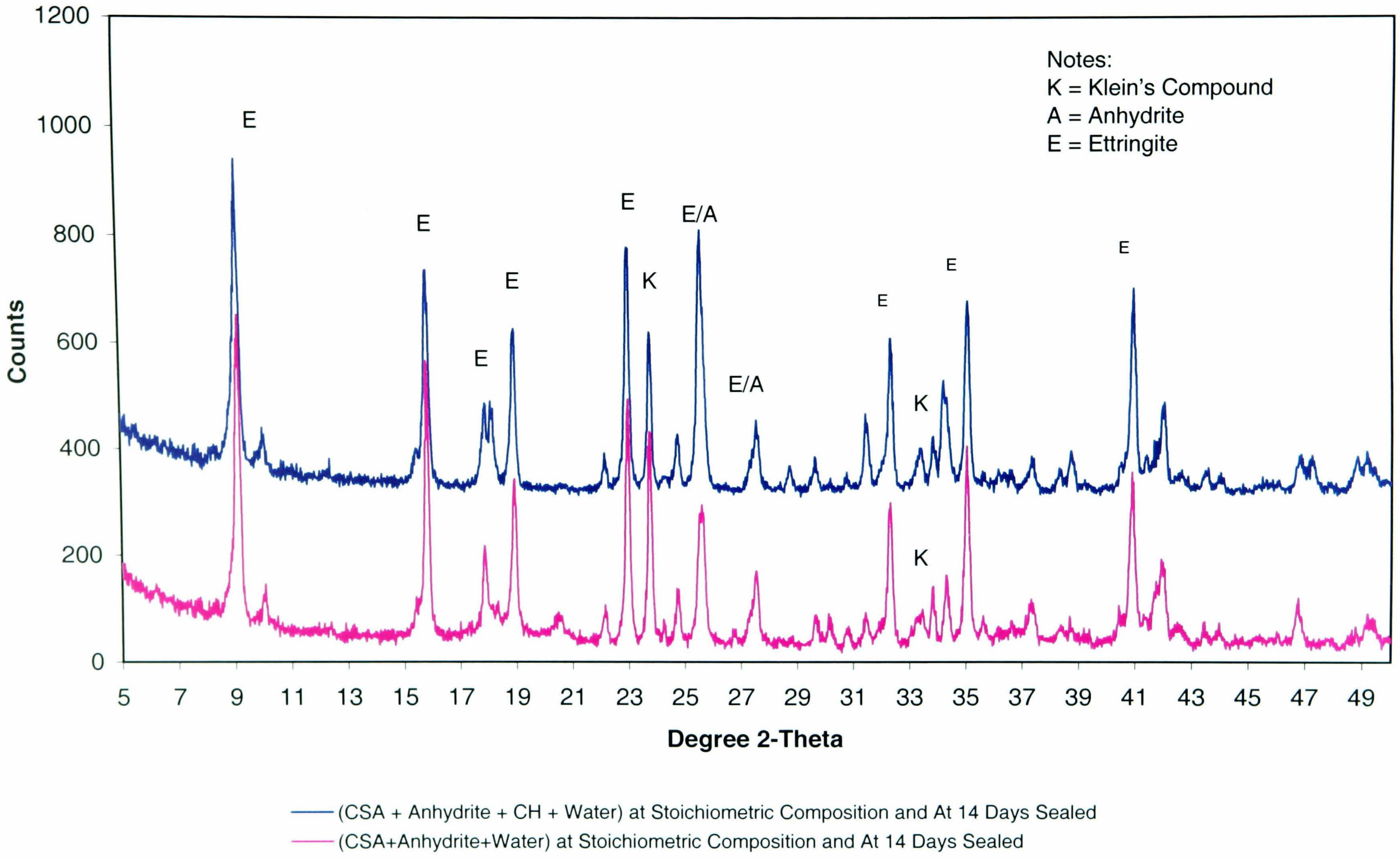


Fig. 6.3: SEM of CSA Mix Containing CH at Stoichiometric Composition (Sealed for 14 Days)

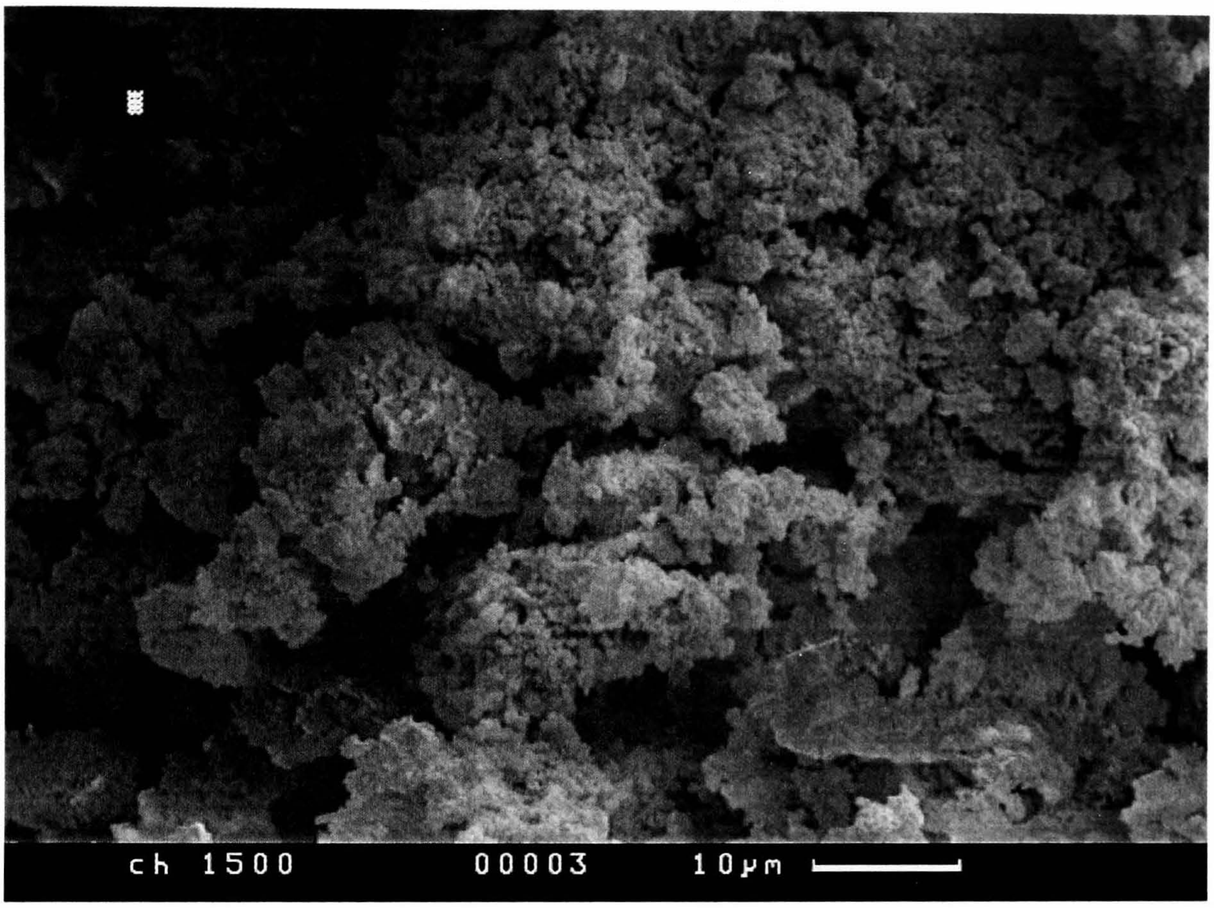


Fig. 6.3.a Magnification of 1500

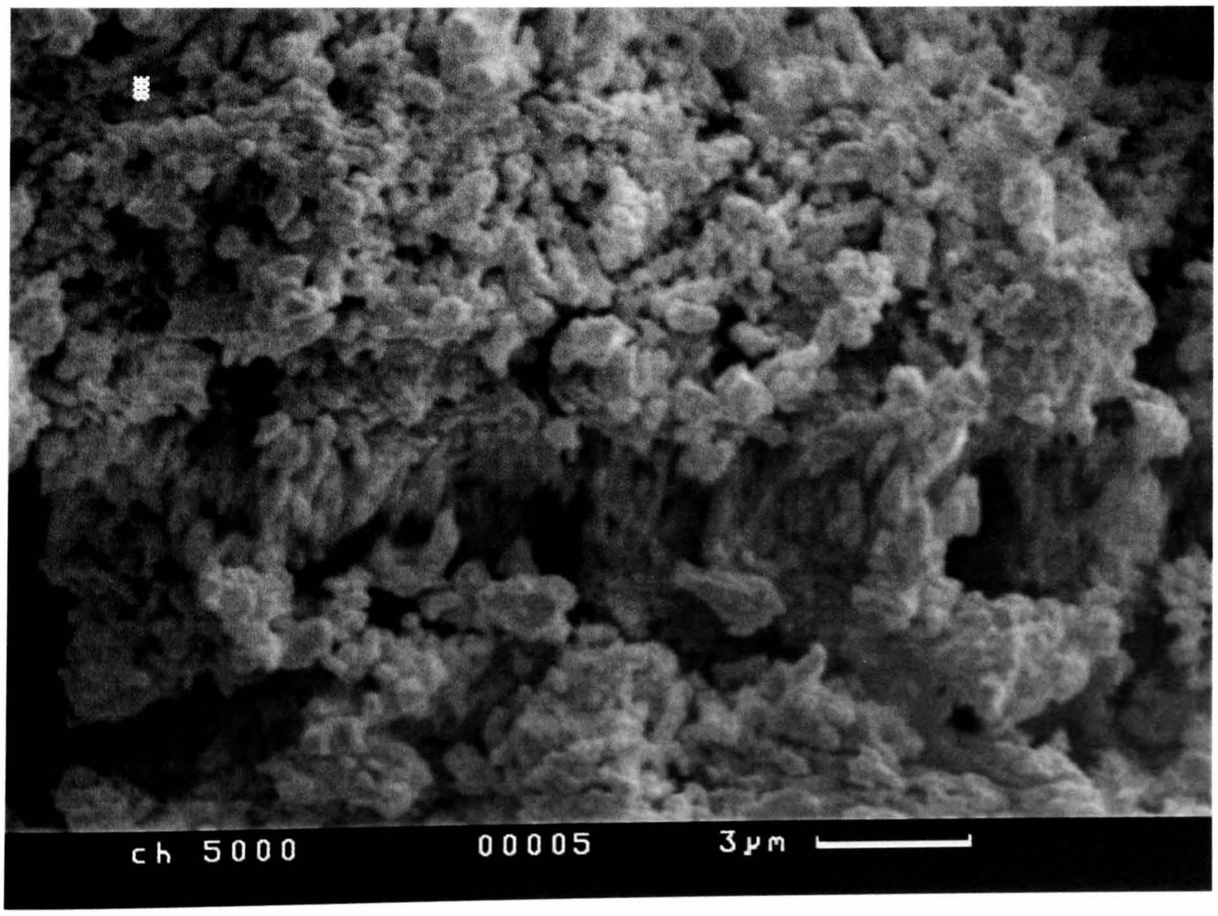


Fig. 6.3.b Magnification of 5000

Fig. 6.4: Comparison of XRD Peaks Between CSA Mix with and without OPC

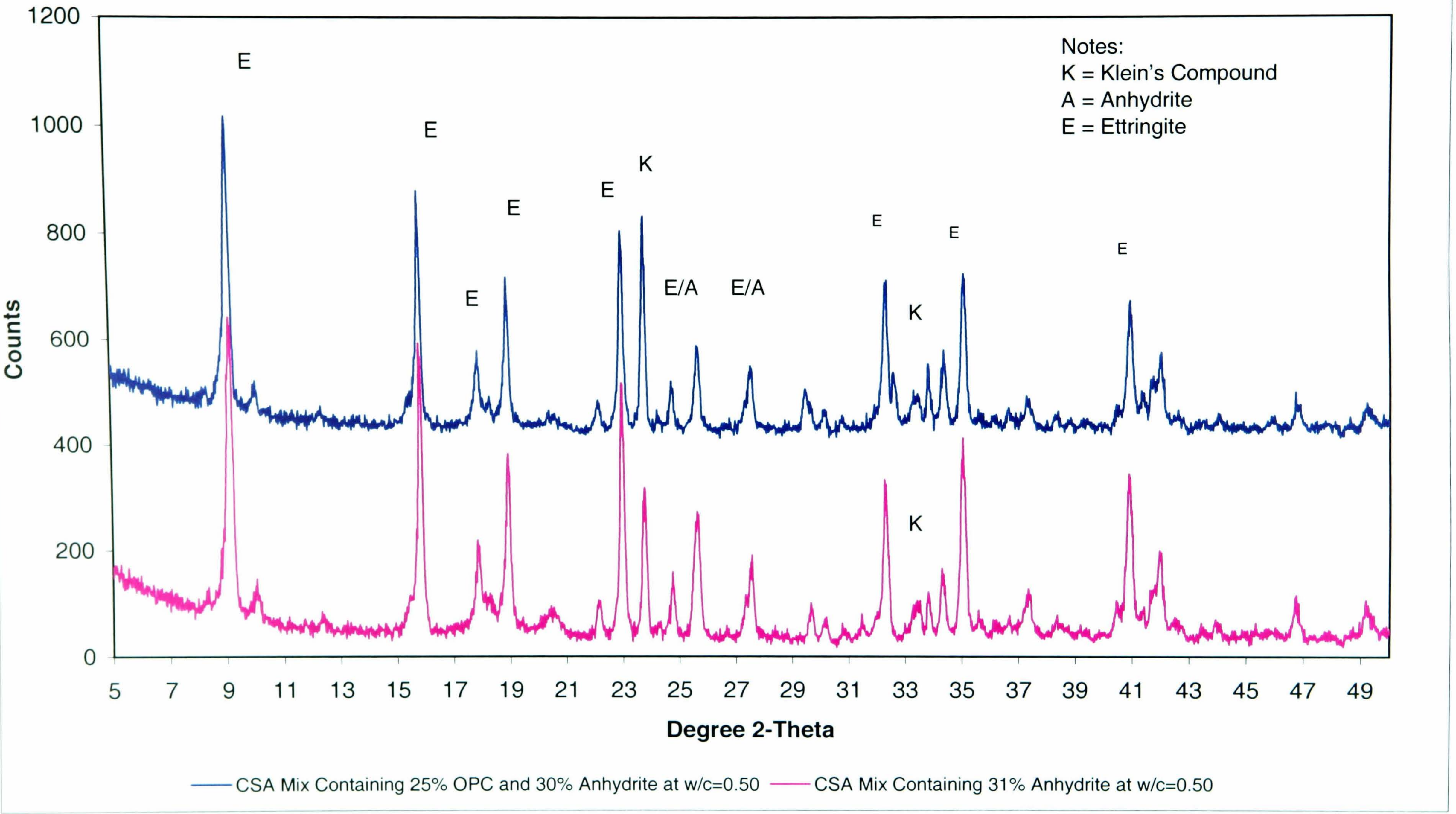


Fig. 6.5: SEM of CSA Mix Containing 25% OPC and 30% Anhydrite at w/cm=0.50 (Cured in Water for 6 month)

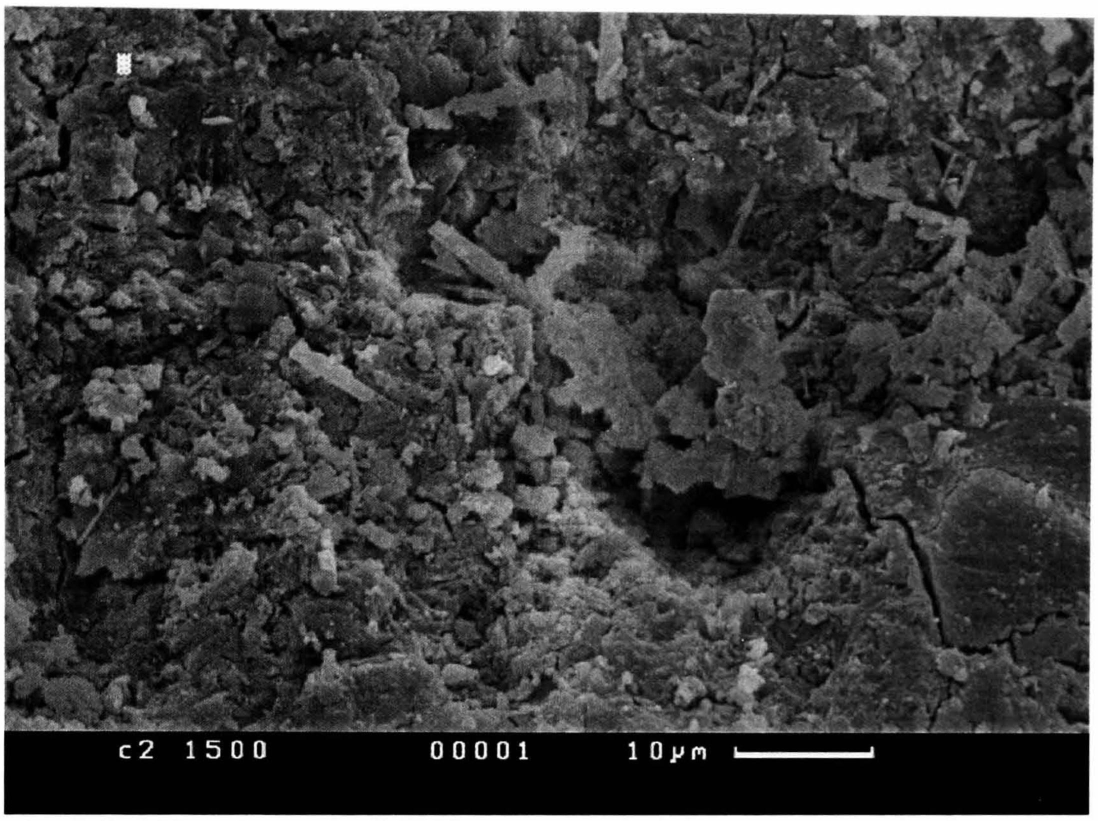


Fig. 6.5.a Magnification of 1500

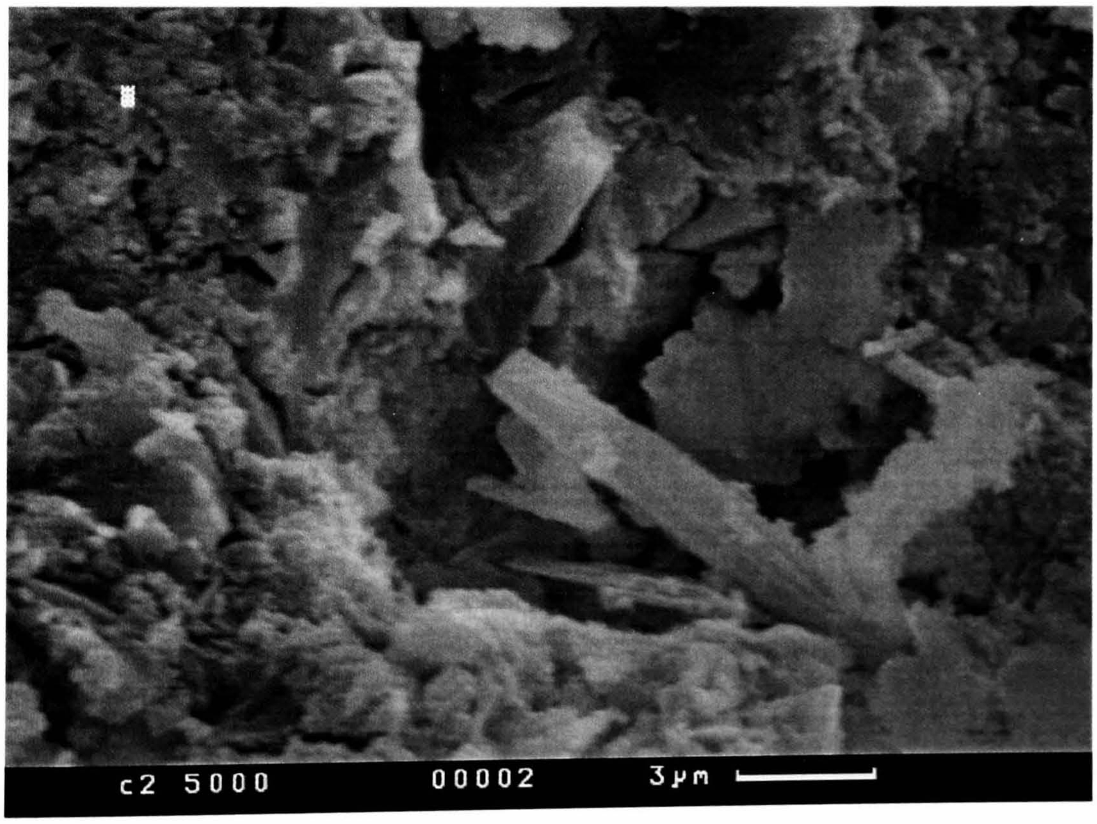


Fig. 6.5.b Magnification of 5000

Fig. 6.6: Length Change Development for CSA Paste Containing 25% OPC

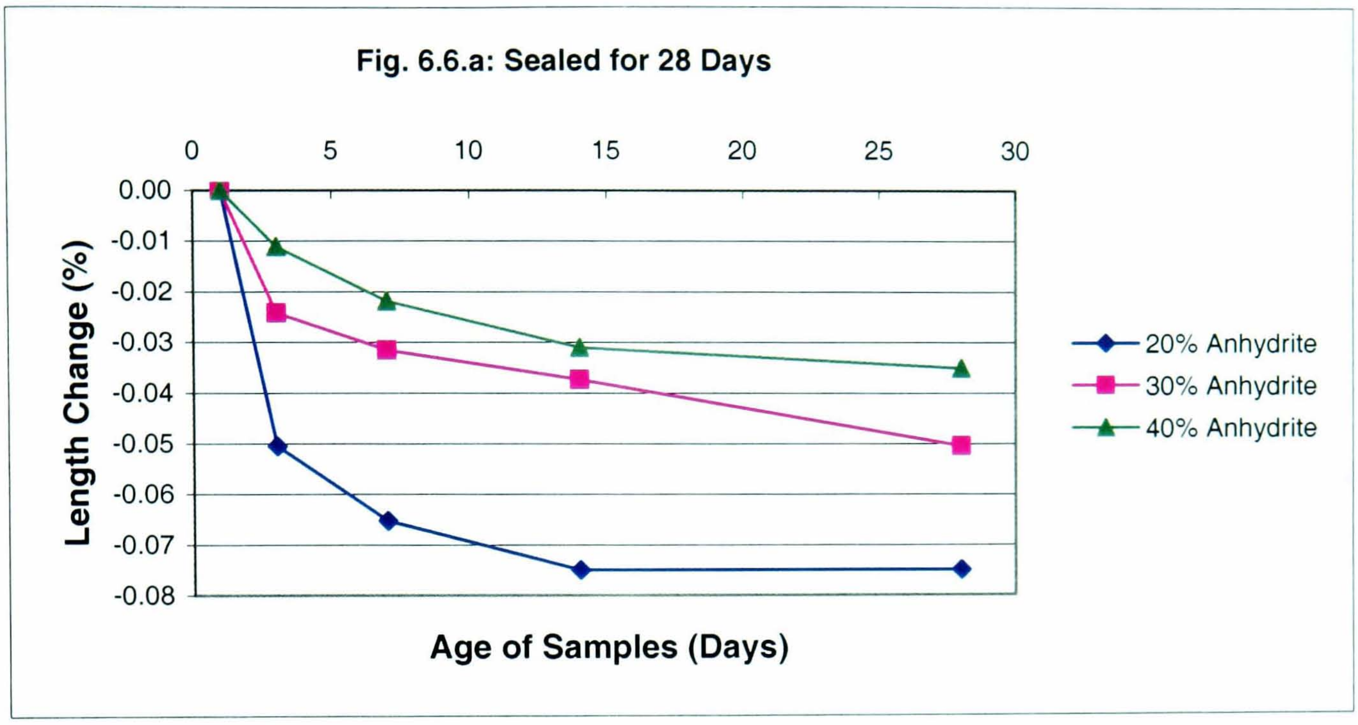


Fig. 6.6.a: Sealed for 28 Days

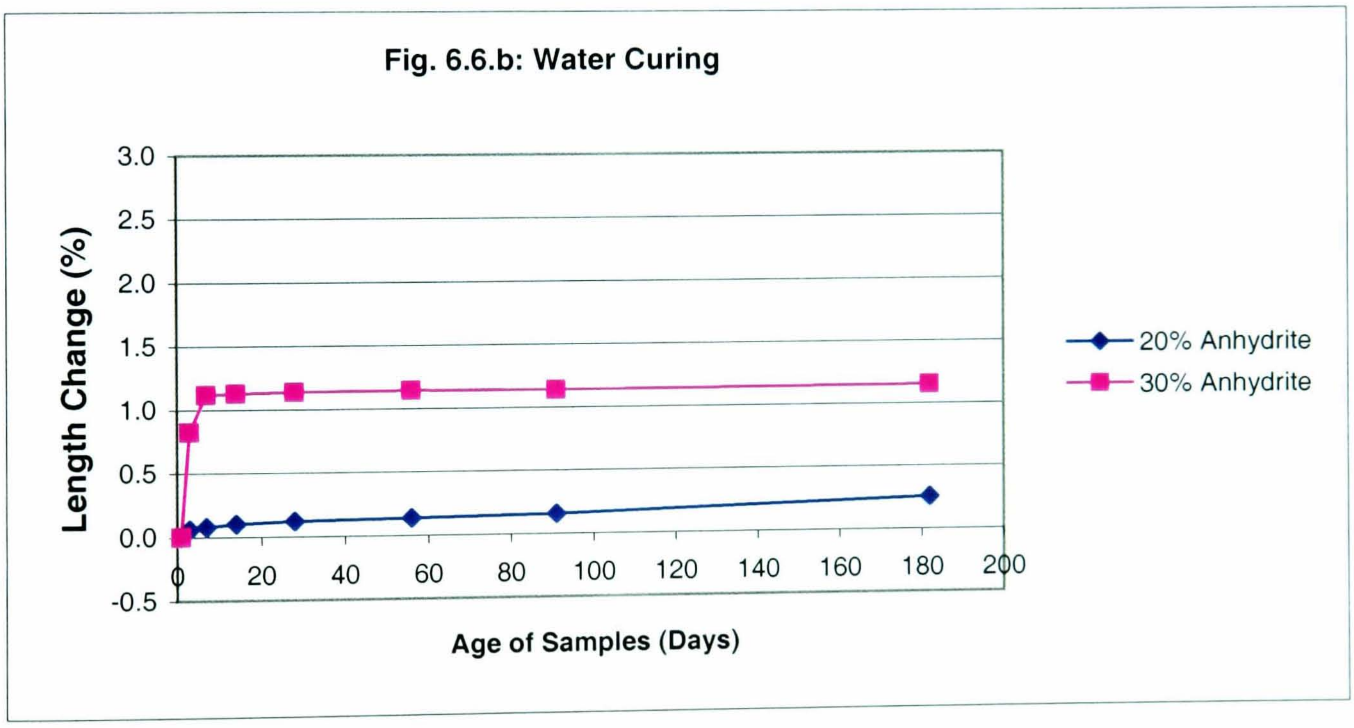


Fig. 6.6.b: Water Curing

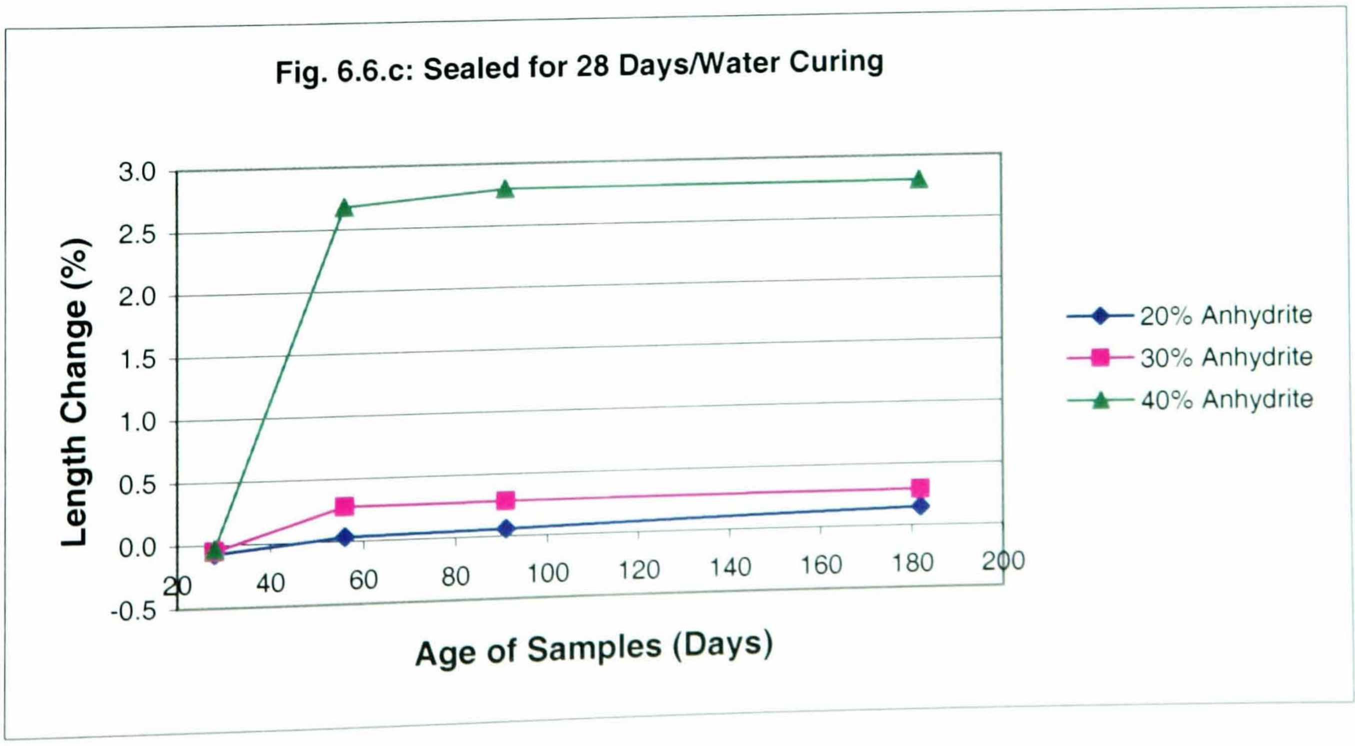


Fig. 6.6.c: Sealed for 28 Days/Water Curing

Fig. 6.7: Weight Change Development of CSA Paste Containing 25% OPC

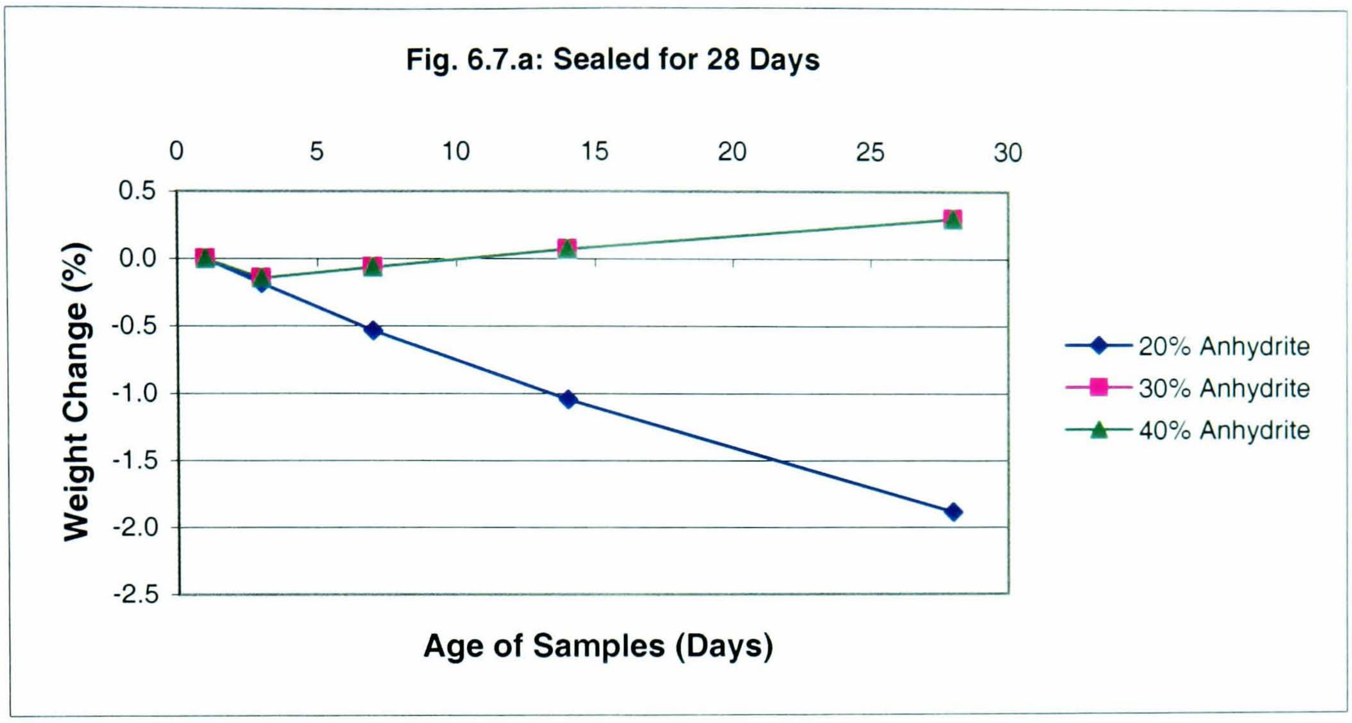


Fig. 6.7.a: Sealed for 28 Days

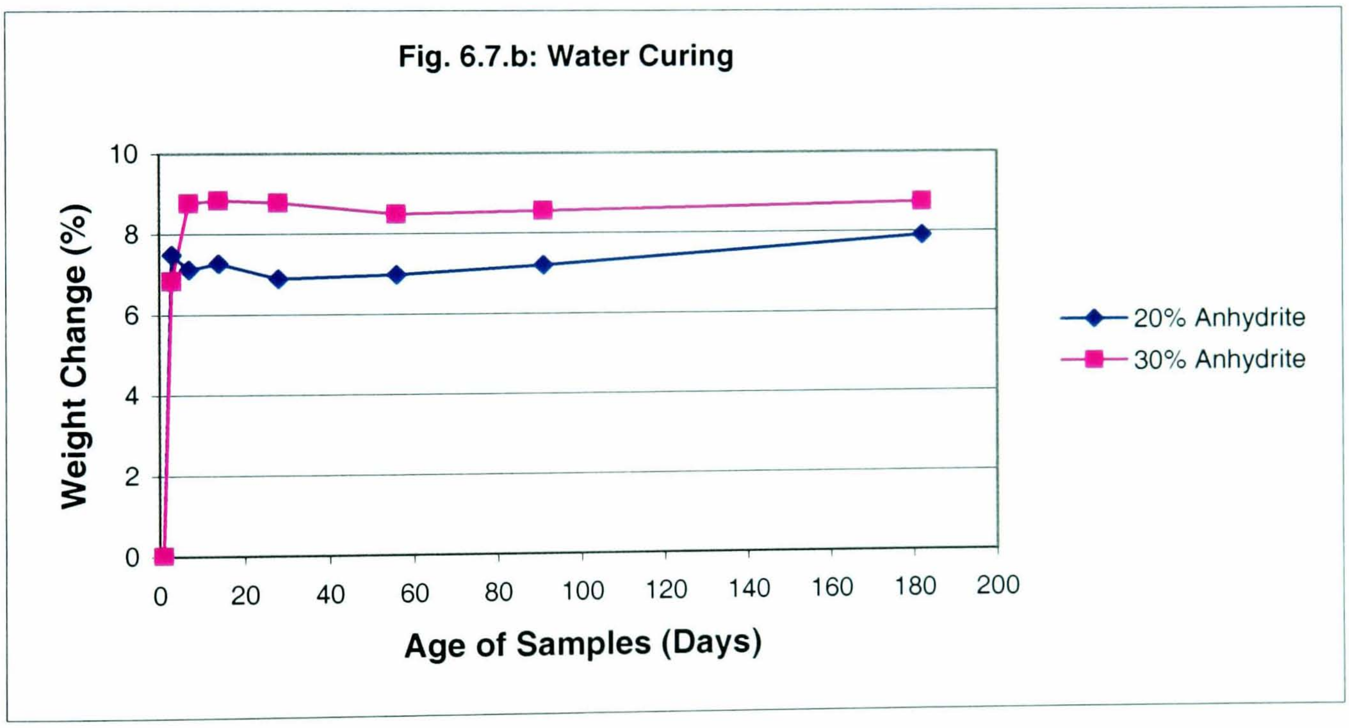


Fig. 6.7.b: Water Curing

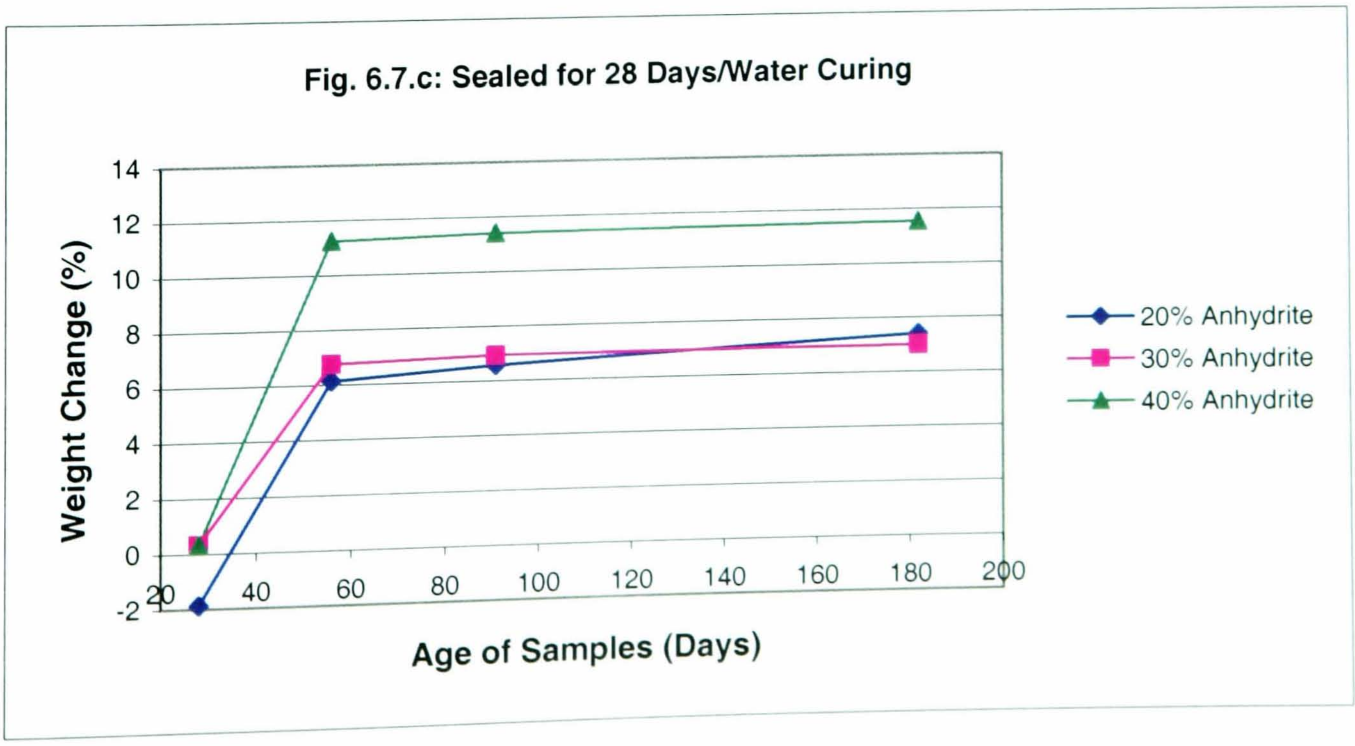


Fig. 6.7.c: Sealed for 28 Days/Water Curing

Fig. 6.8.a: Length Change Development of CSA Paste Containing 25% OPC Sealed for 28 Days/ Immersed in CaSO4 Solution

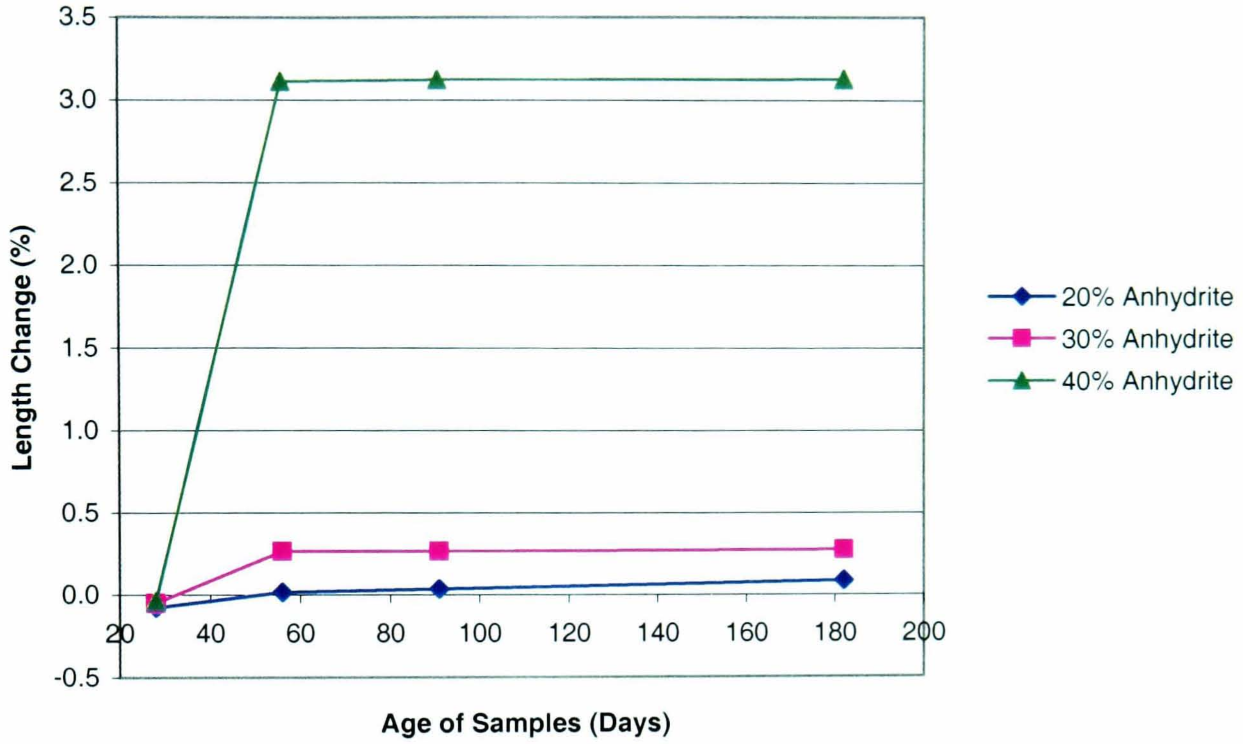


Fig. 6.8.b: Weight Change Development of CSA Paste Containing 25% OPC Immersed in CaSO4 Solution

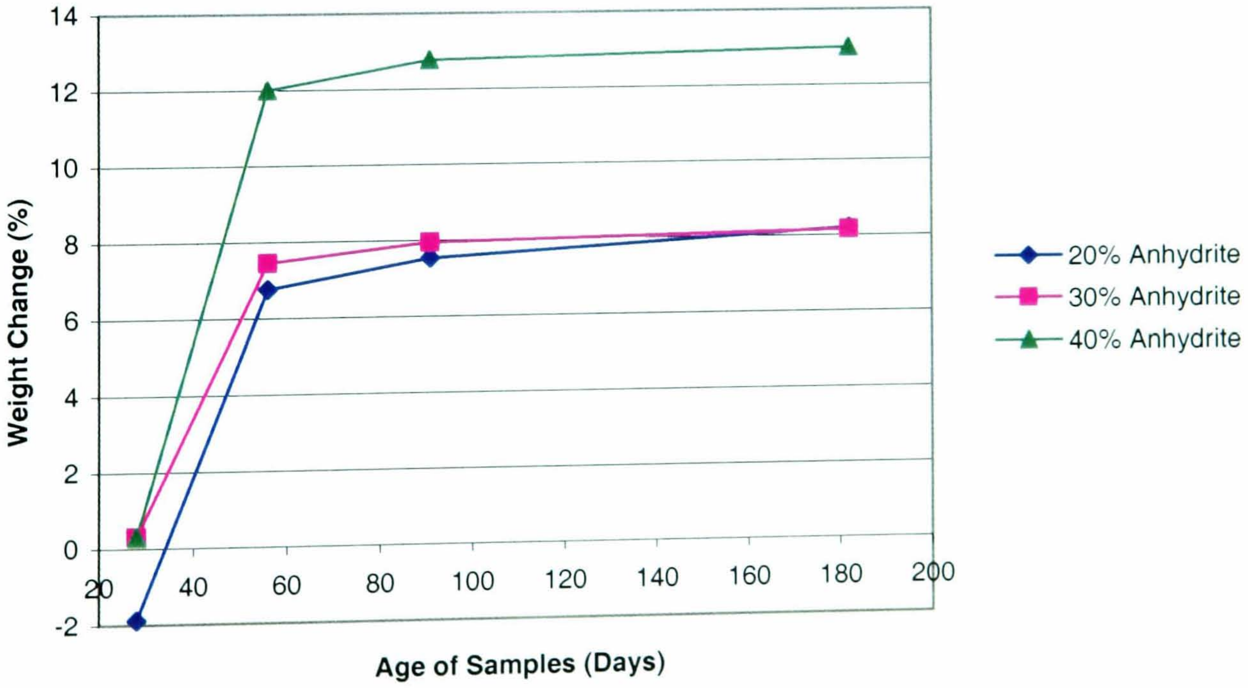


Fig. 6.9: Compressive Strength Development of CSA Paste Containing 25% OPC

Fig. 6.9.a: Water Curing

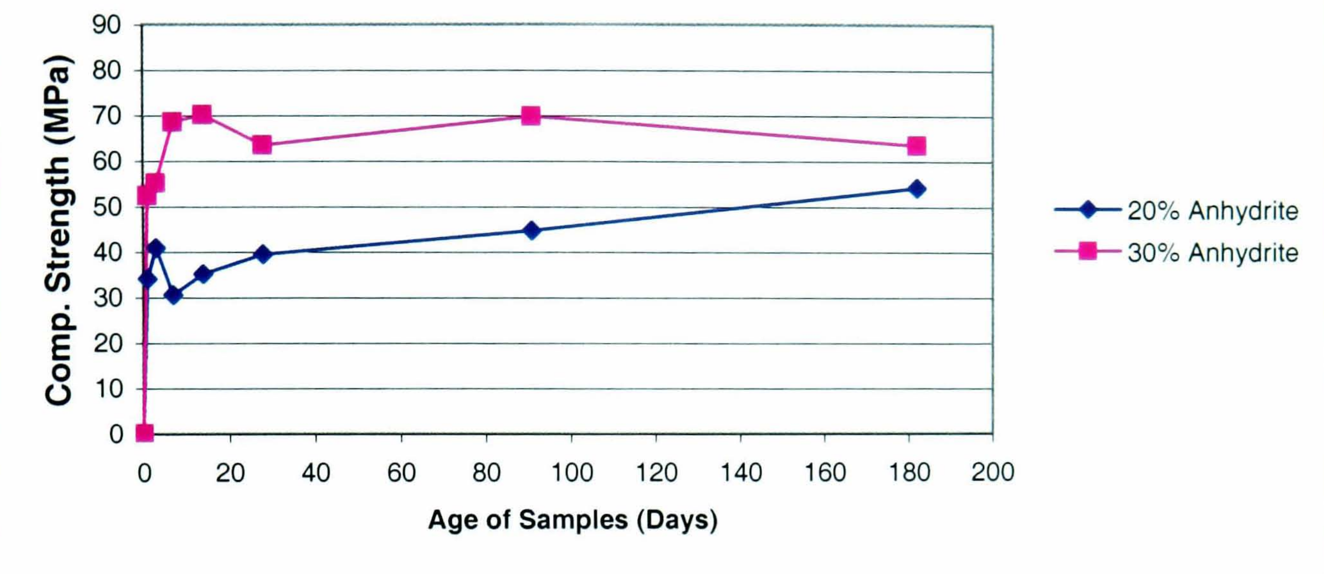


Fig. 6.9.b: Sealed after Demolding

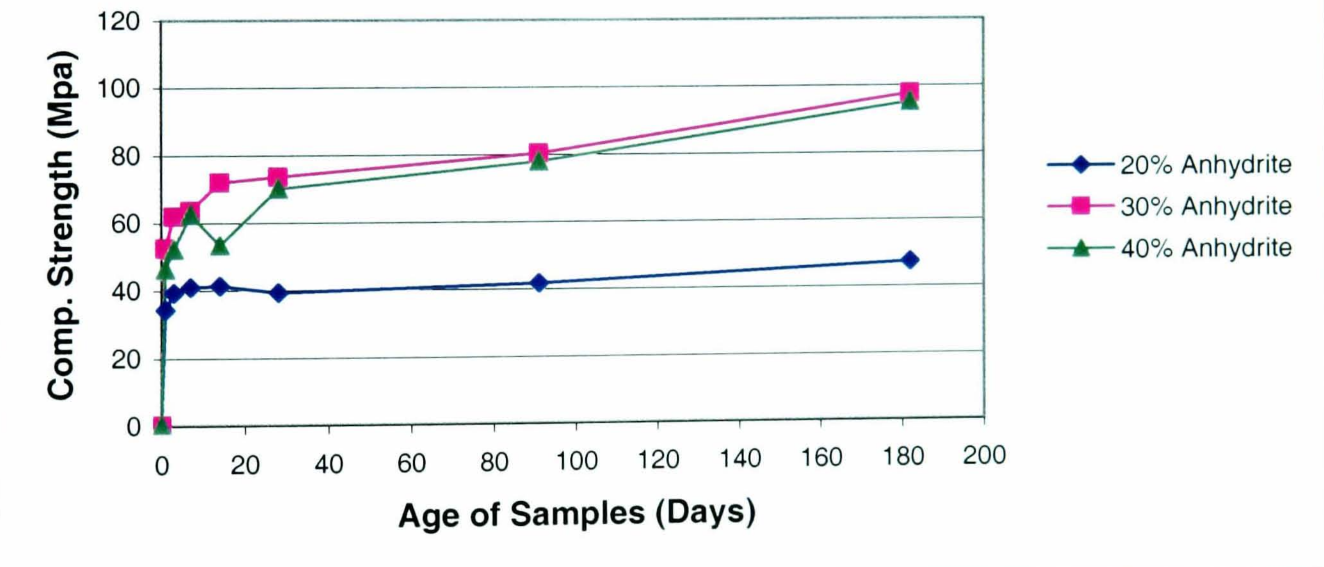


Fig. 6.9.c: Sealed for 28 Days/Water Curing

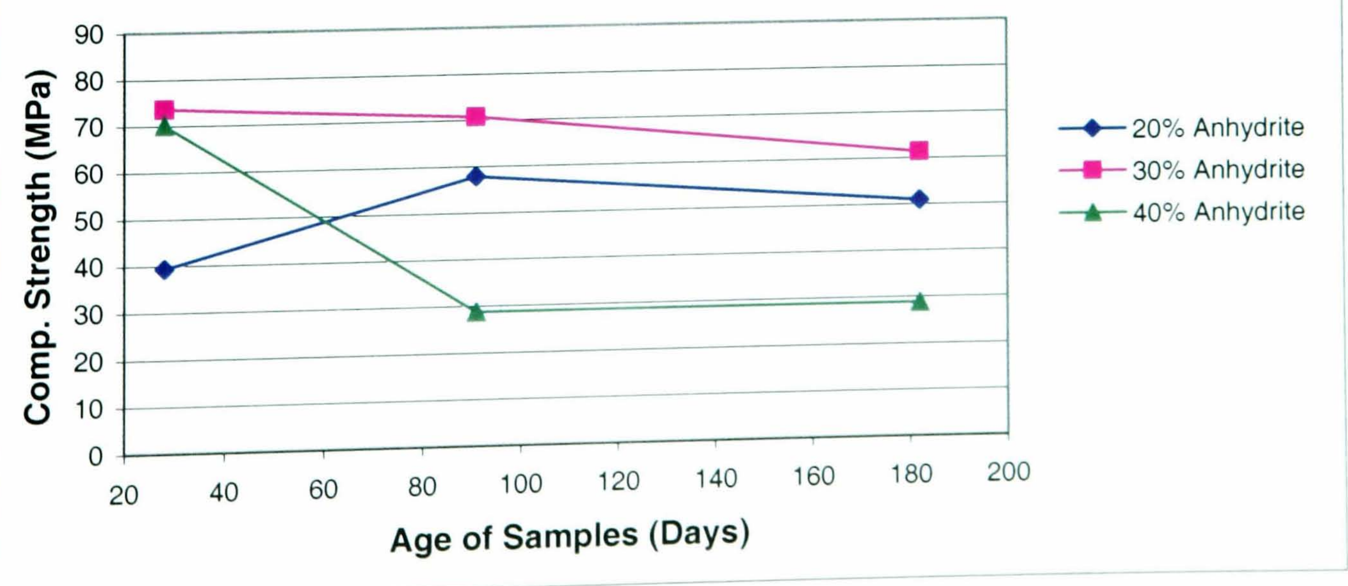
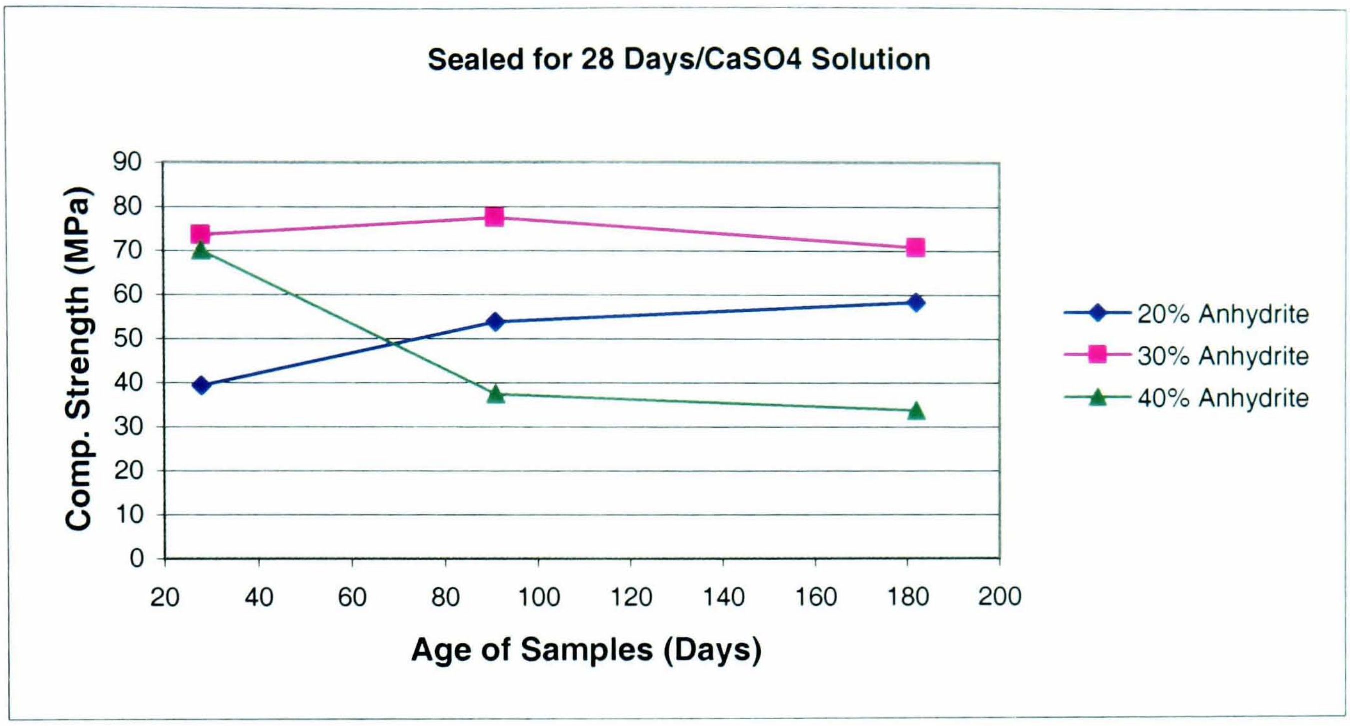


Fig. 6.10: Compressive Strength Development of CSA Paste Containing 25% OPC Sealed for 28 days/immersed in CaSO4 Solution



VII

PROPERTIES OF PASTE MADE FROM COMMERCIALLY MANUFACTURED CSA CEMENT

7.1 Introduction

The use of a commercially manufactured CSA cement in this investigation was intended to develop the research into the properties of CSA paste in a more realistic way. In laboratory manufactured CSA, the purity of the raw materials can be maintained by using AR grade materials, which in turn, given the correct composition of the contributing compounds, nearly pure CSA cement could be produced. This is not the case for commercially manufactured CSA cement. The use of natural resources as raw materials inevitably results in impurities carried by the raw materials besides $C_4A_3\overline{S}$ as the main product.

As shown in table 7.1, the commercially manufactured CSA Cement used throughout the experimental work consisted of only 60% $C_4A_3\overline{S}$. From the XRD test shown in Fig. 7.1, it can clearly be seen that CSA made in the laboratory contained much higher amounts of $C_4A_3\overline{S}$ than the commercially manufactured CSA. CA constitutes 15% of the commercially manufactured cement. Normally with water alone, this phase would directly form calcium aluminate hydrate. With the presence of anhydrite in the system, CA contributes to the formation of ettringite. C_4AF occupying 4% of composition reacts with anhydrite to form iron substitued ettringite (Taylor, 1997). Gehlenite (C_2AS) was found in the cement at around 15%. This phase is much less reactive towards water and might act as a filler to control the expansion. Other minor phases found in the system are $C_{12}A_7$, free lime in a very limited amount, and 0.2% alkali as equivalent Na_2O.

Other principal differences between laboratory made CSA cement and commercially manufactured CSA cement were that the latter had been fired at 1450^{0}C instead of 1350°C and had a specific surface of 450 m^2/kg, which was even finer than that of portland cement.

These differences in properties would certainly create a more complex reaction when compared to the laboratory-made CSA cement. In turn, they would also be expected to affect the properties of the paste. At w/cm ratio of 0.50, the effect of different contents of anhydrite on the properties of CSA paste was examined. The effect of replacing 25% of CSA + anhydrite with OPC on properties of CSA paste was also included as part of this study.

7.2 Setting Times of Commercially Manufactured CSA Cement

7.2.1 Introduction

It is believed that rapid formation of ettringite in CSA cement caused a very fast setting (Janotka and Krajci, 1999; Knofel and Wang, 1994; Zang, et al, 1999). The use of laboratory made CSA cement might, however, delay the initial and final setting times to 1 h 20 min and 2 hours, respectively (Lan and Glasser, 1996). The setting times of commercially produced CSA cement were examined considering the effect of anhydrite variation, inclusion of OPC at different contents and the effect of anhydrite variation at the preferable cement content. As the research was intended to explore the possibility of CSA cement to be used as a binding material in structural concrete, the setting time required was expected to be within the range where the fresh concrete was still suitable to be processed normally.

The water requirement used in the mixes was based on the normal consistency of each mix composition. It was thought to be the most reliable and accurate method to use as the contributing materials in the mixes had different specific gravities and fineness.

The results of the normal consistency and setting times are given in Table: 7.2. The setting times of OPC are included for comparison.

7.2.2 Setting Times of Mix Consisting of CSA Cement and Anhydrite

The contents of anhydrite used in the mixes were 15%, 25%, and 35%. The result is shown in Table 7.2.a. Apparently, the CSA mix was more water demanding than the OPC mix. The explanation for this was related to the lighter specific gravity that caused the increase in volume. Whereas the specific gravity of CSA cement was 2.7, that of OPC was 3.15. Moreover, the finer particles in CSA, where the specific area was 450 m^2/kg, compared to OPC with a specific area of 250 m^2/kg (Neville, 1998). The normal consistency of CSA mix was lower, at a very marginal differential, with increase in the anhydrite content. The fact was that with specific gravity of 2.7, the CSA cement was slightly lighter than anhydrite with specific gravity of 2.9.

The initial and the final setting times of the CSA mix increased with the increase in anhydrite content. As the setting time of CSA cement was dictated by the development of the initial ettringite formation, it seems that the increase of anhydrite caused an increase in acidity of the pore water and then delayed the formation of ettringite (Tattersall and Banfill, 1983)

The initial setting time of OPC was intermediate between the initial setting times of the CSA mixes containing 15% and 25%, while the final setting time of OPC was coincidently the same as the final setting time of the CSA mix containing 15% anhydrite. The time required to reach the final setting times from the initial setting time was on average the same for all CSA mixes, regardless of the anhydrite contents and slower than the time required by OPC to reach the same state. It seems that, with low alkali content of CSA cement as used in the experimental work, the setting times of CSA mixes might be controlled at about the same level as the setting times of OPC by adjusting the anhydrite content.

7.2.3 Setting Times of CSA Cement Mix Containing 25% Anhydrite with Different Contents of OPC.

Different contents of OPC were used as a replacement for the CSA cement containing 25% anhydrite. The result is presented in Table: 7.2.b. Considering that the specific gravity of OPC is higher than the specific gravity of CSA cement and the specific surface of OPC is smaller than the specific surface of CSA cement, the inclusion of OPC into the mix should reduce the water demand. In fact, this was not the case, instead the replacement of 25% CSA cement with OPC increased the normal consistency. An early coagulation caused by the more complex substances in the mix was thought to be responsible for increasing water demand. On the other hand, the presence of OPC in the mix had caused a significant delay in the initial and final setting times.

Replacement of 50% and 75% CSA cement with OPC drastically accelerated the setting time. Increasing the amount of OPC completely changed the pattern of the initial chemical reaction. Increasing the alkalinity carried by the OPC and the availability of CH produced by the finest alite particles were the most likely explanations of the acceleration in the setting times. With the initial setting times below 10 min, these levels of replacement were unsuitable for ordinary structural concrete.

7.2.4 Setting Times of CSA Cement with Different Anhydrite Contents and Incorporating 25% OPC.

The effect of additions of 15%, 25% and 35% of anhydrite on the setting times of CSA cement was investigated. The result is given in Table: 7.2.c. The normal consistency slightly increased with the increase of anhydrite content. On the other hand, the setting times reduced with the increase of anhydrite content.

At 35% anhydrite content, the initial and final setting times were 48 min and 75 min, respectively. This was a considerable drop in the setting times, compared to the mix containing 15% and 25% anhydrite. High availability of anhydrite in the system reacted with initially formed CH and dissolved CSA cement leading to rapid formation of ettringite.

Reducing the anhydrite content to 15% delayed the initial setting time to 260 min compared to 225 min in the mix containing 25% anhydrite. The duration required to reach the final setting time from the initial setting time of the mix containing 15% anhydrite was only 25 min compared to 45 min of the final setting times of mix containing 25% anhydrite.

7.3 Mix Compositions Used in the Experimental Work

The highest anhydrite content in the mix was calculated based on the amount of active materials contributing to ettringite formation in the CSA cement. Taking the stoichiometric requirement for CSA as 31%, with the amount of 60% CSA present in the cement, the need for anhydrite was around 18%. As CA and C_4AF, in the presence of anhydrite can also possibly form ettringite, the highest anhydrite content in the mix was determined to be about 25%. This amount is supported by the appropriate setting times, previously determined. The lower contents of 15% and 20% anhydrite were used to investigate the effect of anhydrite variation in the mix on the properties of the paste. Throughout the experimental work, a w/cm ratio = 0.50 was used.

As the OPC was used as CSA replacement, the setting was the main factor to be considered to determine the content of OPC in the composition. With 25% replacement, suitable setting times have been demonstrated and CSA cement was still a dominant binding material in the mix. At w/cm ratio = 0.50, 25% OPC was included in the CSA mix containing 15%, 20% and 25% anhydrite content for further study.

7.4 Hydration Products

7.4.1 XRD Test

XRD patterns for hydrated commercially manufactured CSA samples with and without incorporation of OPC are shown in Fig 7.2. The samples were taken from mixes containing 25% anhydrite after being cured in water for 28 days. In samples without any OPC, although ettringite was still the main hydration product, the relatively strong peaks of monosulfate present in the samples competed with the domination of ettringite.

The XRD pattern of samples with 25% OPC was similar to the pattern of the laboratory made CSA cement. Ettringite was the main product while monosulfate was represented by weak peaks. OPC in the system enhanced the hydration of CSA and anhydrite. Only a small amount of unhydrated CSA particles were left in the samples

7.4.2 SEM

The SEM image of a commercially manufactured CSA mix without addition of OPC is shown in Fig.: 7.3. The image was taken on samples incorporating 20% of anhydrite after 6 months cured in water at room temperature (20 ± 1) ^{0}C. A compact and dense microstructure of crystalline ettringite was seen among anhydrous particles.

The SEM image of samples incorporating 25% OPC is presented in Fig. 7.4a. The ettringite crystals were surrounded by CSH gel and anhydrous particles At higher magnification (Fig. 7.4.b) long needle-like crystals of ettringite were again observed. This sort of crystal was formed in more porous areas, which provided sufficient space and water for the long needle-like crystals to form.

7.5 Expansion of Commercially Manufactured CSA Paste.

7.5.1 General

The expansion characteristics of hydrated paste specimens made from commercially manufactured cement were expected to be controlled by its chemical composition. The less or non-reactive compounds such as gehlenite would act as filler among the ettringite formed along with the anhydrous particles. This assemblage of products was expected to control the expansion of the paste

The use of 25% OPC as CSA cement replacement in the mixes would further reduce the amount of materials contributing to the formation of ettringite, while the CSH gel formed would act as an additional binder and also additional filler for the crystalline ettringite formed. On the other hand, the CH produced during the hydration would increase the extent of formation of ettringite, which in turn might cause an opposite effect on the expansion.

The effect of these factors on the expansion characteristics of commercially manufactured CSA paste in respect to different anhydrite contents was investigated under different curing conditions. Three curing conditions were applied to the samples. These were water curing, sealed as cast, and water curing after sealing for 28 days. The effect of immersing samples in a saturated concentration of $CaSO_4$ was also considered as part of the investigation. The investigation involved the measurement of the length change and the weight change at various ages of samples (See section 3.3.2.2).

7.5.2 Length Change Development of CSA Paste

7.5.2.1 Samples Sealed for 28 Days Directly After Demolding

The length change development of the CSA samples without addition of OPC is shown in Fig. 7.5.a and the length change development of samples with addition of 25% OPC is shown in Fig. 7.5.b. Because the magnitudes of contraction or expansion were relatively small, the Figures were plotted on a sensitive scale from –0.1% to +0.04%. Generally, the sealed CSA samples without addition of OPC contracted slightly. It is the same observation as for laboratory-made CSA samples. The major part of the contraction occurred at early ages and the development continued slowly beyond 3 days. The magnitude of the contraction of the samples made from commercial CSA cement was slightly lower than the magnitude of contraction of samples made from laboratory CSA (See. Fig 5.17).

Considering the small scale used in the Figure, it seems that the effect of different contents of anhydrite on contraction in commercially manufactured CSA samples without OPC was almost negligible. There was no indication that the contraction had a strong correlation with the content of anhydrite. Samples containing 20% anhydrite underwent slightly greater contraction than samples containing 15% anhydrite, while the lowest contraction was found in samples containing 25% anhydrite.

Contraction was not always the case for samples with 25% added OPC. Early age expansion was found in samples containing 20% and 25% anhydrite. The higher content of anhydrite in the system changed the mechanism of ettringite formation once the CH was produced by OPC hydration. The mix containing 25% anhydrite expanded at a higher rate and the expansion took place up to 7 days of sealing and then followed by the contraction of samples. The samples containing 20% anhydrite expanded at a lower rate and the expansion took place only up to 3 days of sealing and was then followed by contraction of the samples. On the other hand, samples containing 15% anhydrite contracted consistently once the samples were sealed. After 28 days, the magnitudes of the length change of all samples were negative, with the total contraction being higher with reduction in the anhydrite content.

7.5.2.2 Samples Continuously Cured in Water Directly After Demolding

The length change development of samples without OPC is shown in Fig. 7.6.a and the length change development of samples with 25% OPC is shown in Fig. 7.6.b. The use of commercially manufactured CSA cement definitely reduced the expansion of the samples under water curing when compared to the expansion of laboratory made CSA samples. The role of anhydrous particles was probably the most important factor in reducing the expansion.

As for the samples made from laboratory made CSA, the expansion of samples without added OPC continuously developed with time. In the first 7 days, the expansion followed the same pattern as the expansion of the laboratory made CSA samples. To begin with, the expansion was higher with increase in the anhydrite content. After seven days, the pattern started changing where the highest expansion was undergone by samples containing 20% anhydrite, followed by 15% and then 25% of anhydrite. The expansion of samples continued to develop up to 182 days with the maximum expansion being about 0.25%.

Inclusion of 25% of OPC into the CSA mix was supposed to reduce the amount of particles contributing to ettringite formation and hence the observed expansion, but this was not the case in the commercially manufactured CSA paste. The expansion of the samples, especially those containing 15% and 20%, were slightly higher than the expansions of the CSA samples without added OPC at the same anhydrite contents (compare Fig. 7.6.a and Fig 7.6.b).

Only for the first 3 days, the order of the expansion (related to the content of ettringite) was the same as that produced by the laboratory made CSA paste. Beyond that age, the expansion of samples containing 15% and 20% developed much faster than samples containing 25% anhydrite with samples containing 15% always producing the highest expansion. Unexpectedly, the lowest expansion was produced by samples with OPC containing 25% anhydrite. A high expansion rate of samples containing 15% and 20% after 91 days of curing, where during that period the % expansion produced was almost the same as the previous period, was a serious concern for a long-term stability. At 182 days, the maximum expansion, which was produced by samples containing 15% anhydrite was 0.32%. The lowest expansion was less than 0.20% and this was produced by samples containing 25% anhydrite.

7.5.2.3 Samples Cured in Water after Sealing for 28 Days

The expansions of samples with and without added OPC cured in water after sealing for 28 days are shown in Fig.: 7.7.a and 7.7.b, respectively. The expansions of samples followed a similar pattern and a similar magnitude to the expansion observed in samples cured in water directly after demolding. As the initial measurement was taken at 28 days after sealing and samples initially experienced contraction, the expansion after 182 days was slightly lower than the expansion of samples continuously cured in water.

For the anhydrite contents investigated, once again the expansion of the samples without added OPC did not follow a clear pattern with respect to anhydrite content. As for the samples continuously cured in water, those without added OPC containing 20% possessed the highest expansion, followed by the expansion of the samples containing 15% and 25% anhydrite, respectively. For the samples with 25% added OPC, the samples containing 25% anhydrite were less expansive than those containing 15% and 20% anhydrite.

7.5.2.4 Samples Cured in $CaSO_4$ Solution after Sealing For 28 Days

Immersing samples in a saturated solution of $CaSO_4$ did not meaningfully affect the expansion characteristics of commercially manufactured CSA samples with or without added OPC (see Fig. 7.8.a and 7.8.b). The patterns and the magnitudes of expansion of the samples were mostly similar to the pattern and magnitudes of samples cured in water after sealing for 28 days.

7.5.3 Weight Change Development of Commercially Manufactured CSA Paste

7.5.3.1 Samples Sealed Directly After Demolding

The weight change development of commercially manufactured CSA cement samples without OPC sealed directly after demolding is shown in Fig.: 7.9.a. At the earlier ages up to 7 days all the samples experienced some loss of weight. At this stage the evaporation of pore water from the surface was greater than the uptake of water used for continuation of hydration. The rise in temperature during the early hydration enhanced the evaporation.

Beyond 7 days, samples containing 20% and 25% anhydrite gradually gained in weight. Relatively high amounts of initial ettringite formation could retain pore water in the system, while absorption of water took place when the samples were exposed to the ambient atmosphere during length change testing. The absorption was not, however, high enough to regain the weight lost at the earlier ages. On the other hand, the lower amount of ettringite in samples containing 15% of anhydrite caused the amount of water absorbed during the samples exposure to be almost the same as the water evaporated from the system. The weight of samples was therefore relatively constant, up to 28 days.

The weight change development of commercially manufactured CSA cement samples with OPC sealed directly after demolding is shown in Fig. 7.9.b. The loss of weight up to 7 days of sealing of samples containing OPC was higher than for the samples without OPC. The presence of OPC enhanced the early hydration and the heat generation. The expansion at the earlier ages of samples containing 20 and 25% anhydrite created more voids in the system to allow for evaporation during the tests. Up to 28 days, samples containing 25% anhydrite, which were more expansive, underwent greater loss of weight than the samples containing 20% anhydrite, which were less expansive. The samples containing 15% anhydrite, which experienced continuous contraction, slightly gained in weight after 7 days of curing.

7.5.3.2 Samples Continuously Cured in Water Directly After Demolding

The weight change development of the commercial CSA samples without added OPC immersed in water directly after demolding is shown in Fig.: 7.10.a. A considerable gain in weight up to 3 days was due mainly to the absorption of water filling the voids as a replacement for water consumed during the hydration. After 3 days, slow and continuous gain in weight of the samples was due to the absorption of water by ettringite. The highest gain in weight was experienced by the samples containing 20% anhydrite, which correlated with the observation that these samples were the most expansive.

A high gain in weight up to 3 days of curing was also the case for samples with added OPC (see Fig 7.10.b). After 3 days, the weight change development increased at a much slower rate and followed the order of expansion where samples containing less anhydrite experienced higher expansion.

7.5.3.3 Samples Cured in Water after 28 Days of Sealing

Basically, the patterns and the magnitudes of the weight change development of samples with and without OPC cured in water after sealing for 28 days were similar to those cured in water directly after demolding (see. Fig. 7.11.a and Fig. 7.11.b). The main gain of weight at the earlier ages was due to the absorption of water filling the voids as replacement for the water consumed during the hydration and further much slower rate of gain in weight was due to the absorption of ettringite related to the expansion of samples.

7.5.3.4 Effect of Immersion in $CaSO_4$ Solution after 28 Days of Sealing

The effect of immersing the samples into a saturated solution of $CaSO_4$ after being sealed for 28 days on the gain in weight was more or less the same as for those cured in water after being sealed for 28 days. A lower content of $CaSO_4$ in the solution did not significantly change the amount of ettringite in the samples, as a result there was no significant influence on the amount of water absorbed at the later ages (see Fig. 7.12.a and 7.12.b).

7.6 Compressive Strength of Commercially Manufactured CSA Cement Paste

7.6.1 Samples Sealed as Cast Directly after Demolding

The compressive strength of commercially manufactured CSA cement paste samples without added OPC is shown in Fig. 7.13.a. As for laboratory-made CSA cement samples, the compressive strength of commercially manufactured samples developed very fast at early ages, reaching about 50 MPa after only 7 days. However the laboratory made CSA cement samples produced slightly higher compressive strength than that produced by the commercially manufactured CSA cement. After 3 days, the compressive strength had reached on average 70-80% of the compressive strength at 28 days. Except for samples containing 25% anhydrite, where the strength continuously developed at a slow rate until 182 days, the compressive strength of samples containing 20% and 25% anhydrite was constant until the same age.

Unlike laboratory made CSA cement samples, where the compressive strength was higher with increasing anhydrite content, in commercially manufactured CSA cement paste without OPC, there was no clear correlation between compressive strength and anhydrite contents. At 28 days the highest compressive strength was produced by samples containing the lowest anhydrite content and the lowest compressive strength had the highest anhydrite content. After 182 days, however, the highest compressive strength was produced by samples containing the highest anhydrite content and the lowest compressive strength was produced by samples containing 20% anhydrite. The difference in strength of the paste with different anhydrite contents was within a range of 15 MPa.

Inclusion of 25% OPC, as cement replacement, into the commercially manufactured CSA mix slightly reduced the compressive strength of paste (see Fig. 7.13.b). As for the samples without added OPC, there was no clear correlation between compressive strength and anhydrite content. At 28 days the compressive strength was higher with increase in anhydrite content, and at 182 days the compressive strength of samples containing 20% anhydrite was greater than the compressive strength of samples containing 25% by a small amount. The paste samples containing 15% anhydrite produced a much lower compressive strength throughout the curing period. It seems that the use of an appropriate percentage of anhydrite was very important in CSA paste containing OPC, because the presence of CH produced by OPC hydration increased the requirement for anhydrite.

7.6.2 Samples Cured in Water Directly After Demolding

The compressive strength of CSA samples without added OPC cured in water directly after demolding is shown in Fig. 7.14.a. The continuation of rapid hydration for a few days due to the replacement of water used for hydration was maintained by water curing and the expansion during the curing period influenced the compressive strength of samples. At 3 days of curing, the strength of paste cured in water was higher than the strength of paste sealed as cast. From 28 days to 182 days, the strength of samples containing 25% anhydrite constantly developed at a low rate while for samples containing 15% and 20 %, strength slightly reduced up to 91 days but increased again beyond that age. As in samples sealed after demolding, the anhydrite content did not produce a decisive relationship with the compressive strength.

Water curing was more advantageous on samples with OPC. The early age compressive strength was on average as high as the compressive strength of samples without OPC (see Fig.7.14.b). The compressive strength was maintained until 91 days and started to reduce beyond that age. The compressive strength of samples containing 20% and 25% anhydrite was less affected by the curing, but the samples containing 15% anhydrite underwent approximately a 30% reduction at 182 days.

7.6.3 Samples Cured in Water After Sealed for 28 days

The compressive strength of commercially manufactured CSA samples without OPC cured in water after sealing for 28 days is presented in Fig. 7.15.a. Samples containing 25% anhydrite continuously gained strength with time. At 182 days the compressive strength of the samples reached 70 MPa. Samples containing 20% anhydrite developed strength almost at the same rate and magnitude as the samples containing 25% anhydrite until 91 days. Beyond that age the compressive strength reduced at a slow rate until 182 days. Samples containing 15% anhydrite reduced in strength up to 91 days and beyond that age the compressive strength increased at a slow rate. At 182 days, the compressive of samples containing 15% anhydrite was slightly higher than the strength of paste containing 20% anhydrite but lower than the compressive strength of samples containing 25% anhydrite.

The compressive strength of commercially manufactured samples with OPC cured in water after 28 days sealed as cast is presented in Fig. 7.15.b. The samples containing 25% anhydrite produced a consistently slow rate increment of compressive strength up to the 182 days age of paste. Samples containing 15% and 20% anhydrite developed compressive strength up to 92 days and then reduced in strength up to 182 days. The compressive strength of samples at the different anhydrite contents investigated was in a narrow range of 10 MPa. The average compressive strength of samples with OPC was slightly lower than the average compressive strength of samples without OPC.

7.6.4 Effect of Immersing Samples in $CaSO_4$ Solution on Compressive Strength of CSA Paste Containing OPC.

Immersion of the commercially manufactured CSA paste without or with OPC did not seriously affect the compressive strength (see Fig.7.16). The samples containing 25% anhydrite performed as good as those cured in water. The compressive strength of samples steadily developed and did not show a reduction after having been immersed up to 182 days in a saturated solution of $CaSO_4$ (see Fig. 7.16 a and b). It seems that the amount of $CaSO_4$ found in a saturated solution was not big enough to affect further hydration in the paste.

Compressive strength for samples submerged in a saturated $CaSO_4$ solution did not change significantly with changing anhydrite content and no pattern was evident.

7.7 Conclusions

From work conducted on commercially manufactured CSA cement, the paste containing 25% anhydrite has exhibited a good and stable performance throughout the investigation and its use can now be explored in the production of structural grade concrete. It is concluded that:

1. The use of commercially manufactured CSA cement containing low alkali with incorporation of 15% and 25% anhydrite produced a paste with acceptable final setting times of around 3-4 hours. At these levels of anhydrite content, addition of 25% OPC delayed the setting times of the pastes, but they were still acceptable.

2. Ettringite and sometimes monosulfate were the main hydration products of the commercially manufactured CSA cement used in the experimental work. The inclusion of 25% OPC decreased the amount of monosulfate present in the hydration products.

3. The expansion of the commercially manufactured CSA paste was lower than the expansion of laboratory made CSA paste. The use of 25% anhydrite in the paste with or without added OPC produced the lowest expansion.

4. The compressive strength of commercially manufactured CSA paste was lower than the compressive strength of laboratory made CSA paste. Although not the highest, the use of 25% anhydrite in the paste with or without added OPC produced the most stable compressive strength with time under every set of curing conditions.

Table 7.1: Typical Properties of Commercially Manufactured CSA Cement Used in Experimental Work

Physical Properties	
Specific surface area (m^2/kg)	450
Specific gravity	2.7
Colour	Grey
Phase Composition (%)	**(%)**
$C_4A_3\bar{S}$	60
CA	15
C_2AS	15
$C_{12}A_7$	1
C_4AF	4
Free Lime	0.16
Eq. Na_2O	0.2

Table 7.2: Setting Times of Commercially Manufactured Calcium Sulfoaluminate Cement

7.2.a Combination of CSA Cement and Anhydrite

Anhydrite Content %	Normal Consistency %	Setting Times (Minutes)	
		Initial	Final
15	28.8	108	165
25	28.35	160	240
35	28	228	300

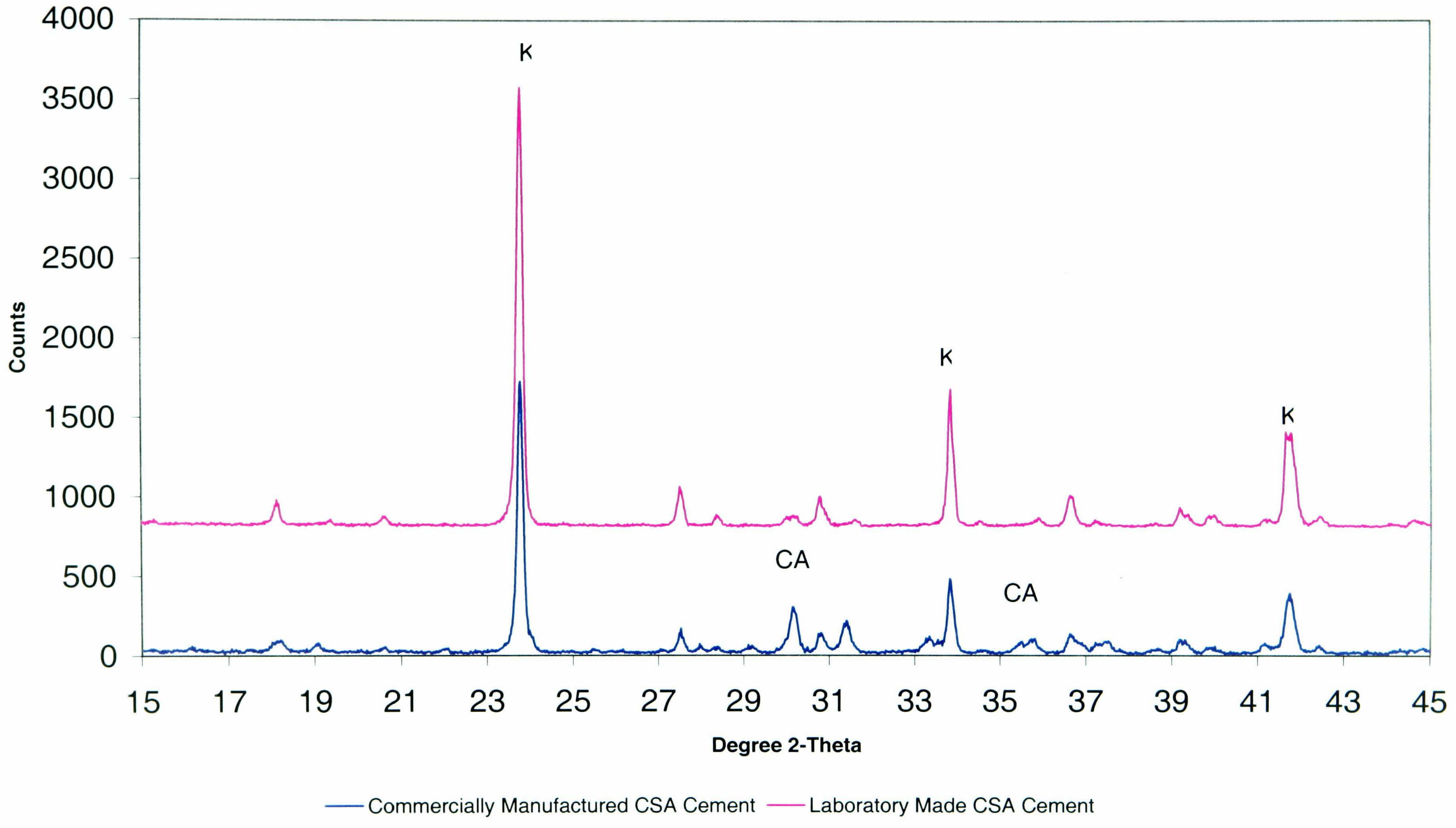
7.2.b: Combination of CSA Cement (Anhydrite Content =25 %) and OPC

Proportion of Material (%)		Normal Consistency (%)	Setting Times (Minutes)	
PC	CSA		Initial	Final
100	0	22.65	138	165
75	25	38.8	6.5	9
50	50	38.1	7.2	9
25	75	31.5	225	270
0	100	28.35	160	240

7.2.c: Combination of CSA Cement and PC (PC Content = 25 %)

Material Proportions (%)		Normal Consistency (%)	Setting Times (Minutes)	
Cement	Anh./(CSA+Anhydrite)		Initial	Final
25	15	31.5	260	285
	25	31.8	225	270
	35	32.1	48	75

Fig.7.1 : Comparison of XRD Pattern Between Commercially Manufactured CSA Cement and Laboratory Made CSA Cement



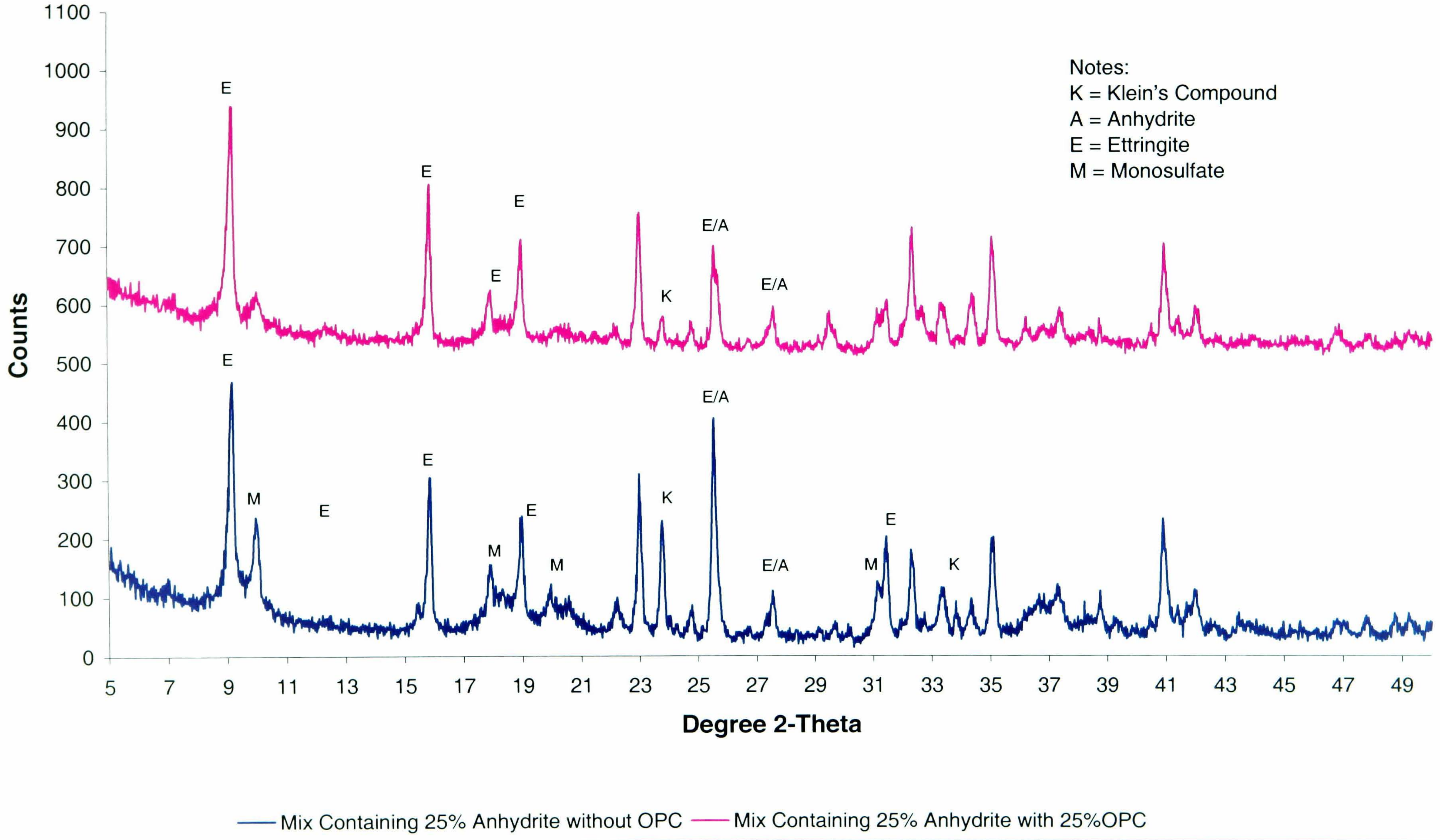


Fig.7.2 : XRD of Commercially Manufactured CSA Cement

Fig. 7.3: SEM of Commercially Manufactured CSA Mix Containing 20% Anhydrite at w/cm=0.50 (Cured in Water for 6 month)

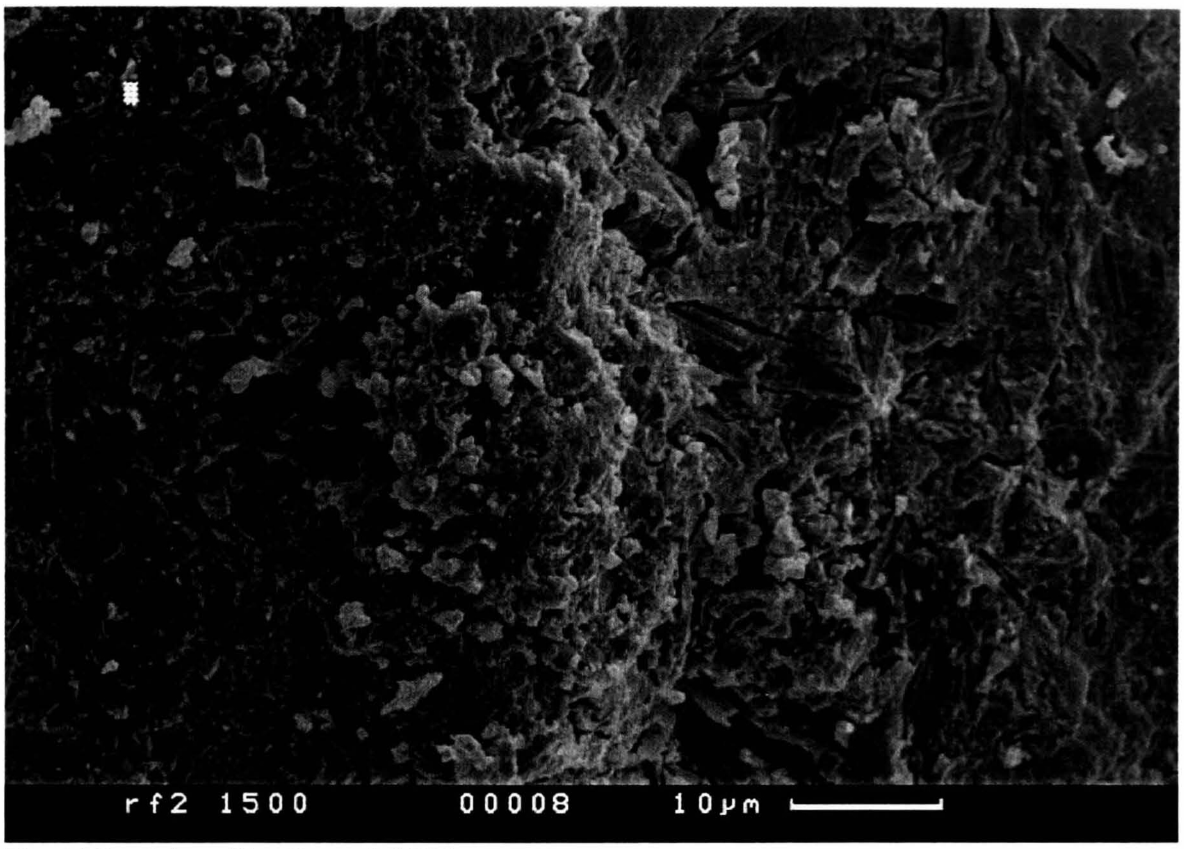


Fig. 7.3.a Magnification of 1500

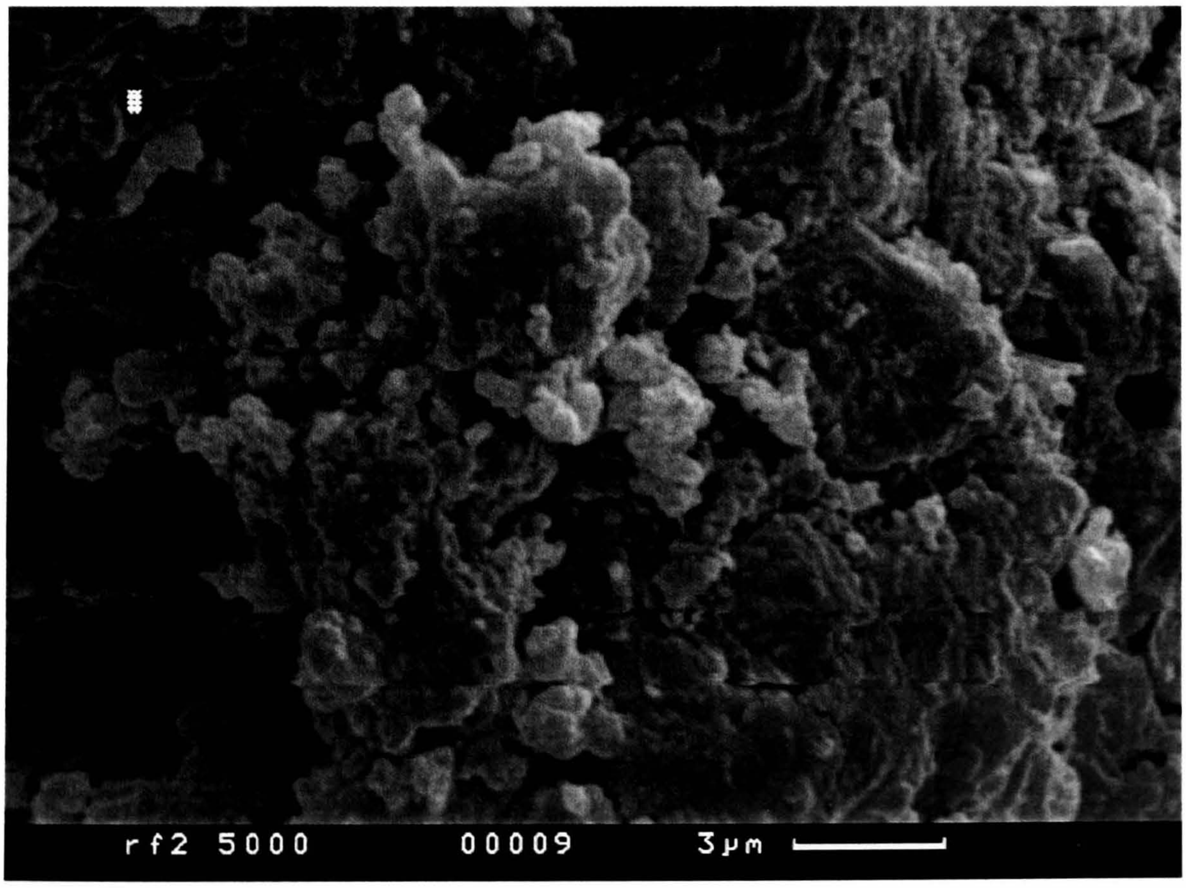


Fig. 7.3.b Magnification of 5000

Fig. 7.4: SEM of Commercially Manufactured CSA Mix Containing 25% OPC and 20% Anhydrite at w/cm=0.50 (Cured in Water for 6 month)

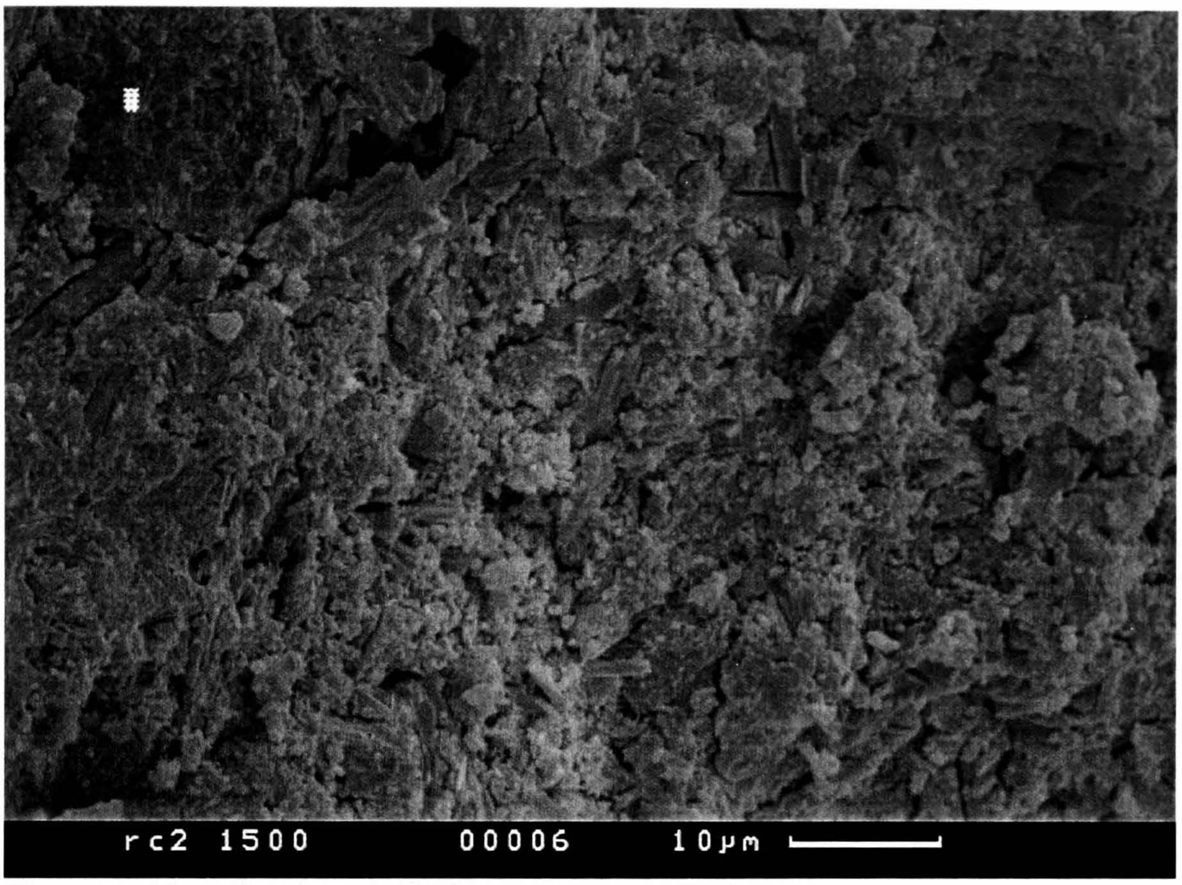


Fig. 7.4.a Magnification of 1500

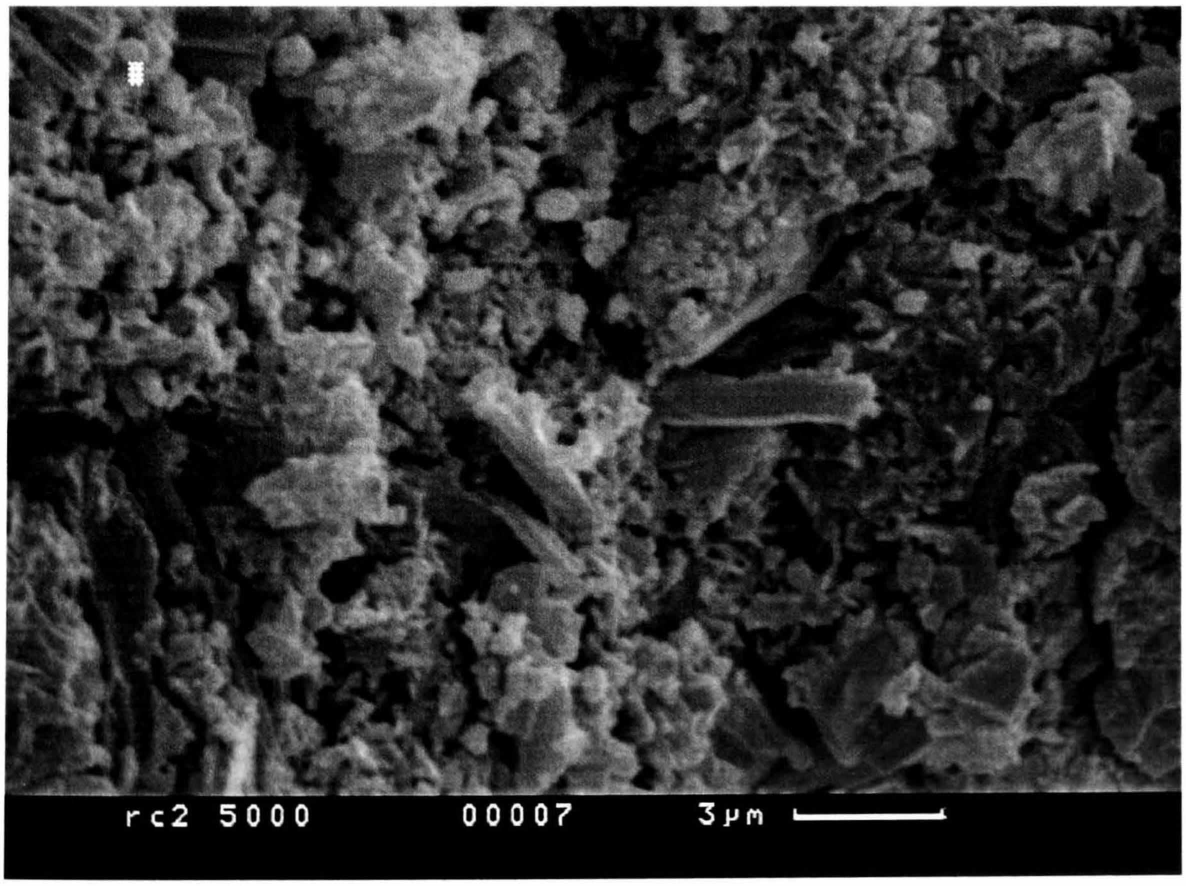


Fig. 7.4.b Magnification of 5000

Fig. 7.5: Length Change Development of Manufactured-CSA Cement Sealed Directly After Demolding

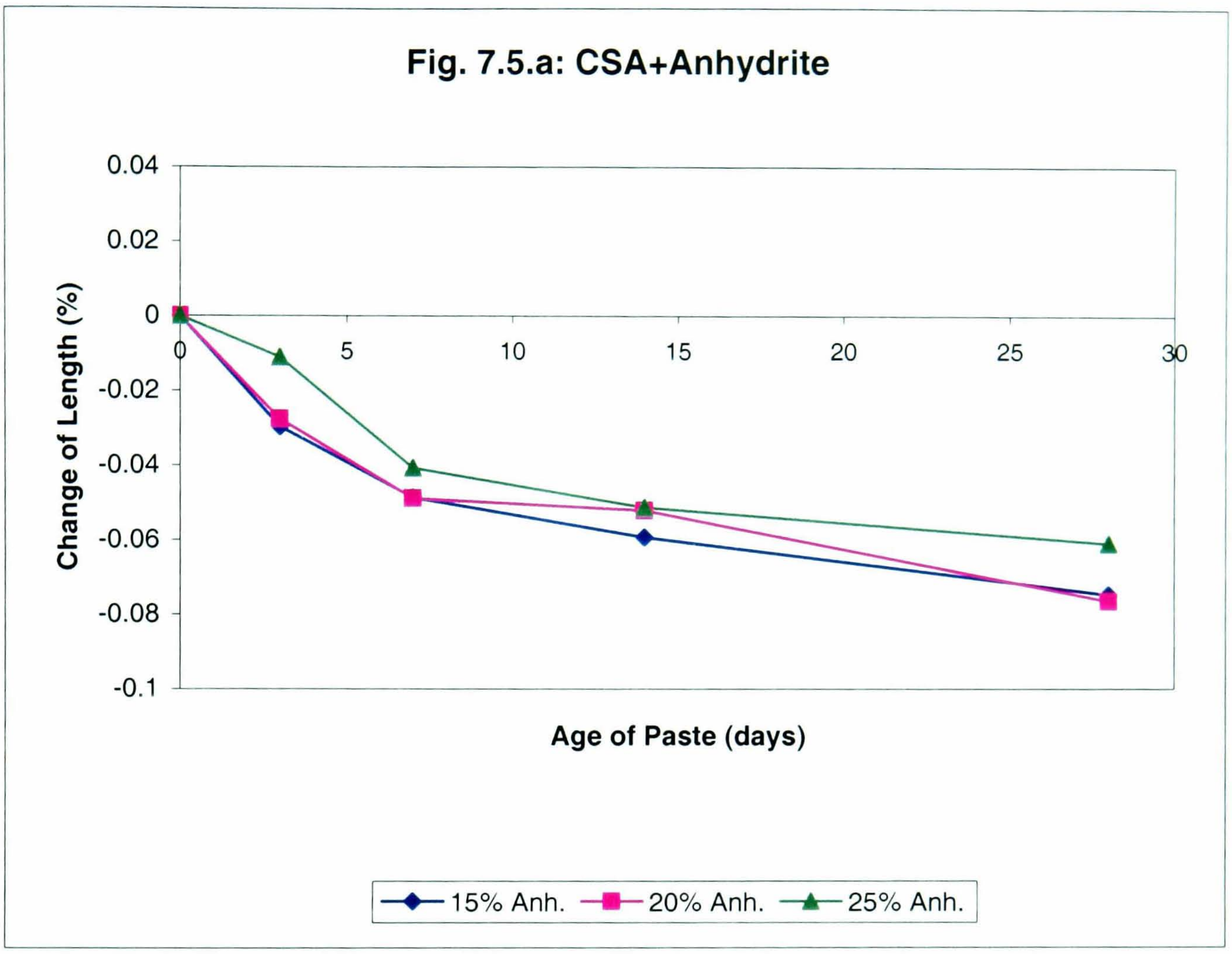


Fig. 7.5.a: CSA+Anhydrite

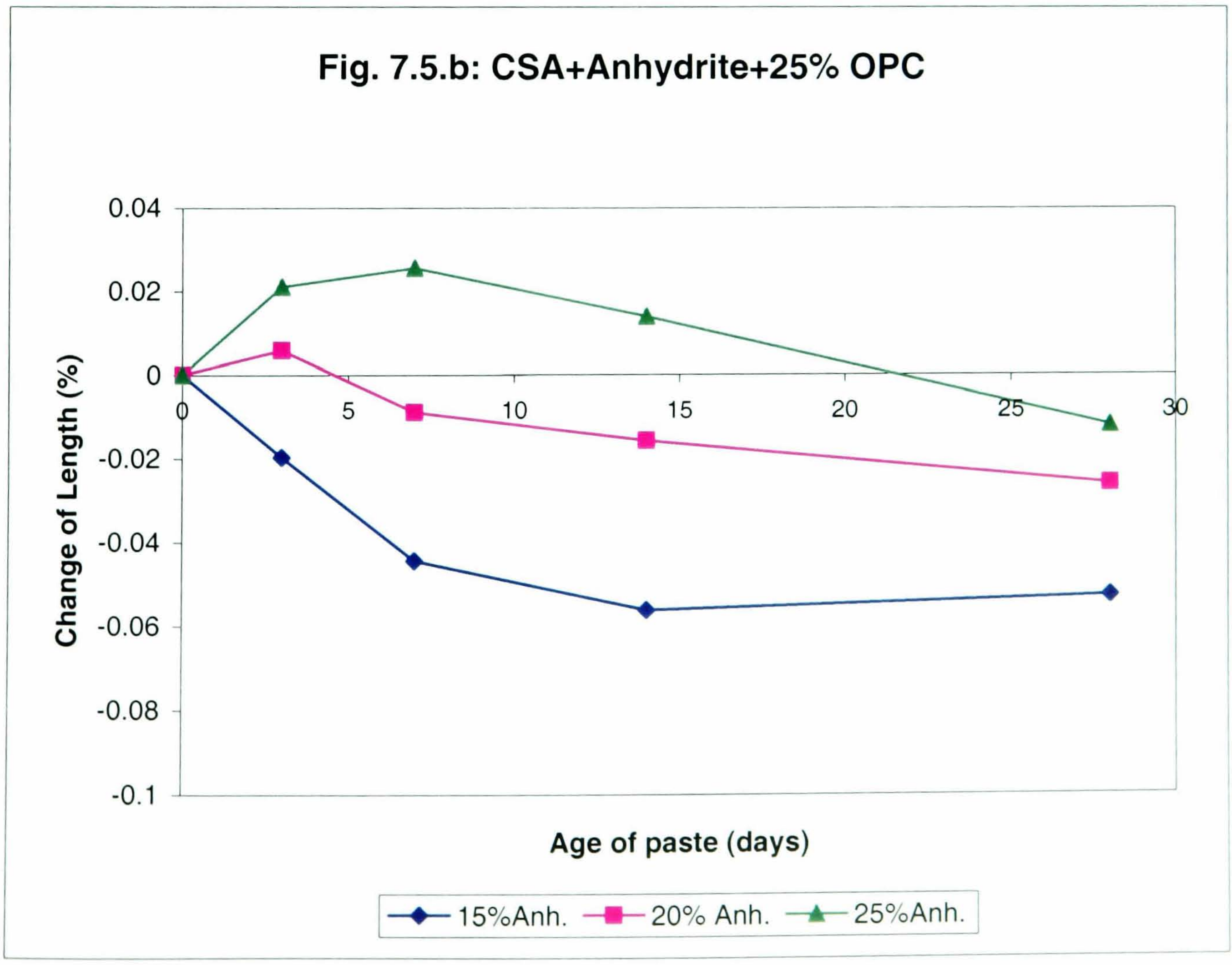


Fig. 7.5.b: CSA+Anhydrite+25% OPC

Fig. 7.6: Length Change Development of Manufactured-CSA Cement Cured in Water

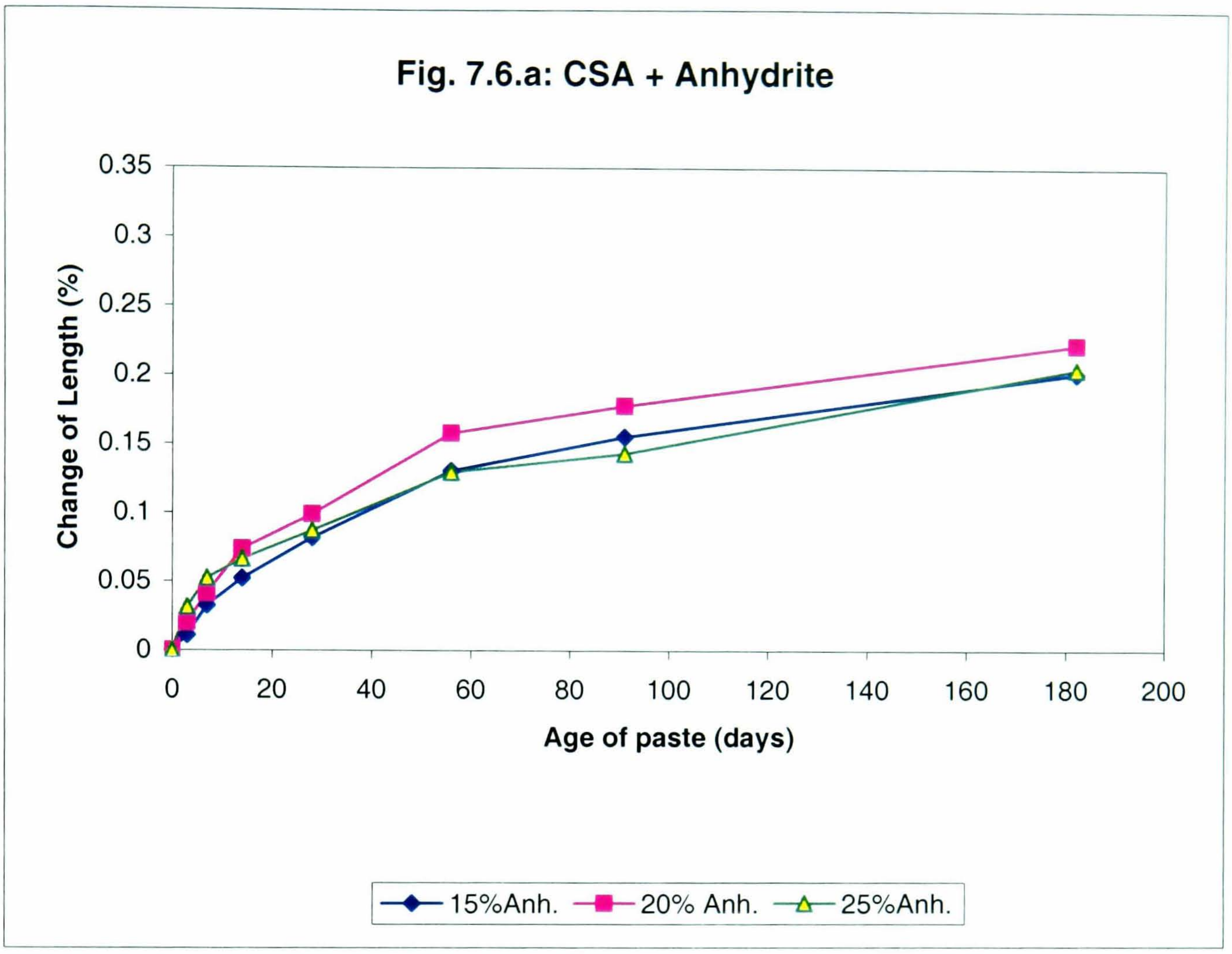


Fig. 7.6.a: CSA + Anhydrite

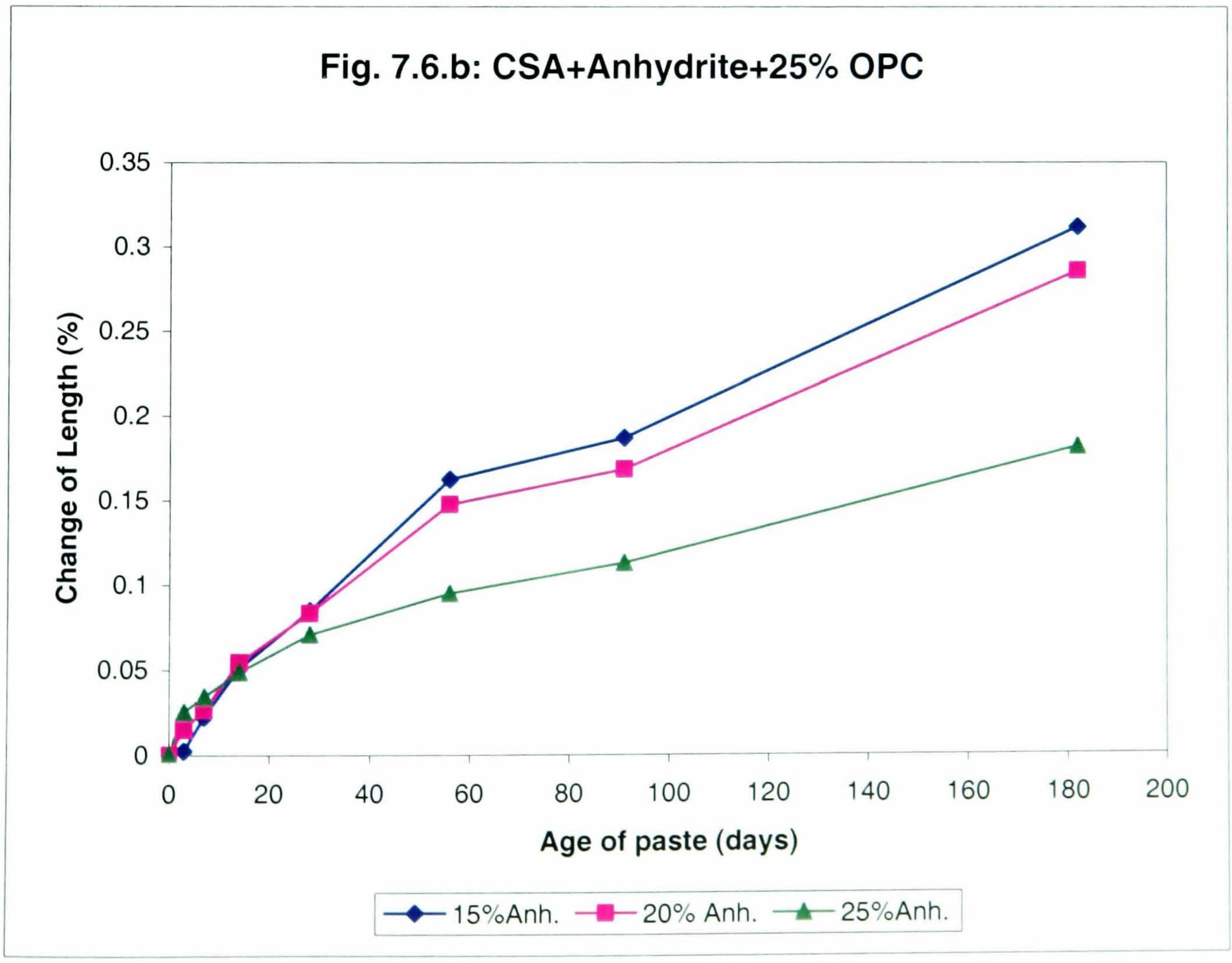


Fig. 7.6.b: CSA+Anhydrite+25% OPC

Fig. 7.7: Length Change Development of Manufactured-CSA Cement Cured in Water after Sealed for 28 Days

Fig. 7.7.a: CSA+Anhydrite

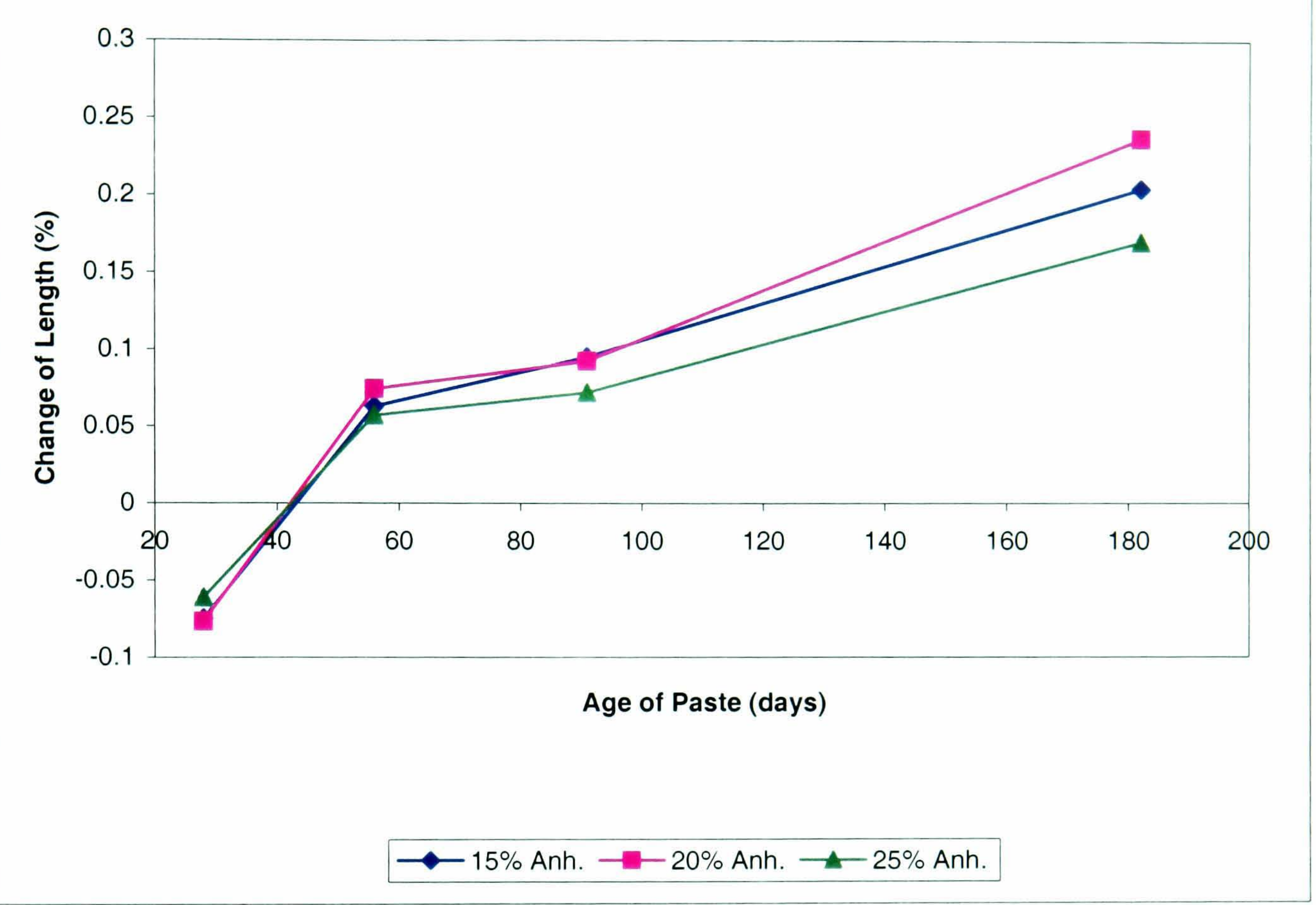


Fig. 7.7.b: CSA+Anhydrite+25% OPC

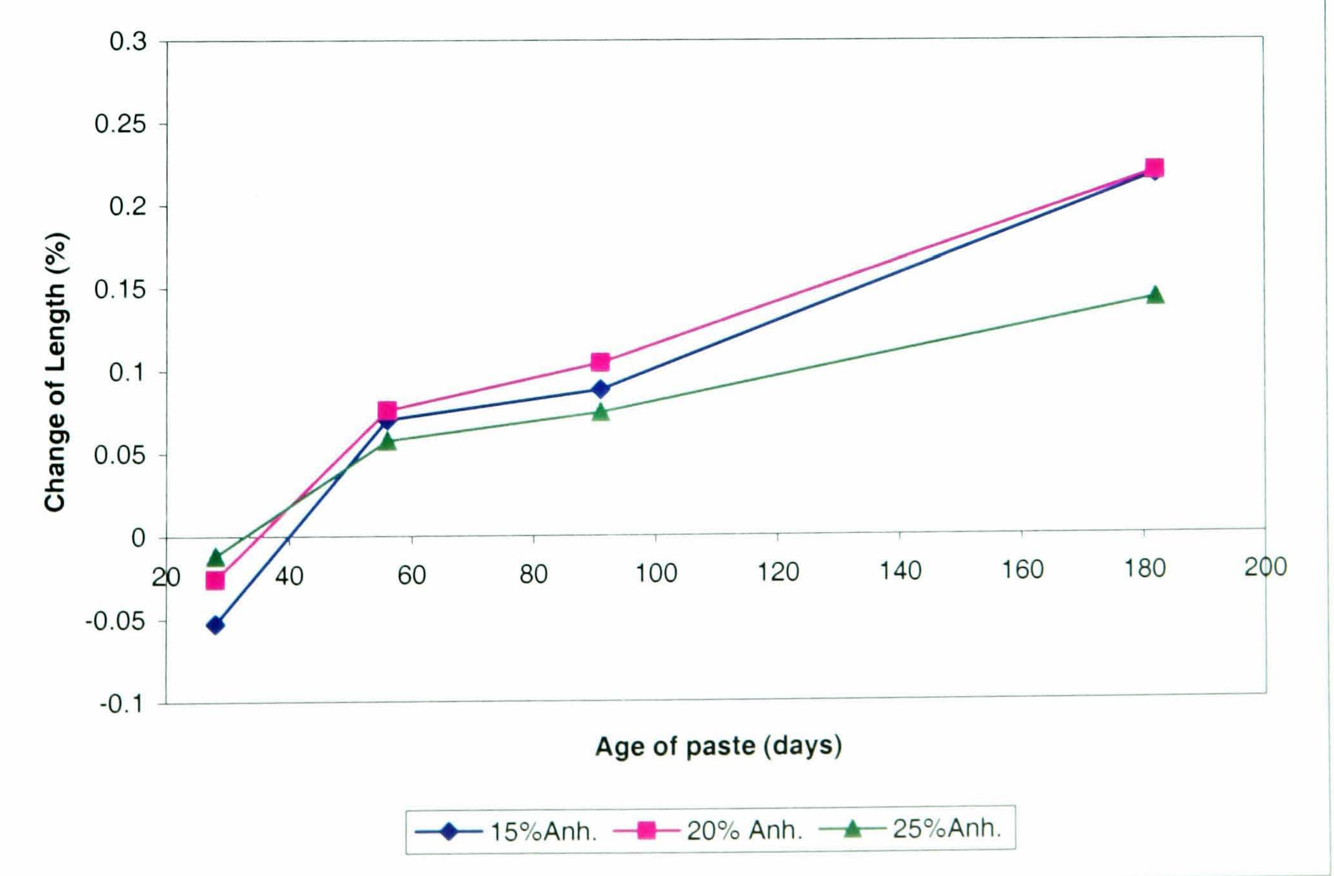
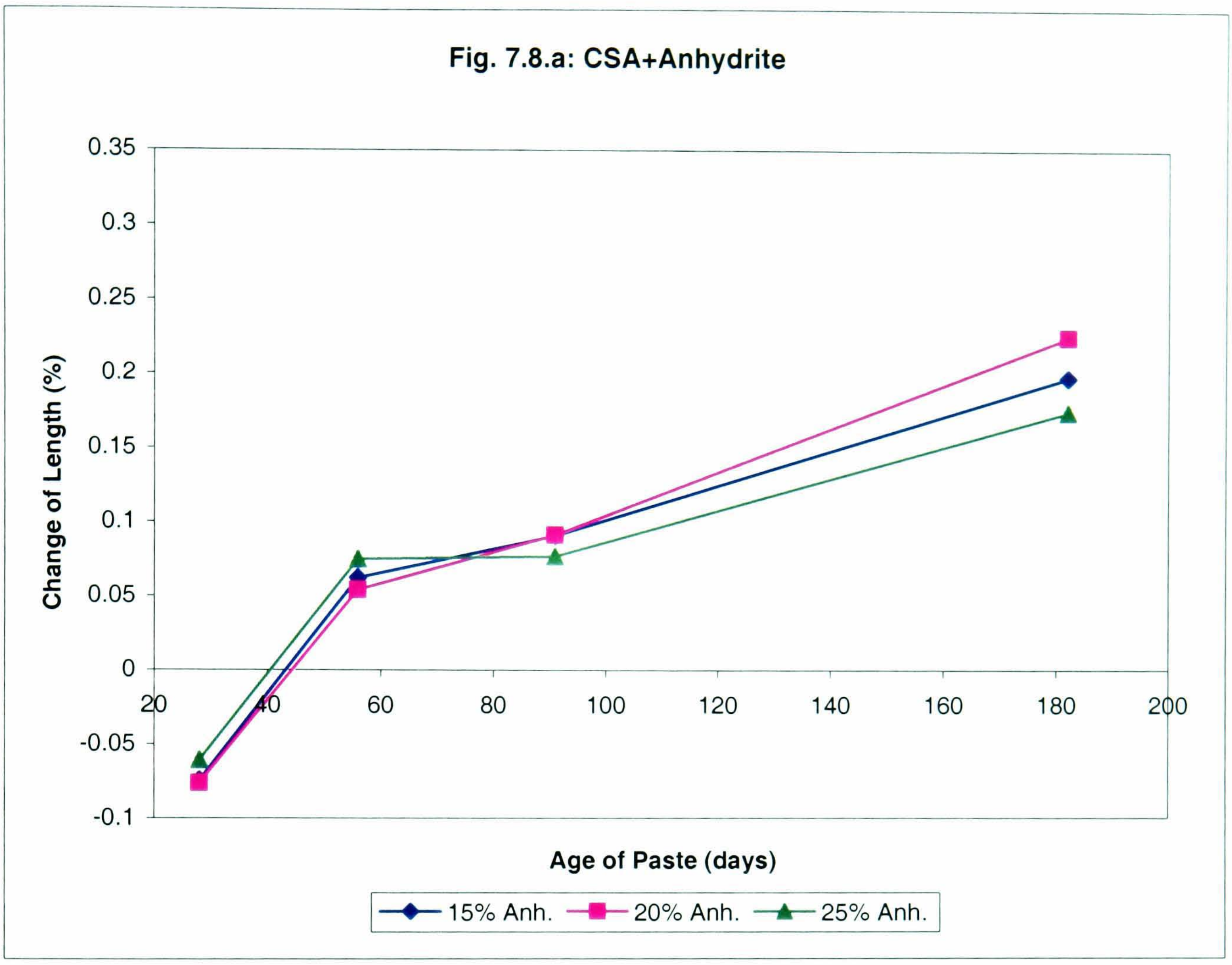


Fig. 7.8: Length Change Development of Manufactured-CSA Cement Cured in CaSO4 Solution after Sealed for 28 Days



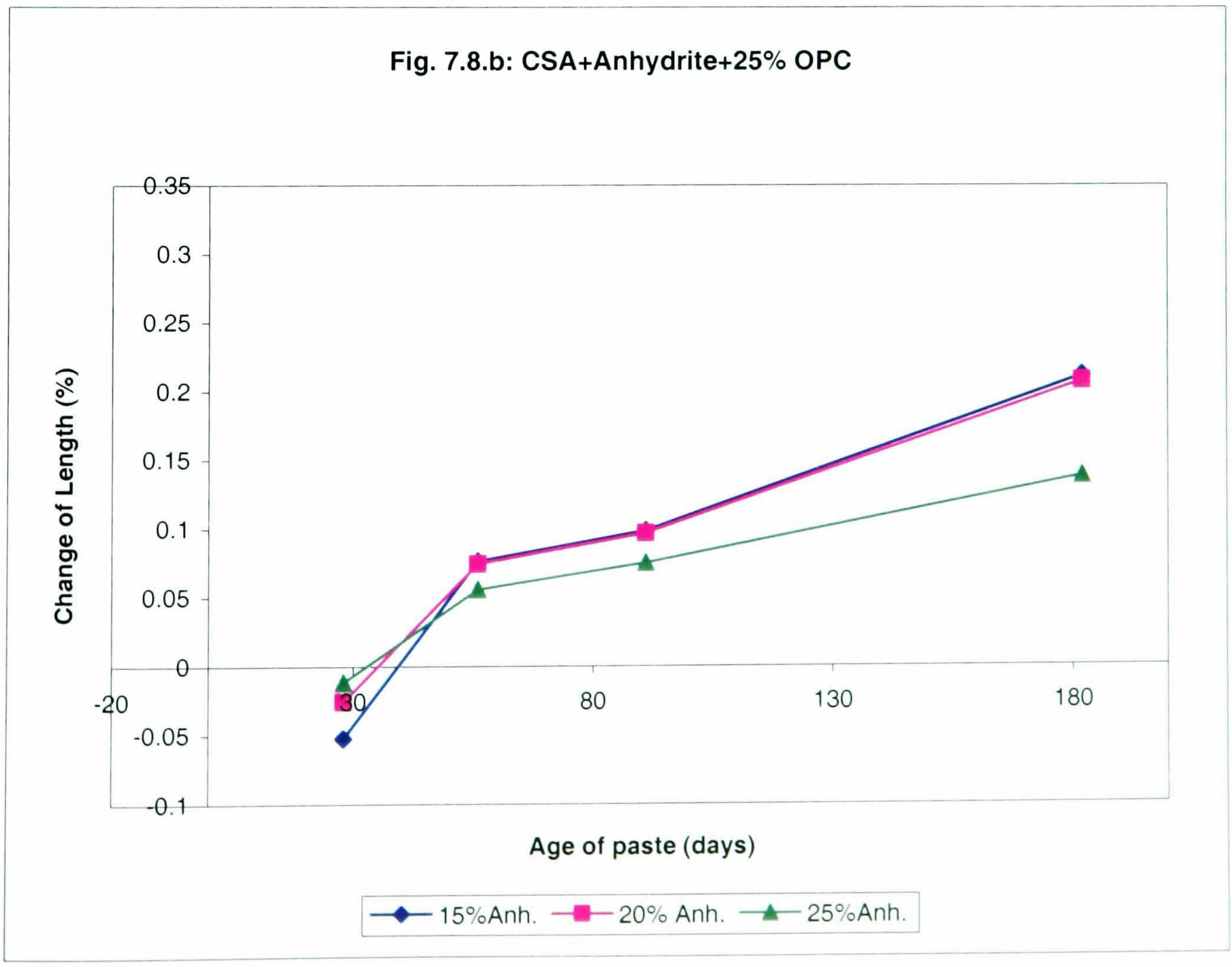


Fig. 7.9: Weight Change Development of Commercially Manufactured CSA Cement Sealed Directly After Demolding

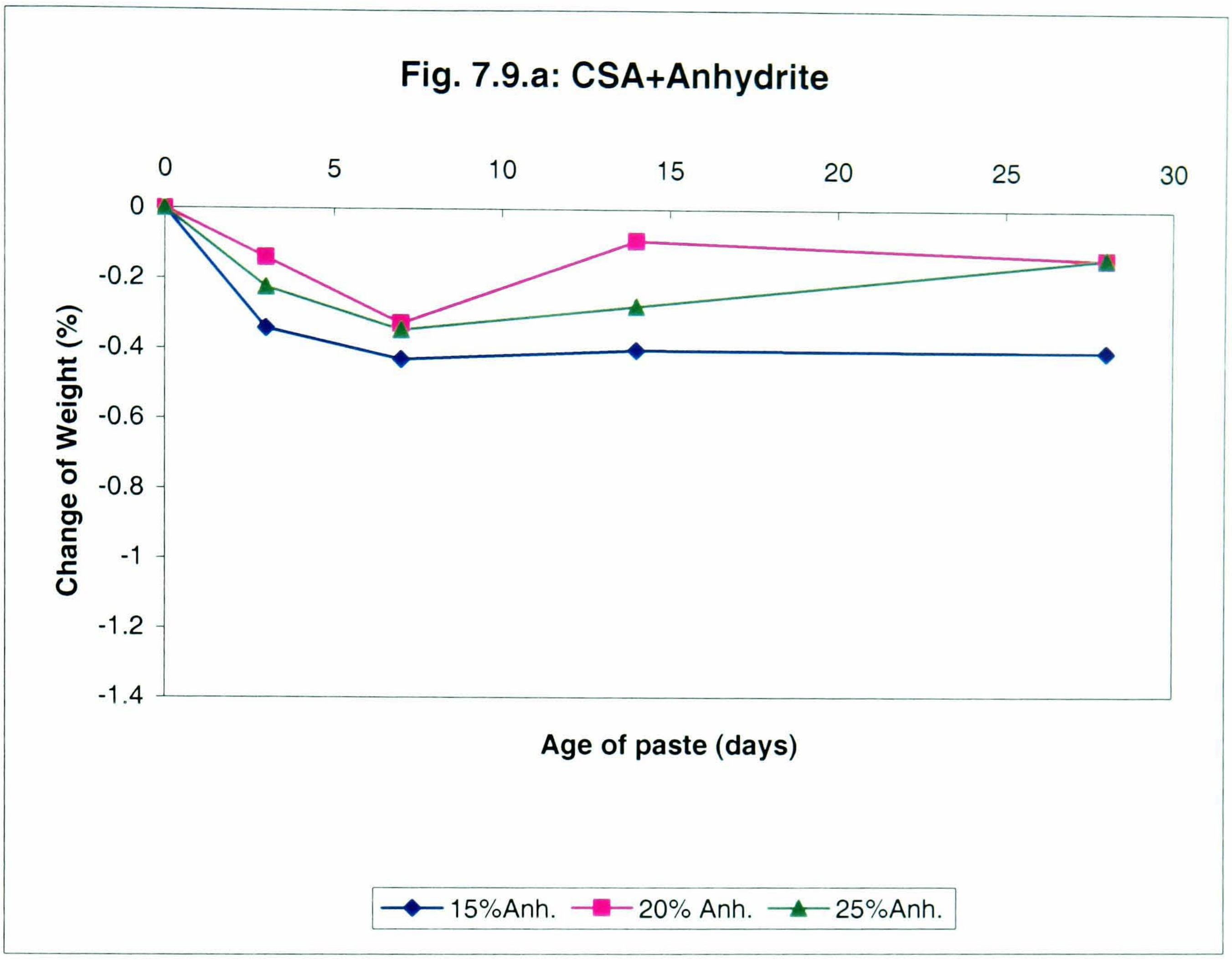


Fig. 7.9.a: CSA+Anhydrite

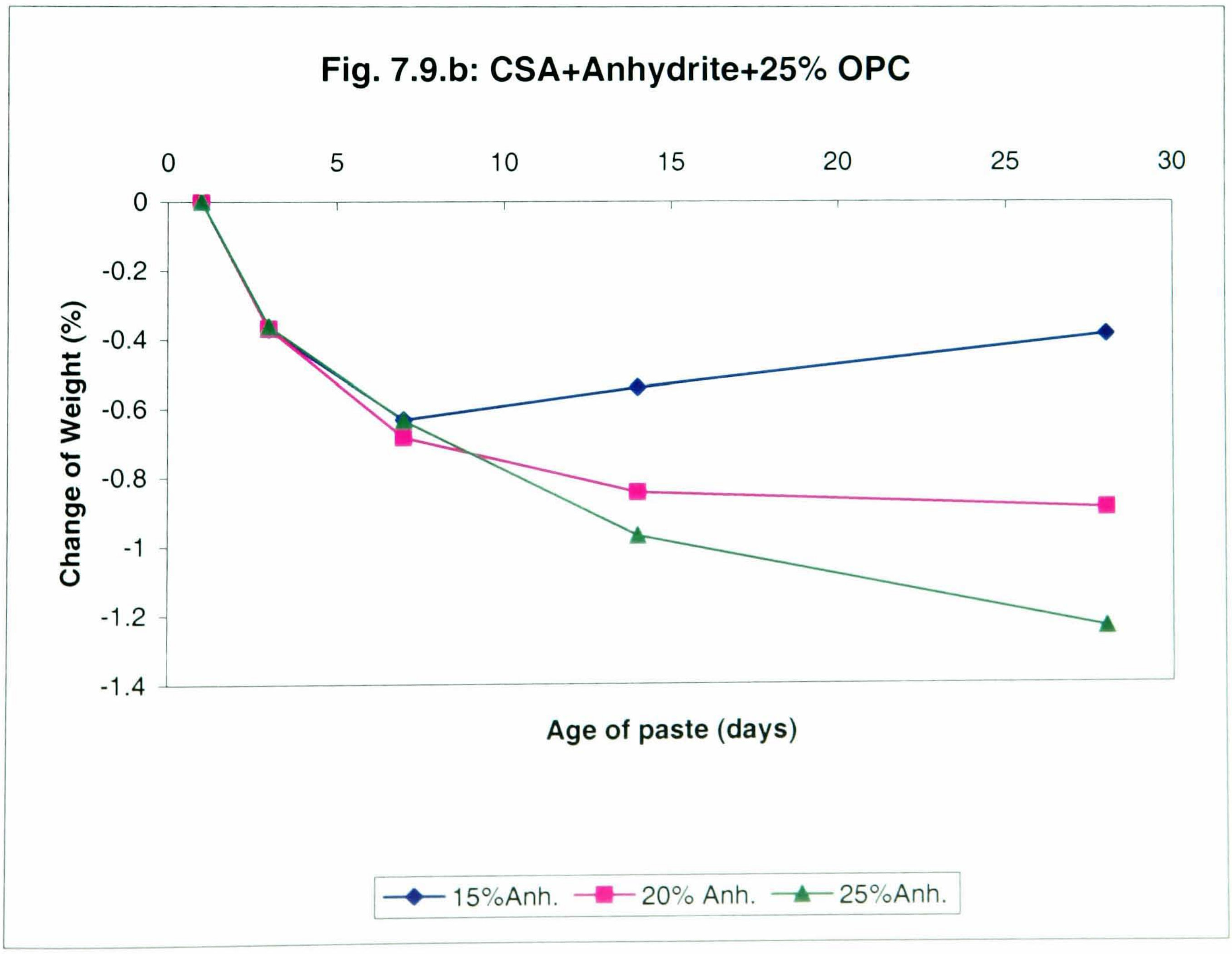


Fig. 7.9.b: CSA+Anhydrite+25% OPC

Fig. 7.10: Weight Change Development of Commercially Manufactured CSA Cement Cured in Water

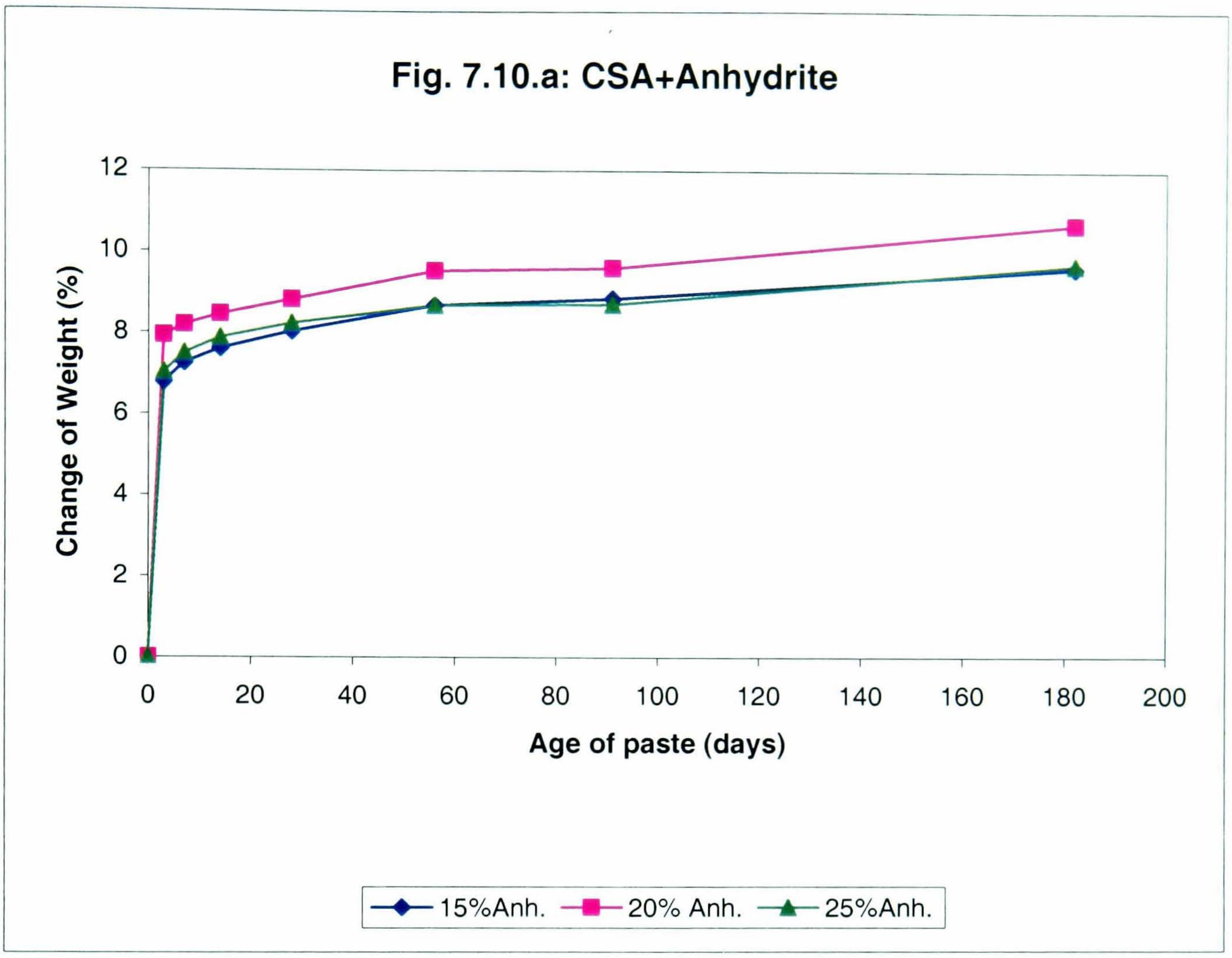


Fig. 7.10.a: CSA+Anhydrite

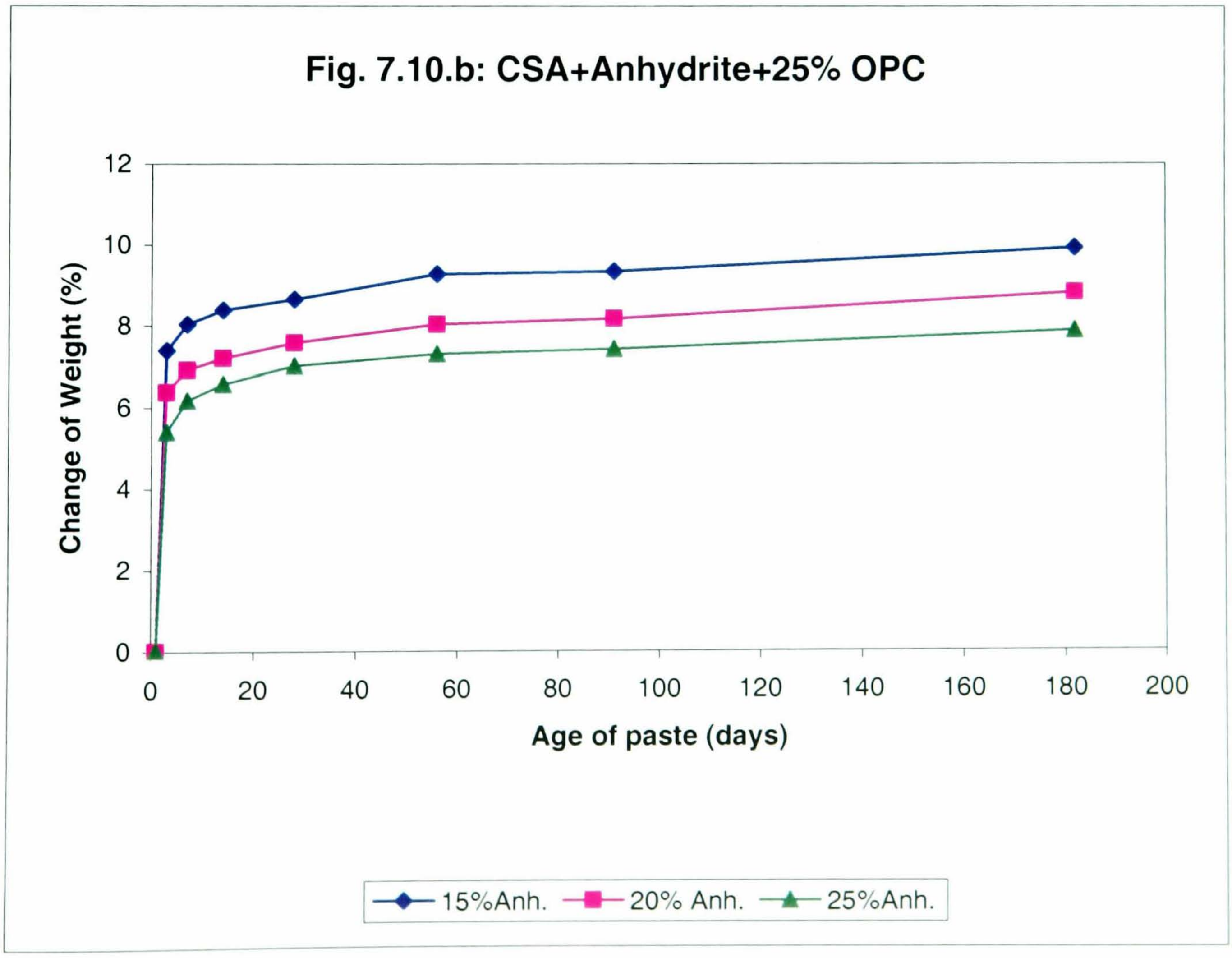
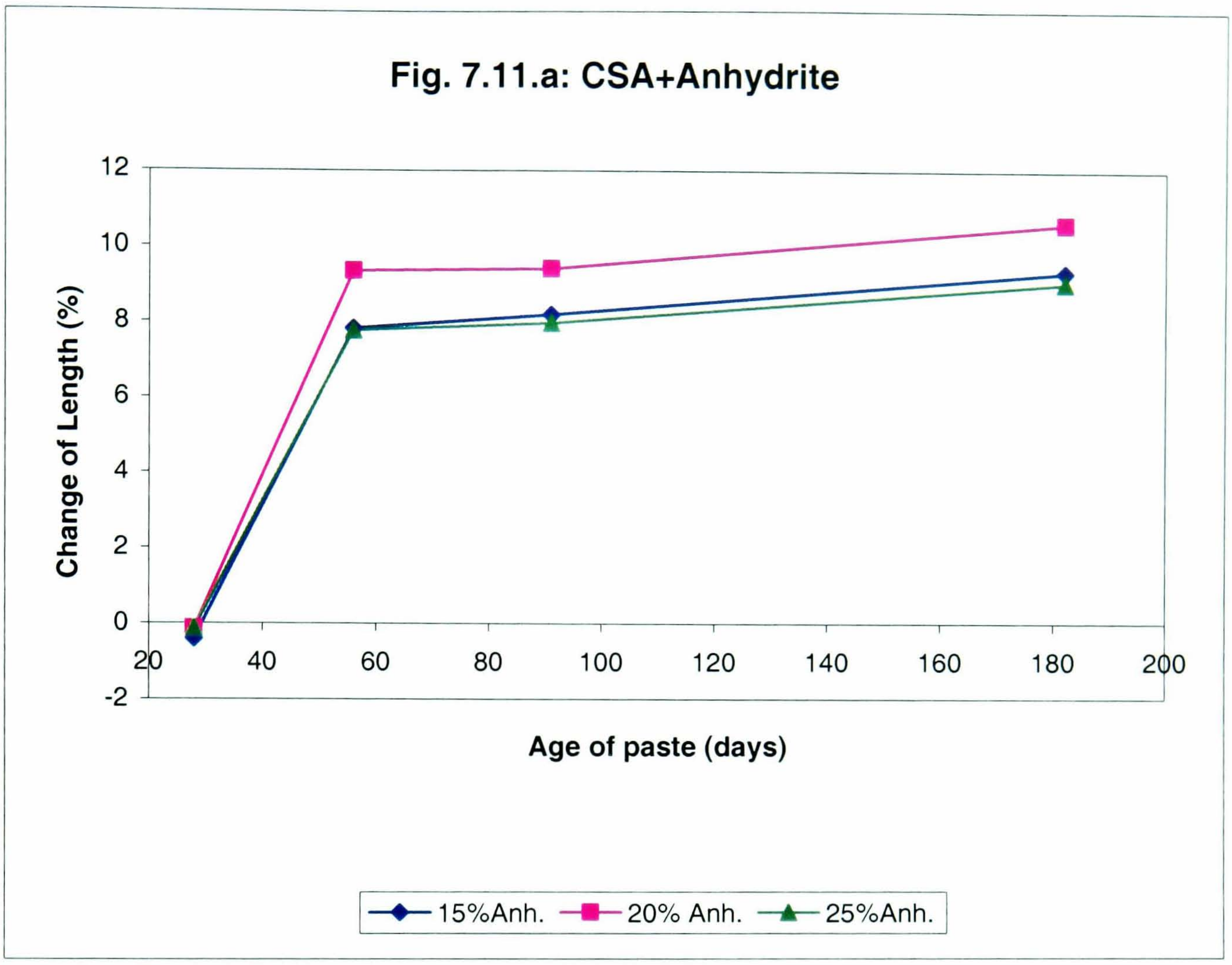


Fig. 7.10.b: CSA+Anhydrite+25% OPC

Fig. 7.11: Weight Change Development of Commercially Manufactured CSA Cement Cured in Water after Sealed for 28 Days



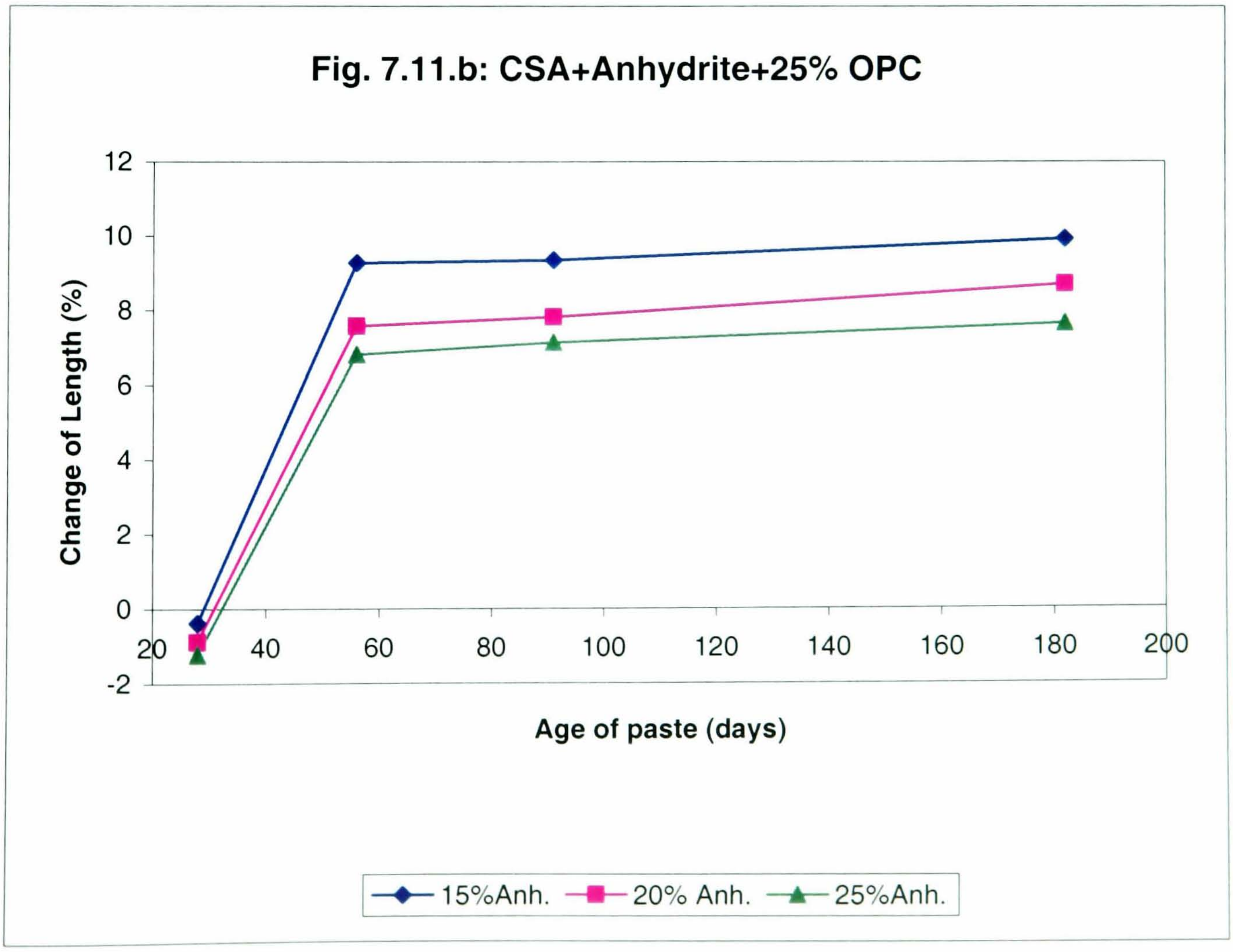


Fig. 7.12: Weight Change Development of Commercially Manufactured CSA Cement Cured in CaSO4 Solution after Sealed for 28 Days

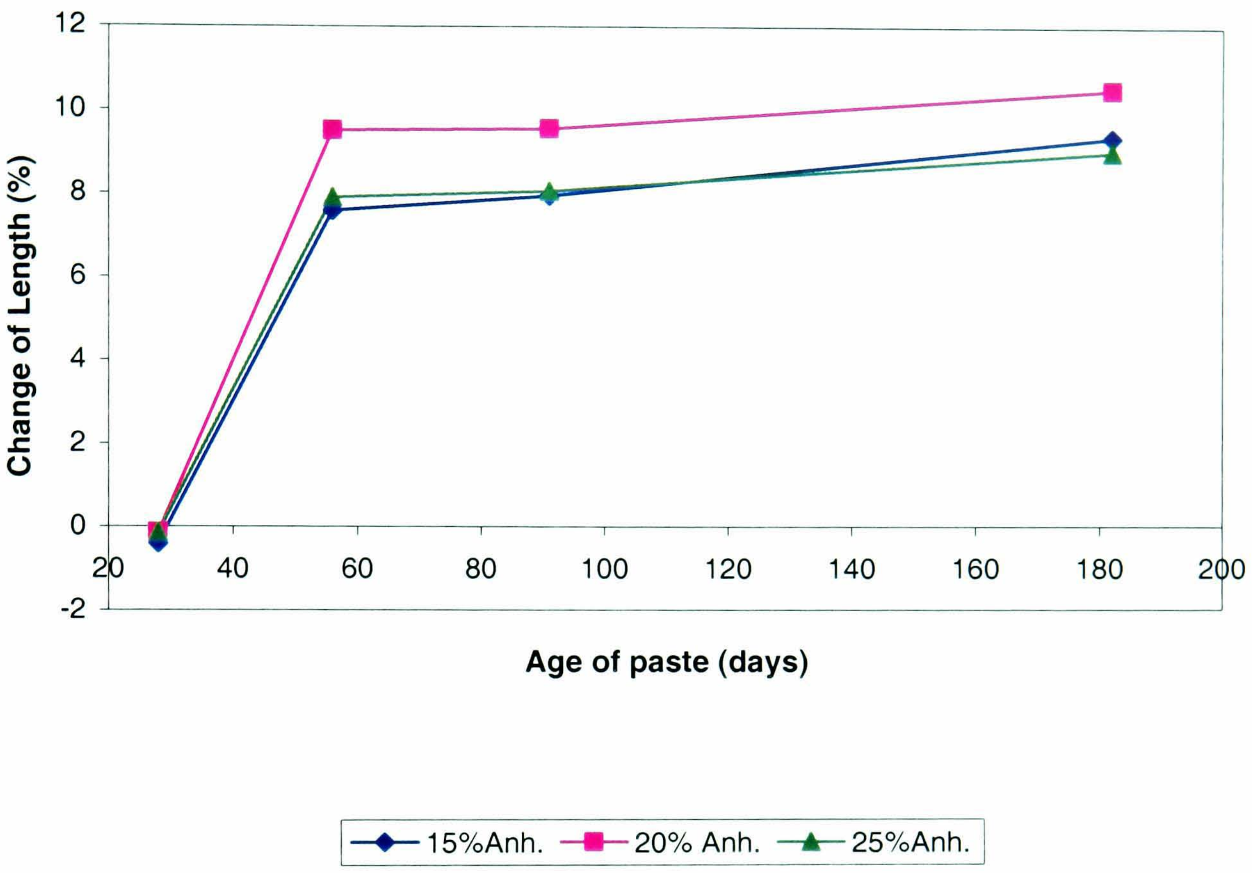


Fig. 7.12.a: CSA+Anhydrite

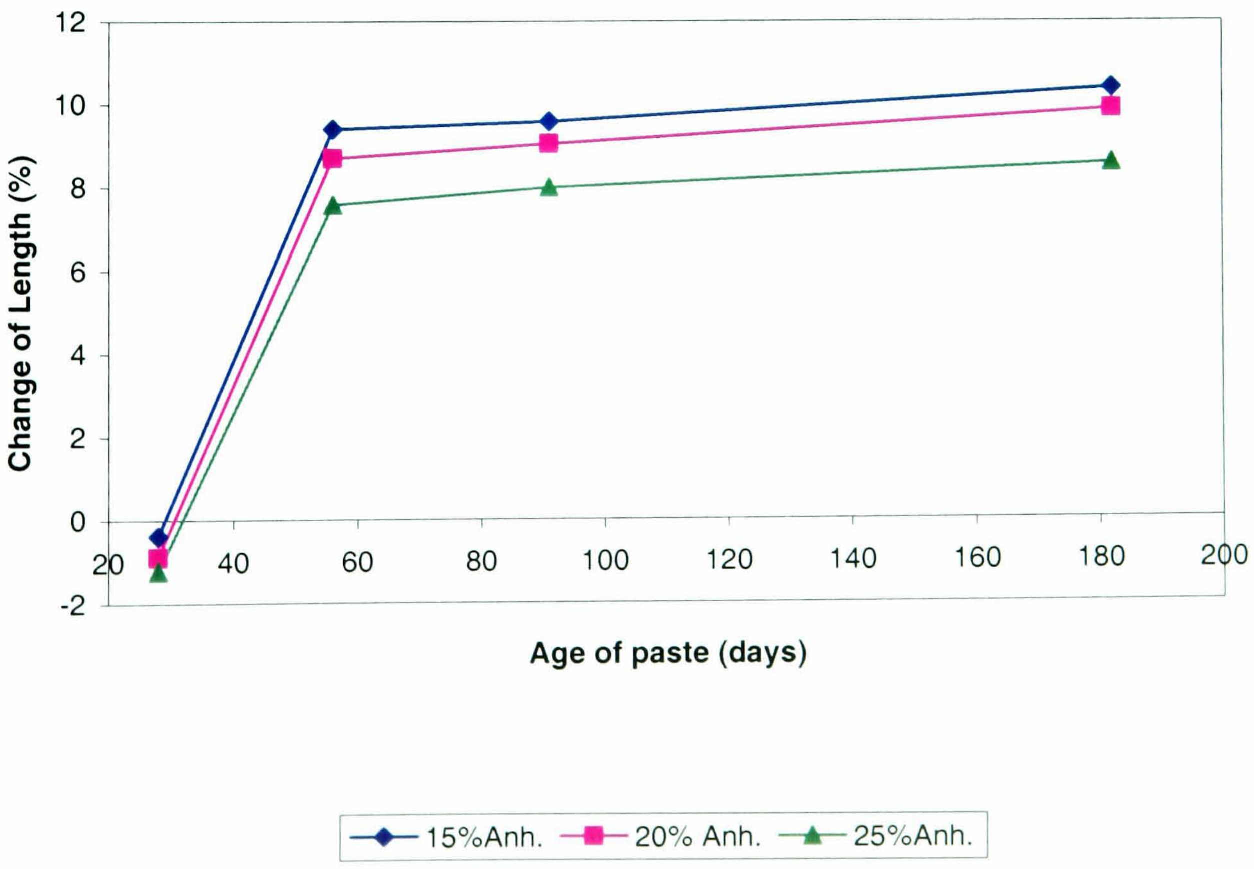
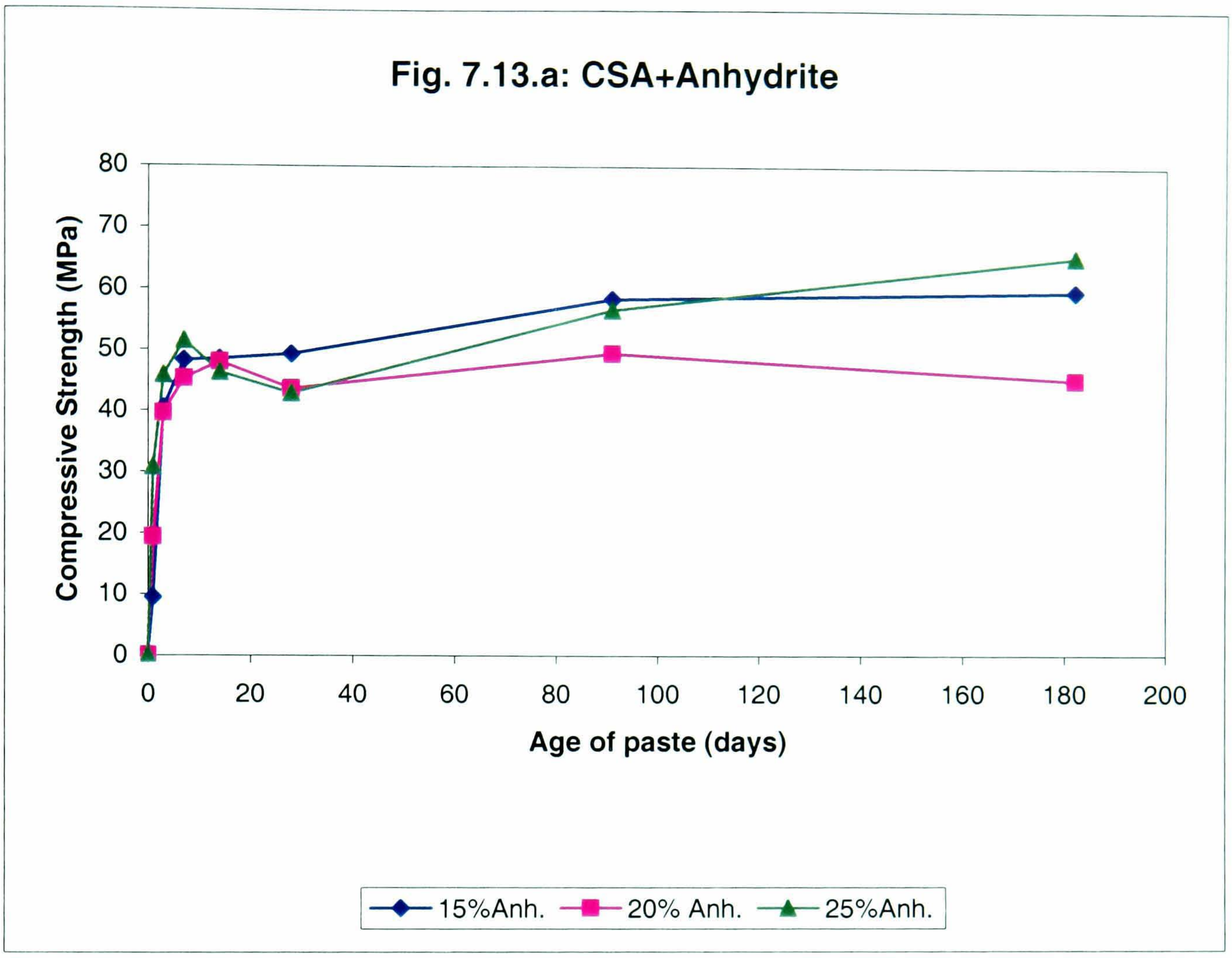


Fig. 7.12.b: CSA+Anhydrite+25% OPC

Fig. 7.13: Compressive Strength Development of CSA Cement Commercially Manufactured (Sealed Directly after Demolding)



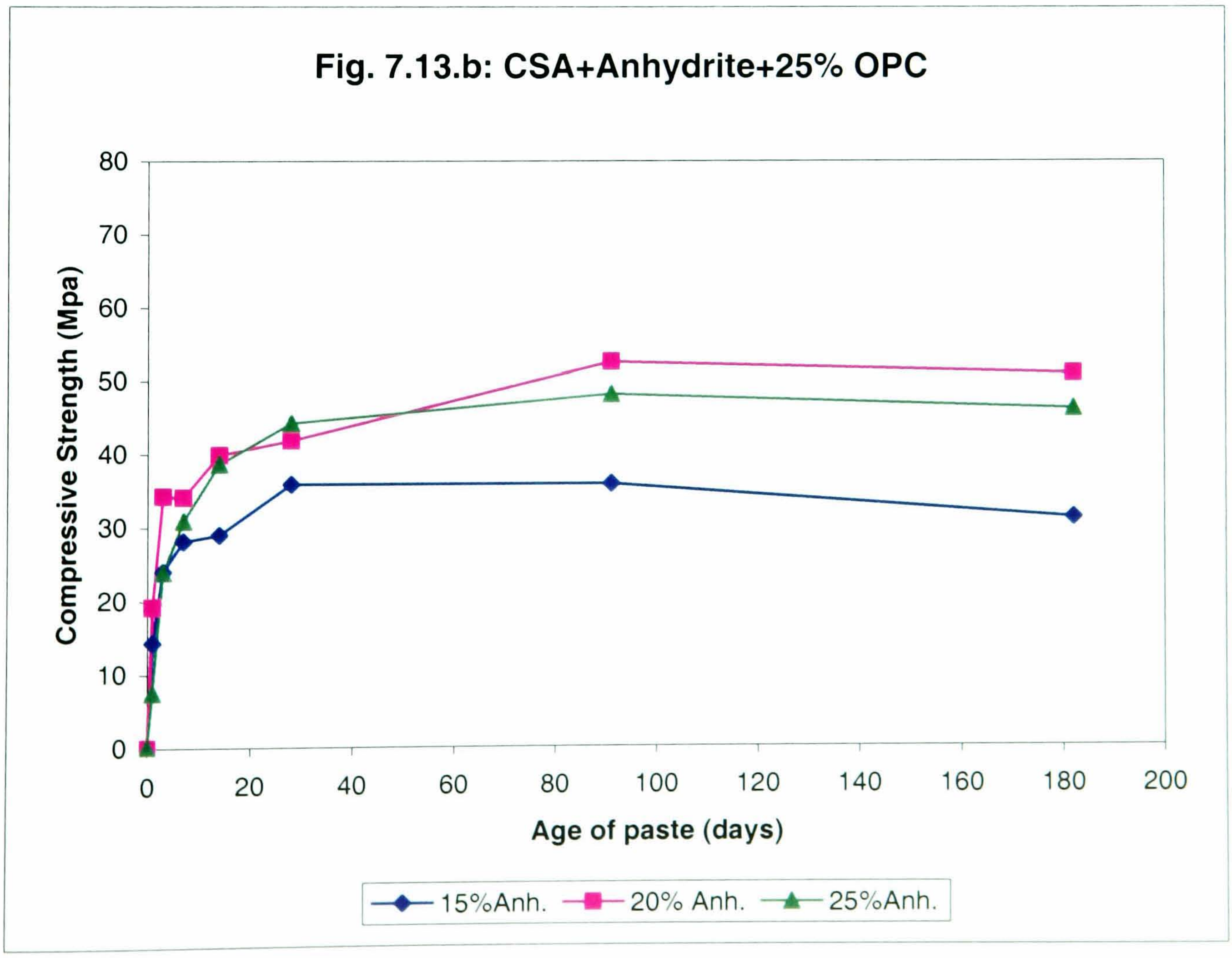
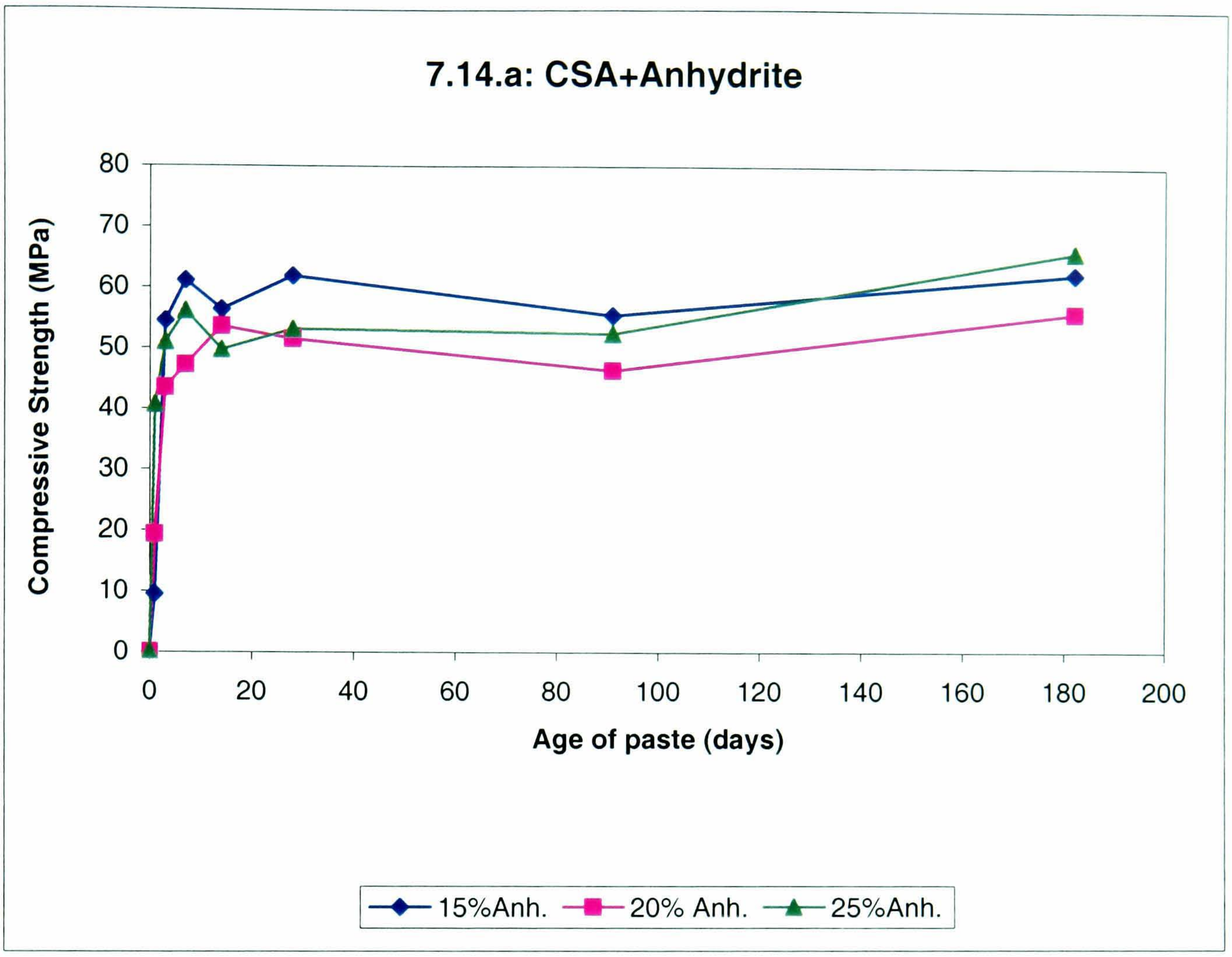


Fig. 7.14: Compressive Strength Development of CSA Cement Commercially Manufactured (Cured in Water)


7.14.a: CSA+Anhydrite

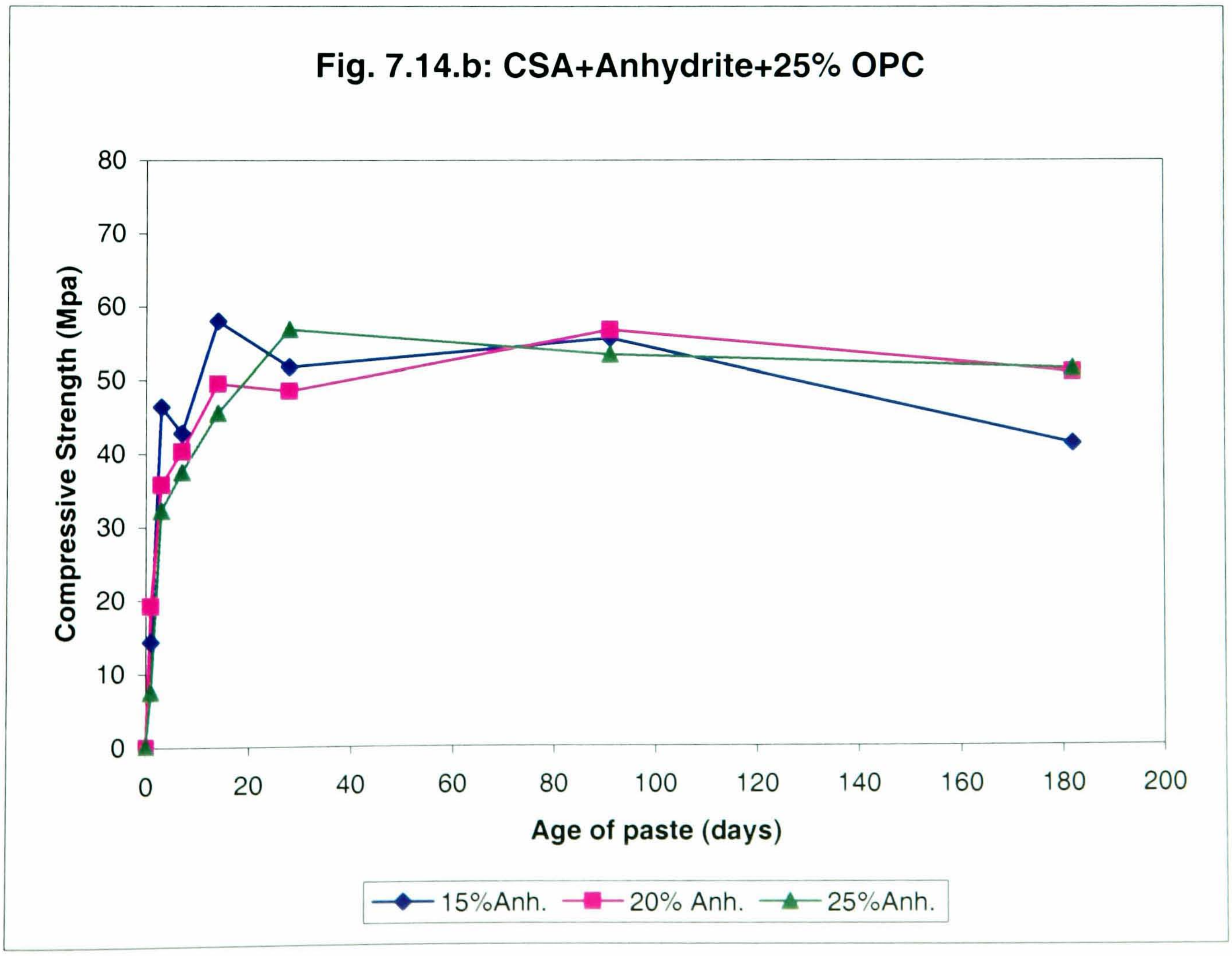


Fig. 7.14.b: CSA+Anhydrite+25% OPC

Fig. 7.15: Compressive Strength Development of Commercially Manufactured CSA Cement (Cured in Water after Sealed for 28 Days)

Fig. 7.15.a: CSA+Anhydrite

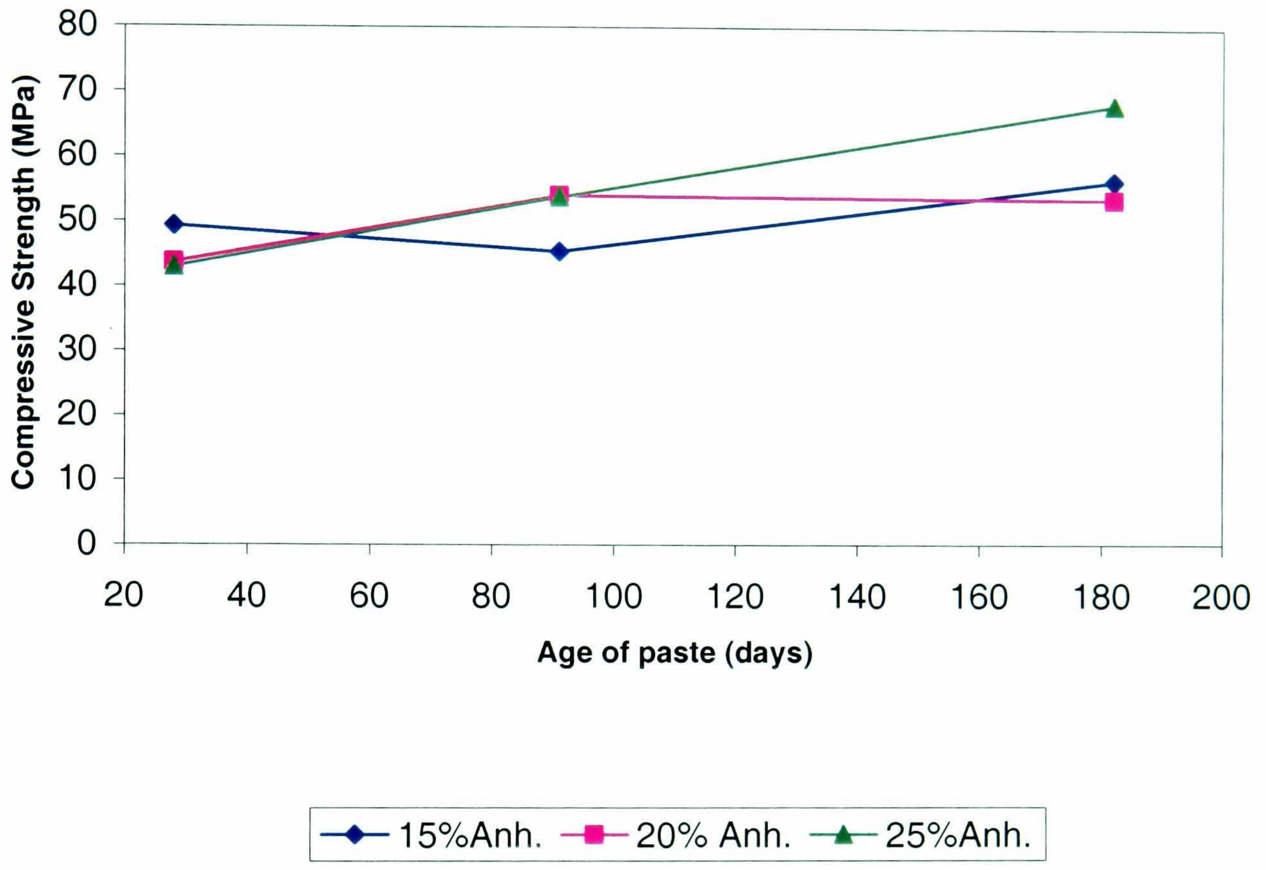


Fig. 7.15.b: CSA+Anhydrite+25% OPC

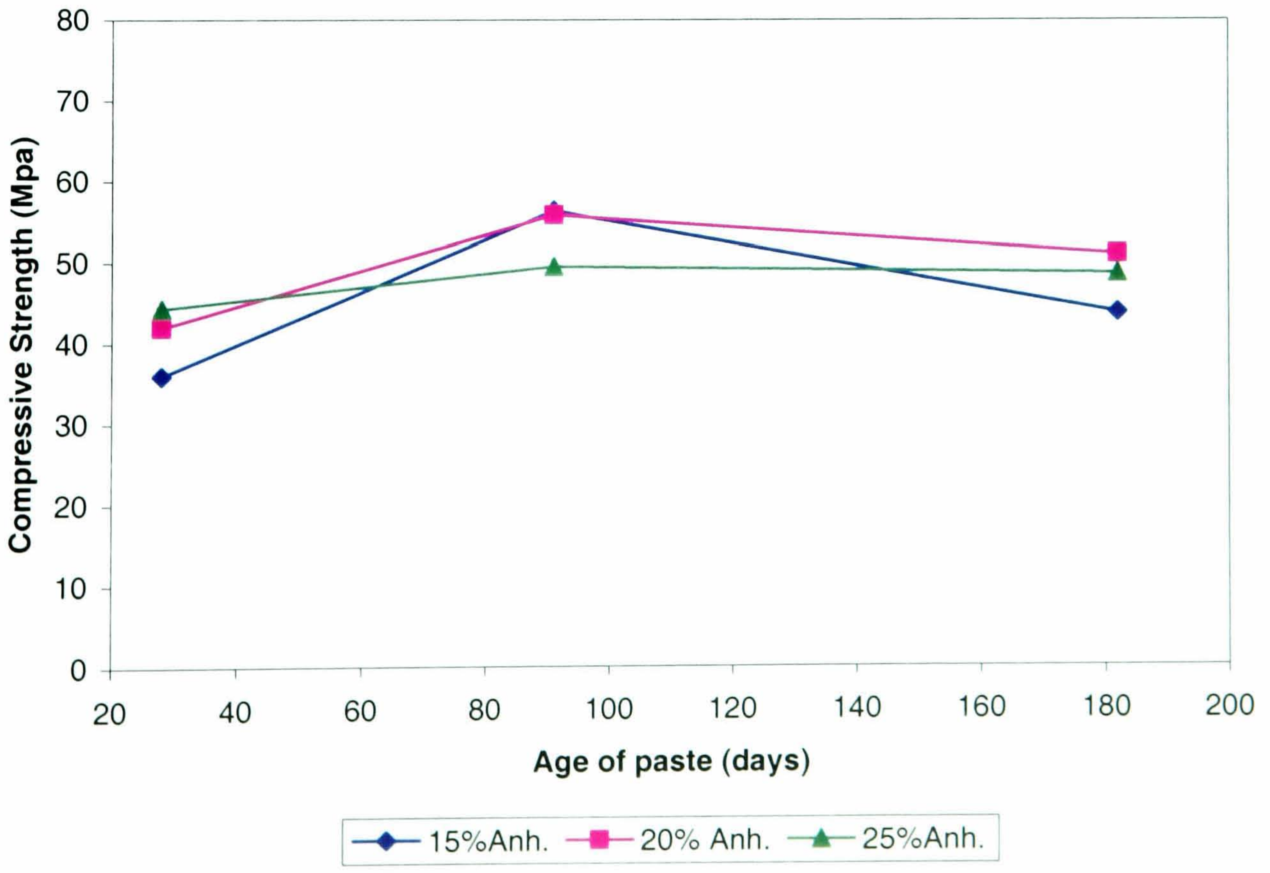


Fig. 7.16: Compressive Strength Development of Commercially Manufactured CSA Cement (Cured in $CaSO_4$ Solution after Sealing for 28 Days)

Fig. 7.16.a: CSA+Anhydrite

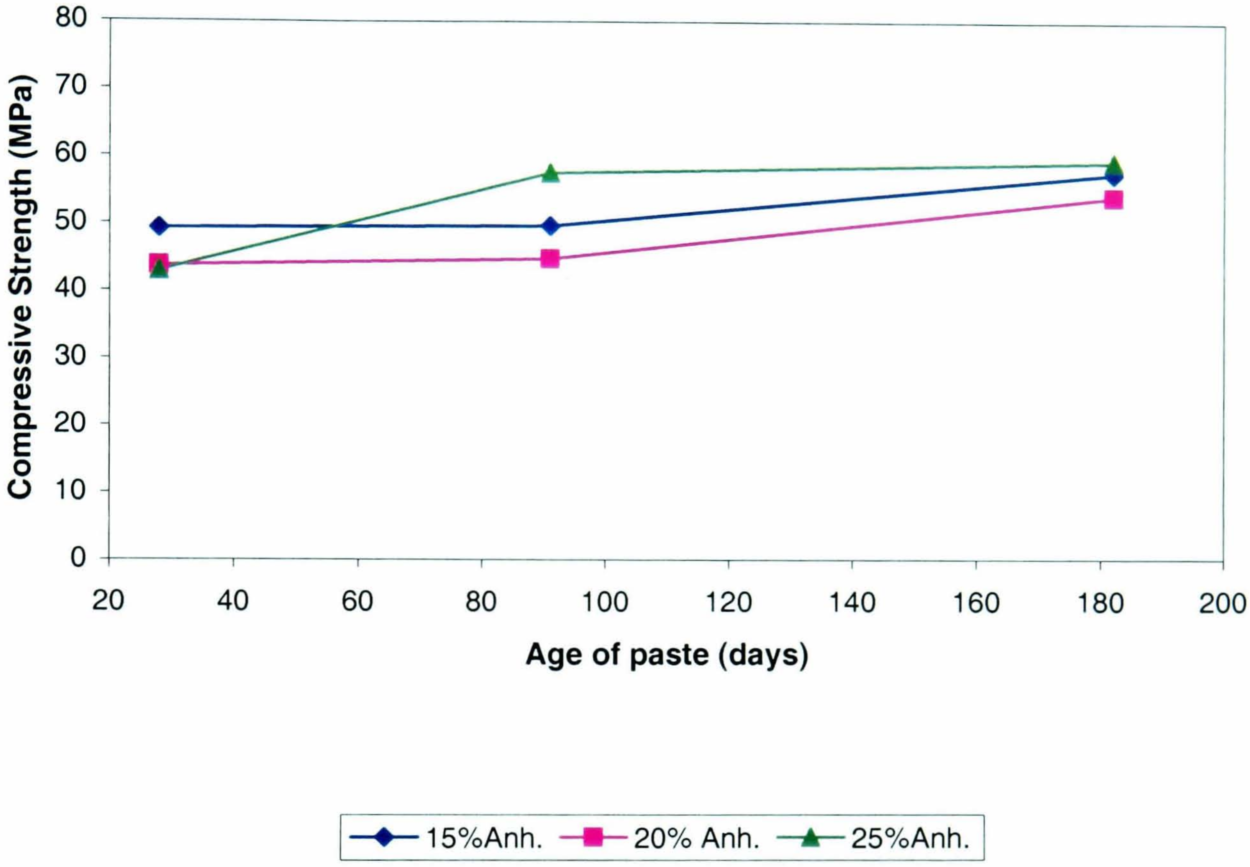
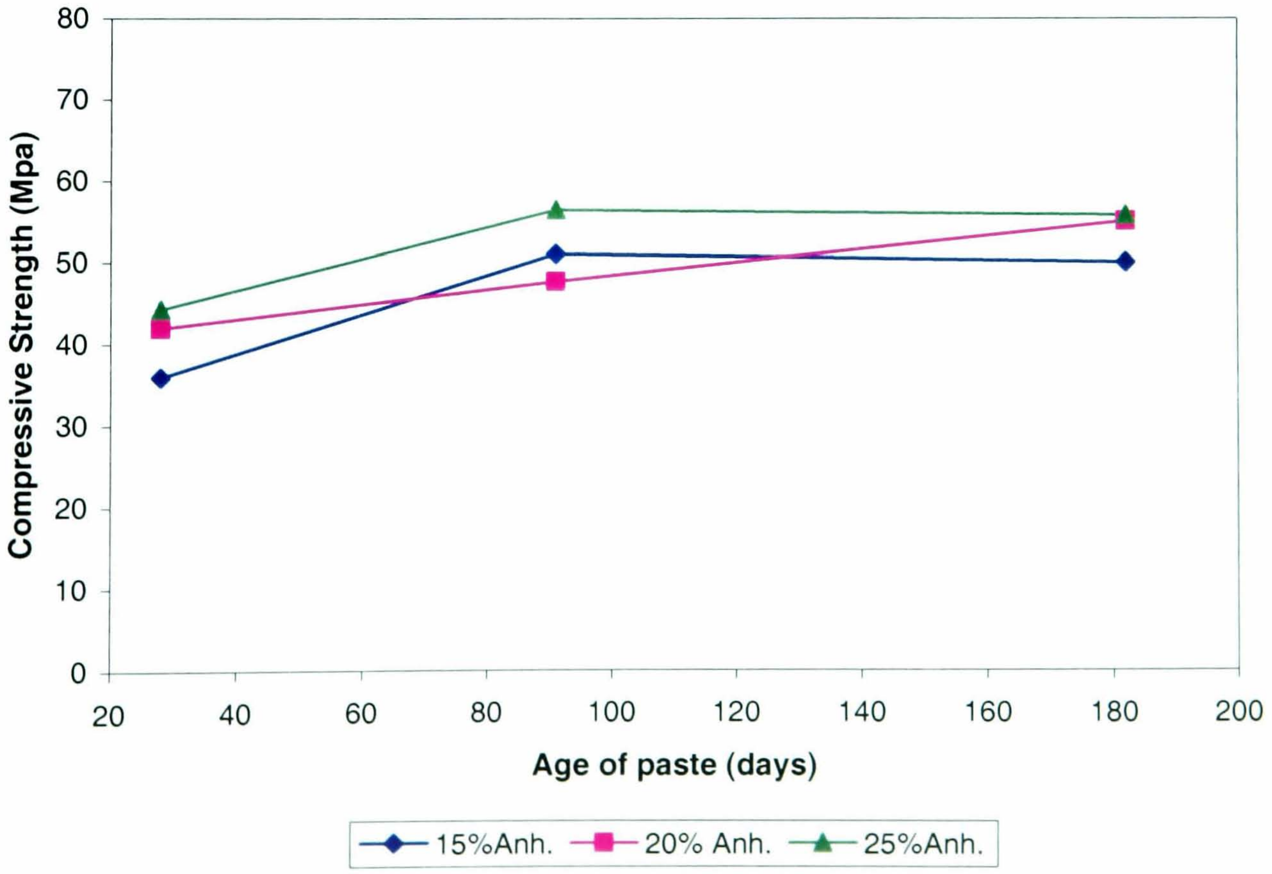


Fig. 7.16.b: CSA+Anhydrite+25% OPC



VIII

PROPERTIES OF CONCRETE MADE FROM COMMERCIALLY MANUFACTURED CSA CEMENT

8.1 Introduction

The investigation on the properties of concrete made with commercially manufactured CSA cement was based on the fact that the properties of the paste were not necessarily equivalent to those of the host concrete. The presence of aggregate particles influences the properties of the fresh and hardened concrete especially in the inter-action between paste and aggregates. The difference in nature between gel produced by hydrated OPC and the crystalline phase produced by hydrated CSA particles and anhydrite is expected to dictate the differences in the bonding characteristics of the two binders and hence, the difference in aggregate/cement interactions.

The investigation carried out on the properties of the CSA paste indicated that the expansion, which is the main problem in ettringite based binders, could be controlled by providing a sufficient amount of filler in the system. In the paste, the filler was provided by the anhydrous CSA cement and anhydrite particles or CSH and anhydrous OPC introduced into the system as cement replacement. In concrete, the presence of aggregates occupying a major part of the concrete volume is thought to reduce further expansion as the aggregates act as a constraint to the expansion of ettringite. The earlier strength development and the high strength produced by the CSA cement paste give CSA cement an advantage over OPC. This can be exploited to improve the efficiency and effectiveness of construction works, as formworks and scaffolding can be removed at an early age.

The investigation on properties of CSA concrete has considered the effects of different anhydrite contents, OPC replacement and different w/cm as parameters that might influence the properties of concrete. For comparison, reference mixes made with OPC at the same level of w/cm ratio and water content were used. The effects of curing conditions on properties of concrete were also examined in this investigation. The properties of concrete under consideration were those of fresh concrete including setting time and workability, and those of hardened concrete including expansion, strength and durability related properties. The design of the concrete mixes has already been described in 3.2.2. The mix proportions of concrete of w/cm ratio equal to 0.50 at different anhydrite contents are given in Table 8.1, while the compositions with a variety of w/cm ratios are available in Tables 8.2 and 8.3.

8.2 Properties of Fresh Concrete

8.2.1 Workability

The workability of CSA cement was measured by slump test, loss of slump and the two-point test (See section 3.3.3.1.2).

8.2.1.1 Slump Test

As the calculation of the mix composition was based on the absolute volume, the volume of the fine material in the CSA concrete mixes was slightly higher than the OPC reference mix. Coupled with the higher specific surface of the CSA cement, the concrete mixes were supposed to be more water demanding compared to the reference mix. In fact, the opposite case was found. At w/cm=0.50 (see Table: 8.1) and at the same water content, the mixes containing the CSA cement and anhydrite only were less water demanding than the reference mix. It was shown by higher slumps produced by these mixes compared to the reference mix. A less amount of water and then a less amount of cement was required to produce the concrete with the same level w/cm ratio and the same slump.

The incorporation of 25% OPC into the system, however, slightly reduced the slump of the concrete. The lowest slump was produced by the mix containing 15% anhydrite and 25% OPC (Mix RC15). The reduction of slump due to the incorporation of OPC into the system, however, was within the limit of the test variation. The effect of different anhydrite contents on the slump was not so pronounced. The CSA mixes containing 25% anhydrite produced the higher slump for both with or without the incorporation of 25% OPC (Mix RC25 & mix RF25, respectively). It seems that the amount of $CaSO_4$ in the mix affected the slump of concrete as the SO_4 ions acted as water reducing agents (Tattersall and Banfil, 1983).

Increasing the w/cm ratio to 0.70 with the same water content did not produce a significant difference in slump test results and similarly when reducing the w/cm ratio to 0.40. This is because the change in the fine material's content in the mix was not so significant as the increase or the decrease in cement volume, due to varying the w/cm, was accompanied by a decrease or increase in the volume of sand.

At very low w/cm ratios (w/cm=0.30), polycarboxylate based superplasticiser was applied into the mix in order to maintain a reasonable cement content and thereby at a low water content achieving a reasonable workability. It is clearly seen that the CSA cement responded to the superplasticiser much better than the OPC. To produce the same level of slump, the CSA concrete only required 0.40% superplasticiser, by weight of cement, compared to 0.75% by weight of cement for the OPC mix. At that composition, the CSA cement produced a more flowing but stickier concrete.

8.2.1.2 Loss of Slump

Although CSA cement has been proven to be able to produce higher slump at the same level of w/cm ratio and water content, the lost of slump is one of the most important aspects to be considered in using relatively new binding material such as this cement. The ability of concrete to retain a certain level of slump during a reasonable period of time is required to guarantee that the concreting process is finalised while the concrete is still workable.

The monitoring of loss of slump was conducted on the mixes with w/cm ratio equal to 0.50 and at the same water content. The variations consisted of OPC as reference (mix REF), CSA cement with 15% and 25% anhydrite and CSA cement with 15% and 25% of anhydrite with 25% OPC replacement. The results are shown in Fig. 8.1.

Generally, CSA concrete underwent a more rapid loss of slump compared to the reference mix. Starting with a very high slump, the CSA concrete mix RF25 experienced loss of slump from 170 mm to 40 mm within 90 minutes and maintained the slump at the same level for a further 60 minutes, while the CSA concrete mix RF15 anhydrite dropped the slump from 150 mm to 40 within 120 minutes but consistently lost the slump up to 0 mm after 150 minutes of mixing. The times required to reach the slump of 40 mm, a value which is thought to be still workable for both mixes, were sufficient to finalise the concreting process in practice.

The CSA concrete mixes containing 25% of OPC rapidly lost their slump and slumps of 40 mm were reached only within 30 minutes. The mixes are considered not suitable for conventional concreting procedures and using conventional concreting equipment.

8.2.1.3 Two-Point Test

A two-point test was carried out in order to develop more understanding of the effect of using CSA cement on workability of concrete. The two-point test was conducted on the same mixes as those used for loss of slump. The test results are presented in Fig. 8.2 and Table 8.4.

Basically, for CSA concrete, the yield value was consistent with the slump of concrete. A higher slump of CSA concrete produced a lower yield value. It is an indication that in the same binding material, the yield value was relative to the consistency of mix. The plastic viscosity did not show a clear relationship with the binding material used. The mix RF25 produced the highest plastic viscosity. This is probably because of segregation of concrete under the torsion force due to the very high slump. Overall, the plastic viscosity of CSA concrete was not much different to the reference mix. It might be said that the CSA concrete can be as workable as the OPC concrete when compared on an equal basis.

8.2.2 Initial Setting Times

Even if the initial setting time of concrete was performed on mortar and not on the parent concrete, the data obtained was still more representative than the setting time of cement paste. As the initial setting time was defined as the resistance to penetration of a standard penetrometer (ASTM C 403-92) reaching 3.5 MPa where the concrete becomes too stiff to be vibrated, the information of the initial setting time is very valuable in concreting work especially in determining the time available for the concreting process to be finalised.

The setting time was conducted on the same mixes as those used for loss of slump. The test results can be seen in Table 8.1. The initial setting times of CSA concrete containing anhydrite without OPC replacement required on average twice as long as the times required for the reference mix. In practice, this longer of setting time of the CSA fresh concrete was a concern especially in protecting the water movement in the fresh concrete caused by the evaporation leading to plastic shrinkage and also in determining the time required before the curing covers can be applied. The use of curing compound is recommended to deal with this situation.

The introduction of 25% OPC into the system accelerated the initial setting times. The setting time of the CSA concrete containing 25% anhydrite with 25% OPC was slightly longer than the initial setting time of the reference mix while the initial setting time of concrete containing 15% anhydrite with 25% OPC was slightly faster than that of the reference mix. There should be a value between those anhydrite contents at which the initial setting time of CSA concrete containing 25% OPC equals that of the reference mix. As the initial setting is predominantly influenced by the initial chemical reactions in the system, the presence of calcium hydroxide in the mix produced by the hydration of C_3S is most likely to be responsible for accelerating the initial setting time of CSA concrete containing OPC.

8.3 Properties of Hardened Concrete

8.3.1 Expansion of CSA Concrete

The expansion of the CSA concrete was assessed by monitoring the length change and the weight change of concrete prisms at different ages and under different curing conditions. The curing regimes applied were:

- continuous curing in water after demolding
- curing in water after sealing as cast for 28 days
- curing in water after storing for 28 days at room temperature and 80% humidity.

The expansion test was conducted on the same mixes as those used for loss of slump. It was carried out on concrete prisms as described in 3.3.3.2. The test results are plotted in Fig. 8.3 and 8.4.

8.3.1.1 Length Change of CSA Concrete

As expected, the length change of the CSA concrete was much lower compared to that of CSA paste samples. The fact is that at the given composition, only approximately 15% of concrete volume is occupied by cement and the rest is filled by aggregates (67%) and water (17%). The predominant aggregates in the system provided a considerable constraint for expansive-prone ettringite. It is thought that the voids often occurring along the interface between mortar and aggregates, due to settlement after compaction provided the space for the expansive ettringite.

Considering Fig. 8.3.a, the highest length change was found about 0.015% in the worst curing condition, where the samples were continuously cured for 6 months in water after demolding. This value of length change was on the safe side as far as the length change for structural concrete is concerned. This length change was produced by the CSA concrete mix RF15 and mix RF25. At the same curing condition and the same age, the CSA concrete mixes with OPC produced lower length changes. For commercially manufactured CSA concrete mix RC15, the length change of samples was approximately the same as that produced by the reference mix. There was no indication that a significant expansion took place before 3 months in all concrete samples continuously cured in water. In fact, at the earlier ages, most concrete samples but the reference mix underwent shrinkage.

The immersion of samples after sealing for 28 days gave lower expansions at the values of around 0.005% at 6 months (see Fig. 8.3.b). Under sealed conditions, samples experienced expansion during the first 3 days and this was followed by contraction. A similar pattern was also found for samples cured in water after 28 days curing at room temperature and 80% humidity (see Fig. 8.3.c). Under this condition, samples mix RC15 underwent the highest expansion after 6 months curing. The expansion of this mix was about 0.015%. The expansions of the rest of the concrete samples were well below this value. For both curing conditions, the expansion measurements for the reference samples never recovered from the earlier contraction, so that the total length change was still below zero.

8.3.1.2 Weight Change of CSA Concrete

The results of monitoring weight change of samples under different curing conditions are given in Fig. 8.4 a, b, and c. Fig, 8.4.a shows the concrete samples cured continuously in water after demolding. The immersion after 3 days in water gives the figure of absorptive characteristics of concrete samples. It is clearly seen that at the same w/cm ratio and the same water content, the reference concrete gives less gain of weight compared to CSA concrete samples. In theory, with the water demand for hydration being less than the water available for the mix in the case of the reference mix, this concrete only absorbed the water from the mix to replace the water used for hydration. At the same time, with the water demand for hydration being more than the water available for the mix in the CSA concrete samples, they absorbed more water and then gained more weight as evident for CSA concrete samples during the first 3 days. Beyond 3 days, a further increment in the weight change occurred mainly because of water ingress to replace the water used in further reactions and also because of the absorption of ettringite. During this period, the weight change took place at a much slower rate. Characteristically, the water absorption of ettringite is much higher than that of CSH-gel, as a result the CSA concrete samples experienced a higher rate of the weight.

A slight reduction in weight occurred when the samples were sealed as cast for 28 days after demolding and this was followed with an increase in weight when the sealed samples were cured subsequently in water. The gain in weight after 6 months was similar to the samples continuously cured in water after demolding (See Fig. 8.4.b). The reference samples cured at room temperature and 80% humidity underwent a higher loss of weight (Fig. 8.4.c) It shows that the OPC concrete is more sensitive to drying than CSA concrete. High water demand for hydration of the CSA concrete caused most mixing water to be consumed for hydration at very earlier ages. As a result, weight measurements are not sensitive to drying since there is less free water to evaporate. On the other hand, the much lesser amount of water required for hydration by OPC concrete at the earlier ages resulted in the pore water evaporating during the period of exposure to the dry environment and hence the samples underwent a considerable amount of weight loss. All samples gained weight when they were cured in water in a similar pattern to that for samples cured continuously in water after demolding.

8.3.2 Strength of CSA Concrete

The difference in the binding mechanism between the CSH gel and crystalline hydrated ettringite in contributing to the strength of concrete is the main factor that must be considered to build up a better understanding of the strength of concrete made from CSA cement. The binding system in OPC concrete was developed by cohesion and adhesion of CSH gel (Neville, 1998). In CSA concrete, with much bigger size of crystals, besides the binding between ettringite crystals and the binding between ettringite and aggregate particles, the ettringite interlocking mechanism also considerably contributes to the strength of concrete.

The compressive strength, the indirect splitting tensile strength and the flexural tensile strength of CSA concrete are discussed for the mixes with w/cm ratio = 0.50 and at the same water content with emphases on the effect of anhydrite content, OPC replacement and different curing conditions. Curing conditions applied to the samples were:

- continuous water curing
- room temperature (20 ± 1^0C) and 80% humidity curing
- seal curing
- water curing after sealing for 28 days

The relationship between w/cm ratio and compressive strength of CSA concrete is also the concern of the discussion.

8.3.2.1 Compressive Strength of CSA Concrete

Under compression, the ettringite interlocking in CSA cement predominantly contributes to the strength of the concrete. This is clearly seen in Fig. 8.5.a, b, c and d where the compressive strengths of CSA concrete were much higher than that produced by the reference mix at the same water/cement ratio and at the same water content in all curing conditions. In this respect, the content of CSA cement could be significantly reduced to produce the same compressive strength as the reference mix. Characteristically, the compressive strength of the CSA concrete was achieved at a very early age. The fast earlier strength development is another advantage of using CSA concrete as structural material as the scaffolding and formworks can be removed much sooner after the casting.

The samples continuously cured in water experienced a reduction in the compressive strength after 6 month of curing (see Fig. 8.5.a) except for concrete samples of Mix RC25, where the strength of concrete slightly increased. Although, in general, the expansion of samples cured in this condition was below the limit which can cause damage in concrete, micro cracks, which might occur in paste due to the expansion was the most likely reason behind the reduction in compressive strength.

Preventing the movement of water in and out of the system by sealing the samples after casting produced higher and more stable compressive strengths in the long term except for samples of mix RF15 where the reduction of strength beyond 6 months was found (See Fig. 8.5.b). Lower hydration, compared to the samples continuously cured in water was compensated by more stable samples as there was no expansion taking place. However this condition hardly affected the compressive strength development of the reference mix.

Allowing the pore water to evaporate by exposing the samples at room temperature and 80% humidity left more anhydrous binding particles. This situation resulted in lower but stable compressive strength of CSA concrete with time compared to the other two curing regimes (See Fig. 8.5.c). The effect of evaporation on the reference mix was pronounced at early ages as the reaction of C_3S was extremely water dependent. The strength of the reference mix at 28 days was lower under this curing condition. In the long term, the continuation of C_2S hydration under humid condition compensated the lower strength at early ages. At 6 months, the strength of the reference mix cured at room temperature and 80% relative humidity was comparable with the compressive strength produced by the samples cured in the other two conditions.

The low compressive strength for the samples stored at room temperature and 80% humidity for 28 days was expected to improve by immersing the samples in water. The water ingress into the system continued the hydration process to produce new binding material in the system. This is the case for all samples but mix RC15 (See Fig. 8.5.d). It is thought that the anhydrite in the mix RC15 had been completely used up before the samples were cured in water. After 2 month of immersion the compressive strength of samples increased faster than the reference mix. As in the case of samples continuously cured in water, the CSA concrete underwent slight loss of compressive strength at 6 months. On the other hand for the same period of curing, the reference mix gradually developed the compressive strength to reach approximately compressive strength of OPC concrete continuously cured in water.

8.3.2.2 Relationship between Compressive Strength and W/CM Ratio of CSA Concrete

The relationship between w/cm ratio and compressive strength of CSA concrete is given in Fig. 8.6.a and b. The relationship was built up using the CSA concrete samples continuously cured in water for 28 days and the concrete stored at room temperature and 80% humidity. Traditionally, it has been well known that the compressive strength of OPC concrete increases with the reduction of w/cm ratio. The reduction of voids as a result of lowering w/cm ratio was believed to be mainly responsible for the increase in strength, even the hydrated particles decreased by the reduction of w/cm. Besides, the hydration may occur through the surface of particles so that the binding ability of CSH with the anhydrous part as nucleus is still reliable in contributing to the compressive strength.

This is not the case in ettringite based binder. It is thought that the contribution of ettringite to compressive strength is affected by the size of crystals, the void content, and the amounts of anhydrous particles, which influence the distance between ettringite crystals. These three factors interact to produce the interlocking and binding ability of ettringite in concrete. The size of ettringite crystals increase with the increase of w/cm ratio. The void content reduces with the reduction of w/cm ratio and the amount of anhydrous particles also increases with the reduction of w/cm ratio. The competition of these three factors caused the relationship between w/cm ratio and compressive strength of CSA concrete to not necessarily be consistent. The compressive strength consistently increased with the decrease of w/cm ratio from 0.70 to 0.50, but the fluctuation appeared at w/cm=0.4 and w/cm = 0.27 (See Fig. 8.6.a)

The effect of lack of curing when the samples were cured at room temperature and 80% humidity (See Fig. 8.6.b) only produced lower compressive strength, but the trend of relationship between w/cm ratio and compressive strength confirmed the results given by samples continuously cured in water.

8.3.2.3 Indirect Splitting Tensile Strength of CSA Concrete

The superiority of ettringite crystal interlocking in compressive strength is not necessarily reproduced when the samples are tested in tension. The CSA concrete samples under indirect splitting tension did not perform as well as they performed under compression testing. Even at 28 days, the indirect tensile strength of most samples was still higher than the reference mix, but the difference was not as wide as that showed in the compressive strength. After 6 months, the indirect splitting tensile strength of most CSA samples was even lower than the reference mix (See Fig.8.7.a).

The indirect splitting tensile strength of the CSA concrete samples sealed directly after demolding gave more consistent results against the curing period (See Fig 8.7.b). As the bonding characteristics of binder play a greater role in dictating the indirect tensile strength than compressive strength and flexural strength, this suggests that the expansion due to water curing possibly had resulted in weakening the bonding between hydrated ettringite and between ettringite and aggregates.

The indirect splitting tensile strength of samples immersed in water after sealing for 28 days is given in Fig. 8.7.c. After 6 months of curing period, the indirect tensile strength of CSA samples was higher than those continuously cured in water but lower than those continuously sealed except for samples containing 25% anhydrite. Samples with 25% OPC replacement underwent more severe effect due to being cured in water. It is thought that the presence of CH produced by the hydration of OPC increases the microcrack induced expansion during the formation of ettringite.

8.3.2.4 Flexural Strength of CSA Concrete

Under flexural load, the ettringite crystal interlocking in the tension area of concrete samples plays a predominant role in contributing to the strength. It is shown by concrete samples containing CSA and anhydrite (See Fig. 8.8.a). At 28 days, the CSA concrete samples produced a higher flexural strength than produced by the reference mix and increased with the increase of the anhydrite content. CSA concrete samples cured in water consistently produced higher flexural strength in respect to anhydrite content. Continuous water curing allowed more ettringite to form in the concrete samples.

Replacing CSA cement and anhydrite with 25% OPC reduced the amount of ettringite in the concrete samples. Besides, the nature of ettringite formation due to the presence of CH caused expansion and then might have caused micro-cracks in the samples. As a consequence, the CSA concrete samples containing 25% OPC had a much lower flexural strength than the samples without OPC. In water curing, the flexural strength of CSA concrete samples containing 25 % OPC was even lower than the reference samples (See Fig. 8.8.a)

After 6 months of curing, the reference samples experienced a loss of strength in all conditions. The CSA concrete samples continuously sealed after demolding slightly increased in flexural strength. In CSA concrete samples continuously cured in water, samples containing 15% anhydrite drastically underwent loss of flexural strength (See Fig. 8.8.b). The micro-crack induced expansion was most likely responsible for the loss of flexural strength and lack of anhydrite caused no further formation of new ettringite. Loss of flexural strength was also found for samples of mix RF25 continuously cured in water, but it was not as high as that experienced by the CSA concrete samples of mix RF15. The continuation of ettringite formation was thought to re-heal the micro-crack induced expansion. After 6 months, the concrete samples of mix RF25 cured in water after sealing for 28 days produced comparable flexural strength to those produced by the same concrete samples continuously sealed.

The CSA concrete samples containing 25% OPC replacement gained flexural strength after continuous seal curing for 6 months. The continuation of C_2S hydration contributed to this increase in the flexural strength. The samples continuously cured in water did not show a significant different in flexural strength after 6 months of curing. The same concrete samples cured in water after sealing for 28 days, performed slightly better after 6 months under flexural load compared to the same concrete samples continuously cured in water at the same period of time (See Fig. 8.8.b).

It is clearly seen that the CSA concrete samples containing 25% anhydrite performed satisfactorily under flexural load under any curing condition. Also this high flexural strength was reached at very early ages and therefore mix RF25 is worth being considered for use in types of structural concrete where flexural strength is one of the main design parameters such as: rigid pavement and pre-stressed concrete.

8.3.3 Durability Related Properties of CSA Concrete

The durability of concrete is mainly influenced by the ease with which harmful substances can penetrate the concrete. In OPC concrete, high strength concrete with low porosity and permeability is mostly more durable against the attack of deteriorating substances such as: sulfates, chlorides, carbonation etc. With a different pore structure in CSA concrete, because of the different hydration mechanism, it was thought important to investigate the durability related properties of the CSA concrete.

The durability related properties of CSA concrete studied cover oxygen permeability, absorption and rapid chloride permeability. The concrete samples used for the tests consisted of OPC concrete as a reference mix, CSA concrete containing 15% and 25% anhydrite with and without 25% OPC as a replacement. The concrete samples used for the investigations were made at a w/cm ratio equal to 0.50 and at the same water content. The effect of different w/cm ratios on oxygen permeability of CSA concrete containing 25% anhydrite was also the concern of the investigation

The curing regimes applied to the concrete samples were continuously cured in water after demolding, sealed continuously after demolding, stored at room temperature (20 ± 1) ^{0}C and 80% humidity and cured in water after sealing for 28 days. In order to prevent the changing in phase of the hydrated particles, the drying process of the concrete samples was not carried out by heating but by storing the samples at room temperature (20 ± 1) ^{0}C for 6 weeks to achieve the constant weight of samples.

8.3.3.1 Oxygen Permeability of CSA Concrete

The results of the oxygen permeability for CSA concrete are given in Fig. 8.9.a, b and c. The curing regimes predominantly affected the results at all ages of curing period. At 28 days (See Fig. 8.9a) concrete samples cured in water performed much better than those cured at room temperature and 80% humidity and those continuously sealed after demolding. Under this curing regime CSA concrete without OPC had oxygen permeability coefficients approximately the same as the reference mix. The CSA concrete samples containing 25% OPC produced two contradictory results. The concrete samples containing 15% anhydrite had the lowest result and the concrete samples containing 25% anhydrite produced the highest permeability. Lack of water, due to the samples were being stored at room temperature and 80% humidity, severely affected the CSA concrete samples containing 15% anhydrite without OPC. As oxygen permeability is mainly relative to the interconnected pores in the samples, low anhydrite content and hence low hydrated ettringite in the samples, because of not properly cured, caused the oxygen to easily penetrate into the samples. The combination of ettringite and CSH in concrete samples containing 25% anhydrite and 25% OPC produced the lowest permeable pore system (See Fig.8.9.a).

Prolonging the curing up to 6 months at room temperature and 80% humidity increased the oxygen permeability of CSA concrete samples without OPC especially for the samples containing 15% anhydrite. The drying process, which would have occurred in samples stored at room temperature and 80% humidity, might be the reason behind the increase in the permeability of those samples. The CSA concrete samples cured in water after 6 months also increased the oxygen permeability. It is thought that continuous curing in water for six months developed the micro-crack induced expansion of ettringite and hence increased the permeability through the cracks formed. The prolonging of curing in sealed CSA concrete samples did not seriously affect the oxygen permeability of CSA concrete samples due to the stability of ettringite under that curing regime. On the other hand, the continuation of OPC hydration compensated the negative effects of ettringite and as a result the effect of delaying curing period did not badly affect the permeability of CSA concrete samples with 25% OPC replacement (See Fig. 8.9.b).

The effect of w/cm ratio on the oxygen permeability of concrete samples containing 25% anhydrite and without OPC replacement is given in Fig. 8.9.c. The curing regimes applied to the samples were water curing and storing at room temperature and 80% humidity. The concrete samples continuously cured in water performed consistently better at all w/cm ratios compared to those stored at room temperature and 80% humidity. At w/cm=0.30 the effect of curing on the oxygen permeability was not so significant. A very impermeable concrete was formed because of low void content created by a very low w/cm ratio and this made the movement of water in and out of the concrete more difficult. As a consequence, the hydration process for both curing regimes at this low w/cm ratio mostly relied on the existing water in the system.

The oxygen permeability of the concrete samples cured at room temperature and 80% humidity increased with the increase of w/cm. This is mainly because of evaporating water from the pore system increases with the increase of w/cm. The oxygen permeability of the concrete samples cured in water reduced with the increase of w/cm ratio up to 0.50 and then increased at w/cm = 0.70. Although the initial permeability of CSA concrete with w/cm 0.40 and 0.50 was relatively higher than that for the concrete of w/cm = 0.30, the conversion of anhydrous particles into ettringite in concrete of w/cm 0.40 and 0.50 during the water curing period resulted in lower permeability for these concretes compared to the samples made with w/cm=0.3. This is because the penetration of water into the 0.3 w/cm concrete was limited by la low initial permeability. Apparently, at w/cm = 0.70, the formation of new ettringite during the curing period could not compensate for a high initial permeability. Less cementitious material in the system due to higher w/cm ratio and more pores created by higher w/cm ratio were responsible for this higher permeability.

8.3.3.2 Absorption

As the concrete samples were not dried by heating process, there was no guarantee that all pores would have been fully emptied from water. Assuming that the capillary pores is completely dry, the absorption value was used instead of porosity measurement to ascertain the amount of water that can be absorbed by 24 hours immersion in water.

To ensure that the absorption values measured for the various systems investigated reflect mainly the interconnected pore structure of the cement paste, the mass of the paste was kept constant for all concrete mixes. This was achieved by varying the sand content to take account of differences in specific gravity of the materials used, whilst maintaining the w/cm ratio and aggregate content constant. The absorption of water by ettringite during the 24 hours immersion was considered negligible.

The results of the absorption tests are given in Table 8.5. As expected, the absorptions of the reference concrete samples were higher than those produced by CSA concrete samples. As water demand for hydration of OPC is lower than the given mixing water, the excess water created a poorer capillary pore system in the reference mix in comparison of CSA concrete. This condition was worsened by lack of curing as shown by the concrete samples sealed directly after demolding or by the concrete samples stored at room temperature and 80% humidity. On the contrary, water demand for hydration of CSA cement is higher than that required for mixing, the CSA concrete samples produced a better capillary pore system since less capillary space is created by excess mixing water, as in case for OPC concrete. Lack of curing allowed the water in the system to evaporate and as a result, increased the absorption of the CSA concrete samples. The amount of hydrated ettringite in the sample clearly affected the absorption. Concrete samples of mix REF25 performed much better than the concrete samples of mix RF15.

The high absorptions of CSA concrete containing OPC replacement were mainly caused by less ettringite in the system as a consequence of the replacement. Besides, the ettringite formation mechanism with the presence of CH, produced by C_3S hydration, caused expansion. The micro-crack induced expansion was possibly responsible for poor pore system in the concrete. It is supported by the fact that the CSA concrete samples of mix RC25 produced the highest absorption in all curing conditions.

8.3.3.3 Chloride Permeability of CSA Concrete.

It is has been a long argument whether chloride permeability test virtually a measurement of electrical conductivity is an accurate method to access the rate of chloride ion transport into the concrete (Neville, 1998 and Shi, 2003). While the electrical conductivity of water saturated concrete depends on the pore structure and the chemistry of the pore solution, the transport of chloride has little to do with the chemistry of pore solutions. The alkalinity of pore solution is one of the important factors influencing the electrical conductivity (Shi, 2003).

The results of chloride permeability of CSA concrete are given in Table 8.5. The test was carried out on samples of w/cm=0.50 and of the same water content under different curing condition upto 28 days. The chloride permeability of concrete is based on charge (Coulomb) passed through the specimen, subjected to 60 volt DC, during 6 hours of testing period. It is not surprising that the reference mix either cured in water or seal cured produced higher charge compared to those produce by CSA concrete. High content of alkali released into pore solution during 28 days of curing produced a high charge in the reference mix. It is different with the concrete samples stored at room temperature and 80% humidity where less alkali was released into the pore solution as the pore water had already evaporated.

The very low alkali content of CSA cement caused the charge produced by the test to be very low. The CSA concrete samples of mix RF25 produced the lowest charge consistently in all curing conditions. It is probably because of more SO_4 ion released into the pore solution. The lowest value of charge produced by the CSA concrete samples can not be taken for granted as a measure that the CSA concrete is less permeable to chloride than the reference mix.

Introduction of OPC into the CSA concrete system significantly changed the test result. Basically the charges produced by CSA concrete samples containing OPC were higher than the CSA concrete samples without OPC. CSA concrete samples R25 cured in water had a charge comparable with the reference mix. It seems that the rapid reduction of $CaSO_4$ in the system during hydration in the presence of CH was a more predominant factor responsible for the high charge produced. It is consistent with the increase of $CaSO_4$ content where the amount of charge drastically reduced.

It is clearly seen that the better performance of the CSA concrete samples, if compared to the OPC concrete, under the chloride permeability test is more because of less alkali in pore system than the indication that the CSA concrete samples were less permeable to chloride. Due to the stated limitations of the rapid chloride permeability test, a less accelerated test (e.g. chloride poundings test needs to be used to verify and calibrate the results found in this investigation.

8.4 Conclusions

1 CSA cement can produce workable concrete suitable for structural applications. The loss of slump reported here is within the limits where the concrete can be handled in a conventional way. The cement was compatible with polycarboxylate based superplasticiser so that the CSA cement can be used to produce high strength or flowing concrete. In all aspects, introduction of OPC as cement replacement gives a negative effect on the workability of CSA concrete.

2 The setting time of CSA cement is significantly longer than the setting times of OPC concrete. Introduction of OPC as a cement replacement reduces the setting times close to those of OPC concrete. Precaution must be taken when the surface of CSA concrete is covered with curing material as a longer setting time may damage the surface if the curing material is applied too early. To avoid the possibility plastic shrinkage occurred due to evaporation of water in association with a long setting time, the use of curing compound is recommended.

3 The expansion of the CSA concrete was not significant enough to cause damage in structural concrete. The internal micro-cracks due to the expansion will probably have affected other properties and the overall performance of concretes.

4 The CSA concrete produced higher compressive strength results at early age. The reduction of cement content to produce the same strength as the reference mix is an advantage of using CSA cement. The effect of lack of curing in the CSA is not as serious as that in OPC concrete. The introduction of OPC as a cement replacement did not give any advantage in compressive strength development.

5 The superior compressive strength of the CSA concrete was not reproduced in the indirect splitting tensile strength test. The indirect tensile strength of the CSA concrete was practically comparable to that

of the reference mix. The presence of OPC in the CSA concrete reduced the indirect tensile strength.

6 The flexural strength of the CSA concrete, especially without OPC, was considerably higher than that of the reference mix. The use of 25% anhydrite in the concrete gave a much better performance.

7 The reference concrete and the CSA concrete containing OPC showed better performance than the CSA concrete without OPC with respect to oxygen permeability.

8 Oxygen permeability values of CSA concrete samples RF15 and RF 25 were significantly higher compared to the reference concrete. Under water curing, oxygen permeability of these concrete samples was comparable with the reference mix at 28 days age of curing and was higher than reference after 6 months of curing. The incorporation of OPC into the system generally improved performance of the oxygen permeability of CSA concrete.

9 The CSA concretes absorbed less water after 24 hours immersion compared to the reference mix, while the CSA concrete without OPC showed a better performance.

10 The CSA concrete was much less permeable compared to the reference mix in the chloride permeability test, but it does not necessarily represent the rating of the concrete in transporting chlorides as the test has many limitations.

11 From the work carried out, CSA cement containing 25% anhydrite without OPC replacement was found to be the best of the binders tested for producing structural grade concrete.

Table 8.1: Composition and Fresh Concrete Properties of Concrete with w/cm = 0.50

Composition (kg/m^3 of concrete)	REF	RF15	RF25	RC15	RC25
Water	166.00	166.00	166.00	166.00	166.00
Anhydrite		49.80	83.00	37.35	62.25
CSA Cement		282.20	249.00	211.65	186.75
PC	332.00			83.00	83.00
Sand	743.19	701.74	704.44	735.99	714.13
Coarse. Aggregates (20 mm)	767.37	767.37	767.37	767.37	767.37
Coarse. Aggregates (10 mm)	328.94	328.94	328.94	328.94	328.94
Total Weight/m^3 (kg)	2337.50	2296.05	2298.75	2330.30	2308.44
Fresh Concrete Properties					
Slump (mm)	120	150	170	85	110
Unit Weight (kg/m^3)	2353.0	2321.5	2324.7	2335.7	2326.6
Calculated Air Content (%)	1.55	2.54	2.59	0.54	1.81
Initial Setting Time (minutes)	379	730	765	333	449

Table 8.2: Composition of CSA Concrete with Different w/cm Ratios

Composition (kg/m^3 of concrete)	Weight of Material/m^3 of Concrete (Kg)				
	RF25-0.7	**RF25-0.6**	**RF25-0.5**	**RF25-0.4**	**RF25-0.3**
w/cm Ratio	0.70	0.60	0.50	0.40	0.30
Water	166.00	166.00	166.00	166.00	135.00
Anhydrite	59.29	69.17	83.00	105.87	112.50
CSA Cement	177.86	207.50	249.00	317.61	337.50
Super-plasticizer					1.80
Sand	793.50	756.39	704.44	704.44	668.08
Coarse. Aggregates (20 mm)	767.37	767.37	767.37	767.37	771.49
Coarse. Aggregates (10 mm)	328.94	328.94	328.94	328.94	330.70
Total Weight/m^3 (kg)	2292.96	2295.37	2298.75	2390.23	2357.07
Slump (mm)	180	170	170	140	200

Table 8.3: Composition of Reference OPC Concrete with Different w/cm Ratio

Composition (kg/m3 of concrete)	Weight of Material/m^3 of Concrete (Kg)				
	REF-0.7	REF25-	REF-0.5	REF-0.4	REF-0.3
w/cm Ratio	0.70	0.60	0.50	0.40	0.30
Water	166.00	166.00	166.00	166.00	135.00
PC	237.14	276.67	332.00	415.00	450.00
Super-plasticizer					3.38
Sand	821.19	788.69	743.19	674.95	720.60
Coarse. Aggregates (20 mm)	767.37	767.37	767.37	767.37	771.49
Coarse. Aggregates (10 mm)	328.94	328.94	328.94	328.94	330.70
Total Weight/m^3 (kg)	2320.64	2327.67	2337.50	2352.26	2411.17
Slump (mm)	140	140	120	100	190

Fig. 8.1: Loss of Slump

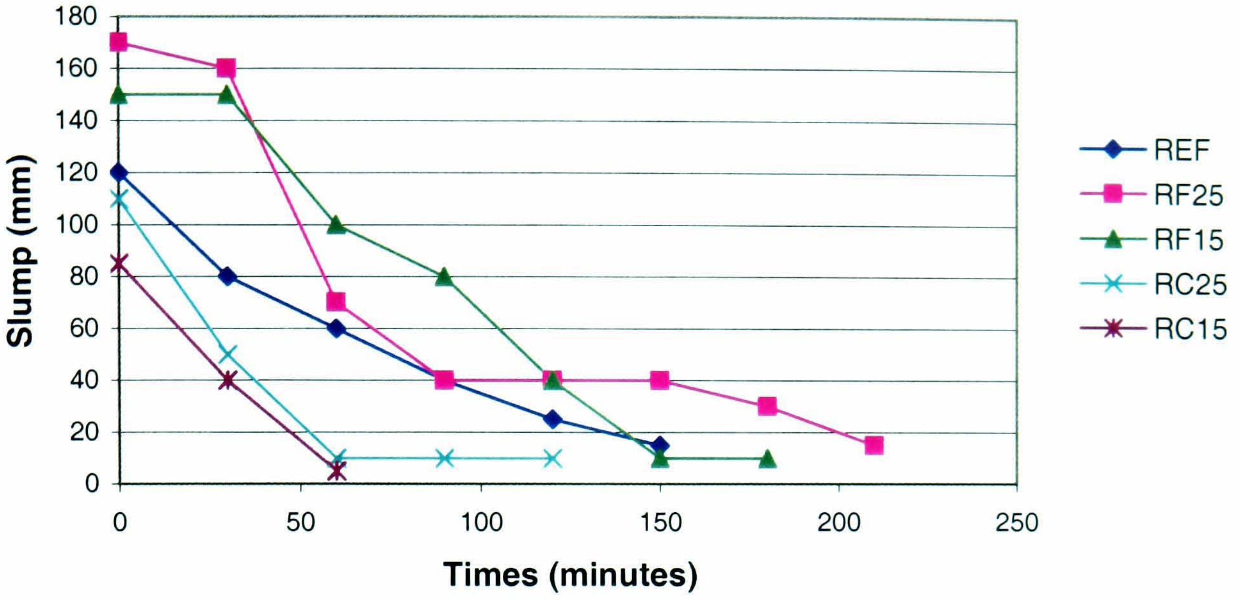


Fig. 8.2: Two Point Test of CSA Concrete

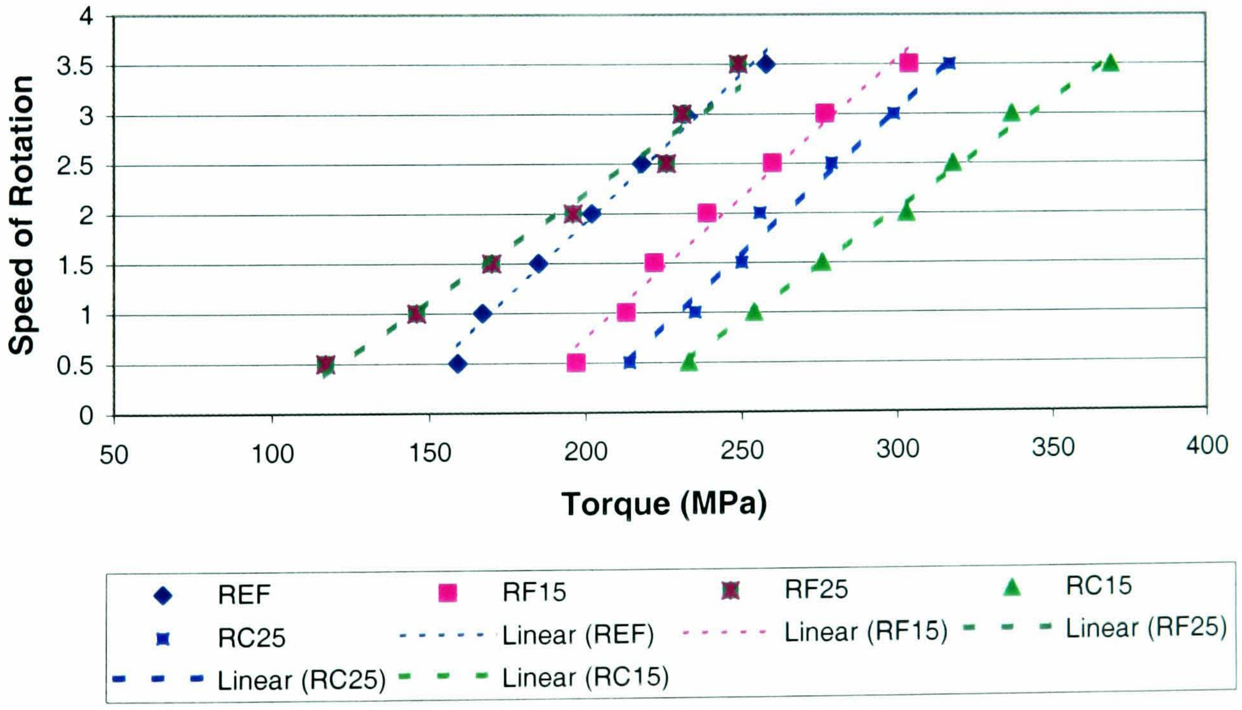


Table 8.4: Parameters of two point test

Mix	Yield Value MPa	Plastic Viscosity MPa s
REF	136.4	33.2
RF15	174.0	35.5
RF25	109.5	45.5
RC15	210.0	38.5
RC25	197.1	33.8

Fig. 8.3.a: Length Change Development of CSA Concrete Cured in Water

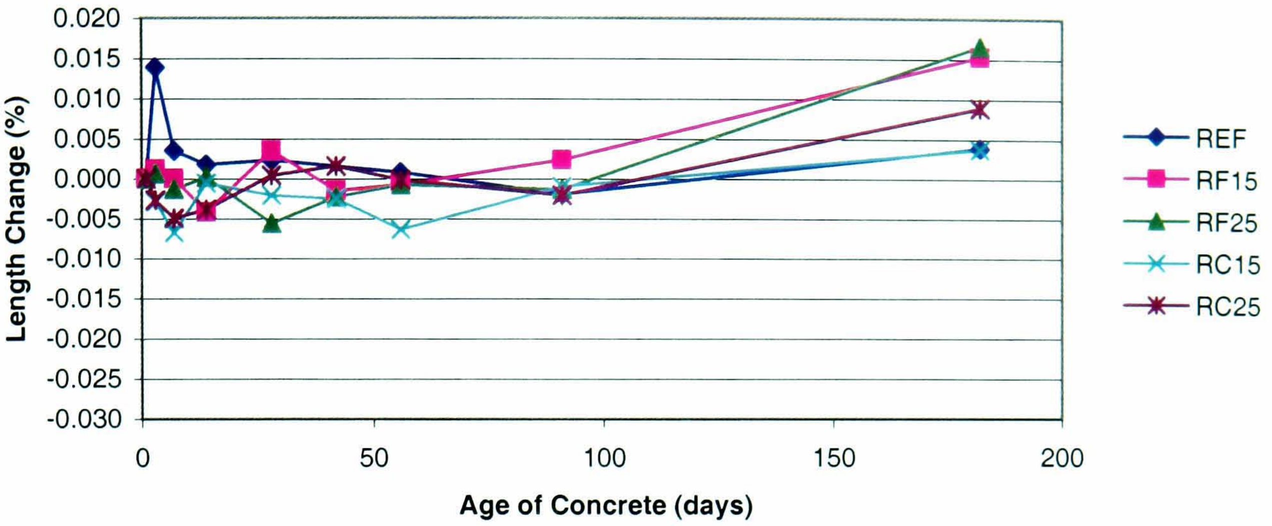


Fig. 8.3.b: Length Change Development of CSA Concrete Cured in Water after Sealed for 28 Days

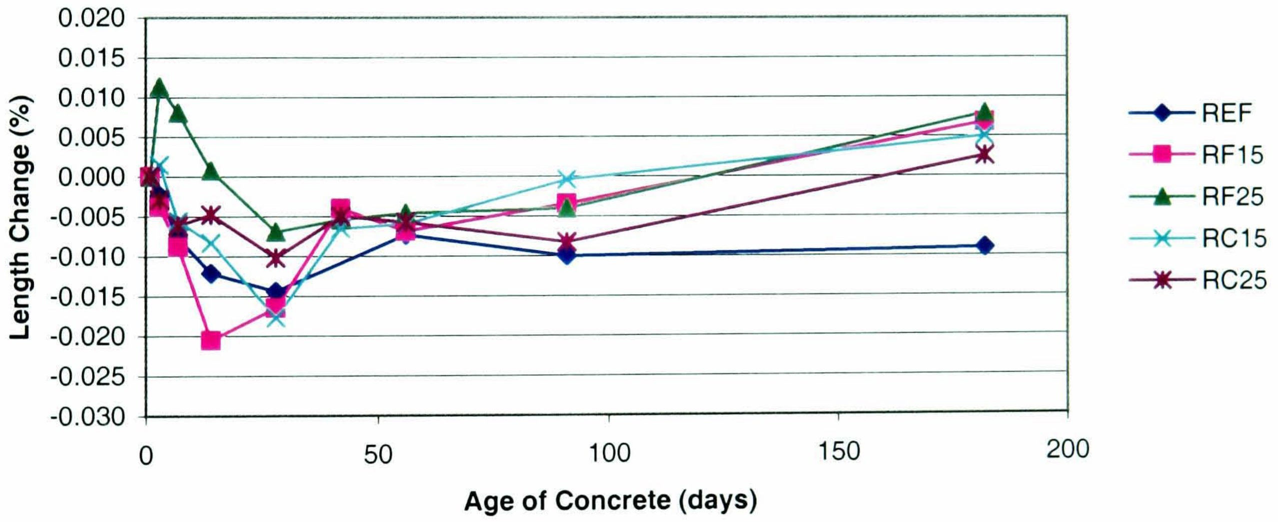


Fig. 8.3.c: Length Change Development of CSA Concrete Cured in Water after Storing at Room Temperature and at 80% Humidity for 28 Days

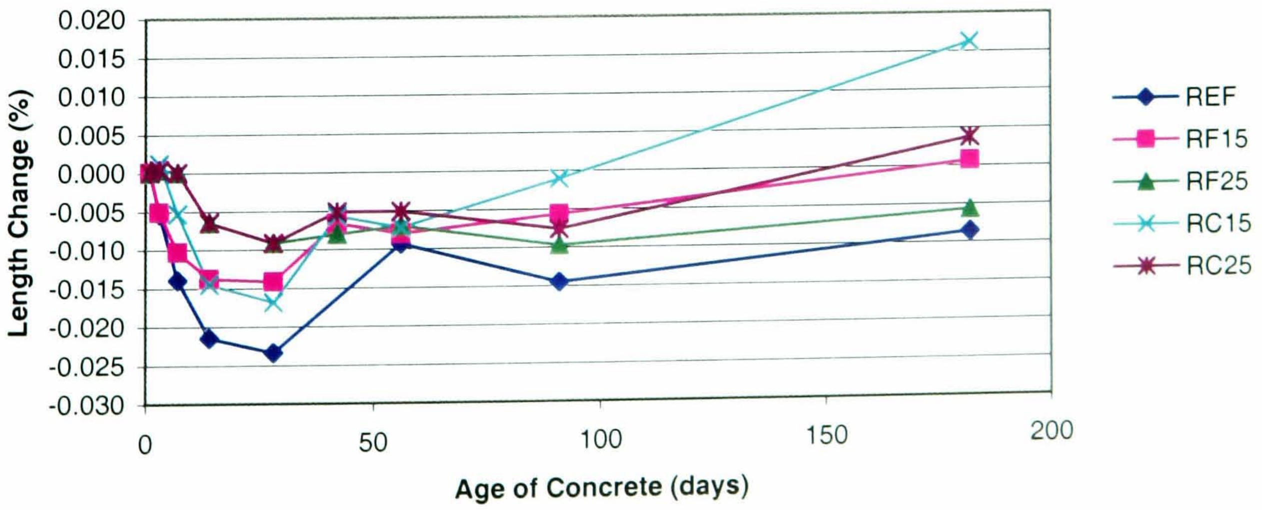


Fig. 8.4.a: Weight Change Development of CSA Concrete Cured in Water

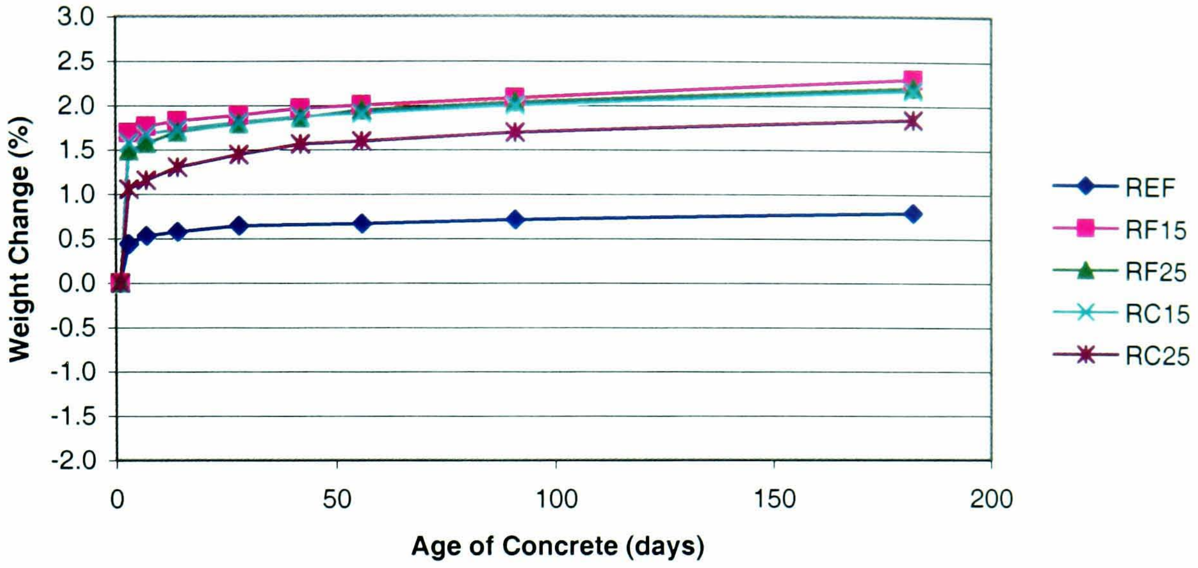


Fig. 8.4.b: Weight Change Development of CSA Concrete Cured in Water after Sealed for 28 Days

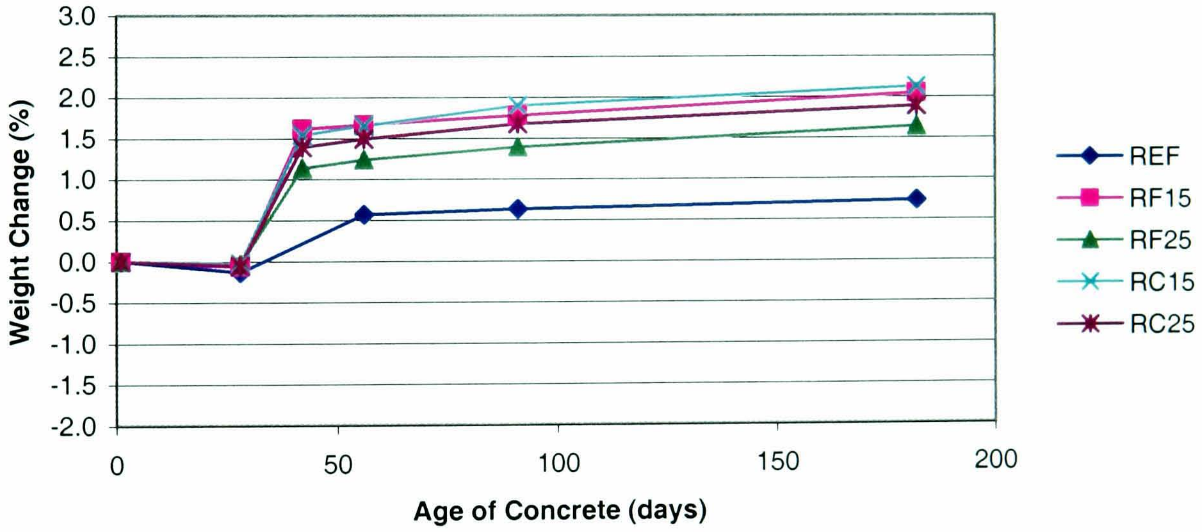


Fig. 8.4.c: Weight Change Development of CSA Concrete Cured in Water after Storing at Room Temperature and at 80% Humidity

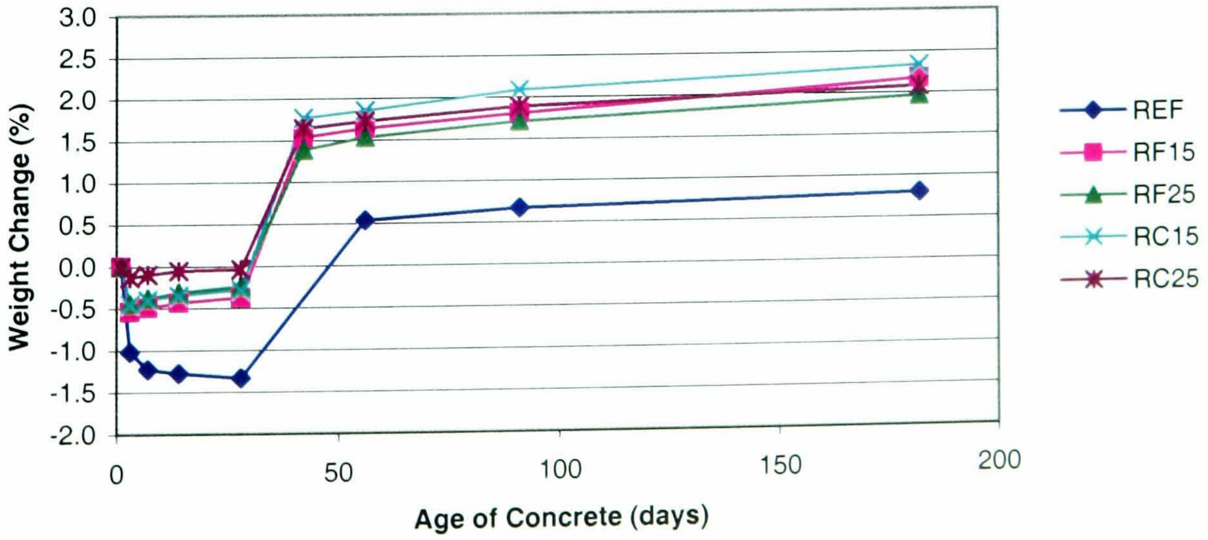


Fig. 8.5.a: Compressive Strength of CSA Concrete Cured in Water (w/cm=0.5)

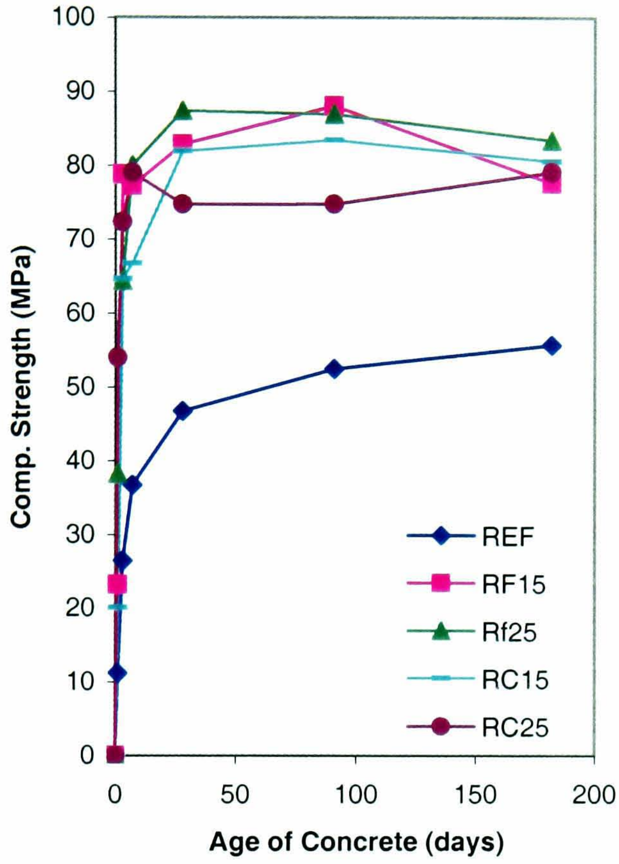


Fig. 8.5.b: Compressive Strength of CSA Concrete Sealed after Demolding (w/cm=0.5)

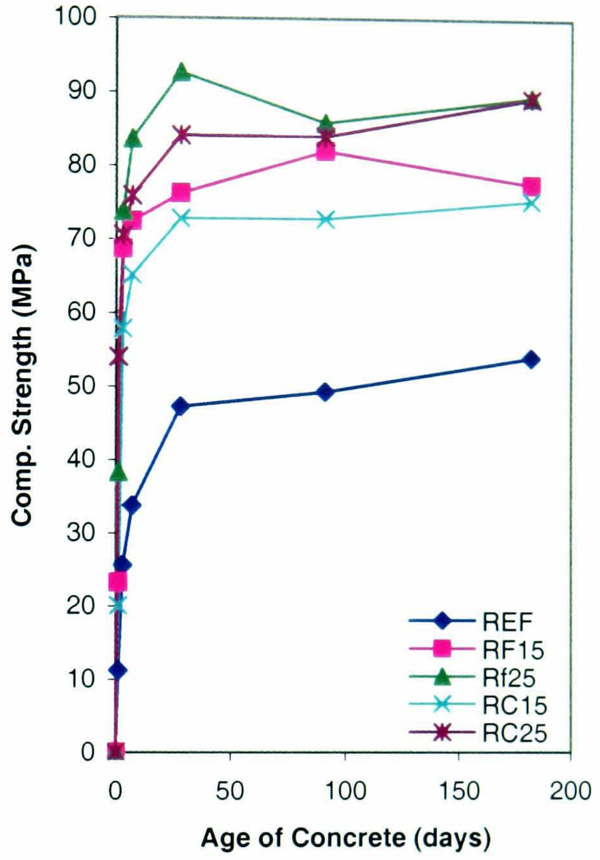


Fig. 8.5.c: Compressive Strength of CSA Concrete Stored at Room Temperature and 80% Humidity (w/cm=0.5)

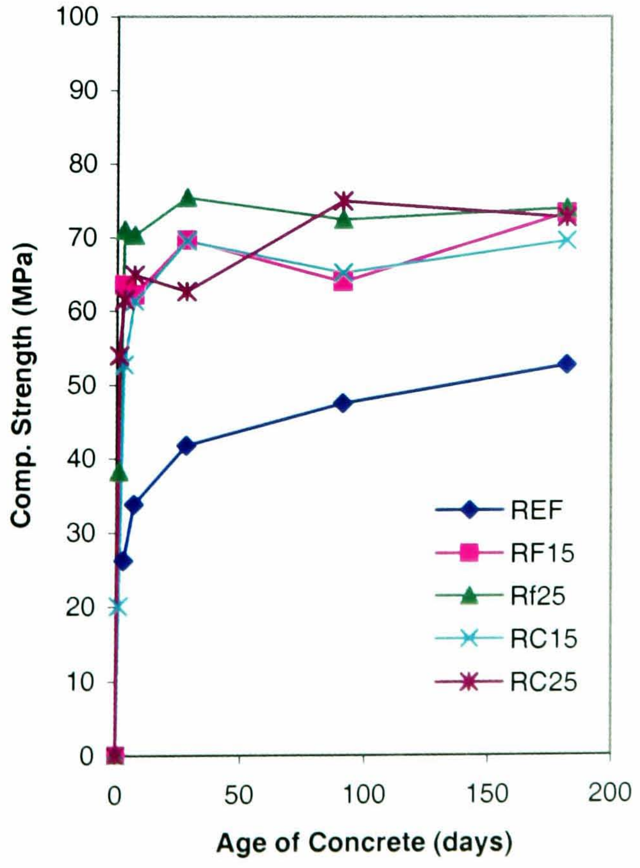
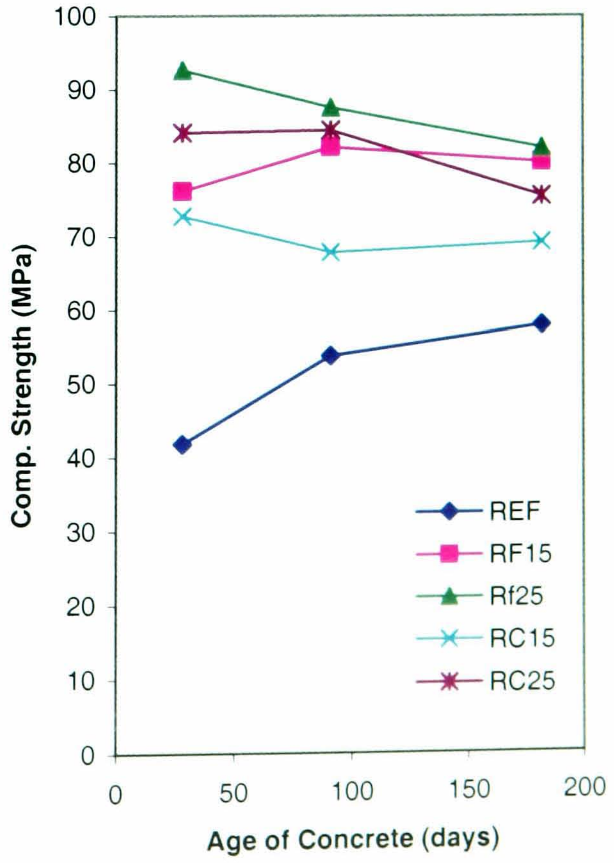


Fig. 8.5.d: Compressive Strength of Concrete Cured in Water after storing in room temperature and 80 humidity for 28 Days



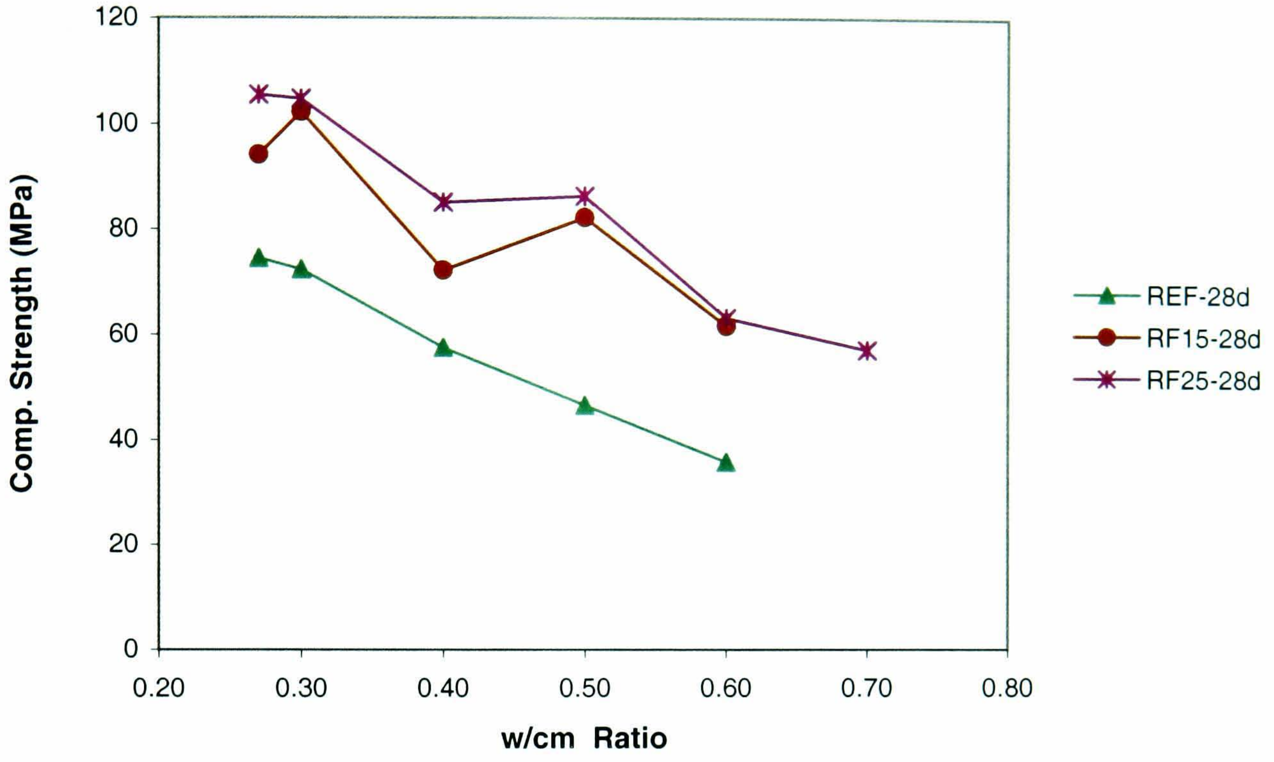


Fig. 8.6.a: Relationship between w/cm ratio and Compressive Strength of CSA Concrete Cured in Water

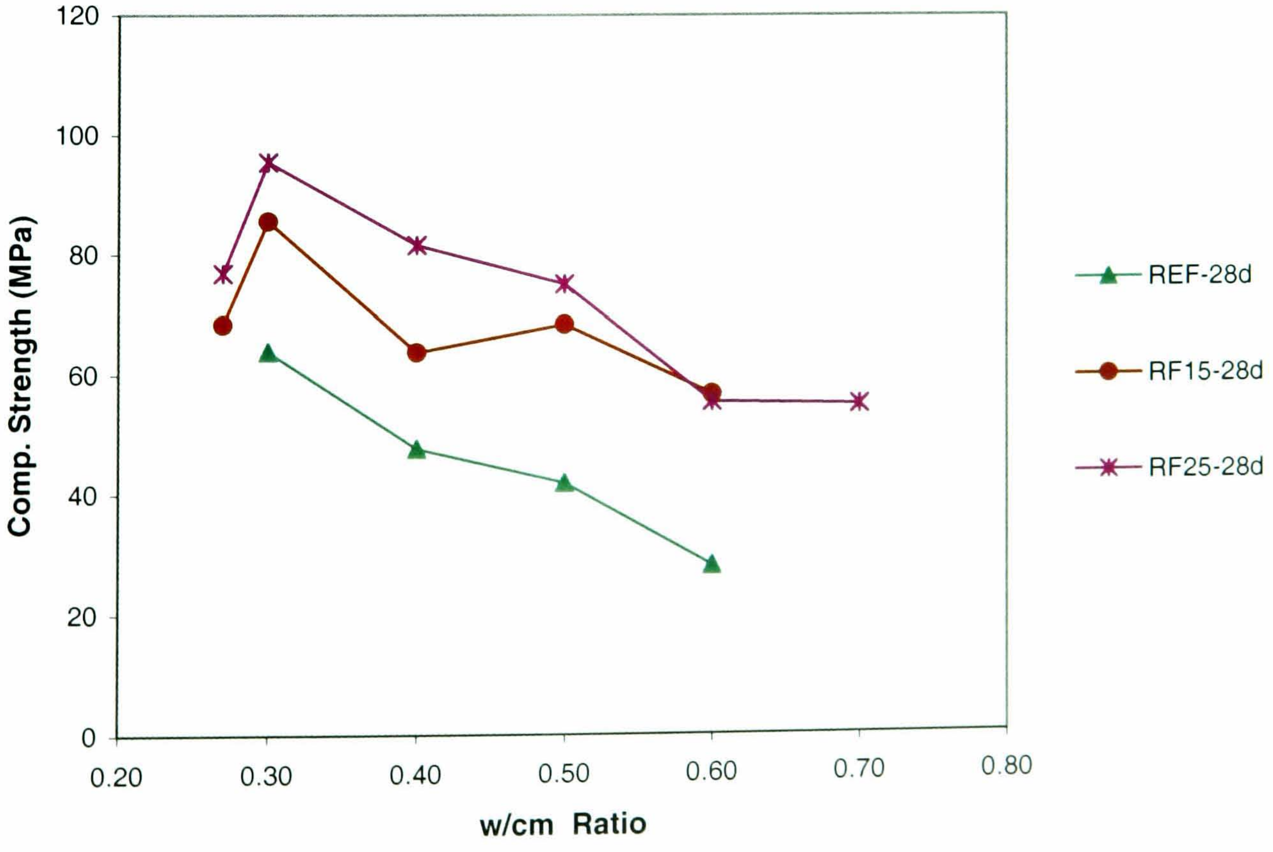


Fig. 8.6.b: Relationship Between w/cm Ratio and Compressive Strength of CSA Concrete Stored at Room Temperature and 80% Humidity

Fig. 8.7.a: Indirect Tensile Strength of CSA Concrete Cured in Water after Demolding (w/cm=0.5)

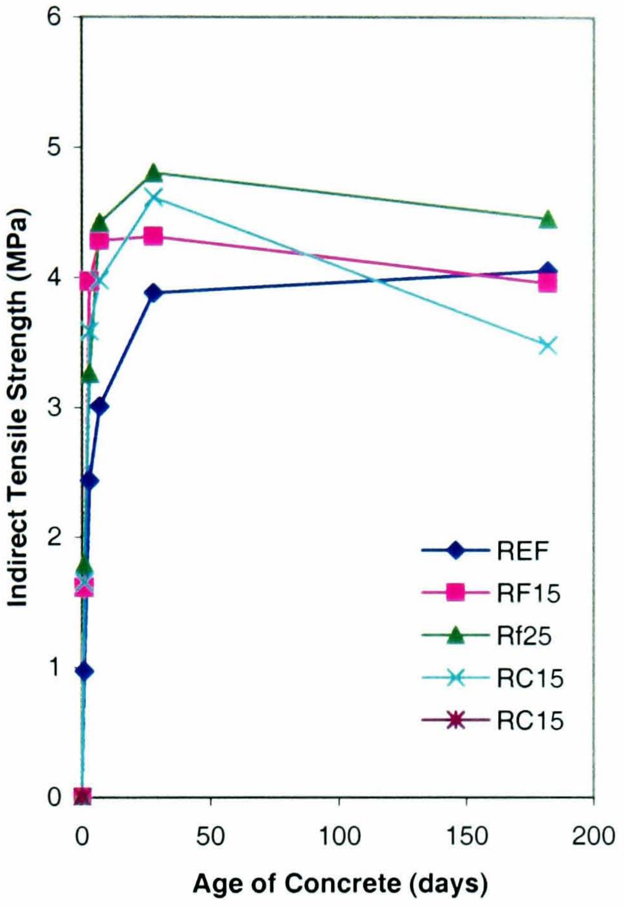


Fig. 8.7.b: Indirect Tensile Strength of CSA Concrete Sealed after Demolding (w/cm=0.5)

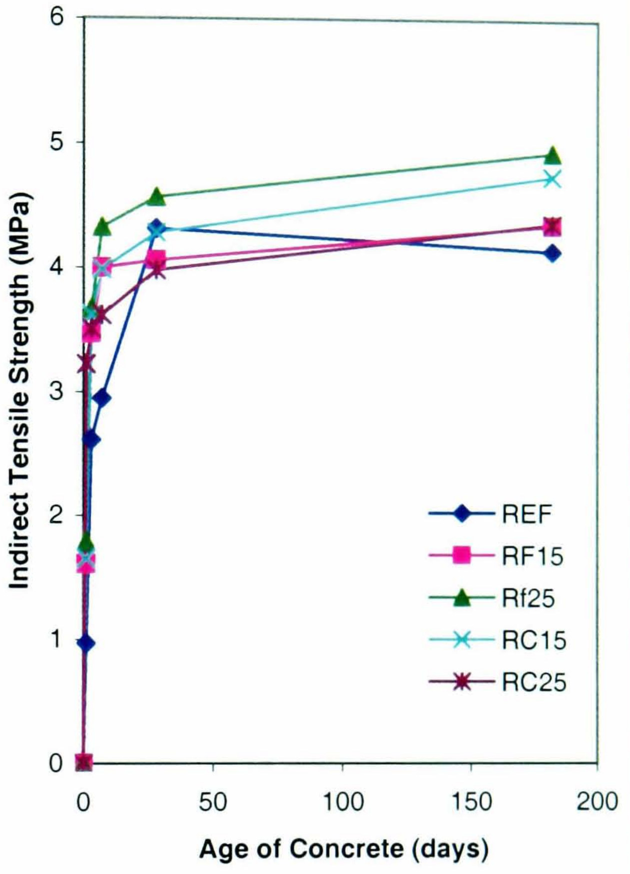
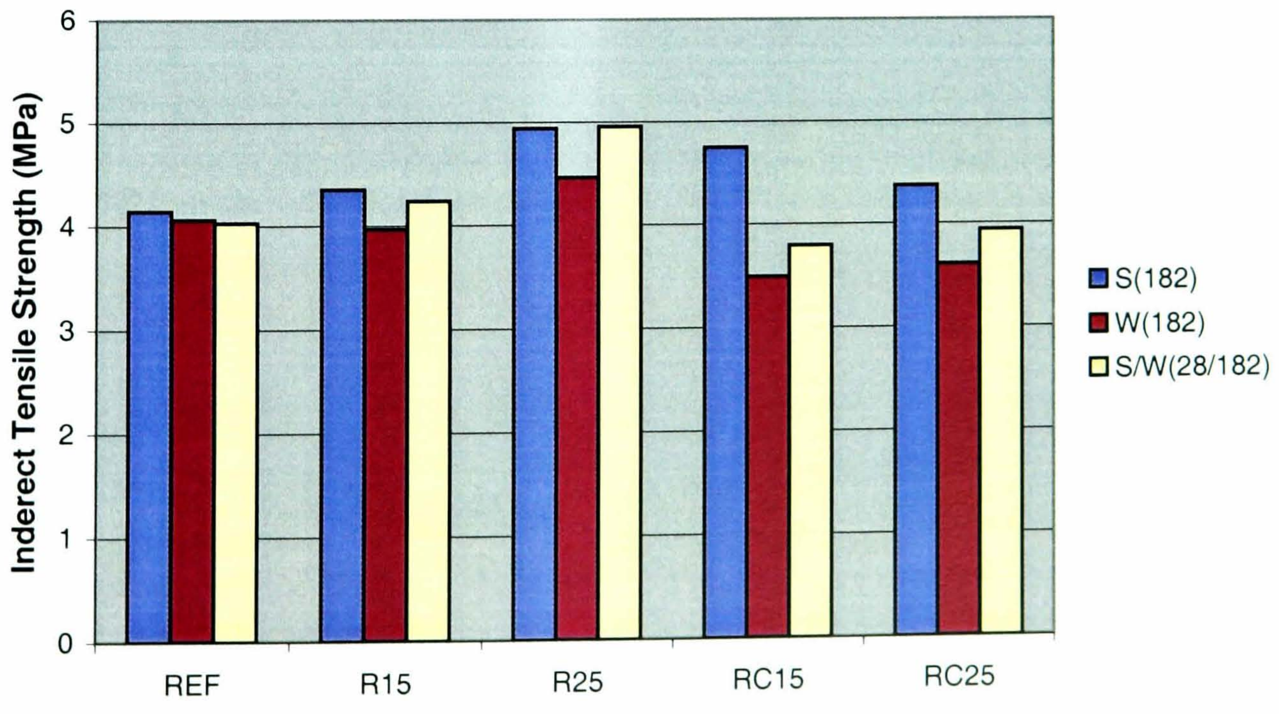


Fig. 8.7.c: Effect of Curing Condition on Indirect Tensile Strength Sealed for 28 days and then Cured in Water (w/cm=0.50)



S = Sealed after demolding W = Cured in water after demolding

S/W = Cured in water after sealing for 28 days.

Fig. 8.8.a: Flexural Strength at 28 Days (w/cm=0.50)

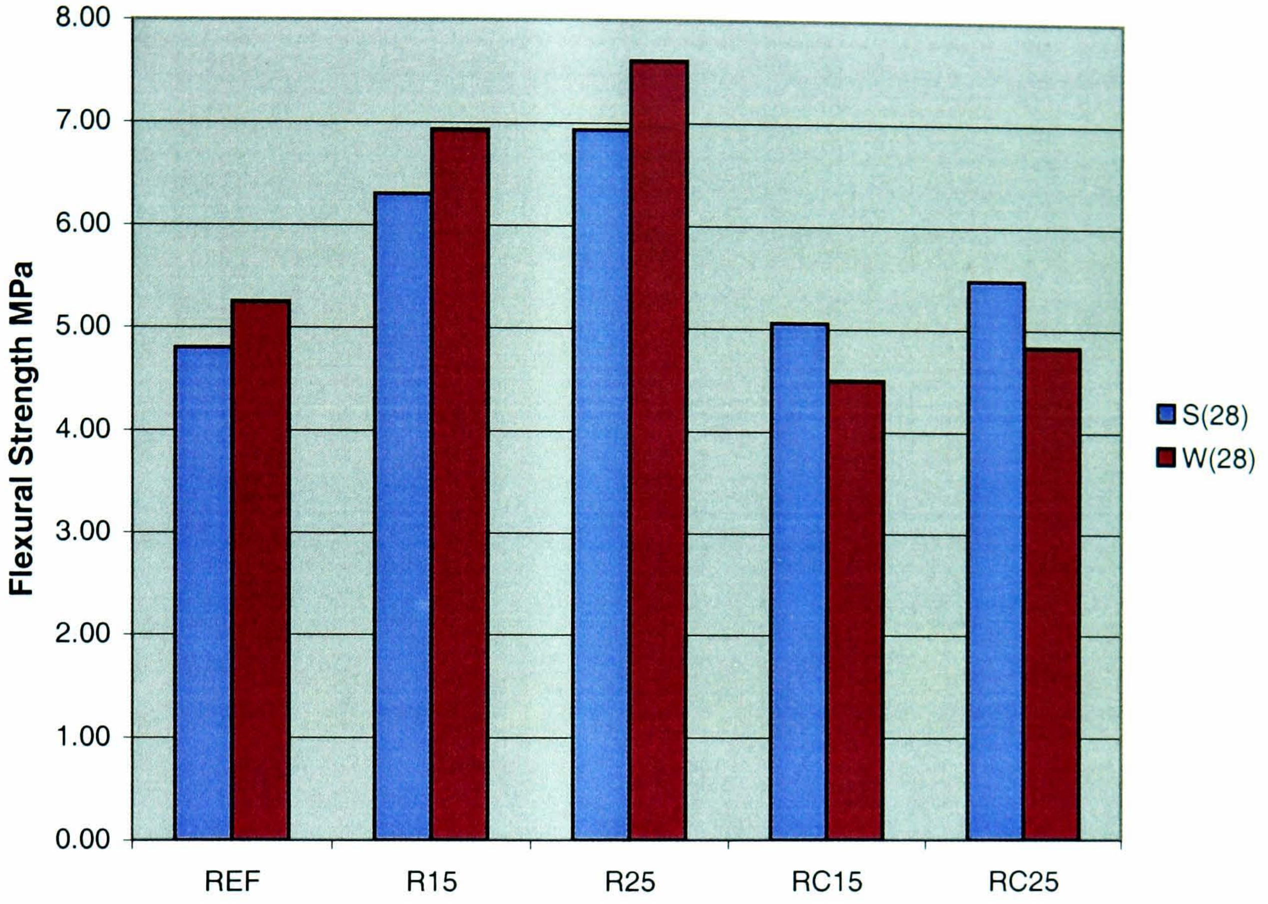
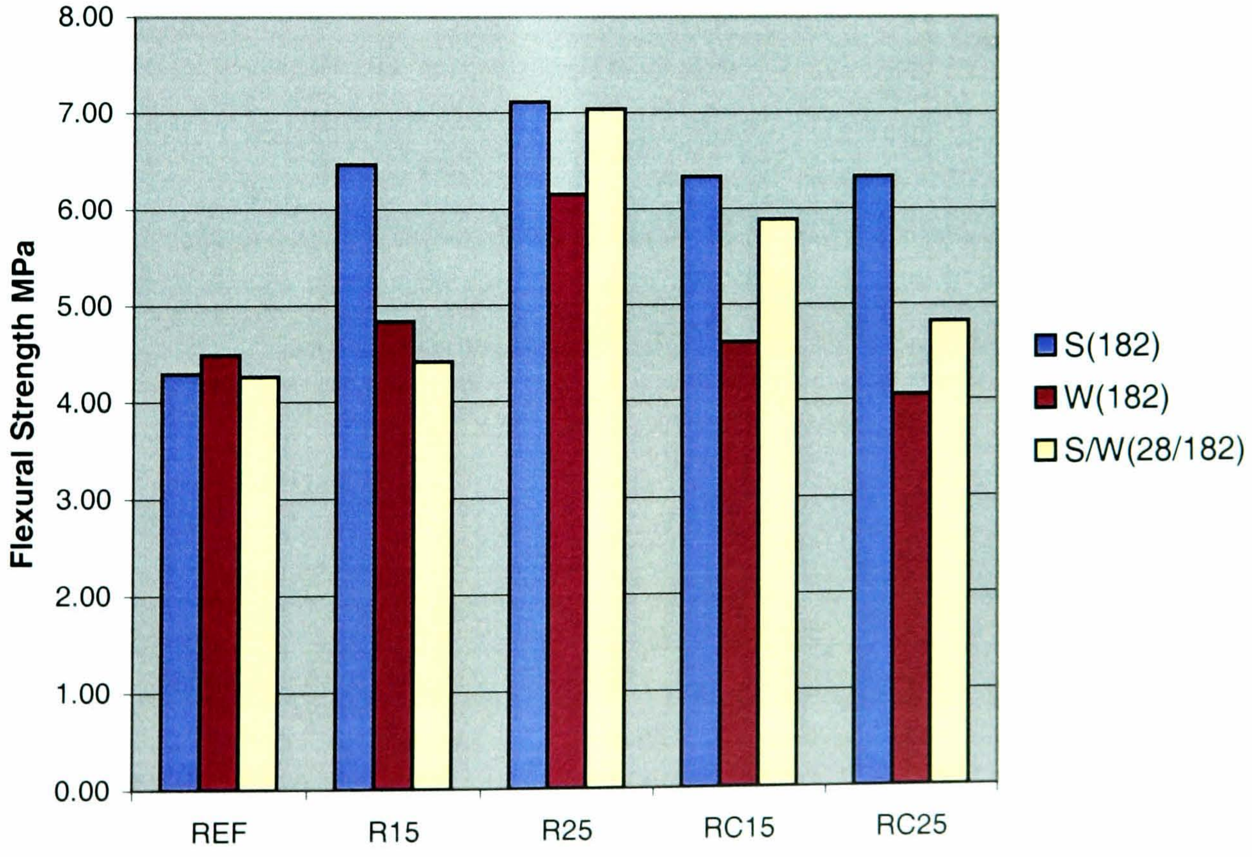


Fig. 8.8.b: Flexural Strength at 182 Days



S = Sealed after demolding W = Cured in water after demolding

S/W = Cured in water after sealing for 28 days.

Fig. 8.9.a: Oxygen Permeability of Sample at w.cm=0.50 after 28 Days of Curing

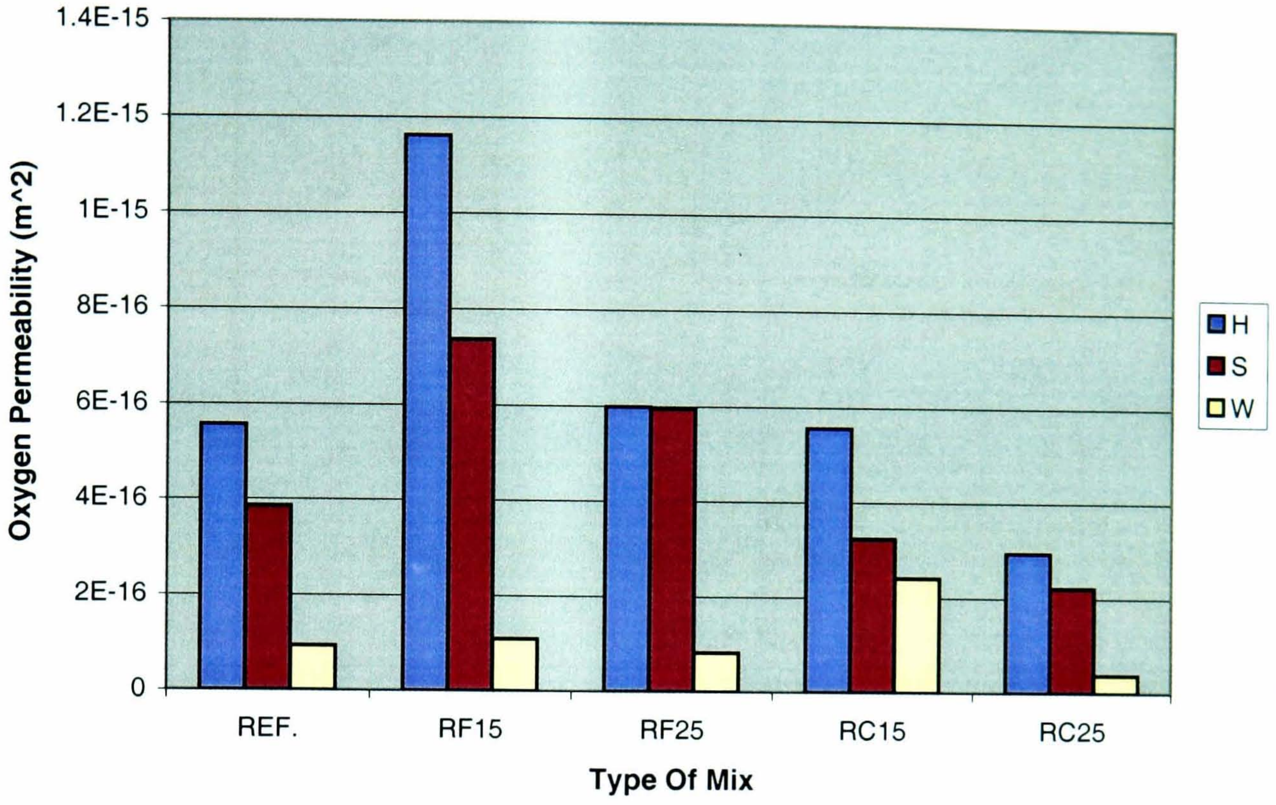
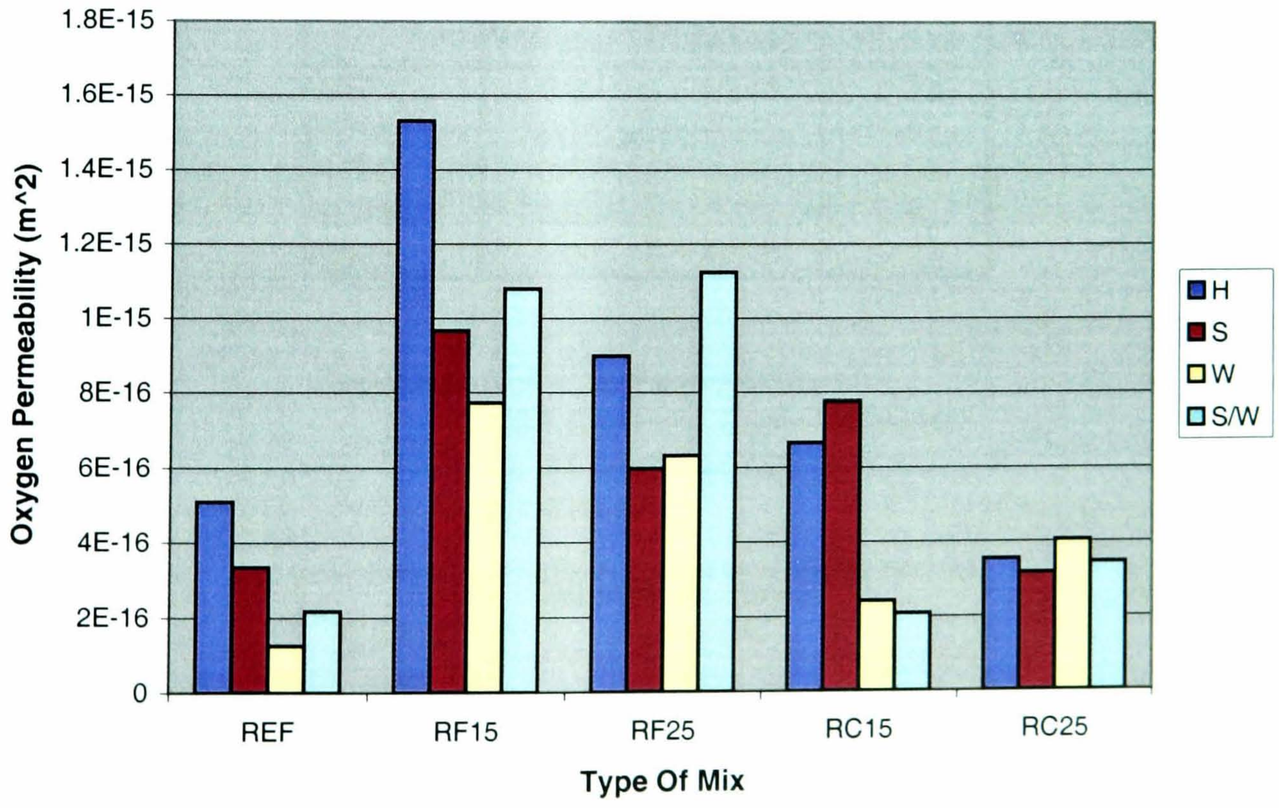


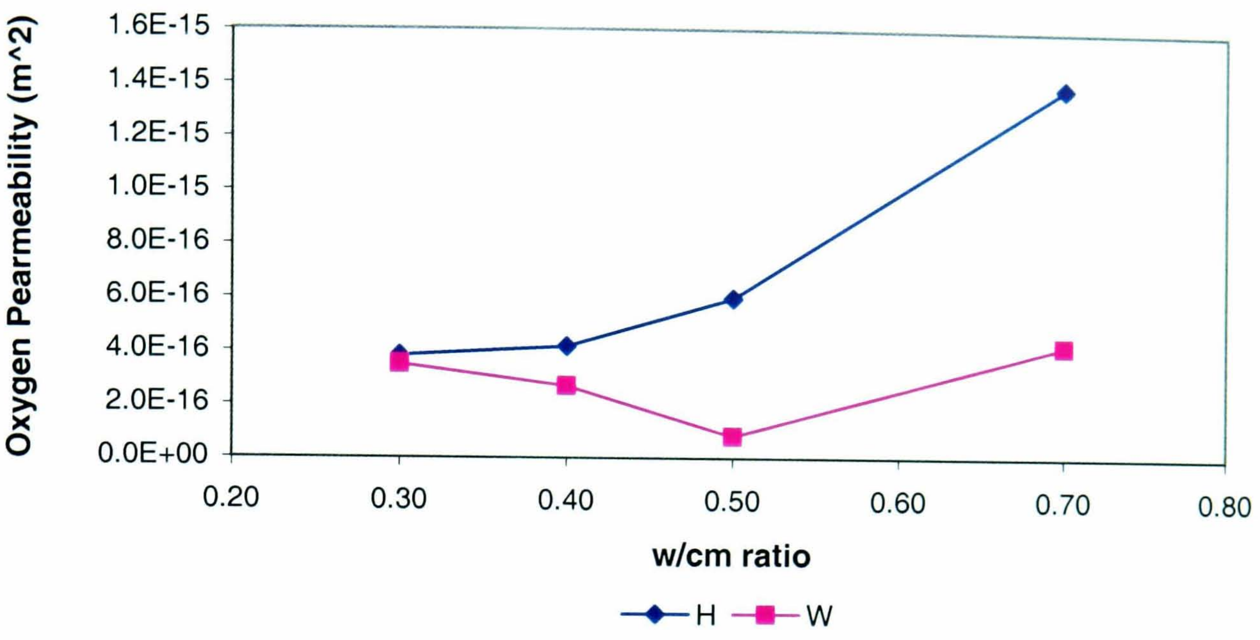
Fig. 8.9.b: Oxygen Permeability of Sample at w/cm=0.50 after 6 Months of Curing



S = Sealed after demolding
H = Cured at room temperature and 80% humidity

W = Cured in water after demolding
S/W = Cured in water after sealing for 28 days

Fig. 8.9.c: Relationship between w/cm Ratio and Oxygen Permeability for CSA Concrete with 25% Anhydrite



H = Cured at room temperature and 80% humidity

W = Cured in water after demolding

Table 8.5: Absorption of CSA Concrete Cured in Water for 28 Days and Conditioned for 6 weeks

Type of Mix	Absorptive Value (%)		
	Water	Curing Sealed	Humid
REF	8.68	10.73	9.27
RF15	2.15	6.37	4.68
RF25	0.77	3.50	2.63
RC15	3.66	5.03	5.80
RC25	5.04	6.50	6.13

Table 8.6: Chloride Permeability of CSA Concrete Cured in Water for 28 Days and Conditioned for 6 weeks

Type of Mix	Chloride Permeability coulombs		
	Water	Curing Sealed	Humid
REF	4870	3135	96
RF15	108	192	291
RF25	98	169	243
RC15	4210	393	468
RC25	578	281	276

IX

Conclusions, Applications and Future Work

9.1 Conclusions

From the work carried out in this thesis, the following conclusions can be drawn.

9.1.1 Properties of CSA Cement Paste

9.1.1.1 Hydration

- Ettringite was found to be the main hydration product of the laboratory-made CSA cement and anhydrite in systems with or without incorporation of OPC (Chapters 5 and 6). Although the ettringite was still the main product, in the commercially manufactured CSA, monosulfate strongly appeared as a second product, especially if the anhydrite was not sufficient to convert all the CSA and CA into ettringite (Chapter 7).

- The hydration process occurred very rapidly. With a given amount of mixing water, the reaction was complete in 7 days. Further hydration of anhydrous particles left in the system can be expected if water from outside enters the concrete.

- The ettringite was produced in crystal form with the size highly dependent upon the space available when the reaction took place. Higher w/cm ratio therefore produced longer crystals of ettringite in the greater available pore volume. The size of ettringite crystals influenced the crystalline interlocking properties and pore system in the CSA paste, which played an important role in contributing to the properties of the hardened concrete.

9.1.1.2 Volume Stability of CSA Paste

- The formation of ettringite from hydration of CSA cement and anhydrite via equation (1.1, Chapter 1) caused a contraction (Chapter 5). When, however, calcium hydroxide was also present in the system, expansion associated with ettringite formation via equation (1.3, Chapter 1) was observed (Chapters 6 and 7). The presence of CH in the system, either purposely introduced or as a product of OPC hydration, caused expansion. This is thought to be due to the forces exerted by the negatively charged ettringite crystals as suggested by Taylor (1997) and Metha and Hu, (1978).

- Hardened CSA paste, with or without OPC, exhibit expansion during continuous water curing. This is believed to be due to the absorptive characteristic of ettringite. The amount of expansion was relative to:

    - the accessibility of water into the system
    - the amount of ettringite in the system
    - the amount of constraint available in the system.

  The accessibility of water closely related to the w/cm ratio. The lower the w/cm ratio, the less was the expansion in the samples. In paste samples made in the laboratory, the constraint was provided by the anhydrous particles, while in paste made from commercially manufactured CSA cement, besides the anhydrous materials, other compounds present in the cement system also acted as a constraint.

- From the investigation carried out, it was found that regardless of the anhydrite contents, the laboratory-made paste samples at low w/cm (e.g. w/cm=0.30) cured in water produced very low expansions, as samples with the low w/cm were less permeable and more difficult to be penetrated by water. Under the same curing conditions, expansions of the laboratory-made samples with low anhydrite content (15% anhydrite) paste also produced very low expansion at all w/cms investigated (Chapter 5). The increase in the residual anhydrous CSA particles with the reduction of anhydrite content was responsible for controlling the expansion as the anhydrous particles acting as a constraint in the system and also because there is les ettringite in the system and hence less expansion.

- In water curing, the CSA samples with OPC produced lower expansion than that produced by CSA samples without OPC. The presence of OPC in the paste system reduced the amount of the substances contributing to the formation of ettringite, while CSH produced from OPC hydration acted as a constraint to the expanding ettringite.

- The use of commercially manufactured CSA cement produced significantly lower expansion than that produced by laboratory-made CSA cement (Chapter 7). This is because of a lower content of Klein's compound in the cement and the presence of less or non-reactive particles (e.g. C_2AS) in the cement system acting as a constraint to expansion.

9.1.1.3 Setting Time of Paste Made with CSA Cement

- In the mix containing CSA cement and anhydrite, the setting time of the paste at 20^0C was longer with the increase in anhydrite content. At an anhydrite content between 15% and 25%, the setting time of CSA paste was similar to that produced by OPC paste.

- Incorporation of 25% OPC into the mix affected the setting times. At 15% and 25% anhydrite contents, the initial setting time of CSA paste was longer than that produced by OPC paste. The initial setting time in the presence of OPC was shorter when the anhydrite content was increased. At 35% anhydrite content, the setting time was only 48 minutes at 20^0C.

9.1.1.4 Compressive Strength of CSA Paste

- In association with the early rapid hydration of CSA cement, the development of compressive strength of CSA paste also occurred at early ages. The seal-cured, laboratory-made CSA pastes developed strength at a slow rate after 7 days of curing. The compressive strength of samples increased with decrease of w/cm. The compressive strength of the laboratory-made CSA pastes cured in water or immersed in saturated $CaSO_4$ was influenced by the degree of damage caused by expansion. At 7 days of curing, the compressive strength increased with the increase in anhydrite content and with the decrease of w/cm. After 7 days of curing, when expansion induced cracks developed, only mixes with w/cms < 0.50 and anhydrite contents < 22.5% remained structurally intact and therefore could maintain the early strength (Chapter 5).

- The incorporation of 25% OPC into the laboratory made CSA paste reduced the compressive strength of seal cured samples. Early development of compressive strength at all levels of anhydrite content could be maintained after 6 months of curing. Curing in water slightly reduced the compressive strength of samples containing 20% and 30% anhydrite. The compressive strength of samples containing 40% anhydrite, however, drastically dropped as the samples experienced severe damage due to expansion (Chapter 6).

- The compressive strength of the commercially manufactured CSA paste was lower than that produced by the laboratory-made CSA samples. As the low expansion of the commercially manufactured CSA paste cured in water did not cause cracks in samples, the compressive strength of samples developed at early ages could be maintained after 6 months. The incorporation of 25% OPC reduced the compressive strength (Chapter 7).

9.1.2 Properties of Commercially Manufactured CSA Concrete

9.1.2.1 Setting Times

- As a consequence of the longer setting times of CSA paste compared to OPC paste, the setting times of concrete made from commercially manufactured CSA based cement were also longer than those for OPC concrete. The presence of CH as a product of OPC hydration when OPC was used as cement replacement, accelerated the initial setting times. Introducing 25% OPC as cement replacement into the system produced initial setting times comparable to the those of OPC.

- Longer initial setting times in CSA concrete may cause a problem in the possibility of losing water due to evaporation and this can cause plastic shrinkage induced cracks and prolonging the application of curing covers if curing compound were not to be used. Also it may increase pressure on formwork.

9.1.2.2 Workability

- Generally, the fresh CSA concrete was more workable than the OPC at the same w/cm ratio and the same water content. CSA concrete produced significantly higher slump at the same level of w/cm ratio and water content. This suggest that for the same slump and w/cm ratio of an OPC concrete, CSA concrete requires less cement content. The use of OPC as a cement replacement in CSA mixes reduced the slump to even lower values than those for control OPC concrete.

- Loss of slump of CSA concrete occurred at a faster rate compared to OPC concrete. The time taken for the slump to drop to the limit where the concrete was still just workable was, however, is still long enough for a normal concreting practice. The use of 25% OPC as a cement replacement adversely accelerated the loss of slump so that the time available was not adequate to handle the concrete using a conventional concreting practice.

- As far as the workability is concerned, the use of OPC as a cement replacement in CSA concrete is not recommended unless the concreting process is done very quickly and the concrete is used in simple concrete structures with no narrow formwork or congested reinforcement.

9.1.2.3 Expansion of CSA Concrete

- The expansions of commercially manufactured CSA concrete with various anhydrite contents, with or without OPC, were very small to structurally cause any damage on concrete. The aggregates occupied more than half of the concrete volume acting as a constraint for expansive ettringite during the water-curing period. The highest expansion was less than 0.02% after 6 months in water and with this amount of expansion, the concrete is categorised as non-expansive concrete. This expansion was reached by CSA samples containing 15% and 25% anhydrite without OPC.

9.1.2.4 Strength of CSA Concrete

- CSA concrete produced considerably higher strength compared to OPC at the same w/cm ratio and cement content. It is thought that the ettringite crystal interlocking considerably contributes to this high compressive strength. To produce an approximately equal compressive strength to that of OPC, the w/cm ratio must be increased, and to produce the same level of workability, the amount of cement must also be reduced. As a consequence, a less cohesive concrete due to lack of fine materials will be the result. Lower cost fine materials, such as pfa and ggbfs, as filler can be considered to compensate for the reduction in CSA cement in concrete. The use of CSA concrete may accelerate the removal of formwork and scaffolding because of the rapid early strength development. Unfortunately, around 10%-20% reduction of strength after 6 months of curing in water has to be expected. This is thought to be due to the development of micro-cracks inside the concrete when the expansion associated with ettringite took place. The introduction of OPC as a cement replacement did not improve the compressive strength of CSA concrete.

- Ettringite crystal interlocking did not work as well under tension. The indirect splitting tension strength was only marginally higher than that produced by the control OPC concrete. The use of OPC as a cement replacement produced even lower indirect splitting tensile strengths than the reference concrete.

- On the other hand, the role of ettringite crystal interlocking was pronounced in CSA concrete under flexural load. The flexural strength of CSA concrete was much higher than the reference mix. Again, the use of OPC as a cement replacement showed a negative effect on flexural strength.

9.1.2.5 Durability Related Properties of CSA Concrete

- Generally, the durability related properties were closely related to the permeability of the concrete. As the water demand for workability of CSA concrete was mostly lower than the water required for hydration, it is expected that the volume of capillary pores were lower than in the OPC concrete where the use of mixing water was always above that required for hydration. This was manifested by the water absorption of the CSA concrete without OPC, which were always lower than that of the OPC concrete. The oxygen permeability of CSA concrete was higher than that of the reference mix. The results of the rapid chloride permeability test carried out on CSA concrete are not conclusive due to the limitations of the test.

9.2 Applications of CSA Concrete

- Based on the research carried out on CSA concrete in this investigation, the applications of the concrete are widely open to various types of structures. Better workable concrete and reasonable duration of slump loss make CSA concrete suitable for application using conventional concreting processes. The longer initial setting times could be a problem as far as the evaporation of water and application of curing covers is concerned. The use of OPC as a cement replacement is not recommended from a workability point of view.

- The good compatibility between CSA cement and polycarboxylate based superplasticiser is beneficial in using CSA cement in flooring and self-levelling concrete or screed application.

- The higher strength of CSA concrete compared to that of OPC concrete is an advantage in using the concrete in various types of structure. The possibility of compressive strength reduction of about

10-20% due to curing in water for six months, as shown in Chapter 8, should be taken into consideration in design calculation. Higher flexural strength is an advantage of the CSA concrete if it is used as the material in pre-stressed concrete structures and rigid pavement. As for workability, the use of OPC replacement is not recommended, as the OPC adversely affected the strength of CSA concrete.

- The low alkalinity of CSA concrete is an advantage when glass fibres are used as reinforcement in concrete since these fibres are vulnerable to a high alkali and high pH environment. The low alkalinity of the concrete will, however, be a problem for steel reinforced concrete structures due to the increased potential for corrosion. As a result, CSA concrete for structural application needs to be of low permeability, or externally sealed to prevent water ingress.

9.3 Future Research

- The long-term durability of CSA concrete is the main concern to be researched in the future especially the effect of water curing and the effect of interference of other substances, such as those leading to sulphate attack and carbonation.

- As the CSA cement produces a higher strength than that produced by OPC, the effect of using lower cost fine material as filler is also worth considering in order to reduce the use of CSA cement in respect to achieving a lower strength of concrete. The introduction of a high content of entrapped air will be a benefit in creating the space for expansion if it is taking place. The use of pfa and ggbfs will be an interesting research topic, as both materials may act as cement replacement in reducing the strength and may act as an expansion constraint as well. The use of a latent cementitious material such as ggbfs may be expected, to some extent, to increase the ultimate strength of concrete and may provide a more stable structure with respect to moisture change. A number of MSc and undergraduate projects in the Department of Civil and Structural Engineering have already started investigating the above. The use of finely divided waste-rubber as filler does not only benefit in reducing cost but is also more environmentally friendly. From an engineering point of view, the high elasticity of finely divided waste rubber is an advantage in accommodating the expansion of ettringite and also it is expected to improve the dynamic properties of concrete.

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