uOttawa

L'Université canadienne
Canada's university

FACULTÉ DES ÉTUDES SUPÉRIEURES ET POSTOCTORALES

uOttawa

L'Université canadienne
Canada's university

FACULTY OF GRADUATE AND POSDOCTORAL STUDIES

Mukesh Pokharel
AUTEUR DE LA THÈSE / AUTHOR OF THESIS

M.A.Sc. (Civil Engineering)
GRADE / DEGREE

Department of Civil Engineering
FACULTÉ, ÉCOLE, DÉPARTEMENT / FACULTY, SCHOOL, DEPARTMENT

Geotechnical and Environmental Responses of Paste Tailings Systems to Coupled Thermo-Chemical Loadings

TITRE DE LA THÈSE / TITLE OF THESIS

Mamadou Fall
DIRECTEUR (DIRECTRICE) DE LA THÈSE / THESIS SUPERVISOR

CO-DIRECTEUR (CO-DIRECTRICE) DE LA THÈSE / THESIS CO-SUPERVISOR

EXAMINATEURS (EXAMINATRICES) DE LA THÈSE / THESIS EXAMINERS

Jim Beaudoin

O. Burkan Isgor

Gary W. Slater
Le Doyen de la Faculté des études supérieures et postdoctorales / Dean of the Faculty of Graduate and Postdoctoral Studies

GEOTECHNICAL AND ENVIRONMENTAL RESPONSES OF PASTE TAILINGS SYSTEMS TO COUPLED THERMO-CHEMICAL LOADINGS

By

Mukesh Pokharel

Thesis submitted to the Faculty of the Graduate and Postdoctoral Studies in partial fulfillment of the requirements for the M.A.Sc.degree in Civil Engineering

Department of Civil Engineering
Faculty of Engineering
University of Ottawa

Your file Votre référence
ISBN: 978-0-494-48631-3
Our file Notre référence
ISBN: 978-0-494-48631-3

Dedicated to my family

Acknowledgement

First, I would like to thank my supervisor, Professor M. Fall for accepting me as a M.A.Sc student in the Civil Engineering Department at the University of Ottawa. I express my sincere thanks to him for his expertise, invaluable suggestions, tireless efforts, encouragement and motivation to finish this research work within time. The hotly debated and useful discussion in the subject matter with him encouraged me to finish the writing of this thesis.

I also want to thank Dr. J.J. Beaudoin, Dr. T. Sato of NRC, Ottawa, Canada, for their help and interest in this research. My special thanks go to Mr. G. Chan of NRC for his invaluable time and co-operation during the XRD examination of the sample.

I am also thankful to my collegues Jean Claude Celestine, Juan Marin, and Othman Nasir for their help during the research. I am also thankful to Kulan Ambalavanar and Majeed Muslim for their tireless support during laboratory work.

Finally, this thesis would not be completed without the help of my spouse, Susma and son, Sanchit. I am very much thankful for her moral support as well as sharing difficulties during my Master's degree.

Abstract

Geotechnical and environmental responses of paste tailings systems to coupled thermo chemical loadings.

Cement paste tailings (CPT) and tailings shotcrete (TS) are investigated for thermo-chemo coupled effects on mechanical strength, durability and reactivity. CPT are made from Portland cement type I (PCI) and PCI-slag with 0 ppm, 5000 ppm, 15000 ppm and 25000 ppm of sulphate, cured at 2°C, 20°C, 35°C and 50°C and tested for UCS at 28, 90, and 150 days respectively. The mechanical strength depends upon both sulphate and temperature. Sulphate concentration, up to 15000 ppm, contributes positively to the strength whereas 25000 ppm reduces the strength at 50°C. Sulphate adsorption by calcium silicate hydrate (C-S-H) at 35°C and 50°C is also noticed. CPT used in cold mines is also found less durable than CPT used in hot mines (20°C -35 °C). The reactivity of the CPT system depends upon pyrite content and type of binder as well as curing time. Reactivity increases with increase of pyrite content and decreases with increase of curing time. The reactivity also increases with increase of curing temperature.

TS samples made from PCI, PCI-slag and PCI-fibre with 0 ppm, 2500 ppm and 5000 ppm of sulphate, are prepared and cured at 2°C, 20°C, 35°C and 50°C and

tested for UCS at 1, 7, 28 and 120 days respectively, to study the thermo-chemical effect on mechanical strength, durability and reactivity. The results show that sulphate and temperature significantly affect the mechanical strength, durability and reactivity of TS. Sulphate content up to 2500 ppm is found to contribute positively to the strength whereas 5000 ppm at higher temperatures shows deterioration in strength due to sulphate attack (adsorption of sulphate by C-S-H gel). PCI- slag performs better than PCI in sulphate and non - sulphate environments at 20°C and 35°C, but PCI-slag show poor performance at 2°C and 50°C. Fibre does not contribute any additional gain in strength to the TS. PCI performs very well at 50°C in sulphate as well as non - sulphate environments. The TS with PCI-Slag shows the lowest fluid transport ability. The reactivity of TS also depends upon percentage of pyrites and types of binder.

Table of Contents

List of Figures

List of Tables

List of Abbreviations

AMD	: Acid mine drainage
ASTM	: American Society of Testing Materials
C_3S	: Tricalcium silicate
C_2S	: Dicalcium silicate
C_3A	: Tricalcium aluminate
CH	: Calcium hydroxide
CPS	: Counts per second
CPT	: Cement paste tailings
C-S-H	: Calcium silicate hydrate
CWA	: Capillary water absorption
GGBFS	: Ground granulated blast furnace slag
kPa	: Kilo Pascal
MAC	: Mining Association of Canada
MPa	: Mega Pascal
PCI	: Portland cement type I
PPM	: Parts per million
TS	: Tailings Shotcrete
SEM	: Scanning electron microscopy
UCS	: Uniaxial compressive strength
XRD	: X-ray diffraction

1 Chapter 1: Introduction and background

1.1 General problem statement

Canada is rich in natural resources and ranks top as a mineral producing nation in 2006 with $40 billion as a production value (Stothart, 2007). It stands first in rank globally in the production of potash and uranium. In the same way, it is second in the production of nickel and cobalt, and third in aluminum, magnesium and gypsum (Stothart, 2007). These mineral industries are extracting huge amounts of metal ores from underground resources to recover precious metals through chemical and mining processes. These mining processes generate significantly large amounts of waste.

In Canada, approximately 500 million tonnes of mining waste are produced annually (Amaratunga and Yaschyshyn, 1997). The disposal of such waste can create several problems. Loss of fertility of land, soil erosion, landslides, formation of acid mine drainage (AMD), failure of tailing dams as well as contamination of water bodies are some examples of aesthetic, monetary and environmental impacts associated with the disposal of mining waste (Ritcey, 2005). Public perception and strict government regulations regarding the disposal of such waste compelled the mining industry into thinking and developing new strategies which are environmentally sound and cost effective. In this scenario,

recycling of such waste is gaining popularity in Canada and other parts of the world. Cemented paste tailing (CPT) is a new technology which is practiced extensively in Canadian mining sites (Fall et al., 2008). CPT is a heterogeneous material produced by mixing tailings with a solid percentage between 70% and 85%, water that is either fresh or mine processed, and hydraulic binder, which is usually 3% to 7% by weight (Fall and Benzaazoua, 2005; Fall and Samb, 2006). This technology has economical as well as environmental benefits for the mining industry. The use of CPT in the voids, created during the mining operation, allows the mining industry to extract additional ores (Fall et al. 2004, Benzaazoua et al., 2004). CPT technology significantly reduces the quantity of mining waste that has to be managed on the earth's surface (Fall and Samb, 2007). In addition to this, the hardened CPTs provide ground support for the surrounding mines structure and also a safe working environment for the mine workers (Kesimal et al, 2005). The use of CPT in the mining industry also reduces the construction of tailings dams. These tailings dams have the potential to pollute the ground water as well as tendency to destroy the aesthetic beauty of nature from tailings dam failure due to leakage, instability and liquefaction (Zou and Sahito, 2004). Rico et al. (2008) identified the failure of 147 tailing dams throughout the world.

CPT technology significantly recycles mine waste, in the same way the tailings shotcrete (TS) is another technique of recycling mine waste which is still in the research phase. Conventional shotcrete is widely used in mining as well as the construction industry. If the aggregate part of the conventional shotcrete can be

replaced by tailings, then it will be a great achievement to the mining industry from an environmental as well as economical point of view (Zou and Sahito, 2004). Some researches have been conducted on tailings in order to determine its suitability for usage in TS. It is prepared by mixing tailings with around 22% binder and 27% water by mass in the total mixture (Zou and Sahito, 2004). Polymer fibre (1.6%) or steel fibre (1.2%) is also added to increase the flexural strength. TS have many applications in the mining industry. It can be used in barricades construction, support of ground openings, tunnels and open pit slopes (more details are given in section 2.3.2).

The design criteria of CPT and TS (called paste tailings systems in this thesis) include geotechnical (mechanical stability, durability) and environmental (reactivity, fluid transportability) properties.

CPT and TS should have sufficient mechanical strength in order to be used underground for the safety of mine workers as well as increase ore recovery. In addition to mechanical stability, their resistance to sulphate attack is another parameter which influences the durability of CPT and TS structures. Most of the tailings contain pyrite as a source of sulphate (Elberling et al, 1994). Fall and Benzaazoua (2005) pointed out that the long term mechanical strength will reduce due to presence of sulphate. Sulphate attack also gives rise to cracks in the CPT system resulting in the possibility of generation of acid mine drainage (AMD). Temperature is another factor which significantly influences strength.

Heat of hydration of cement, geographical location of the mine, depth of the mine, mine ventilation, and blasting operations (Fall and Samb, 2006) significantly increase the temperature of the mine site, and CPT and TS structure. The coupled effect of temperature and sulphate (coupled thermo-chemical effects) on the mechanical strength and durability of the paste tailings system is still unknown. There are several literature items on CPT (e.g., Fall and Benzaazoua, 2005; Fall and Samb, 2006; Kesimal et al, 205) which either deal with sulphate or temperature alone, but in reality, at the mine site, both exist, so the information available in the literature will not simulate a field condition for establishing a standard design criteria for CPT and TS structures.

Furthermore, the response of the CPT and TS systems to these thermo–chemical effects needs to be investigated in order to better understand the durability and environmental behavior of paste tailings systems. Hence, fluid transportability (sorption, hydraulic conductivity) and oxygen consumption capability will provide the required information about the durability and reactivity of tailings. The fluid transport ability of the CPT and TS system provides information about the ways that it eases fluids, such as water, oxygen etc which can enter and move (Neville, 1995) into the system. This will provide indirectly, the amount of oxygen and water available for the further oxidation of sulphide minerals within the system. The presence of oxygen and moisture inside the CPT and TS system will increase the sulphate concentration from the oxidation of sulphide tailings. This results in the reduction of strength and favors the AMD

formation representing long term durability and environmental problems. Reactivity of the CPT and TS system using an oxygen consumption (OC) test is also important to judge if surface or underground CPT and TS can develop AMD and also whether the CPT system can produce sulfate. The OC test gives the amount of oxygen consumed by the CPT system containing different percentages of pyrites. It will indicate the reactivity of the CPT systems to judge the potential of AMD formation.

1.2 Background

1.2.1 Sources of sulphate in backfill operations

Sulphate is either available externally or internally in cementitious materials. For most of the concrete structures situated in the ground, sulphate enters into it externally from either ground water or soil (Park et al., 1999) through various mechanisms, such as diffusion, sorptivity or capillary suction (Adhikari, 2007; Neville, 1995). In the case of CPT and TS, the majority of sulphate is available internally within the systems. Most of the tailings used in the CPT system contain ferrous sulphide minerals in the form of pyrite and pyrrhotite (Elberling et al, 1994). These tailings may contain from 2% to 60% sulphide (Fall and Benzaazoua, 2005) depending upon the composition of ores. These sulphides in the presence of oxygen and moisture become oxidized and produce effluent that contains high concentration of sulphate with reduced pH (Elberling et al, 1994). In addition, the use of mine process water as mixing water (Fall and

Benzaazoua, 2005) can significantly increase the sulfate content in the CPT system. Finally, the presence of gypsum in the binder also contributes to sulphate.

1.2.2 Sources of temperature in backfill operations

Temperature is one of the major parameters that influence the mechanical strength of the CPT system. The recent trend of progressive depletion of ores at shallow depths compels the mining industry to consider alternative resources located at greater depths. The excavation of ores located at 3500-5000 meters from the earth surface will increase the heat load of the mining site due to geothermal gradient (Rawlins, 2003). Rawlins and Philips (2001) reported the variation of temperature with depth in an investigation carried out in a South Africa gold mine. According to this investigation, it is found that the temperature at 2000 meters is 37°C, 48°C for 3000 meters and 70°C for 5000 meters. In addition to the geographical location of the mine, blasting operations, and heat of hydration of cement also contribute to increasing the temperature of the mining site. Moderate heat can be added to the CPT system during its preparation to increase its early age strength (Fall et al, 2007). More detailed information about the sources of temperature in mines and backfill operations are published in Fall et al. (2008b).

1.2.3 Effect of sulphate on cementitious materials.

Sulphate attack is the process of deterioration of strength in cementitious materials when exposed to sulphate salt. Many cement concrete structures, such as bridges, piers, foundations etc., that are located in a sulphate environment become deteriorated due to expansion, cracking from the phenomenon of sulphate attack (Al-Akhras and Nabil, 2006). The sulphate attack is further classified as external and internal depending upon the source of sulphate in the cementitious materials. The phenomenon of the sulphate attack where the concrete structure loses its strength has become a major concern to the scientific community over the last few decades (Sahmaran et al, 2007). According to Bing and Cohen (2000), the two main chemical reactions involved in the sulphate attack mechanism are: 1) formation of ettringite due to the reaction between sulphate ions and C_3A along with its hydration products, and 2) formation of gypsum due to the reaction between sulphate ions and CH. The presence of ettringite and gypsum in the hardened cementitious material is harmful from a durability point of view (Sahmaran et al, 2007). The formation of ettringite produces expansion in cementitious materials resulting in the cracking of concrete (Fu and Beaudoin, 1996; Bing and Cohen, 2000; Fall and Benzaazoua, 2005). The formation of gypsum in cementitious materials is also harmful. According to Bing and Cohen (2000), whether the formation of gypsum in concrete leads to expansion is still controversial. Al-Akhras and Nabil (2006)

pointed out that the formation of gypsum and ettringite leads to expansion, cracking, deterioration and disruption of concrete structures.

Sulphate attack is a complex durability problem for cementitious materials and depends upon many factors, such as cement type, w/c ratio, CH content, porosity and permeability, mineral admixtures, types of salt, concentration of the salt, temperature, drying wetting cycles, etc. (Fu et al, 1997; Hekal et al, 2002; Al-Akhras and Nabil, 2006; Salah and Al-Dulaijan, 2007). Sulfate concentration is an important parameter that influences the durability of the cementitious materials. Concentrations of 0-150 ppm, 150-1500 ppm, 1500-10000 ppm and above 10000 ppm are classified as mild, moderate, severe and very severe respectively (Akoz et al, 1995) for concrete. However, sulphate concentration classification with regards to the damage of CPT did not exist until now. The cation present in the sulfate salt also plays a significant role in the deterioration of concrete strength and behaves differently with the product of its hydration. Both sodium sulphate and magnesium sulphate deteriorate concrete and the extent of deterioration is high in a magnesium sulphate environment (Park et al, 1999). In the case of sodium sulphate salt, formation of gypsum and ettringite will have an adverse effect on the durability of cementitious materials. If the concrete structures are subjected to a magnesium sulphate environment, then in addition to gypsum and ettringite, brucite and M-S-H (Baghabra and Al-Amoudi, 2002; Fall and Benzaazoua, 2005) will be produced due to the decalcification of C-S-H.

M-S-H is a non cementitious, non cohesive mass which significantly reduces the strength of cementitious materials (Baghabra and Al-Amoudi, 2002)

The adverse effect of sulfate on cementitious materials can be reduced to some extent by using type V cement (C_3A: 3.64%) which is found to perform better than type I cement (C_3A: 8.52%) in the sulphate bearing environment due to lower amount of C_3A (Salah and Al-Dulaijan, 2007). A lower amount of C_3A will limit the formation of ettringite, but on other hand, lower C_3A cement will have a high quantity of C_3S/C_2S. Increase of this ratio will produce a higher amount of CH from the hydration of the cement which again, aid in the formation of gypsum and causing loss of strength (Salah and Al-Dulaijan, 2007). Hence, in addition to C_3A, the ratio of C_3S to C_2S also has a significant effect on sulfate resistance (Baghabra and Al-Amoudi, 2002). Sahmaran et al. (2007) concluded from their research that sulphate resistant Portland cement with 3.6 % C_3A may not perform very well in a high sulphate environment due to high ratio of C_3S / C_2S.

Blended cements are widely used in a sulphate bearing environment to minimize the deterioration of cementitious materials. The use of type V cements with low C_3A (3.6%) results in lower strength than blended cements (Sahmaran et al. 2007). Various research, such as those by Baghabra and Al-Amoudi, 2002; Salah and Al-Dulaijan 2007, illustrate the role of the binder in reducing the adverse effect of sulphate. It is found that type I cement deteriorates more (Salah and Al-Dulaijan 2007) due to the presence of high amounts of C_3A. When PCI is

blended with pozzolanic materials, such as fly ash, ground granulated blast furnace slag (GGBFS), and silica fume, then it will resist the sulphate attack more than being used alone (Salah and Al-Dulaijan, 2007). The benefit of blended cement is the consumption of CH through pozzolanic reactions in the presence of moisture producing secondary C-S-H. The formation of secondary C-S-H in the cement gel makes the cementitious materials more impermeable and strong, minimizing the ingress of adverse chemicals in it (Baghabra and Al-Amoudi, 2002). In addition to the pozzolanic reaction, replacement of cement by pozzolanic materials in the system also reduces the quantity of C_3A which again, minimizes the potential of ettringite formation (Baghabra and Al-Amoudi, 2002). The hydration products of blended cement when observed through a scanning electron microscopy (SEM) that are exposed to a sulphate bearing environment for a long time, show no or fewer amounts of ettringite and gypsum in the cement matrix (Sahmaran et al, 2007). Due to this behavior of blended cement, they are highly recommended for use in high sulphate bearing environment (Salah and Al-Dulaijan, 2007).

Several studies of sulphate attack on conventional concrete and mortar (Akoz et al, 1995; Fu and Beaudoin, 1996; Turker et al , 1997; Akoz et al, 1999; Park et al, 1999; Baghabra and Al-Amoudi, 2002; Hekal et al, 2002; Mohammed et al, 2006; Sahmaran et al, 2007; Salah and Al-Dulaijan, 2007) are available in the literature. The above mentioned studies particularly deal with external sulfate attack whereas very few studies are available with respect to the CPT

system where the sulfate attack is internal. Some of the research work on CPT, such as Benzaazoua et al., 2004, Kesimal et al., 2004, Fall and Benzaazoua, 2005, indicate the strength loss due to the adverse effect of sulfate. Fall and Benzaazoua (2005) found that the adverse effect of sulphate on CPT also depends upon the concentration, curing time and binder type. At an earlier age, the sulphate plays a positive role in the gain in strength of CPT due to the precipitation of hydration products, such as CH, gypsum and ettringite in the micro pores of the CPT, resulting in the decrease of internal porosity. At an advanced age, depending upon the sulphate concentration, CPT becomes worse in strength due to the expansive pressure of these hydration products in the system. However, it should be mentioned that our understanding of sulphate attack on CPT and TS is still lacking.

Delayed ettringite formation (DEF) is another type of internal sulphate attack which is also known as heat induced internal sulphate attack (Escadeillas et al, 2007). In high temperatures above 70°C, especially in pre cast products and mass concreting, concrete and mortar will expand due to DEF when exposed to moisture at lower temperatures (Ramlochan et al, 2004). The high temperature inhibits the formation of ettringite and a considerable amount of sulphate is adsorbed by C-S-H gel (Fu et al, 1994; Ramlochan et al, 2004). The amount of sulphate adsorbed by C-S-H gel is also related to the concentration of the sulphate in the pore fluid. The sulphate thus adsorbed will be released at a later age and form ettringite in the hardened concrete. The

mechanism involved in the adsorption of sulphate by C-S-H gel is still not well defined (Ramlochan et al, 2004).

Cementitious materials also deteriorate by the formation of thaumasite which is another type of sulphate attack produced in the cement matrix due to the chemical reaction between sulphate and carbonate ion with C-S-H gel in an aqueous medium. The reaction between sulphate and CH produces gypsum which again reacts with $CaCO_3$ and C-S-H and produces thaumasite (Mingyu et al. 2006). The thaumasite will be continuously formed in the cement matrix as long as there is the availability of external sulphate and carbonate. The silica component will be available from the C-S-H gel and produces thaumasite which results in the softening of cement matrix. This produces white incohesive mushy products (Crammond, 2003). The thaumasite formation depends upon various factors; among them, cold temperature, sources of sulphate and carbonate, sources of silica and presence of water are the major parameters in the cement matrix. It was reported that thaumasite generally form in cold climates with temperatures below 15°C. Some thaumasite will form at 25°C, but in this case, the rate of formation is very low (Crammond, 2003).

1.2.4 Effect of temperature on cementitious materials

Temperature influences the mechanical properties of cementitious materials. Some of the previous research, such as Escalante-Garcia et al, 2001; Kim et al, 2002; Lothenbach et al, 2007, on concrete materials show that the increased temperature increases the fast precipitation of hydration products of cement leading to high early strength. In contrast, low temperatures decrease the hydration reaction, producing less hydration products and less dense C-S-H, resulting in low early strength. Strength development at lower temperatures is very slow whereas it is faster when the temperature is increased above room temperature (Lothenbach et al, 2007). The research on the effect of raised temperature on concrete (Escalante-Garcia et al, 2001; Kim et al, 2002; Lothenbach et al, 2007) shows that at an early stage (during 7 days of curing) temperature increases the strength. However, it has a negative effect on the strength at a later age of 28 days as reported by Kim et al. (2002). This leads to inferior mechanical properties with lower compressive strength. This lower strength at high temperatures during the later stage is due to the formation of dense hydrated phase which surrounds the unreacted cement particles and preventing them from further hydration (Barnett et al, 2006). There is adequate information available in the literature dealing with the effect of temperature on the mechanical strength of concrete (e.g., Escalante-Garcia et al, 2001; Kim et al, 2002 Lothenbach et al, 2007). As CPT is a different construction material than

normal concrete (Benzzazoua et al, 2004), hence, the results obtained from the concrete may not be fully applicable to CPT (Fall and Samb, 2006).

There is limited information in the literature about the effect of temperature on the mechanical properties of CPT and TS cured for a long period of time. Fall and Samb (2006) studied the impact of curing temperatures (0°C, 20°C, 35°C and 50°C) on the mechanical properties of CPT at early ages (up to 28 days). It was observed that the curing temperature has a significant influence on the strength development of CPT. Increasing the curing temperature increases the strength of CPT. CPT cured at low temperatures (0°C) exhibit lower strength due to inhibition of hydration reaction at low temperatures as well as the formation of ice lenses within the cement matrix which damages the CPT (Fall and Samb, 2006). The TG/DTA analysis of CPT cured at higher temperatures (20°C - 35°C) shows the presence of hydration products, such as C-S-H, ettringite, CH, and calcite. The amount of these hydration products is found to increase with an increase of curing temperature (Fall and Samb, 2006). The elastic modulus of the CPT sample is also found to increase linearly with curing temperature, supporting the formation of high amounts of hydration products within the cement matrix. The CPT samples cured at 50°C contain fine pores with low porosity and void ratio in comparison to the sample cured at 0°C which contains more voids. Presence of such finer voids and less porosity as well as void ratio in CPT cured at 50°C indicates possession of high strength. The capillary water absorption (CWA) test also demonstrates that the sample cured at 50°C absorbs the lowest amount of

water than other samples cured at 0°C, 20°C and 35 °C. The sample cured at 0°C absorbs more water due to high porosity (Fall and Samb, 2006; Fall and Samb, 2007). This suggests that CPT cured at higher temperature has a finer pore structure at early ages. Despite the tremendous progress made by the aforementioned studies on understanding the impact of temperature on CPT, our knowledge about the effect of temperature on the long term properties of CPT and TS is still limited. Furthermore, there is no study about the coupled effect of temperature and sulphate on the properties of CPT. There is a need to address these issues as explained above.

1.2.5 Shotcrete in underground mines

Shotcrete is an engineered material prepared from mixing cement, aggregate, and water in required proportion to suit the ground application. The proportion of this ingredient usually depends upon the specified compressive strength (Sahito, 2003). Shotcrete is generally mixed with admixtures, such as accelerators, and plasticizers to improve the performance for suiting ground conditions. Shotcrete is also reinforced with fibre or mesh and bolts to make it durable and as an economical means of ground support (Bernard, 2008).The presence of fibres in shotcrete improves its mechanical properties, such as ductility, toughness, flexural strength, impact resistance, etc. Shotcrete is extensively used as rock support in mines and civil engineering projects. It has been used as rock support for more than 40 years (Malmgren et al, 2005). The use of shotcrete in mining operations had started rapidly from the 1980s and still used today (Sahito, 2003). Shotcrete helps stabilize rock mass by preventing the

disintegration of rock particles. Shotcrete has many applications in mining as well as construction industries. Among them, the following are some examples of shotcrete applications (Sahito, 2003):

a) used in underground mine roofs,
b) used as tunnel lining, protecting slope and erosion, repairing civil engineering structures, and
c) used to prevent seepage of water from cracked surfaces, thermal insulation of tunnel etc.

1.2.6 Tailings containing sulphide

Mine tailings are the finely ground waste that remains after the extraction of metal ores. Generally, they have a particle size in the range of 100 to 200 μm (Elberling and Nicholson, 1996). The chemical composition of these mine tailings depend upon the composition of ores. Most of the tailings contain ferrous sulphide minerals (pyrite and pyrrhotite) (Elberling at al, 1994). In tailings impoundment, these sulphides become oxidized when exposed to the atmospheric oxygen and water. The oxidation of the sulphide minerals produces low pH (2-4) effluent rich in toxic metals with high concentration of sulphate. This acidic metal-rich leachate may contaminate water bodies, creating serious environmental problems, also known as AMD or Acid Rock Drainage (ARD). The common source of AMD are open pit mining works, mining waste rock, processing tailings, temporary or permanent stockpiles of sulphide minerals (Witt

et al, 2004). These sources remain active in the production of AMD for decades or even centuries after mine closure.

The oxidation of pyrite in the presence of atmospheric oxygen and water can be described by the following chemical reaction:

$$2FeS_2 + 7O_2 + H_2O = 2Fe^{2+} + 4SO_4^{2-} + 4H^+$$

However, it be mentioned that the describing the overall reaction for pyrite oxidation, in fact, consists of a series of complex subreactions with reaction mechnanisms that, in some cases, are not full understood (Herbert, 1999).

1.3 Objectives

The main objectives of this research programs are:

1) to study the coupled thermo-chemical effects on strength development of CPT systems (CPT, TS),

2) to study the coupled thermo-chemical effects on fluid transportability of paste tailings systems, and

3) to study the reactivity of paste tailings systems under various thermal conditions.

1.4 Organization of manuscript

This thesis has five chapters. Chapter 1 deals with the introduction and background of the research with its objectives, identifying the research needs

with some background of the problems. Chapter 2 concentrates on the coupled thermo-chemical (temperature and sulphate) effects on strength development of CPT systems. The experimental parts and results of these coupled processes on the mechanical strength of CPT and TS at early and advanced ages are thoroughly discussed, followed by conclusions and recommendations. Chapter 3 provides the experimental output of coupled thermo-chemical effect on fluid transportability of CPT and TS. The results obtained from the hydraulic conductivity of CPT and capillary test for TS are thoroughly analyzed and presented followed by conclusions and recommendations. Chapter 4 deals with the reactivity of paste tailings systems under various thermal conditions. It provides the information about the AMD formation as well as sulphate production potentials of various cemented and uncemented paste tailing systems. Finally, summary and conclusions as well as recommendations for further research are presented in Chapter 5.

2 Chapter 2: Coupled thermo-chemical effects on the strength development of cemented paste tailings systems

2.1 Introduction

CPT is the latest technology used in mining industries to fill the voids produced during excavation of metal ores. TS are another approach used in the mining industries to construct barricades, and reinforcing underground openings. TS is still in the research phase. Extensive research was carried out to find the suitability of tailings for use in TS. The CPT and TS systems should have sufficient mechanical strength for use in mining operations. They should be durable for the safety of worker as well as economical benefit. Paste tailings are used as an aggregate for such paste tailings systems (CPT, TS systems). Depending upon the composition of the ores, these tailings may contain different amounts of sulphide. Every mine has a unique temperature. The mechanical strength of CPT and TS is found to be influenced by curing temperature. Several research on CPT show that mechanical strength also depends upon its sulphate content. The thermo–chemical coupled effect on mechanical properties of CPT and TS is still lacking knowledge. Hence, extensive laboratory investigation was carried out to study the coupled effect on the mechanical strength of CPT and TS.

2.2 Cemented paste tailings

2.2.1 Abstract

Almost 200 samples were tested for uniaxial compressive strength (UCS) cured at different temperatures of 2°C, 20°C, 35°C, 50°C at 28, 90 and 150 days with sulfate concentrations of 0 ppm, 5000 ppm, 15000 ppm and 25000 ppm. PCI and PCI-slag (50/50) were used to observe the effect. The results showed that sulfate with concentrations of 5000 ppm, and 15000 ppm has a beneficial effect on the strength development of the CPT up to the period under study. The 25000 ppm sample also shows good strength, but lower than that of the 5000 ppm and 15000 ppm sample at 28 days. The 25000 ppm sample at 90 days cured at 50°C shows a sudden drop of strength. It is concluded that CPT with a 4.5% binder up to 15000 ppm does not exhibit the phenomenon of sulfate attack. If the sulfate content is in the range of 25000 ppm, then UCS will be reduced after 90 days in hot curing temperatures. Most of the results of the CPT sample show that the PCI–slag performed better with sulfate than PCI.

2.2.2 Introduction

The mechanical properties of the CPT depend upon various factors, such as tailings material characteristics, type of binders, water cement ratio, chemical composition of water, curing temperatures, sulfate content etc. The problems will arise when the CPT materials are rich in sulphate. Depending upon the concentration, it may have positive and negative effects on the performance of the CPT (Fall and Benzaazoua, 2005). Temperature is another parameter that also affects the UCS of CPT. Fall and Samb (2006) concluded that mechanical properties of CPT increase with increases in curing temperature at an early age of 28 days. The above studies were implemented taking only one parameter, either sulphate or temperature, at a time. In reality, both temperature and sulphate exist together. Thus, the impact of sulfate and temperature at the same time on the UCS of CPT still lacks information. In the best knowledge of the author, there is no information available in literature about this coupled effect on the mechanical strength of CPT. Hence, this issue should be resolved in order to determine the exact solution for use in CPT operation to address economical as well as safety concerns. In this scenario, the prime objective of this research is to investigate the coupled thermo-chemical effects on the mechanical strength of CPT.

After this introduction, materials and methods will be discussed, followed by specimen preparation. The experimental results are presented and discussed in the results and discussion, and finally, conclusion of the research is drawn at the end.

2.2.3 Materials and methods

2.2.3.1 Materials

2.2.3.1.1 Binders used

CPT gains strength by mixing with binder. Portland cement is widely used as a binder in various proportions in order to achieve the required strength. The cost and strength of CPT are found to be proportional to the amount of binder used. Generally, alternative cementitious materials, such as GGBFS and fly ash are also mixed with Portland cement in certain proportions to reduce the cost (Fall and Samb, 2006) and also to take advantage of the pozzolanic reaction. Hence, in this study, commercially available ordinary PCI and GGBFS are used to prepare the samples. In the case of PCI–slag, PCI and slag were used (50:50 % by weight). The binder was added in the mix at a rate of 4.5% by weight in all samples. Table 2.1 shows the chemical properties of the cement and slag as well as their relative density.

Table 2-1 Chemical properties of the binders used

Binder	MgO	CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	Rel.density
PCI	2.65	62.82	18.03	4.53	2.7	3.82	3.1
Slag	10.98	41.14	34.23	9.54	------	3.87	3.3

Rel.: relative

2.2.3.1.2 Water used

Distilled water was used to prepare all specimens. The purpose of using distilled water is to accurately maintain the desired concentration of sulfate in the sample. Furthermore, tap water may contain undesirable chemicals that can affect the behaviors of CPT. Required amounts of sulfate salt ($FeSO_4.7H2O$) with molecular weight 278.01 was added to the distilled water in order to achieve 5000 ppm, 15000 ppm and 25000 ppm of sulfate concentration. The water cement ratio was maintained at 7.5.

2.2.3.1.3 Tailings

Commercially available artificial tailings, known as SILCOSIL106, were used to prepare the entire sample. These artificial tailings are made from ground silica which contains 99.8 % of SiO_2. The grain size of the artificial tailings is very similar in the physical characteristics of the natural tailings available at the mining sites in eastern Canada (Fall and Samb, 2007). The grain size distribution of the ground silica used in the research is given in Figure 2.1. The same figure also

illustrates the grain size distribution of natural tailings from 9 Canadian mines from eastern Ontario. The main objective of using artificial tailings is to have an accurate control of the mineralogical and chemical composition of the tailings; the exact initial amount of concentration of sulfate in the mix. Furthermore, the natural tailings may contain varying amounts of sulfate and other undesirable minerals which can significantly influence the results of the study. The physical and chemical properties of the tailings are given in Tables 2.2 and 2. 3.

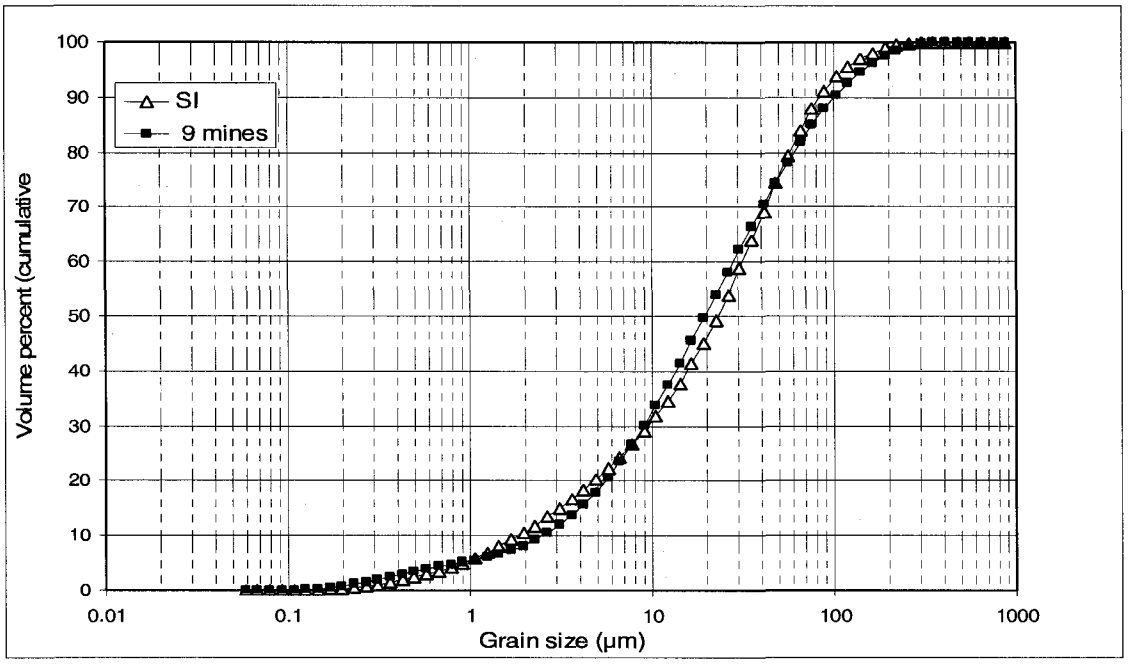

Figure 2-1 Grain size distribution of tailings used and average grain size (9 mines) of tailings from eastern Canada

Table 2-2 Physical properties of the tailings

Element	Gs	D_{10}	D_{30}	D_{50}	D_{60}	D_{90}	C_u	C_c
Unit	-	µm	µm	µm	µm	µm	-	-
	2.7	1.9	9.0	22.5	31.5	88.9	16.2	1.3

Table 2-3 Chemical properties of the tailings by percentage (Source: US Silica Company)

SiO_2	Fe_2O_3	Al_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	LOI	pH
99.8	0.035	0.05	0.02	0.01	<0.01	<0.01	0.02	0.1	7

2.2.4 Specimen preparation

Required amounts of tailings and binder were mixed in a dry container until a homogeneous color was obtained. Required amounts of sulfate salt were added into the distilled water to achieve 5000 ppm, 15000 ppm and 25000 ppm of concentration of sulfate in the mix. The distilled water containing sulfate salt was added to the dry mix of binder and tailings, and mixed together to obtain a homogeneous paste. Table 2.4 shows the ingredients of the mix used in this research. The CPT samples were kept in a plastic cylinder sized 5 cm in diameter and 10 cm in height. The samples were then vibrated manually to remove the entrapped air from the molded samples. The prepared samples were sealed with a plastic cover to prevent the evaporation of water. They were cured in an environmental chamber with controlled temperatures of 2°C, 20°C, 35°C and 50°C for 28, 90 and 150 days. Almost 200 samples were prepared for this study.

Table 2-4 Different ingredients used in the research for CPT

Binder Types	Binder ratio	% of Binder	W/C ratio	Sulphate (ppm)
PCI	--	4.5	7.5	0
PCI	--	4.5	7.5	5000
PCI	--	4.5	7.5	15000
PCI	--	4.5	7.5	25000
PCI + Slag	50/50	4.5	7.5	0
PCI + Slag	50/50	4.5	7.5	5000
PCI + Slag	50/50	4.5	7.5	15000
PCI + Slag	50/50	4.5	7.5	25000

2.2.5 Testing procedures

2.2.5.1 Uniaxial compressive strength test

UCS testing as per ASTM C 39 was performed to evaluate the mechanical strength of the samples after 28, 90 and 150 days of curing times for the different temperatures under consideration. The load was applied at a slow rate of 1

mm/min. Each test was repeated at least twice to ensure the repeatability of the results.

2.2.5.2 Water content test

The water content of the CPT sample was determined as per ASTM standard D2216-05. The water content allows us to determine indirectly, the advancing of the binder hydration and also quantity of water absorbed by the cement hydration products and sulphated hydration products. It should be mentioned that the determination of water content does not inform about the hydration degree, but can provide a relative comparison of the quantity of water absorbed by the hydration products and expansive minerals, such as ettringite, and gypsum of the cementitious materials.

The hydration degree of cementitious materials can be determined by using several methods, such as (Aziz et al, 2005):

1) Determination of free lime content with ammonium acetate methods,
2) Determination of evaporable and non - evaporable water content, and
3) SEM observation.

2.2.5.3 X-Ray analysis test

X-ray analysis tests on selected samples were implemented to gain information about the coupled effects of temperature and sulphate on the mineralogical

composition of the samples. For these tests, water cement paste with (w/c = 2) were prepared by adding required amounts of sulphate to obtain 5000 ppm, 15000 ppm and 25000 ppm of sulphate. The samples were cured at 2°C, 20°C, 35°C, 50°C for 28, 90 and 150 days. X-ray tests were performed after 28 and 150 curing days.

2.2.5.4 SEM observations

SEM observations were implemented on cemented paste samples to identify the binder hydration product and/or the nature of sulphated minerals formed under various thermo-chemical loadings.

2.2.6 Results and discussions

2.2.6.1 Coupled effects of sulphate and temperature on PCI-CPT strength

2.2.6.1.1 Early ages

Figure 2.2 represents the 28 day UCS value of CPT made from PCI cured at 2°C, 20°C, 35°C and 50°C with 0 ppm, 5000 ppm, 15000 ppm and 25000 ppm of sulphate concentration. In general, the UCS of all samples increases with increase of curing temperature. As the curing temperature increases, the hydration reaction of cement will be accelerated, thus more hydration products will be produced in the CPT system resulting in the gain of UCS value (Fall and Samb, 2006; Lothenbach et al, 2007).The XRD results in Figures 2.3, 2.4 and 2.5 show the variation of presence of CH in the CPT system due to raised temperatures. The peak of CH, especially at 18 degrees 2-theta at 20°C (Fig 2.4) and 50°C (Fig 2.5) with 25000 ppm of sulphate is greater than the peak of CH produced at 2°C for 28 days resulting in a higher value of UCS with raised temperatures. This suggests a higher binder hydration degree in CPT samples cured at hotter temperatures (20°C, 50°C).

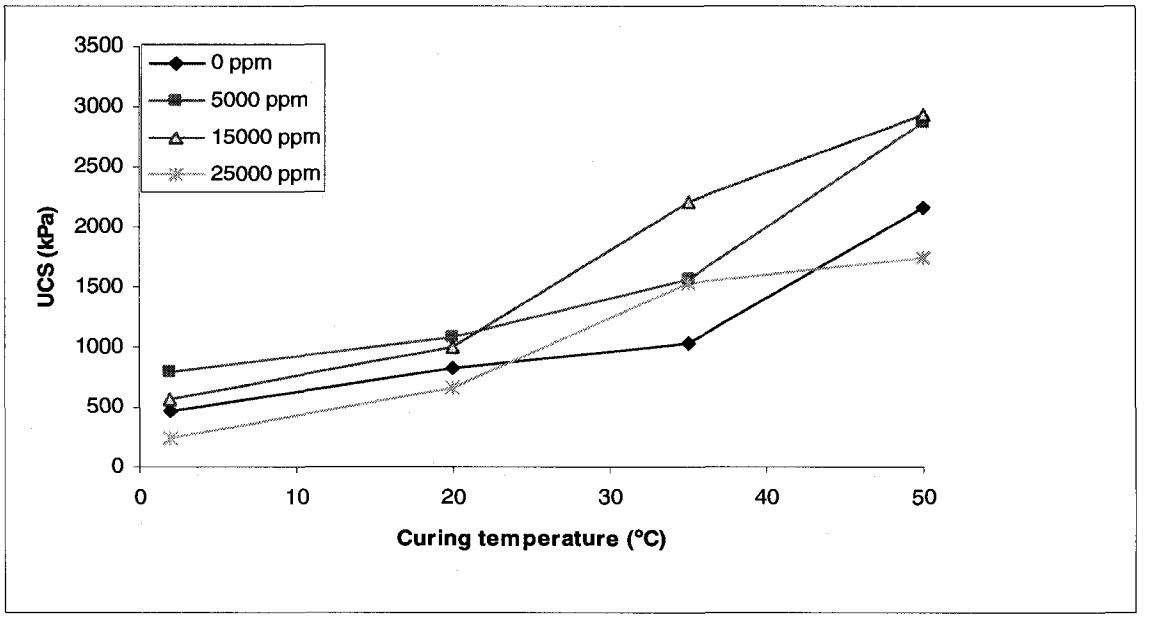

Figure 2-2 28 day UCS of CPT made from PCI with different sulphate at different curing temperatures

Figure 2.2 also shows that the UCS of samples containing sulphate is comparatively higher than those without sulfate with the exception of the 25000 ppm samples. The CPT sample cured at 2 °C exhibits lower strength. This lower strength is due to the inhibition of cement hydration at low temperatures. The sample cured at low temperatures has very low cement hydration rate as mentioned in sub paragraph 1.2.4, producing less C-S-H (Barnett et al, 2006; Fall and Samb, 2006; Lothenbach et al, 2007). This results in a lower value of compressive strength.

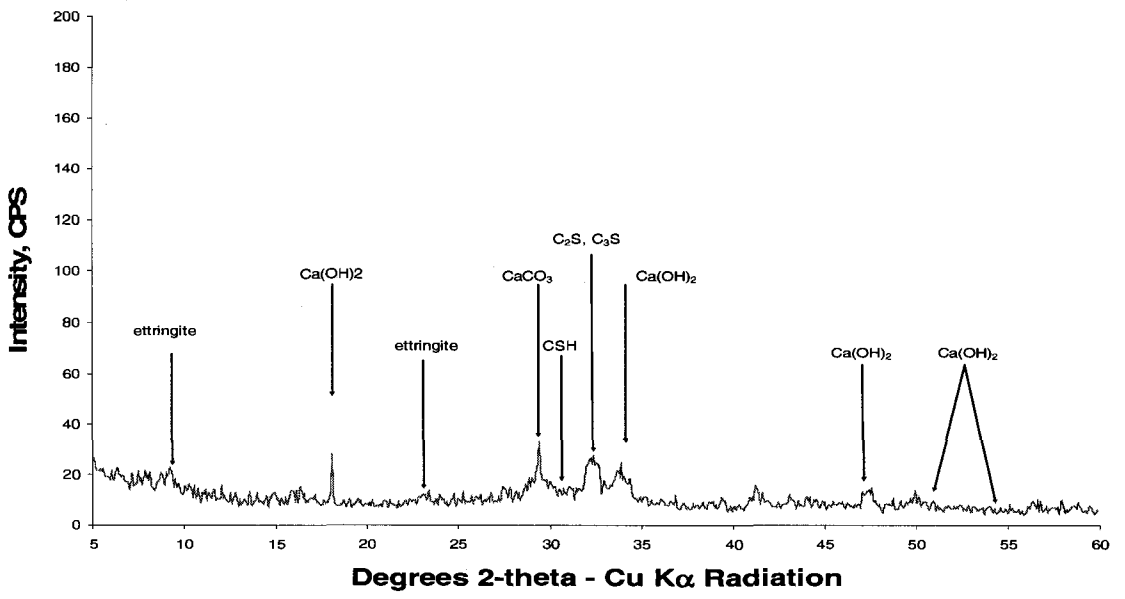

Figure 2-3 XRD result of 25000 ppm of cemented paste made from PCI cured at 2°C for 28 days.

The 5000 ppm and 15000 ppm of sulphate samples have higher values of UCS than 0 ppm sample at 2°C, 20°C, 35°C and 50°C. This increase of UCS value with raised temperatures was also reported by Akoz et al. (1999). The higher value of UCS of 5000 ppm and 15000 ppm samples is due to the precipitation of both hydration products and secondary gypsum, and ettringite in the cement matrix by the reaction of sulphate with CH and C_3A (Nehdi and Hayek, 2005). The formation of such secondary gypsum and ettringite along with hydration products fills the void space and micro pores within the CPT system. Such mechanism of precipitation of minerals rearranges the micro structure of CPT which decreases the internal porosity, resulting in the higher strength of the CPT (Akoz et al, 1999; Fall and Samb, 2006).

Figure 2.2 also shows that the 15000 ppm samples cured at 35°C has the highest value of UCS than the rest of the samples cured at the same temperature. This may be due to the higher amount of ettringite precipitated which still contributes positively to the strength. The 28 day UCS value at 50°C of 0 ppm and 5000 ppm samples increases sharply from 35°C whereas 25000 ppm sample at 50°C shows a lower value of UCS. This sharp increase is due to the continuous precipitation of hydration products due to high curing temperatures. In addition to these hydration products, precipitation of secondary ettringite and gypsum also contributes to the sharp gain of UCS of 5000 ppm sample at 50°C. This lower UCS value for 25000 ppm sample at 50°C could be attributed to the phenomenon of adsorption of sulphate by C-S-H gel (Fu et al, 1994) so that there will be no or very small amounts of sulphate remaining for the precipitation of secondary gypsum and ettringite in the CPT system.

The XRD result in Figure 2.5 shows the absence of secondary gypsum and ettringite, but the presence of high amounts of CH. This XRD result shows the sulphate adsorption by C-S-H gel at high curing temperatures. Hence, there is not enough sulphate remaining in the system to react with CH. Additional mechanism that can contribute to the decrease of ettringite at 50°C, is the fact that the stability of ettringite decreases at high temperatures (Escadeillas et al, 2007). One can observe a higher peak of CH in Figure 2.5 although the sample contains 25000 ppm of sulphate. The sample with 25000 ppm of sulphate shows a reduced strength at 50°C at the earlier age of hydration. This reduction of

strength of 25000 ppm of sample may be due to adsorption phenomenon. The adsorption of high amounts of sulphate by C-S-H, can have led to the formation of C-S-H gel of lower quality, thereby resulting in the decrease of UCS. Indeed, C-S-H is the main binding phase in cemented systems. Another mechanism; the inhibition of cement hydration at an early age by the high initial sulphate content can be suggested as an additional cause of the low UCS of the 25000 ppm sample at 50°C. From Figure 2.2, it can also be observed that the 25000 ppm samples have a lower value of UCS in all temperatures in comparison to 5000 ppm and 15000 ppm.

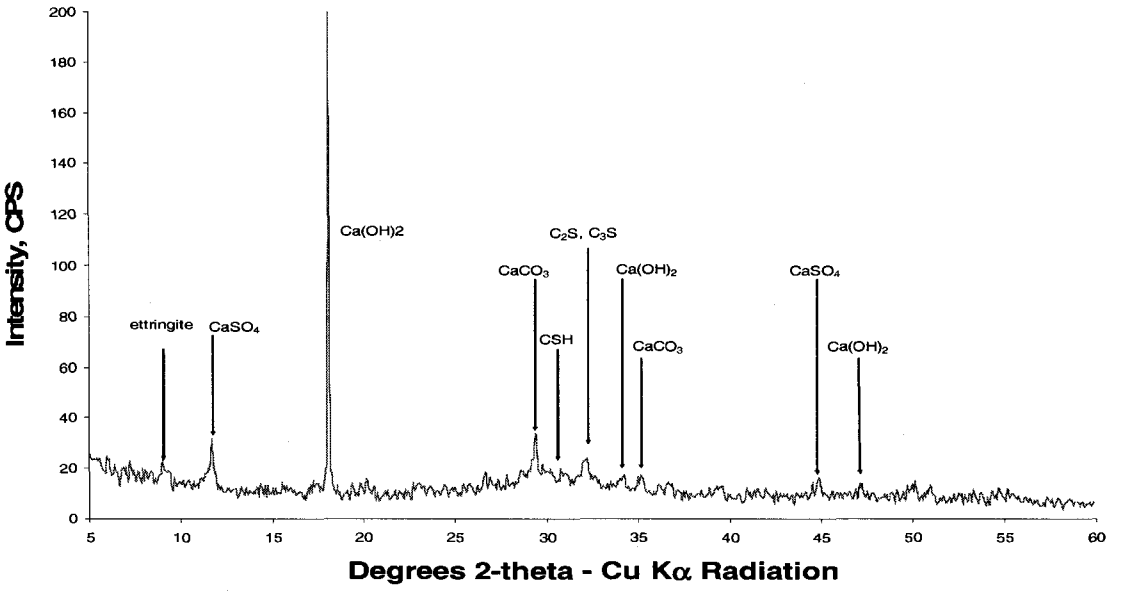

Figure 2-4 XRD result of 25000 ppm of cemented paste made from PCI cured at 20°C for 28 days.

The lower value of UCS of the 25000 ppm sample can be explained by the strong inhibition of hydration reaction due to the presence of sulphate at 2°C and

20 °C. Fall and Benzaazoua (2005) explained that this effect is due to the presence of sulphate which strongly inhibits the early hydration of C_3A.

The XRD results in Figures 2.3, 2.4 and 2.5 show that the 25000 ppm sample still has unreacted C_2S and C_3S. This means that the samples are not fully hydrated. The gain of strength is very slow as temperature increases from 2°C to 20°C, but shows a sharp increase from 20°C to 35°C. This increase is due to the formation of additional hydration products along with secondary ettringite.

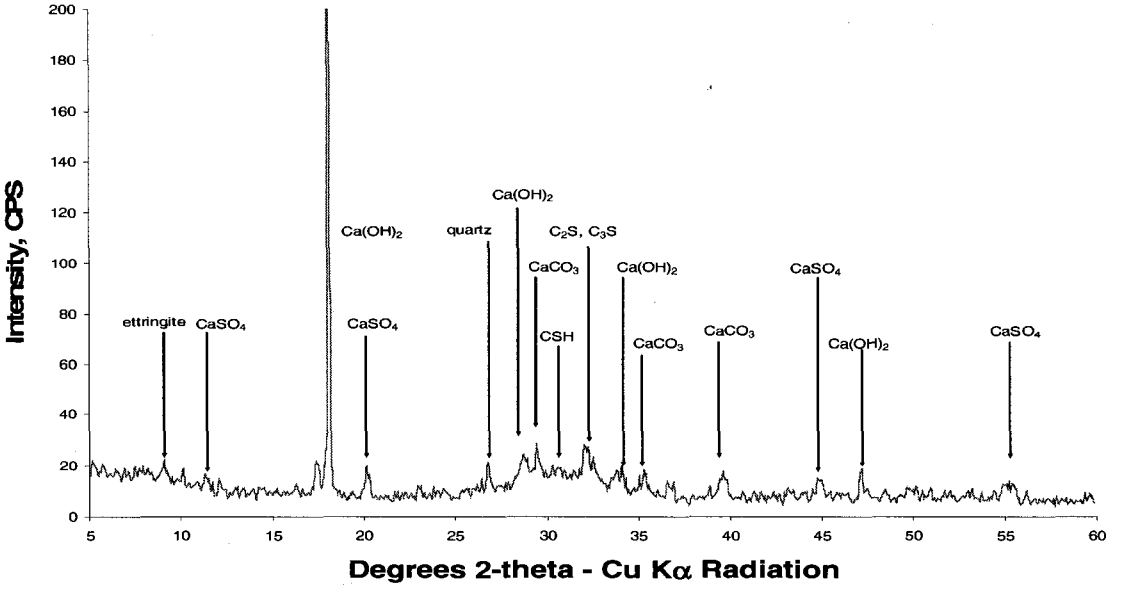

Figure 2-5 XRD result of 25000 ppm of cemented paste made from PCI cured at 50°C for 28 days .

2.2.6.1.2 Advanced ages

Figures 2.6 and 2.9 present the UCS of CPT at 90 and 150 days made from PCI cured at 2°C, 20°C, 35°C and 50°C with 0 ppm, 5000 ppm, 15000 ppm and 25000 ppm of sulphate concentration.

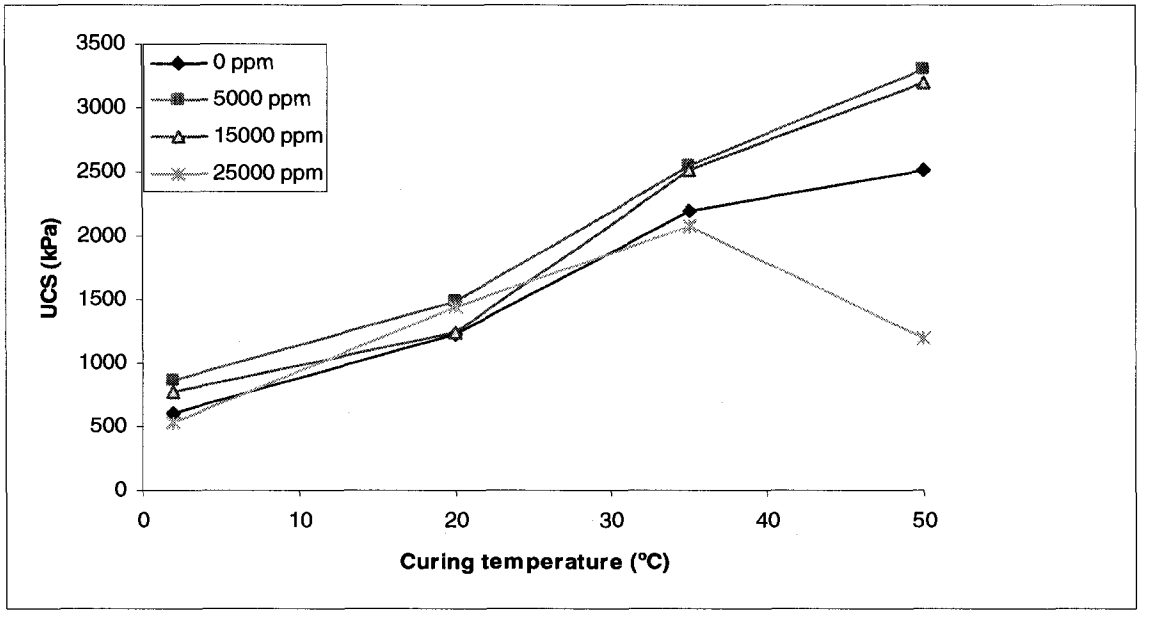

Figure 2-6 90 day UCS of CPT made from PCI with different sulphate contents at different curing temperatures

Like the 28 day value, the 90 day UCS value of all the samples increases with increase of curing temperature with the exception of the 25000 ppm sample at 50°C. The increase of the strength of the 0 ppm sample is entirely due to formation of an additional quantity of CH and C-S-H due to rise in temperatures (Fall and Samb, 2006, Lothenbach et al, 2007). On the other hand, formation of

gypsum, and ettringite in addition to the CH, C-S-H contributes in the gain of UCS value of 5000 ppm, 15000 ppm and 25000 ppm samples (Fall and Benzaazoua, 2005).

At 2 °C, the 5000 ppm and 15000 ppm samples show somewhat higher strengths than 0 ppm samples while the 25000 ppm sample has a lower value of UCS in comparison to the rest of the samples. As mentioned above, the lower value of UCS of the 25000 ppm sample in comparison to other samples is due to the presence of elevated amounts of sulphate which strongly inhibit the hydration reaction.

The trend of evolution of UCS from 28 to 90 days at 2°C for these samples shows that the rate of strength gain is 117%, 35%, 7% and 30% for 25000 ppm, 15000 ppm, 5000 ppm and 0 ppm samples, respectively. This is due to the continuous hydration of cement with curing time. The 25000 ppm sample at 2°C has very low 28 day UCS value due to a high amount of sulphate. The presence of sulphate for 90 days in 25000 ppm samples contributes positively to the UCS value due to the formation of expansive minerals as explained above. In addition to this, the continuous hydration of cement with curing time makes its gain of strength higher in comparison to other samples at 2°C.

The 90 day UCS value of the 5000 ppm sample (Fig 2.6) is found to be higher than that of the other samples at all curing temperatures. The 5000 ppm sample

cured at 2°C at 90 days is 40%, 10% and 60% stronger than 0 ppm, 15000 ppm and 25000 ppm samples at the same curing times and temperatures. This difference in strength between the 5000 ppm sample and rest of the samples at 2°C can be attributed to the formation of a higher quantity of CH along with gypsum and ettringite. In contrary to this, 15000 ppm and 25000 ppm samples will have smaller amounts of CH at 2°C due to the high sulfate content.

CPT sample without sulphate (0 ppm) will form a high quantity of CH and C-S-H from the hydration of cement. However, it does not have any sulphate except for a few sulphate ions from the cement which is considered negligible in this study. Thus, there is no possibility of formation of expansive minerals. Hence, it has less strength than the 5000 ppm and 15000 ppm samples at 2°C.

The 5000 ppm sample shows a higher value of UCS at 20°C than the rest of the samples and has almost the same value as the 15000 ppm sample at 35°C and 50°C. This can be explained by the fact that because of the low sulfate concentration of the 5000 ppm sample, there is enough hydration of the cement. The sulphate reacts with available CH and forms expansive minerals. These minerals play a beneficial role of filling voids, thereby contributing positively to the strength of the samples and showing high value of UCS at all temperatures.

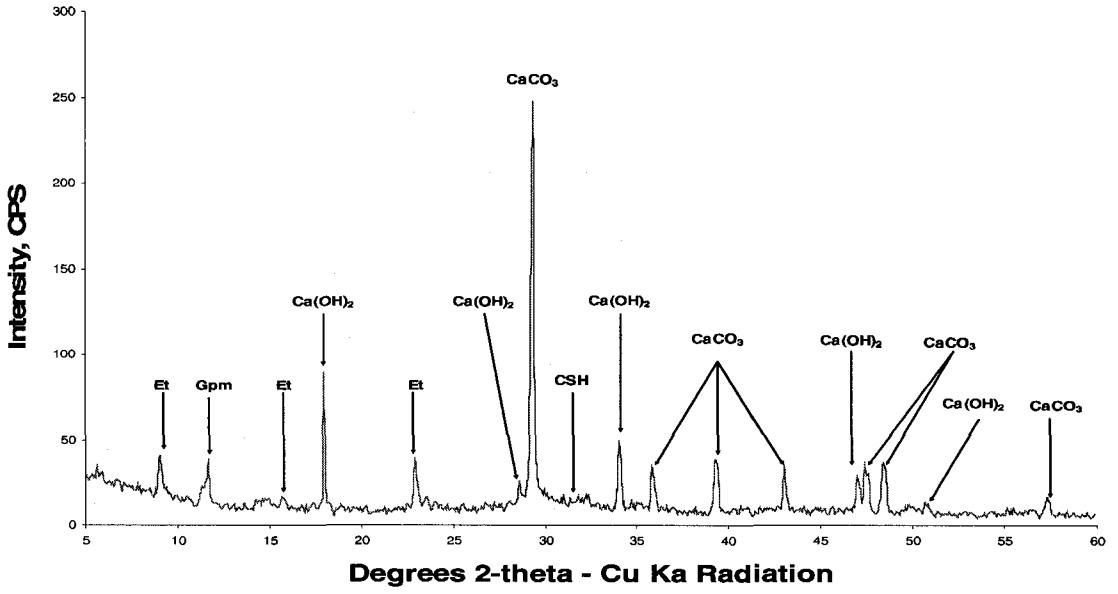

Figure 2-7 XRD result of 5000 ppm cemented paste made from PCI cured at 20°C for 150 days

The 15000 ppm and 25000 ppm samples still show less strength than the 5000 sample at 20°C due to less formation of hydration products. This is because of the high concentration of sulphate in those samples. When the temperature rises above 20 °C, the hydration reaction accelerates, producing more and more CH. The CH reacts with sulphate, producing expansive minerals filling the voids. This results in the high strength of the 15000 ppm sample at 90 days at 35°C and 50°C. This argument is also supported by the result of the 90 day water content presented in Figure 2.8. This figure illustrates that when the temperature increases, the sample is consuming more and more water. Thus, the hydration rate of cement increases, producing more and more hydration products (e.g. C-S-H, CH), leading to high strength of CPT samples at advanced ages.

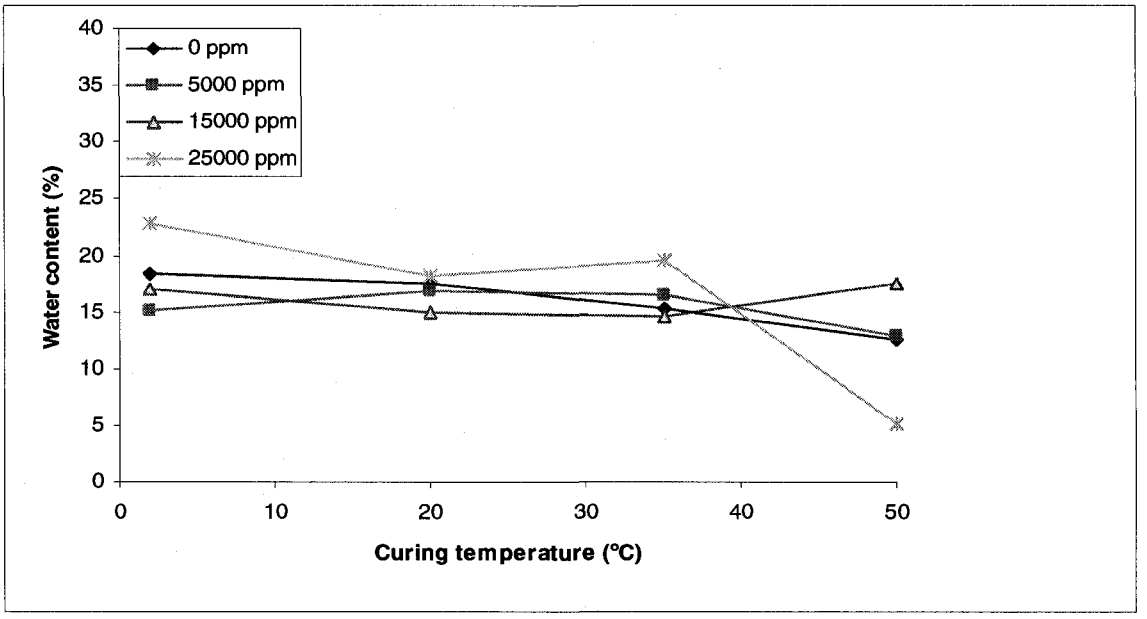

Figure 2-8 90 day water content of CPT made from PCI with different sulphate contents at different curing temperatures

In contrary to this, the 25000 ppm sample at 90 days behaves differently. It shows a sharp rise in strength up to 35°C. After that, the strength drops at 50°C. The trend of the growth of the UCS curve of the 25000 ppm sample from 2°C to 20°C and from 20°C to 35°C shows that the slope of the curve declines from 20°C to 35 °C in comparison to 2°C to 20 °C, and at 50°C, there is considerable loss of strength of the 25000 ppm sample. The reduced strength can be mainly attributed to the adsorption of sulphate by the C-S-H gel which is described below more in detail.

Figure 2.9 illustrates the 150 day UCS of CPT cured at different temperatures with various initial sulphate contents. As the 90 day strength, the 150 day UCS results also show that the strength of the samples increases with increase of curing temperature with the exception of 25000 ppm at 50°C. The 5000 ppm

sample has a higher compressive strength at 2°C than the rest of the samples. The XRD result in Figure 2.7 shows the formation of ettringite and gypsum in the 5000 ppm sample cured at 20°C. These expansive minerals (in non excessive proportion) contribute to the strength gain of the 5000 ppm sample. The XRD result of the 25000 ppm sample at 20°C in Figure 2.11 also shows excessive formation of expansive minerals. The UCS value shows reduced strength. This may be due to the formation of excessive amounts of ettringite that produced expansive pressure, deteriorating the strength of the 25000 ppm CPT at 20°C (Fall and Benzaazoua, 2005). The 25000 ppm sample at 20°C shows the effect of sulphate attack with lower UCS value than the rest of the samples at the same temperature.

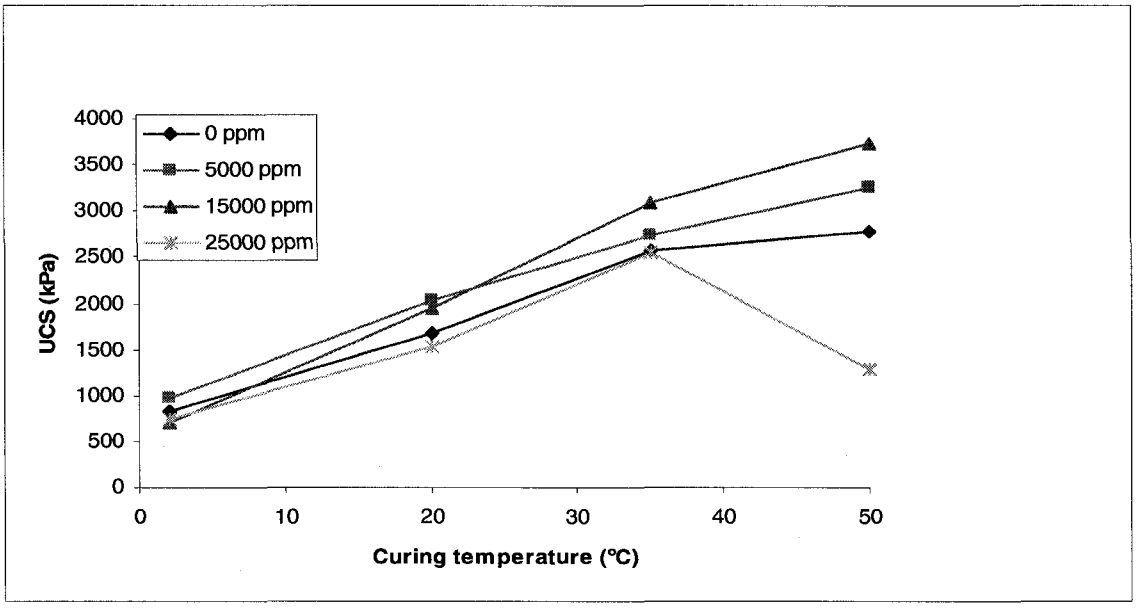

Figure 2-9 150 day UCS of CPT made from PCI with different sulphate content at different curing temperatures

The 15000 ppm sample has approximately the same strength as the 5000 ppm sample at 20°C. This is because of the formation of secondary expansive minerals contributing positively to the strength. The XRD result of the 5000 ppm sample at 20°C in Figure 2.7 shows the presence of an adequate amount of ettringite, gypsum, CH and absence of any C_2S and C_3S. This indicates that almost all cement gets hydrated.

The UCS of the 15000 ppm sample increases sharply from 2°C to 35°C, exceeding the strength of the 5000 ppm sample at 35°C. The slope of evolution of UCS from 2°C to 35°C of the 15000 ppm sample shows sharp and constant rate of strength gain, whereas there is a change of slope from 35°C to 50°C, showing slower rate of strength gain. The rate of gain in strength for the 15000 ppm sample at this range of temperature is lower than that for the temperature 2°C to 35°C, indicating the possibility of adsorption of sulphate by C-S-H gel.

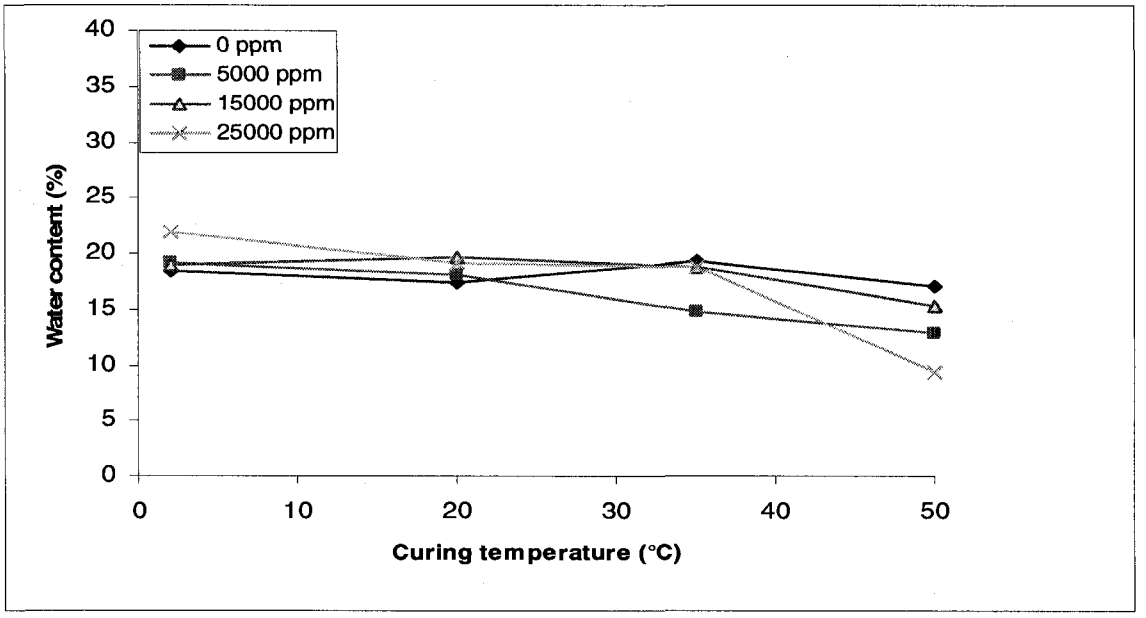

Figure 2-10 150 day water content of CPT made from PCI with different sulphate contents at different curing temperatures

After 20°C, the strength of the 5000 ppm sample at 35°C and 50°C is lower than that of the 15000 ppm sample. This can be due to the depletion of the sulphate in the 5000 ppm sample while reacting with available CH. The rate of gain in strength in the 5000 ppm sample beyond 20°C may be mainly attributed to the formation of additional hydration products from the continuous hydration of the cement. The XRD result of the 5000 ppm sample at 50°C in Figure 2.13 shows a higher peak of CH at 18, 28.5 and 34 degrees 2-theta in comparison to the XRD result of the same sample at 20°C in Figure 2.7. This can indicate a smaller reaction of sulphate and CH at 50°C.

The XRD result also shows less formation of ettringite in comparison to the 5000 ppm sample cured at 20°C. This means that the sample cured at 50°C also

shows adsorption of sulphate by C-S-H gel. However, due to the low quantity of sulphate, the amount adsorbed by C-S-H gel will be low and complete hydration of cement of the 5000 ppm sample makes its UCS value higher than that of the 25000 ppm sample at 50°C. The XRD result (Fig 2.12) of the 0 ppm sample cured at 50°C is very straight forward. There is not any unreacted C_2S and C_3S, and the strength gain of this sample is fully due to the continuous hydration of cement. The observed small quantity of ettringite and gypsum can be attributed as resulting from the gypsum used in cement clinker.

The result of the 150 day water content in Figure 2.10 also illustrates that there is continuous consumption of water by the 5000 ppm sample as the temperature rises from 2°C to 50°C.

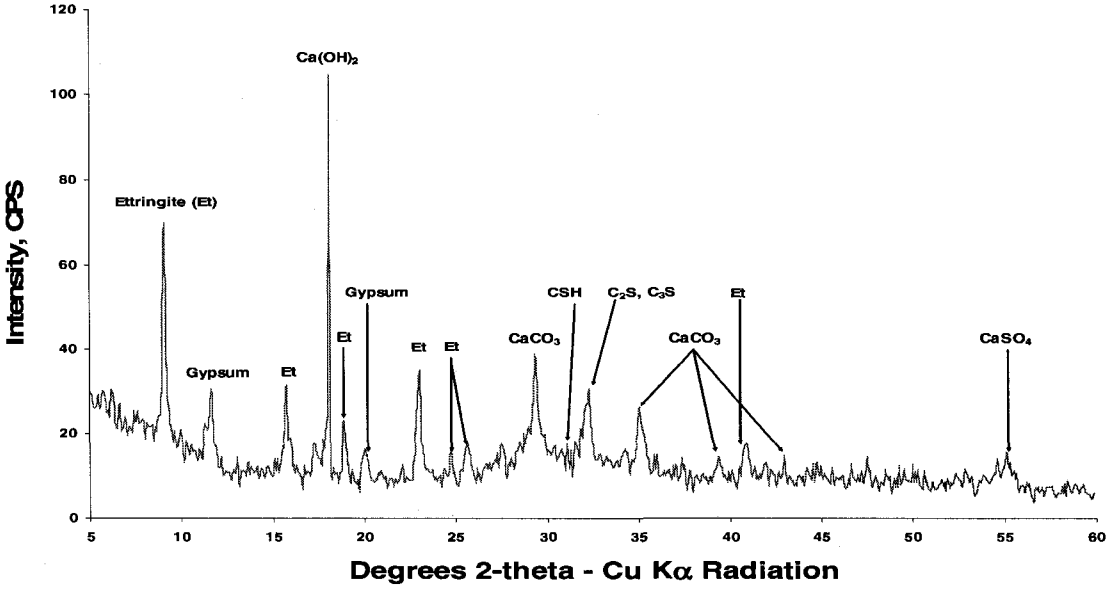

Figure 2-11 XRD result of 25000 ppm cemented paste made from PCI cured at 20°C for 150 day .

The UCS value of the 25000 ppm CPT sample at 50°C is much lower than that of all the samples. The XRD result of the 25000 ppm sample at 50°C in Figure 2.14 shows the presence of very low amounts of expansive minerals. The same XRD result also shows the presence of adequate CH. The intensity of CH peak is greater than that in the 25000 ppm sample cured at 20°C as illustrated by the XRD result in Figure 2.11. This means that the sulphate is not available for CH to produce adequate expansive minerals for the 25000 ppm sample cured at 50°C. In this case, the sulphate is adsorbed by C-S-H gel (Fu et al, 1999). This assumption is fully supported by the XRD result of the 25000 ppm sample at 20°C in Figure 2.11 which has adequate secondary ettringite and gypsum.

The adsorption of sulphate in C-S-H gel may have led to the formation of lower quality of C-S-H which lowers the strength of the 25000 ppm CPT samples at 50°C. It should also be mentioned that high concentration of sulphate favors the adsorption of sulphate by C-S-H gel (Ramlochan et al, 2004). The destabilization of ettringite at high temperatures can be considered as an additional cause of the low quantity of ettringite observed in figure 2.14.

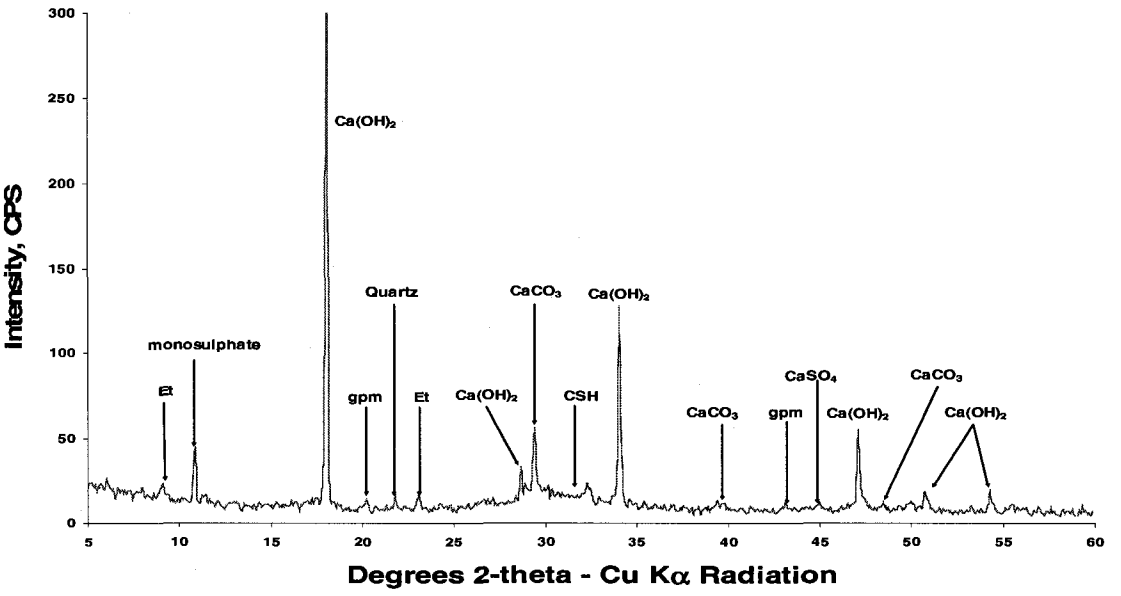

Figure 2-12 XRD result of 0 ppm cemented paste made from PCI cured at 50°C for 150 days

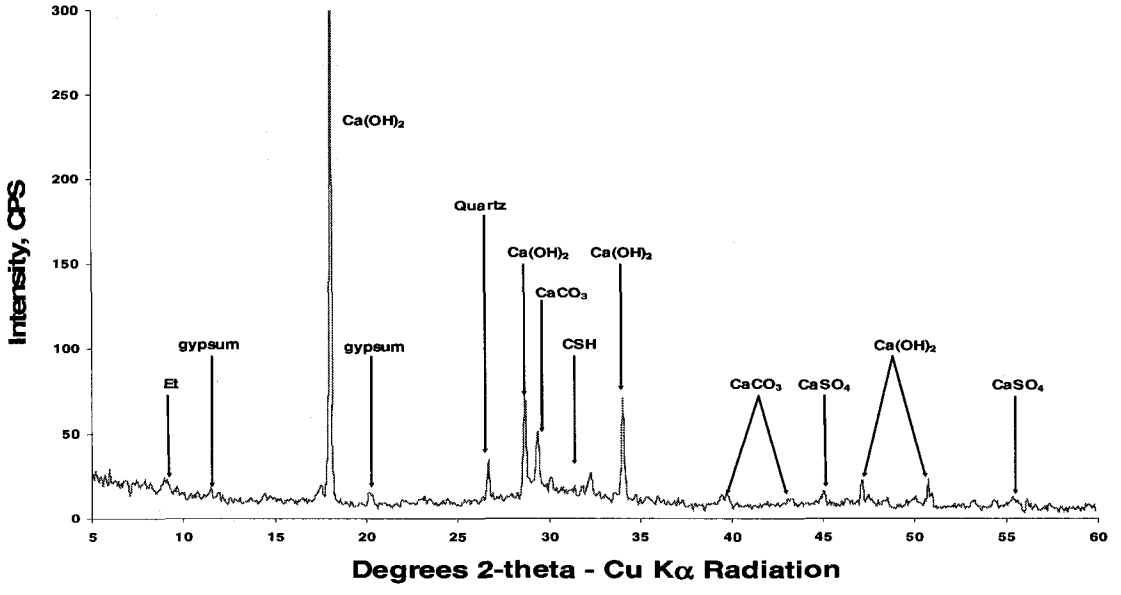

Figure 2-13 XRD result of 5000 ppm of CPT made from PCI cured at 50°C for 150 days .

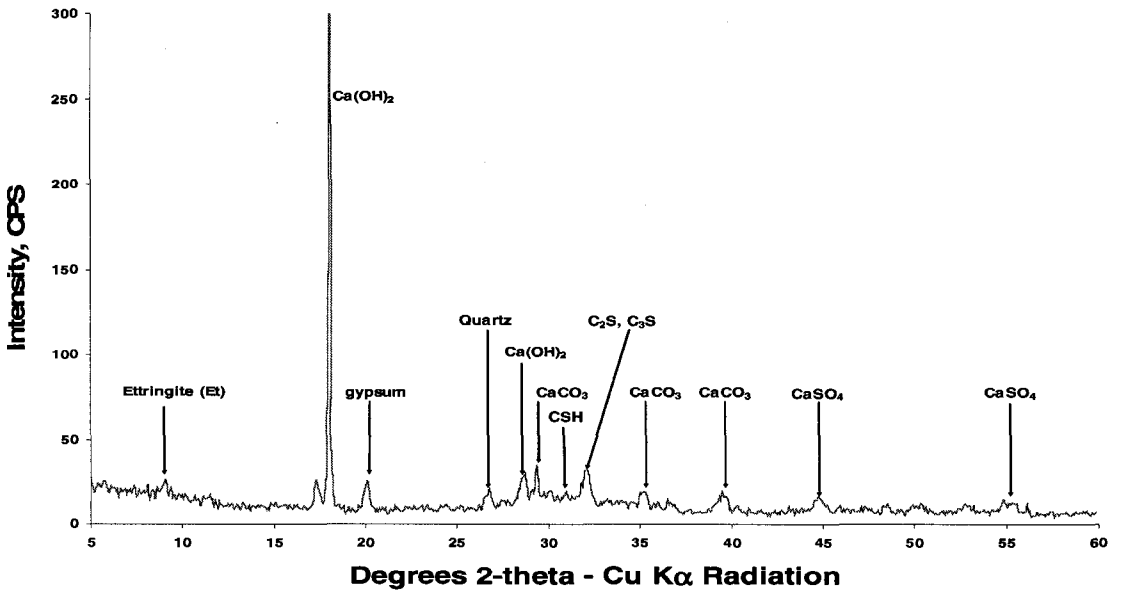

Figure 2-14 XRD result of 25000 ppm cemented paste made from PCI cured at 50°C for 150 days.

2.2.6.2 Coupled effects of sulphate and temperature on PCI – slag CPT strength

2.2.6.2.1 Early ages

Figure 2.15 illustrates the results of the 28 day UCS values of CPT made from PCI-slag cured at 2°C, 20°C, 35°C and 50°C with sulphate concentrations of 0 ppm, 5000 ppm, 15000 ppm and 25000 ppm. Globally, the 28 day UCS value of all samples increases with increase of curing temperature. At 2°C, the 28 day UCS value of all samples are lower than those at 20°C, 35°C and 50°C. This means that at 2°C, the hydration of cement starts very slowly and leads to the formation of less dense C-S-H (Lothenbach et al, 2007). It is also observed from

Figure 2.15 that at 2°C, the UCS values of the 25000 ppm, 15000 ppm and 5000 ppm samples are lower than those of 0 ppm samples. The lower UCS value can be attributed to the presence of high quantities of sulphate in the cement matrix which significantly retard the hydration reaction of the cement. The sulfate present in the sample strongly inhibits the hydration of C_3A which is responsible for early strength of cement (Fall and Benzaazoua, 2005).

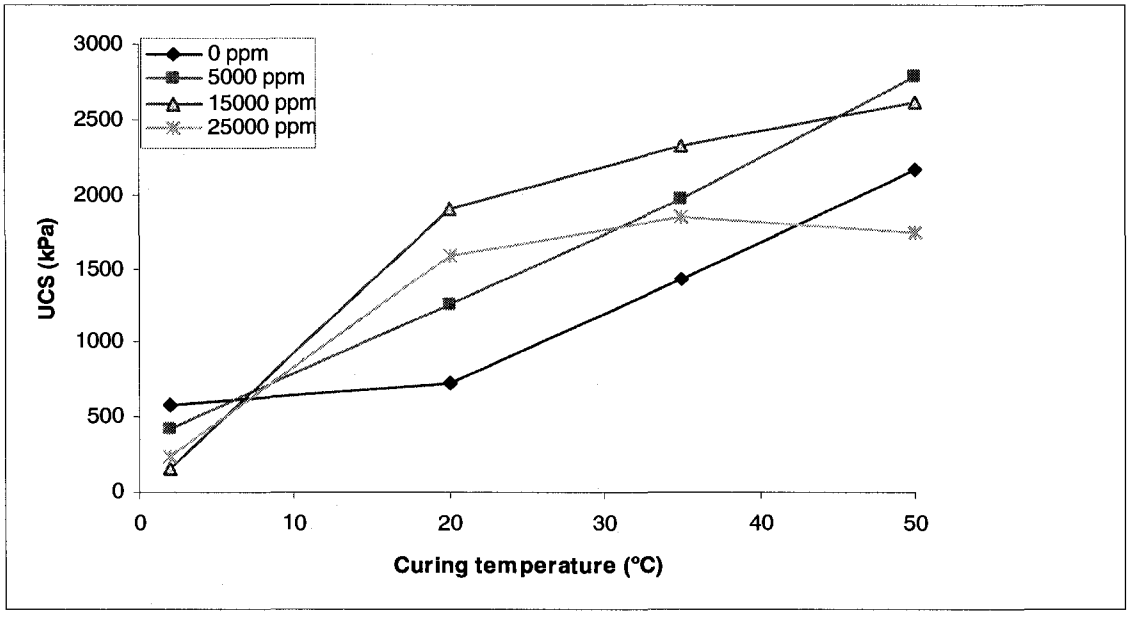

Figure 2-15 28 day UCS of CPT made from PCI-slag with different sulphate contents at different curing temperatures

The water content curve in Figure 2.16 shows that the 25000 ppm samples have consumed very low amounts of water in comparison to other samples during the hydration process at 2°C. This suggests a lower hydration degree of samples containing 25000 ppm sulphate.

At 20°C, samples containing sulphate shows reverse behavior in comparison to 2°C. The 28 day UCS value of all samples containing sulfate is higher than the 0 ppm sample at the same curing time and temperature. The 15000 ppm sample shows the highest UCS value. The 15000 ppm sample is 160%, 51% and 19% stronger than the 0 ppm, 5000 ppm and 25000 ppm respectively.

It is interesting that UCS varies with variation of sulphate concentrations cured at the same temperature and time. The possible reason of such variation in UCS can be attributed to the concentration of sulphate in the samples. The formation of gypsum and ettringite in the 15000 ppm sample reduces the porosity and makes it stronger than the 0 ppm samples. The lower value of UCS of the 25000 ppm rather than the 15000 ppm sample at 20°C may be due to the precipitation of excessive amounts of expansive minerals in the cement matrix, which reduces the strength due to conventional sulphate attack. Another possible cause of reduced strength may be the fewer formation of expansive minerals in comparison to the 15000 ppm samples due to lower hydration of cement because there is a high amount of sulphate (inhibition of cement hydration). The absorption of sulphate by C-S-H gel can be considered as an additional mechanism that leads to the decrease of ettringite and gypsum in the CPT system. Indeed, higher concentrations of sulphate also favor the sulphate adsorption phenomenon (Ramlochan et al, 2004).

The 5000 ppm sample at 20°C has a higher value of UCS than the 0 ppm sample, but lowers than the 15000 and 25000 ppm samples at the same curing temperature. The formation of secondary ettringite and gypsum by the reaction of sulphate ion with CH and cement hydration products (Akoz et al, 1999, Fall and Benzaazoua, 2005) makes the 5000 ppm sample stronger than the 0 ppm sample. The lower quantity of sulphate in the 5000 ppm sample in comparison to the 15000 ppm and 25000 ppm samples may have produced a lower amount of ettringite and gypsum. This can increase the internal porosity and thus, the 5000 ppm sample has lower value of UCS in comparison to the 15000 ppm and 25000 ppm samples.

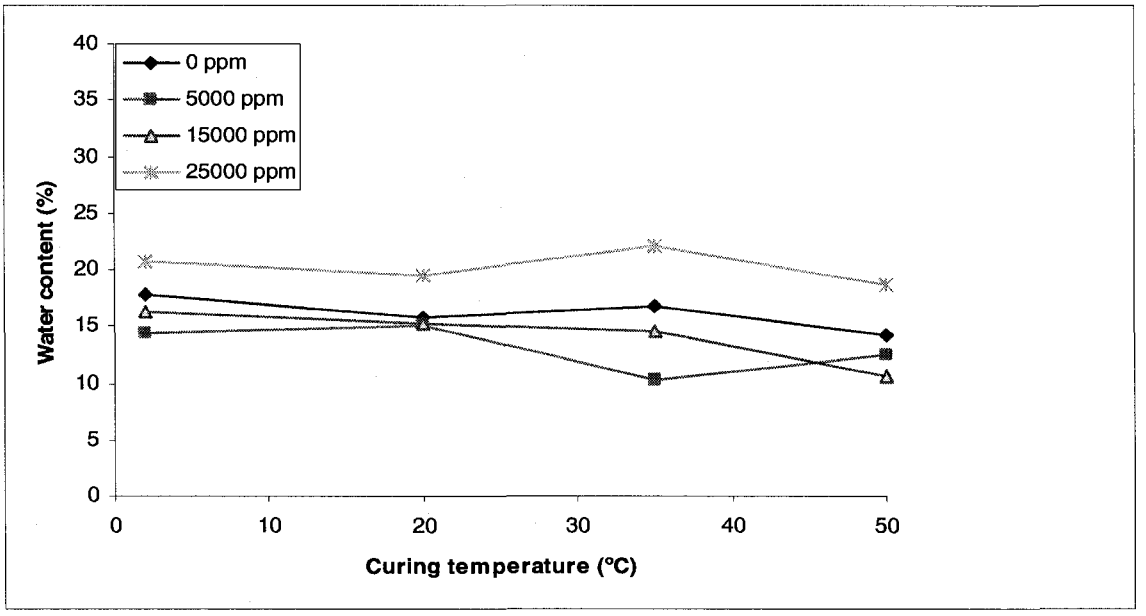

Figure 2-16 28 day water content of CPT PCI-slag at different temperatures with different sulphate contents

Barnett et al. (2006) pointed out that the strength development of concrete containing GGBFS is significantly influenced by curing temperature. Mortar with 70% GGBFS achieves a 3 day compressive strength of 26 N / mm ^{2} when cured at 50°C, but only 2 N / mm ^{2} at 10°C. Escalante and Sharp (2001) also observed that 30°C is the optimum temperature suitable for the strength development of slag blended cement. This observation indicates that at 2°C and 20°C, the pozzolanic reaction of slag contributes minimally in the strength development process. Hence, at this early age (≤ 28 days), the strength development of these samples containing sulphate up to 20°C is mainly due to both the continuous hydration of cement and precipitation of ettringite and gypsum in the system.

At 35°C, the 28 day UCS value of all samples containing sulfate is still higher than that of the 0 ppm sample. The 15000 ppm sample still has higher value of UCS than the rest of the samples. The trend of the gain in strength rate of the 15000 ppm and 25000 ppm samples from 20°C to 50°C is different than that of the 0 ppm and 5000 ppm samples. The 0 ppm and 5000 ppm samples show a sharper rate of strength gain from 20°C to 50°C. The continuous hydration of cement with increased temperatures as well as formation of secondary C-S-H due to the reaction between slag and CH (Hekal et al, 2002) made the 0 ppm sample consistently grow in UCS with curing temperature. In addition to this, the formation of secondary ettringite and gypsum also contribute to the strength development (Fall and Benzaazoua, 2005) for the 5000 ppm sample. On other hand, the rate of gain of strength of the 15000 and 25000 ppm samples is mild.

The decreasing trend of UCS value is observed in the case of 15000 and 25000 ppm of sulphate at 50°C.

The 28 day UCS value of the 25000 ppm sample at 35°C is found to be lower than the 5000 ppm sample at the same temperature .The lower value may be due to the adsorption phenomenon of sulphate by C-S-H gel (Fu et al, 1994). In this case, at high curing temperatures, there will be depletion in the sulfate in the cement matrix so that smaller amounts of expansive minerals (for filling the voids) are precipitated in the 25000 ppm samples. Another possible reason for reduced strength is the formation of inferior quality of C-S-H from the adsorption of sulphate. The rate of gain in strength due to increase of temperature at 50°C of the 15000 ppm sample is slow. Also, the 25000 ppm sample shows lowering of strength at 50°C. As explained earlier, the drop of strength of the 25000 ppm and lower strength gain rate of 15000 ppm samples at 50°C can be attributed to the adsorption of sulphate by C-S-H at high curing temperatures. Hence, it can be concluded that the reduced strength is not due to conventional sulfate attack by the formation of excessive expansive minerals as explained in several research (e.g. Fall and Benzaazoua, 2005; Hekal et al, 2002; Salah and Al-Dulaijan, 2007), The reduced strength of the 25000 ppm and 15000 ppm samples at 50°C can be mainly attributed to the formation of inferior quality of C-S-H due to the coupled effect of sulfate and temperature.

2.2.6.2.2 Advanced ages

Figure 2.17 presents the 90 day UCS of CPT PCI-slag cured at 2°C, 20°C, 35°C and 50°C with sulfate concentrations of 0 ppm, 5000 ppm, 15000 ppm and 25000 ppm. In general, the 90 day UCS of all CPT samples increases with increase of curing temperature except for the 25000 ppm sample at 50°C. From Figure 2.17, it is observed that the 90 day UCS value of 5000 ppm, 15000 ppm and 25000 ppm samples at 2°C is higher than that of the 0 ppm sample.

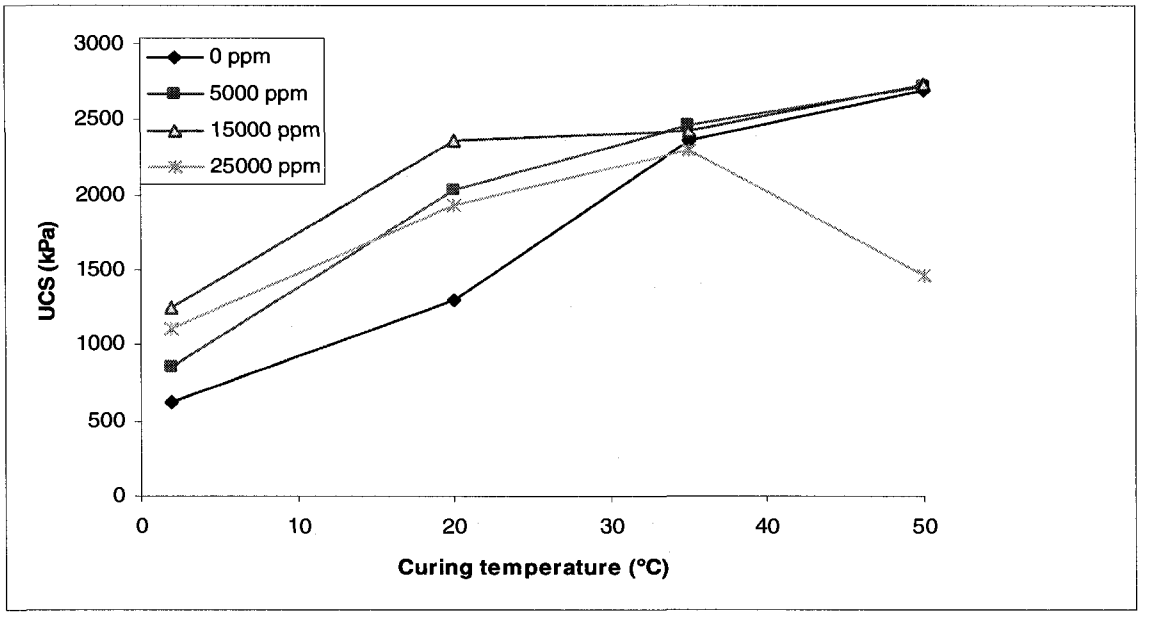

Figure 2-17 90 day UCS of CPT made from PCI-slag at different temperatures with different sulphate contents.

The 90 day UCS value of 15000 ppm, 25000 ppm, 5000 ppm and 0 ppm samples cured at 2°C shows high gain of strength when compared to the same samples cured at 28 days. It is 713%, 375%, 65% and 7% higher than the 28 day samples respectively. The higher strength of the samples containing sulphate is

mostly due to the formation of secondary ettringite and gypsum. The 90 day UCS value of 25000 ppm is lower than that of 15000 ppm, but higher than 5000 ppm at 2°C. This indicates that the hydration rate of 25000 ppm is still lower than 15000 ppm, and sulphate is still playing an inhibition role. The 5000 ppm sample at 2°C shows strength slightly higher than 0 ppm and lower than 15000 and 25000 ppm samples. This may be due to the formation of lower quantity of expansive minerals in the samples due to the presence of lower quantities of sulphate. With increase of curing temperature, the strength of all samples increases except for 25000 ppm at 50°C.

The 90 day UCS value of the 15000 ppm sample at 20°C is higher than that of all samples. This is due to the formation of a hydration product, secondary C-S-H from pozzolanic reaction of slag and also precipitation of ettringite and gypsum in the cement matrix pores. The 25000 ppm sample at 90 days at 20°C has a lower strength than the 15000 ppm and 5000 ppm sulphated samples. The lower UCS value can be from the precipitation of excessive amounts of expansive minerals contributing negatively to the strength (Fall and Benzaazoua, 2005). Another possible reason of reduced strength can be adsorption of sulphate by C-S-H gel as mentioned above. At 35°C, almost all samples have the same strength.

The 90 day UCS value of 25000 ppm CPT at 50°C shows sharp drop of strength. This may be due to the phenomenon of adsorption of sulphate by C-S-H which is explained below in detail.

Figure 2.18 shows the 150 day UCS of CPT samples cured at 2°C, 20°C, 35°C, 50°C with 0 ppm , 5000 ppm , 15000 ppm , 25000 ppm of sulfate. This figure also illustrates that the 150 day UCS of the sample increases with increase of curing temperature.

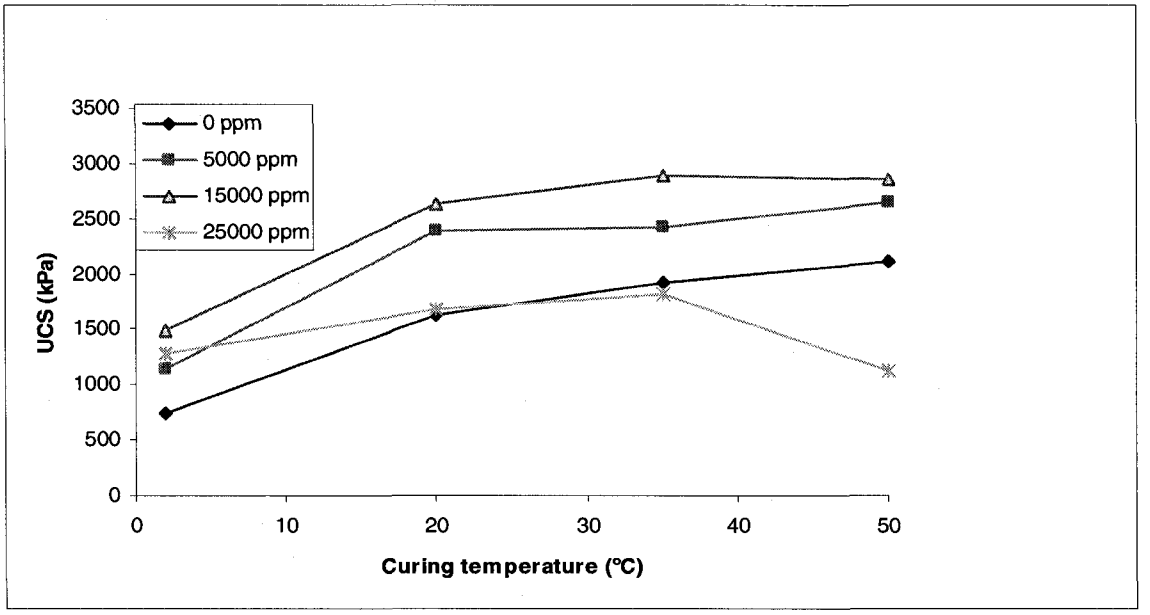

Figure 2-18 150 day UCS of CPT made from PCI-slag at different temperatures with different sulphate contents

The XRD result in Figure 2.19 shows the mineralogical composition of the 0 ppm sample made from PCI-slag cured at 20°C for 150 days. It shows that the sample is fully hydrated. The ettringite and monosulphate present in the sample is due to the presence of gypsum which is added during the manufacturing of cement. Sulphate was not added to the 0 ppm sample, so this sample will not produce any expansive minerals. The XRD result in Figure 2.19 also shows that the sample does not have any expansive minerals. Hence, the strength development

is due to the continuous hydration of cement. As the curing temperature increases to 35°C, the UCS value also increases. This increase of strength, as mentioned earlier, is due to the continuous hydration of cement. In addition to this, the formation of secondary C-S-H from the pozzolanic reaction of slag also contributes to the development of strength.

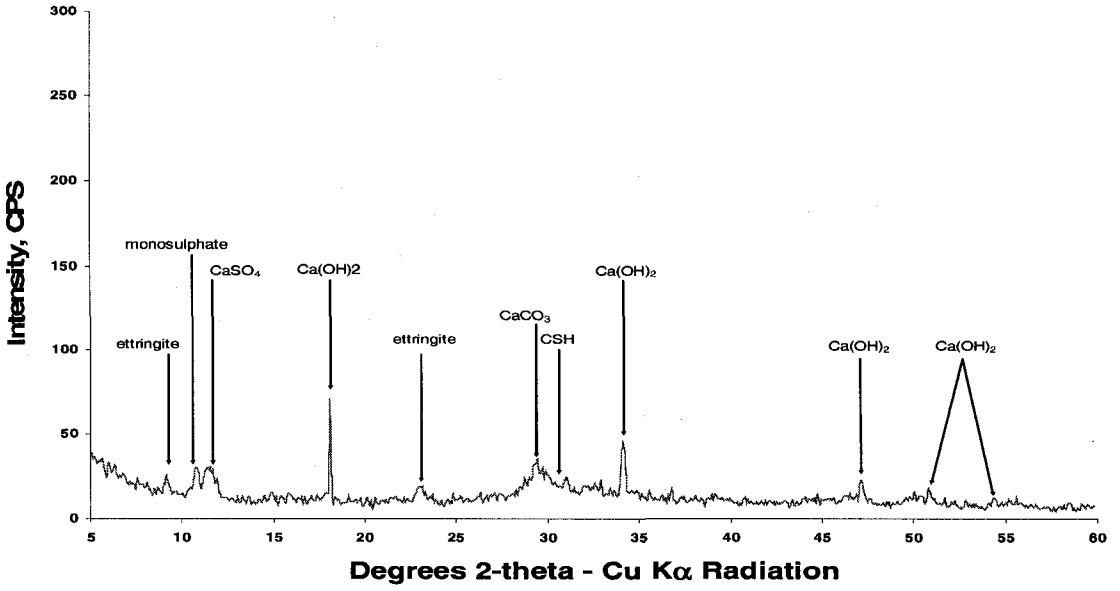

Figure 2-19 XRD result of 0 ppm of cemented paste made from PCI-slag cured at 20°C for 150 days

The XRD result in Figure 2.20 also shows the presence of a high quantity of hydration products in the 0 ppm sample cured at 35°C. The intensity of CH is found higher for the 0 ppm sample cured at 35°C (Fig. 2.20) than at 20°C (Fig 2.19). It is observed that the intensity of CH at 18 degrees 2-theta is 75 CPS in the case of the 0 ppm sample at 20°C whereas at 35°C, this intensity is approximately 95 CPS. In the same way, the intensity of CH at 34, 47, 51 degrees 2-theta for the 0 ppm sample cured at 35°C (Fig 2.20) is a little bit

higher than that of the 20 °C samples (Fig 2.19). Both XRD results of the 0 ppm sample do not have any presence of C_2S and C_3S, indicating complete hydration of this clinker phase.

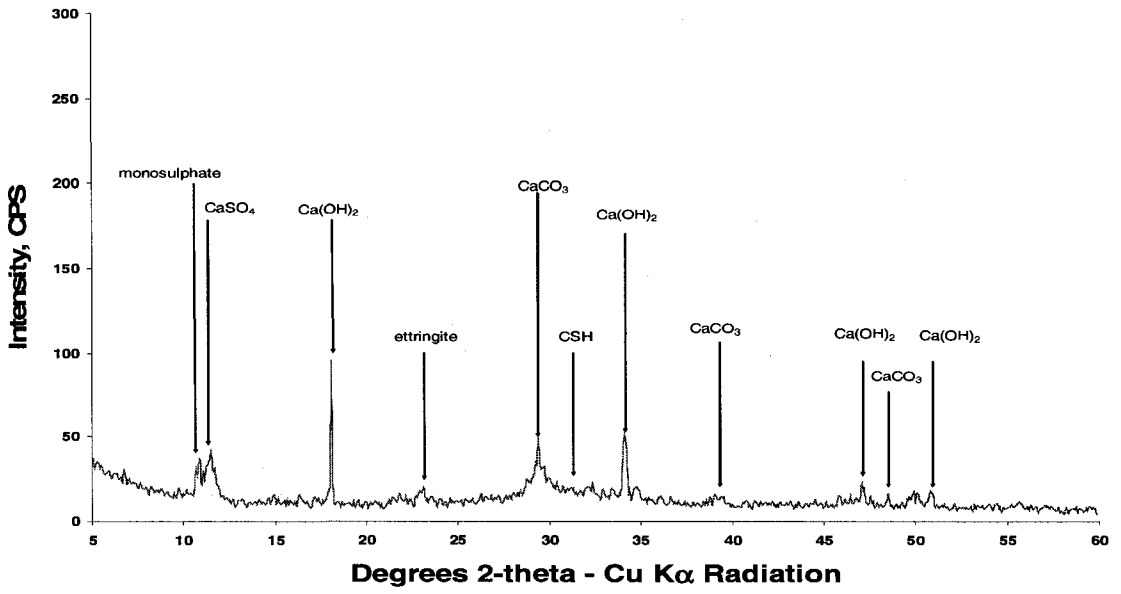

Figure 2-20 XRD result of 0 ppm cemented paste made from PCI-slag cured at 35°C for 150 days

The 150 day UCS value of all samples except for the 25000 ppm sample at 35°C and 50°C containing sulphate is higher than that of the 0 ppm sample. As explained above, this higher value of UCS in the sulfated sample can be attributed to the formation of additional secondary gypsum and ettringite in the cement matrix. This fact is also supported by comparing the XRD result of the 0 ppm and 15000 ppm samples cured at 20°C and 35°C as shown in Figures 2.19, 2.20, 2.21 and 2.22. The XRD results of the 15000 ppm sample cured at 20°C and 35°C in Figures 2.21 and 2.22 shows the presence of high amounts of secondary ettringite in comparison to the 0 ppm sample at 20°C and 35°C.

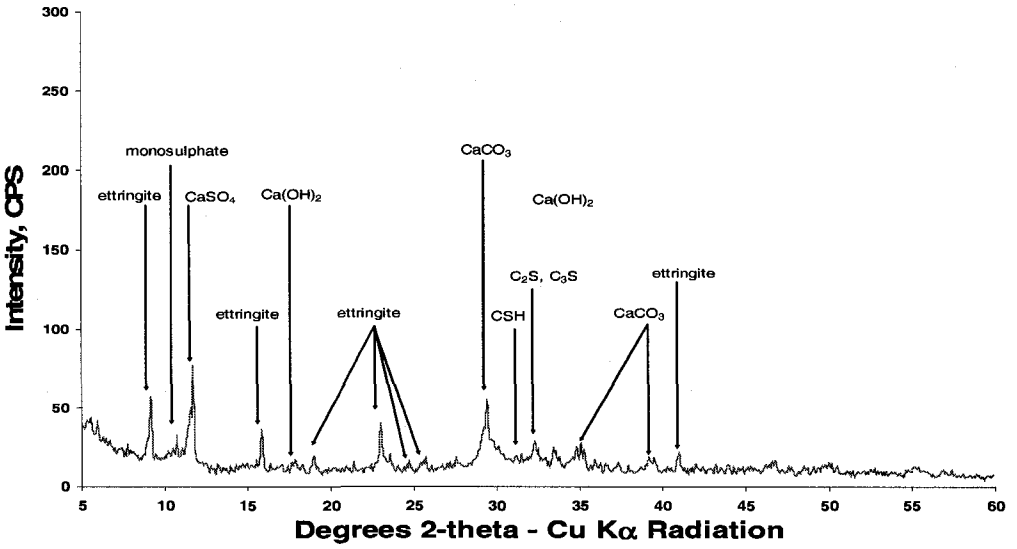

Figure 2-21 XRD result of 15000 ppm cemented paste made from PCI – slag cured at 20°C for 150 days

The XRD result of the 15000 ppm sample cured at 35°C in Figure 2.22 shows the presence of ettringite. It is also observed from the XRD results that the peak of ettringite in the 15000 ppm sample at 35°C (Fig 2.22) is lower than at 20°C (Fig 2.21) even though the UCS value at 35°C is higher. The lower peak of ettringite can be explained by the adsorption of sulphate by C-S-H. The destabilization of ettringite by high temperatures should be considered as an additional cause of this depletion of ettringite. The XRD result of the 15000 ppm sample at 35°C (Fig 2.22) does not show the presence of CH in the cement matrix. This means all available CH is consumed partly by the sulphate and partly by slag through pozzolanic reactions. This is because slag is very reactive around 30°C (Escalante and Garcia, 2001). Due to this pozzolanic reaction and formation of expansive minerals (fill the pores), the CPT has a high value of UCS.

The 25000 ppm sample at 20°C shows a lower UCS value than the 5000 ppm and 15000 ppm and its UCS value is approximately equal to the 0 ppm samples (Fig 2.18). The XRD result of the 25000 ppm at 20°C (Fig 2.23) shows presence of adequate amounts of ettringite along with low amounts of unreacted CH. It is very similar to the XRD result of the 15000 ppm at 20°C (Fig 2.21). The only difference is that the 25000 ppm has a higher intensity peak of ettringite at 9 degrees 2–theta. These two XRD results show approximately the same kind of mineralogical composition, but the 15000 ppm sample at 20°C has a higher UCS than the 25000 ppm at 20°C (Fig 2.18). The reduced UCS can be attributed to the presence of excessive amounts of expansive ettringite which deteriorate the strength of CPT due to phenomenon of conventional sulphate attack.

The XRD result of the 25000 ppm sample at 35°C in Figure 2.24 shows much smaller amounts of ettringite in comparison to the same CPT at 20°C in Figure 2.23. For the 25000 ppm sample at 35°C, no or very small amounts of sulphate is available for the formation of ettringite. In this case, sulphate is adsorbed by the C-S-H gel. The 25000 ppm CPT sample cured at 50°C at 150 days in Figure 2.18 shows considerable drop of strength in comparison to the rest of the sample. As explained above, this can be mainly attributed to the adsorption of sulphate in C-S-H gel due to high curing temperatures as reported by Fu et al. (1994). The adsorption of sulphate in C-S-H gel may result in formation of inferior quality of C-S-H in the cement matrix which reduces the strength of CPT. In addition to this, the SEM observation (Figures 2.40, 2.41, 2.42) of the 25000 ppm sample at

50°C shows the presence of colloidal ettringite which cannot be detected by x-ray tests and is also responsible for decrease of strength. The details about the colloidal ettringite are presented in Section 2.2.6.3.2

The XRD results of the 25000 ppm and 15000 ppm samples at 35°C show the presence of $CaSO_4$ and $CaCO_3$. The formation of these minerals is due to the presence of CH. At high pH, due to the presence of adequate CH, the formation CO_3^{2-} is faster than that of SO_3^{2-}, thus more $CaCO_3$ will be formed. Once there is a drop of pH, then $CaSO_4$ will form in the samples (Martinez, 1999). The formation of this compound is found in almost all of the samples. The XRD results in Figures 2.19, 2.20, 2.21, 2.22 show the presence of these compounds, but they have good UCS value. Hence, the effect of these compounds on the mechanical properties of samples should be further investigated.

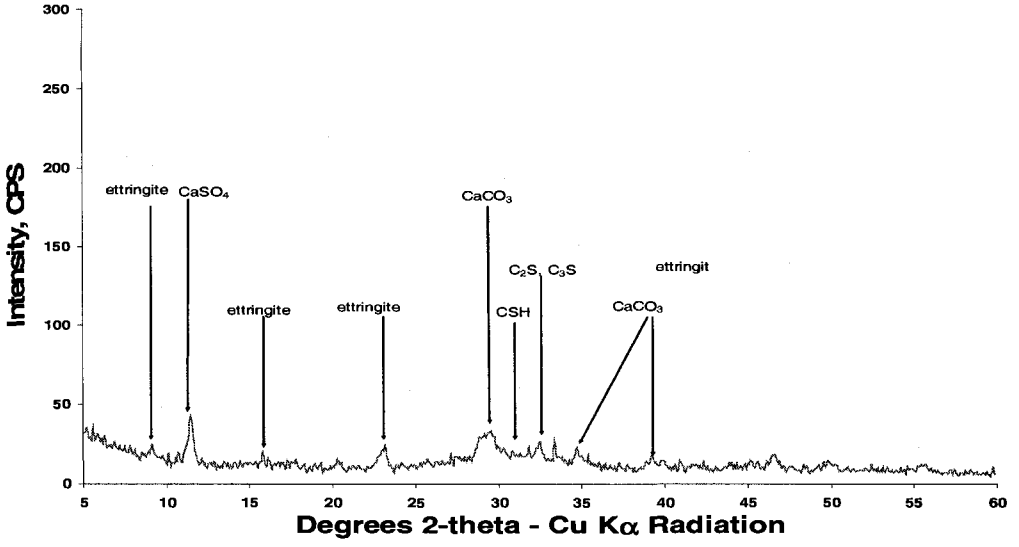

Figure 2-22 XRD result of 15000 ppm cemented paste made from PCI-slag cured at 35°C for 150 days

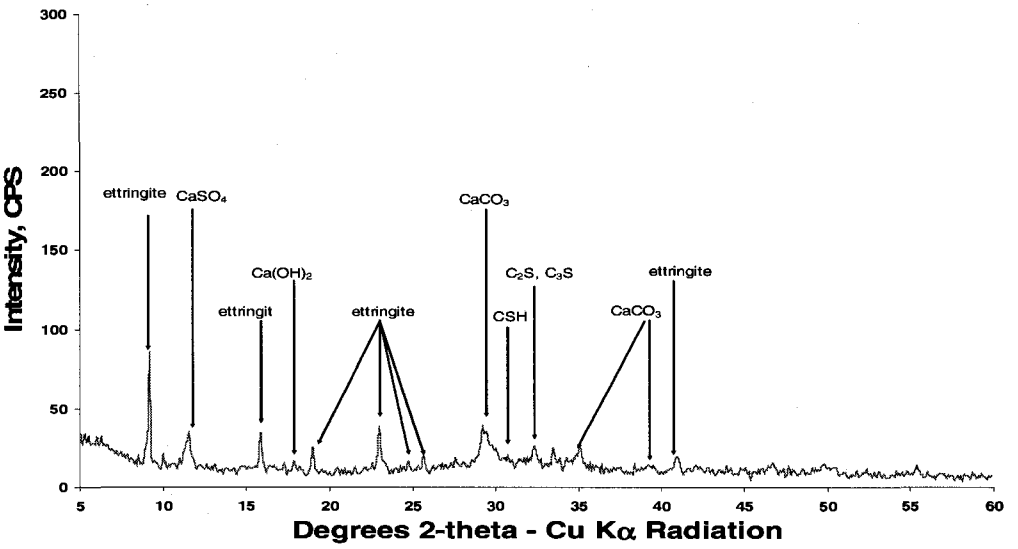

Figure 2-23 XRD result of 25000 ppm cemented paste made from PCI-slag cured at 20°C for 150 days

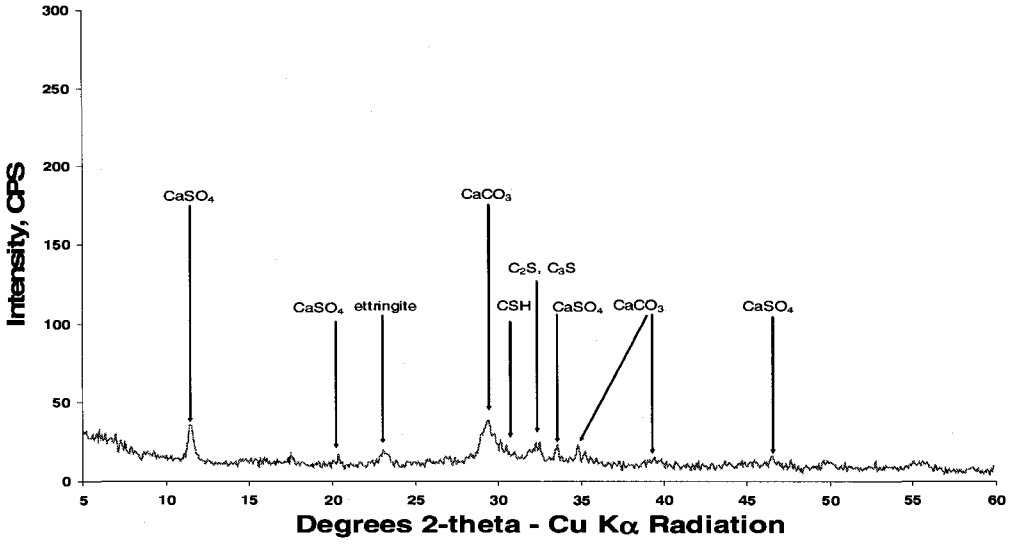

Figure 2-24 XRD result of 25000 ppm cemented paste made from PCI-slag cured at 35°C for 150 days

2.2.6.3 Comparison between CPT-PCI and CPT PCI-slag behavior

2.2.6.3.1 Early ages

Figure 2.25 shows the comparison of the 28 day UCS of CPT made from PCI and PCI-slag (50 % wt of slag) without sulphate for various curing temperatures. The UCS of both CPT samples increases with increase of temperature. The hydration reaction of PCI and PCI-slag is influenced by the curing temperature (Lothenbach et al, 2007). As the curing temperature increases, the hydration reaction will be accelerated, thus more hydration products will be produced in the cement matrix which enhances the development of the strength of both cements (Barnett et al, 2006; Fall and Samb, 2006). At 2°C, both samples show almost the same value of UCS at 28 days of curing. This value is very low in comparison to other values at higher temperatures with the same curing time. It was observed during the test that these samples at 2°C have adequate amount of unreacted water when removing from the mould. This means that at low temperatures, the hydration reaction starts very slowly and will take time to precipitate the hydration product in the cement matrix. This produces less dense C-S-H (Lothenbach et al, 2007).

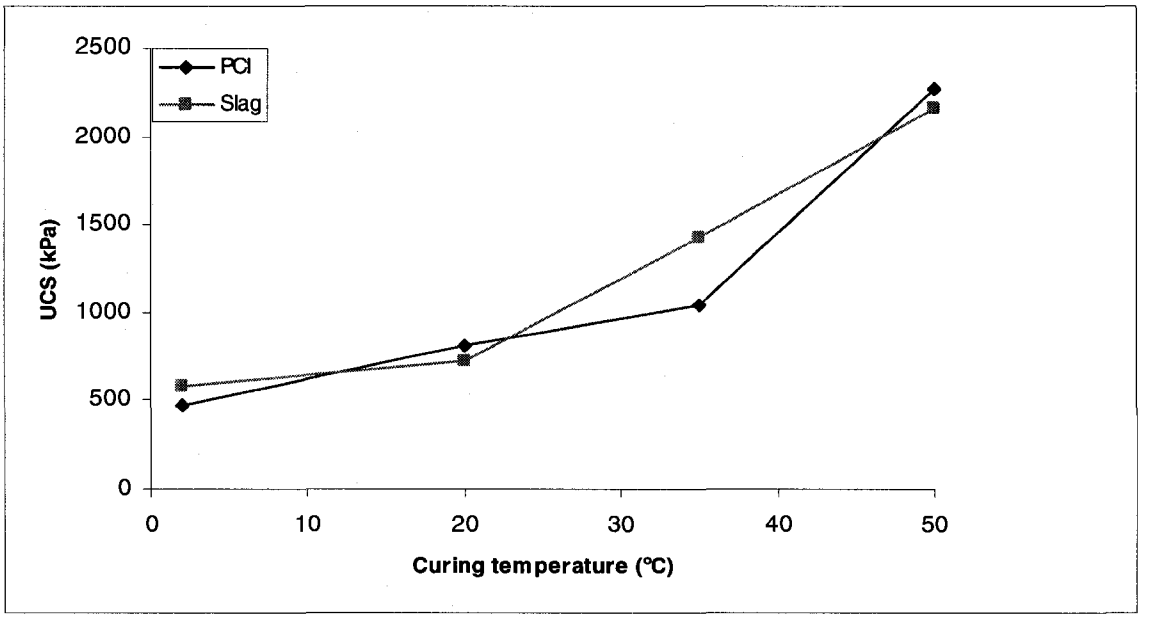

Figure 2-25 28 day UCS value of CPT PCI and PCI- slag without sulphate at different temperatures.

At 20 °C, the UCS value of both samples is approximately the same. The rate of gain in strength of blended cement at 28 days from 2°C to 20°C is slow in comparison to PCI at the same curing time and temperature. The PCI shows a 73% rate of gain in strength whereas blended cement shows only 25% when the temperature increases from 2°C to 20°C. This lower strength development behavior of blended cement with GGBFS under 20°C was also observed by previous researchers (Escalante and Sharp, 2001; Fall and Benzaazoua, 2005; Barnett et al, 2006). One of the main drawbacks reported in the literature for the use of blended cement with GGBFS is the slow rate of strength development in comparison to PCI (Barnett et al, 2006).

As the curing temperature increases to 35°C, the 28 day UCS value of blended cement is comparatively higher than that of PCI cement by almost 36%. This is due to the fact that higher temperatures (35-50°C) accelerate the hydration reaction of cement resulting in the formation of more C-S-H and CH that contributes to the development of the strength of CPT. The slag, in turn, reacts with CH, producing extra additional secondary C-S-H in the case of blended cement. The formation of this additional secondary C-S-H in blended cement makes the slag-CPT sample stronger than the samples made from PCI. It is also observed that higher hydration temperature will increase the reactivity of slag (Escalante et al,2001) and the hydration of GGBFS is more sensitive to the temperature than ordinary Portland cement (Barnett et al, 2006; Escalante et al, 2001)

At 50 °C, the 28 day UCS value of CPB made from blended cement is slightly lower than that of CPB made from PCI. This can be explained by the formation of dense hydrated phase around the unreacted slag grains which retards further hydration resulting in the lower strength (Barnett et al, 2006).

Figures 2.26, 2.27, 2.28 shows the result of 28 day UCS value of CPT samples cured at different temperatures containing 5000 ppm, 15000 ppm and 25000 ppm of sulphate. These results illustrate that at 2°C, the 28 day UCS value of blended cement is significantly lower than that of PCI cement in the sulphate environment. As explained earlier, this is due to the slower rate of hydration of the blended cement. As the curing temperature increases to 20°C, the blended cement samples show higher UCS values than samples made from PCI cement.

The difference of strength depends upon the sulphate concentration. As the sulphate concentration of the sample increases, the difference between the 28 day strength of blended cement and PCI cement cured at 20°C increases (Figures 2.26, 2.27, 2.28).

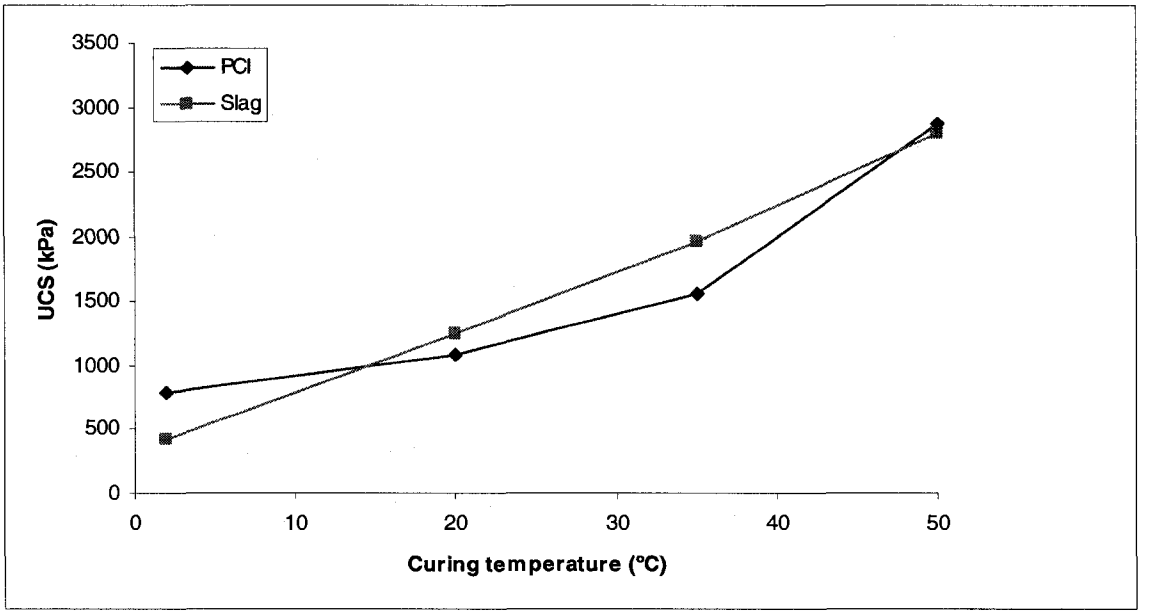

Figure 2-26 28 day UCS value of CPT PCI and PCI- slag with 5000 ppm of sulphate at different temperatures

The increase of strength at 20°C is approximately 16%, 89% and 138% for 5000 ppm, 15000 ppm and 25000 ppm of sulphate, respectively. The presence of sulphate ions activates the hydration of slag in blended cement (Aziz et al, 2005). Hence, these higher values of UCS (due to higher concentrations of sulphate) of CPT made from blended cement at 20°C result from the formation of secondary C-S-H from a pozzolanic reaction (Fall and Benzaazoua, 2005).

The 28 day UCS value of CPT made from blended cement is still higher than that of PCI-CPT at 35°C for all sulphated samples and almost equal to the PCI at 50°C. At 50°C, there is retardation of hydration of the slag cement. Such was also observed by other researchers (Barnett et al, 2006; Fall and Samb, 2006) The reduced strength can be attributed to the formation of hydration rims.

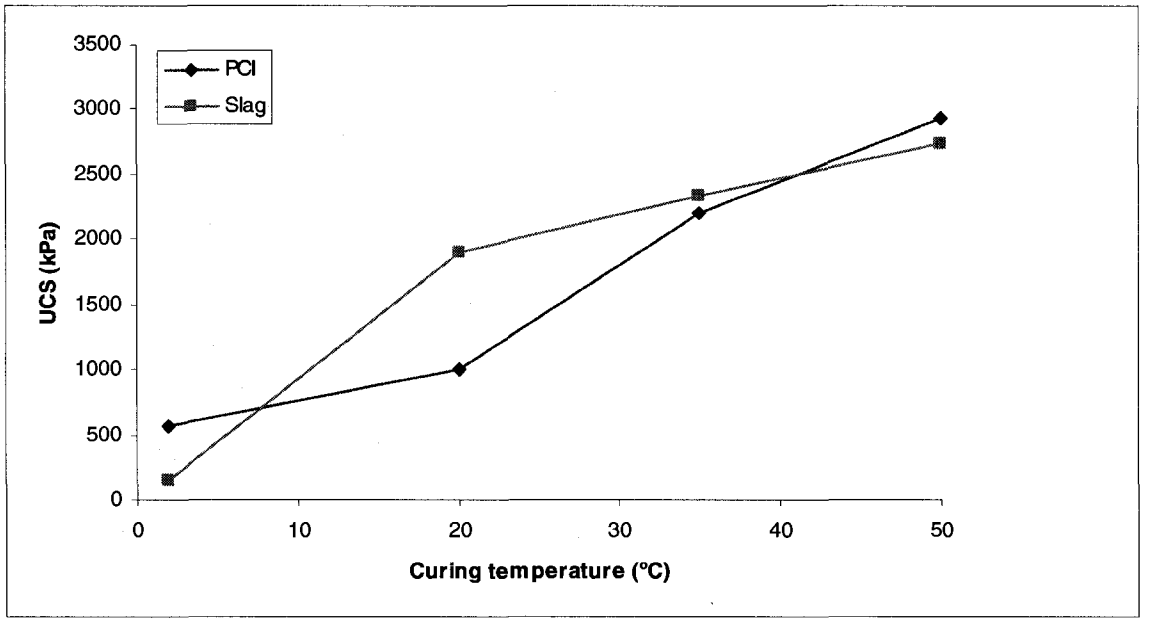

Figure 2-27 28 day UCS value of CPT PCI and PCI- slag with 15000 ppm of sulphate at different temperatures.

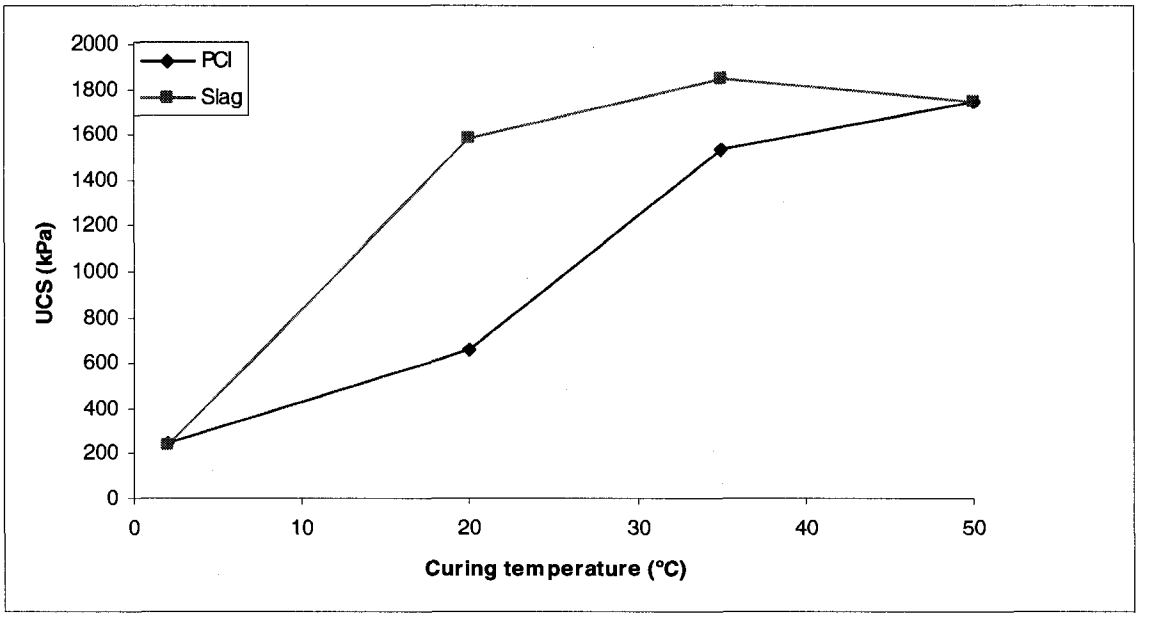

Figure 2-28 28 day UCS value of CPT PCI and PCI- slag with 25000 ppm of sulphate at different temperatures.

2.2.6.3.2 Advanced ages

Figure 2.29 shows the result of the 150 day UCS value of the CPT PCI and PCI-slag cements cured at 2°C, 20°C, 35°C and 50°C without sulphate. The 150 day UCS of the CPT sample increases with increase of temperature due to continuous hydration of unhydrated products in the cement. The 150 day UCS value of CPT made of blended cement is similar to PCI at low temperatures (2°C, 20°C) and significantly lower than PCI-CPT at 35°C and 50°C. A similar result was also observed by previous studies (e.g. Cakir and Akoz, 2008). The high strength of PCI-CPT at 35°C and 50°C is due to the continuous hydration of cement as it has adequate clinker portions for the strength. The lower value of

UCS of PCI-slag at 150 day at all temperatures in comparison to PCI cement may be due to the lower amount of C_2S and C_3S (Aziz et al, 2005).

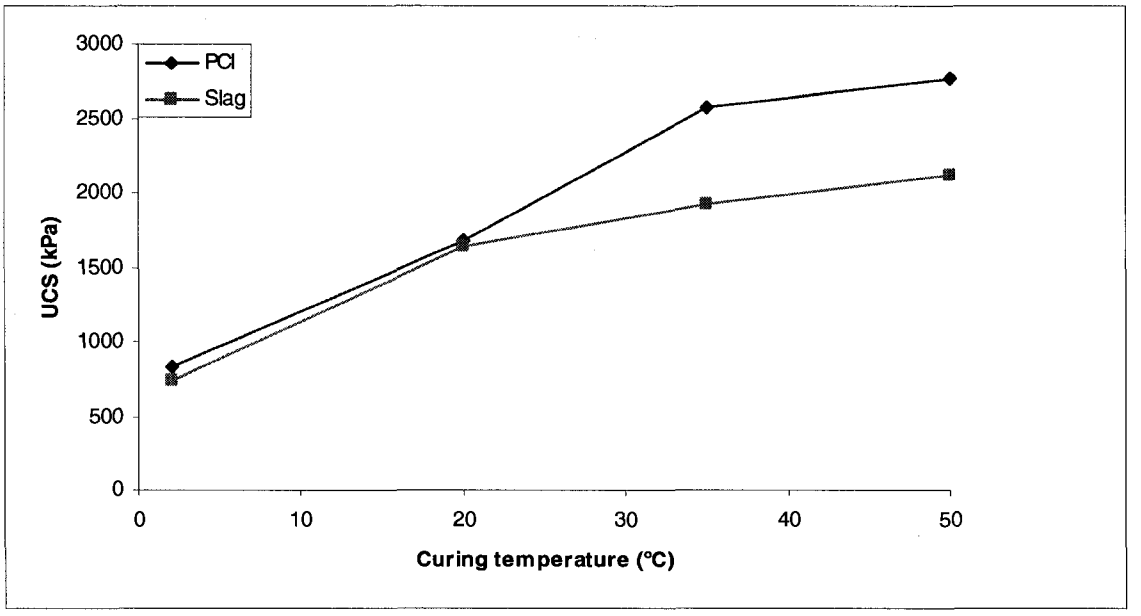

Figure 2-29 150 day compressive strength of CPT of PCI and PCI-slag without sulphate at different temperatures.

The partial (50%) replacement of cement with GGBFS caused this blended cement to have only 50% of C_2S and C_3S in comparison to PCI. Hence, at advanced ages, as curing time increases, the quantity of C_3S and C_2S is reduced due to the hydration reaction in the cement matrix and thus the blended cement is producing smaller amounts of C-S-H and CH. Cakir and Akoz (2008) found that the UCS of the blended cement decreases with increase of GGBFS percentage. On other hand, the PCI-CPT cement has adequate quantity of this clinker phase in the cement matrix. Hence, PCI cement is continuously producing higher amounts of CH and C-S-H in comparison to the CPT made

from blended cement. In addition to inadequate amount of clinker phase in PCI-slag, the formation of hydration rims at higher temperatures also reduces the UCS value of CPT made from PCI-slag at 35°C and 50°C.

Figures 2.30, 2.31 and 2.32 show the 150 day UCS value of CPT at 5000 ppm, 15000 ppm and 25000 ppm of sulphate. The UCS value of CPT made from PCI-slag at 2°C and 20°C is higher than that of PCI-CPT for all concentrations of sulphate whereas at 35°C and 50°C, the UCS value of PCI sample has a higher value than that of PCI-slag.

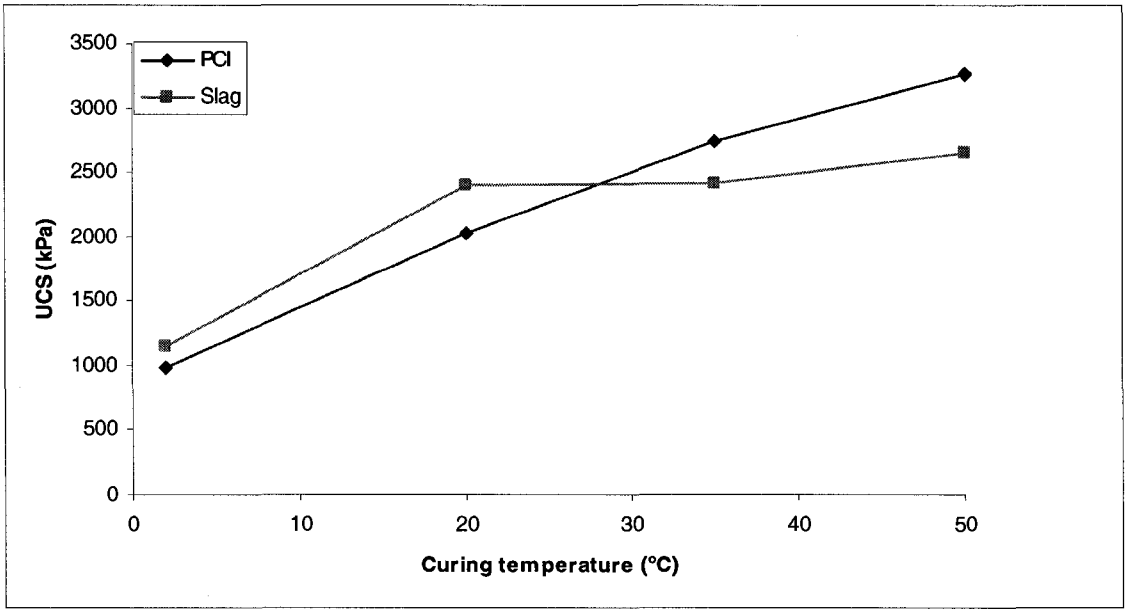

Figure 2-30 150 day UCS value of PCI and PCI- slag CPT with 5000 ppm of sulphate at different temperatures

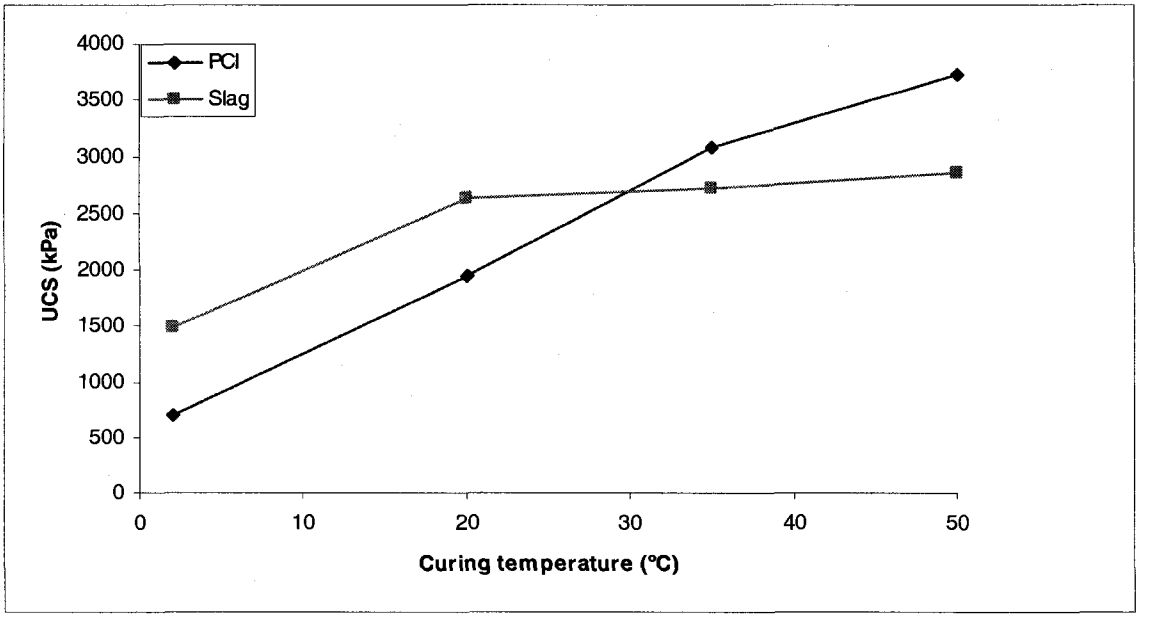

Figure 2-31 150 day UCS value of CPT PCI and PCI- slag with 15000 ppm of sulphate at different temperatures.

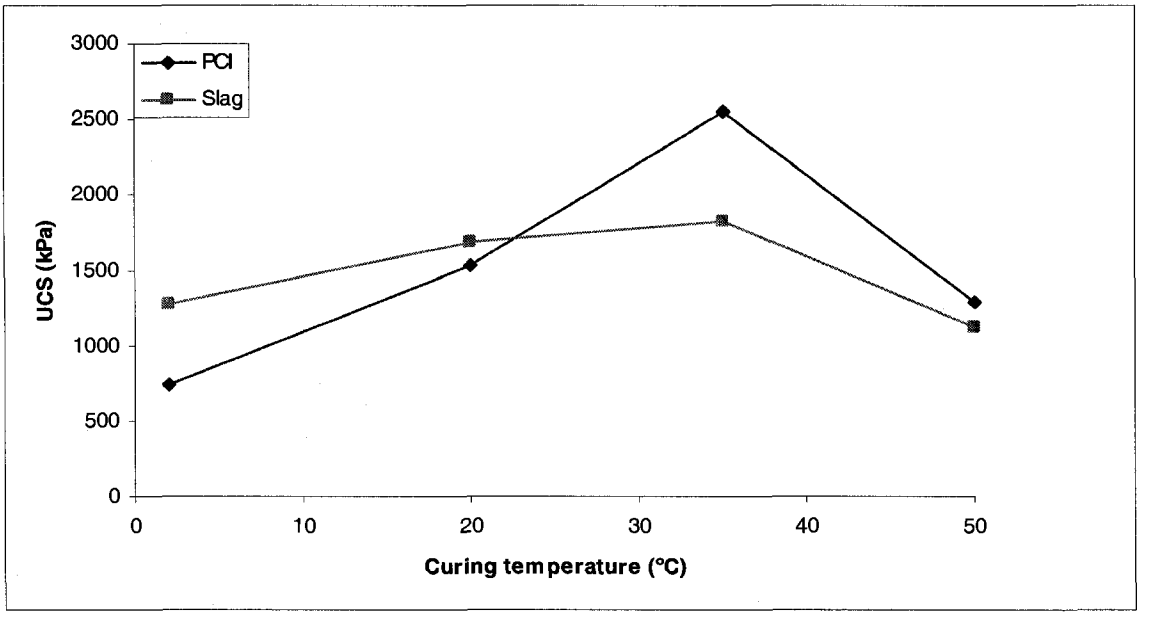

Figure 2-32 150 day UCS value of CPT PCI and PCI- slag with 25000 ppm of sulphate at different temperatures.

The increase of the UCS value of blended cement at 2°C and 20°C may be due to the pozzolanic reaction between liberated CH and slag. The XRD result of the 5000 ppm sample made from PCI cement at 20°C in Figure 2.7 shows high amounts of CH along with ettringite and gypsum. Hence, the UCS value is mainly due to the formation of these expansive minerals and hydration products. On other hand, the same sample made from blended cement at 20°C in Figure 2.30 shows a higher strength than the CPT sample made from PCI. The additional strength is due to the consumption of CH through pozzolanic reactions. This assumption of formation of secondary C-S-H due to the pozzolanic reaction in the PCI-slag is further supported by comparing the peak of CH at 18 degrees 2-theta in the XRD result of the 25000 ppm of CPT sample made from PCI and PCI- slag cured at 20°C in Figures 2.11 and 2.23 respectively. The intensity of CH at 18 degree 2-theta for PCI-slag cement (Fig 2.23) is about 20 CPS whereas in PCI cement, the intensity of CH is 110 CPS (Fig 2.11). It clearly shows that in addition to the hydration product, the CPT sample made from PCI-slag contains additional secondary C-S-H resulting in a higher UCS value than PCI.

At 35°C and 50°C, the 150 day UCS value of the PCI-slag sample with sulphate (Figures 2.30, 2.31, 2.32) is considerably lower than that of the PCI sample. Particularly, in Figures 2.30 and 2.31, the UCS value increases with increase of curing temperature whereas in the case of the PCI – slag samples, the UCS value remains relatively constant when temperature increases to 50°C from 35°C. No increase of the UCS can be attributed to the formation of rims of

hydration products (Escalante and Sharp, 2001) which prevents the further hydration of unhydrated slag grain. In addition, the partial replacement of cement by slag also reduces the clinker portion. This also decreases the strength of PCI-slag samples as explained earlier.

The 25000 ppm sample at 50°C in figure 2.32 shows very low value of UCS at 150 days. This lower value can be explained by the adsorption of sulphate ion by C-S-H gel (Fu et al, 1994) at high curing temperatures as described earlier. It is assumed that the adsorption of sulphate in C-S-H gel may have produced inferior quality of C-S-H with reduced strength.

SEM observations of the 25000 ppm sample cured at 50°C for 150 days in Figures 2.40, 2.41 show the presence of colloidal ettringite. The energy dispersive X-ray analysis (EDAX) of the same sample in figure 2.42 shows the major peaks of Ca, S, Al, and Si. This indicates the formation of ettringite, which can lead to the decrease of strength. This colloidal ettringite does not have high bindery forces and seems to be porous. However, the SEM observation of the 0 ppm sample at 50°C cured for 150 days in Figures 2.37, 2.38 shows the absence of collodoil ettringite. The EDAX of the 0 ppm sample in figure 2.39 shows a major peak of Ca, Si, O, indicating there is no formation of colloidal ettringite.

Figures 2.33, 2.34, 2.35 and 2.36 present the evolution of UCS of CPT samples made from PCI and PCI – slag with 5000 ppm, 15000 ppm and 25000 ppm of

sulphate cured at 2°C, 20°C, 35°C and 50°C. The UCS value of almost all samples increases with curing time. At 2 °C in Figure 2.33, samples made from PCI - slag shows lower strength at early days whereas UCS values increase as the curing time increases. At an advanced age, the UCS value of PCI- slag is greater than PCI cement.

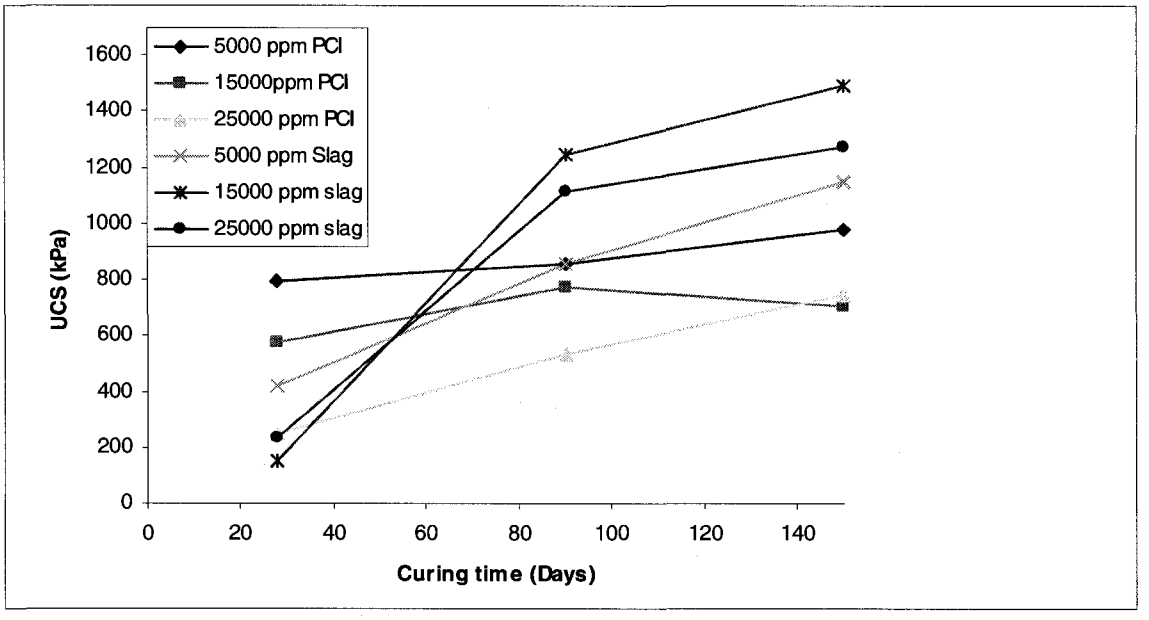

Figure 2-33 Evolution of UCS of CPT sample with different sulphate concentration at 2°C at different curing days.

Figure 2.34 shows that the PCI- slag still has higher values of UCS than PCI cement at 20°C. The higher UCS is due to the additional strength caused by the secondary C-S-H produced from the pozzolanic reaction. The samples made from the 15000 ppm PCI–slag shows higher value of UCS at this temperature in comparison to the rest of the samples followed by the 25000 ppm samples. The UCS value of the 25000 ppm samples at 20°C made from both cements

increases from 28 days to 90 days, but the strength shows a gradual decreasing trend at 150 day, showing the negative effect of sulphate. The 5000 ppm and 15000 ppm samples made from both binders show continuous increase of UCS value with curing time and do not show any signs of sulphate attack at 20°C in both the early and advanced ages of curing.

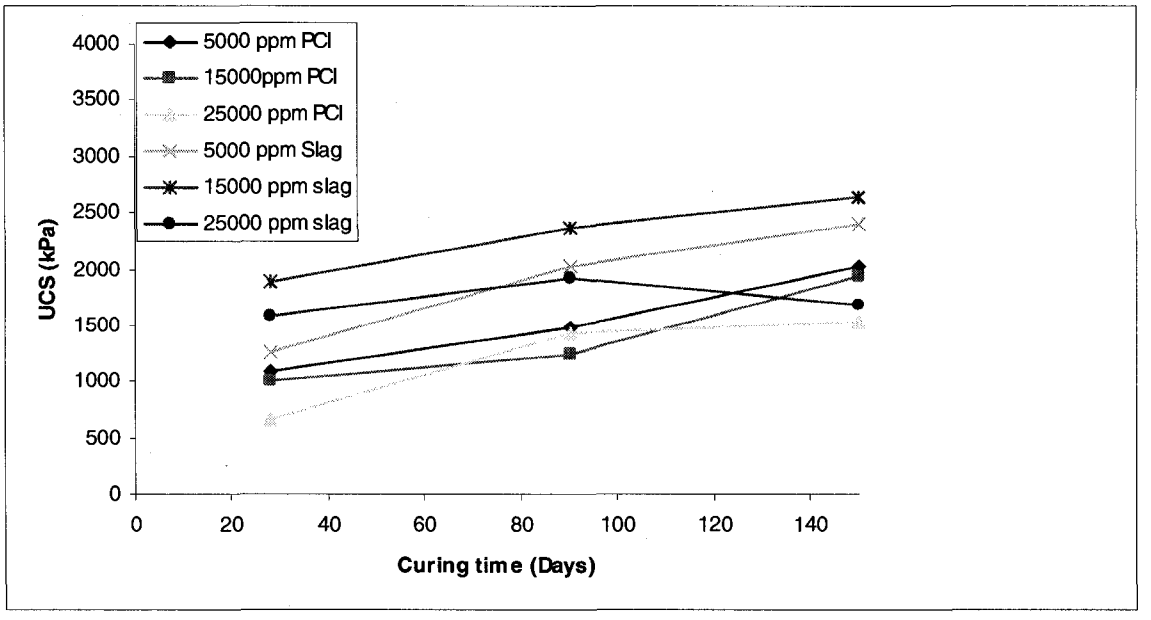

Figure 2-34 Evolution of UCS of CPT sample with different sulphate concentration at 20°C at different curing days

At 35°C, as illustrated in Figure 2.35, the 15000 ppm sample made from PCI–slag shows high UCS value during the early days of curing, but in the advanced age of curing, the UCS value is lower than the same sample made from PCI. In general, all samples made from PCI-slag show higher UCS value at an earlier age whereas they have a lower value of UCS at 150 days in comparison to PCI samples. The early higher strength of CPT samples made from PCI-slag may be

due to the formation of secondary C-S-H at 28 and 90 days. The reduced strength of the CPT samples made from PCI-slag at an advanced age may be due to the smaller quantity of clinker phase C_3S and C_2S present in the cement matrix so that smaller amounts of hydration products will be formed during the advanced age due to continuous hydration with time.

Samples made from PCI with 15000 ppm of sulphate show good strength at the advanced age in comparison to the rest of the samples. This can be attributed to the continuous hydration of cement in addition to the formation of expansive minerals which contribute positively to the strength of CPT. The 25000 ppm samples made from PCI-slag show lower UCS value than the 5000 ppm and 15000 ppm samples made with PCI-slag at the earlier as well as in the advanced age. The lower value at the earlier age can be caused by the presence of high quantities of sulphate which inhibit the hydration reaction, and also the adsorption of sulphate at 35°C by the C-S-H is another possible reason for the reduction in the value of UCS for the 25000 ppm samples.

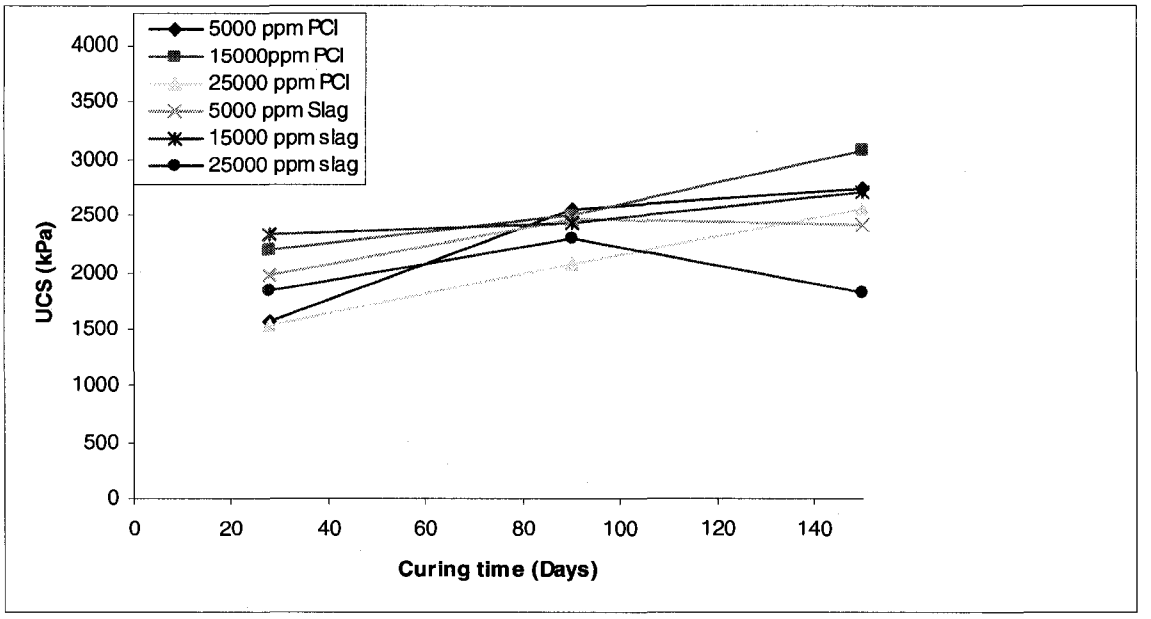

Figure 2-35 Evolution of UCS of the CPT sample with different sulphate concentration at 35°C at different curing days.

Figure 2.36 presents the evolution of UCS of all samples made from PCI and PCI-slag at 50°C with 5000 ppm, 15000 ppm and 25000 ppm of sulphate. The result shows that the sample made from PCI-slag has a lower value of UCS than the sample made from PCI at 50°C. This can be due to the formation of hydration rims which prevent the further hydration of unhydrated slag grains. Another possible reason may be the presence of lower amounts of clinker phase in PCI-slag.

The 25000 ppm samples with PCI and PCI-slag at 50°C in Figure 2.36 show the same value of UCS in all curing periods and have UCS value lower than other samples with low amounts of sulphate. The lower value is due to the adsorption

of sulphate which produces lower quality of C-S-H gel thereby reducing the strength of CPT samples.

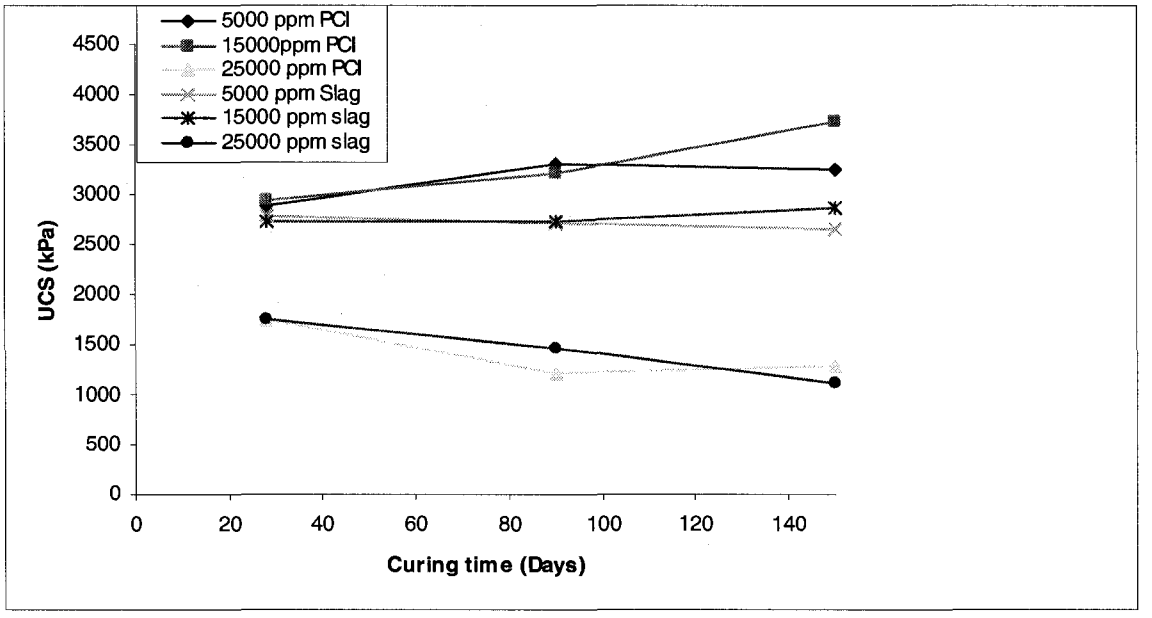

Figure 2-36 Evolution of UCS of CPT sample with different concentration of sulphate at 50°C at different curing days

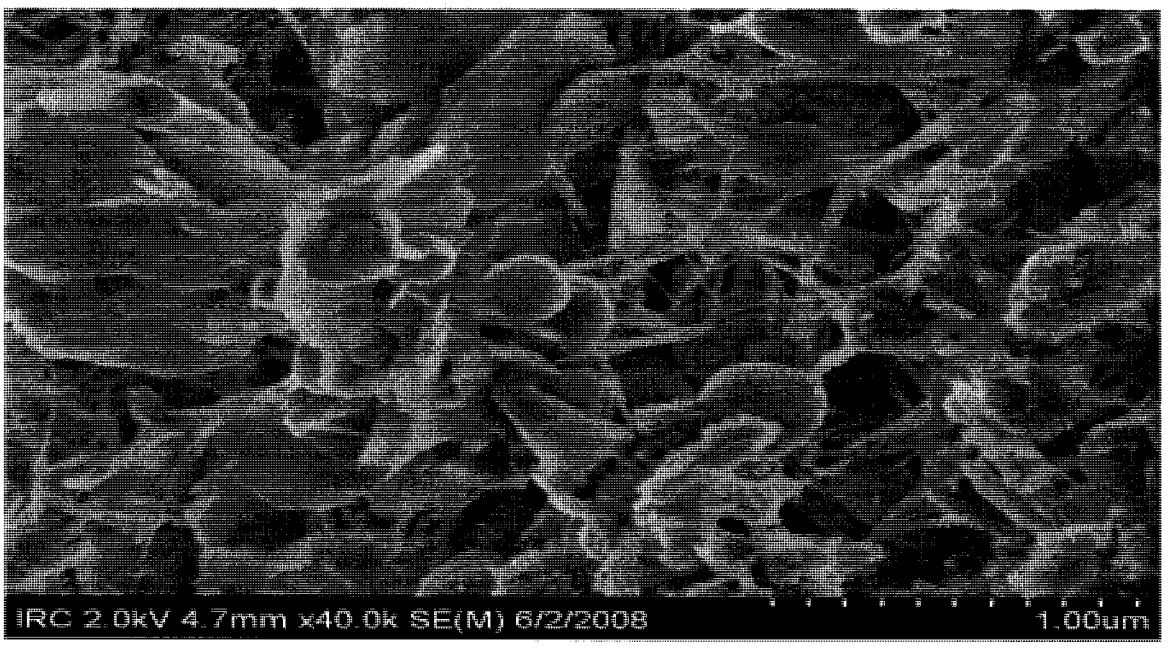

Figure 2-37 SEM observation of 0 ppm sample made from PCI at 50°C cured for 150 days

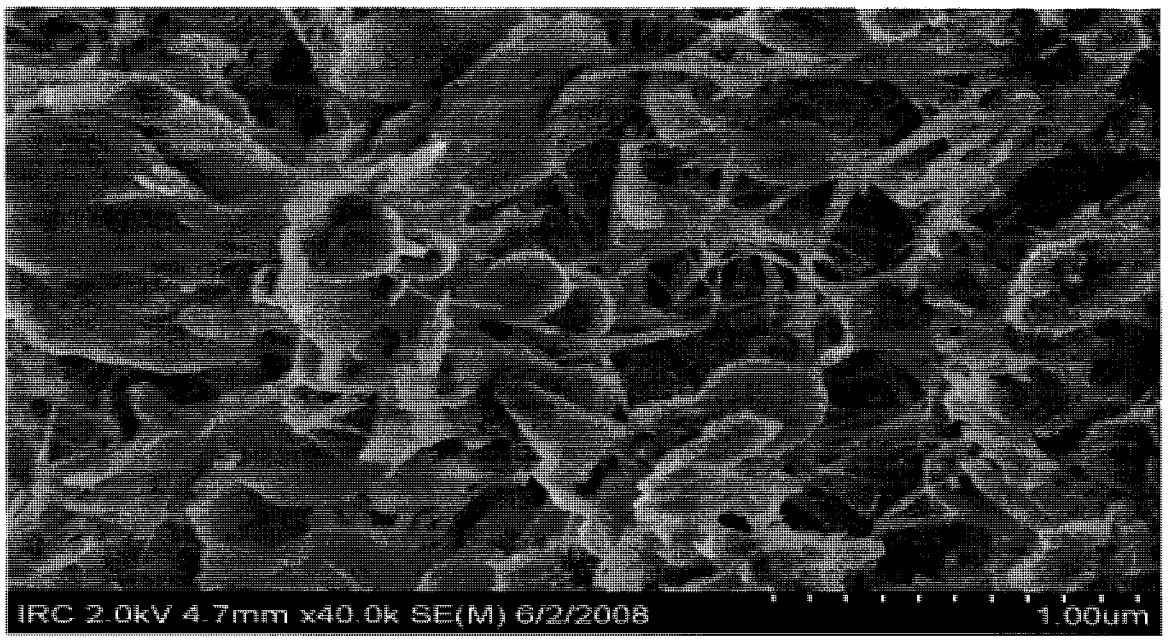

Figure 2-38 SEM observation of 0 ppm sample made from PCI at 50°C cured for 150 days

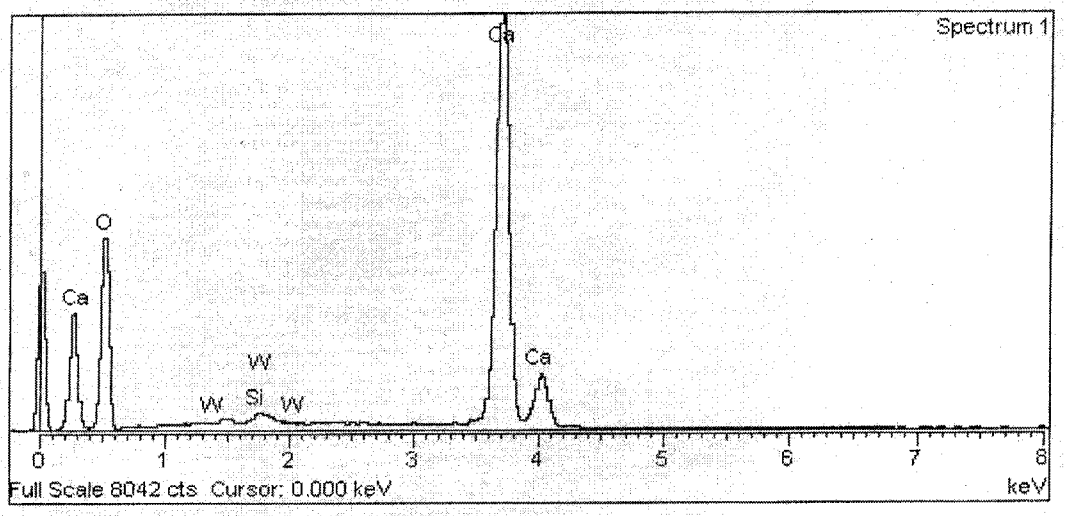

Figure 2-39 EDAX of 0 ppm sample made from PCI at 50°C cured for 150 days

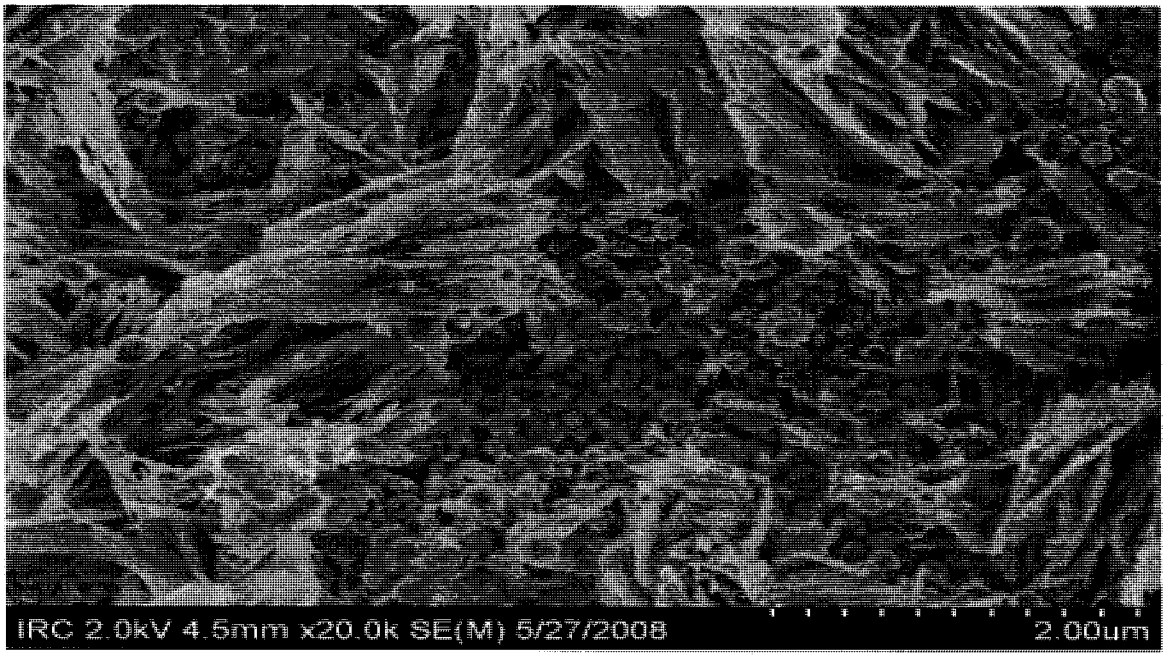

Figure 2-40 SEM observation of 25000 ppm samples made from PCI at 50° C cured for 150 days.

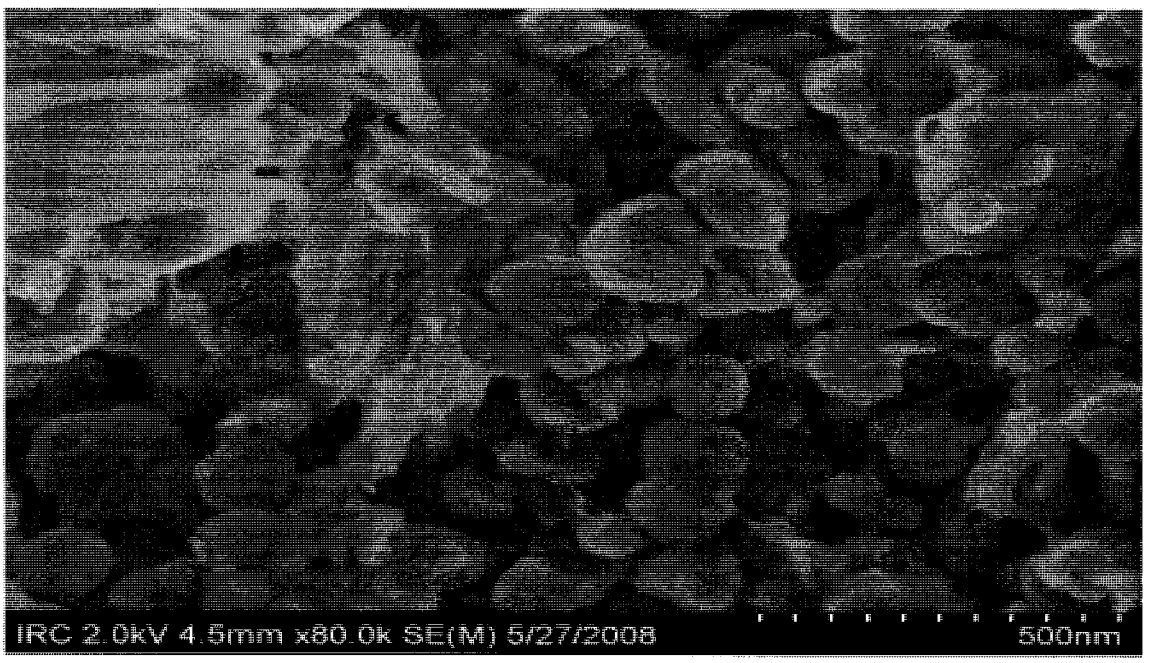

Figure 2-41 SEM observation of 25000 ppm samples made from PCI at 50° C cured for 150 days.

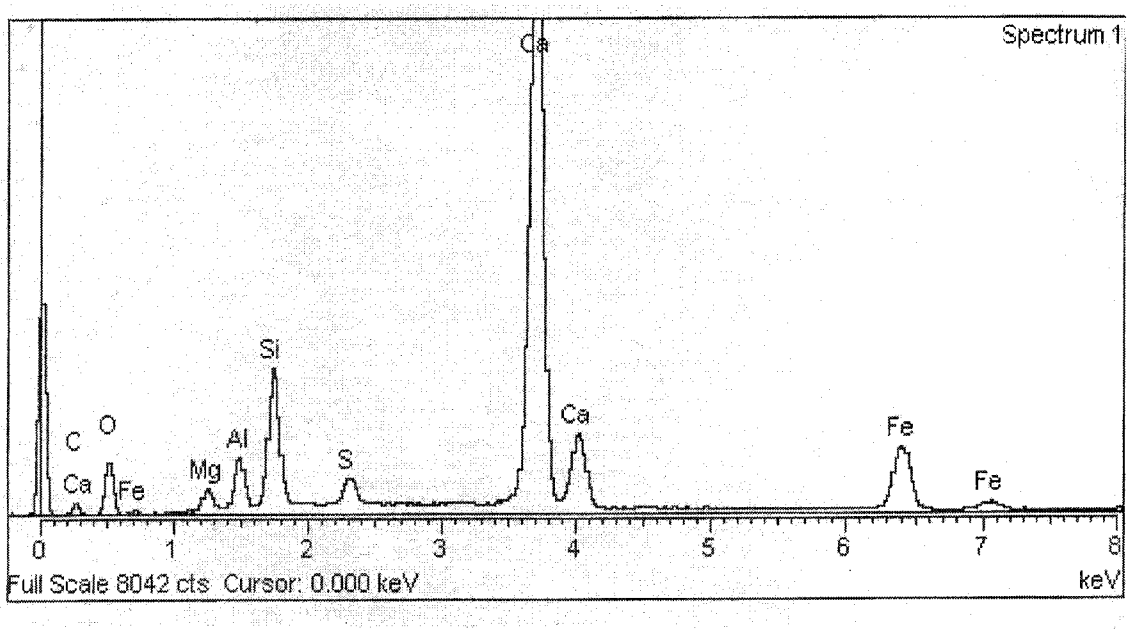

Figure 2-42 EDAX of 25000 ppm samples made from PCI at 50° C cured for 150 days

2.2.7 Conclusions and recommendations

Almost 200 samples are prepared with 0, 5000, 15000 and 25000 ppm of sulphate cured at 2°C, 20°C, 35°C and 50°C for 28, 90 and 150 days to study the thermo-chemical coupled effect on the UCS of CPT. Deterioration in the strength of CPT is found due to conventional sulphate attack for 25000 ppm sulphate at 20°C. The CPT sample with 25000 ppm at 50°C shows considerable loss of strength. This may be due to the formation of inferior quality of C-S-H gel due to the adsorption of sulphate by C-S-H gel. The study shows that the mechanical strength of CPT is largely influenced by this thermo-chemical effect. Sulphate content up to 15000 ppm contributes positively to the strength of CPT for the studied temperatures.

Sulphate attack is a very complex subject and most of the mechanism is still either controversial or unanswered. In this context, the effect of sulphate with raised temperatures on mechanical properties on CPT is more complex than sulphate attack at room temperature. This may be the first study implemented for the coupled thermo - chemical effect on CPT. There is not enough literature available in this area. Hence, further studies are necessary in for increased and better understanding of this problem.

2.3 Tailings shotcrete

2.3.1 Abstract

Tailings shotcrete (TS) is a new construction material with the potential to be used in the mining industry. TS is still in the research phase. Very few researches in TS have been carried out to find its suitability for use in mining applications. Previous research has encouraging results. In the continuation of the research, almost 300 samples, including PCI, PCI-slag and PCI-fibre with 0 ppm, 2500 ppm and 5000 ppm of sulphate, are prepared and cured at 2°C, 20°C, 35°C and 50°C and tested for 1, 7, 28 and 120 days respectively, to study the thermo-chemical effect on mechanical strength. Almost 18 MPa of UCS is obtained in this study with PCI cement at 50°C without using any additives. Sulphate content up to 2500 ppm is found to contribute positively to the strength whereas 5000 ppm at higher temperatures shows deterioration in strength due to sulphate attack (adsorption of sulphate by C-S-H gel). PCI- slag performs better than PCI in sulphate and non sulphate environments at 20°C and 35°C, but PCI-slag shows poor performance at 2°C and 50°C. Fibre does not contribute any additional gain in strength to the PTS. PCI performs very well at 50°C in sulphate as well as non sulphate environments.

2.3.2 Introduction

Metal industries are the prime industries for the economical development of any country. The mining process is growing every day, due to industrial development and advancement of technology (Saxena and Dhimole, 2006). The mining industries are using huge amounts of metal ores as raw materials to extract valuable metals. In general, ores contain very small concentrations of targeted metals, for example 1-2% for copper and 0.05% of uranium in their respective ores (Saxena and Dhimole, 2006). Thus, during the process of extraction of metals from their ores, large amounts of impurities will be produced as tailings in the processing plants. The chemical composition of these tailings mainly depends upon the composition of the original ores. The heavy metal ores generally contain sulphide minerals, such as pyrite or pyrrhotite (Elberling et al, 1994). The presence of sulphide minerals in the tailings creates a huge environmental problem (Kesimal et al, 2005) when they come into contact with oxygen and water. The well known phenomenon of acid rock drainage formation (ARD) or acid mine drainage (AMD) due to the oxidation of sulphide mineral will develop as a result (Ritcey, 2005).

The tailings are discharged in the form of slurry and parts of them are stored in tailings dams. In modern mines, around 40% to 100% of the total tailings are managed in tailings ponds (Benzaazoua et al, 2004). The major environmental

degradations due to surface storage of tailings according to Ritcey (2005) are: 1) contamination of streams by seepage of acidic water, 2) stream contamination due to surface runoff from the storage of tailings, 3) air and water contamination from blowing around of dry tailings from the wind, and 4) risk of tailings dam failure etc.

The environmental risks associated with tailings impoundment, risk of tailings dam failures, and huge operation and maintenance costs of the tailings impoundment compels the engineering community to consider alternative usage of the tailings. The use of tailings in the mining industries as CPT and production of bricks and copper tailings used in highway construction are some of the examples of the recycling of tailings (Ritcey, 2005). The use of tailings as a CPT is extensively practiced in Canadian underground mines as well as other parts of the world which offers a number of technical, economical as well as environmental benefits (Fall et al, 2008).

The use of CPT to fill underground voids in the mining industry reduces up to 60% of tailings that are stored on the surface (Fall and Samb, 2007). However, the mining industry still has to manage huge quantities of unused tailings on the earth surface. Hence, some studies were carried out to investigate the possibility of using these tailings in shotcrete. Zou and Sahito (2004) investigated that mine tailings have the potential to be used as shotcrete materials. If it can be used as shotcrete, then significant amounts of tailings can be reutilized in the mining

operation which helps to reduce environmental problems as well as costs associated with the surface impoundment of tailings.

Shotcrete has many applications in the construction industry for ground support (Zou and Sahito, 2004). It is commonly used in the repair and rehabilitation of concrete structures, tunnel linings and also to stabilize rock and soil slopes. In the mining industry, shotcrete is used to support the underground opening and strengthen the rock pillar. To be used as shotcrete, it should have a compressive and also high flexural strength in order to be compatible with different ground conditions. Hence, shotcrete is generally reinforced with steel or synthetic fibre to improve its flexural strength. The fibre reinforced shotcrete will sustain a higher bending load and withstand large deformations (Zou and Sahito, 2004). The compressive strength (uniaxial) is the most used parameter to evaluate the resistance and durability of shotcrete.

As mentioned earlier, most of the heavy metals tailings contain pyrite and pyrrhotite as a source of sulphate. In addition to this, mine process water (Fall and Benzaazoua, 2005) used in the mixing of TS also produces a significant quantity of sulphate in paste tailings shotcrete. Another characteristic is the variation of temperature which depends upon the parameters, such as depth, surrounding rocks, geographical location, mine ventilation, types of rock etc. (Fall and Samb, 2006). A previous study by Fall and Samb (2006) concluded that the mechanical strength of CPT is largely influenced by curing temperature. Other

studies (Kesimal et al., 2004; Fall and Benzaazoua, 2005) experimentally verified that the sulphate can have positive as well as negative impacts on the strength of the CPT depending upon its concentration and time.

The aforementioned studies were carried out by considering only either the isolated effect of temperature or sulphate on CPT strength. However, in reality, the effects of temperature and sulphate are strongly coupled. Furthermore, these studies deal with CPT. Since CPT is different from TS, thus their applicability will remain limited. Furthermore, previous studies performed on TS (Zhou and Sahito, 2004), didn't address the resistance of shotcrete to sulphate attack as well as to coupled effects of sulphate and temperature. To the best knowledge of the author, there are no studies on the coupled effect of sulphate and temperature on the strength development of TS. Hence, this coupled effect on the mechanical strength as well as durability of TS is necessary for study in order to evaluate the suitability for mine TS as a ground support. Hence, this study will be carried out to understand the coupled effect of temperature and sulphate on the strength development of TS.

After this introduction, materials and methods will be discussed, followed by specimen preparation. Then, the experimental results are presented and discussed. Finally, the conclusion of the research is drawn at the end.

2.3.3 Materials and methods

2.3.3.1 Materials

2.3.3.1.1 Binders and fibre used

Two types of binder are used in this research. Ordinary PCI, which is frequently used to achieve the strength in cementitious material, is one of the binders. In addition, GGBFS (50% by wt) is another binder used to prepare the samples. Polymer fibre is also used with PCI to observe the role of fibre in the development of UCS under thermo-chemical loading. The nylon fibre is mixed at a rate of 1.75% of solid mix and the binder is kept as 22% of the tailings to obtain a reasonable strength (Zou and Sahito, 2004). Table 2.1 gives the chemical properties of the binders with relative densities.

2.3.3.1.2 Water used

Distilled water is used throughout the experiment to prepare the specimens. The objective of using distilled water is mentioned in 2.1.3.1.2 for control on the sulphate concentration. $FeSO_4.7H_20$ is used in different quantities to obtain 2500 and 5000 ppm of sulphate concentration. Water is added as 27% of the solid mix

as per a previous study by Zou and Sahito (2004) to achieve optimum strength of the tailings shotcrete.

2.3.3.1.3 Tailings

This part is described in detail in 2.2.3.1.3. The grain size distribution of tailings is shown in Figure 2.1. The physical and chemical properties of the tailings are given in Tables 2.2 and 2.3 respectively.

2.3.4 Specimen preparation

Required amounts of tailings and binder were mixed in a dry container until a homogeneous color was obtained. Sulphate salt was added to the distilled water to achieve 2500 ppm and 5000 ppm concentration of sulphate in the mix. The distilled water, when all the sulphate salt dissolved, was added to the dry mix of binder and tailings, and mixed together to obtain a homogeneous paste. Table 2.5 shows the ingredients of the mix. The TS samples were kept in a plastic cylinder sized 5 cm in diameter and 10 cm in height. The samples were then vibrated manually to remove the entrapped air. They were sealed with a plastic cover to prevent the evaporation of water. The samples were cured in an environmental chamber with controlled temperatures at 2°C, 20°C, 35°C and 50°C for 1, 7, 28 and 120 days. Almost 300 samples were prepared for this research.

Table 2-5 Different recipes used in the study for tailing shotcrete

Binder Type	Binder ratio	% of Binder	W/C ratio	Sulphate (ppm)
PCI	-	22	1.45	0
PCI	-	22	1.45	2500
PCI	-	22	1.45	5000
PCI + Slag	50/50	22	1.45	0
PCI + Slag	50/50	22	1.45	2500
PCI + Slag	50/50	22	1.45	5000
PCI + Fibre	-	22	1.45	0
PCI + Fibre	-	22	1.45	2500
PCI +Fibre	-	22	1.45	5000

2.3.5 Testing procedures

2.3.5.1 Uniaxial compressive strength test

A UCS test per ASTM C-39 was performed to evaluate the mechanical strength of the samples after 1, 7, 28 and 120 days of curing time for the different temperatures under consideration. The load was applied at a slow rate of 1 mm/min. Each test was duplicated to ensure the reliability of the results.

2.3.5.2 Water content test

The water content test is described in 2.2.5.2 in detail.

2.3.6 Results and discussions

2.3.6.1 Coupled effects of sulphate and temperature on PCI shotcrete strength

2.3.6.1.1 Early ages

Figure 2.43 illustrates the 1 day UCS of TS made from PCI with 0, 2500, and 5000 ppm of sulphate cured at 2°C, 20°C, 35°C and 50°C. The results show that the UCS of all samples increases with increase of curing temperature. Increase of curing temperature promotes the hydration reaction of cement resulting in the rapid precipitation of hydration products which are responsible for early strength development (Barnett et al, 2006; Escalante and Sharp, 2001; Fall and Samb, 2006; Lothenbach et al, 2007). At 2 °C, the sample has almost the same value and the UCS value is very low in comparison to other higher curing temperatures. This is because the hydration starts very slowly (Lothenbach et al, 2007) due to the lower temperature. The strength of these tailings shotcrete increases almost at the same rate due to the continuous hydration of cement as

the temperature rises to 20°C. The TS with 0 ppm, 2500 ppm and 5000 ppm of sulphate also shows approximately the same UCS value at 20°C.

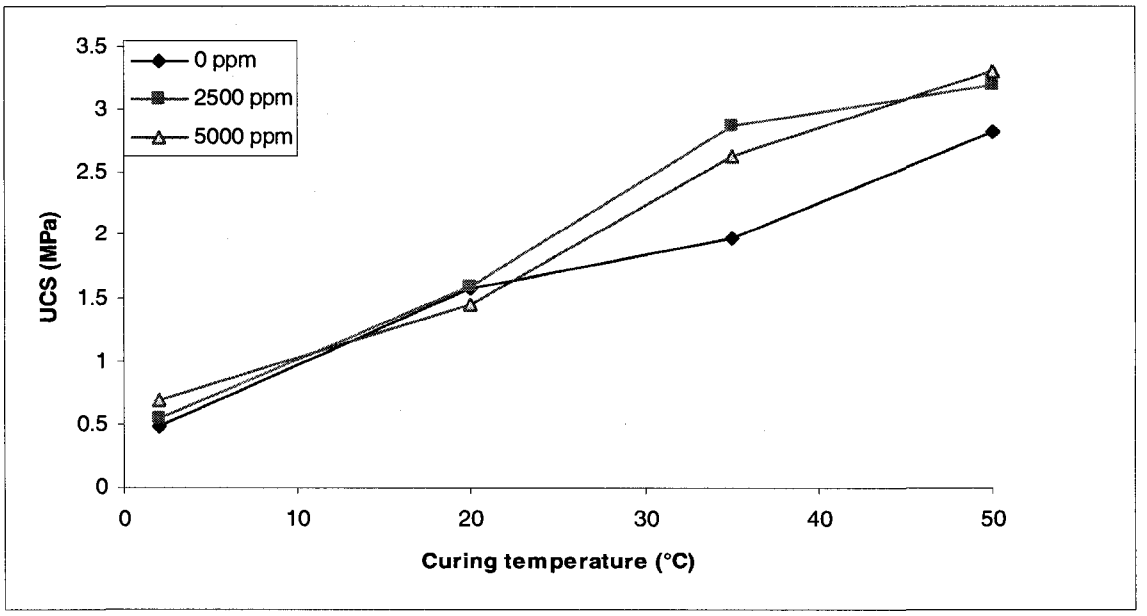

Figure 2-43 1 day UCS of PCI-tailings shotcrete with different sulphate concentrations at different temperatures

TS samples with 2500 ppm and 5000 ppm sulphate show higher 1 day UCS values at 35°C and 50°C than the 0 ppm samples. This higher strength can be due to the precipitation of gypsum and ettringite in the cement matrix produced from the reaction between sulphate and CH (Fall and Benzaazoua, 2005; Hekal et al, 2002; Salah and Dulaijan, 2007). The formations of gypsum and ettringite at an earlier age fill the pores and voids and contribute to the formation of a denser structure, resulting in high strength of the TS (Fall and Benzaazoua, 2005; Hekal et al, 2002). Such behavior was also reported in previous studies

(Akoz et al, 1995; Fall and Benzaazoua, 2005; Hekal et al, 2002; Salah and Dulaijan, 2007).

The higher value of UCS of the 2500 ppm than 5000 ppm sample at 20°C and 35°C can be attributed to the inhibition of the binder hydration of the 5000 ppm sample by high sulphate concentration. The sulphate partly prevents the formation of CH so higher amounts are expected in the 2500 ppm sample than the 5000 ppm samples due to less sulphate. Hence, the 2500 ppm sample will form more expansive minerals at 20°C and 35°C due to the release of CH from hydration of cement.

At 50°C, the 1 day UCS value of the 5000 ppm sample is higher than that of the 0 ppm and 2500 ppm samples. This high value is due to the positive contribution of expansive minerals. With increase of curing temperature, the continuous hydration of cement along with formation of expansive minerals in the pores of the TS caused the 5000 ppm sample to be stronger than the 2500 ppm and 0 ppm samples at 50°C.

The evolution of UCS in the 0 ppm sample is due to the formation of hydration products, such as CH and C-S-H. As they have no additional sulphate, there will be no precipitation of secondary expansive minerals in the pores that could have resulted in a decrease of the porosity of the 0 ppm sample. This leads to lower

UCS value. Hence, the UCS value of the 0 ppm sample is lower than the 2500 and 5000 ppm samples at 35°C and 50°C.

The 7 day UCS value of tailings shotcrete, as shown in Figure 2.44, also increases with increase of temperature except at 50°C. The 7 day UCS value of all samples at 2°C and 20°C is almost the same. The rate of development of strength in TS shows that at 7 day, the 0 ppm sample at 2°C is 380% higher than 1 day whereas for the 2500 ppm, it is 250%. For the 5000 ppm sample, the 7 day strength is 270% greater than the 1 day strength at 2°C.

TS with 5000 ppm of sulphate at 35°C and 50°C have lower strength than 0 ppm and 2500 ppm. On the other hand, the 2500 ppm sample at 35°C shows the highest UCS value which may be due to the positive contribution of expansive minerals as mentioned above. The lower UCS value of the 5000 ppm sample at 35°C can be attributed to the adsorption phenomenon of sulphate by C-S-H gel. The 0 ppm sample has constant growth of UCS from 2°C to 35°C due to continuous hydration of cement. At 50°C, all samples show reduced strength. The reduced strength of the 0 ppm samples can be due to the negative impact of high curing temperatures on UCS value also known as the phenomenon of the cross over effect (Kim et al, 2002). Figure 2.44 also illustrates that the 5000 ppm and 2500 ppm sample at 50°C has lower UCS value than at 35°C. This may be due to the formation of inferior quality of C-S-H due to the adsorption of sulphate (Fu et al, 1994). The 2500 ppm sample has good 7 day strength at 35°C.

However, it also shows reduced strength at 50°C. Nevertheless, the 2500 ppm sample at 50°C has a UCS value greater than that of the 5000 ppm sample at 50°C. This is due to the lower quantity of sulphate present in the 2500 ppm sample because high sulphate concentration in the pores of samples favors higher adsorption of sulphate by C-S-H (Ramlochan et al, 2004).

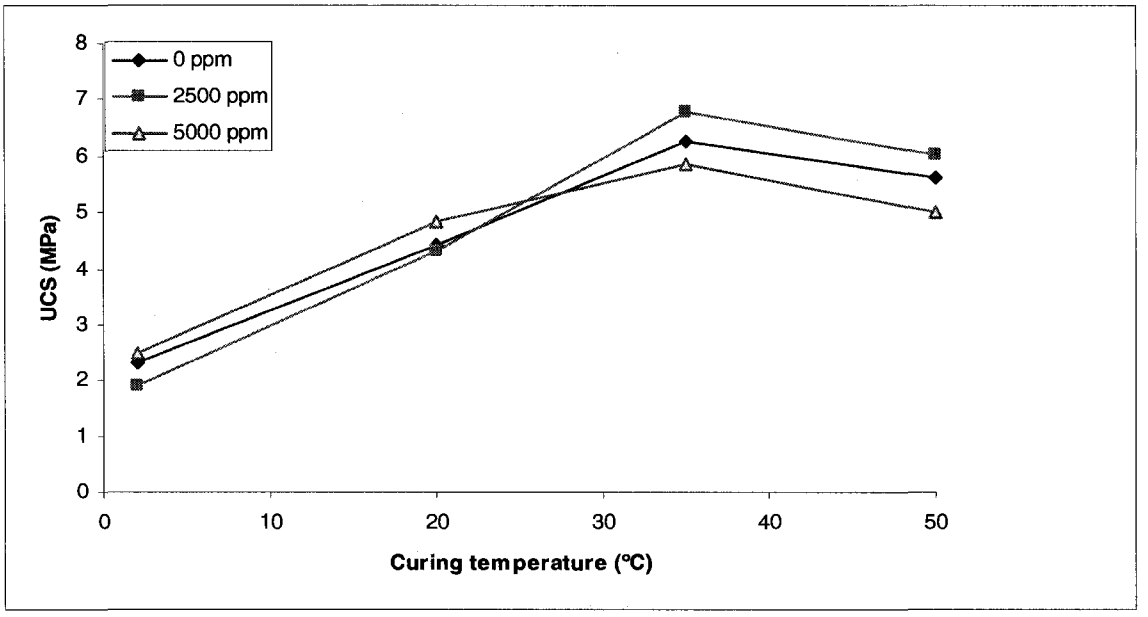

Figure 2-44 7 day UCS of PCI-tailings shotcrete with different sulphate concentrations at different temperatures

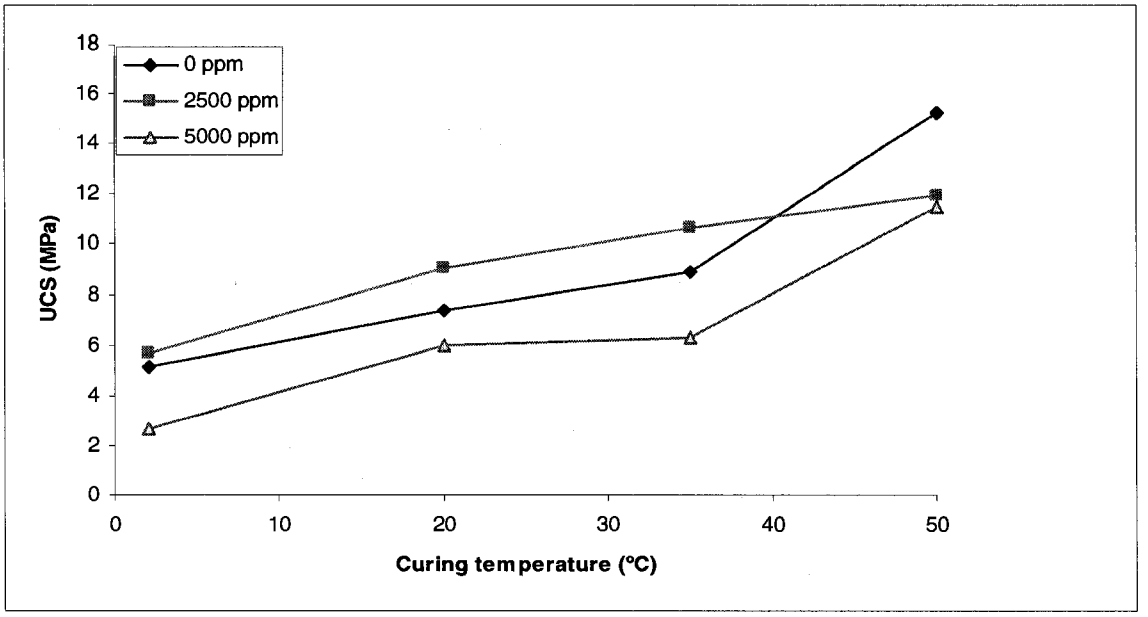

Figure 2-45 28 day UCS of PCI tailings shotcrete with different sulphate concentrations at different temperatures

Figure 2.45 illustrates that the 28 day UCS value of TS also increases with increase of curing temperature. The 28 day UCS value shows that the 2500 ppm sample has a higher strength at almost all temperatures except 50°C. On other hand, the UCS of the 5000 ppm sample shows a lower value than the rest of the samples at all temperatures studied. At 2°C, the 5000 ppm sample shows much lower strength. At this lower temperature, it has 2.5 MPa of UCS value while the 0 ppm and 2500 ppm samples show almost 6 MPa. The water content curve for the 28 day sample in Figure 2.46 also shows that the 5000 ppm sample at 2 °C has higher water content than rest. This water content data also support that the hydration degree is lower for the 5000 ppm sulphate sample. Hence, it has a very low value of UCS at 2°C mainly due to the inhibition of the binder hydration by high sulphate content and low curing temperatures (Fall and Samb, 2006).

The 2500 ppm sample has the highest strength at 2°C, 20°C and 35°C. The 28 day water content curve in figure 2.46 also illustrates that the 2500 ppm sample is consuming more water than the 5000 ppm sample. Hence, from the hydration of cement, there will be enough hydration products along with secondary gypsum and ettringite which makes the 2500 ppm sample stronger than the 0 ppm and 5000 ppm samples. The 28 day UCS value of the 0 ppm sample is very consistent. It is between that of the 2500 ppm and 5000 ppm samples. The uniform rate of gain in strength of the 0 ppm sample is due to continuous hydration of cement with increase of temperature (Fall and Samb, 2006; Lothenbach, 2007). The 5000 ppm samples at 20°C and 35°C still exhibit very low UCS values, even lower than that of 0 ppm. The 28 day water content curve in Figure 2.42 still shows high water content. The reduced strength of the 5000 ppm samples at 20 °C and 35°C can be attributed either to lower binder hydration and/or due to excess formation of expansive minerals in the cement matrix.

At 50°C, the 28 day UCS value of the 0 ppm sample is the highest. The continuous hydration of cement with raised temperatures allows the formation of adequate hydration products in the 0 ppm sample. This causes the 0 ppm sample to reach a higher value of UCS at 50°C. Both the 2500 ppm and 5000 ppm samples show approximately the same strength. These lower UCS values can be attributed to the adsorption of sulphate by C-S-H. This can result in the

formation of C-S-H of a lower quality. Furthermore, the destabilization of ettringite at high temperatures can lead to the coarsening in the pore structure of the matrix of the tailings, and thus contributing to the increase of the porosity, i.e. decrease of the UCS.

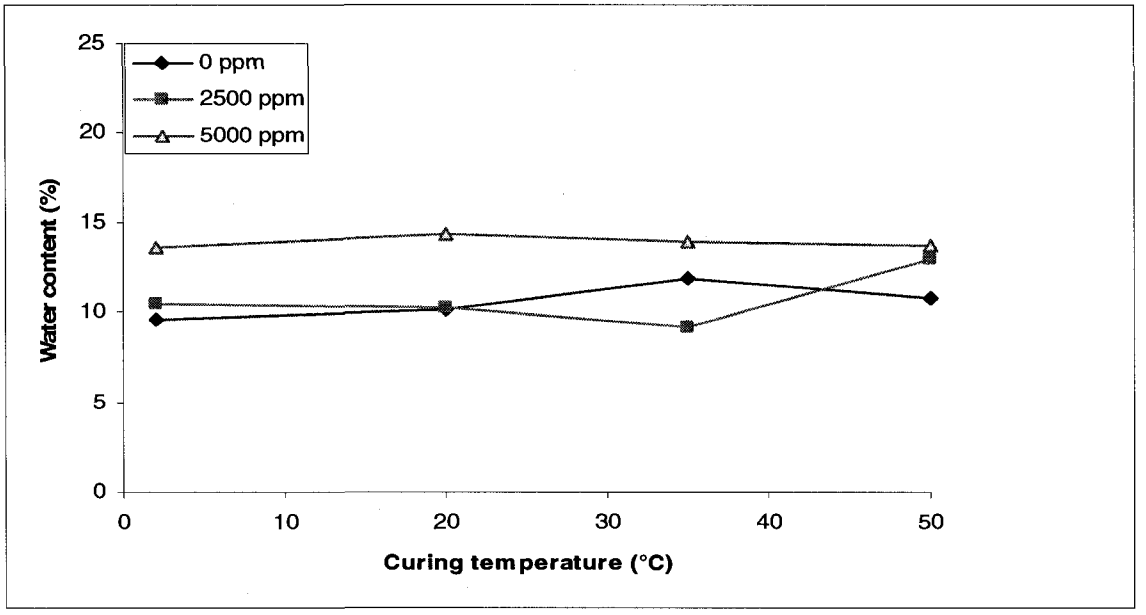

Figure 2-46 28 day water content of PCI-tailings shotcrete with different sulphate concentrations at different temperatures

2.3.6.1.2 Advanced ages

Figure 2.47 shows the 120 day UCS value of the TS made from PCI with 0 ppm, 2500 ppm and 5000 ppm sulphate cured at 2°C, 20°C , 35°C and 50°C. The 120 day UCS value of all TS also increases with increase of curing temperatures. At 2°C and 20°C, the 2500 ppm and 5000 ppm samples have almost the same UCS

values. The same figure also illustrates that the TS sample containing sulphate has a higher UCS value than the 0 ppm sample at 2°C and 20°C. The 120 day UCS value of samples containing sulphate is approximately 21% and 17% higher than that of 0 ppm samples at 2°C and 20°C. This increase of UCS at 2°C and 20°C of samples containing sulphate is due to the precipitation of secondary ettringite and gypsum.

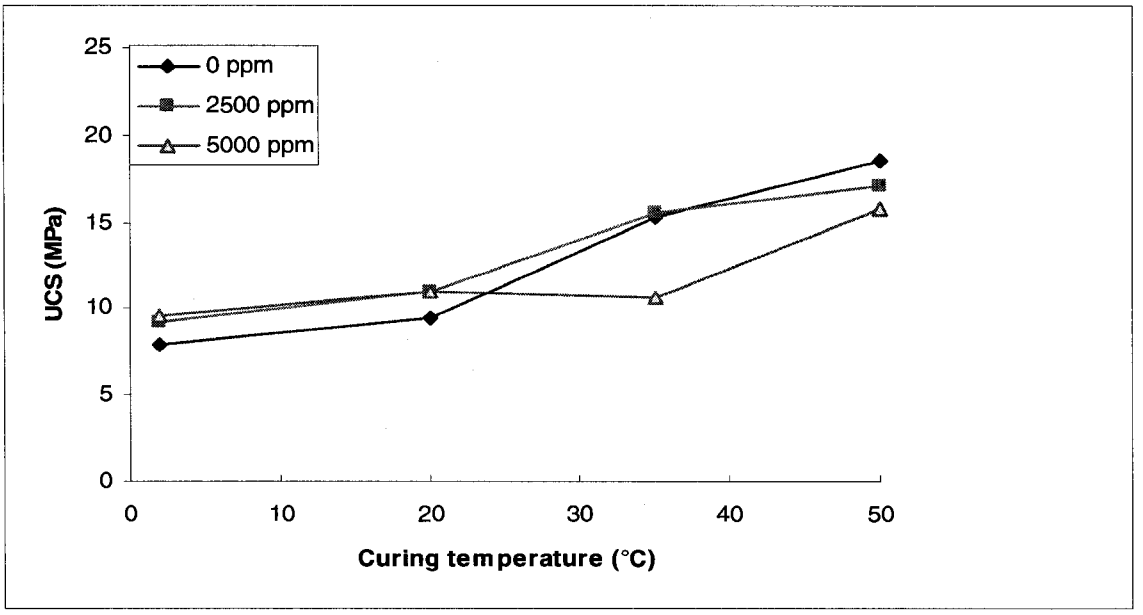

Figure 2-47 120 day UCS of PCI-tailings shotcrete with different sulphate concentrations at different temperatures

This is also supported by comparing the XRD results of the 0 ppm and 5000 pm samples at 20°C as shown in Figures 2.73 and 2.7. The 5000 ppm sample cured at 20°C in Figure 2.7 shows the precipitation of higher amounts of expansive minerals. The same figure also shows the depletion of CH due to the reaction

between CH and sulphate. On other hand, the 0 ppm sample cured at 20°C in Figure 2.73 shows the lower quantity of ettringite and higher amounts of CH.

At 35°C, the 0 ppm sample shows good strength. The 120 day UCS value of 0 ppm sample is almost the same as that of the 2500 ppm sample. It is also significantly higher than that of the 5000 ppm sample. The increase of the strength is entirely due to the continuous hydration of cement. The formation of expansive minerals in the 2500 ppm sample at 35°C still plays a positive role in the development of compressive strength. The lower value of UCS of the 5000 ppm sample at 35°C is due to sulphate attack where ettringite and gypsum contribute negatively to the strength, reducing the 120 day UCS value of TS (Fall and Benzaazoua, 2005). The UCS of the 5000 ppm sample at 50°C (explained below) is still higher than 35°C, hence there is no or very limited amount of sulphate that will adsorbed by C-S-H.

Figure 2.47 also shows that at 50°C, the 0 ppm sample reaches a higher UCS value than the rest of the samples. The XRD result in Figure 2.12 shows the formation of high quantities of CH and C-S-H along with ettringite and gypsum. The precipitation of these hydration products significantly reduces the capillary porosity, thereby resulting in high 120 day UCS value. The 5000 ppm sample at 50°C shows an increase of strength in comparison to 35°C. This is due to the precipitation of both hydration products and fewer amounts of expansive minerals in the cement matrix which play positive roles in the strength development

because of the limited availability of sulphate due to adsorption by C-S-H gel. The 5000 ppm sample at 50°C is not able to make enough ettringite and gypsum in comparison to 20°C due to shortage of sulphate. This can be again, supported by the XRD result in Figure 2.13. This figure shows an adequate amount of unreacted CH due to shortage of sulphate. Again, the peak of CH at 18, 28.5, 34, 47 and 51 degrees 2-theta in the XRD result of the 5000 ppm samples at 50°C is higher than 20°C in Figure 2.7.The lower peak of CH in Figure 2.7 is due to the higher availability of sulphate because of the lower curing temperature. In this case, the quantity of CH is reduced due to the reaction between CH and the available sulphate. For this reason, adequate ettringite and gypsum are found in the sample in comparison to the 5000 ppm sample cured at 50°C. Hence, at 50°C, the 2500 ppm and 5000 ppm samples clearly exhibit the adsorption phenomenon. However, due to the relatively low amount of free sulphate present in the sample, it still shows good strength.

2.3.6.2 Coupled effects of sulphate and temperature on PCI-Slag tailings shotcrete strength

2.3.6.2.1 Early ages

Figure 2.48 represents the result of 1 day UCS value of TS made from PCI and slag in the ratio of 50/50 by weight cured at 2°C, 20°C, 35°C and 50°C with 0 ppm, 2500 ppm and 5000 ppm of sulphate concentration. In general, the 1 day UCS value of all TS samples increases with increase of curing temperature. Raised temperatures of the TS enhance the hydration reaction of cement, thereby leading to more precipitation of the hydration products in the cement matrix, thus resulting in early high strength (Akoz et al, 1999; Escalante and Sharp, 2001; Fall and Samb, 2006; Lothenbach et al, 2007) .The same figure also shows that the 1 day UCS value of TS without sulphate is higher than that of the samples containing sulphate at all temperatures studied. The 1 day UCS value of 0 ppm TS at 2°C is found to be 60% and 130% stronger than the 2500 ppm and 5000 ppm TS respectively. The lower UCS value of TS containing sulphate is due to the presence of sulphate which prevents the hydration of cement (Fall and Benzaazoua, 2005). The 1 day water content curve in Figure 2.49 also supports the above assumption. The sample with sulphate has a lower rate of hydration than those without sulphate.

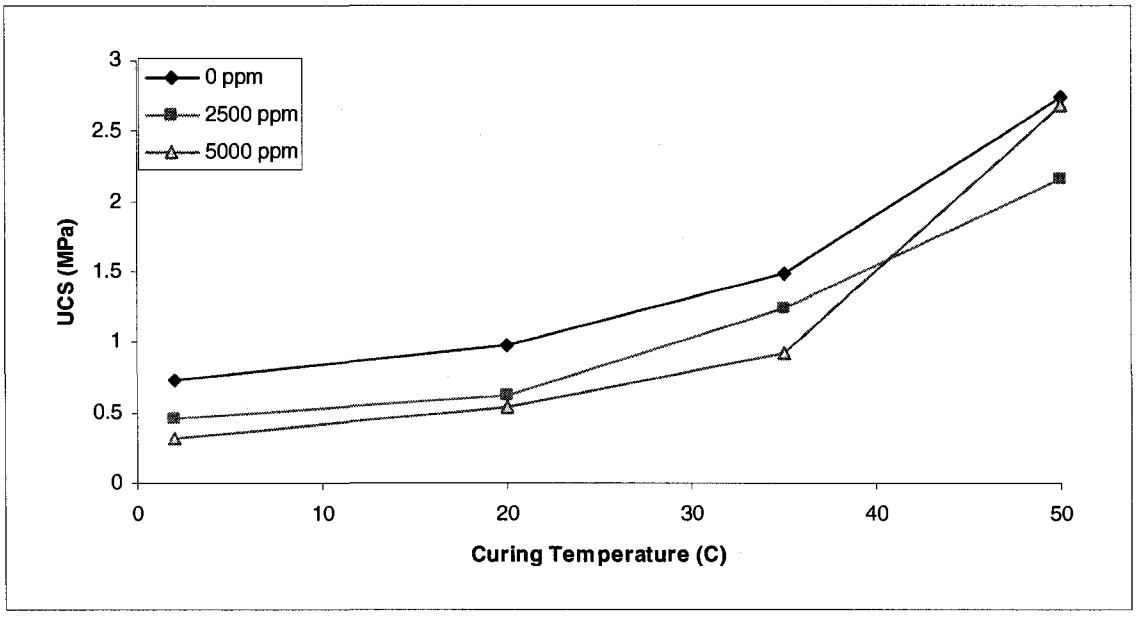

Figure 2-48 1 day UCS of PCI-slag tailings shotcrete with different sulphate concentrations at different temperatures

The water content curve in Figure 2.49 also illustrates that the 0 ppm sample uses more water than the 2500 ppm and 5000 ppm samples at all temperatures studied. The consumption of water by the 2500 ppm and 5000 ppm samples is lower. Thus, there is less hydration of cement than the 0 ppm TS resulting in the lower value of UCS.

Figure 2.48 also shows that the 1 day UCS value of 2500 ppm TS is somewhat higher than the 5000 ppm sample at 2°C, 20°C and 35°C, but lower than the 5000 ppm at 50°C. The higher strength can be attributed to the lower concentration of sulphate. This is due to the fact that high concentration of sulphate prevents the early hydration of C_3A (Fall and Benzaazoua, 2005).

Again, the water content curve in Figure 2.49 also shows that the water used by the 2500 ppm sample is a little bit higher than the 5000 ppm sample at 2°C, 20°C and 35°C whereas at 50°C, the 5000 ppm sample absorbs more water, resulting in the high UCS value .

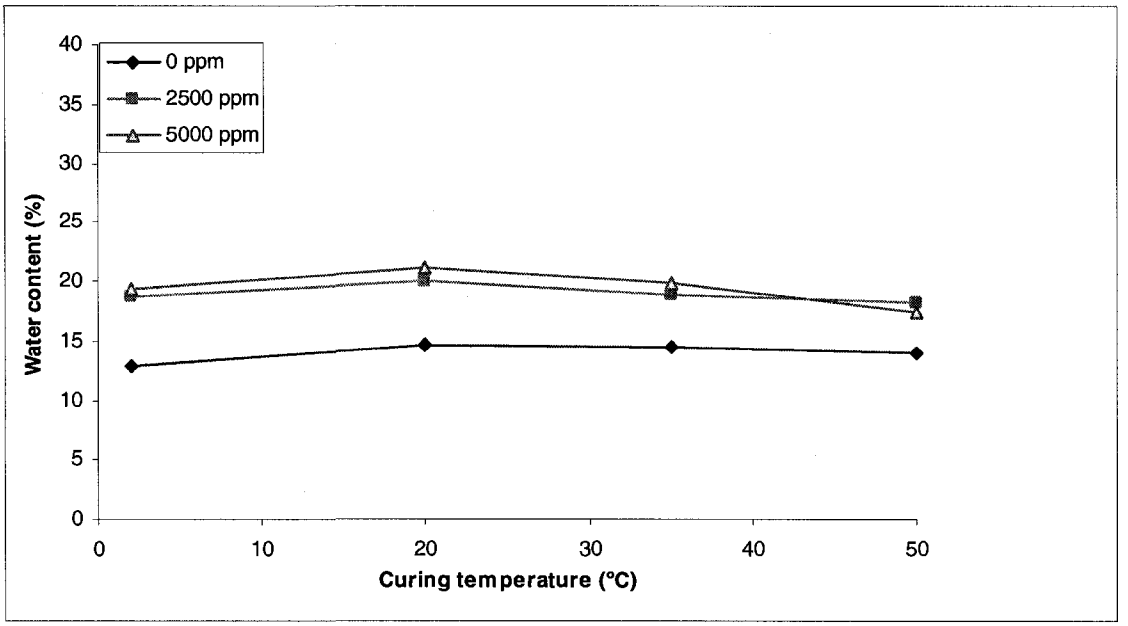

Figure 2-49 1 day water content of PCI-slag tailings shotcrete with different sulphate concentrations at different temperatures

An interesting observation in Figures 2.48 and 2.49 is the behaviour of the 0 ppm and 5000 ppm samples at 50°C. They have an almost equal UCS value at 50°C, but the water content curve shows that the water consumed by the 0 ppm sample is significantly more at the same temperature. The water is solely used by the 0 ppm sample to hydrate the cement and attain a good strength due to the

formation of hydration products. As it does not have any sulphate, the strength is mainly due to the formation of C-S-H. Also, the full pozzolanic reaction of slag will not be expected at such an early age because slag needs a longer curing period for slag activation (Escalante and Sharp, 2001).

However, the 5000 ppm sample uses 25% less water at 50°C. Hence, the formation of hydration products is assumed to be less. As it contains adequate amounts of sulphate, the sulphate can react with CH and produce gypsum and ettringite. Hence, the precipitation of these expansive minerals fills the pores, thereby reducing the porosity. C-S-H can compel the strength of the 5000 ppm sample and reach the same 1 day UCS value as that of the 0 ppm sample.

Figure 2.50 presents the result of the 7 day UCS value of TS cured at 2°C, 20°C, 35°C and 50°C with 0 ppm, 2500 ppm and 5000 ppm of sulphate concentrations. In general, the 7 day UCS value of all TS made from PCI-slag increases with increase of curing temperature. The result also shows that they have almost the same UCS value at all temperatures except at 50°C. The 7 day UCS value of TS at 2 °C is found to be 90%, 190% and 355 % stronger than the 1 day UCS values for 0 ppm, 2500 ppm, and 5000 ppm whereas at 20°C and 35°C, the rate of gain in strength of these samples are much higher than 2°C. The 7 day UCS value of 0 ppm , 2500 ppm and 5000 ppm TS at 20°C and 35°C will be 410%, 670%, 888% and 490%, 570%, 750% respectively higher than the 1 day UCS value at the same temperatures. Such increase of the strength in the 0 ppm shotcrete

sample is partly the result of continuation hydration of unhydrated cement particles. Furthermore, the formation of secondary C-S-H from the pozzolanic action of slag (Hekal et al, 2002; Sahmaran et al, 2007) contributes to the observed strength increase.

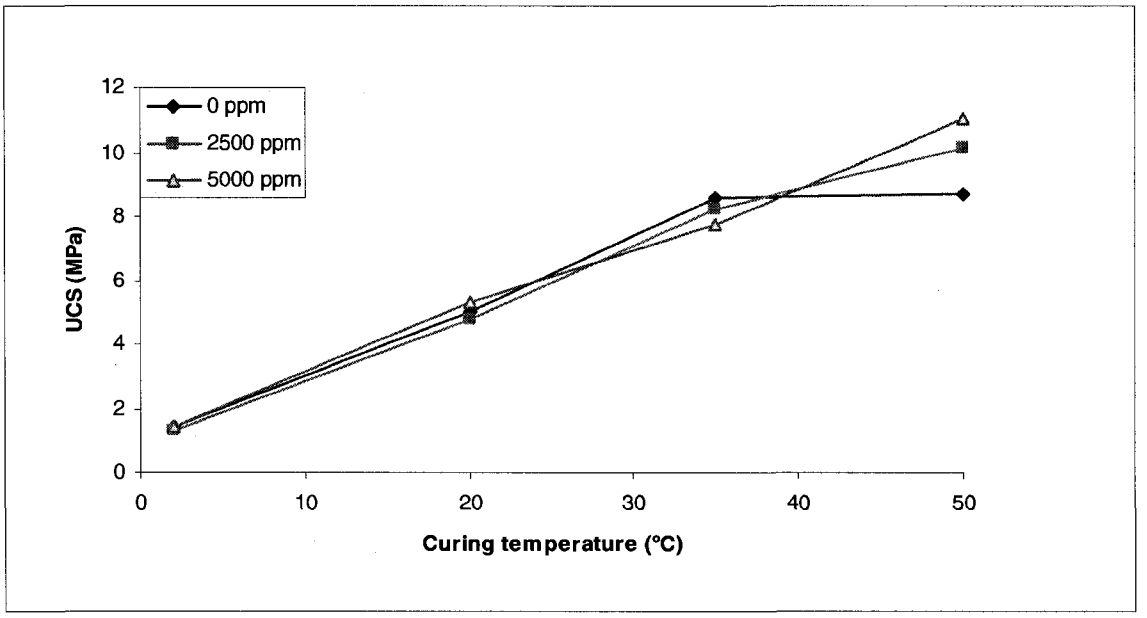

Figure 2-50 7 day UCS of PCI-slag tailings shotcrete with different sulphate concentration at different temperatures

Figure 2.50 also illustrates that at 50°C, TS has different 7 day UCS values. The 5000 ppm sample has the highest value. The 0 ppm sample shows almost the same value at 35°C and 50°C. In this case, the higher UCS value of samples containing sulphate is also due to the presence of expansive minerals as mentioned above. The TS at 7 day does not show any sulphate attack and reduced strength from the adsorption of sulphate. One of the possibilities here may be due to the presence of slag which forms additional secondary C-S-H by

pozzolanic reactions. The secondary C-S-H fills the pores of the cementitious materials, reducing the porosity and forms a dense compact body (Aziz et al, 2005). The additional strength gained by the pozzolanic reaction can dominate the strength loss due to adsorption of sulphate at the early ages of tailings shotcrete.

Figure 2.51 represents the 28 day UCS value of TS made from PCI-slag cured at 2°C, 20°C, 35°C and 50°C containing 0 ppm, 2500 ppm and 5000 ppm of sulphate. It also illustrates that the 28 day UCS value of all samples increases with increase of curing temperature. The TS has almost the same value of UCS at 2°C. At 20°C, the 28 day UCS value of samples containing sulphate is a little bit higher than the 0 ppm sample. This increase is due to the additional contribution of ettringite and gypsum produced from the reaction of sulphate and CH (Fall and Benzaazoua, 2005). At 35°C, the 0 ppm and 2500 ppm samples have the same strength whereas the 5000 ppm sample shows reductions in its UCS value. This may be either due to formation of adequate expansive minerals in the cement matrix reducing the strength due to conventional sulphate attack or adsorption of sulphate by C-S-H gel which produces inferior quality of C-S-H. At 50°C, the 0 ppm sample has a little bit higher value of UCS in comparison to samples containing sulphate. The higher value is from the precipitation of C-S-H with continuous hydration of cement with curing time. The reduced value of the 2500 ppm and 5000 ppm samples can be due to adsorption of sulphate by C-S-H gel resulting in the inferior quality of C-S-H. An additional mechanism, i.e. the

coarsening of the pore structure of the TS through the dissolution of ettringite at high temperatures can contribute to the reduction of strength.

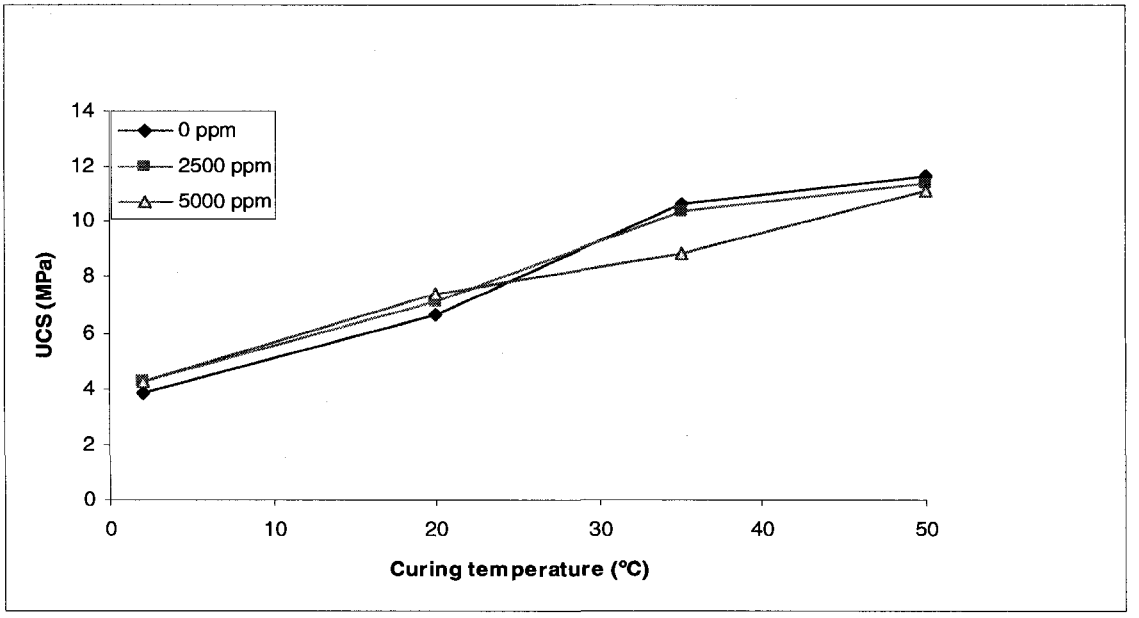

Figure 2-51 28 day UCS of PCI-slag tailings shotcrete with different sulphate concentration at different temperatures

2.3.6.2.2 Advanced ages

Figure 2.52 shows the 120 day UCS value of TS made from PCI-slag with 0 ppm, 2500 ppm and 5000 ppm of sulphate cured at 2°C, 20°C, 35°C and 50°C. The results show that the 120 day UCS value of TS increases with increase of curing temperature except at 50°C. At 2°C, almost all samples have the same strength. The 5000 ppm sample has the value of 11.7 MPa at 2°C. The gain in strength of TS samples containing 0 ppm, 2500 ppm and 5000 ppm sulphate is 190%, 155%, and 175 % from 28 days to 120 days at 2°C. The water content curve in Figure 2.53 also illustrates that the water consumption by the 2500 ppm and 5000 ppm samples at 2°C is almost the same whereas the 0 ppm sample consumes a little bit higher amount of water. At 2°C, the gain in strength of the 2500 ppm and 5000 ppm samples is partly due to the formation of secondary ettringite, gypsum and partly by the precipitation of hydration products, including secondary C-S-H. The precipitation of these minerals in the sulphate samples still plays a positive role in the strength development of TS at 2°C. The UCS values of all samples increases as temperature increases to 20°C. The 2500 ppm sample attains the highest value at 20°C followed by 0 ppm. The 5000 ppm sample exhibits lowest value of compressive strength. However the difference in the strength is very low. The 2500 ppm sample is 6% and 13% stronger than the 0 and 5000 ppm samples. This somewhat higher strength of the 2500 ppm

sample is mainly due to the precipitation of gypsum and ettringite which are still contributing to the strength (Fall and Benzaazoua, 2005).

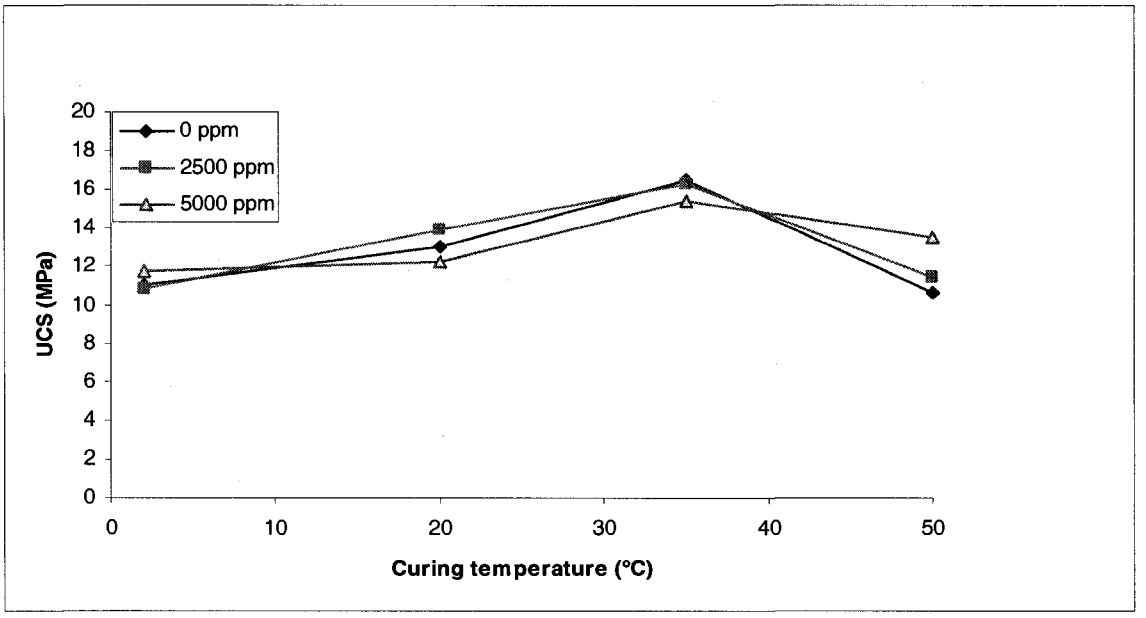

Figure 2-52 120 day UCS of tailings shotcrete PCI-slag with different sulphate concentration at different temperatures

The 0 ppm sample at 20°C has a lower 120 day UCS value than the 2500 ppm sample due to absence of gypsum and ettringite. The continuous hydration of unhydrated cement components (Hekal et al, 2002) of the 0 ppm sample with time and formation of secondary C-S-H from the pozzolanic reaction (Akoz et al, 1999) makes the 120 day 0 ppm TS sample stronger than 28 day 0 ppm sample. The XRD result in Figure 2.19 shows the presence of adequate CH.

The lower 120 day UCS value of the 5000 ppm sample at 20°C than the 0 and 2500 ppm samples may be either from conventional sulphate attack due to precipitation of excessive amount of gypsum and ettringite in the cement matrix contributing negatively to the strength. Another possible reason can be attributed to the slight inhibition of the binder hydration by the high concentration of sulphate (5000 ppm).

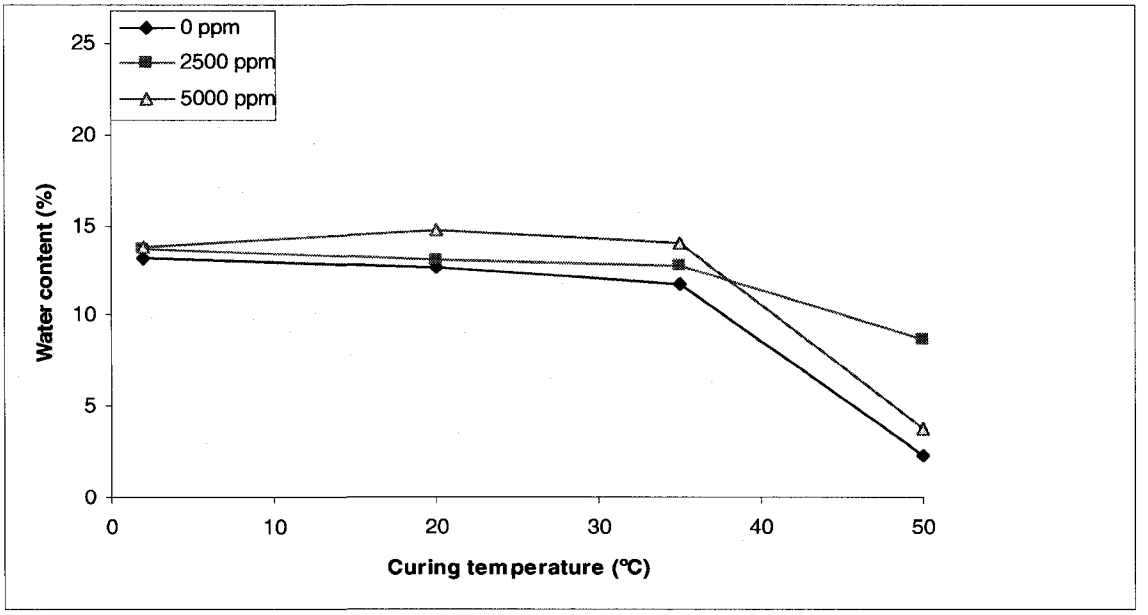

Figure 2-53 120 day water content of tailings shotcrete PCI-slag with different sulphate concentration at different temperatures

Figure 2.52 also shows that at 35°C, TS made from PCI-slag shows its highest 120 day UCS value. The maximum compressive strength achieved at this temperature is 16.5 MPa, 16.3 MPa and 15.4 MPa for 0 ppm, 2500 ppm, and 5000 ppm samples respectively. These high UCS values are due to the high

reactivity of slag. The high reactivity of slag is also observed by previous researchers (Barnett et al, 2006; Escalante and Sharp, 2001) who noticed the temperature dependence of the hydration of slag. Escalante and Sharp (2001) found the presence of many anhydrous or only slightly hydrated slag grains at 10°C whereas at 30 °C, some partially or fully hydrated slag grains are present in the cement paste when observed through BEI micrographs. The 120 day UCS value of the 0 ppm and 2500 ppm samples are almost the same at 35°C. The XRD result of the 0 ppm sample at 35°C made from PCI-slag in Figure 2.20 shows the formation of high quantities of CH more than the 0 ppm samples cured at 20°C and especially at 18 and 34 degrees 2-theta in Figure 2.19. This shows that the high UCS value of the 0 ppm sample is due to the continuous hydration of cement.

The 5000 ppm sample has a lower 120 day UCS value than the 0 ppm sample at 35°C, but higher than the 5000 ppm sample cured at 20°C. This may be due to the coupled effects of adsorption of sulphate at high temperatures and formation of expansive minerals in the cement matrix. Another possible reason of reduced strength can be the inhibition of binder hydration by the high quantity of sulphate. Adsorption of sulphate and inhibition of cement hydration tend to reduce the strength whereas expansive minerals in small quantities tend to increase the strength. Hence, it can be assumed that the results of this coupled effect render the 5000 ppm sample at 35°C to achieve a somewhat lower UCS value than the

0 ppm and 2500 ppm samples and higher UCS value than the 5000 ppm at 20°C.

Figure 2.52 also illustrates that at 50°C, the 120 day UCS of all TS made from PCI-slag shows a lower value than at 35°C. The 120 day UCS value of the 0 ppm and 2500 ppm samples at 50°C is lower than 20 °C. Such behavior of slag cement with inversion of compressive strength at high temperatures during longer periods of curing time was also observed by other researchers (Barnett et al, 2006; Escalante and Sharp, 2001). The 0 ppm sample shows a significant reduction in compressive strength when the curing temperature changed from 35°C to 50°C. This lower strength is due to the formation of hydration rims around the unhydrated slag grain (Barnett et al, 2006; Escalante and Sharp, 2001).

The unhydrated slag grains in slag cement are surrounded by the rims of hydration products at higher temperatures which prevent further hydration of slag grains. There will be smaller amounts of secondary C-S-H due to the low pozzolanic reaction which significantly lowers the UCS value of the 0 ppm TS at 50°C than 35°C. The 120 day water content curve in Figure 2.53 also illustrates that the 0 ppm sample at 50°C consumes more water than 35°C. In spite of this, huge water consumption at 50°C by the 0 ppm sample lowers the UCS value more than at 35°C. This can be explained by the fact that a large amount of water is used by the 0 ppm sample to hydrate its main component C_3S and C_2S which produces adequate amounts of C-S-H and CH .The problem is that they

can not use enough CH to produce secondary C-S-H from a pozzolanic reaction due to the limited availability of slag grains which is surrounded by rims of hydration products (Barnett et al, 2006). Thus, even the water content curve shows high consumption of water at 50°C by the 0 ppm sample with lower strength due to an inadequate pozzolanic reaction.

Like the 0 ppm sample, the 120 day UCS values of 2500 ppm and 5000 ppm samples at 50°C also show lower strength than 35°C. The water content curve of Figure 2.53 also indicates that these samples consume more water than they did at 35°C. The sample is using more water to hydrate its alite and belite component of cement and producing enough CH and C-S-H. The high temperature prevents the further hydration of slag grain since it is surrounded by rims of hydration products (Lothenbach et al, 2007). Thus, there is no or low pozzolanic reaction. Most of the sulphate present at this high temperature can be considered adsorbed by C-S-H (Fu et al, 1994) and there is either no or very low amounts of sulphate available to react with CH. Hence, the 2500 and 5000 ppm samples are unable to produce adequate amounts of gypsum and ettringite at 50°C. The 120 day UCS value of 2500 ppm and 5000 ppm samples at 50°C are significantly lower than 35°C due to the dual effect of adsorption of sulphate and formation of rims of hydration at high temperatures.

2.3.6.3 Coupled effects of sulphate and temperature on strength of PCI shotcrete with fibre

2.3.6.3.1 Early ages

Figure 2.54 shows the 1 day UCS value of TS made from PCI with fibre cured at 2°C, 20°C, 35°C and 50°C with 0 ppm, 2500 ppm and 5000 ppm of sulphate. The 1 day UCS value of all samples increases with increase of curing temperature. At 2°C, almost all of the samples show very low strength in comparison to the ones at high curing temperatures. This is entirely due to the slow hydration reaction of cement at low temperatures. Thus, hydration products will take time to precipitate in the cement matrix, resulting in less dense C-S-H (Lothenbach et al, 2007).

Figure 2.54 also illustrates that the 0 ppm and 2500 ppm samples have almost the same UCS value at 2 °C whereas the 5000 ppm sample has the lowest value. The 1 day water content curve (Figure 2.55) also shows that the 5000 ppm sample cured at 2°C has consumed lower amounts of water in comparison to the 0 ppm and 2500 ppm samples at the same temperature.

The low consumption of water by the 5000 ppm sample indicates lower hydration degree of cement, thus producing less C-S-H. The lower 1 day UCS value may be due to the presence of high amounts of sulphate in comparison to that of the 0

ppm and 2500 ppm samples which strongly inhibit the early hydration of C_3A (Benzaazoua et al , 2004; Fall and Benzaazoua , 2005).

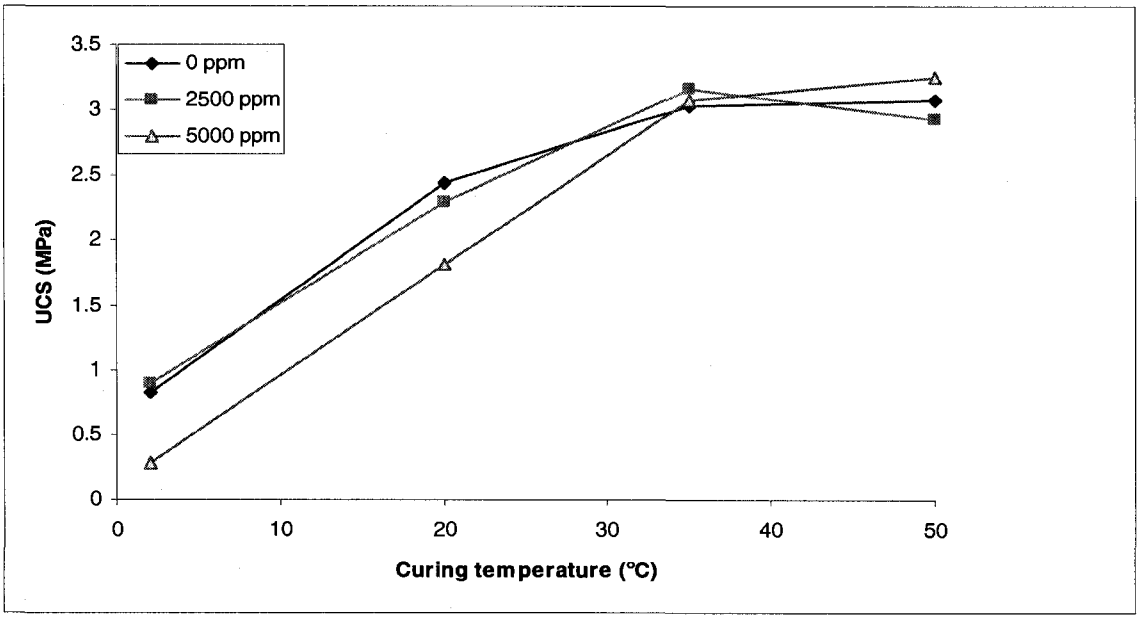

Figure 2-54 1 day UCS of TSPCI-fibre with different sulphate concentration at different temperatures

As the temperature increases to 20°C, all samples show a very sharp gain of strength. The strength gain of 0 ppm, 2500 ppm and 5000 ppm samples is respectively 200%, 160% and 500% when curing temperatures increase from 2°C to 20°C. The 1 day water content curve in Figure 2.55 also illustrate that the 5000 ppm sample consumes more water at 20°C than 2 °C. This sharp rate in gain of strength is caused by the precipitation of hydration products in cement matrix from the fast hydration reaction of cement due to high temperatures (Lothenbach et al, 2007).

At 20°C, the 5000 ppm sample is still showing a low value of UCS in comparison to the 0 ppm and 2500 ppm samples due to the presence of high sulphate whereas the 0 ppm sample without sulphate shows a little bit higher 1 day UCS value than the 2500 ppm.

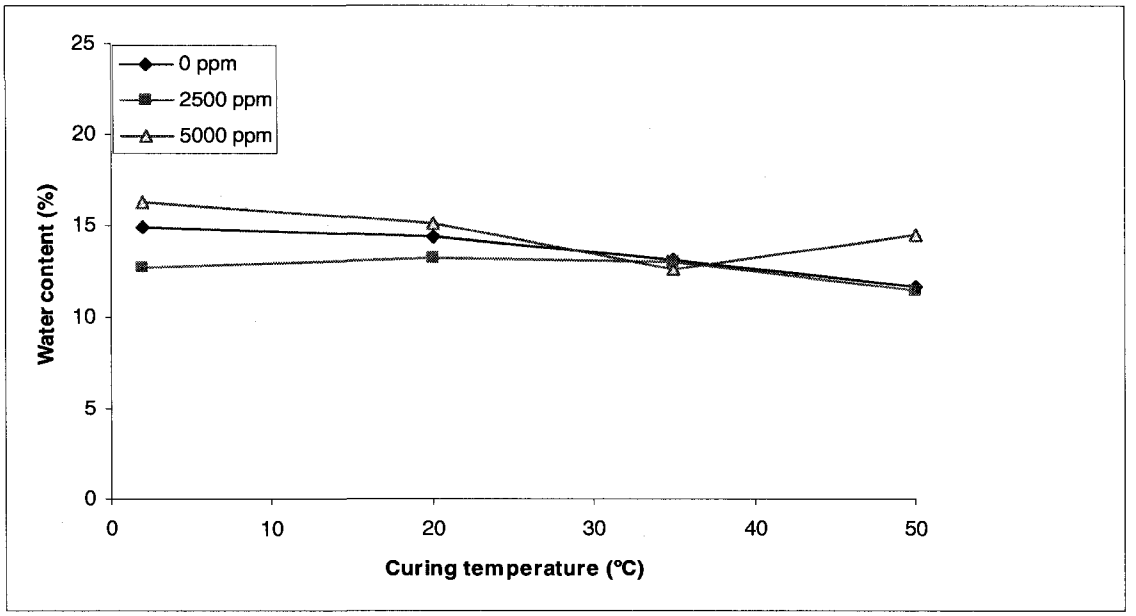

Figure 2-55 1 day water content of TSPCI-fibre with different sulphate concentration at different temperatures

At 35°C, all samples show almost the same 1 day UCS value in spite of sulphate content. The rate of gain in strength and water consumption patterns of the 5000 ppm sample shows the dependency of cement hydration of high sulphate bearing samples with temperature. The 1 day water content curve at 35°C in figure 2.55 shows that all samples use the same amount of water and have almost the same strength.

The 1 day UCS value of the 5000 ppm sample at 50°C is found to be higher than the 0 ppm and 2500 ppm samples which may be due to the precipitation of gypsum and ettringite. In this case, higher temperature increases the hydration reaction and produces adequate amount of CH in the cement matrix. The CH will react with sulphate and produces gypsum and ettringite which contribute to the strength (Fall and Benzaazoua, 2005).

Figure 2.56 illustrates the 7 day UCS value of shotcrete made from PCI with fibre at 2°C, 20°C, 35°C and 50°C with 0 ppm, 2500 ppm and 5000 ppm of sulphate. The 7 day UCS value of the shotcrete also increases with increase of curing temperature because of the fast hydration of cement matrix (Fall and Samb, 2006; Lothenbach et al, 2007). The 2500 ppm and 5000 ppm samples at 2°C show the same values of UCS at 7 days where as the 0 ppm sample has the lowest value at 2°C. The higher value of UCS at 7 days of shotcrete samples containing sulphate can be explained by the precipitation of ettringite and gypsum which contribute positively to the compressive strength. The strength development of shotcrete samples at 2°C from 1 day to 7 day is the maximum for 5000 ppm. The 7 day 5000 ppm sample is 500% stronger than the 1 day sample at 2°C, whereas this value is almost 200% for the 0 ppm samples.

Figure 2.56 also illustrates that at 20°C, the 5000 ppm sample shows a higher 7 day UCS value than the rest of the samples at the same temperature. The 7 day

UCS value of the 2500 ppm sample at 20°C is also a little bit higher than that of 0 ppm samples.

The higher UCS value of samples containing sulphate as described earlier is also due to the formation of expansive minerals as well as precipitation of hydration products in the cement matrix which reduce the porosity of the tailings shotcrete. This results in higher UCS value of the 2500 ppm and 5000 ppm samples than 0 ppm samples at 20°C. The continuous hydration of cement with raised temperature is responsible for the increase of UCS for the 0 ppm samples.

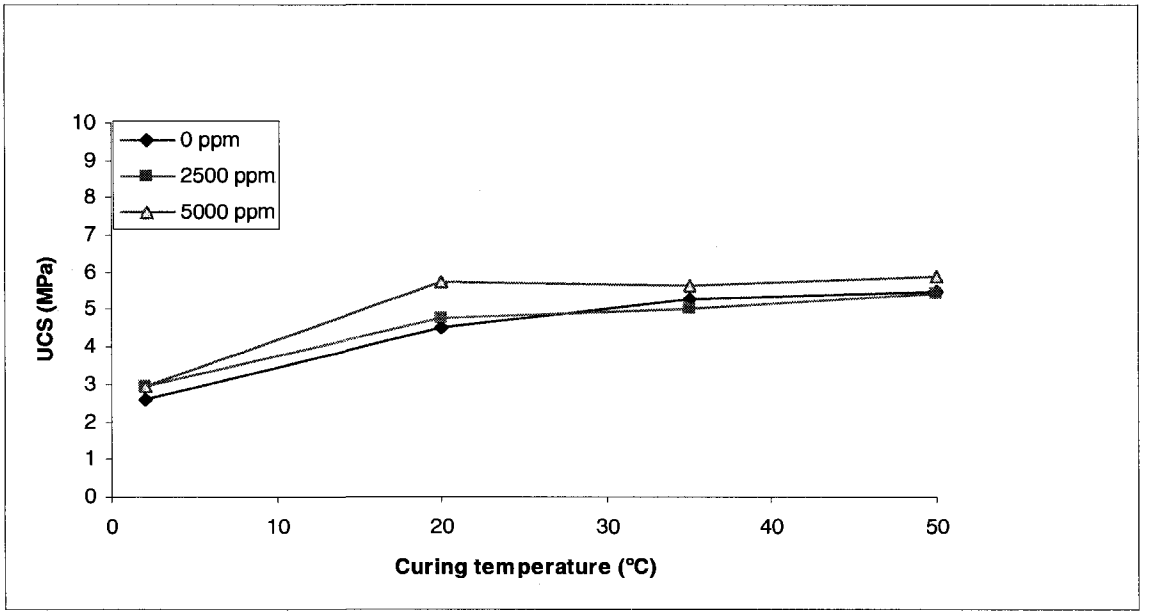

Figure 2-56 7 day UCS of TS PCI-fibre with different sulphate concentration at different temperatures

The 5000 ppm sample exhibits somewhat lower strength at 35°C and 50°C in comparison to 20°C. This sample uses more and more water (Figure 2.57) as the temperature increases from 20°C to 50°C. However, Figure 2.56 shows that the 5000 ppm sample is not showing any increment in its 7 day UCS value with increase of temperature. This may be due to the combined phenomenon of precipitation of CH gel on fibre (Hamou et al, 2005) and adsorptions of sulphate by C-S-H gel at higher temperatures (Fu et al, 1994) which prevents the formation of gypsum and ettringite. This leads to a lower value of 7 day UCS at 35°C and 50°C for samples with sulphate. However, the 5000 ppm sample is still stronger than the 0 ppm and 2500 ppm samples at 35°C and 50°C.

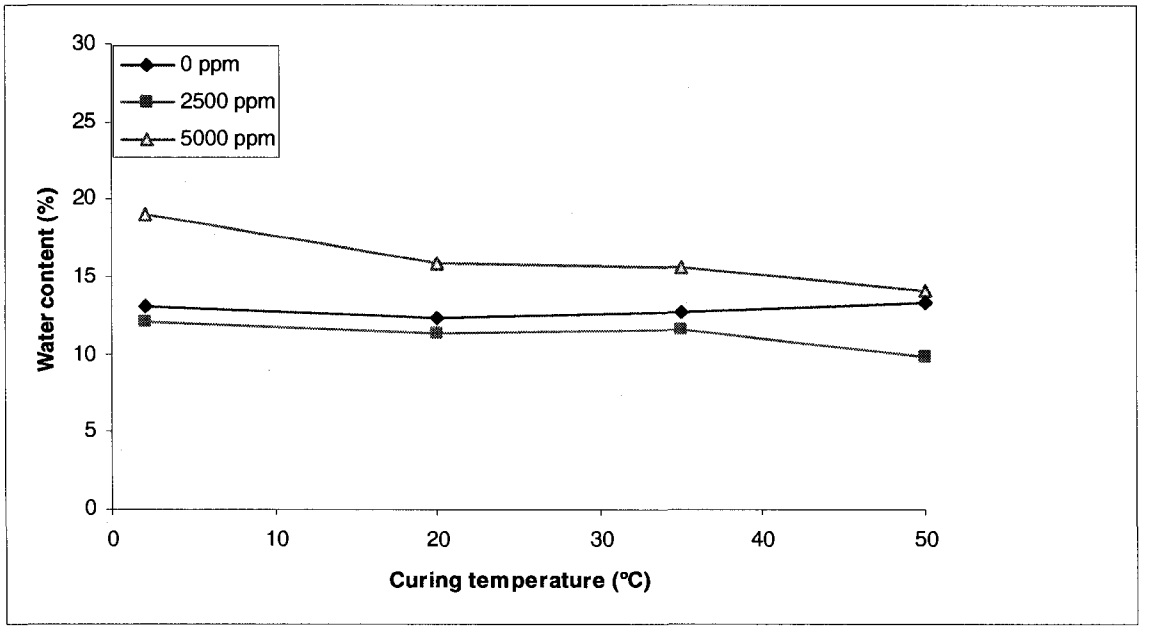

Figure 2-57 7 day water content of TS PCI-fibre with different sulphate concentration at different temperatures

Figure 2.58 illustrates the 28 day UCS value of shotcrete sample made from PCI with fibre at 2°C, 20°C, 35°C and 50°C with 0 ppm, 2500 ppm and 5000 ppm of sulphate concentrations. The 28 day compressive strength of the sample also increases with increase of curing temperature. At 2°C and 20°C, 28 days UCS value of all TS is almost the same. The 28 day result shows that there is not that much variation in the UCS of TS at 2°C, 20°C and 35°C. At 35°C, the 5000 ppm sample has the lowest UCS value whereas the 2500 ppm sample shows a little bit of a higher value than the rest. The higher UCS value of the 2500 ppm at 35°C is due to the formation of expansive minerals playing a positive role to the strength as explained earlier. The reduced strength of the 5000 ppm sample at 35°C can be due to phenomenon of conventional sulphate attack and/or adsorption of sulphate by C-S-H gel. Another possible reason of reduced strength is the inhibition of the cement hydration by high sulphate content.

Figure 2.58 also illustrates that the 28 day UCS of 0 ppm TS cured at 50°C has a higher value than the 2500 ppm and 5000 ppm sample. The gain in strength of the 0 ppm sample from 35°C to 50°C is very sharp and the higher strength of the 0 ppm sample in this case is due to the formation of hydration products from continuous hydration of unhydrated clinkers particles which fill the pores of the samples. The 2500 ppm and 5000 ppm samples at 50°C have almost the same 28 day UCS values, but lower than the 0 ppm sample. The adsorption of sulphate with C-S-H gel at 50°C can form an inferior quality of C-S-H in the case

of the 2500 and 5000 ppm samples, resulting in lower UCS value. The destabilization of the ettringite that fill some voids of the tailings shotcrete at high temperatures can be also considered as an additional cause of this lower strength. Indeed, the high temperature can have led to more voids in the cement matrix of TS because of the dissolution of ettringite, thereby reducing the strength.

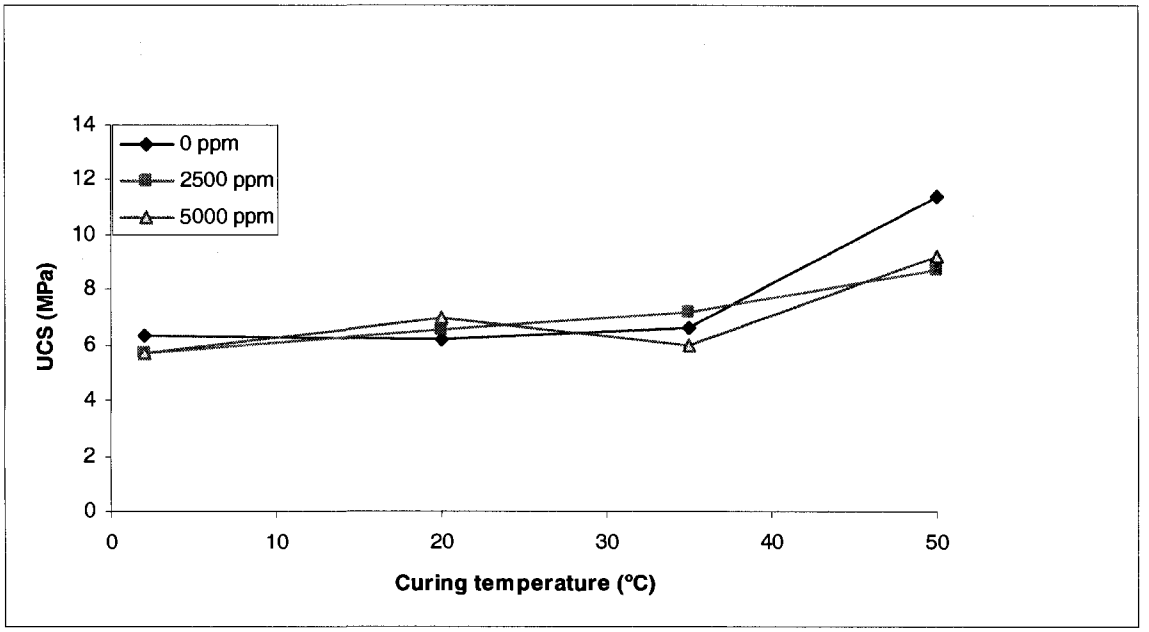

Figure 2-58 28 day UCS of PCI-fibre TS with different sulphate concentrations at different temperatures

2.3.6.3.2 Advanced ages

Figure 2.59 represents the 120 day UCS value of TS made from PCI-fibre cured at 2°C, 20°C, 35°C and 50°C containing 0 ppm, 2500 ppm and 5000 ppm of sulphate. The 120 day UCS value of the TS also increases with increase of curing temperature. Figure 2.59 also shows that the 120 day UCS value of the 0 ppm, 2500 ppm, and 5000 ppm samples of shotcrete containing fibre is almost the same at 2°C.There is not that much variation in the value of UCS of TS samples at 20 °C. The gain in strength of these TS with increases of temperature up to 35°C is very low.

The XRD result of the 5000 ppm sample with PCI at 20°C without fibre in Figure 2.7 shows precipitation of adequate expansive minerals, but the 2500 ppm and 5000 ppm samples do not show any contribution of strength from expansive minerals at 20°C and 35°C. One of the reason can be the precipitation of CH in fibre (Hamou et al, 2005), preventing the formation of such expansive minerals. The 120 day water content curve in Figure 2.60 at 20 °C shows that the 2500 ppm and 5000 ppm samples have consumed more water than 0 ppm samples, even though the strength of 2500 ppm and 5000 ppm samples is the same as that of the 0 ppm sample. With consumption of adequate water, the 2500 ppm and 5000 ppm samples are supposed to be producing enough CH. The CH thus produced should be expected to react with sulphate ion to produce gypsum and

ettringite. Depending upon the quantity of these minerals formed within the 2500 ppm and 5000 ppm samples, it should have either higher or lower strength than the 0 ppm sample. In contrary to this, the 2500 ppm and 5000 ppm samples show the same strength as that of the 0 ppm sample. Hence, fibre can play a role in preventing the formation of these expansive minerals. Further studies will be necessary to elucidate the interaction between fibre, sulphate and CH, and their effect of the resistance of shotcrete to sulphate attack.

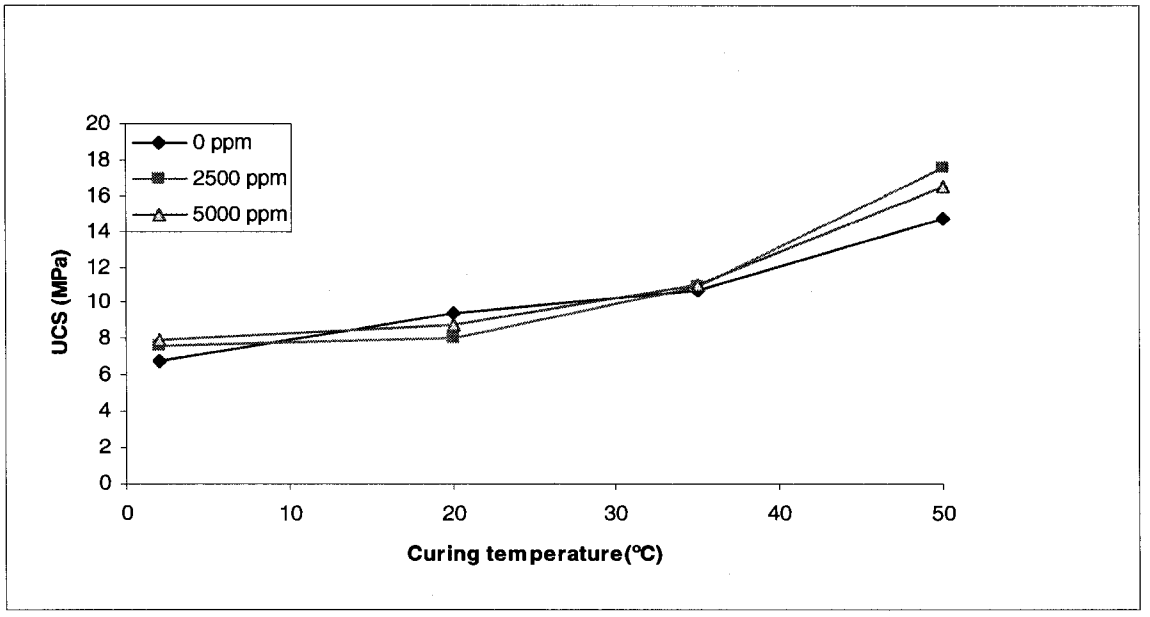

Figure 2-59 120 day UCS of TSPCI-fibre with different sulphate concentrations at different temperatures.

Figure 2.59 also shows that at 50°C, the 2500 ppm sample has a higher 120 day UCS value followed by the 5000 ppm sample. The 0 ppm sample has the lowest 120 day UCS value at 50°C. The strength development of the 0 ppm sample is entirely due to the hydration of cement products. The additional strength of TS

with sulphate samples can be the contribution of expansive minerals. This is in accordance with the results of the water content at 120 days. The 120 day water content curve in Figure 2.60 shows that at 50°C, the 2500 ppm and 5000 ppm samples consume high amounts of water. High consumption of water by the expansive minerals may be the cause of this lower water content. The 5000 ppm sample has a lower UCS value than the 2500 ppm sample. This may be due to the adsorption of sulphate by C-S-H gel at higher temperatures and at high sulphate content so that only part of the sulphate reacts with CH to form limited amounts of expansive minerals. The sulphate adsorption also depends upon the percentage of sulphate (Ramlochan et al, 2004). Thus, a higher percentage of sulphate in the cement means a higher amount of sulphate adsorbed in the cement matrix. Hence, a lower amount of sulphate can be adsorbed in C-S-H gel in the 2500 ppm sample. There will be the possibility of the formation of higher amounts of these expansive minerals in the 2500 ppm than 5000 ppm of samples. This may explain why the 2500 ppm sample has a higher UCS value. The XRD result of the 5000 ppm samples at 50°C in Figure 2.13 also shows the formation of expansive minerals. This also supports that the 120 day UCS value of 5000 ppm is higher than the 0 ppm sample due to the positive contribution of these expansive minerals. The strength development for the 0 ppm sample is due to the continuous hydration of cement.

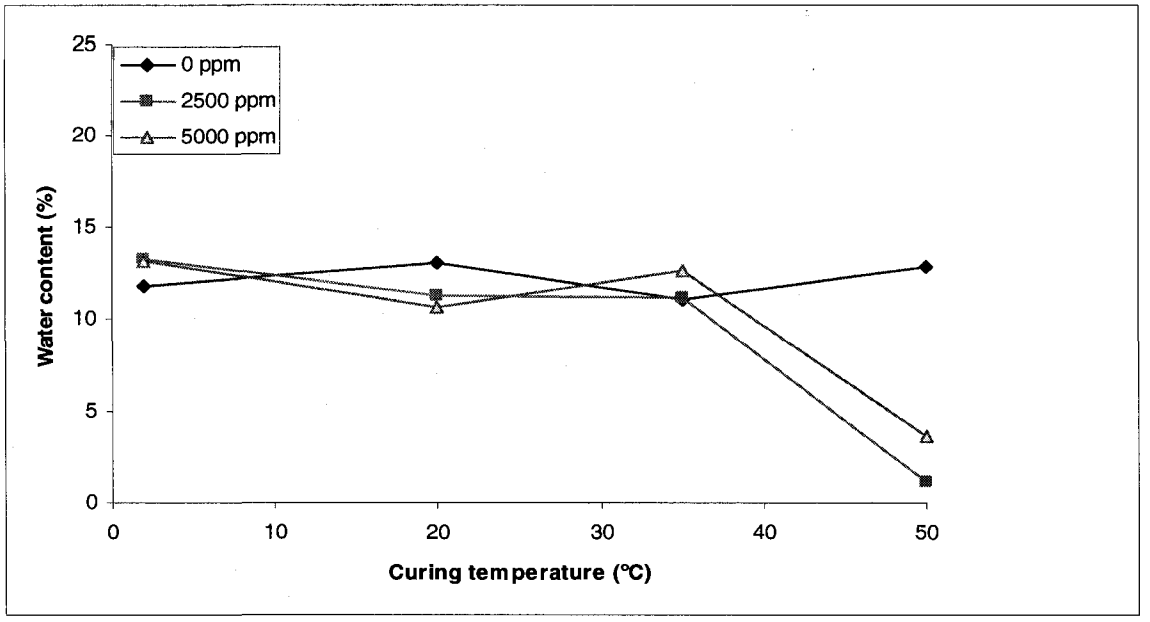

Figure 2-60 120 day water content of TSPCI-fibre with different sulphate concentration at different temperatures

2.3.6.4 Comparison between PCI, PCI-slag, PCI-fibre tailing shotcrete.

2.3.6.4.1 Early ages

Figures 2.61, 2.62 and 2.63 represent the 1 day UCS value of TS made from PCI, PCI-slag and PCI with fibre at 2°C, 20°C, 35°C and 50°C containing 0 ppm, 2500 ppm and 5000 ppm of sulphate. The 1 day UCS value of all TS made from the above binder increases with increase of curing temperature. This is due to the faster cement hydration reaction when the curing temperature increases.

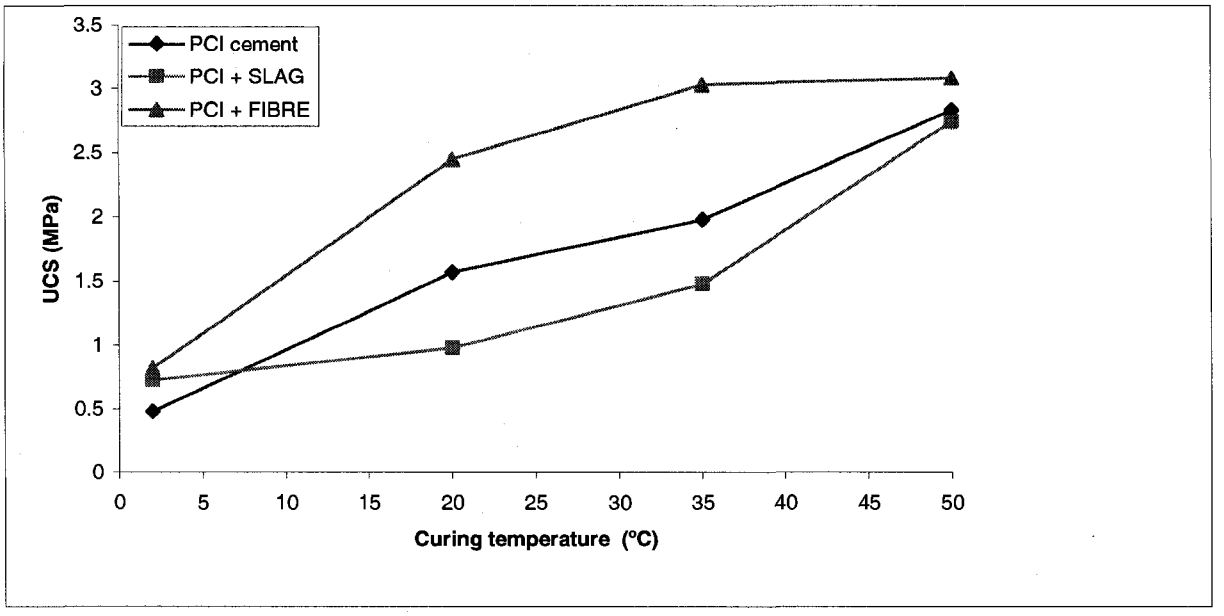

Figure 2-61 1 day UCS of TS made from PCI, PCI-slag and PCI-fibre with 0 ppm of sulphate at different temperatures

The TS made from PCI with fibre containing 0 ppm, 2500 ppm and 5000 ppm of sulphate has a higher 1 day UCS value than rest of the shotcrete samples at all curing temperature with some exception at 2°C. In fresh cementitious materials, the uniform distribution of fibres reinforced against the formation of plastic shrinkage crack and increases the compressive strength of the cementitious materials (Puertas et al, 2003). The TS made from PCI with 0 ppm, 2500 ppm and 5000 ppm of sulphate shows that the 1 day UCS value is in between TS with slag and TS made from fibre at almost all curing temperatures.

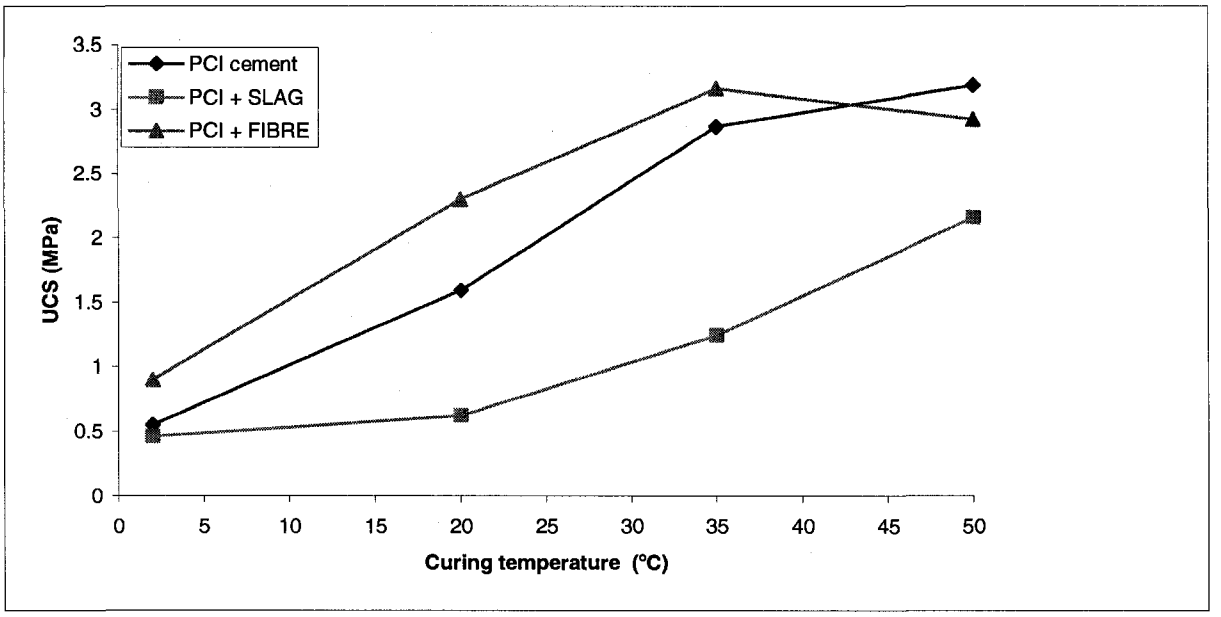

Figure 2-62 1 day UCS of TS made from PCI, PCI-slag and PCI-fibre with 2500 ppm of sulphate at different temperatures

Figures 2.61, 2.62 and 2.63 also show that the TS made from PCI-slag has the lowest 1 day UCS value at all curing temperatures with different sulphate contents. The lower 1 day UCS value is due to the presence of slag which is very unreactive at early ages (Escalante and Sharpe, 2001). In addition to this, the presence of slag in the cement matrix already replaces 50% of C_3A, C_3S, and C_2S from the TS, hence smaller amounts of hydration product will be expected. Fall and Samb (2006) also observed similar results.

Figures 2.62 and 2.63 also illustrate that the TS made from PCI and PCI with fibre for 2500 ppm and 5000 ppm of sulphate has high rates of gain of strength in comparison to the TS made from PCI-slag. This is also due to the presence of

high percentage of clinker in PCI which is responsible for the strength development of cementitious materials. In addition to this, slag has very low reactivity at an early age. Another possible reason of high strength gain by PCI and PCI with fibre in comparison to PCI-slag can be the precipitation of more gypsum and ettringite in the pores of cementitious materials produced from the reaction between CH, C_3A and sulphate ions. The precipitation of such minerals in the pores of the TS significantly reduces the internal porosity and increases the strength (Fall and Benzaazoua, 2005).

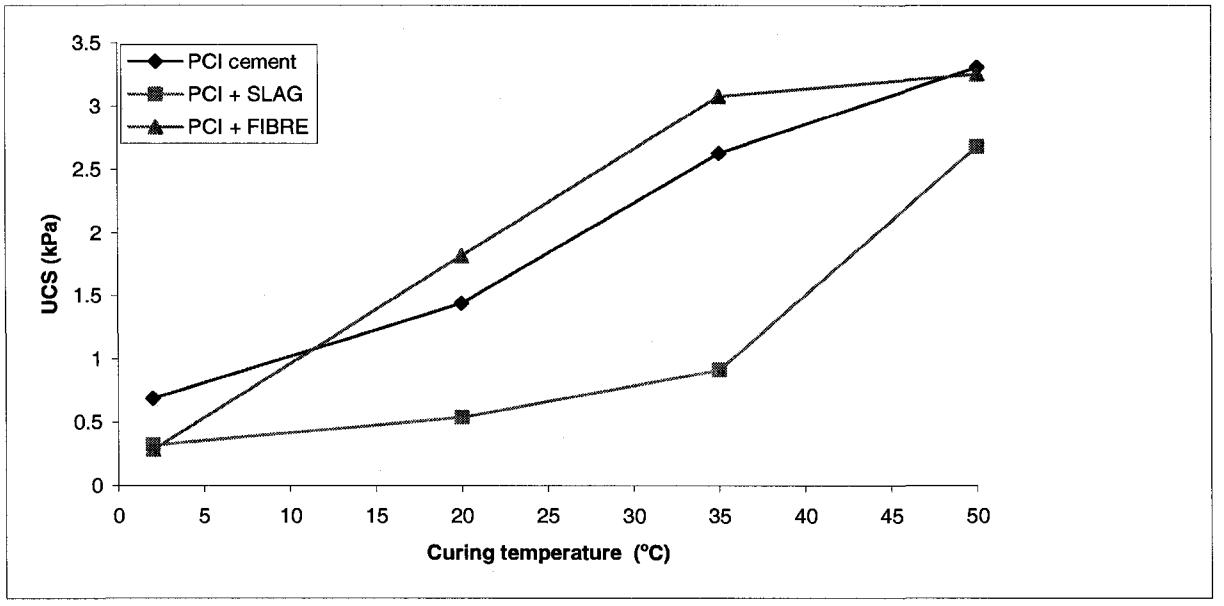

Figure 2-63 1 day UCS of TS made from PCI, PCI-slag and PCI-fibre with 5000 ppm of sulphate at different temperatures

Figure 2.64 illustrates the 7 day UCS value of TS cured at 2°C, 20°C, 35°C and 50°C containing 0 ppm of sulphate. The 7 day UCS value of all TS increases with increase of curing temperature except TS made from PCI at 50°C.The 7 day

UCS value of TS made from PCI and PCI with fibre at 2°C has the same strength as that of 0 ppm sulphate and higher than TS made from PCI-slag. The higher strength of TS made from PCI and PCI with fibre is due to the ability of this mix to produce more hydration products from higher clinker portion. This is because low temperatures are not favorable for slag cement hydration (Barnett et al, 2006). At 20°C , 35 °C and 50°C the TS made from PCI-slag shows 7 day UCS value higher than TS made from PCI and PCI-fibre containing 0 ppm of sulphate. The higher strength of shotcrete sample made from PCI-slag cement is due to the formation of additional secondary C-S-H from the pozzolanic reaction between CH and slag (Escalante and Sharp, 2001). The TS made from PCI-slag shows almost the same UCS value at 35°C and 50°C. This may be due to the formation of hydration rims because of higher curing temperature in the PCI-slag TS sample which prevents the further hydration of slag grains.

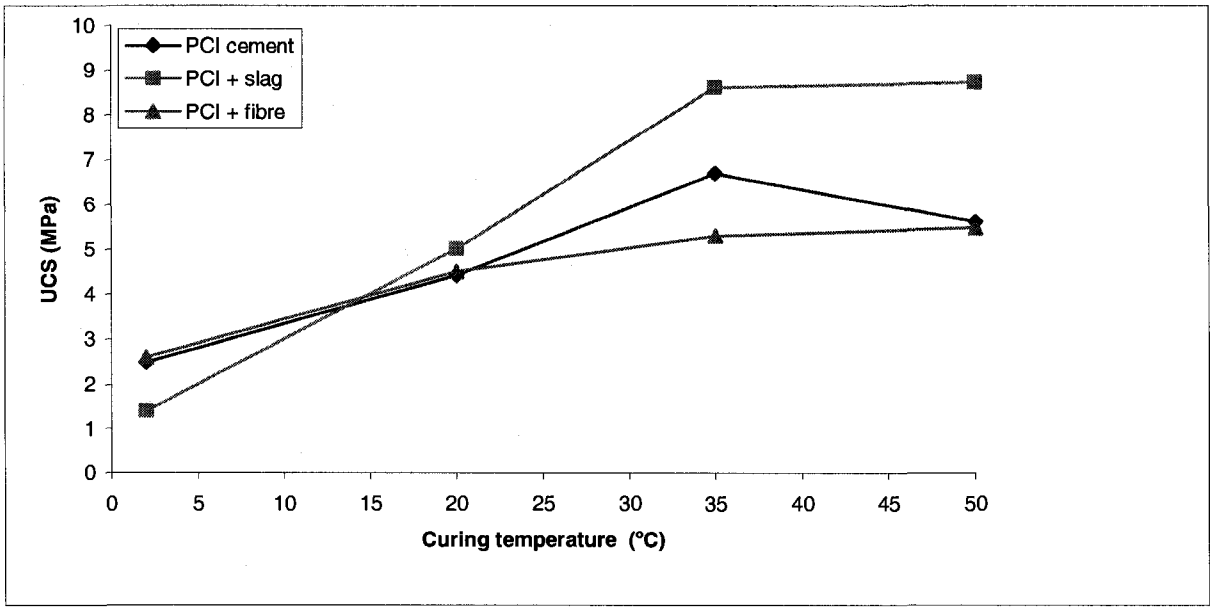

Figure 2-64 7 day UCS of TS made from PCI, PCI-slag and PCI-fibre with 0 ppm of sulphate at different temperatures

The TS containing fibre has the lowest strength at 35°C and attain the same strength as that of TS made from PCI at 50°C with 0 ppm of sulphate. The lower UCS value may be due to the presence of fibre. Aulia (2002) mentioned that "the fibres function as the initiator of the micro cracking because of their low modulus of elasticity compared to the cement matrix. The formed mechanical bond with the cement matrix is thus low" (Aulia, 2002). The same type of behavior of lower compressive strength of concrete mortar with the use of fibre was also reported by a previous researcher (Soroushian et al, 1993).

At 50°C, all samples show different types of behavior. There are no increases in the UCS value for PCI-slag and PCI-fibre, whereas PCI shows a decline. This lower strength of the TS at higher curing temperatures may be due to the

formation of hydration rims. Lothenbach et al. (2007) also observed such a type of reduced strength of Portland limestone cement at 50°C and explained this phenomenon as due to the slowdown of hydration because of the formation of hydration rims which surrounds the unhydrated grains at higher curing temperatures. This results in heterogeneous distribution of the hydration products, providing a coarser porosity.

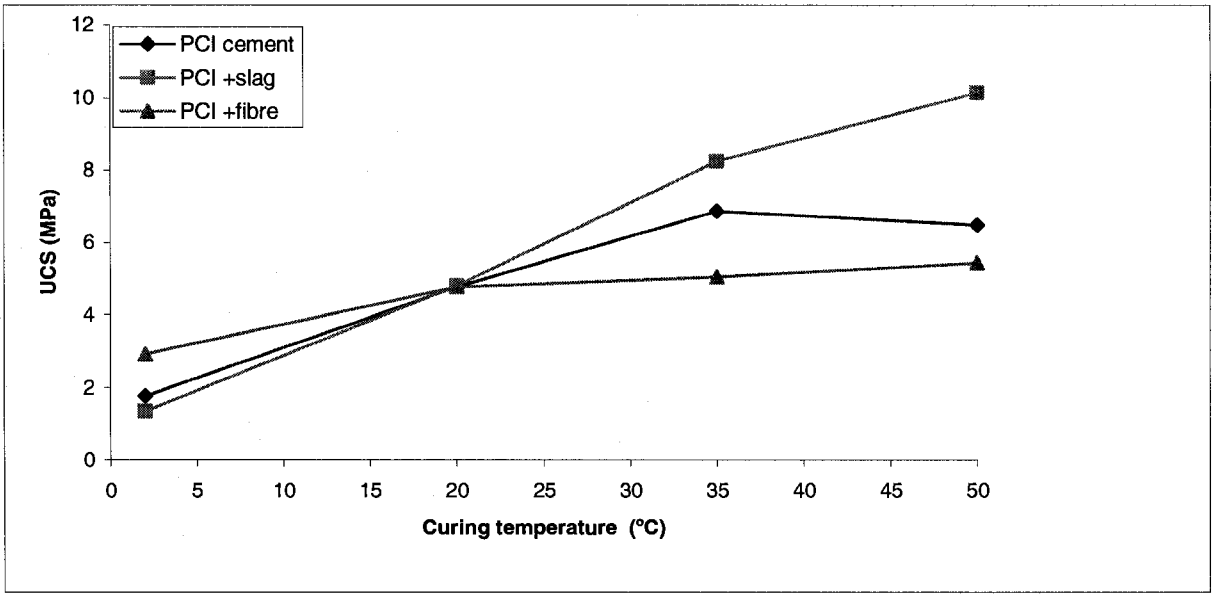

Figure 2-65 7 day UCS of TS made from PCI, PCI-slag and PCI-fibre with 2500 ppm of sulphate at different temperatures

Figures 2.65 and 2.66 illustrate the 7 day UCS value of TS made from different types of binder with 2500 ppm and 5000 ppm of sulphate at different curing temperatures. These results also show that the 7 day UCS value of TS containing slag at 2°C has a lower strength than the rest of the samples at the

same temperature and the UCS value increases with increase of curing temperature. Figure 2.65 also illustrates that at 20°C, all TS samples with 2500 ppm of sulphate show the same 7 day UCS value. However, beyond 20°C, TS made from PCI-slag shows higher strength than the rest of the samples. At 35°C and 50°C, the higher UCS value of the PCI-slag is due to the positive contribution of secondary ettringite and gypsum as well as additional secondary C-S-H formed in the cement matrix from pozzolanic reaction of the slag.

The TS made from PCI-slag containing 5000 ppm of sulphate at 50°C shows higher strength than the 2500 ppm sample at the same temperature. The 7 day UCS value of TS made from PCI-slag at 50°C with 5000 ppm of sulphate is almost 10% stronger than the 2500 ppm sample at the same curing temperature. This higher value may be due to the precipitation of additional amounts of gypsum and ettringite in the 5000 ppm samples. The precipitation of additional minerals in the cement matrix fills additional pores and voids which reduce the internal porosity of the sample resulting in the formation of a compact and dense structure contributing positively to the strength (Fall and Benzaazoua, 2005). It is also observed from Figure 2.66 that the 7 day UCS value of TS with PCI and PCI with fibre has approximately the same UCS at all curing temperatures. The strength development of these samples is mainly due to the formation of additional hydration products and with the precipitation of expansive minerals.

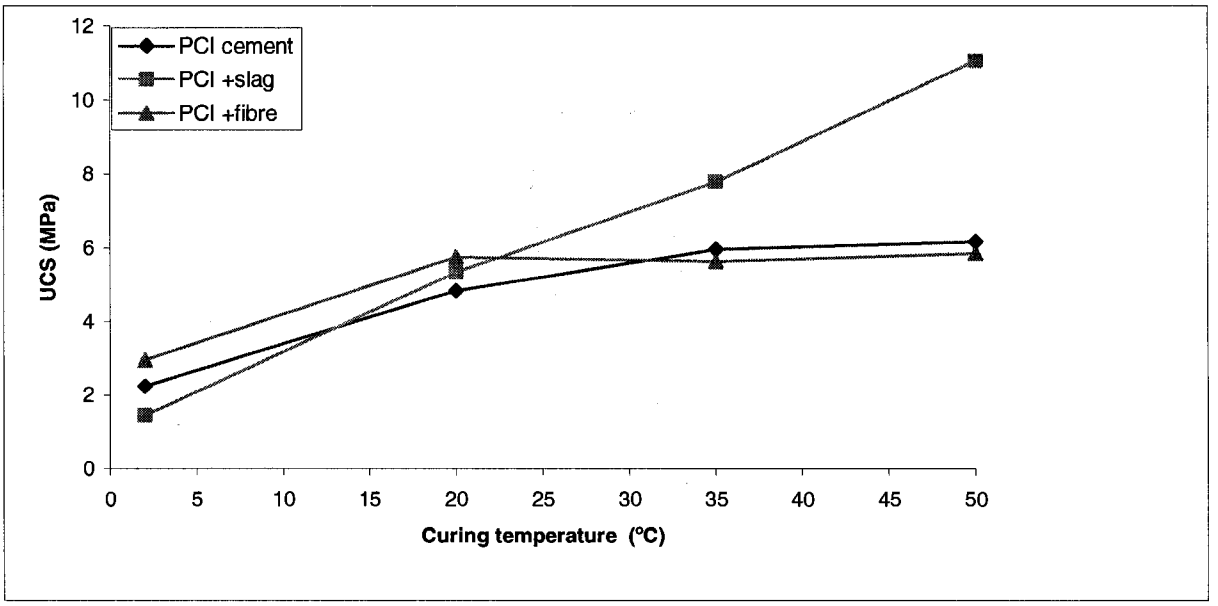

Figure 2-66 7 day UCS of TS made from PCI, PCI-slag and PCI-fibre with 5000 ppm of sulphate at different temperatures

Figures 2.67, 2.68 and 2.69 present the 28 day UCS value of TS with different binders at different curing temperatures with various sulphate concentrations. In general, the 28 day UCS value of all TS samples increases with increase of curing temperature with some exception at 35°C for 5000 ppm of sulphate.

Figure 2.67 illustrates the 28 day UCS value of shotcrete made from PCI, PCI-slag and PCI-fibre with 0 ppm of sulphate at different curing temperatures. It also illustrates that at 2°C, the TS containing fibre has the highest 28 day UCS. The PCI-slag sample with 0 ppm of sulphate has the lowest value. At 20°C, most of the samples show approximately the same strength. Due to high reactivity of slag, as explained earlier, TS with PCI-slag shows higher 28 day UCS value at 35°C.The TS made from PCI have UCS value less than PCI-slag at 35°C. At

50°C, TS made from PCI-slag has a lower 28 day UCS value than TS made from PCI. The rate of gain in strength of PCI-slag from 35°C to 50°C is slower in comparison to PCI with 0 ppm sulphate concentration. This is due to the formation of hydration rims in which the unhydrated slag grains are prevented from further hydration (Barnett et al, 2006; Escalante and Sharpe, 2001).The TS made from PCI with 0 ppm of sulphate has a higher 28 day UCS value at 50 °C that is due to the formation of additional hydration products which fill the pores of the cement matrix resulting in the reduction of internal porosity, thus contributing to the UCS value.

The figure 2.68 represents the 28 day UCS of TS with different binders at different temperatures containing 2500 ppm of sulphate. This figure shows that the TS made from PCI and PCI-fibre at 2°C has same 28 day UCS value and this value is higher than 28 day UCS value of PCI-slag. The high 28 day UCS value of PCI in comparison to PCI-slag at 2°C is due to the presence of high quantity of clinker particles which are responsible for the gain of strength of the cementitious materials .The continuous hydration of this clinker made the PCI TS to exhibit higher strength than PCI-slag at 2°C.

At 20°C, the presence of adequate amount of clinker particles contributes higher strength to PCI TS in comparison to the PCI-slag tailings shotcrete. In spite of the low amount of clinker in the PCI-slag sample, it shows the same value of UCS as that of PCI at 35°C and 50°C. The significant increase of strength of

PCI-slag after 20°C is due to the high reactivity of slag, which consumes CH produced from the hydration reaction. This results in the formation of secondary C-S-H which contributes positively to the strength of the TS (Sahmaran et al, 2007).

The TS made from PCI-fibre shows the lowest 28 day UCS values at 20°C, 35°C, and 50°C. In this case, fibre does not contribute positively in the compressive strength. This lower value can be due to the formation of a lower mechanical bond between the cement matrix and fibre as explained above. In addition to this, increase of porosity as a result of inadequate compaction due to presence of fibre may be another reason for the lower compressive strength (Leung et al, 2005)

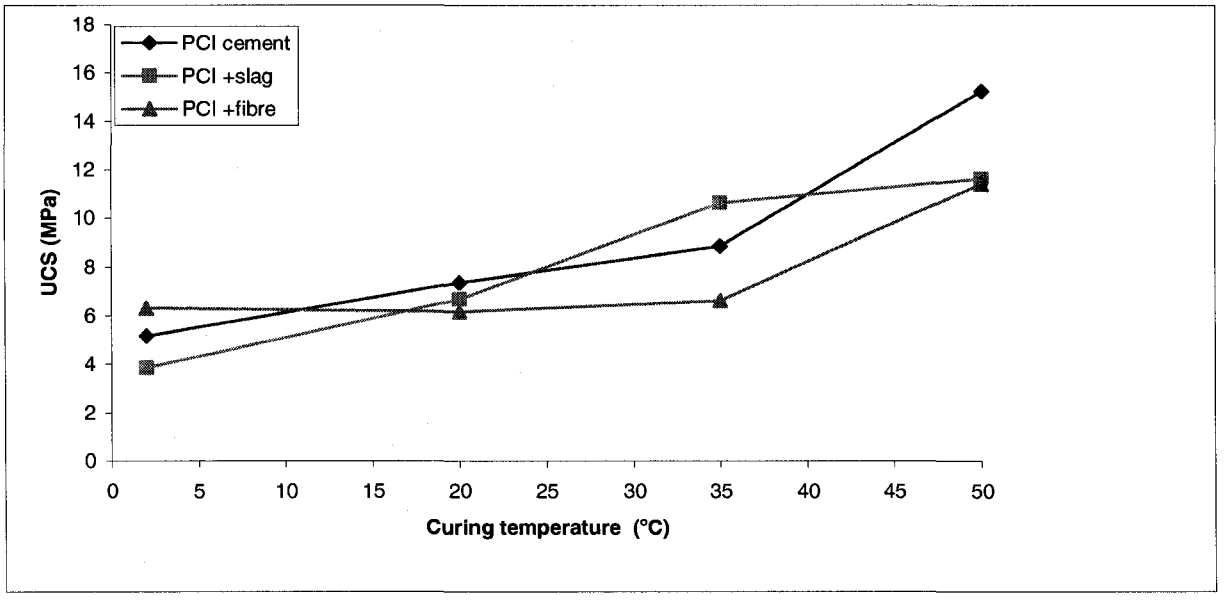

Figure 2-67 28 day UCS of TS made from PCI, PCI-slag and PCI-fibre with 0 ppm of sulphate at different temperatures

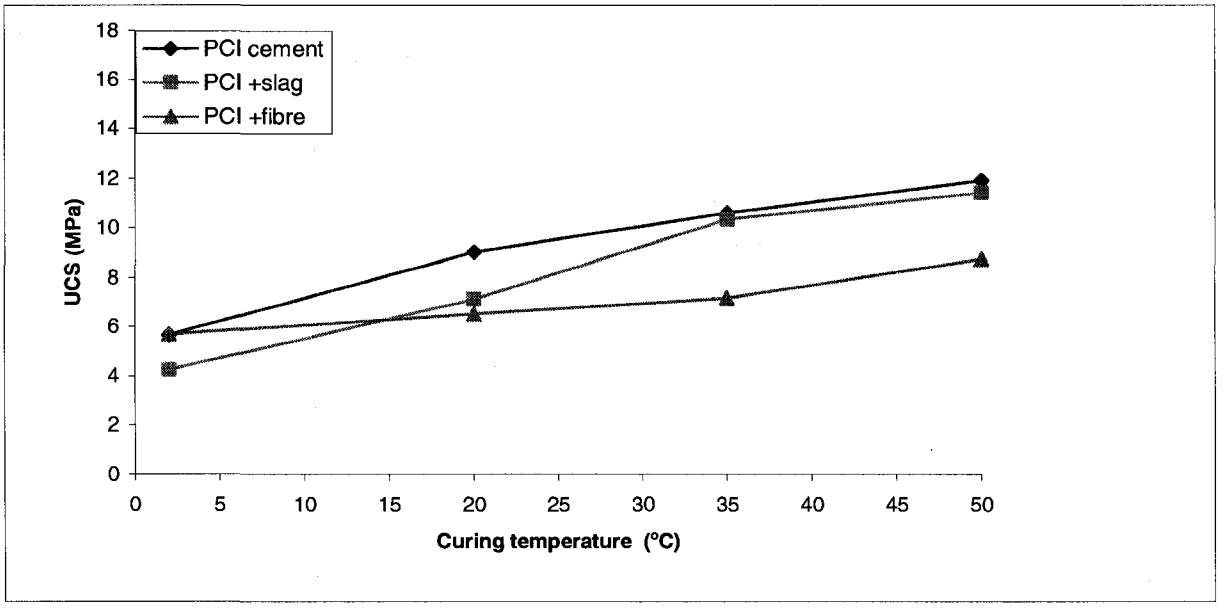

Figure 2-68 28 day UCS of TS made from PCI, PCI-slag and PCI-fibre with 2500 ppm of sulphate at different temperatures

Figure 2.69 represents the 28 day UCS value of the TS made from PCI, PCI-slag and PCI-fibre at different curing temperatures with 5000 ppm of sulphate. At 2°C, it shows a higher strength than the rest of the samples. The 28 day UCS value of TS made from PCI-slag at 2°C with 5000 ppm sample shows strength value between that of the TS made from PCI and that of PCI-fibre. The higher 28 day UCS value of TS with PCI-slag in comparison to TS made from PCI at 2°C is due to the contribution of secondary C-S-H in the cement matrix.

The 28 day UCS value of TS made from PCI-slag with 5000 ppm of sulphate increases with increase of curing temperature and exhibits higher value at 20°C, and 35°C. This is the result of the precipitation of additional secondary C-S-H

along with hydration products in the pores of TS in comparison to TS made from PCI and PCI-fibre whereas the gradual increase of UCS of TS made from PCI is due to continuous hydration of cement and formation of expansive minerals.

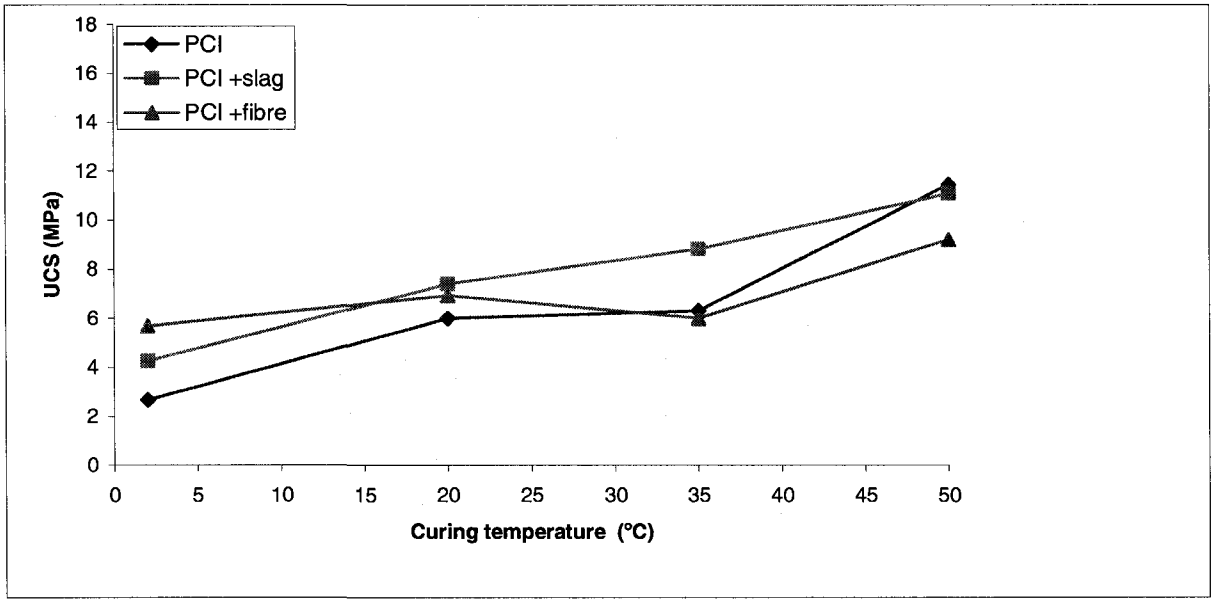

Figure 2-69 28 day UCS of TS made from PCI, PCI-slag and PCI-fibre with 5000 ppm of sulphate at different temperatures

2.3.6.4.2 Advanced ages

Figures 2.70, 2.71, 2.72 represent the 120 day UCS value of TS made from PC-I, PCI-slag and PCI-fibre with 0 ppm, 2500 ppm and 5000 ppm of sulphate cured at

different curing temperatures respectively. The 120 day UCS value of all shotcrete with or without sulphate increases with increase of curing temperature except TS with slag at 50°C with 0 ppm , 2500 ppm and 5000 ppm of sulphate which shows a decline in the compressive strength.

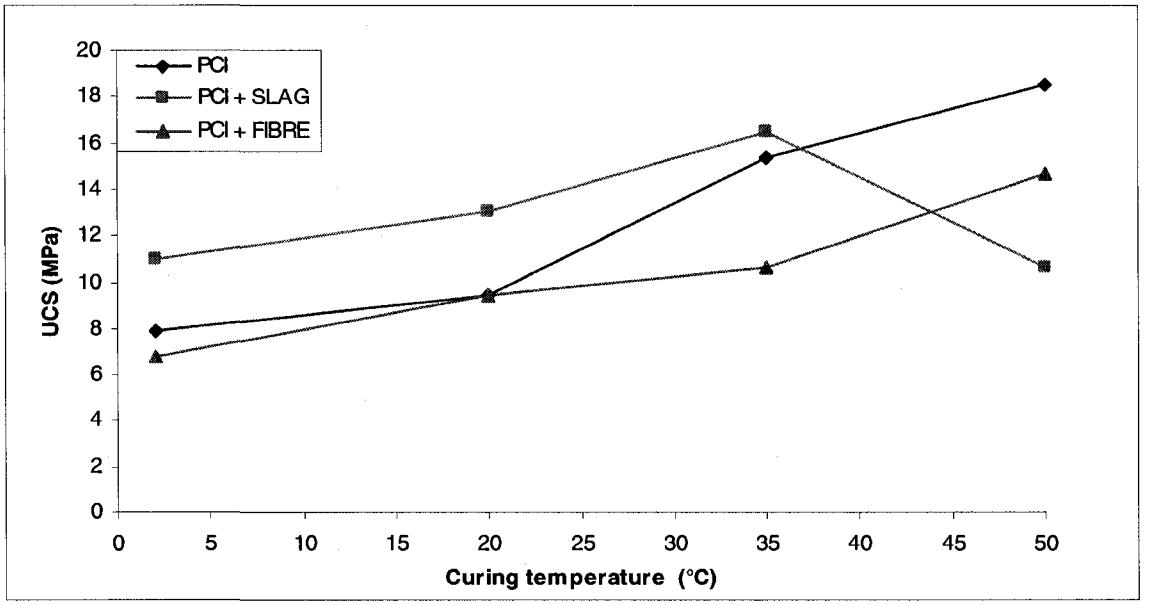

Figure 2-70 120 day UCS of TS made from PCI, PCI-slag and PCI-fibre with 0 ppm of sulphate at different temperatures

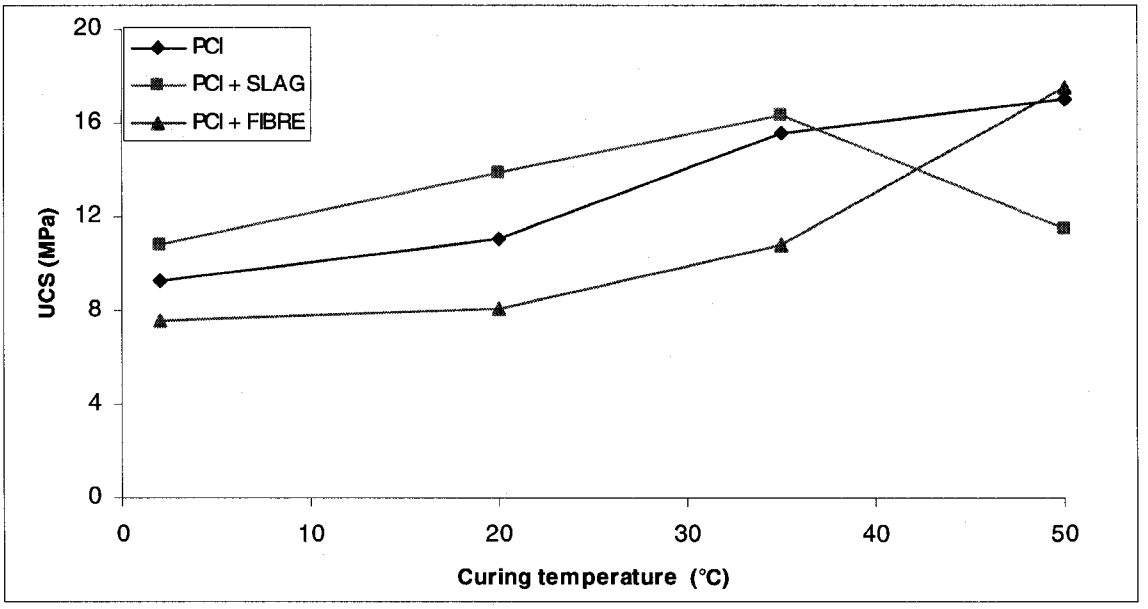

Figure 2-71 120 day UCS of TS made from PCI, PCI-slag and PCI-fibre with 2500 ppm of sulphate at different temperatures

The 120 day UCS value of TS made from slag cement with 0 ppm, 2500 ppm and 5000 ppm sulphate shows higher strength than the rest of the TS samples at 2°C, 20°C and 35°C. The higher strength is due to the formation of secondary ettringite and gypsum. In addition to the precipitation of these expansive minerals, secondary C-S-H also contributes to the strength. At 50°C, the TS containing slag with or without sulphate shows a considerable drop of 120 day UCS value. This is due to the formation of hydration rims in the slag cement which surrounds the unhydrated slag grains, preventing them from further hydration (Barnett et al, 2006). In addition to this, the adsorption of sulphate by C-S-H gel at 50°C can also contribute to strength decrease. The TS made from PCI and PCI-fibre does not exhibit such decline. It is also observed from the 120

day result that TS made from PCI has a higher 120 day UCS value at 50°C containing 0 ppm of sulphate. This is due to the adequate hydration of cement at higher temperatures, producing adequate hydration products as well as secondary gypsum and ettringite that precipitate in the cement matrix.

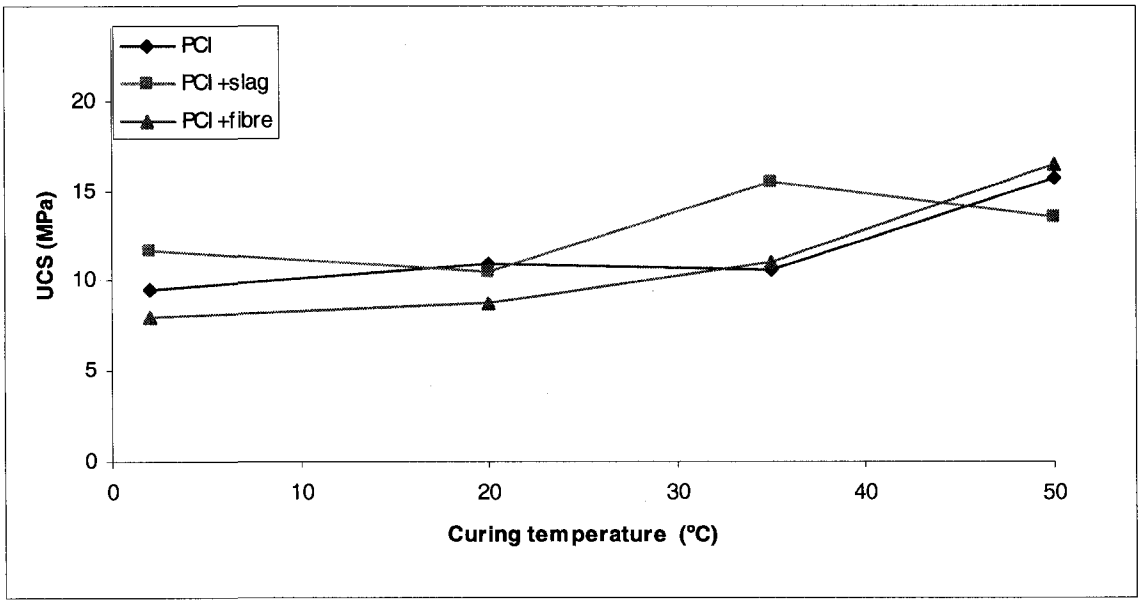

Figure 2-72 120 day UCS of TS made from PCI, PCI-slag and PCI-fibre at different temperatures with 5000 ppm of sulphate concentrations

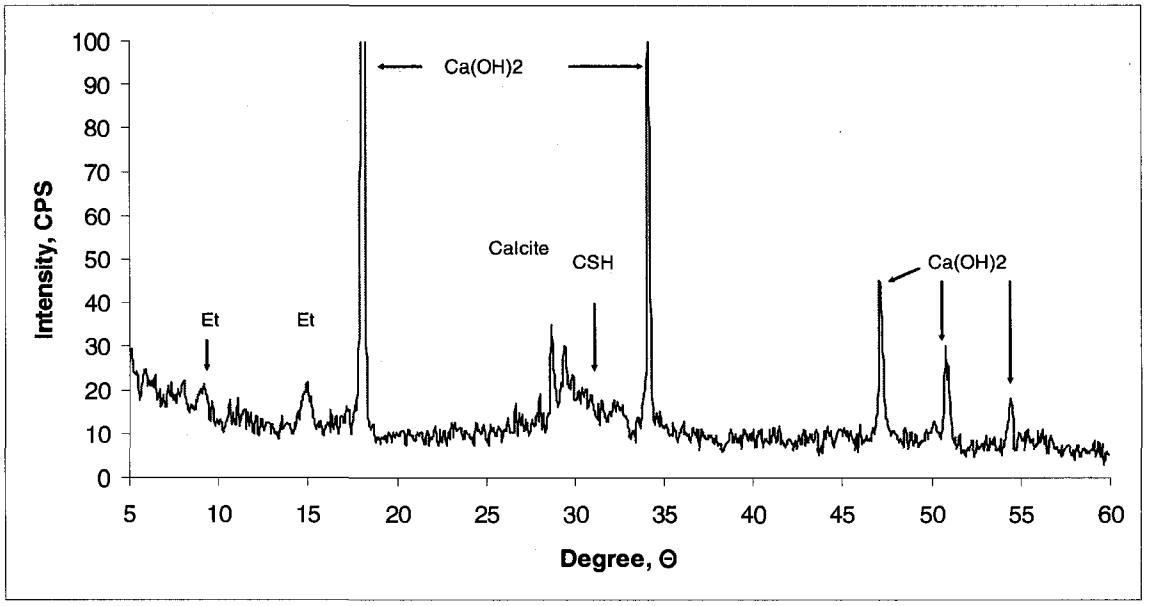

Figure 2-73 XRD result of 0 ppm cement paste made from PCI cured at 20°C for 150 day .

2.3.7 Conclusions and recommendations

Almost 300 samples are made with 0 ppm, 2500 ppm and 5000 ppm of sulphate cured at 2°C, 20°C, 35°C,and 50°C and tested at 1, 7, 28, and 120 days. The TS is made from PCI, PCI-slag and PCI-fibre. The research shows that the mechanical strength of TS is significantly influenced by coupled thermo-chemical effect. The maximum value of compressive strength obtained in this study is almost 18 MPa for the TS made from PCI cured at 50°C for 120 days. The addition of fibre in the TS does not contribute to any additional compressive strength gain. The UCS value of fibre TS is a little bit lower than that of PCI shotcrete. The performance of PCI-slag is found to be better than PCI in sulphate as well as non sulphate bearing environments at the temperature range between

20°C to 35°C. Blended cement performs poorly at 2°C and 50°C. Sulphate is found to contribute positively or negatively to the strength of TS depending upon the curing temperature and concentration. The 2500 ppm sulphate within 35°C temperature does not show any significant deterioration in the mechanical strength whereas the 5000 ppm sulphate concentration in the range of 35°C to 50°C shows reduction in the compressive strength. Adsorption of sulphate by C-S-H gel is observed at higher curing temperature with 5000 ppm of sulphate, reducing the strength of TS. It is assumed in this study that the adsorption of sulphate by C-S-H gel can produce inferior quality of C-S-H, reducing the strength. It requires further study to explore the mechanism associated with the adsorption of sulphate by C-S-H gel, interaction between fibre, sulphate and CH and also the role of these mechanisms in the strength development of TS.

3 Chapter 3: Coupled thermo-chemical effects on the fluid transportability of paste tailing systems

3.1 Abstract

Capillary adsorption and hydraulic conductivity (HC) tests are carried out to study the fluid transport ability and durability of TS and CPT respectively. Capillary adsorption test is conducted on TS made from PCI, PCI-slag and PCI-fibre with 0 ppm, 2500 ppm and 5000 ppm of sulphate cured at 2 °C, 20 °C, 35 °C and 50 °C for 150 days. In the same way, the HC test was conducted on the CPT made from PCI and PCI-slag with 0 ppm, 5000 ppm, 15000 ppm and 25000 ppm of sulphate cured at 2 ° C, 20 ° C, 35 ° C and 50 ° C for 90 days. The test results show that both sulphate and temperature influence the fluid transportability of the CPT systems. Generally, increase in curing temperatures lowers the fluid transportability with some exception at 50 °C. The fluid transportability of the tailings system also shows dependency on the composition of the binder. The TS with PCI-slag will have less environmental problems due to very low ability to transport fluid, indicating low potential of sulphide oxidation in comparison to PCI and PCI-fibre. PCI-fibre shows higher fluid transportability and will have less durability performance.

The HC of CPT also decreases with increase in curing temperature except for the 25000 ppm at 50 °C. The results of the HC test show that the HC of CPT

made from PCI is somewhat lower than CPT made from PCI-slag. The results also illustrate that the CPT will allow lower fluid movement in the temperature range of 20 °C to 35 °C, but the movement of fluid will increase if the curing temperature reached 50 °C with 25000 ppm of sulphate. The CPT samples also show higher HC at 2 °C. The HC of the tested samples ranges between 10^{-5} to 10^{-8} cm / sec. The results show that CPT samples cured at 2 °C demonstrate the highest value of HC in the range of 10^{-5} cm/sec in comparison to HC at other curing temperatures. This indicates that CPB cured in cold mine environments will be less durable due to its higher HC. This higher permeability will favor the fluid (oxygen / water) transport through the CPB, thus the oxidation of the sulphide minerals. The mine site with average temperatures (20 °C - 35 °C) will be more environmentally friendly for the CPT due to lower HC in the range of 10^{-6} to 10^{-8} cm/sec. This low permeability does not allow much fluid inside it, preventing further oxidation of tailings systems. The mine site with hot temperatures (> 35 °C) is also less favorable for the durability of CPT with high sulphate concentrations.

3.2 Introduction

The mine tailing has different constituencies with different chemical compositions depending upon the type of ore mined (Saxena and Dhimole, 2006). Most of these tailings are rich in pyrite, and pyrrhotite (Elberling et al, 1994). When these sulphides come in contact with water and oxygen, they impose a high risk to the environment due to the potential of formation of AMD. AMD is a low pH (2-4) acidic effluent generated from the chemical and biological reaction between sulphide containing minerals and atmospheric oxygen in the presence of water (Wang et al, 2006). AMD favors the solubilization of heavy metals and can pollute groundwater from the infiltration (Ritcey, 2005).

The drawback of tailings to be used in paste tailings system is the fact that the tailings often contain relative high amounts of sulphide minerals (e.g. pyrite, pyrrhotite). In addition to AMD described above, the oxidation of these sulphides (e.g. pyrite, pyrothite) can produce sulphate inside the cemented paste systems. The CPT system can lose strength due to internal sulphate attack which is described in detail in Chapter 2. Thus, the ingress of oxygen and water in it through the voids can deteriorate the performance of the CPT system in the long term and/or lead to AMD development. The movement of these fluids in the tailings system depends upon factors, such as porosity, pore diameter, distribution, pores continuity etc (Kunhanandan and Ramamurthy, 2007).Thus,

the pore structure within CPT systems is one of the parameters which determine the strength as well as fluid movement inside the tailings system (Fall and Samb, 2007). Knowing the fluid transport ability of the cemented paste tailings system will give us indirectly valuable information about the pore structure of the materials.

The mechanical strength of the CPT system is frequently evaluated by the 28 day UCS test in the field as well as laboratory due to the very simple nature of testing and can be performed in a short period of time. The 28 day UCS test of CPT gives an idea of the early strength to design any CPT system, but will not provide enough information about the durability and behavior of CPT containing sulphide for long term periods of time. The movement of fluid inside the CPT system will determine its durability because the system will lose strength due to internal sulphate attack. The sulphide inside the tailings system will only oxidize if the system permits the flow of aggressive elements, such as oxygen and water. The fluid transport ability of cementitious materials can be determined by permeability, water absorption, and sorption. Permeability is the process of determining the flow of water under pressure in saturated porous media (Kunhanandan and Ramamurthy, 2007). The CPT system is almost saturated (Fall and Samb, 2006) and hence, HC testing can be performed to gain information about the ability of CPT to transport fluid, and thus evaluate its durability (Tasdemir, 2003). However, due to the high cement content in the TS, they have very fine pores and so the time required for completion of permeability

testing is very high. It is also found (Khatib and Clay, 2003; Kunhanandan and Ramamurthy, 2007) that HC will not give accurate results of fluid transport ability in unsaturated media, such as TS. The fineness of the capillary pores allows shotcrete to absorb water (Khatib and Clay, 2003) from the capillary suction. Hence, the sorption coefficient gives reliable results about the pore structure and fluid transport ability of TS.

HC as well as sorption tests will give information about the fluid transport ability of the CPT system. The results can be used to estimate the long term durability (Khatib and Clay, 2003) and environmental performance of CPT containing sulphide bearing tailing. Hence, it is necessary to have an idea about the fluid transport ability of CPT system so that it can be incorporated into the design. The fluid transport ability is a function of temperature and sulphate. However, to the best knowledge of the author there are no studies published about the coupled thermo-chemical effects on the fluid transport ability of cemented paste tailings system. This background inspired the author to conduct HC and sorption tests to study the fluid transport abilities of the CPT system containing various amounts of sulphate with different temperatures. This study will provide useful information for estimating the fluid transport ability of CPT with sulphate at different concentrations at different mining sites with different temperatures. The author believes that the outcome of this research will help the engineering community working in the cement paste tailings system field for consideration in the design and durability evaluation of the aforementioned structures, and will also help in

the prediction of AMD formation potential of the paste tailings systems containing sulphate.

After this introduction, materials and methods will be discussed. This is followed by specimen preparation. After that, the experimental results are presented and discussed. Finally, conclusion of the research is drawn at the end of the paragraph.

3.3 Materials and Methods

3.3.1 Materials

3.3.1.1 Binders used

The description of binders used in this study is already given in 2.2.3.1.1 and 2.3.3.1.1 for HC and sorption tests respectively.

3.3.1.2 Water

The details of water used for this research is described in 2.3.3.1. 2

3.3.1.3 Tailings

The details of tailings used for this research is described in 2.3.3.1.3

3.4 Specimen preparation

The specimen preparation for this research is explained in 2.2.4 for HC tests and 2.3.4 for sorption testing. The ingredients used for this research is given in Tables 2.4 and 2.5 respectively.

3.5 Testing Procedure

3.5.1 Capillary Test

Sorption of cementitious material is a phenomenon where water is absorbed into it by capillary action (Khatib and Clay, 2003). The sorptivity can be determined by placing one side of the sample over water (2 to 5 mm) and the weight of the water absorbed by the sample is measured in a certain period of time. The pores of the cementitious materials allow water to move into it by capillary action. Hence, the capillary test also gives indication about the pore structure (Khatib and Clay, 2003). If the porosity of cementitious materials is high with interconnection between the pores, then the fluid transport ability will be high. If the materials have high volume of porosity, but lack continuity of pores, then it will reduce the capillary absorption of water (Neville, 1995).

Water absorption through capillaries is found to be proportional to the square root of time during the initial absorption period (Gonen and Yazicioglu, 2007; Tasdemir, 2003) according to following equation

$$i = s\sqrt{t}$$

i denotes the amount of water absorbed per cross sectional area of the specimen that is in contact with water, t is the time in seconds and s is the sorptivity coefficient of the specimen measured in $gms/m^2 * \min^{1/2}$. The value of s can be determined from the slope of the linear part of the i vs $\sqrt{t}$.

Figure 3-1 Sorption test of TS with various sulphate contents and cured at different temperatures after 150 days.

The TS samples for this test is made with 0 ppm , 2500 ppm and 5000 ppm of sulphate cured at 2°C , 20°C, 35°C and 50°C for 150 days. The samples were removed from the mould and dried at 50°C until a constant mass. The sides of each sample are covered with plastic tape as shown in Figure 3.1 for a unidirectional flow of water (Gonen and Yazicioglu, 2007). The sample was then kept in a covered box over water to avoid evaporation. The water level was maintained at 5 mm from the bottom of the samples throughout the experiment (Gonen and Yazicioglu, 2007; Menadi et al, 2008). The weight was taken at 5 minute time intervals during the start of the test and increased accordingly as the test proceeded. The bottom part was wiped with soft tissue to remove any water before the weight measurement for reliable results. The sample was then placed back into the box containing water. The test was conducted for more than 30 days.

3.5.2 Hydraulic Conductivity Test

The HC of CPT samples made from PCI and PCI-slag with 0 ppm, 5000 ppm, 15000 ppm and 25000 ppm of sulphate cured at 2 °C, 20 °C, 35 °C and 50 °C was tested after 90 days. The HC which is also known as the coefficient of permeability test is conducted as per the standards and procedures described in ASTM D 5084-00 (2002). The sample was kept under tap water for half an hour to aid saturation.

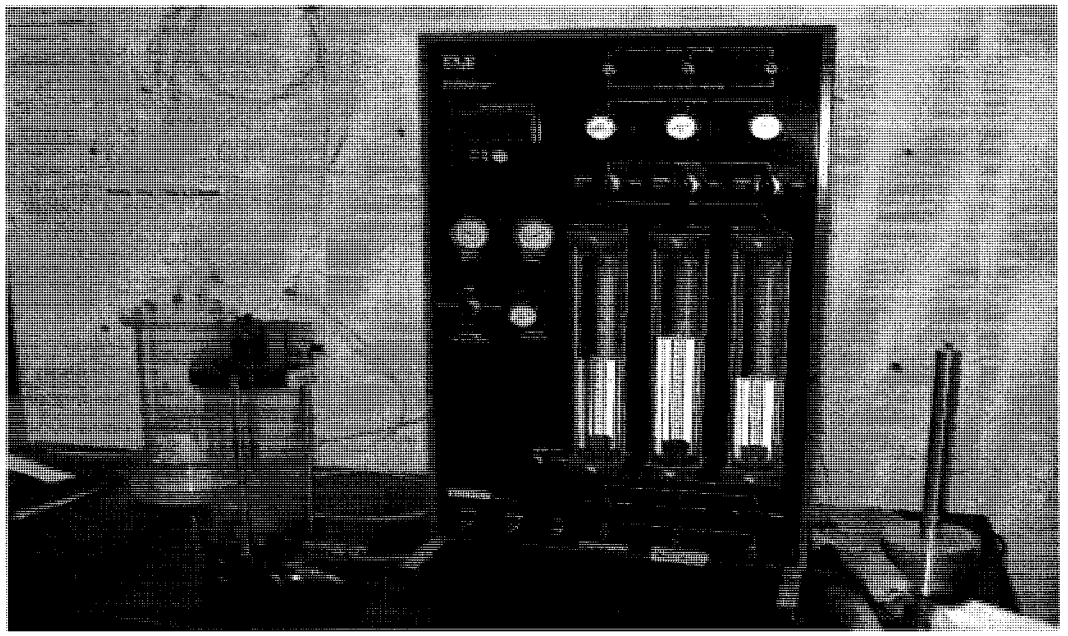

Figure 3-2 Experimental set up for the hydraulic conductivity test

Two porous stones with the same diameter as the sample were kept at the bottom and top parts of the sample in the permeameter cell. Two pieces of filter paper were also placed in between the sample and porous stone to avoid the clogging of the porous stone by the sample grains. A flexible membrane was then used to cover whole sample, including porous stone with the help of a membrane expander. O rings were inserted at the bottom and top part of the system to seal the membrane to the base and at the top in the permeameter cell. The flow tubings were then fixed at their position inside the cell and the permeameter cell was assembled. Then the cell was filled with water. The permeameter cell containing the sample and water was connected to the triaxial cell to start the HC test. Constant head method was used to calculate the HC of

the sample. For this purpose, the hydraulic gradient as suggested by ASTM D 5084-00 is used. The HC k of the sample is calculated as follows:

$$k = \frac{\Delta Q * L}{A * h * \Delta t}$$

Where k = HC m/s

ΔQ = quantity of flow (m^3) for given time interval Δt.

L = length of the specimen, m

A = cross sectional area in m^2

Δt = Interval of time over which the flow ΔQ occurs $(t_2 - t_1)$

t_1 = time at the start of the test secs

t_2 = time at the end of the test secs

h = average head loss across the permeameter

3.6 Results and discussions

3.6.1 Capillary absorption of paste tailings shotcrete

3.6.1.1 Capillary absorption of TS -PCI

Figure 3.3 illustrates the capillary absorption (CWA) of water by TS made from PCI containing 0 ppm of sulphate at 2°C, 20°C, 35°C and 50°C cured for 150 days. In general, the results show that the CWA by TS decreases with increase of curing temperature. TS at 2°C shows high amount of water absorption during the initial day in comparison to other samples. In the same way, TS at 50°C has a low amount of water absorption and samples cured at 20°C and 35 °C had a CWA between 2°C and 50°C.

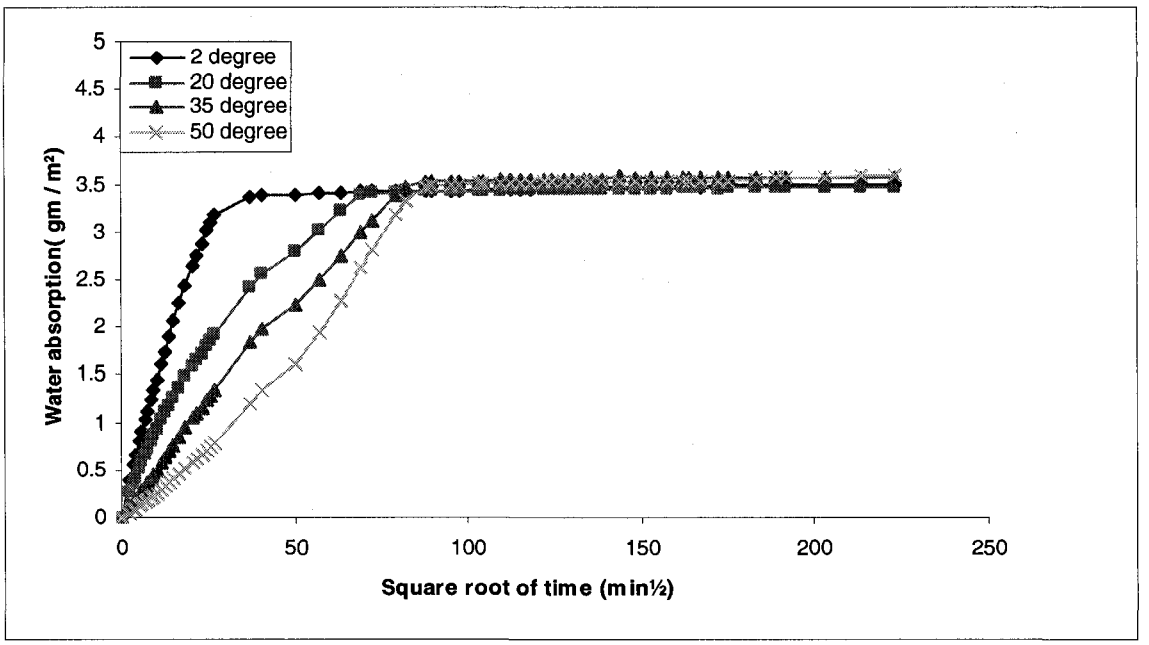

Figure 3-3 Capillary absorption of water by TS made from PCI with 0 ppm of sulphate at different curing temperature

The variation of CWA with curing temperature is due to the quantity of hydration products precipitated in TS (Fall and Samb, 2007). The lower value of CWA of TS cured at 50°C is due to the precipitation of adequate hydration products in the cement matrix due to higher curing temperatures which decrease the pore volume in the cement matrix and also reduce the pore connectivity (Fall and Samb, 2007). The higher CWA of TS cured at 2°C is due to the lower curing temperature. At 2°C, the cement hydration reaction proceeds very slowly (Lothenbach et al, 2007) and less hydration products will precipitate in the cement matrix. This confers high porosity to the cementitious materials in comparison to the sample cured at high temperatures. The precipitation of hydration products in the 35°C sample is more than the 20°C sample. Hence the TS cured at 20°C shows a higher value of CWA.

It is also observed from Figure 3.3 that during the early period of testing up to 7 days, the TS sample has a very high rate of water adsorption. After 7 days, the TS show gradual increase of CWA and are almost the same for all TS. The initial high rate of water absorption is due to the filling of pores of TS occupied by air and at later days of testing, almost all of the voids were saturated with water and showed very small amounts of water absorption.

The slope of the CWA curve of TS cured at 2°C is very sharp and there is reduction of the slope as the curing temperature increases. Finally, the slope of the TS cured at 50°C is very mild indicating that the water absorption is very low in comparison to other samples.

Figures 3.4 and 3.5 illustrate the CWA of TS made from PCI cement at 2°C, 20°C, 35°C and 50°C containing 2500 ppm and 5000 ppm of sulphate. It is observed from these figures that the fluid transportability of TS is highly influenced by the coupled effect of curing temperature and sulphate. Such behavior of CPT system was also observed by Fall and Samb (2007). In general, the CWA of TS decreases with increase of curing temperature except at 50°C. The 2500 ppm and 5000 ppm shotcrete samples cured at 2°C in Figures 3.4 and 3.5 also show higher amounts of CWA. The higher water absorption is due to the fewer formation of hydration products and also the presence of

sulphate inhibit the hydration reaction (Fall and Benzaazoua, 2005) resulting in less precipitation of hydration products in the cement matrix.

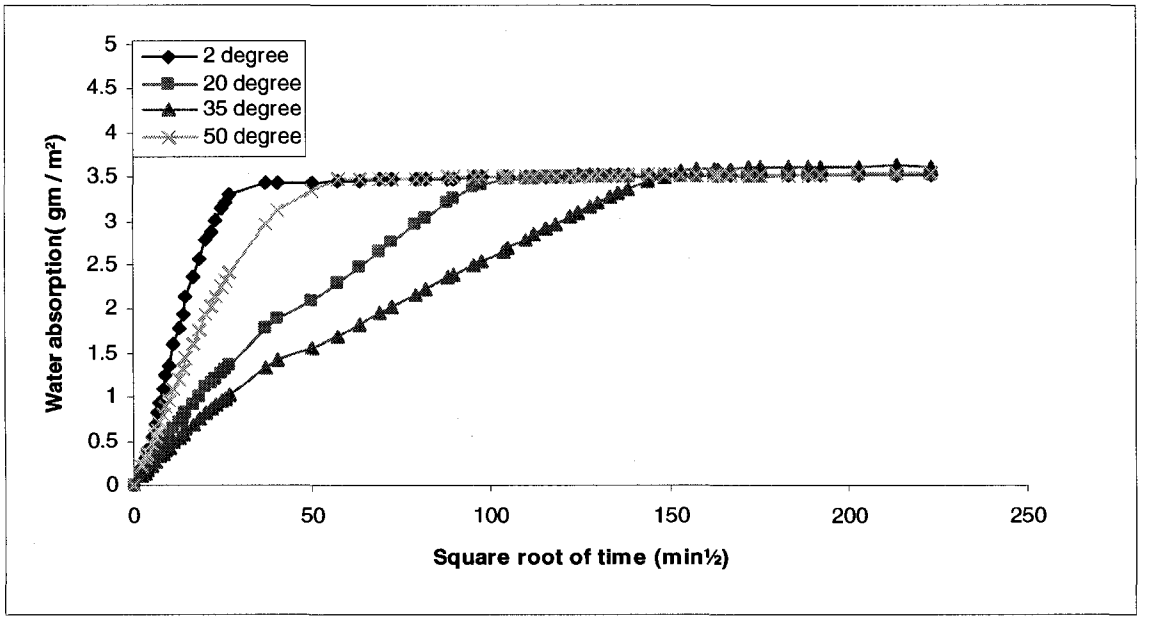

Figure 3-4 Capillary absorption of water by TSmade from PCI with 2500 ppm of sulphate at different curing temperatures

It is also observed from Figures 3.3, 3.4 and 3.5 that the slope of the TS with sulphate is relatively milder than without sulphate at the same temperature with the gypsum and secondary ettringite formed by the reaction between sulphate and CH (Fall and Benzaazoua, 2005) are also filling the voids of the cement matrix in the case of TS containing sulphate.

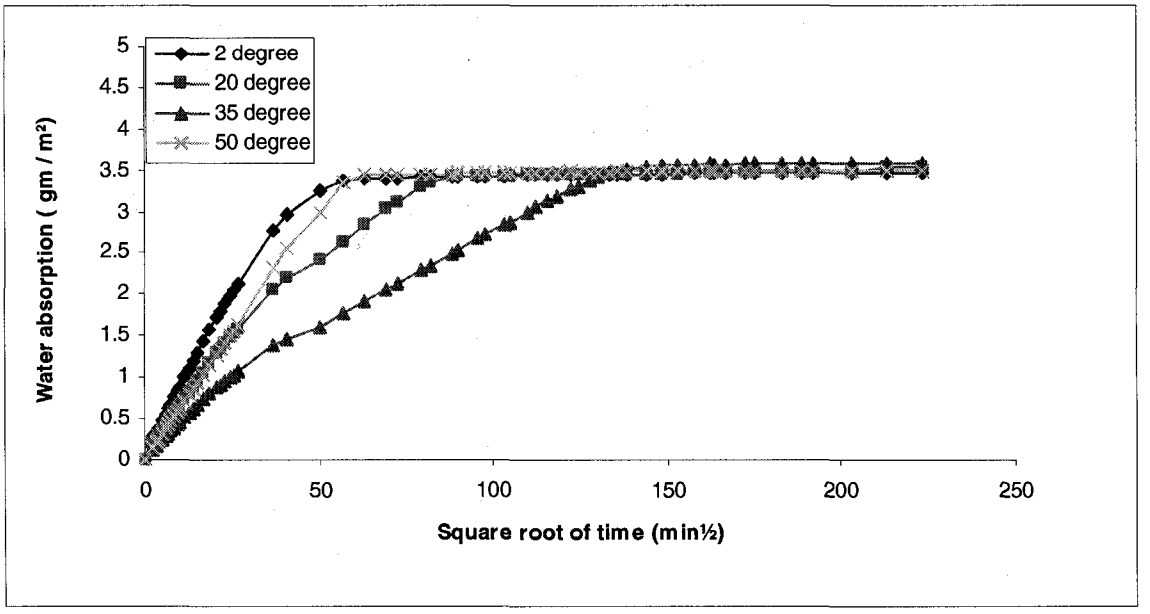

Figure 3-5 Capillary absorption of water by TS made from PCI with 5000 ppm of sulphate at different curing temperatures

The precipitation of these additional expansive minerals in the voids and pores of the TS rearrange the micro structure resulting in less internal porosity (Fall and Samb, 2007).

The XRD result of the 5000 ppm samples at 20 °C in Figure 2.13 shows the precipitation of the expansive minerals along with other hydration products. Hence, the CWA of TS cured at 20°C and 35°C containing 2500 ppm and 5000 ppm shows low value. Figures 3.4 and 3.5 also show that the TS sample cured at 35°C shows less fluid transport ability than 20°C with 2500 ppm and 5000 ppm of sulphate. This difference in fluid transport ability of TS with different curing temperatures can be the difference in amount of expansive minerals as well as hydration product precipitating in the cement matrix.

The TS samples containing 2500 ppm and 5000 ppm of sulphate cured at 50°C show different behavior than the rest of the samples. The CWA is between those of samples at 2°C and 20°C. This indicates that the samples are more porous than samples cured at 20°C and 35°C. This different behavior can be due to the phenomenon of adsorption of sulphate by C-S-H (Fu et al, 1994) and also the destabilization of ettringite at high temperatures (Ramlochan et al, 2004). These two mechanisms can lead to the increase of the porosity of the TS, thereby resulting in higher CWA. Indeed, the absorption of sulphate by C-S-H will make less sulphate available to form expansive minerals that can reduce the porosity of the TS. The dissolution of ettringite at high temperatures leads to higher porosity.

This argument is further supported by comparing the XRD results of the 5000 ppm sample cured at 50°C and 20°C in Figures 2.13 and 2.7 respectively. The XRD result of the 5000 ppm at 20°C in Figure 2.7 shows a higher precipitation of ettringite and gypsum in comparison to the one at 50°C in Figure 2.13. The peak of these expansive minerals especially at 9, 11.5, 16, 23 degrees 2 theta, is higher for 5000 ppm samples at 20°C, indicating a high precipitation of these expansive minerals in the pores of 5000 ppm TS whereas the 5000 ppm sample at 50°C shows the presence of a high peak of CH especially at 18, 28.5, 34, 47, 51 degrees 2-theta in comparison to the ones at 20°C. The presence of high

amounts of CH indicates that the adsorption of sulphate by C-S-H gel could have resulted in the higher value of CWA of the 5000 ppm samples at 50°C.

Figure 3.6 shows the sorptivity of TS made from PCI with 0 ppm, 2500 ppm and 5000 ppm of sulphate at 2°C, 20°C, 35°C and 50°C. The sorptivity curves are obtained by calculating the slope of the linear part (Tasdemir, 2003) of the results of the CWA curve as shown in Figures 3.3, 3.4 and 3.5.

It is observed from Figure 3.6 that the TS sample with different sulphate concentrations has different values of sorptivity at different temperatures. In general, the sorptivity of TS decreases with increase of curing temperature except for samples containing 2500 ppm and 5000 ppm of sulphate at 50°C.

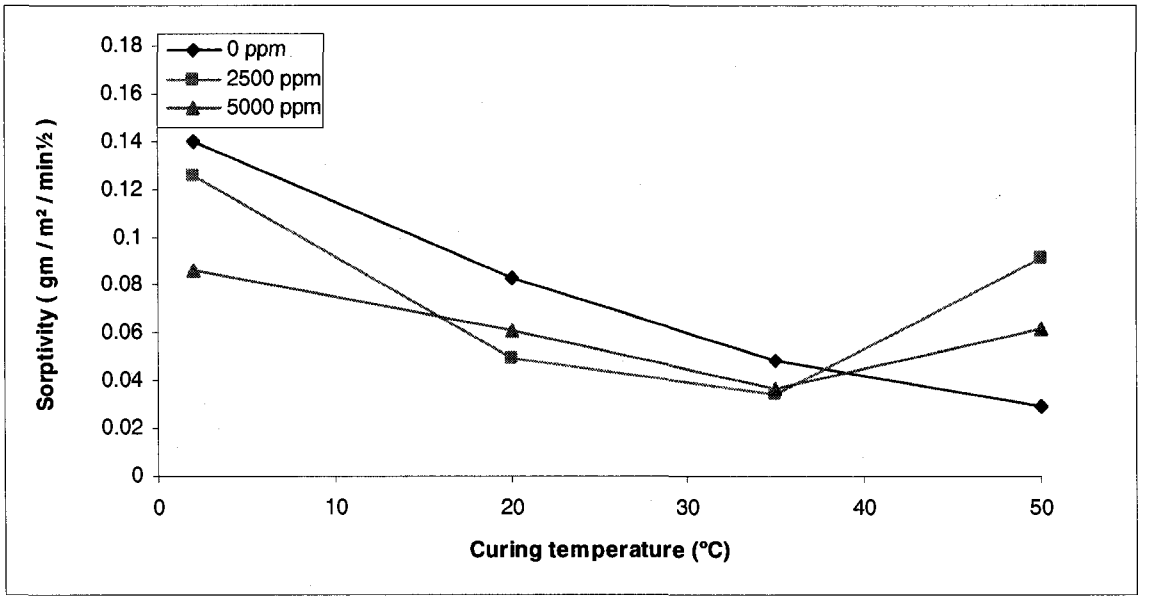

Figure 3-6 Sorptivity of TS made from PCI containing sulphate at different curing temperatures

As the curing temperature increases, the TS with 0 ppm sulphate in Fig 3.6 shows rapid fall in the value of sorptivity. This may be due to the filling of pores by the formation of additional hydration products in the sample which rearrange the pore structure.

This rearrangement of pores due to additional hydration products reduces the pore connectivity in the cement matrix that significantly lowers the capillary sorption of the samples (Fall and Samb, 2006). The TS made from PCI with 2500 ppm and 5000 ppm of sulphate shows lower value of sorptivity at 20°C, 35°C than 0 ppm of sulphate. The lower value is due to the formation of secondary gypsum and ettringite which fills the micro pores of the cement matrix making the sample denser, resulting in the lower capillary absorption of water.

The TS containing 0 ppm, 2500 ppm and 5000 ppm of sulphate cured at 2°C shows high value of sorptivity. The higher value is due to the slow hydration of cement at lower temperatures (Fall and Samb, 2006; Lothenbach et al, 2007). At this low temperature, the voids of the samples are not filled with enough hydration products. This results in the formation of coarser pore structure which increases the sorptivity of the samples. The sorptivity of TS with 5000 ppm of sulphate is lowest at 2°C. The sorptivity of 2500 ppm of sulphate is between that of the 0 and 5000 ppm samples. The lower value of sorptivity of TS containing sulphate in comparison to the 0 ppm sample is due to the presence of sulphate. The precipitation of secondary gypsum and ettringite from the reaction of sulphate with the hydration product (CH) of cement fills the voids of the sample (Fall and Benzaazoua, 2005) which reduces the internal porosity and lowers the sorptivity of the TS containing sulphate.

Figure 3.6 also shows that the sorptivity of TS samples made from 2500 ppm and 5000 ppm at 20°C and 35°C are almost the same and lower than the 0 ppm sample. This lower value is due to the formation of expansive minerals in addition to the hydration products. The shotcrete sample containing 2500 ppm and 5000 ppm at 50°C shows high value of sorptivity, even higher than the sorptivity of TS cured at 20°C and 35°C.The high sorptivity of 2500 ppm and 5000 ppm at 50°C is due to the adsorption of sulphate by C-S-H gel (Fu et al, 1994) and the dissolution of ettringite at high curing temperatures as explained above.

3.6.1.2 Capillary absorption of TS - PCI-Slag

Figures 3.7, 3.8 and 3.9 show the CWA curves of TS made from PCI-slag with 0 ppm , 2500 ppm and 5000 ppm of sulphate, respectively, and cured at 2°C, 20°C, 35°C and 50°C. Figure 3.7 illustrates that the capillary adsorption of TS made from PCI-slag depends upon the curing temperature.

During the beginning of the testing, all samples were showing the same capillary absorption of water. As the test proceeded, the TS cured at 50°C showed a higher value of CWA. The higher value can be attributed to the formation of hydration rims around the unhydrated slag grains (Escalante and Sharpe, 2001). This prevented the further hydration of slag cement at higher temperatures.

Formation of hydration rims in the blended cement prevents the precipitation of hydration products in the cement matrix so that the pores are not adequately filled thereby resulting in the increase of internal porosity. This will increase the CWA value of TS at 50°C.

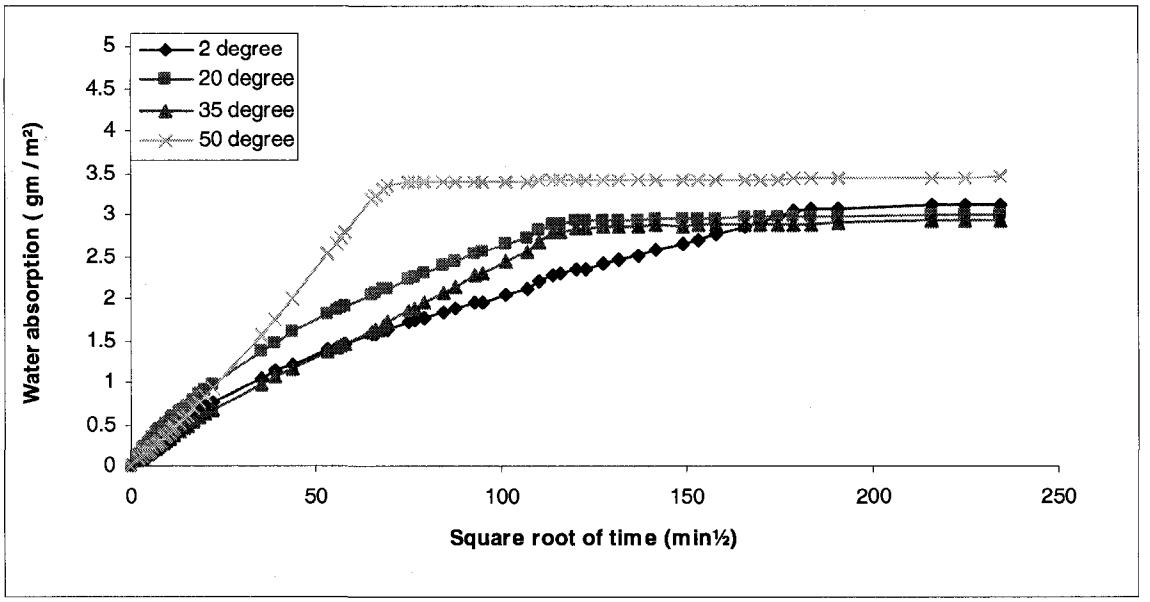

Figure 3-7 Capillary absorption of water by TS made from PCI-slag with 0 ppm of sulphate at different curing temperature

Figure 3.7 also illustrates that the TS cured at 2°C shows the lowest value of CWA followed by TS at 35°C. The lowest value of CWA of the 2°C sample can be explained by the fact that the unreated slag grains (because of the low temperature) play a role of filler effect thereby resulting in finer pore structure.

The lower value of CWA of TS at 35 °C is mainly due to the high pozzolanic reaction of slag which is very reactive around 35 °C (Escalante and Sharpe,2001) . At 35°C, the hydration reaction of cement is very fast and slag also reacts with CH and produces secondary C-S-H. The precipitation of hydration products and secondary C-S-H in the pore lowers the internal porosity resulting in the lower value of CWA. The TS cured at 20°C has a CWA value between that of the 50°C and 35°C samples. It indicates that the porosity of the 20°C TS sample is somewhat higher than the 35°C sample. The XRD result of

the 0 ppm sample at 35°C made from PCI-slag in Figure 2.20 shows higher amount of hydration products at 18, 51, 54.5 degrees 2-theta position in comparison to the 0 ppm sample at 20°C in Figure 2.19.

Figure 3.8 illustrates the capillary absorption of TS made from PCI-slag with 2500 ppm of sulphate at 2°C, 20°C, 35°C and 50°C. The TS cured at 50°C shows the highest value of CWA in comparison to the rest of the samples followed by TS cured at 35°C. The higher value can be explained by the formation of hydration rims in the slag cement. In addition to this, sulphate is adsorbed by C-S-H gel (Fu et al, 1994) which can form lower quality of C-S-H gel resulting in the high CWA. The destabilization of ettringite at higher temperatures can be considered as an additional cause. The dissolution of ettringite leads to higher porosity, thus resulting in higher value of CWA.

Figure 3.8 also illustrates that the CWA of TS cured at 35°C is between those of samples cured at 50°C and 20°C. This lower CWA (in comparison to 50°C sample) can be attributed to the combined effects of the following mechanisms: a) due to lower temperatures, there is less adsorption of sulphate by C-S-H gel thus a higher amount in expansive minerals will be present, b) the lower temperature causes a lower dissolution of ettringite which in turn, produces lower porosity, and c) the high reactivity of slag will produce high amounts of secondary C-S-H gel.

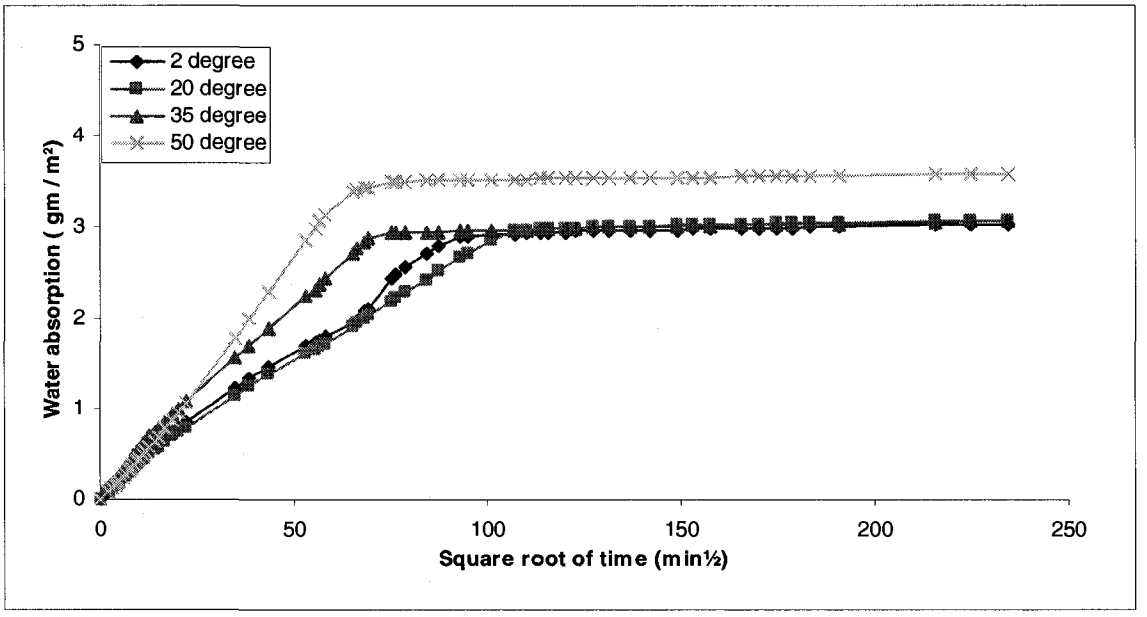

Figure 3-8 Capillary absorption of water by TS made from PCI-slag with 2500 ppm of sulphate at different curing temperature

Figure 3.8 also illustrates that the TS made from PCI-slag with 2500 ppm of sulphate and cured at 2°C and 20 °C shows relatively low value of CWA. The low value is due to the precipitation of hydration products as well as formation of secondary C-S-H and expansive minerals. In addition, these low temperatures (≤ 20°C) are not favorable for the adsorption of sulphate by C-S-H and the destabilization of ettringite. It means that there is no increase of porosity due to the aforementioned mechanism. The precipitation of hydration products in addition to the expansive minerals fills the pore space of the TS cured at 2°C and 20°C. This reduces the internal porosity as well as CWA value resulting in the formation of a dense and compact body of TS (Fall and Benzaazoua, 2005).

Figure 3.9 shows the CWA of TS made from PCI-slag containing 5000 ppm of sulphate at 2°C, 20°C, 35°C and 50°C. In this case, TS cured at 50°C shows the lowest value of CWA whereas at 35°C shows highest value of sorptivity. At 50°C, the phenomenon of hydration rims and adsorption of sulphate by C-S-H should increase the CWA of TS. In contrary to this, it shows a lower value of CWA at an earlier day of the test. In this case, some of the sulphate is adsorbed by the C-S-H gel and dissolution of some of the ettringite in the samples rendered very low amounts of ettringite. This low amount of ettringite will not be able to exert significant amount of pressure on the cemented matrix so that the formation of crack will be localized. This can result in the discontinuity of the pore space within the TS. If the voids are not interconnected, they will show a lower value of CWA, even if the porosity of the sample is higher (Neville, 1995).

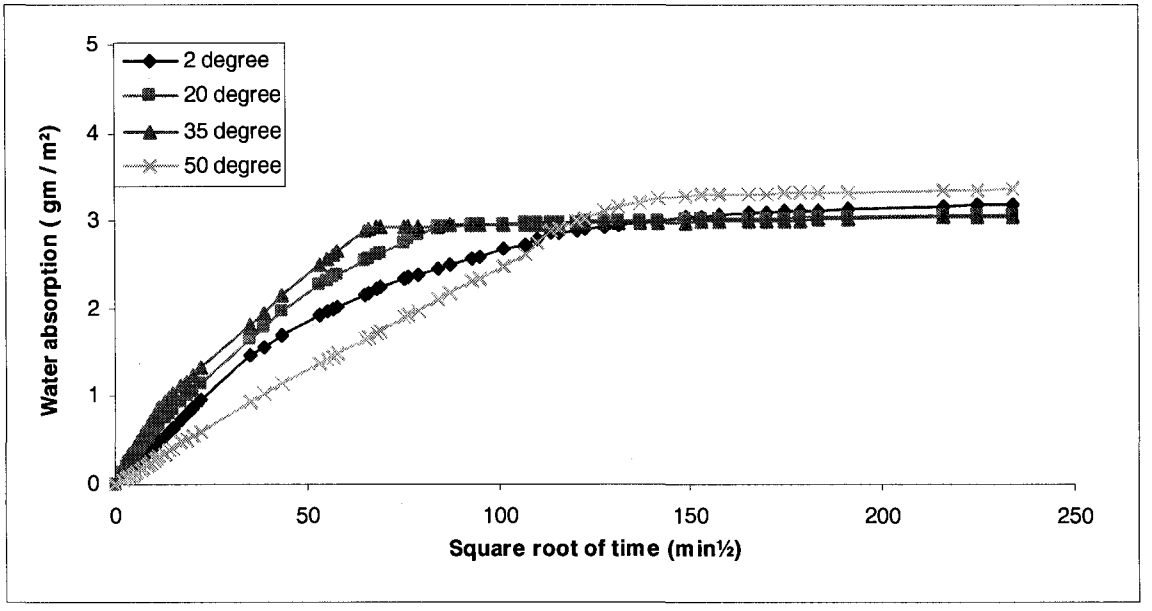

Figure 3-9 Capillary absorption of water by TS made from PCI-slag with 5000 ppm of sulphate at different curing temperature

After 7 days of the testing, again, the same TS cured at 50°C shows higher absorption rate. This shows that the sample is highly porous, but the voids are discontinuous at the bottom part of the sample. The higher capillary water adsorption after 7 days of testing indicates the presence of interconnected voids. As explained earlier, the adsorption of sulphate and formation of hydration rims (Barnett et al, 2006; Escalante and Sharp, 2001) prevents the hydration of slag grains resulting in the porous microstructure of the TS which increases the CWA of TS cured at 50°C.

Figure 3.9 also illustrates that the TS cured at 35°C shows the highest value of CWA. The higher value may be due to conventional sulphate attack and/or adsorption of sulphate by C-S-H gel. In addition to this, the dissolution of ettringite at higher curing temperatures also contributes to the high CWA value of 35°C TS. The TS cured at 2°C shows lower value of CWA than 20°C and 35°C. Its CWA value lies between those of 20°C and 50°C. This lower value may be due to the precipitation of adequate amounts of secondary C-S-H from the pozzolanic reaction of slag. In addition to the pozzolanic reaction, filler effect of slag, formation of secondary ettringite and gypsum in the pores of TS from the reaction between CH and sulphate also contribute to the refinement of the pores. This leads to the reduction in the internal porosity which considerably lowers the CWA value of TS cured at 2°C.

Figure 3.10 represents the sorptivity of TS made from PCI-slag containing 0 ppm, 2500 ppm and 5000 ppm of sulphate at curing temperatures 2°C, 20°C, 35°C and 50°C. In general, the TS samples containing sulphate show higher value of sorptivity than without sulphate with some exceptions. The TS with 2500 ppm and 5000 ppm of sulphate has the same value of sorptivity at 2°C and this value is higher than that of the 0 ppm TS at 2°C. The higher value may be due to the presence of sulphate which inhibits the hydration of cement at lower temperatures (Fall and Benzaazoua, 2005) so that these TS have lower amount of hydration products in comparison to the TS without sulphate. The formation of micro cracks in the cemented matrix of these TS, because of the pressure produced by the expansive minerals, can be considered as an additional cause of the higher sorptivity.

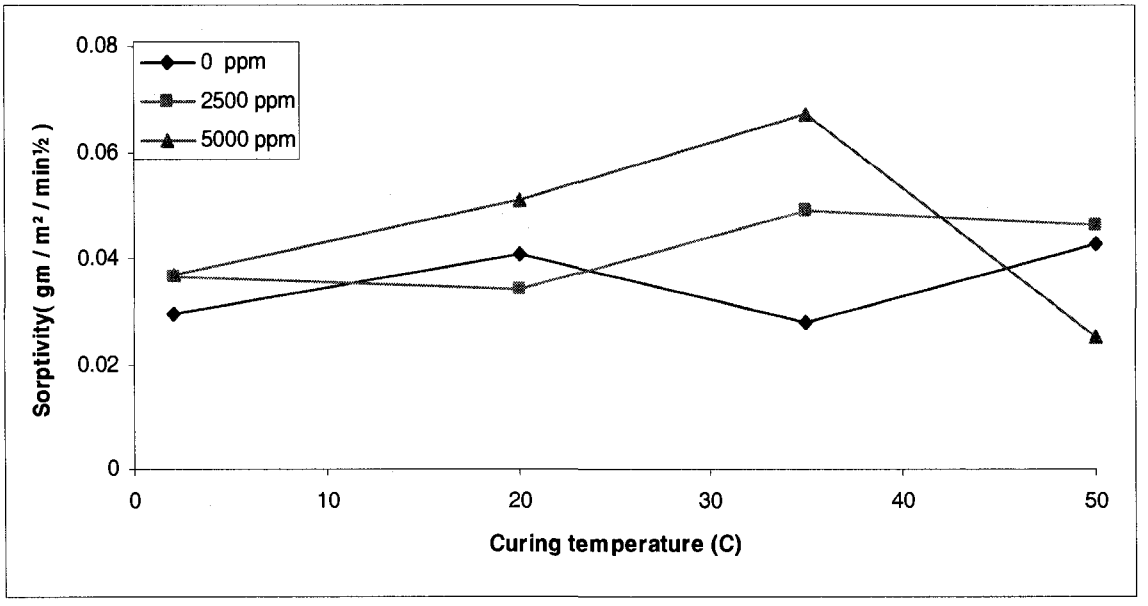

Figure 3-10 Sorptivity of TS made from PCI-slag containing sulphate at different curing temperatures

At 20°C and 35°C, TS with 5000 ppm of sulphate shows higher value of sorptivity than the rest of the samples at the same temperature. It means that the 5000 ppm TS cured at 20°C and 35°C has a higher amount of capillary pores. The higher value of sorptivity can be due to the effect of sulphate attack. The expansive minerals exert expansive pressure on the pore structure resulting in the formation of cracks. The higher value of sorptivity of TS with 5000 ppm of sulphate at 35°C can be attributed to the adsorption of sulphate by C-S-H gel and the destabilization of ettringite which results in the increase of CWA. The 0 ppm sample at 35°C has the lowest sorptivity. This can be due to the precipitation of additional hydration products with time as well as with increase of curing temperatures. This assumption of formation of hydration products with curing temperature is again supported by comparing the XRD results of the 0 ppm samples cured at 20°C and 35°C in Figures 2.19 and 2.20 respectively. In addition to this, the formation of secondary C-S-H in the pores of the 0 ppm samples at 35°C also contributes to lowering the internal porosity.

Figure 3.10 also shows that at 20°C, the 2500 ppm sample has the lowest value of sorptivity. This can be due to the positive contribution of gypsum and secondary ettringite which are still filling the voids of the cement matrix and reducing the porosity of samples. At 50°C, both 0 ppm and 2500 ppm samples show approximately equal value of sorptivity. The sorptivity of the 0 ppm sample at 50°C is higher than 35°C. The higher value can be due to the formation of

hydration rims at high curing temperatures which surround the unhydrated slag grains and prevent further hydration.

The 5000 ppm sample shows lower value of sorptivity at 50°C. As discussed earlier, this can be due to discontinuity of the pores in the cement matrix.

3.6.1.3 Capillary absorption of TS PCI-Fibre

Figure 3.11 shows the CWA of TS made from PCI- fibre containing 0 ppm of sulphate at 2°C, 20°C, 35°C and 50°C. The results show that the CWA decreases as the temperature increases with the exception of TS cured at 50°C which shows the highest value of CWA.

The higher value of CWA is mainly due to the formation of denser hydration rims (Barnett et al, 2006; Lothenbach et al, 2007) at higher temperatures which prevents the hydration of unhydrated cement grains, thereby resulting in the coarsening of porosity. The TS cured at 35°C shows lowest value of CWA. This lowest value is due to the precipitation of hydration products in the cement matrix which fills the pores and voids, and thus resulting in the lower porosity cemented matrix. The TS cured at 2°C and 20°C exhibits a CWA value between those of 50°C and 35°C.

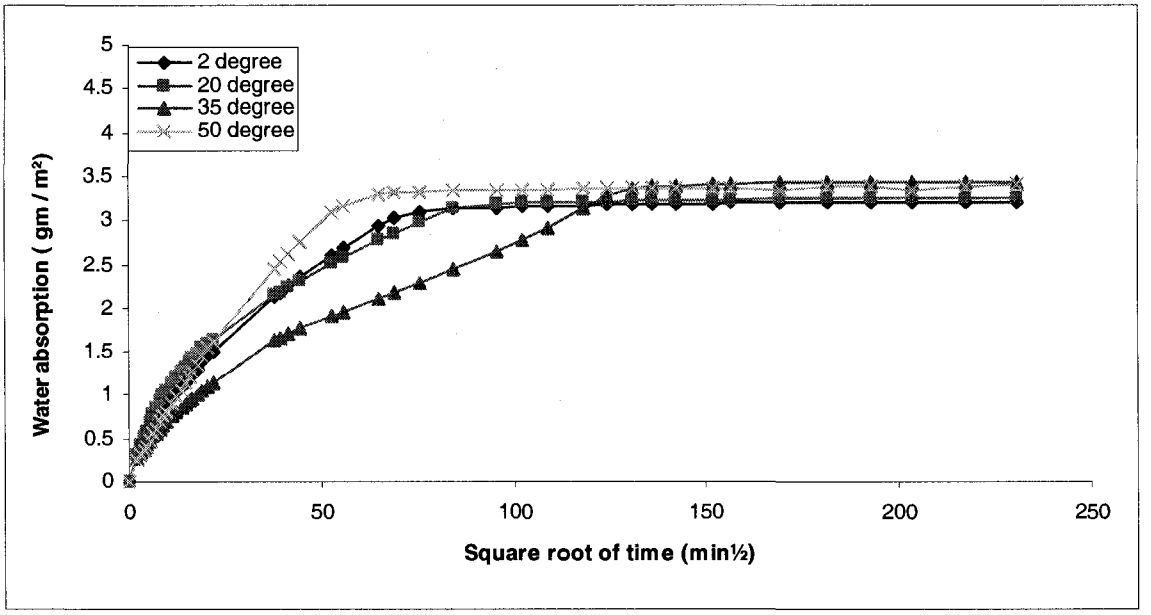

Figure 3-11 Capillary absorption of water by TS made from PCI-fibre with 0 ppm of sulphate at different curing temperature

Figures 3.12 and 3.13 illustrate the CWA results of TS made from PCI-fibre containing 2500 ppm and 5000 ppm of sulphate. In both of these figures, TS cured at 50°C shows the highest value of CWA. This is due to combined effects of adsorption of sulphate by C-S-H gel, formation of hydration rims and dissolution of ettringite at high temperature.

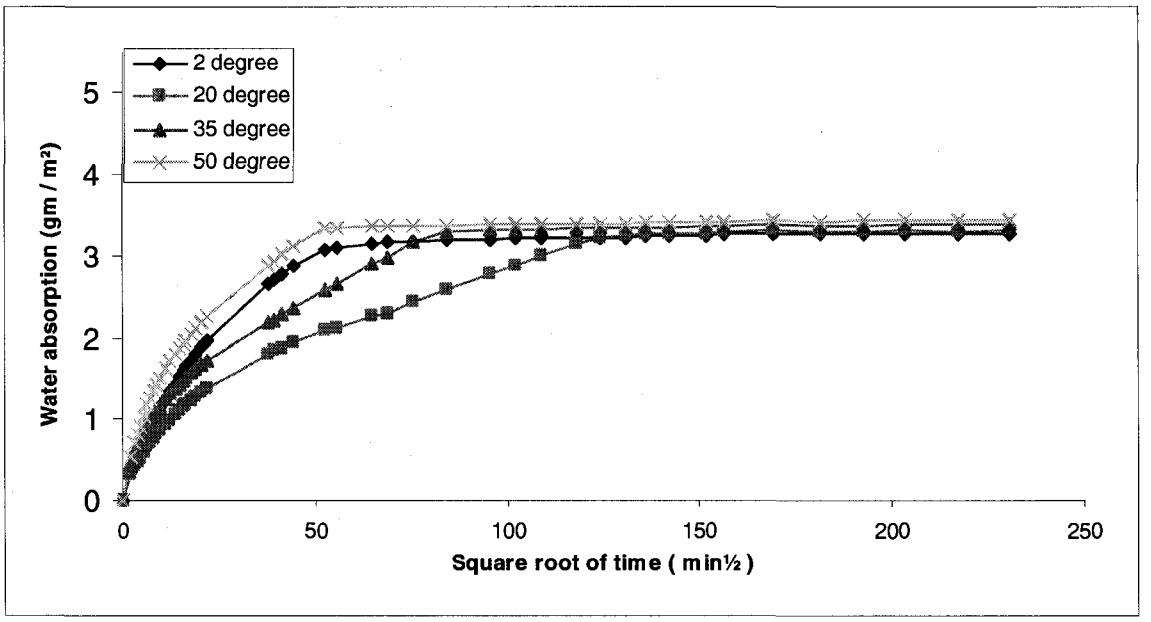

Figure 3-12 Capillary absorption of water by TS made from PCI-fibre with 2500 ppm of sulphate at different curing temperature

All of these factors contribute to the coarsening of the pore structure and thus producing higher CWA values. The TS samples cured at 20°C show lowest value of CWA for both sulphate concentrations. The lowest value of TS at 20°C is due to the filling of pores by the precipitation of hydration products and expansive minerals.

Figures 3.12 and 3.13 also show that the TS at 35°C has a CWA value higher than TS at 20°C. This may be due to the adsorption of sulphate by C-S-H gel so that less sulphate will be available for formation of ettringite and gypsum. In addition, the dissolution of ettringite at high curing temperatures can be another cause of increase.

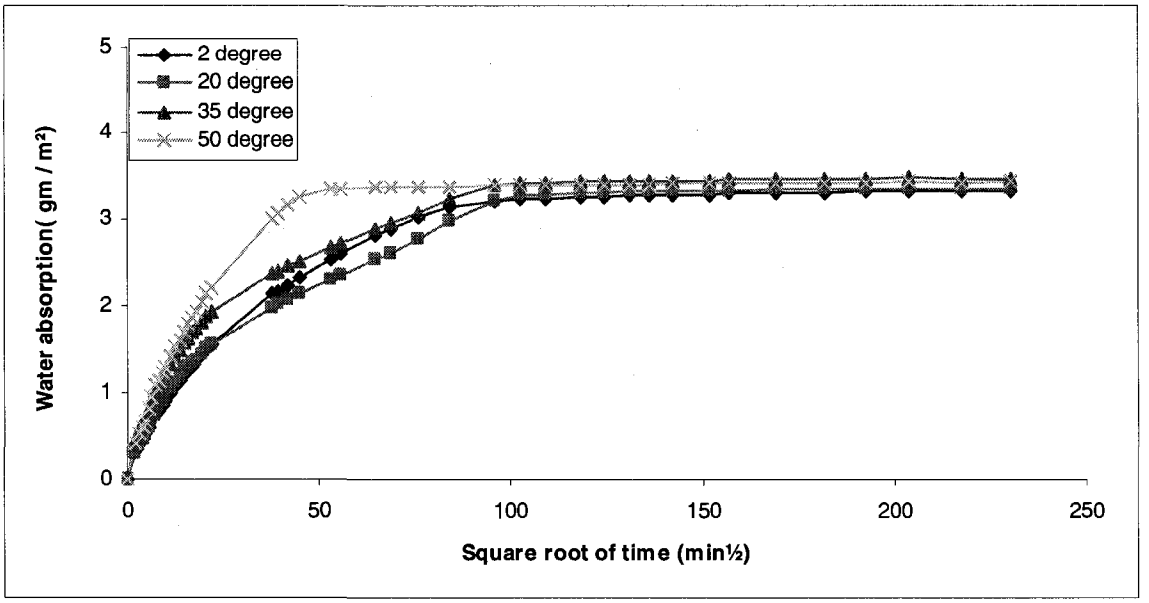

Figure 3-13 Capillary absorption of water by TS made from PCI-fibre with 5000 ppm of sulphate at different curing temperature

Figure 3.12 also illustrates that the TS at 2°C containing 2500 ppm of sulphate has a high value of CWA than 20°C and 35°C, but lower than 50°C.The higher value can be due to the presence of sulphate which inhibits the hydration of cement at low temperatures. In addition, unreactivity of slag at lower temperatures also causes higher value of CWA whereas the CWA value of 2 °C sample containing 5000 ppm (in Figure 3.13) shows a CWA value in between that of the 35°C and 20°C sample. TS cured at 2°C has a higher value of CWA than that of the 20°C sample because of the presence of high sulphate which prevents the hydration of cement at lower temperatures. The 5000 ppm shotcrete cured at 2°C has a lower CWA value than that of the 35°C sample and can be explained by the adsorption of sulphate which may form fewer amounts of expansive materials due to less available sulphate from the adsorption

phenomenon. The dissolution of ettringite at higher temperatures can be another possibility of increasing CWA value of TS cured at 35°C, reducing the ettringite phase in the cement matrix. Hence, the smaller presence of sulphate at 35°C due to the adsorption phenomenon and high presence of ettringite in the cement matrix of the 20°C TS, render this 2°C tailings sample to exhibit a CWA between those of the 20°C and 35°C samples.

Figure 3.14 illustrates the sorptivity of TS with 0 ppm, 2500 ppm and 5000 ppm of sulphate at temperatures 2°C, 20°C, 35°C and 50°C made from PCI- fibre. In this case, the TS with sulphate show higher value of sorptivity than without sulphate except at 20°C. At 2°C, the 2500 ppm sample shows higher value of sorptivity than the rest of the samples whereas the 5000 and 0 ppm samples have the same value of sorptivity. The higher value can be attributed to inhibition of hydration reaction of cement by the sulphate. The continuous precipitation of hydration products in the 0 ppm sample results in lower value of CWA. The 5000 ppm samples may have some expansive minerals so that it has the same value of CWA as the 0 ppm samples.

As the curing temperature increases to 20°C, the sorptivity of the 2500 ppm and 5000 ppm samples is lower than the 0 ppm samples. The lower value of sorptivity is due to the precipitation of expansive minerals and hydration products in the voids. The precipitation of additional expansive minerals renders these samples with a lower value of CWA.

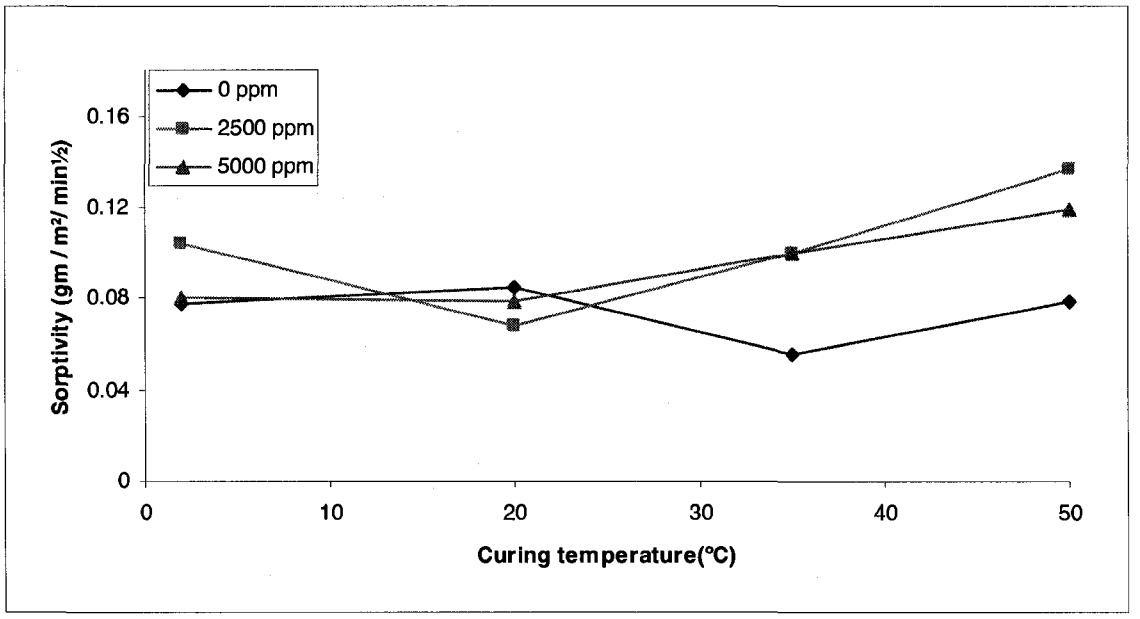

Figure 3-14 Sorptivity of TS made from PCI-fibre containing sulphate at different curing temperatures

The 2500 ppm and 5000 ppm samples show the same value of sorptivity at 35°C and this is higher than the sorptivity value of the 0 ppm TS sample at 35°C. The adsorption of sulphate by C-S-H gel and dissolution of ettringite by high temperatures can be the reason for high sorptivity of TS made from PCI-fibre at 35°C and 50°C (as mentioned above).

Figures 3.15, 3.16 and 3.17 present the comparison of the sorptivity of TS made from PCI, PCI-slag and PCI-fibre cured at different temperatures containing 0 ppm, 2500 ppm and 5000 ppm of sulphate respectively. Figure 3.15 shows that at 0 ppm of sulphate, the TS made from PCI-slag shows very low value of sorptivity in comparison to the TS made from other binders at almost all curing

temperatures with the exception of 50°C. This suggests that TS made from PCI-slag has a fine pore structure and thus, better durability properties.

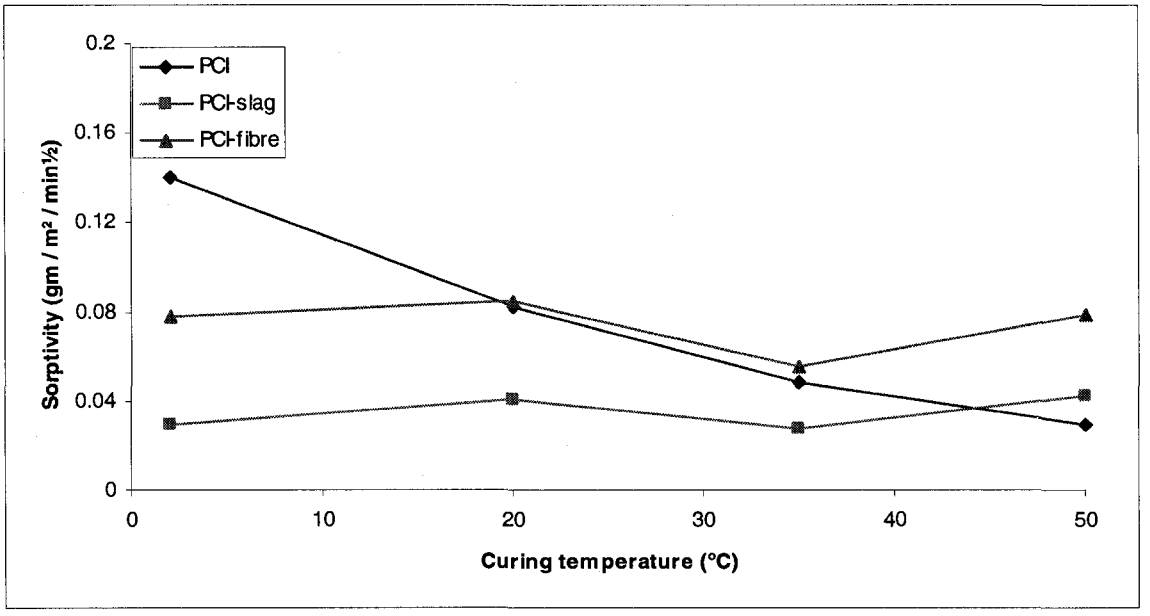

Figure 3-15 Sorptivity of TS with 0 ppm of sulphate made from different binders at different curing temperatures

The filler effects (Tasdemir, 2003) of slag due to fine particle size distribution also contribute to the refinement of the pores, resulting in the reduction of internal porosity. In addition to this filler effect, the reduction in the porosity is also due to the pozzolanic reaction (Akoz et al, 1995; Gopalan, 1996) which produces secondary C-S-H by consuming available CH and decreases the value of sorptivity by filling the micro pores of the cement matrix.

The previous study performed by Peiwei et al. (2007) illustrates that the volume of the pores in the case of blended cement is lowered. The same study

concluded that when the pozzolanic material is mixed with the normal cement, the pore radius larger than 100 nm is decreased due to the filling of pores by the fine slag particles.

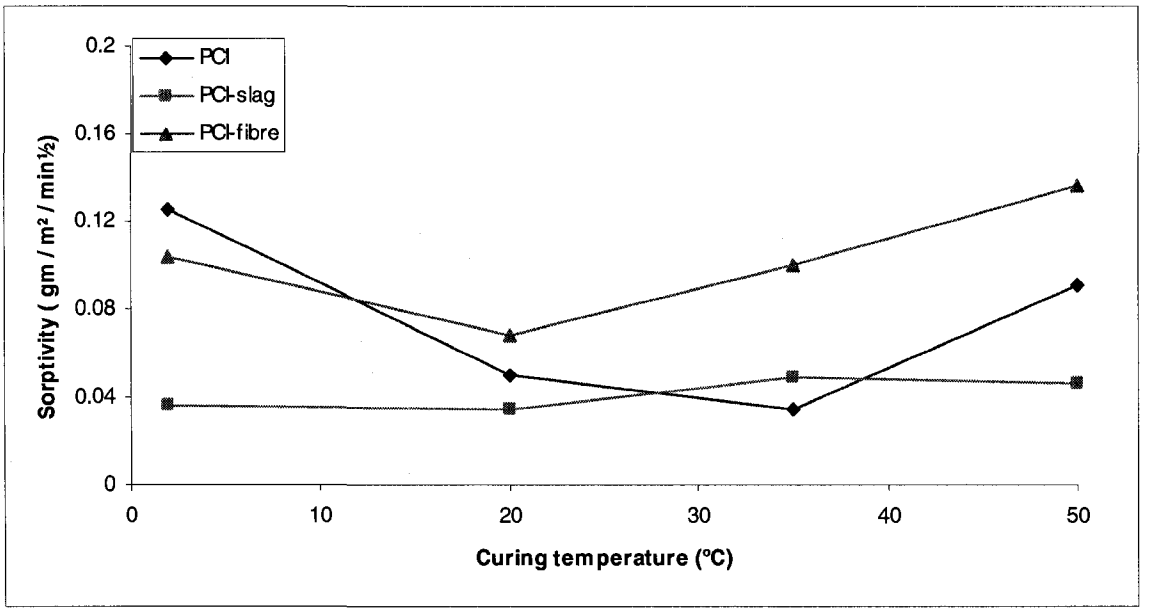

Figure 3-16 Sorptivity of TS with 2500 ppm of sulphate made from different binders at different temperatures

At 0 ppm of sulphate, the TS made from PCI-slag cured at 2°C shows lower value of sorptivity followed by TS made from PCI-fibre. The TS with PCI shows higher value of sorptivity at 2°C. The higher value can be due to the lack of the filler effect of slag. Another possible reason is the absence of secondary C-S-H (from the reaction of CH with slag) in the PCI TS.

The sorptivity of PCI and PCI-fibre has almost the same value at 20°C and 35°C. Figure 3.15 also shows that the PCI-slag has a lower value of sorptivity than that

of PCI and PCI-fibre at 35°C due to contribution of secondary C-S-H and filler effect of the slag. At 50°C, TS made from PCI-slag shows a higher value of sorptivity than at 35°C. This is due to the formation of hydration rims where the unhydrated slag grains were surrounded by rims of hydration products and will prevent the slag grain from further hydration (Escalante and Sharpe, 2001).

Figures 3.16 and 3.17 also show that the TS made from PCI-slag and containing 2500 ppm and 5000 ppm has lower value of sorptivity than those containing the same amount of sulphate. The lower value of CWA of TS made from PCI-slag can be due to the formation of secondary C-S-H from the pozzolanic reaction in the cement matrix. In addition, the filler effect of slag as explained earlier, can also contribute to the lower value of the CWA.

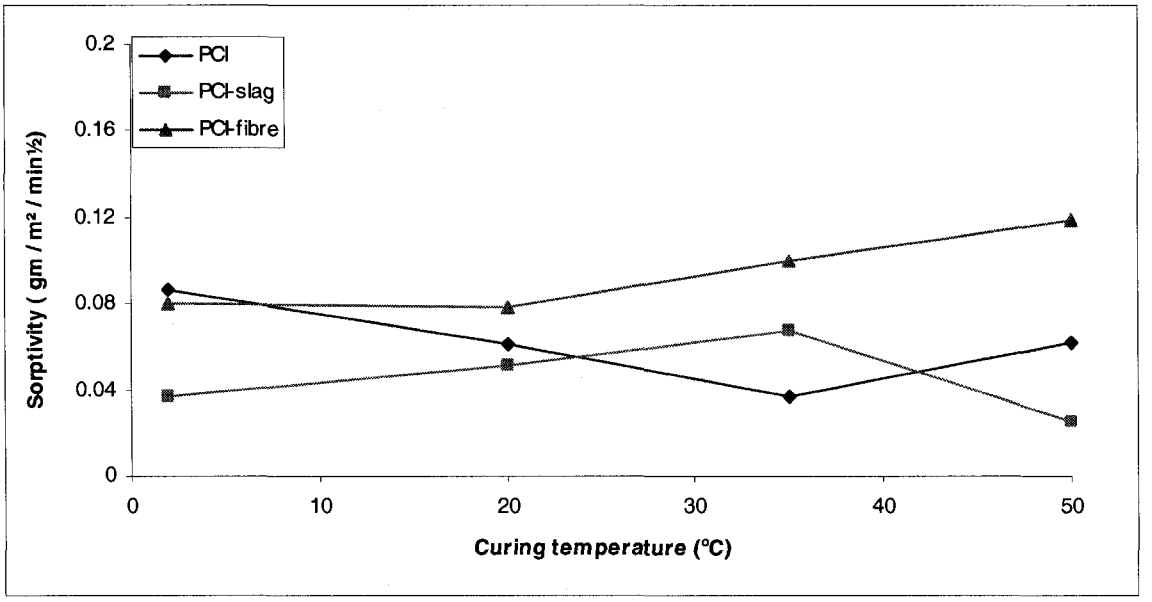

Figure 3-17 Sorptivity of TS with 5000 ppm of sulphate made from different binders at different temperatures

TS made from PCI cement with 2500 ppm and 5000 ppm of sulphate shows decrease in the value of sorptivity as the curing temperature increases from 2°C to 35°C, whereas its sorptivity increases when temperature increases from 35°C to 50°C.The continuous hydration of cement with curing temperature and precipitation of expansive minerals in the cement matrix are mainly responsible for the lowering of CWA in TS made from PCI. At 50°C, the combined effects of ettringite dissolution at high temperature and adsorption of sulphate may lead to the higher value of sorptivity for both samples made from PCI and PCI-fibre.

TS made from PCI-fibre containing 2500 ppm and 5000 ppm of sulphate in Figures 3.16 and 3.17 shows higher value of sorptivity than TS made from PCI and PCI-slag at almost at all curing temperatures. The higher value of sorptivity is due to the formation of weaker bonds formed between fibre and cement matrix. Fibres also aid in the formation of micro cracking (Aulia, 2002) which can be the main reason for the higher value of CWA of TS made from PCI-fibre. Furthermore, Hamou et al. (2005) indicated that CH can precipitate in the fibre. This can be also considered as an additional cause of the higher sorptivity. It makes CH unavailable to form gypsum, thus contributing to the coarsening of the pore structure of the fibre shotcrete.

3.6.2 Hydraulic conductivity of cemented paste tailings

3.6.2.1 Hydraulic conductivity of CPT-PCI

Figure 3.18 illustrates the HC of CPT samples made from PCI containing 0 ppm, 5000 ppm, 15000 ppm and 25000 ppm of sulphate cured at 2 °C, 20°C, 35°C and 50°C for 90 days. In general, the HC of CPT sample depends upon both temperature and sulphate concentration. The HC of all samples with or without sulphate decreases with increase of curing temperature except for 25000 ppm of sulphate at 50 °C.

The higher HC of samples at 2 °C is due to the formation of low amounts of hydration products in the cement matrix because of slow hydration reaction (Fall and Samb, 2006, Lothenbach et al, 2007) of cement due to lower curing temperatures. Figure 3.18 also illustrates that the 15000 ppm and 25000 ppm samples at 2 °C shows a higher HC than 0 ppm samples whereas the 5000 ppm sample has a lower HC at 2 °C in comparison to the 0 ppm sample. The higher HC is due to the presence of high sulphate concentration which significantly inhibits the hydration of cement at lower temperatures preventing the precipitation of hydration products in the pores of the cement matrix. This results in the formation of more porous structures. The lower HC of the 0 ppm sample than that of 15000 ppm and 25000 ppm samples is due to the continuous hydration of cement. The 5000 ppm sample has the lowest HC at 2 °C. This is from the precipitation of expansive minerals along with hydration products in the pores of the cement matrix.

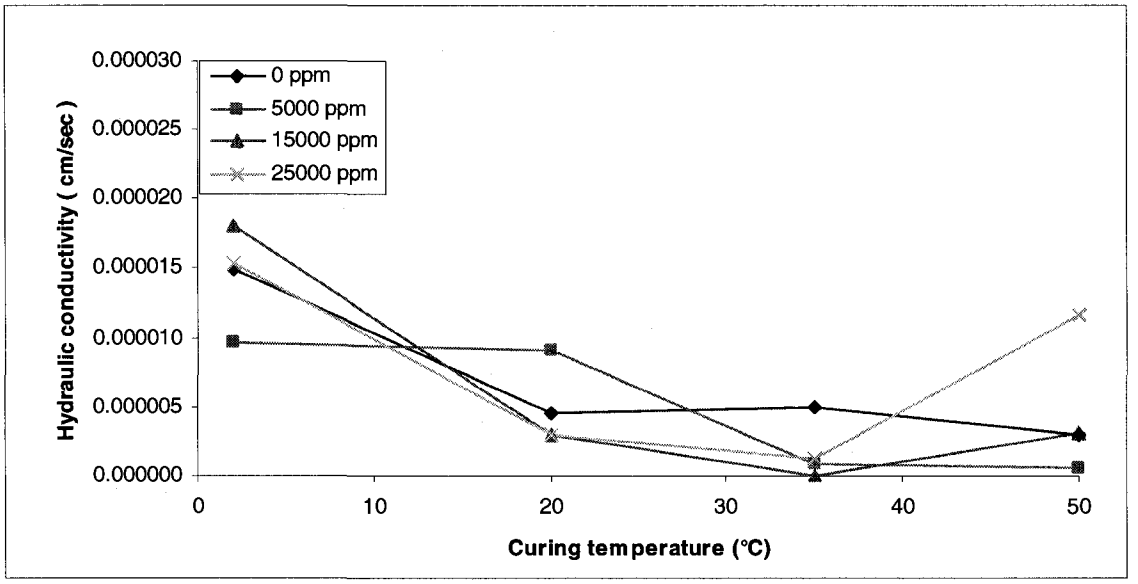

Figure 3-18 Hydraulic conductivity of CPT made from PCI with different sulphate contents at different curing temperatures

As the curing temperature approaches to 20 °C, the HC of all CPT samples decreases. This is because of the increase of curing temperature which significantly accelerates the hydration rate of the cement paste (Lothenbach et al, 2007).Fall and Samb (2007) also observed the increase in the formation of CH, C-S-H and calcite with increase of curing temperature by performing thermal analysis on hardened cemented paste of CPT. The XRD results of Chapter 2 also illustrated that the high curing temperature allows CPT samples to form high amounts of hydration products. These fill the voids and reduce the porosity so that the sample has low HC as higher curing temperatures.

At 20 °C, the HC of CPT samples with 15000 ppm and 25000 ppm sulphate is lower than the 0 ppm samples. This may be due to the fact that the 0 ppm sample does

not have any sulphate so only CH and C-S-H will form from the cement hydration. The 15000 ppm and 25000 ppm sample has enough sulphate in it so expansive minerals such as secondary ettringite and gypsum also precipitate in addition to this hydration products which lowers the HC of sulphated samples at 20 °C.

The HC of all samples cured at 35 °C is further lower than that of samples cured at 20 °C. Fall and Samb (2006) also observed the similar behaviour that the CPT cured at hot temperature (35 - 50 °C) seems to have finer pores and lower total porosity as well as lower void ratio than CPT samples cured at lower temperature. At 35 °C, the HC of sulphated samples are significantly lowers than 0 ppm samples. The formation of additional hydration products due to rise of temperature as well as precipitation of expansive minerals in the pores of the CPT lowers the HC of sulphated samples. The 15000 ppm samples cured at 35 °C has the lowest value of HC, which is found to be 1.4×10^{-8} cm/sec. In the same way, the HC of the 5000 ppm sample at 35 °C is almost the same as that of the 15000 ppm whereas the 25000 ppm sample has a slightly higher value of HC. The 25000 ppm sample has almost 1.6×10^{-6} cm/ sec. However, it still has a lower value of HC than the 0 ppm sample. The higher value can be due to the adsorption of sulphate by C-S-H gel and also the dissolution of ettringite at higher temperatures.

Figure 3.18 also illustrates that the CPT sample shows different types of behaviour at 50 °C. The 0 ppm samples show decrease in the value of HC as curing temperature increases to 50 °C. In contrary to this, CPT samples containing sulphate show increase in the value of HC. Among the three sulphate samples, the 25000

ppm sample shows the highest value of HC followed by the 15000 ppm and 5000 ppm samples. The higher value of HC of CPT samples containing sulphate can be due to the adsorption of sulphate by C-S-H gel at higher temperatures (Fu et al, 1994) as well as the destabilization of ettringite at high temperatures. This leads to the lower amounts of expansive minerals in the pores of the CPT thereby coarsening its pore structure. This assumption is also consistent with the XRD result of 25000 ppm sample at 20 °C and 50 °C in figures 2.11 and 2.14. The 25000 ppm sample at 20 °C shows presence of high amounts of expansive minerals due to availability of sulphate to react with CH. The XRD result of the 25000 ppm at 50 °C in figure 13 shows the presence of very low amounts of these minerals. The peak of CH is also high especially at 18 degrees 2-theta. The 25000 ppm sample at 20 °C in Figure 2.11 does not have any CH in 28.5 degrees 2-theta whereas the ones at 50 °C contain CH. Hence, these XRD show clearly that at higher curing temperatures, sulphate is adsorbed by C-S-H gel and/or ettringite is destabilized which results in high HC.

The adsorption of sulphate by C-S-H gel also depends upon the concentration of sulphate (Ramlochan et al, 2004). Higher concentration of sulphate in samples means higher amount of sulphate adsorbed by the C-S-H. The 5000 ppm and 15000 ppm samples have an HC that is lower than the 25000 ppm samples at 50 °C. This can be due to the lower percentage of sulphate so that lower amounts are absorbed in C-S-H gel.

3.6.2.2 Hydraulic conductivity of CPT-PCI slag

Figure 3.19 represents the hydraulic conductivity of CPT made from PCI-slag containing 0 ppm, 5000 ppm, 15000 ppm and 25000 ppm of sulphate cured at 2 °C, 20 °C, 35 °C and 50 °C for 90 days. In general, the HC of CPT samples made from PCI-slag decreases with increase of curing temperature with some exception at 50 °C.

At 2 °C, the CPT samples with 25000 ppm of sulphate shows a higher value of HC than that of the other samples. The 0 ppm, 5000 ppm and 15000 ppm samples have almost the same value of HC at 2 °C. The higher value of HC of the 25000 ppm sample is due to the presence of high amounts of sulphate which inhibit the hydration of cement (Fall and Benzaazoua, 2005).

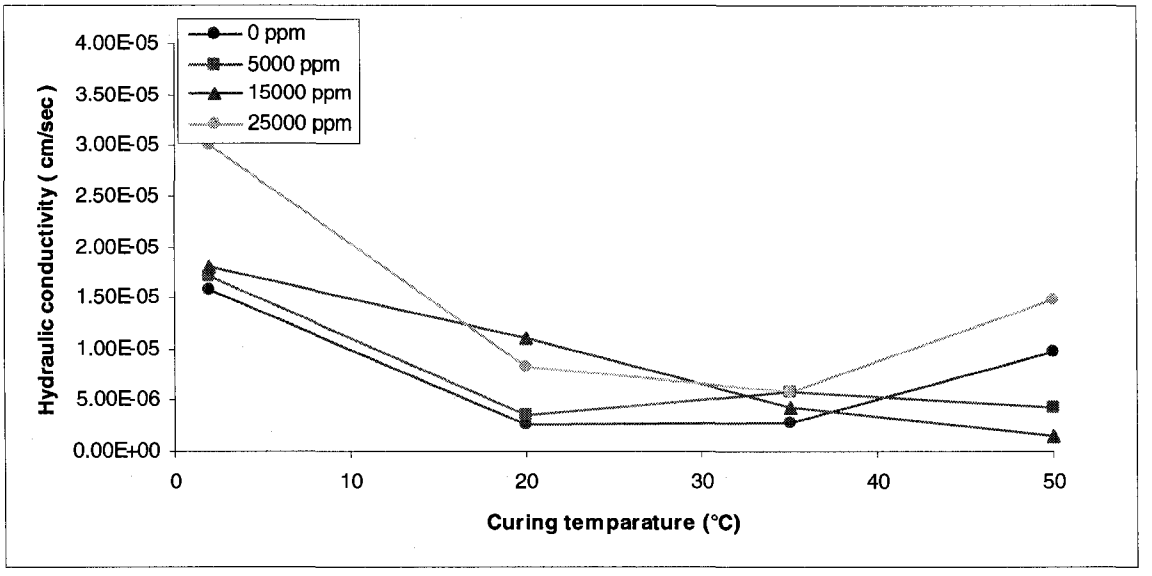

Figure 3-19 Hydraulic conductivity of CPT made from PCI-slag with different sulphate contents at different curing temperatures

The HC of all CPT samples with or without sulphate decreases when the curing temperature increases to 20 °C. Figure 3.19 also illustrates that at 20 °C, the CPT samples with sulphate has a higher HC than 0 ppm samples.

The higher HC of the 25000 ppm and 15000 ppm samples can be explained by the effect of conventional sulphate attack where the formation of secondary ettringite and gypsum is exerting pressure on the wall of the pore resulting in a higher value at 20 °C. The HC of 25000 ppm and 15000 ppm CPT samples shows decrease in value when temperature changes to 35 °C. This is due to the increase of hydration products as temperature increases. The higher value of HC of the 25000 ppm sample at 50 °C can be due to the adsorption of sulphate by C-S-H gel, the dissolution of ettringite by high temperatures and also the formation of hydration rims than can prevent the further hydration of some slag grains.

The 0 ppm sample made from PCI-slag does not contain any sulphate, but it has higher HC at 50 °C than the 15000 ppm and 5000 ppm samples. The higher HC is due to the formation of hydration rims at high curing temperatures preventing the further hydration of slag grains. The 5000 ppm and 15000 ppm samples at 50°C are still showing a lower value of HC in spite of the adsorption phenomenon by C-S-H gel. This can be due to the lower percentage of sulphate. Parts of the sulphate are available for the precipitation of secondary ettringite gypsum, and

the formation of secondary C-S-H from the pozzolanic reaction in the pores of the CPT system lower the HC.

3.7 Conclusions and recommendations

TS samples with 0 ppm, 2500 ppm and 5000 ppm of sulphate cured at 2 °C, 20 °C, 35 °C and 50 °C for 150 days made from PCI, PCI-slag and PCI-fibre are tested through the capillary adsorption test to study the fluid transport ability of the TS. This can give valuable information about the durability of sulphate or no sulphate bearing TS under various thermal loadings. The sorptivity of TS decreases with increase of curing temperature except at 50 °C. The adsorption phenomenon of sulphate and formation of hydration rims as well as the destabilization of some ettringite at higher temperatures makes the shotcrete samples more porous.

TS made from PCI-slag perform very well, showing very low fluid transportability in comparison to PCI and PCI-fibre in all curing temperature with or without sulphate. The filler effect due to smaller particles size and pozzolanic action of slag contribute positively to reduce the value of sorptivity of TS made from PCI-slag. This means that TS with PCI-slag will have higher durability properties due to lower oxidation potential of sulphide minerals. Hence, PCI-slag will be more environmentally friendly than other binders because of smaller potential for formation of AMD. The TS made from PCI-fibre shows higher value of sorptivity

than the rest of the TS. This means the TS with fibre is less durable and has more potential to form sulphate and thus reduce the service life of the structure.

HC tests are carried out on CPT samples with 0 ppm, 5000 ppm, 15000 ppm and 25000 ppm of sulphate made from PCI and PCI-slag cured at 2 °C, 20 °C, 35 °C and 50 °C for 90 days. It is observed that the HC of CPT depends upon temperature, sulphate, and also binder types. In general, HC of CPT decreases with increase of temperature except for the 25000 ppm at 50 °C. The HC of CPT samples is found to be influenced by binder type. CPT samples made from PCI-slag are found to be relatively more permeable than CPT made from PCI. This may be due to the higher amount of clinker phase in PCI cement than PCI-slag. In most of the temperatures, the sulphate present in the CPT system lowers the HC of the CPT samples made from PCI whereas sulphate behaves oppositely for PCI-slag.

Thus, samples with lower HC are less susceptible to the formation of AMD. The 25000 ppm samples at 50 °C show a high value of HC. The higher value of HC may be due to the adsorption of sulphate by C-S-H, and the destabilization of ettringite at high temperature can produce a coarser pore structure. The mechanism of adsorption of sulphate by C-S-H still needs to be investigated in detail. There is scarce information regarding this mechanism of coarsening of pore structure in cementitious materials containing high amounts of sulphate at

high curing temperatures, so further studies are needed to investigate this behavior.

4 Chapter 4: Reactivity of paste tailing systems under various thermal loadings

4.1 Abstract

Oxygen consumption (OC) tests are performed to study the reactivity of CPT systems (CPT and TS). CPT are made from PCI and PCI-slag with 5%, 15%, 45% of pyrite cured for 2°C, 20°C, 35°C and 50°C up to 56 days of curing time. TS is also made with PCI, PCI-slag and PCI-fibre with 5% and 15% of pyrite cured at 2°C, 20°C, 35°C and 50°C for 56 days. Uncemented paste tailings are prepared with 5%, 15% and 45% of pyrite with 50%, 75%, 85% and 95% degrees of saturation and cured for 7 days. The OC test results show that the reactivity depends upon both binder type and amount of pyrite in the case of CPT and TS. The reactivity of CPT is found to decrease with increase of curing time. PCI-slag shows high reactivity at the 7 day curing time whereas its reactivity decreases and even lower than the reactivity of CPT made from PCI cement at 28 and 56 days of curing time. The reactivity of CPT cured at high temperatures is found to be higher than lower temperatures. The uncemented paste tailings also show dependence of reactivity on both pyrite content and degree of saturation. The uncemented paste tailings with degree of saturation higher than 75% in an undrained condition do not show any reactivity at 7 days of curing time.

4.2 Introduction

The underground storage of tailing as CPT reduces the amount of tailings that have to manage on the earth surface up to 60 % (Fall and Samb, 2007). The underground storage of the mining waste as CPT has both environmental as well as economical benefits (Fall and Samb, 2006). In addition, another approach that uses tailings as an aggregate in the TS also reduces a considerable amount of tailings on the earth surface. The tailings which are used in CPT and TS have various chemical compositions depending upon the composition of the ores that are mined. Most of the heavy metal ores are rich in ferrous sulphide minerals (Elberling et al, 1994). However, the associated disadvantage is the potential of formation of AMD with various chemical and biological reactions (Benzaazoua et al, 2002; Kesimal et al, 2005; Ritcey, 2005). This is the natural phenomenon of oxidation of sulphide mineral in tailings when exposed to atmospheric oxygen in the presence of water. After oxidation, these tailings contain acid with low pH and dissolve many base metals, such as arsenic, selenium etc (Ritcey, 2005). This leachate is harmful from an environmental point of view because it can contaminate ground water as well as deteriorate the surrounding ecosystem (Ouellet et al, 2003).

Furthermore, the oxidation of the sulphide minerals present in the CPT and TS can produce sulphate ions within the aforementioned materials. These ions can deteriote the CPT and TS through sulphate attack. In the same way, the sulphide present in the CPT also has potential to develop AMD. It needs to be evaluated

in order to be used in CPT and shotcrete. There is scarce information available about the reactivity of paste tailings systems in the literature. The environmental impact by incorporating these sulphide bearing minerals in CPT and TS should be investigated before placing these tailings underground in the mining industries.

Chapter 2 already dealt with the effect of sulphate on the mechanical properties of CPT and TS. The high presence of sulphate within the CPT and TS system can reduce the strength, thereby resulting in deterioration. Among various sources of sulphate, self oxidation of pyrite minerals within the tailings systems in the presence of moisture and oxygen is one of the contributing sources. The oxidation of tailings is strongly dependent on the amount of oxygen and water available in the tailings materials. Higher oxygen will mean higher reactivity of tailings. In CPT systems, the presence of binder in the cement matrix reduces the internal porosity due to precipitation of its hydration products (Fall et al. 2004). In addition, the presence of high quantities of water within CPT systems limits oxygen availability because of the low diffusion of oxygen in water.

Water behaves like a barrier for the ingress of oxygen into the CPT system. For these reasons, the reactivity of tailings in the CPT is mostly considered as low. However, it should be mentioned that only few studies are implemented on the reactivity of CPT until now. This means there is a lack of fundamental knowledge about the reactivity of tailings on CPT systems. Previous studies (Fall et al, 2004;

Ouellet et al, 2003) on reactivity of CPT already observed that reactivity depends upon both binder as well as pyrite content. They concluded that the reactivity of tailings will be significantly reduced by keeping them in the CPT. The same studies also illustrated that the reactivity of uncemented paste tailings depend upon the percentage of pyrite and degree of saturation. However, all were carried out in room temperature. The oxidation of sulphide is itself a chemical reaction which is significantly influenced by temperature. Furthermore, every mine and backfill structure has its unique temperature (Fall and Samb, 2006). As well, the depletion of ores on the earth surface means that the mining activities will go deeper and deeper for each coming day and this means that temperature is a vital component due to geothermal gradient. However, the effect of temperature on the reactivity of CPT is still unknown. In addition, the aforementioned previous studies were performed on CPT made of natural tailings. These tailings contain various chemical elements and buffer minerals that can significantly affect the reactivity of the sulphide minerals with CPT. In other words; the question how reactive is pyrite in CPT has not been answered. No studies are conducted on the reactivity of TS at room temperature, or subjected to various thermal loading conditions. Hence, the objective of this study is to obtain detailed information about the reactivity of CPT systems containing different amounts of pyrite and cured at different curing days with different binders.

After this introduction, materials and methods will be discussed, followed by specimen preparation. The experimental results are presented and discussed in results and discussion. Finally, the conclusion of the research is drawn at the end.

4.3 Materials and methods

4.3.1 Materials

4.3.1.1 Binder used

The description of the binders used in this study is already given in 2.2.3.1.1 and 2.3.3.1.1 for CPT and tailings SC respectively.

4.3.1.2 Water

The details of water used for this study is given in 2.3.3.1.2

4.3.1.3 Tailings

The details of tailing used for this study is given in 2.3.3.1.3

4.3.1.4 Pyrite

Commercially available pyrite (FeS_2) with molecular weight 119.98 in powder form is used in this study. The size of the pyrite particles is close to that of pyrite minerals commonly found in natural tailings. The physical properties of the pyrite are given in Table 4.1. The percentage of pyrite used in the CPT system and uncemented paste tailings is shown in Table 4.2.

Table 4-1 Physical properties of the pyrite

Bulk density	Density @ 20 °C	Melting point	pH	Sp. Gravity
2.2 – 2.5 gm/cm3	4.7 gm/cm3	1193°C	4 - 6	4.6

4.4 Specimen preparation

Required amounts of tailings and binder were mixed in a dry container. Calculated amounts of pyrite were added in order to obtain 5%, 15% and 45% of pyrite content in the mix. The materials were again mixed until a homogeneous color was obtained. Required amounts of distilled water was added and mixed together for a homogeneous paste. The mixture was then poured into plastic cylinders of 10 cm in diameter and 20 cm in height. The cylinders were manually vibrated to remove any air while pouring the paste. They were then covered with a plastic lid to prevent the evaporation of water. Then they were placed into an environmental chamber with controlled temperatures of 2 °C, 20 °C, 35 °C and 50 °C. For uncemented paste tailings, the required amount of water was added in the dry mix to obtain saturation degrees of 50%, 75%, 85% and 95%. Tables 4.2, 4.3 and 4.4 show the different combinations of samples used in this study. Altogether, 36 large samples were made and tested.

Table 4-2 Different ingredients used in CPT

Binder	Binder ratio	% of binder	% of pyrite	Curing temperature(°C)	Testing temperature(°C)
PCI	-	4.5	5, 15, 45	20	20
PCI	-	4.5	45	20	2, 35, 50
PCI	-	4.5	45	2, 35, 50	20
PCI+Slag	50/50	4.5	5, 15, 45	20	20
PCI+ Slag	50/50	4.5	45	2, 35, 50	20

Table 4-3 Different ingredients used in tailings SC

Binder	Binder ratio	% of binder	% of pyrite	Curing temperature(°C)	Testing temperature(°C)
PCI	-	22	5,15	20	20
PCI	-	22	15	35	20
PCI+Slag	50/50	22	5,15	20	20
PCI+Slag	50/50	22	15	35	20
PCI+ Fibre	-	22	5,15	20	20
PCI+Fibre	-	22	15	35	20

Table 4-4 Different recipes ingredients in uncemented paste tailings

Binder	Degree of saturation	% of pyrite	Curing temperature (°C)	Testing temperature (°C)
UCP	95	5,15,45	20	20
UCP	85	5,15,45	20	20
UCP	75	5,15,45	20	20
UCP	50	5,15,45	20	20

4.5 Testing procedure

4.5.1 Oxygen consumption tests

An OC test is an alternative method purposed by Elberling et al. (1994) to determine the oxidation rate by measuring the depletion of oxygen concentration with respect to time in a closed container covering the sulphide minerals. The depletion is due to diffusion of oxygen and oxygen used by sulphide minerals for oxidation (Ouellet et al, 2003). The main assumption behind this test is that the steady state condition ($\delta c / \delta t = 0$) will be maintained from beginning to the end of the test. Elberling and Nicholson (1996) purposed to monitor the oxygen concentration in a closed chamber containing an oxygen sensor for every 300 seconds to over 6000 seconds. The OC test was carried out in the lab by digging a 2 cm oxygen chamber in the cylinder before the beginning of the test. A special

type of oxygen sensor GC33-200 manufactured by GC industries California (Elberling and Nicholson, 1996) was used to measure the oxygen concentration. This oxygen sensor is connected to the voltmeter and the voltage thus produced is directly proportional to the partial pressure of oxygen in the gas phase (Ouellet et al, 2003). To start the test, the oxygen sensor was carefully fixed inside the cylinder space above the reactive materials and covered with the lid of the cylinder. The lid was made airtight to maintain a steady state condition. The voltage produced by the voltmeter was recorded at every 5 minutes up to 2 hours. Figure 4.1 shows the arrangement used to carry out the OC test.

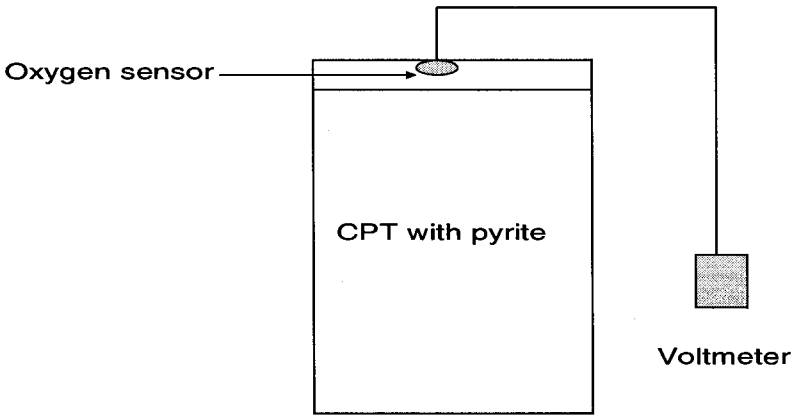

Figure 4-1 Experimental set up for oxygen consumption test

4.6 Results and discussions

4.6.1 Reactivity of PCI-CPT

Figures 4.2, 4.3, 4.4 and 4.5 present the OC of the CPT sample made from PCI containing 5%, 15% and 45% of pyrite cured at 20 ° C for 7, 14, 28 and 56 days respectively. In general, all of these figures illustrate that the OC of CPT made from PCI depend upon the pyrite content. The CPT samples with 45% pyrite show the highest value of OC whereas 5% pyrite shows the lowest value of OC. The same type of behavior was also observed by Fall et al. (2004) and Ouellet et al. (2003).

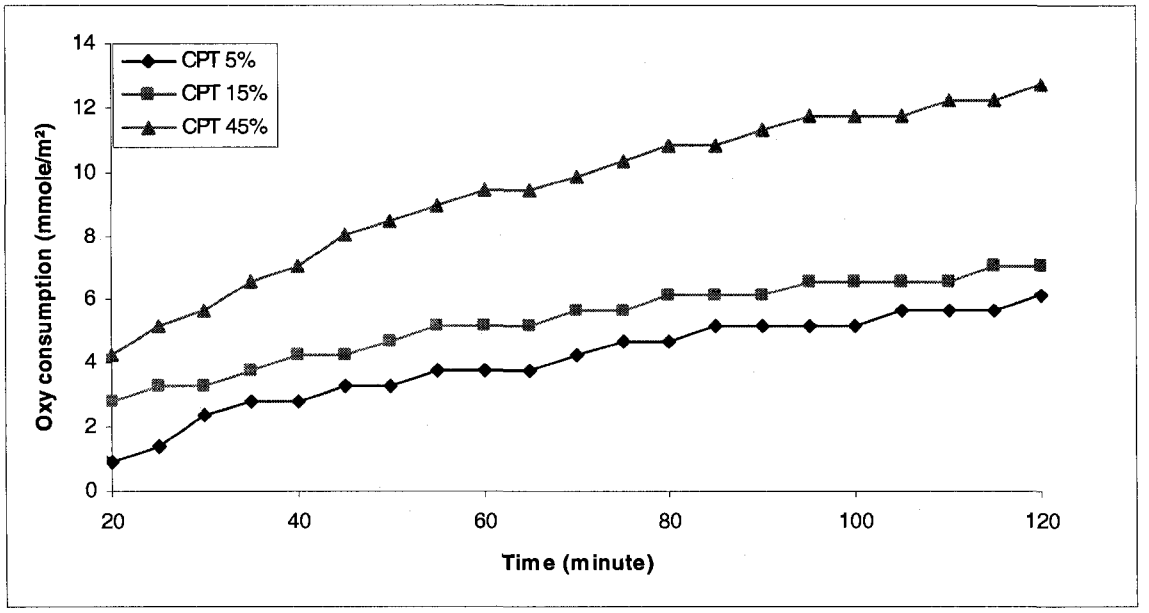

Figure 4-2 OC by CPT made from PCI with different percentages of pyrite at 20 ° C cured for 7 days

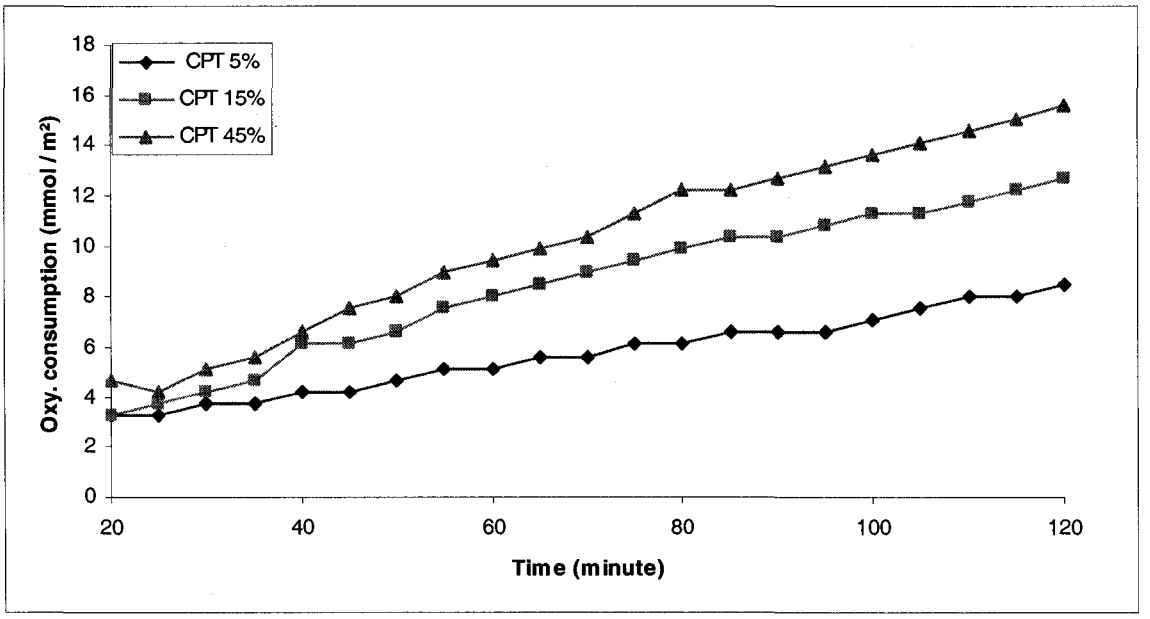

Figure 4-3 OC by CPT made from PCI with different percentages of pyrite at 20° C cured for 14 days

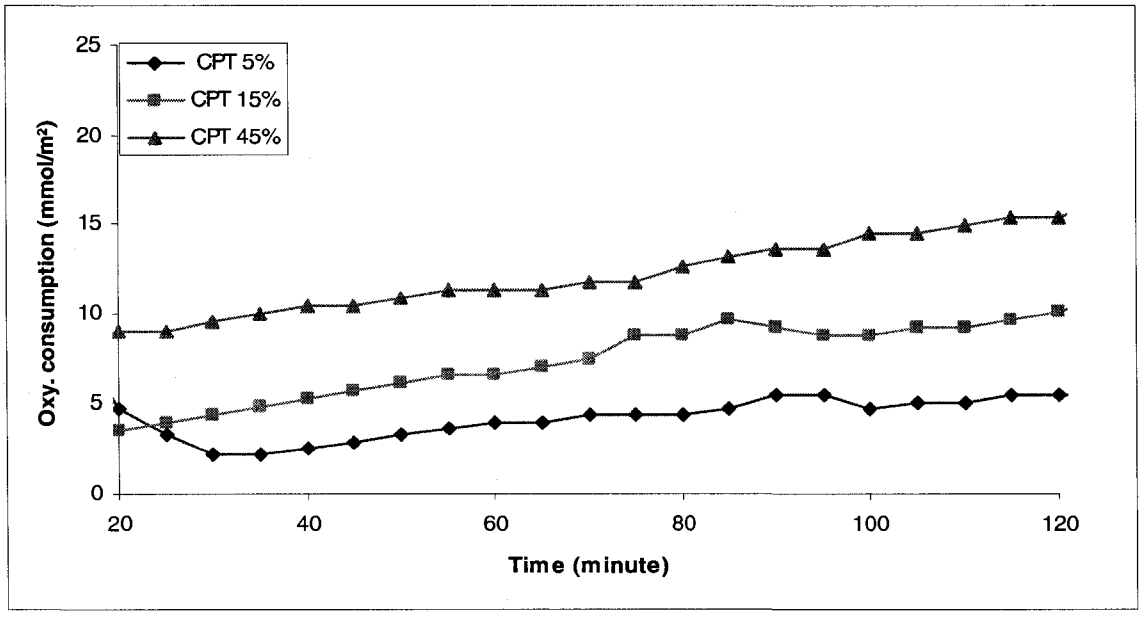

Figure 4-4 OC by CPT made from PCI with different percentages of pyrite at 20 ° C cured for 28 days

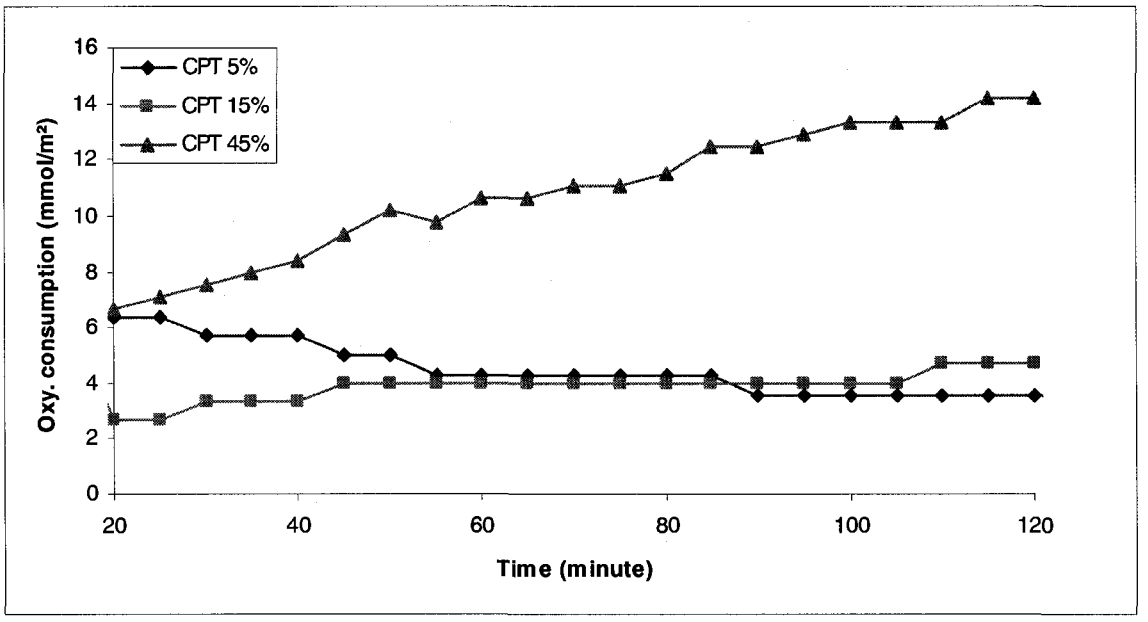

Figure 4-5 OC by CPT made from PCI with different percentages of pyrite at 20 ° C cured for 56 days

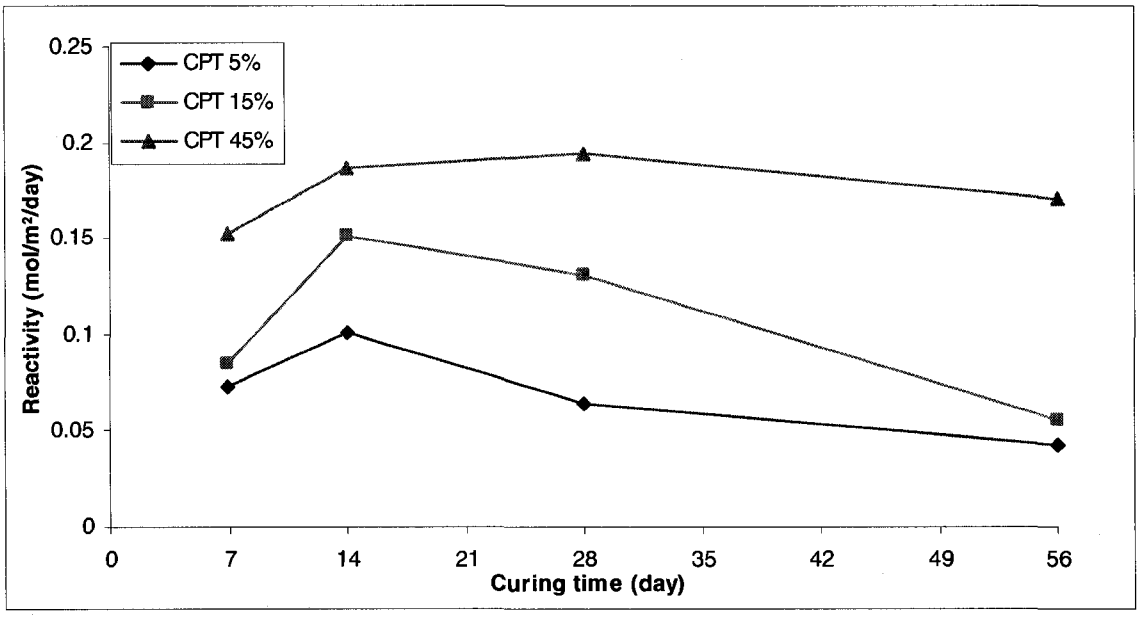

Figure 4-6 Reactivity of CPT made from PCI with different percentages of pyrite at 20° C cured for various curing times

Figure 4.6 shows the reactivity of CPT made from PCI containing different amounts of pyrite with different curing days. The reactivity also depends upon the pyrite content. The CPT with high amounts of pyrite shows highest reactivity whereas low amounts of pyrite have low reactivity. Figure 4.6 also shows that at 7 days, CPT has a low OC rate whereas it increases for the14 days of curing time. The lower value of OC rate of all CPT at 7 days may be due to the higher degree of saturation of CPT. As curing time increases to 14 days, all CPT samples show higher values of OC than the 7 days. This may be due to the self desiccation of the CPT sample (Nasir and Fall, 2008). After 14 days of curing time, the CPT samples with 5% and 15% of pyrite are showing smaller amounts of OC. This can be due to the precipitation of hydration products in the pores of the CPT which fills the voids and reduces the diffusion of oxygen. The CPT with 5% and 15% of pyrite have very a low OC rate at 56 days of curing time due to the precipitation of more hydration products.

The CPT sample with 45% pyrite at 28 days shows a slightly higher value of OC than 14 days. It shows a gradual decrease of the OC rate after 28 days of curing time. The gradual decrease of the OC rate beyond 28 days can be due to the continuous precipitation of hydration products in the cement matrix. As it has a high percentage of pyrite, CPT with 45 % pyrite does not follow the same trend of decrease in OC rate as 5 % and 15% pyrite.

Figure 4.7 illustrates the OC of CPT-PCI containing 45% of pyrite cured at 20 ° C and tested at 2°C and 20°C for different curing days to observe the variation in OC due to the effect of temperature. The samples were kept in an environmental chamber with required testing temperature 2 hours before the experiment in order to stabilize them. After testing, the samples were again placed back to the original environment chamber maintained at 20 ° C for further curing.

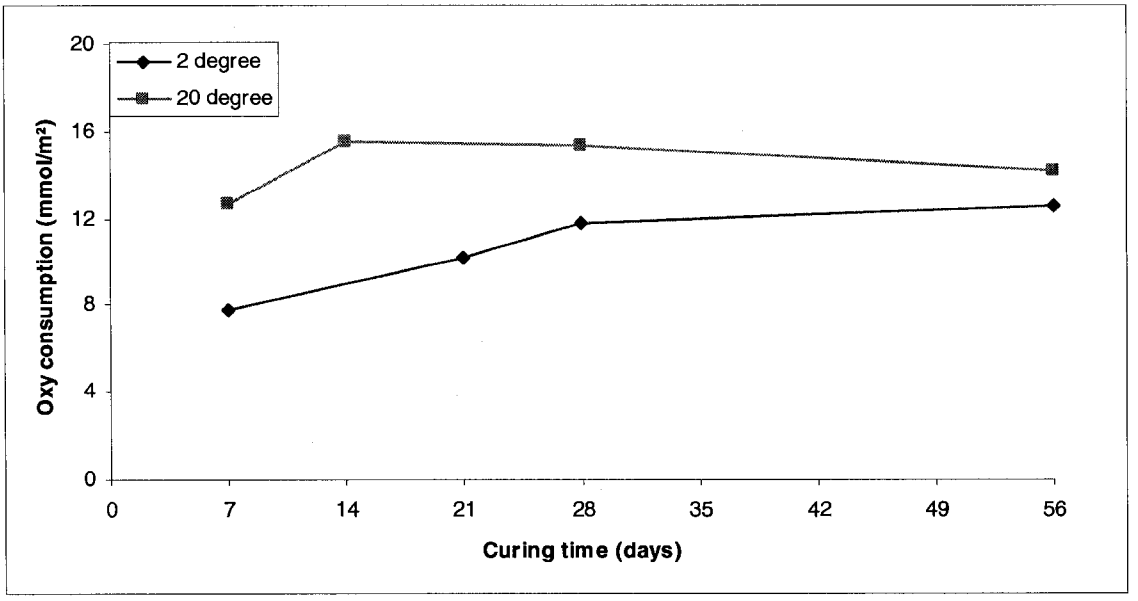

Figure 4-7 OC by CPT-PCI with 45% of pyrite after 120 minutes of testing, cured at 20° C and tested at different temperatures for different curing days

This result shows that even if the samples have the same amount of pyrites and cured at the same temperature, the OC value will be affected by the testing temperature.

Figure 4.8 represents the OC results of PCI-CPT containing 45% pyrite cured at 2 ° C, 20 ° C, 35 ° C and 50 ° C and tested at 20 ° C to observe the effect of the curing temperature. As in Figure 4.7, the samples cured at different curing temperatures are kept in the environmental chamber, maintained at 20 ° C for 2 hours before the OC test to stabilize the samples.

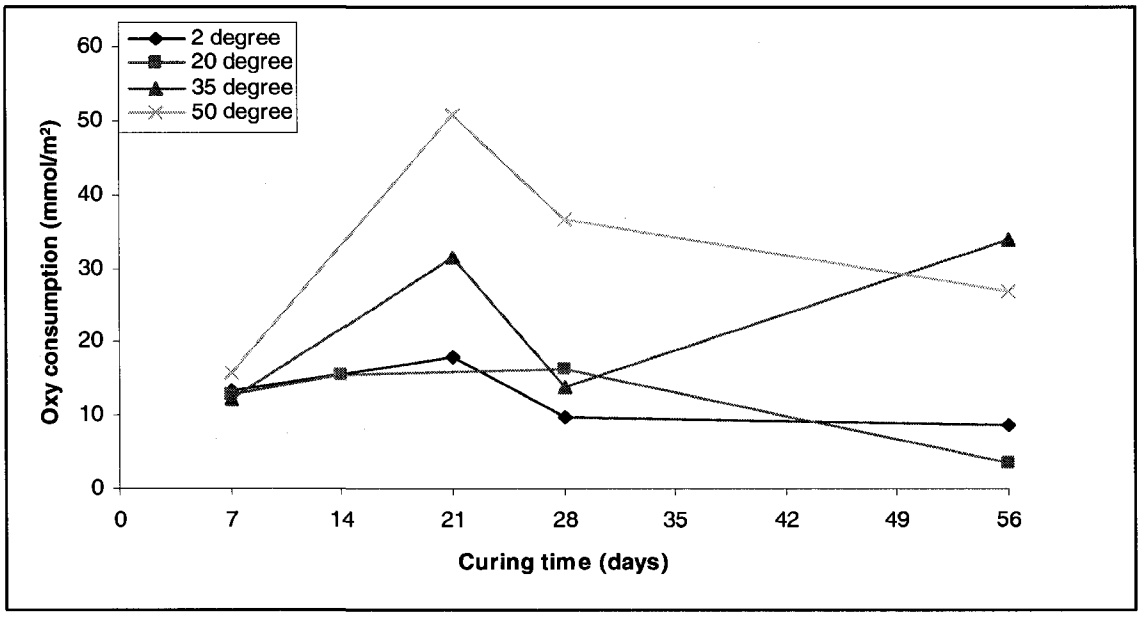

Figure 4-8 OC by CPT-PCI with 45% of pyrite after 120 minutes of testing, cured at different temperatures and tested at 20 ° C for different curing days

Figure 4.8 shows that the reactivity of the PCI-CPT sample containing 45% of pyrite is significantly affected by curing temperature. In general, it is observed that the reactivity of CPT increases with increase of curing temperature and the reactivity mostly decreases with increase of curing time except for those cured at 35 ° C at 56 days. At 7 days, almost all of the samples cured at different

temperatures show almost the same value of OC. At 21 days, the OC of all samples increases with increase of curing temperature. The increase of reactivity with higher curing temperatures can be explained by the fact that a higher curing temperature leads to higher self dessication of the CPT, thus lower degree of saturation of the CPT. Lower degree of saturation is linked with higher oxygen diffusion.

At 21 days, the CPT sample cured at 50 ° C shows 51 mmol consumption of oxygen per square meter after 120 minutes of testing. In the same way, the CPT samples cured at 35 ° C and 2 ° C consumed 32 mmol and 18 mmol of oxygen per square meter after 120 minutes of the testing. At 28 days, the PCI-CPT samples containing 45% of pyrite cured at different temperatures show decrease in the value of OC in comparison to 21 days. This can be due to the formation of additional hydration products which fill the pores thereby reducing the diffusion of oxygen. Furtermore, after 21 days the saturation degree of CPT remains almost constant. The PCI-CPT samples cured for 56 days show almost the same trend of increase of reactivity with increase of curing temperature except for CPT samples at 35 ° C. The reactivity at 56 day CPT samples cured at 2 ° C, 20 ° C and 50 ° C is lower than the reactivity of the same samples cured at 28 days which can be due to precipitation of additional hydration products in the pores of the cement matrix as explained earlier. Formation of such hydration products will reduce the diffusion of oxygen through the samples.

4.6.2 Reactivity of PCI- Slag CPT

Figures 4.9, 4.10, 4.11 and 4.12 illustrate the OC results of CPT made from PCI-slag containing 5%, 15%, 45% of pyrite at 20 ° C cured for 7, 21, 28, and 56 days respectively. These results also illustrate that the OC by CPT made from PCI-slag depends upon the percentage of pyrites. CPT with 45% of pyrite shows the highest value of OC for all curing days whereas CPT with 5% pyrite has the lowest value of OC. Since OC includes both oxygen used for the oxidation of pyrite and diffusion (Elberling and Nicholson, 1996), hence, more oxygen will be needed to oxidize higher amounts of pyrite. This can be the main reason for higher OC with higher percentages of pyrite in CPT systems.

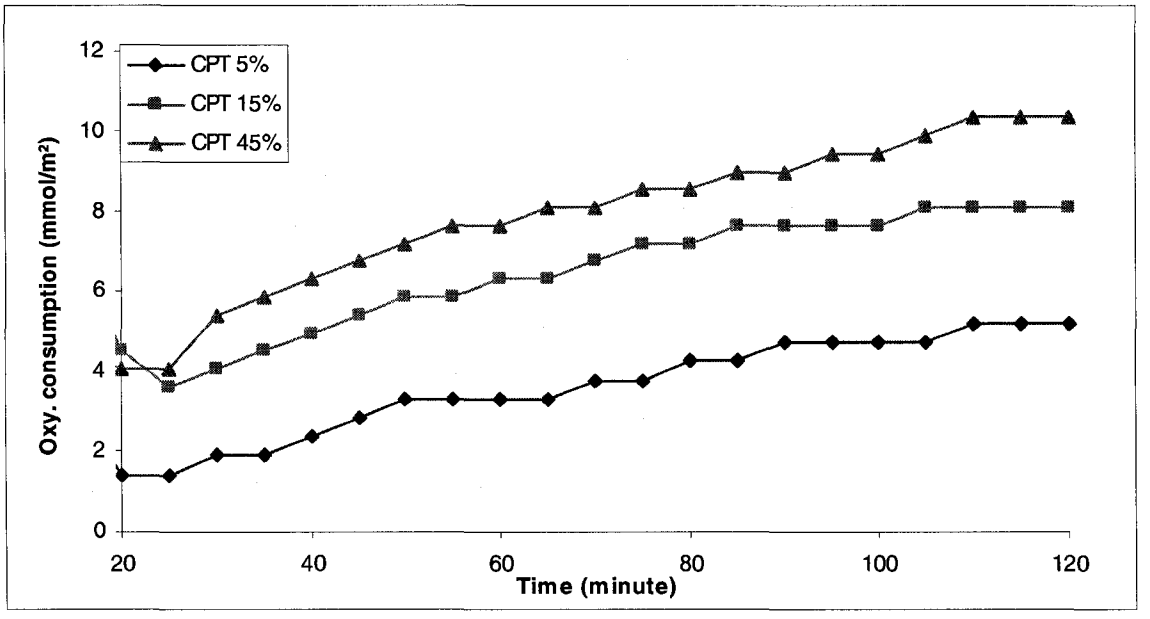

Figure 4-9 OC by CPT made from PCI-Slag with different percentages of pyrite at 20 ° C cured for 7 days

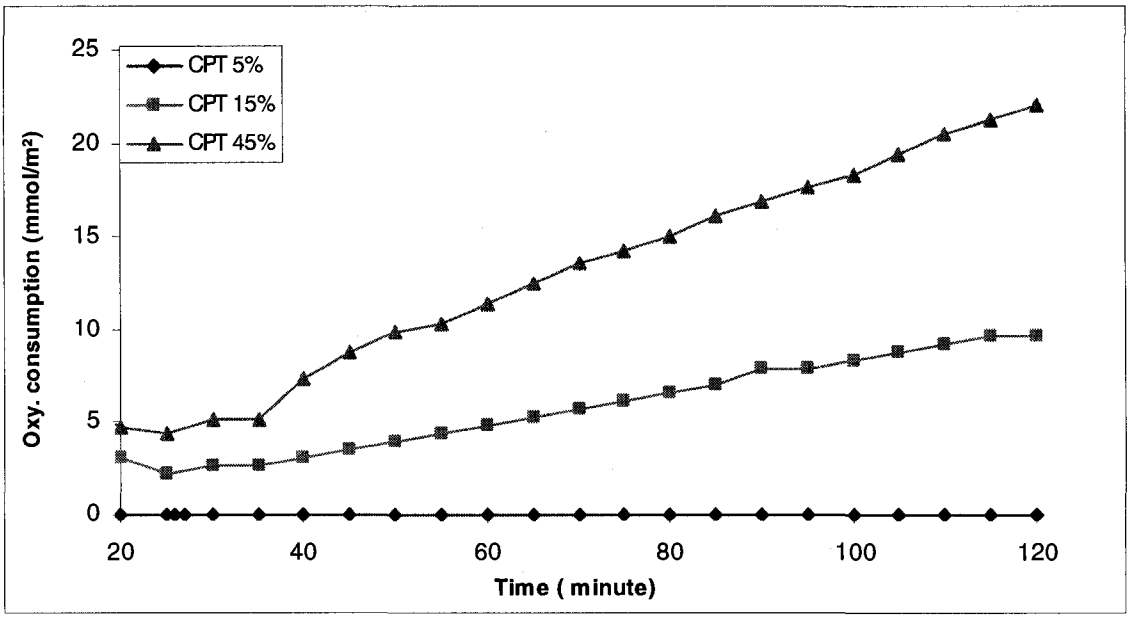

Figure 4-10 OC by CPT made from PCI-slag with different percentages of pyrite at 20 ° C cured for 21 days

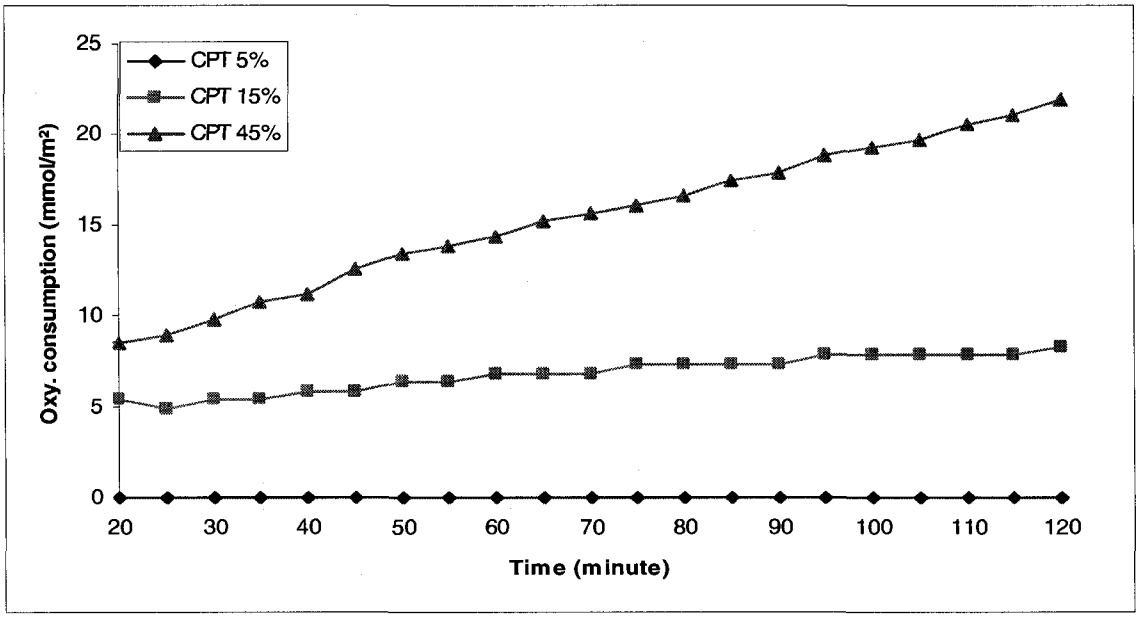

Figure 4-11 OC by CPT made from PCI-slag with different percentages of pyrite at 20 ° C cured for 28 days

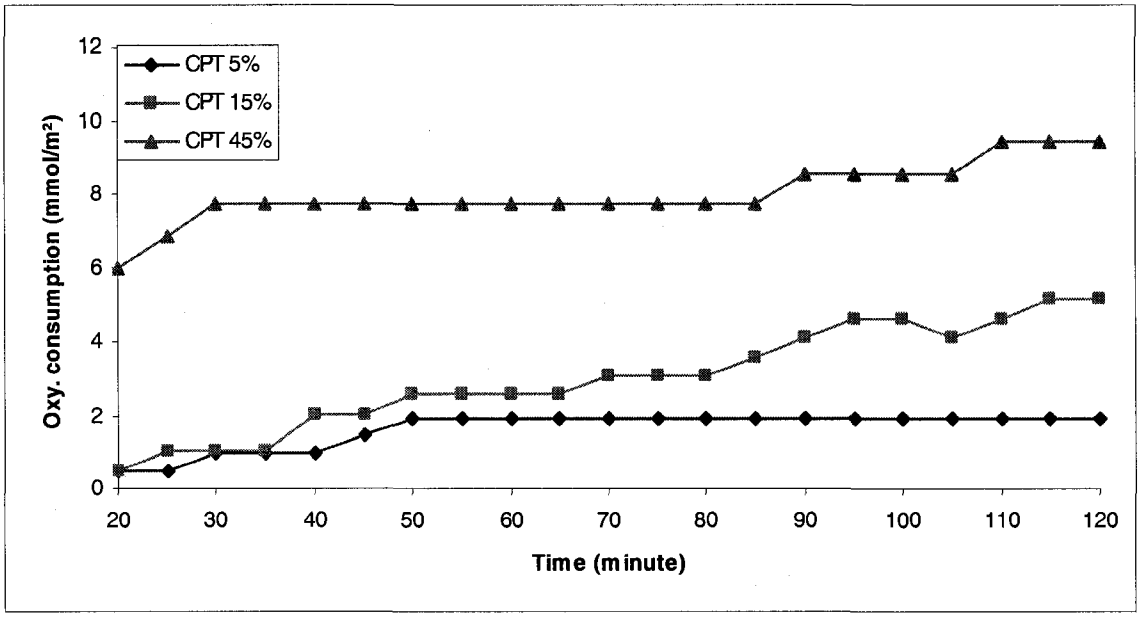

Figure 4-12 OC by CPT made from PCI-slag with different percentages of pyrite at 20 ° C cured for 56 days

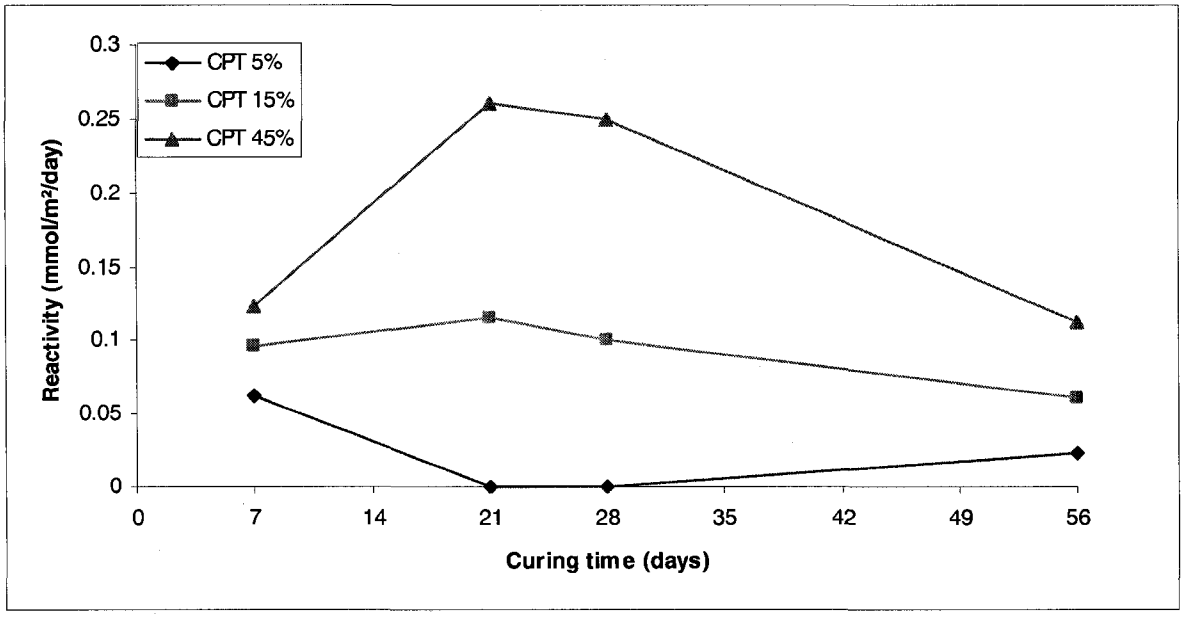

Figure 4-13 Reactivity of CPT made from PCI-slag with different percentages of pyrite at 20 ° C

The CPT with 5% of pyrite at 21 and 28 days shows no consumption of oxygen, but at 56 days, the samples show some OC.

Figure 4.13 shows the reactivity of CPT made from PCI-slag containing different percentages of pyrite for different curing days. The results show that the reactivity of CPT with 45% and 15% pyrite increases from 7 to 21 days of curing. The lower reactivity at 7 days can be explained by the high initial saturation degree (around 97%) of CPT. However, as the curing days increase, CPT show higher reactivity. This is due to the self-desiccation of the CPT materials. The reactivity of the CPT again decreases after 21 days of curing. It shows a greater decline in reactivity beyond 28 days. The decrease is due to the continuous precipitation of hydration products in the voids of the cement matrix which fills the voids and reduces the diffusion of oxygen through it. Due to lower diffusion, the reactivity decreases at advanced days of curing.

The CPT sample made from PCI-slag with 5% of pyrite as shown in Figure 4.13 shows no consumption of oxygen at 21 and 28 days due to very low percentages of pyrite. As explained earlier, this can be due to the precipitation of hydration products in the cement matrix and lower amounts of pyrite present in the CPT system which reduces diffusion as well as oxygen required for oxidation.

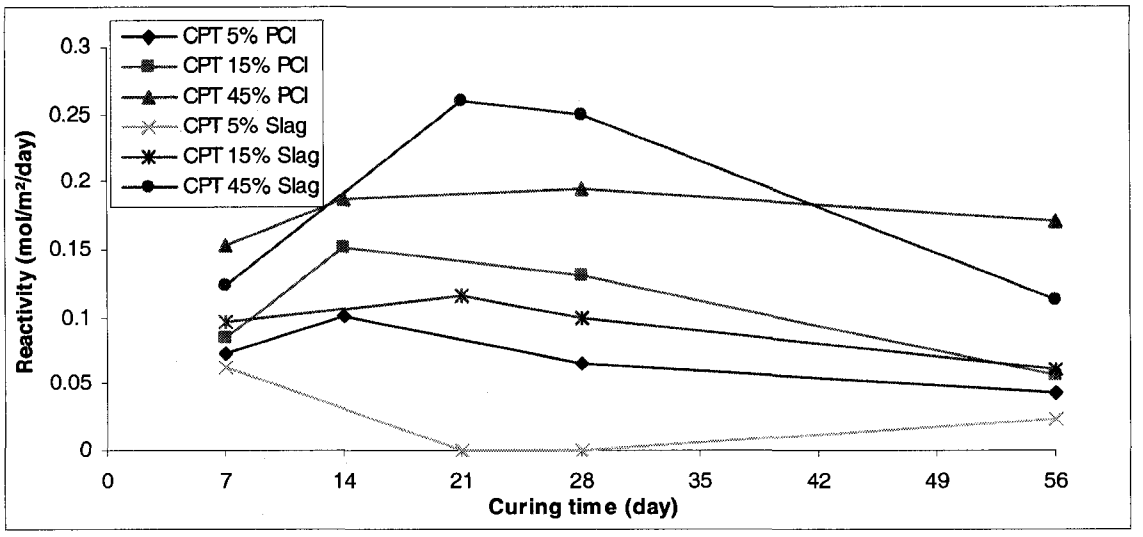

Figure 4-14 Reactivity of CPT made from PCI and PCI-slag with different amounts of pyrite at 20 °C

Figure 4.14 illustrates the reactivity of CPT made from PCI and PCI-slag with different amounts of pyrite cured at 20 °C. This figure compares the reactivity of CPT systems. The CPT containing 45% slag shows a higher reactivity than CPT made from PCI at an early age up to 28 days. The higher reactivity of CPT made from PCI-slag can be explained by the slow hydration of slag at early stages of hydration. The reactivity decreases after 28 days and there is lower reactivity than the CPT made from PCI with 45% pyrite. This lower value of reactivity at advanced age is due to the precipitation of hydration products as well as the formation of secondary C-S-H in the cement matrix which fills the voids and reduces the diffusion of oxygen through the cement matrix. In addition, the filler effect of slag (Peiwei et al, 2007) causes it to fill the pores of the cement matrix thus reducing the reactivity of CPT.

Figure 4.14 also shows that the CPT made from PCI with 15% of pyrite has a lower reactivity at 7 days than CPT made from PCI-slag with 15% pyrite. This is due to the slower reactivity of slag at early stages of hydration. At 21 and 28 days, the reactivity of CPT made from PCI-slag is lower than that made from PCI with 15% of pyrite. This is caused by the combination of the filler effect of slag, precipitation of hydration products as well as formation of secondary C-S-H. At an advanced age of 56 days, the CPT made from PCI-slag shows almost equal value of reactivity with CPT made from PCI. This may be due to the filling of pores with hydration products as well as complete or nearly complete oxidation of pyrite.

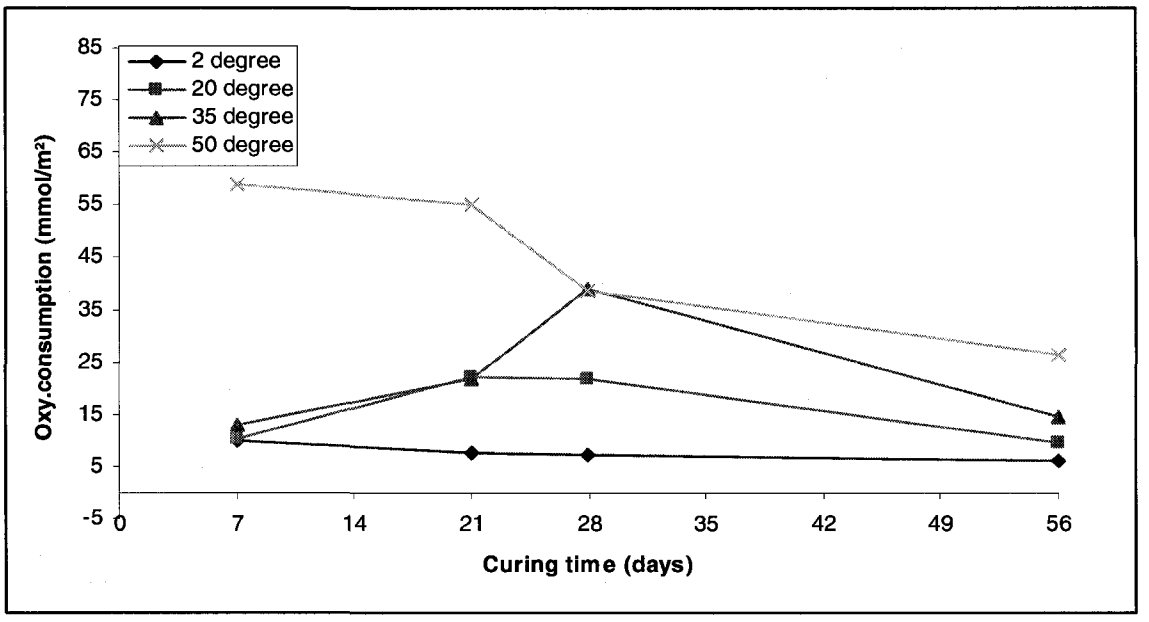

Figure 4-15 OC by CPT PCI-slag after 120 minutes of testing with 45% pyrite cured at different temperatures and testing at 20 ° C for different curing days

Figure 4.15 represents the OC of CPT made from PCI-slag containing 45% of pyrite cured at 2 °C, 20 °C, 35 °C and 50 °C for different curing times. The OC testing of these samples was done by keeping them at 20 °C, 2 hours before the test. In general, the figure illustrates that the reactivity of CPT made from PCI-slag increases with increase of curing temperature and decreases with curing time. The increase of reactivity with higher curing temperatures can be attributed to the higher self-dessication (lower water saturation degree) with higher curing temperatures. The diffusion of oxygen will be significantly increased by lower degree of saturation. The figure also shows that at 7 days of curing time, the OC of CPT samples cured at 2 °C, 20 °C and 35 °C have the same value whereas

the OC of the CPT sample cured at 50 ° C show a higher value. The reason for this behavior is a high self dessication. The value of OC of CPT cured at 50 ° C decreases with curing time. At 28 days of curing time, its value of OC is similar to the one cured at 35 ° C and higher than other CPT samples cured at 2 ° C and 20 ° C. The CPT sample cured at 2 ° C shows the lowest value of OC at 28 days. It may be due to the lower curing temperature which favors a lower self-dessication i.e. higher saturation degree. At 56 days, the results in the figure show that the OC is significantly influenced by the curing temperature. The CPT samples cured at 50 °C has the highest value of OC (due to higher self-dessication) than all CPT samples whereas the CPT sample cured at 2 ° C shows the lowest value of OC. It is also observed from the figure that the reactivity of CPT samples decreases with increase of curing time which can be due to the formation of additional hydration products in the cement matrix reducing the voids which decrease the diffusion of oxygen.

4.6.3 Reactivity of uncemented paste tailings

Figures 4.16, 4.17, 4.18 illustrate the OC of uncemented paste tailings with 5%, 15% and 45% of pyrite at 50%, 75%, 85% and 95% degrees of saturation, cured for 7 days. In the first 7 days, the uncemented paste samples were not drained. As well, the top part of the sample was covered to prevent evaporation. The 7 day OC results in Figures 4.16, 4.17 and 4.18 shows that OC of uncemented

paste tailings depends upon both saturation degree as well as percentage of pyrite. The uncemented paste tailings with 50% of degree of saturation with 5%, 15% and 45% of pyrite show the highest consumption of oxygen. The uncemented tailings with degree of saturation that is more that 75% do not show any OC for the 7 days. The same observation was also reported by Ouellet et al. (2003) in previous research. This lower or no consumption of oxygen with higher degree of saturation of uncemented paste tailings is due to the presence of water which decreases the diffusion coefficient (Elberling and Nicholson, 1996; Fall et al, 2004; Ouellet et al, 2003).

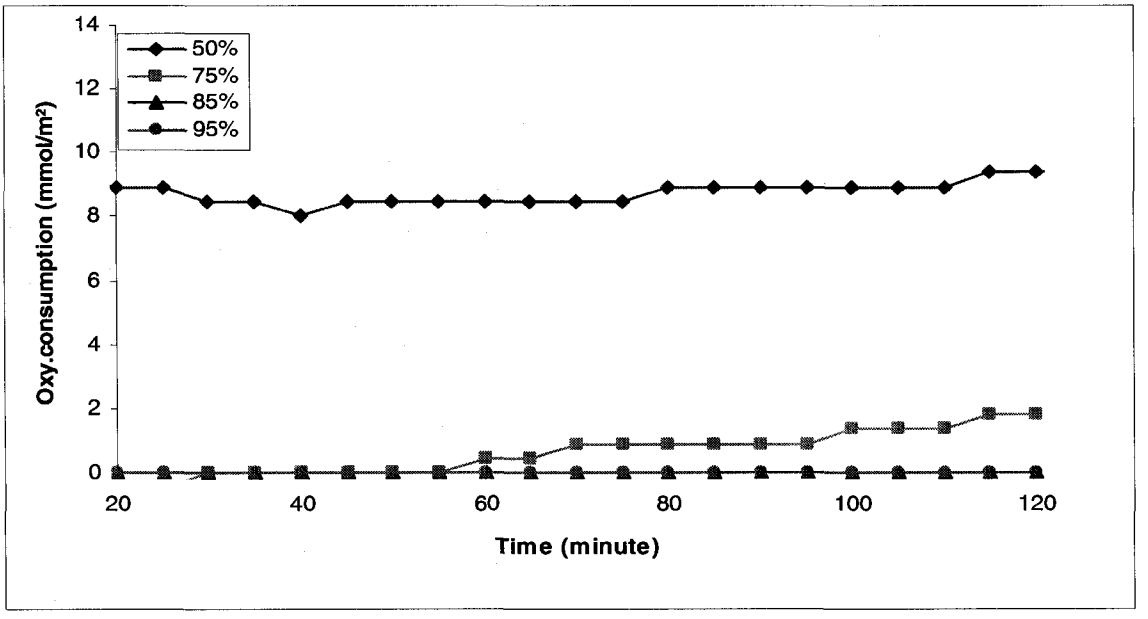

Figure 4-16 OC by uncemented paste tailings with 5% of pyrite at 20 ° C cured for 7 days at different degrees of saturation.

Figure 4.17 shows the OC results of uncemented paste tailings with 15% pyrite with different degrees of saturation for 7 days of curing. This result is similar to the 7 day result in Figure 4.16. As in the 5% pyrite, uncemented paste tailings containing 50% and 75% degrees of saturation with 15% pyrite also show some reactivity. The reactivity of the 15% pyrite with 50% degree of saturation is a little bit higher than the 5% pyrite. At a saturation value of 50%, 11 mmol oxygen per square meter are consumed by uncemented paste tailings with 15% pyrite after 120 minutes whereas this value for 5% pyrite with 50% degree of saturation is only 9 mmol per square meter. The uncemented paste tailings at 75% degree of saturation with 15% pyrite are somewhat more reactive than 5% pyrite. This reactivity is due to the presence of higher amounts of pyrite in the uncemented paste tailings. The uncemented paste tailings with degree of saturation more than 75% containing 15% of pyrite also do not show any value of OC due to presence of water as explained earlier.

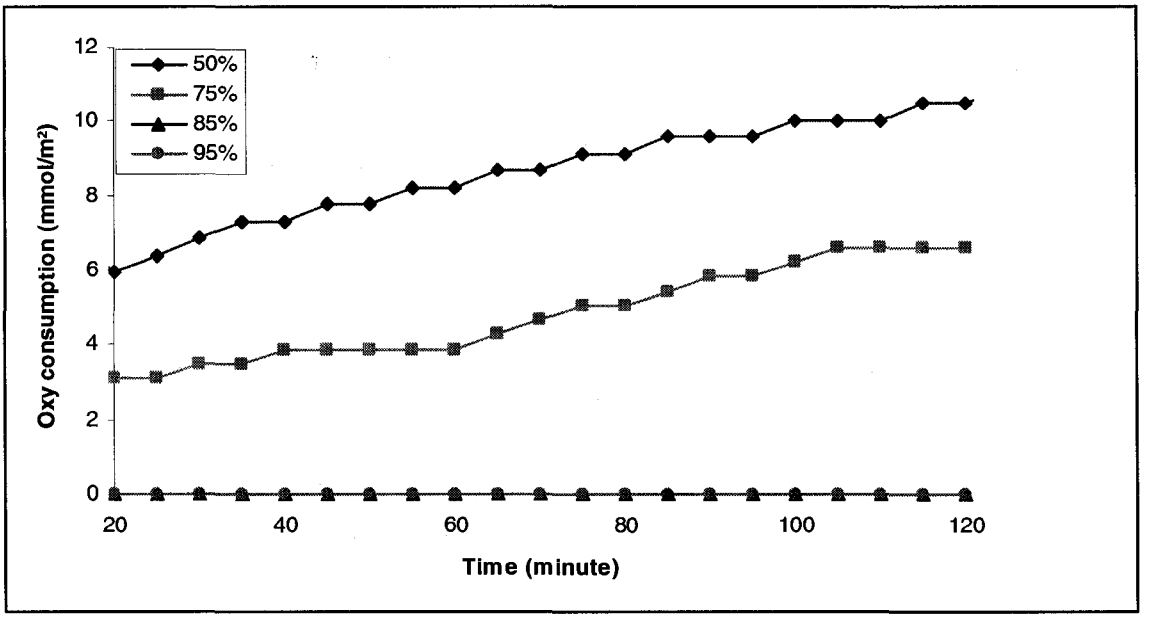

Figure 4-17 OC by uncemented paste tailings with 15% of pyrite at 20 ° C cured for 7 days at different degrees of saturation.

Figure 4.18 shows the OC of uncemented paste tailings containing 45% of pyrite with different degrees of saturation, cured for 7 days. The uncemented paste tailings also show a similar result as the ones with 5% and 15% of pyrite. The uncemented paste tailings with 50% degree of saturation show high reactivity in comparison to other high degrees of saturation. At a saturation degree of 50%, 21 mmol of oxygen per square meter is consumed by uncemented paste tailings with 45% pyrite after 120 minutes whereas this value for 5% pyrite with 50% degree of saturation is only 9 mmol per square meter cured for 7 days. This shows that the reactivity of uncemented paste tailings depends upon the pyrite concentration (Fall et al, 2004; Ouellet et al, 2003). It is also observed from the figure that the uncemented paste tailings with 75% degree of saturation containing 45% pyrite is less reactive than 50% degree of saturation. It shows

OC in the range of 5 mmol per square meter. This higher reactivity of the 50% saturation degree sample is mainly due to increase of the effective diffusion coefficient (Ouellet et al, 2003; Fall et al., 2004). As in the 5% and 15% pyrite content, the uncemented paste tailings with more than 75% degree of saturation containing 45% pyrite does not show any OC due to presence of water.

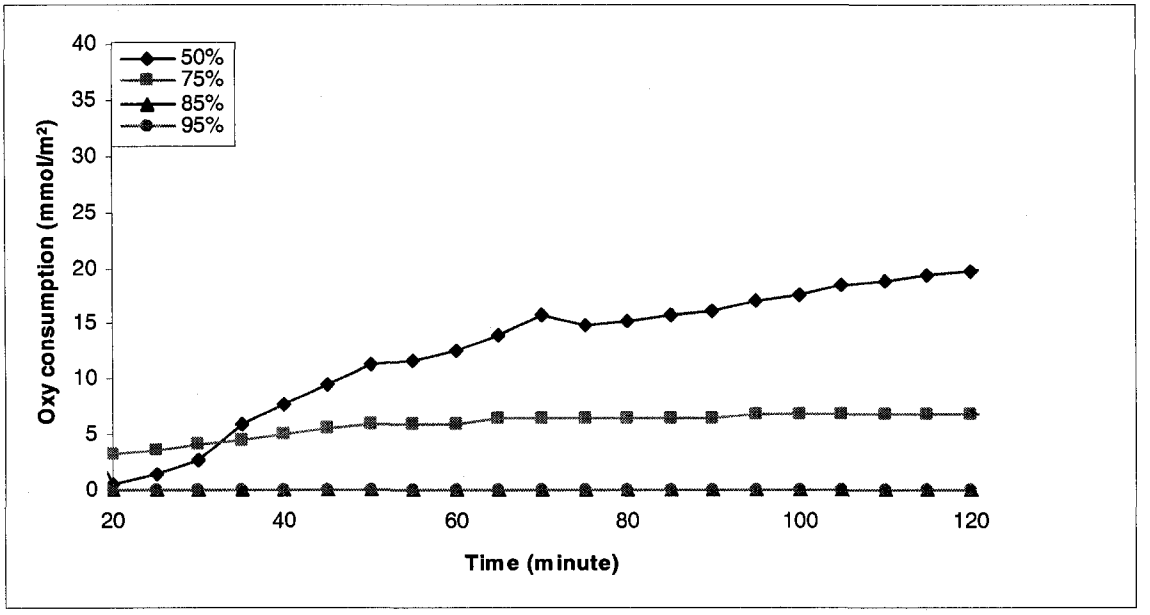

Figure 4-18 OC by uncemented paste tailings with 45% of pyrite at 20 ° C cured for 7 days at different degrees of saturation.

4.6.4 Reactivity of TS with PCI, PCI-Slag, PCI-Fibre

Figure 4.19 illustrates the results of OC by shotcrete made from PCI, PCI- slag and PCI-fibre containing 5% and 15% of pyrite at 20° C cured for 7 days. In general, the 7 day OC curve of TS shows that the reactivity of shotcrete depends upon binder type, percentage of pyrites and presence of fibre. It is also observed from the same figure that the OC of TS increases with the increase of contained pyrite. TS containing 15% pyrite shows higher OC than TS containing 5% pyrite. At 7 days of curing time, reactivity of shotcrete is also found to be influenced by the binder types. TS made from PCI have the lowest OC rate in comparison to PCI-slag and PCI-fibre.

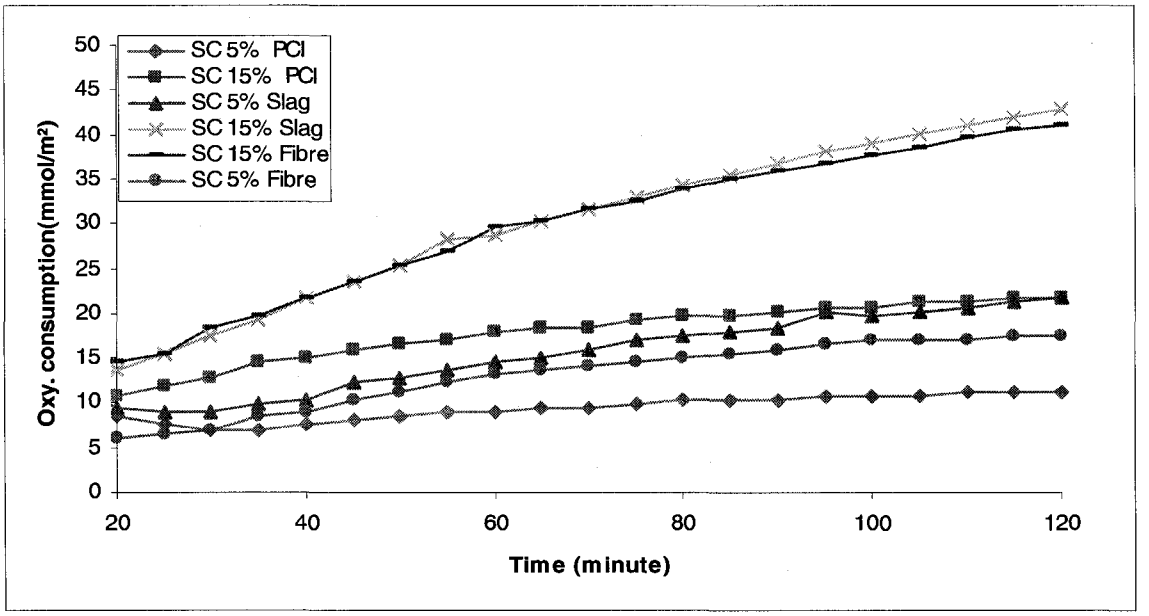

Figure 4-19 OC by TS made from different binders with different percentages of pyrite at 20 ° C cured for 7 days

The lower rate of OC of TS with PCI cement is due to the precipitation of adequate hydration products in the cement matrix which fill the pores and significantly reduce the diffusion of oxygen through it.

The hydration of slag is very slow at an early age (Barnett et al, 2006). Hence, in the case of TS made from PCI-slag, due to lower binder hydration at an early age, the pores of the sample are not adequately filled by the hydration products in comparison to the TS made from PCI. Hence, diffusion of the oxygen through the TS made from slag will be higher, resulting in the higher consumption of oxygen. Another possible reason can be due to the presence of low amounts of C_3A. The replacement of 50% of PCI by slag will reduce almost 50% of C_3S and

C_3A which are more responsible for early hydration of cement. Thus precipitation of fewer hydration products will increase the porosity and hence, a high consumption of oxygen.

Figure 4.19 also shows that the TS containing 5% pyrite made from PCI-fibre demonstrates higher consumption of oxygen than the TS made from PCI with the same amount of pyrite. However, it has a lower OC rate than PCI-slag. The TS made from PCI-fibre with 15% of pyrite also shows a higher rate of OC than the one made from PCI whereas it has almost the same pattern of OC as that of TS made from slag containing 15% of pyrite.

The high amount of OC of TS made from PCI-fibre is due to the weaker mechanical bond between fibre and cement matrix (Aulia, 2002). This is favourable for the development of high porosity at the interface between the fibre and the cement matrix. Fibre favors the formation of cracks which makes the sample porous. The presence of fibre also reduces the compaction efficiency (Leung et al, 2005) that can result in a porous structure which increases the diffusion of oxygen. This behavior of fibre compels the TS to attain a high OC.

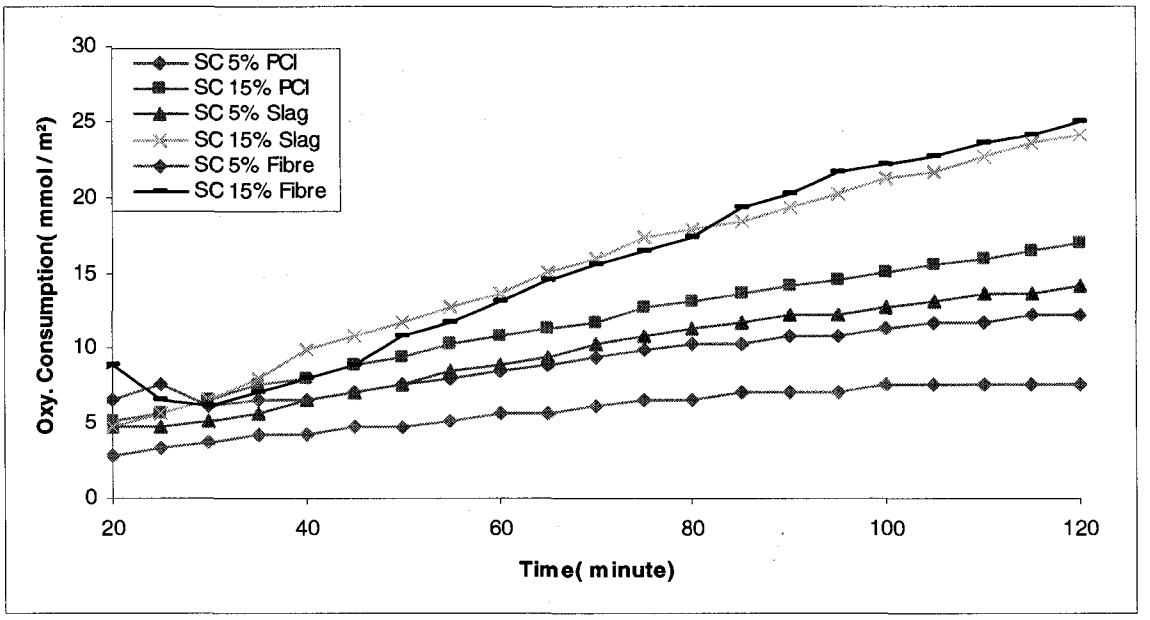

Figure 4-20 OC by TS made from different binders with different percentages of pyrite at 20° C cured for 14 days

Figure 4.20 illustrates the OC by TS with different binders containing different percentages of pyrite cured at 20°C for 14 days. The 14 day pattern of OC also shows the same trend as that of 7 days. The 14 day data as shown in Figure 4.20 also indicate that the OC is a function of pyrite content. The TS containing 15 % pyrite shows a higher value of OC than TS with 5% pyrite.

The TS made from PCI-fibre and PCI-slag with 15% of pyrite has almost the same value of OC. This value is higher than that of OC of TS made from PCI containing the same amount of pyrite. The higher value is due to the mechanism explained earlier. The higher consumption of oxygen by PCI-slag TS can be due to slow hydration of slag so that PCI-slag is unable to produce sufficient

hydration products in the cement matrix. The PCI TS has the lowest value of OC among the 15% pyrite group cured at 14 days which may be due to the precipitation of hydration products in the pores of the cement matrix which fill the voids and significantly reduce the diffusion coefficient.

Figure 4.20 also illustrates that the TS made from PCI-slag containing 5% pyrite cured for 14 days has higher OC rate than TS made from PCI-fibre and PCI. The reasons for this behavior are already explained above.

Figures 4.21 and 4.22 show the OC results of TS made from different binders with 5% and 15% of pyrite cured for 28 and 56 days at 20 °C respectively. In general, it can be concluded from these figures that the OC by TS depends upon pyrite content, binder type and presence of fibres. The 28 day results in figure 4.24 also show that the TS with 15% pyrite have a higher OC rate than TS containing 5% of pyrite. The TS made from PCI-fibre with 15% of pyrite has the highest value of OC whereas TS made from PCI and PCI-slag has almost the same value of OC at 28 days. The lower value is due to the decrease of diffusion of oxygen through the samples because of the precipitation of CH and C-S-H from the hydration of cement. In the case of TS made from PCI-slag, secondary C-S-H will be produced due to the pozzolanic reaction of slag. In addition, secondary C-S-H and other hydration products precipitate in the void of TS made from PCI-slag. Precipitation of such hydration products lowers the oxygen diffusivity that decreases the OC rate.

TS made from PCI containing 5% of pyrite still show the lowest value of OC than TS made from PCI-slag and PCI-fibre cured for 28 days.

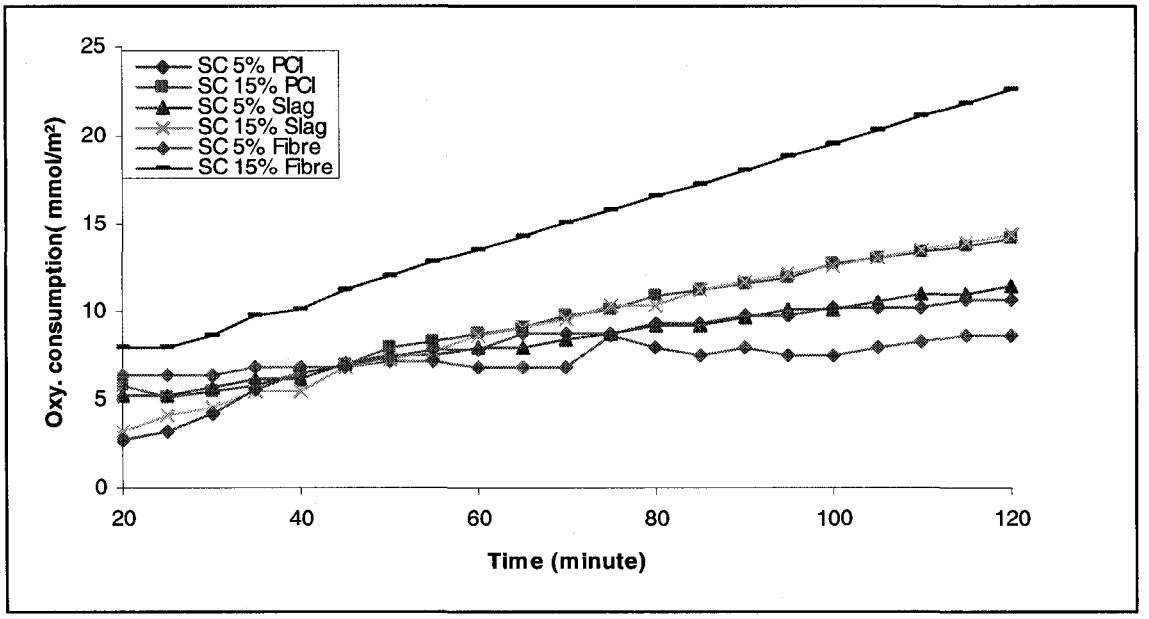

Figure 4-21 OC by TS made from different binders with different percentages of pyrite at 20° C cured for 28 days

Figure 4.22 shows the OC of TS made from different types of binder with 5% and 15% of pyrite cured for 56 days at 20° C. The TS made from PCI-slag has a lower OC rate than PCI-fibre and PCI TS samples cured for 56 days. The TS made from PCI-slag with 5% pyrite does not show any OC. This may be due to the full hydration of slag which produces secondary C-S-H in addition to the primary C-S-H. Such behavior was also reported by Fall et al. (2004) and Ouellet et al. (2003). The TS made from PCI-fibre containing 5% pyrite still has a high value of OC among the 5% pyrite group. In the same way, the OC of TS made

from PCI-fibre with 15% pyrite has the highest value followed by TS made from PCI. Among the 15% pyrite group, TS made from PCI-slag shows lowest value of OC due to the positive contribution of the pozzolanic reaction of slag that fill the voids within the cement matrix thus reducing the OC value.

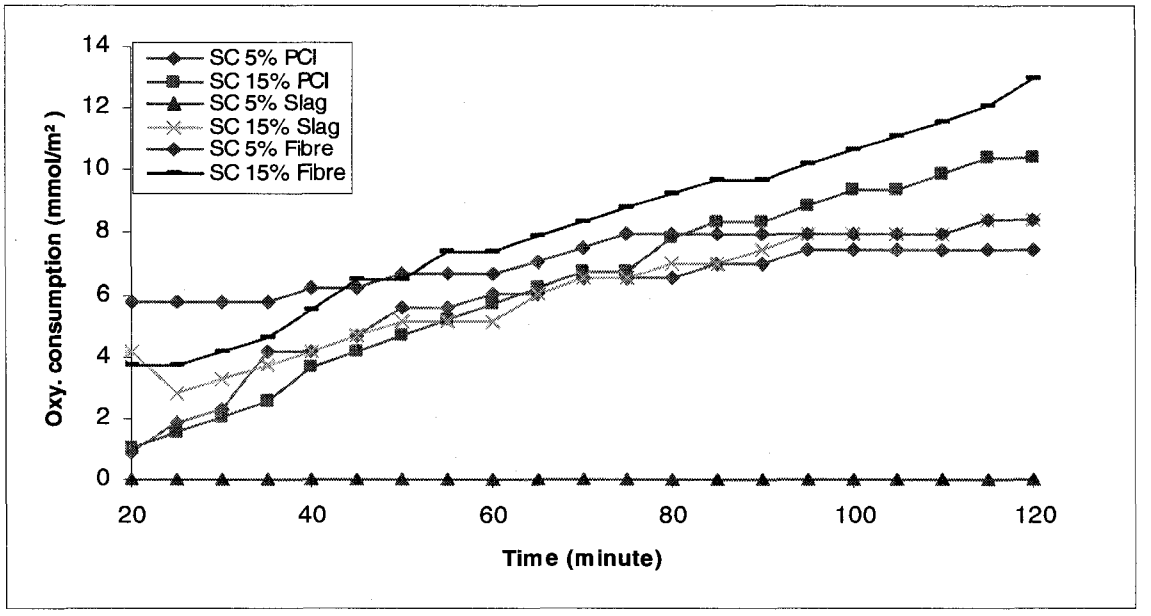

Figure 4-22 OC by TS made from different binders with different percentagesof pyrite at 20° C cured for 56 days

Figure 4.23 represents the reactivity of TS made from PCI, PCI-fibre and PCI-slag with 5% and 15% of pyrite. In general, the reactivity of all TS decreases with increase of curing days. It also depends upon the amount of pyrite and the binder type. The TS with 15% pyrite shows a higher reactivity than TS with 5 % pyrite. The TS with 15% pyrite made from PCI-fibre and PCI-slag shows a higher reactivity at early days than TS made from PCI. The lower value of reactivity of PCI TS in comparison to other TS at earlier ages can be due to the precipitation

of more hydration products in the pores of the cement matrix as discussed earlier.

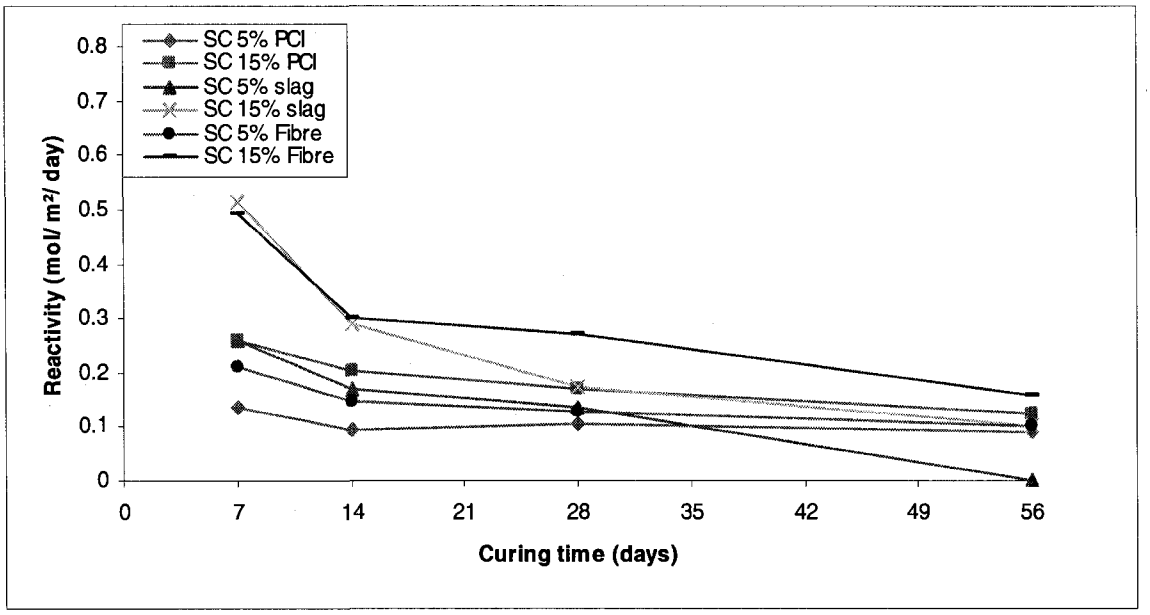

Figure 4-23 Reactivity of TS made from different binders with different percentages of pyrite at 20° C cured for 56 days

The TS made from slag shows a higher value of reactivity at the early age of 7 days due to poor hydration of slag. The TS made from PCI-slag has very low reactivity at an advanced age. The 5% pyrite content tailings made from PCI-slag shows almost no reactivity at 56 days. The reactivity of the TS with 15% pyrite made from PCI-slag is very low among the 15% pyrite group which is due to the formation of secondary C-S-H in the pores of the TS as mentioned above.

Figure 4.24 illustrates the evolution of the void ratio of SC with different amounts of pyrite for different curing days. The trend of the evolution of void ratio also

indicates that there is precipitation of hydration products in the cement matrix with increasing curing time. Hence, the void ratio (ratio of volume of voids to volume of solids) of the sample decreases with increase of curing time.

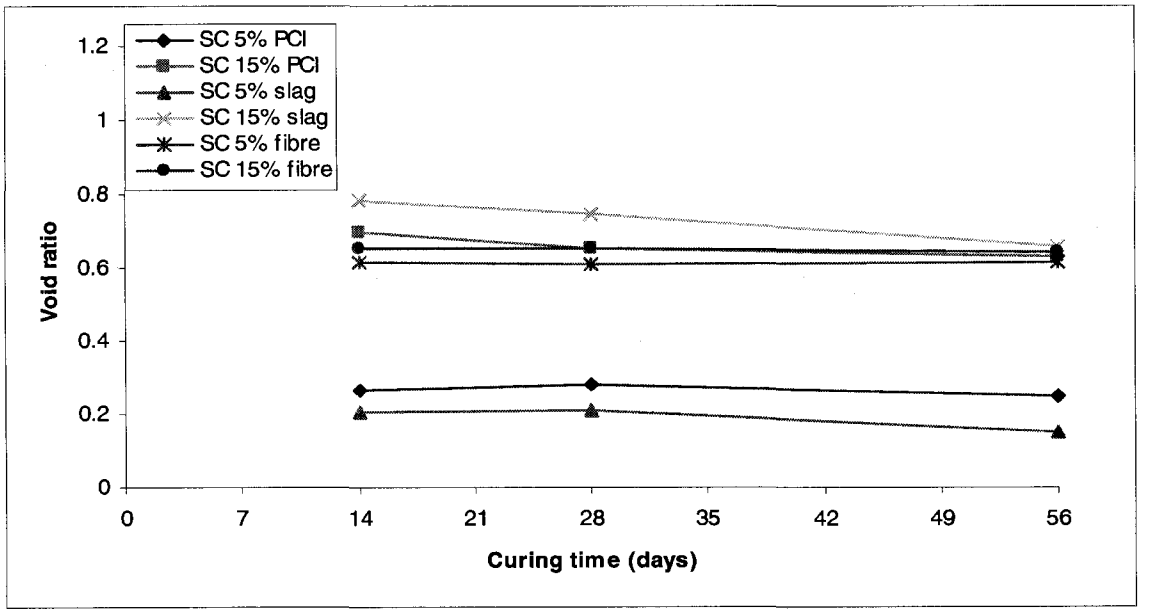

Figure 4-24 Evolution of void ratio of SC with different amounts of pyrite for different curing times

Figure 4.25 represents the OC results of SC containing 15% of pyrite made from different types of binder cured at 35 ° C for different curing times. This OC test is carried out by keeping samples at 20 ° C two hours before the test.

It is clearly observed that the reactivity of tailings SC with 15% of pyrite depends upon both binder and curing time. At 7 days of curing time, tailings SC made from PCI-slag shows the highest value of OC in comparison to tailings SC made from PCI and PCI-fibre. Tailings SC made from PCI-slag consumed almost 95 mmol of oxygen per square meter at 7 days of curing time after 120 minutes of testing whereas this value for PCI and PCI-fibre is 77 and 79 mmol of oxygen per

square meter respectively. The higher value can be due to the less reactivity of slag during the early days of curing time.

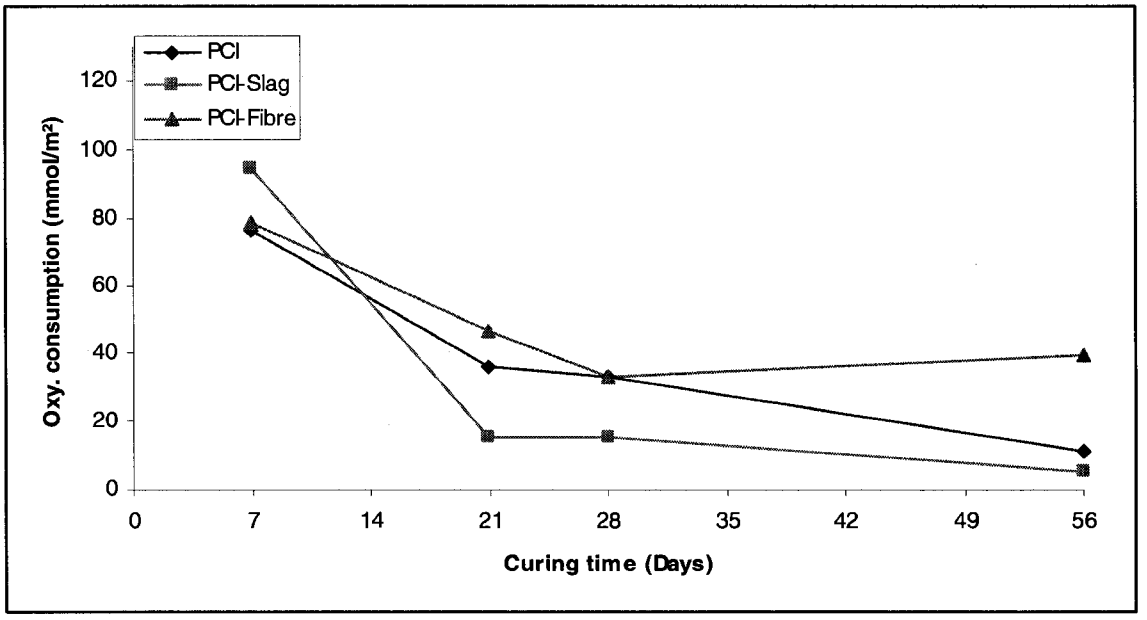

Figure 4-25 OC by shotcrete with 15% of pyrite made from different binders cured at 35° C and tested at 20 ° C for different curing days after 120 minutes of testing.

The reactivity of all TS decreases with increase of curing time except for PCI-fibre at 56 days. The decrease of the reactivity is mainly due to the precipitation of hydration products in the cement matrix. The hydration products fill the pores and reduce the internal porosity resulting in the reduction of diffusion of oxygen gas.

The reactivity of TS made from PCI-slag is found to be lower than that made from PCI and PCI-fibre at 21, 28 and 56 days of curing time. This can be due to the

pozzolanic reaction of slag as mentioned earlier. The TS made from PCI-fibre are more reactive than other TS at 21, 28 and 56 days of curing time. This is due to the presence of fibre which will form a weaker bond in the cement matrix (leads to high porosity at the interface fibre-cement matrix) and helps the formation of cracks which increases the diffusion coefficient resulting in the increase value of OC.

Figure 4.26 compares the reactivity in terms of OC for TS containing 15% of pyrite cured at 20 ° C and 35 ° C made from different types of binder for different curing times. The OC test is carried out at 20 ° C of all tailings SC to monitor the reactivity at different curing temperatures. The above figure shows that the reactivity of TS cured at 35 ° C is higher than 20 ° C at 7, 14, 21, 28 days of testing with the exception of TS made from PCI-slag which has an OC value similar to 20 ° C after 21 days of curing. The higher value of OC with higher temperatures is due to higher self-dessication of the shotcrete. At an advanced age of 56 days, almost all of the TS cured at 20 °C and 35 °C show similar reactivity. This can be explained by the fact that at advanced ages, the shotcrete tends to have relative similar degrees of water saturation.

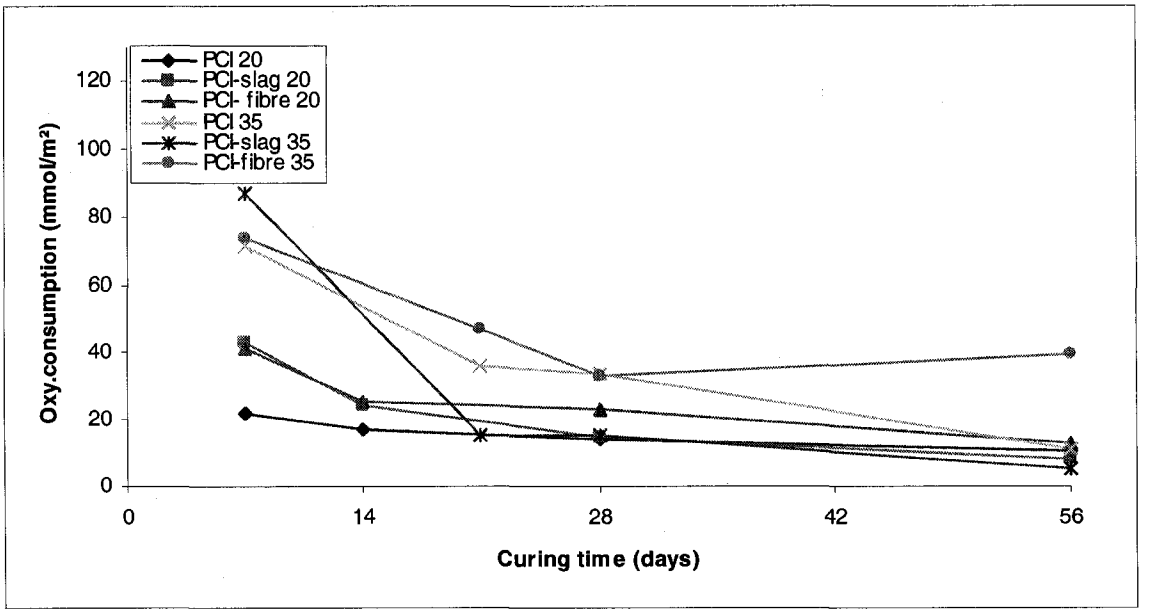

Figure 4-26 OC by shotcrete with 15% of pyrite made from different binders cured at 20 ° C and 35° C tested at 20 ° C for different curing days after 120 minutes of testing.

4.7 Conclusions and recommendations

Extensive laboratory experiments are performed to investigate the reactivity of paste tailings systems under various thermal load conditions. The reactivity of paste tailings systems depends upon various factors, such as binder type, amount of pyrite as well as curing time and temperature. CPT containing 45% of pyrite shows a higher degree of reactivity than 5% and 15% of pyrite. CPT made from PCI-slag shows a higher reactivity at 7 days of curing time than PCI. The reactivity is found to decrease with curing time. At 28 and 56 days of curing time, the reactivity of all CPT samples is found to decrease. The CPT made from PCI-

slag is found to be less reactive than PCI. TS also exhibit the same behavior. They show dependence on amount of pyrite, binder type, presence of fibre and curing time. Uncemented paste tailings with higher degree of saturation that is greater than 75% do not show any reactivity at 7 days in an undrained condition. The CPT made from both PCI and PCI-slag containing 45% of pyrite shows bigger potential of AMD formation at an earlier age and this potential decreases with time. This is also true for TS which behaves like CPT.

5 Chapter 5: Final summary and conclusions

5.1 Summary and conclusion

Since the paste tailings systems are subjected to coupled thermo-chemical loadings during their service, the combined effects of sulphate and temperature on the geotechnical (strength, durability) and environmental properties (fluid transport ability, reactivity) properties of paste tailings are studied.

Laboratory experiments are performed to study these coupled effectes. CPT samples are made with 0 ppm, 5000 ppm, 15000 ppm and 25000 ppm of sulphate and cured at 2 °C, 20 °C, 35 °C and 50°C. PCI and PCI-slag are used to prepare samples. The UCS test is carried out on these samples after 28, 90 and 150 days. The result shows that the 0 ppm, 5000 ppm and 15000 ppm sample does not show any decrease in UCS value at all studied temperatures.The 25000 ppm sample at 50 °C shows decline in strength at 90 and 150 days of curing time. The XRD result of the 25000 ppm sample at 50 °C does not show a high amount of ettringite. The same XRD result shows the adsorption of sulphate by C-S-H. The SEM observation implemented on the same sample shows the presence of colloidal ettringite. Hence, it is concluded that the reduced strength of 25000 ppm at 50 °C can be due to the formation of an inferior quality of C-S-H gel due to adsorption of sulphate by the C-S-H gel.

TS are also investigated for this coupled process. They are made with 0 ppm, 2500 ppm and 5000 ppm of sulphate and cured at 2 °C, 20 °C, 35 °C and 50 °C from PCI, PCI-slag, and PCI-fibre. The UCS of the TS is tested for 1, 7, 28, 120 days of curing time. The result shows that the mechanical strength of TS is significantly influenced by the thermo chemical coupled process. Sulphate is found to be contributing positively or negatively to the mechanical strength depending upon its concentration as well as temperature. The adsorption of sulphate by C-S-H gel is also observed for the TS with 5000 ppm of sulphate at 50°C. HC and sorption testing are carried out for CPT and TS respectively to investigate durability. The OC test is also carried out to gain an idea about environmental impacts of these materials to be used in the mining industries. The experimental result shows that the CPT used in cold mines will be less durable due to high HC which will favor fluid transport. The CPT used in an average environment (20 °C-35 °C) will be more environmentally friendly due to lower HC. The durability of TS is found to increase with increase of curing temperature except at 50 °C. TS cured at 50 °C is not found to be much more durable than TS cured at lower temperatures due to the formation of hydration rims and adsorption of sulphate. The presence of fibre in the TS does not contribute positively to the durability. The TS made from PCI-slag are more durable than PCI and PCI-fibre. The OC test on the CPT system shows that the reactivity depends upon pyrite content, curing time, curing temperature and also with binder types. The result shows that the reactivity of the CPT system increases with increase of pyrite content and decreases with increase of curing time. The

reactivity of tailings systems strongly depends upon the binder type. At early ages of curing, tailings SC made from PCI-slag show higher reactivity, but with increase of curing time, they are less reactive and even lower than tailings SC made from PCI and PCI-fibre. The reactivity of uncemented paste tailings depends upon degree of saturation and pyrite content. Saturation higher or equal to 75% is not reactive when tested undrained. CPT and TS with higher pyrite content are susceptible to the formation of AMD at early days of curing and the environmental impact of these tailings systems decrease with curing time.

5.2 Recommendation for further research

CPT systems are investigated for development of UCS with 0 ppm, 5000 ppm, 15000 ppm and 25000 ppm of sulphate at different curing temperatures up to 150 days for curing time. The interaction of sulphate with raised temperature is found to be a complex issue. The XRD result illustrates formation of various mineralogical compositions that depend upon both temperature and sulphate concentration. Due to limited time, all required information can not be obtained, especially the deep explanation of decline in strength of the 25000 ppm sample at 50 °C. It is concluded that the C-S-H adsorbs sulphate at high temperatures and assumed that adsorption of sulphate produces an inferior quality of C-S-H which drops the strength. Hence, it will be the subject of further research to determine the exact mechanism that leads to decline in strength of sulphate bearing cementitious materials at high curing temperatures, to better understand

the temperature induced absorption of sulphate by C-S-H and the consequences on the mechanical properties of CPT and TS.

Furthermore, detailed mineralogical and microstructure investigation will be necessary to better understand the coupled effect of sulphate and temperature on the mineralogical composition and microstructure of CPT systems as well as on the binder hydration in the aforementioned system. This investigation should perfomed at the microstructural and nano-level.

6 References

Adhikari GR, Durability of blended cement against sodium sulphate attack and alkali silica reaction. Master thesis (2007) , Ryerson University,Toronto

Akoz F, Turker F, Koral S, Yuzer N. Effects of raised temperature of sulfate solutions on the sulfate resistance of mortars with and without silica fume. J Cement and Concrete Research 29 (1999) 537-544

Akoz F, Turker F, Koral S, Yuzer N. Effects of sodium sulfate concentration on the sulfate resistance of mortars with and without silica fume. J Cement and Concrete Research. 25 6 (1995) 1360-1368

Al-Akhras, Nabil M, Durability of metakaolin concrete to sulphate attack. J Cement and Concrete Research 36 (2006) 1727-1734

Amaratunga L.M., Yaschyshyn D.N. Development of a high modulus paste Fill using fine gold mill tailings. J Geotechnical and Geological Engineering 15 (1997) 205–219.

Aulia TB, Effects of Polypropylene fibres on the properties of high strength concrete. J LACER 7 (2002) 43-59.

Aziz M Abd El, Aleem Abd El, Heikal M, Didamony H El. Hydration and durability of sulphate-resisting and slag cement blends in Caron's Lake water. J Cement and Concrete Research 35 (2005) 1592-1600

Baghabra S.O, Al-Amoudi, Attack on plain and blended cements exposed to aggressive sulphate environments. J Cement Concrete Composite 24 (2002) 305-316

Barnett SJ, Soutsos MN, Millard SG, Bungey JH. Strength development of mortars containing ground granulated blast-furnace slag: Effect of curing temperature and determination of apparent activation energies. J Cement and Concrete Research. 36 (2006) 434-440

Benzaazoua M, Belem T, Bussiere B. Chemical factors that influence the performance of mine sulphidic pste backfill. J Cement and Concrete Research 32 (2002) 1133-1144

Benzaazoua M, Fall M, Belem T. A contribution to understanding the hardening process of cemented pastefill. J Minerals Engineering 17 (2004) 141-152

Bernard ES. Early age load resistance of fibre reinforced shotcrete linings. J Tunnelling and Underground Space Technology 23 (2008) 451-460

Bing T, Cohen MD. Does gypsum formation during sulphate attack on concrete lead to expansion. J Cement and Concrete Research 30 (2000) 117-123

Cakir O, Akoz F. Effect of curing conditions on the mortars with and without GGBFS.J Construction and Building Materials 22 (2008) 308-314

Crammond NJ. The thaumasite form of sulphate attack in the UK. J Cement and Concrete Composite 25 (2003) 809-813

Elberling B, Nicholson RV, Scharer JM. A combined kinetic and diffusion model for pyrite oxidation in tailings: a change in controls with time. Journal of Hydrology. 157 (1994) 47-60

Elberling B, Nicholson RV. Field determination of sulphide oxidation rates in mine tailings. J Water Resources Research 32 6 (1996) 1773-1784.

Escalante JI, Gomez LY, Johal KK, Mendoza G, Mancha H, Mendez J. Reactivity of blast-furnace slag in Portland cement blends hydrated under different conditions. J Cement and Concrete Research 31 (2001) 1403-1409

Escadeillas G, Aubert JE,Segerer M, Prince W, Some factors affecting delayed ettringite formation in heat-cured mortars. J Cement Concrete Research 37 (2007) 1445-1452

Escalante-Garcia JI, Sharp JH, The microstructure and mechanical properties of blended cements hydrated at various temperatures. J Cement and Concrete Research. 31 (2001) 695-702

Fall M, Celesttin JC, Pokharel M, Mechanical properties and binder consumption of cemented tailings backfill as function of the temperature. Journal of underground space technology .2008 b (to be submitted)

Fall M, Benzaazoua M, Saa EG. Mix proportioning of underground cemented tailings backfill. J Tunnelling and Underground Space Technology 23 (2008) 80-90

Fall M, Nasir, O., Celestin J.C. Paste backfill response in deep mine temperature conditions. Symposium Mine Fill 2007.

Fall M, Samb SS. Pore structure of cemented tailings materials under natural or accidental thermal loads. J Materials Characterization 59 (2007) 598-605.

Fall M, Samb SS. Influence of curing temperature on strength, deformation behavior and pore structure of cemented paste backfill at early ages. J Construction and Building Materials xxx (2006) xxx-xxx

Fall M, Benzaazoua M. Modeling the effect of sulphate on strength development of paste backfill and binder mixture optimization. J Cement and Concrete Research 35 (2005) 301-314.

Fall M, Benzaazoua M, Ouellet S. Effect of tailings properties on paste backfill performance. Proceedings 8th International Symposium on Mining with Backfill in Beijing, China, 2004, 193-202

Fu Y, Ding J, Beaudoin JJ. Expansion of Portland cement mortar due to internal sulphate attack. J Cement and Concrete Research 27 9 (1997) 1299-1306.

Fu Y, Beaudoin JJ. Microcracking as a precursor to delayed ettringite formation in cement systems. J Cement and Concrete Research 26 10 (1996) 1493-1498.

Fu Y, Xie P, GU Ping, Beaudoin JJ. Effect of temperature on sulphate adsorption/desorption by tricalcium silicate hydrates. J Cement and Concrete Research 24 8 (1994) 1428-1432

Gonen T, Yazicioglu S. The influence of mineral admixtures on the short and long term performance of concrete. J Building and Environment 42 (2007) 3080-3085

Gopalan MK, Sorptivity of fly ash concretes. J Cement and Concrete Research 26 8 (1996) 1189-1197

Hamou AT, Vanhove Y, Petrov N. Microstructural analysis of the bond mechanism between polyolefin fibres and cement pastes. J Cement and Concrete research 35 (2005) 364-370

Hekal EE, Kishar E, Mostafa H. Magnesium sulfate attack on hardened blended cement pastes under different circumstances. J Cement and Concrete Research 32 (2002) 1421-1427.

Herbert RB, Sulphide Oxidation in Mine Waste Deposits, A Review with Emphasis on Dysoxic Weathering ,MiMi Print Dept.Geol and Geoch Stockholm Univ .S-106 91,Sweden,1999

Kesimal A, Yilmaz E, Ercikdi B, Alp I, Deveci H. Effect of properties of tailings and binder on the short–and long-term strength and stability of cemented paste backfill. J Materials Letters 59 (2005) 3703-3709

Kesimal A, Yilmaz E, Ercikdi B. Evaluation of paste backfill mixtures consisting of sulphide-rich mill tailings and varying cement contents. J Cement and Concrete Research 34 (2004) 1817-22.

Khatib JM, Clay MR. Absorption characteristics of metakaolin concrete. J Cement and Concrete Research.34 1 (2003) 19-29

Kim JK, Han Sh, Song YC. Effect of temperature and aging on the mechanical properties of concrete part I. Experimental results .J Cement Concrete Research 32 (2002) 1087-1094

Kunhanandan EK, Ramamurthy K. Sorption characteristics of foam concrete.J Cement and Concrete Research 37 (2007)1341-1347

Leung CKY, Lai R, Lee AYF. Properties of wet-mixed reinforced shotcrete and fibre reinforced concrete with similar composition. Cement and Concrete Research 35 (2005) 788-795.

Lothenbach B, Winnefeld F, Alder C, Wieland E, Lunk P. Effect of temperature on the pore solution, microstructure and hydration products of Portland cement pastes. J Cement and Concrete Research 37 (2007) 483-491

Malmgren L, Nordlund E, Rolund S. Adhesion strength and shrinkage of shotcrete. J tunneling and Underground Space Technology 20 (2005) 33-48

Martinez- Ramirez S, Influence of SO2 deposition on cement mortar hydration .J Cement and Concrete Research 29 (1999) 107-111

Menadi B,Kenai S, Khatib J, Mokhtar AA. Strength and durability of concrete incorporating crushed limestone sand. Construction and Building Materials xxx (2008) xxx-xxx

Mingyu Hu, Fumei L, Mingshu T, The thaumasite form of sulphate attack in concrete of Yongan Dam. J Cement and Concrete Research 36 (2006) 2006-2008

Mohammed SA, Mohammed BH, Al-Gadhib Ali H. Predicting residual strength in unsaturated concrete exposed to sulfate attack. J Materials in Civil Engineering. 18 3 (2006) 343-354.

Nasir, O, Fall M. Coupling temperature, binder hydration and strength development of underground cemented paste backfill. J Tunnelling and underground space technology (submitted)

Nehdi M, Hayek M. Behavior of blended cement mortars exposed to sulphate solutions cycling in relative humidity. J Cement and Concrete Research 35 (2005) 731-742

Neville A.M, 1995. Properties of concrete, fourth edition page 663

Ouellet S, Bussiere B, Benzaazoua M, Aubertin M, Fall M,Belem T. Sulphide reactivity within cemented paste backfill: Oxygen consumption test results. J Canadian geo technical 2 (2003) 176-181

Park YS, Suh JK, Lee JH, Shin YS. Strength deterioration of high strength concrete in sulfate environment. J Cement Concrete Research. 29 (1999) 1397-1402.

Peiwei G, Xiaolin L, Chuanxi Y, Xiaoyan Li, Nannan S, Shaochun J. Microstructure and pore structure of concrete mixed with superfine phosphorous slag and superplasticizer. J Construction and Building Materials. 22 (2008) 837-840

Puertas F, Amat T, Fernandez- Jimenez A, Vazquez T, Mechanical and durable behaviour of alkaline cement mortars reinforced with polypropylene fibres . J Cement Concrete Research . 33 12 (2003) 2031-2036

Ramirez SM. Influence of SO_2 deposition on cement mortar hydration Cement and Concrete Research 29(1999)107-111

Ramlochan T, Zacarias P, Thomas MDA, Hooton RD. The effect of pozzolans and slag on the expansion of mortars cured at elevated temperature. Part I: Expansive behaviour. J Cement and Concrete Research 33 (2003) 807-814

Ramlochan T, Thomas MDA, Hooton RD. The effect of pozzolans and slag on the expansion of mortars cured at elevated temperature. Part II: Microstructural and microchemical investigations. J Cement and Concrete Research 34 (2004) 1341-1356

Rawlins CA, Backfill heat load contribution in deep level mining operations. 30th International Conference of Safety in Mines Research Institutes, South African Institute of Mining and Metallurgy. (2003) 373-384

Rawlins CA, Phillips HR, Reduction of in mine heat loads. 7th International Mine Ventilation Congress. Poland 55(20010 381-389

Rico M, Benito G, Salgueiro AR, Diez-Herrero A, Pereira HG, Reported tailings dam failures. A review of the European incidents in the worldwide context.J Hazardous Materials 152 (2008) 846-852

Ritcey MG. Tailing management in gold plants. J Hydrometallurgy 78 (2005) 3-20

Sahmaran M, Erdem KT, Yaman OI, Sulfate resistance of plain and blended cements exposed to wetting-drying and heating-cooling environments. J Construction and Building Materials. 21 (2007) 1771-1778.

Sahito W. Suitability of mine tailings for shotcrete as a ground support. MASC thesis (2003) Dalhousie University.

Salah U, Al-Dulaijan. Sulfate resistance of plain and blended cements exposed to magnesium sulfate solutions. J Construction and Building Materials 21 (2007)1792-1802

Saxena M, Dhimole LK. Utilization and value addition of copper tailing as an extender for development of paints. Journal of Hazardous Materials B 129 (2006) 50-57

Soroushian P, Tlili A,Alhozaimy A, Khan A.Development and characterization of hybrid polythene-fibre-reinforced cement composites. J Construction and Building Materials 7 4 (1993) 221-229

Stothart P. Facts and figures, 2007. A report on the state of the Canadian mining industry. The Mining Association of Canada . 72 p

Tasdemir C. Combined effects of mineral admixtures and curing conditions on the sorptivity coefficient of concrete. J Cement and Concrete Research 33 (2003) 1637-1642

Tommy Y.Lo, Cui HZ, Nadeem A, Li ZG. The effects of air content on permeability of lightweight concrete.J Cement and Concrete Research 36 (2006) 1874- 1878

Turker F, Akoz F, Koral S, Yuzer N. Effects of magnesium sulfate concentration on the sulfate resistance of mortars with and without silica fume. J Cement and Concrete Research 27 2 (1997) 205-214.

US Silica Company, Berkeley, Springs, WV

Wang HL, Shang JQ, Kovac V, Ho KS. Utilization of atikokan coal fly ash in acid rock drainage control from Mussel white mine tailings. J Can. Geotech 43 (2006) 229-243

Zou DH, Sahito W. Suitability of mine tailings for shotcrete as a ground support. Can.J.Civ. Eng. 31 4 (2004) 632-636