

# **Reactivity of Cemented Paste Backfill**

by

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## **ABSTRACT**

Mining has been one of the main industries in the course of the development of human civilization and economies of various nations. However, every industry has issues, and one of the problems the mining industry has faced is the management of waste, especially sulphide-bearing tailings, which are considered to be a global environmental problem. This issue puts pressure on the mining industry to seek alternative approaches for tailings management. Among the several different types of methods used, cemented paste backfilling is one of the technologies that offers good management practices for the disposal of tailings in underground mines worldwide.

Cemented paste backfill (CPB) is a cementitious composite made from a mixture of mine tailings, water and binder. This technology offers several advantages, such as improving the production and safety conditions of underground mines. Among these advantages, CPB is a promising solution for the management of sulphidic tailings, which are considered to be reactive materials (i.e., not chemically stable in an atmospheric condition) and the main source of acid mine drainage, which constitutes a serious environmental challenge faced by mining companies worldwide. Such tailings, if they come into direct contact with atmospheric elements (mainly oxygen and water), face oxidation of their sulphidic minerals, thus causing the release of acidic drainage (i.e., acid mine drainage) and several types of heavy metals into surrounding water bodies and land.

Therefore, the reactivity of sulphidic tailings with and without cement content can be considered as a key indicator of the environmental behavior and durability performance of CPB systems. For a better understanding of the reactivity, it is important to investigate the influencing factors. In this research, several influencing factors are experimentally studied by conducting oxygen consumption tests on different sulphidic CPB mixtures as well as their tailings under different operational and environmental conditions. These factors include time, curing temperature, initial sulphate content, curing stress, mechanical damage, binder type and content, and the addition of mineral admixtures. In addition, several microstructural techniques (e.g., x-ray diffraction and scanning electron microscopy) are applied in order to understand the changes in the CPB matrices and identify newly formed products.

The results reveal that the reactivity of CPB is affected by several factors (e.g., curing time, initial sulphate content, ageing, curing and atmospheric temperature, binder type and content,

vertical curing stress, filling strategy, hydration and drainage, etc.), either alone or in combination. These factors can affect reactivity either positively or negatively. It is observed that CPB reactivity decreases with increasing curing time, temperature (i.e., curing and atmospheric temperatures), curing stress, binder content, the addition of mineral admixtures, degree of saturation, and the binder hydration process, whereas reactivity increases with increases in sulphide minerals (e.g., pyrite), initial sulphate content, mechanical damage, and with decreased degrees of saturation and binder content. The effect of sulphate on the reactivity of CPB is based on the initial sulphate content as well as curing time and temperature. It is concluded that the reactivity of CPB systems is time- and temperature-dependent with respect to other factors. Also, binders play a significant role in lowering CPB reactivity due to their respective hydration processes.

## **DEDICATION**

I gratefully dedicate this work to all members of my family, especially to: my parents, Majed and Nourah, my beloved wife, Maryam, and my lovely sons and daughters: Majed, Sarah, Noura, Nouf, Fahad, Khalid, and Lulua, for their love, support, and patience during times of my study.

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## List of Symbols

AFm: Monosulfate (calcium monosulfate aluminate hydrate)  
AMD: Acid Mine Drainage  
ARD : Acid Rock Drainage  
As: Arsenic  
ASTM: American Society for Testing and Materials  
BHC: Blended Hydraulic Cement  
C/T %: Cement to Tailings ratio  
C: Cement  
C<sub>2</sub>S: Dicalcium Silicate  
C<sub>3</sub>A: Tricalcium Aluminate  
C<sub>3</sub>AF: Tetracalcium Aluminoferrite  
C<sub>3</sub>S: Tricalcium Silicate  
Cd: Cadmium  
CH: Portlandite (Calcium Hydroxide, Ca(OH)<sub>2</sub>)  
C<sub>o</sub>: atmospheric concentration of oxygen  
CPB: Cemented Paste Backfill  
CPT: Cemented Paste Tailings  
C-S-H: Calcium silicate hydrate  
CUS: Curing Under Stress  
D<sub>e</sub>: effective diffusion coefficient of oxygen  
Et.: Ettringite (AF<sub>t</sub>)  
FA: Fly ash  
F<sub>L</sub>: Flux  
GDP: Gross Domestic Product  
G<sub>s</sub>: Specific Gravity (Sp. Gravity)  
GT: Gold Tailings  
GU: General Use cement  
K<sub>r</sub>: the first-order reaction rate coefficient  
μM : micrometer  
MEND: Mine Environment Neutral Drainage (MMS Canada)  
MIP: Mercury Intrusion Porosimetry  
ML: Metal Leaching  
OC: Oxygen Consumption test  
PC I: Portland Cement Type I  
PF: Portland and Fly ash Cement  
PS: Portland and Slag Cement  
PS: Slag

PSD: Pore Size Distribution  
SCA: Canadian Standard Association  
SCM: Supplementary Cementing Material  
SEM: Scanning Electron Microscope  
SEM/EDS: Scanning Electron Microscopy / Energy Dispersive X-Ray Spectroscopy  
SO<sub>4</sub><sup>2-</sup>: Sulphate  
SSA: Specific Surface Area  
ST: Silica Tailings  
T: Tailings  
TG/DTG: Thermal Gravimetric/ Derivative thermogravimetric analysis  
THMC: Thermal Hydraulic Mechanical Chemical process  
UCS: Unconfined Compressive Strength  
w/b: water to binder ratio  
w/c: water to Cement ratio  
W: Water  
wt% : Percentage by weight  
XRD: X-Ray Diffraction Spectroscopy  
ZT: Zinc Tailings

# **Chapter 1: General Introduction**

## **1.1 Introduction**

The mining industry has and will continue to play a vital role in human civilization as well as in many developing and developed countries worldwide. Canada is considered to be a leading mining country, producing more than 60 types of minerals and metals. The mining industry in Canada is one of the most important sectors of the economy, and provides many jobs. In 2014, the mining sector in Canada contributed \$63 billion of the nominal GDP and employed nearly 380,000 Canadians (Marshall, 2015).

On the other hand, the Canadian mining industry is considered as the largest producer of solid waste in Canada (e.g., rocks, tailings). Figure 1.1 presents the primary types of solid waste streams in Canada for 2012. From the figure, it is evident that the volume of mine tailings is much greater than that of municipal solid waste. In addition to the large volume, mine waste often contains acid-generating sulphides (e.g., pyrite, pyrrhotite), heavy metals (e.g., arsenic (As) and cadmium (Cd)), and other contaminants that may spread into the surrounding environment (e.g., surface and groundwater, soil). Therefore, mine waste needs to be properly managed to prevent or minimize its environmental risk and social and economic impacts (Benzaazoua et al., 2008).

Among the different types of mine waste, sulphide-bearing waste and its handling and disposal require more attention from mining companies due to its substantial volume and potential to generate acid mine drainage (AMD) (Dold, 2014; Ohlander et al., 2012). Although AMD (also called acid rock drainage (ARD)) can be generated naturally, mining activities increase the rate of acid formation by exposing a large volume of sulphidic waste to atmospheric conditions (Kumari, Udayabhanu, & Prasad, 2010). In mining operations, AMD can be generated as a product characterized by a low pH and high concentration of sulphate ions and heavy metals (Kumari et al., 2010). AMD is considered to be the most serious issue facing the mining industry worldwide due to its environmental, social and economic impacts, which can last for a very long time.

The handling, storing and disposal of sulphide bearing tailings are serious challenges that the mining industry is facing globally due to the fineness of their grain size as well as their substantial volume. It is well known that in the presence of air (i.e., oxygen) and water, sulphidic tailings (commonly containing pyrite) oxidize and form AMD (Buckby et al., 2003). This product can then reduce the pH of the surrounding streams and soil/rock, and cause the leaching of toxic

trace metals (e.g., As, Cd) (Benzaazoua et al., 2008). The fineness of the tailings materials increases the oxidation rate of the sulphide minerals and thus can lead to serious economic and environmental consequences. As a result, the management of sulphidic tailings has been considered a significant challenge and a high priority of the mining industry (Levei et al., 2013). To prevent and/or minimize the negative impacts of sulphidic tailings, several disposal or mine waste management methods have been proposed and put into practice, such as desulphurization, paste tailings (cemented paste tailings (CPT)), and/or a combination of these approaches (Benzaazoua et al., 2008; Bois et al., 2012).

Among these technologies, cemented paste backfilling, as a novel approach, has been proven as an appropriate and cost-effective technology for the disposal of sulphidic tailings. Therefore, cemented paste backfilling has become a widely adopted technology for mine waste management in many parts of the world (e.g., North America, Australia, and Germany). Cemented paste backfill (CPB) is an engineered mixture that consists of three main components: tailings, binder and water.

To assess the environmental behaviour and durability performance of CPB, the chemical reactivity of a paste backfill system that contains sulphides is used. There are a number of testing methods that have been used to measure the reactivity of sulphidic materials, such as humidity cells, kinetic columns, and oxygen consumption (OC) tests. The latter is simple and fast, relatively accurate and economical as compared to other methods.

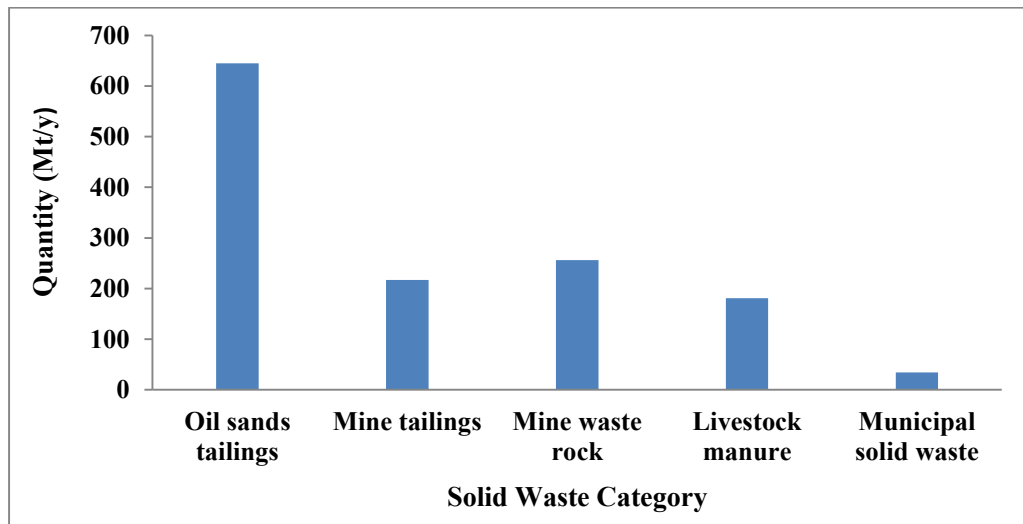


Figure 1.1. Major categories of solid waste streams in Canada - 2012 (Statistics Canada, 2012)

Many factors affect a CPB system during its operational life, such as temperature, curing time, water content, sulphide content and type, initial sulphate content, cracking, and damage stress. Any one of these factors, alone or in combination, may cause positive and/or negative impacts on the reactivity of a backfill system. These factors can originate from the backfill system itself (internal source) and/or from the surrounding mine environment (external source).

## **1.2 Problem Statement**

The incorporation of tailings that contain sulphide in cemented backfill appears to be an effective disposal method in underground and surface mines (Fall et al., 2004; Benzaazoua et al., 2008). However, there are still a number of unanswered questions about the reactivity of CPB systems in the short and long term. Also, another issue is the effect of backfill reactivity on the environmental behavior and durability of the backfill system itself. In the literature, most previous studies have focused on the physical and mechanical properties of CPB systems and their main components, but have neglected their chemical reactivity. Only a few studies have investigated the reactivity of sulphidic tailings without cement (e.g., Demers et al., 2009; Elberling et al., 1994; Elberling and Nicholson, 1996; Kempton and Atkins, 2009; Mbonimpa et al., 2003, 2002) and with cement (e.g., Fall et al., 2004; Ouellet et al., 2006, 2003; Pokharel, 2008). However, these studies have focused on assessing the influence of factors, such as curing time, sulphide concentration, water content and degree of saturation on the reactivity by conducting OC testing. Despite their significant findings, these studies did not take into account other equally important factors, such as curing and ambient mine temperatures, cracks and damage, ageing, initial sulphate content, curing stress, proportion and type of binder, and type and replacement level of mineral admixtures, either by themselves or combined. These factors could significantly impact the reactivity and thus lead to serious safety, environmental and economic ramifications. Hence, this research will experimentally investigate the influence of the neglected factors on the reactivity of CPB systems. The research results will provide significant information for mining engineers to better understand the reactivity of CPB systems and the influence of these factors, both individually and/or combined. This can lead to minimizing environmental as well as economic consequences and enhancing the durability of CPB systems.

### **1.3 Research Objectives**

The overall goal of this thesis is to provide a better understanding of the reactivity of CPB systems. The specific objectives of the research work are summarized below:

- To study the effects of time and mechanical damage at different loading levels and the associated microstructural changes on the reactivity of CPB for various curing times
- To investigate the effect of curing and ambient atmospheric temperatures on the reactivity of CPB
- To investigate the effect of the initial sulphate content on the reactivity of CPB
- To study the combined effects of initial sulphate content and curing temperature on the reactivity of CPB
- To study the effect of curing stress of CPB (cured at room temperature) on its reactivity

### **1.4 Research Approach and Methods**

In this thesis, the influence of a number of factors on the reactivity of CPB systems is experimentally investigated in order to achieve the above-mentioned objectives. Figure 1.2 shows the research method flow chart.

To better understand the reactivity of CPB systems and its influencing factors, several materials are used, such as different types of tailings materials (either artificial tailings materials such as ground silica sand or natural materials such as zinc and copper), proportions and types of binders (e.g., Portland cement, blended cement), and types of mixing water (distilled, tap water and water that contains sulphides). In addition, some other materials are used, including mineral admixtures (e.g., slag and fly ash) to partially substitute for Portland cement, and commercial pyrite powder which is added and mixed with specific amounts of ground silica to create artificial pyritic tailings with the desired sulphide content. These materials also include compounds such as ferrous sulphate heptahydrate. Desired amounts of ferrous sulphate are added to the mixing water to investigate the effect of internal sulphate attacks on the reactivity of CPB systems. Furthermore, various CPB mixtures are cured under different environments and operational conditions which approximately simulate mining environments.

During all of the experiments, oxygen consumption (OC) testing is used as the primary means to determine the reactivity of CPB and tailings without cement. The reactivity value is

measured as the average of three specimens and expressed in terms of the oxygen diffusion rate (moles  $O_2/m^2/y$ ). In addition to the OC test, several microstructural approaches (e.g., x-ray diffraction (XRD), scanning electron microscopy (SEM), mercury intrusion porosimetry (MIP), and thermogravimetric/derivative thermogravimetric (TG/DTG) analysis) are conducted on selected specimens to investigate the changes in the CPB microstructure. Also, other tests are carried out in accordance with American Society for Testing and Materials (ASTM) standards, including water content, slump, grain size distribution, specific gravity, etc.

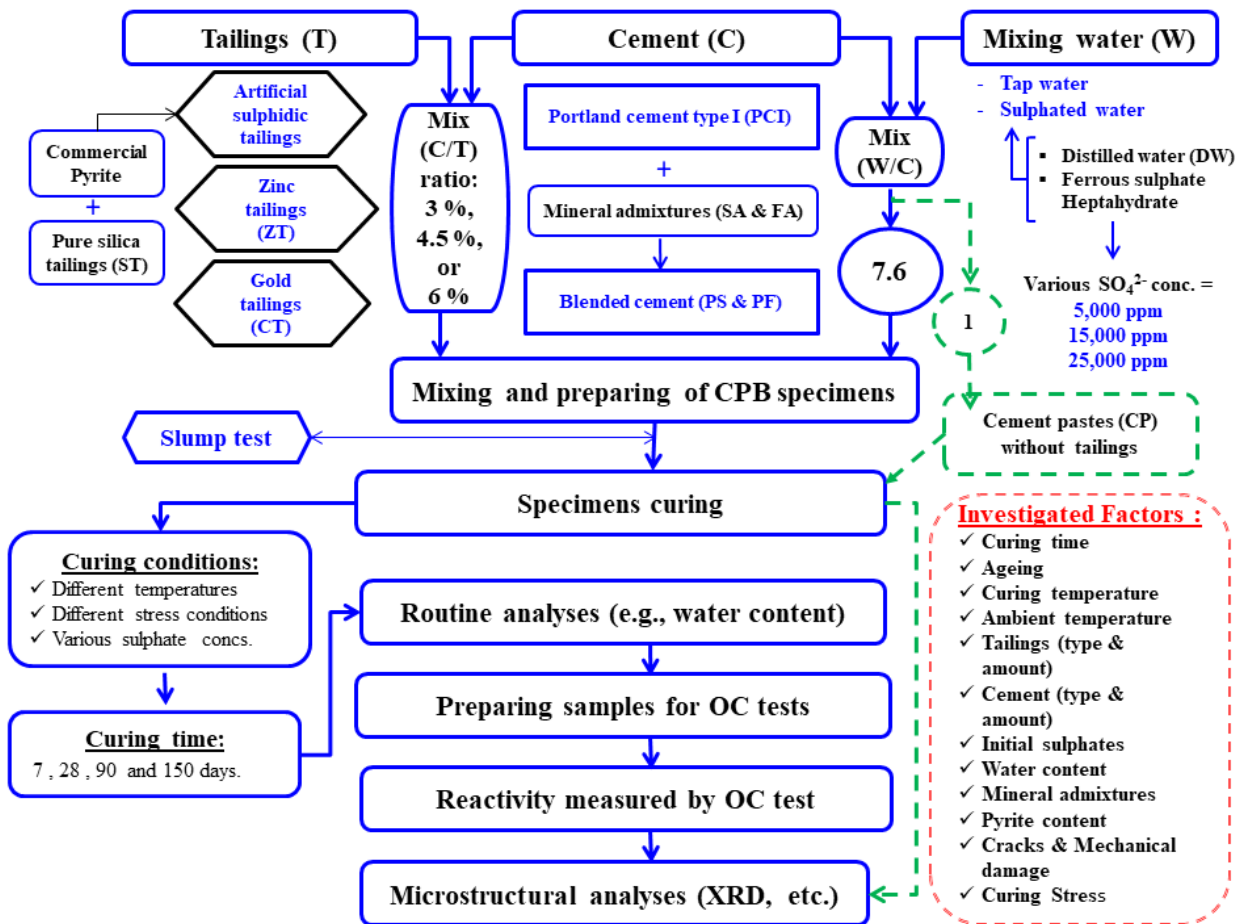


Figure 1.2. Flow chart of research method

## 1.5 Organization of the Thesis

The thesis is organized into nine chapters, as follows. Figure 1.3 shows the organization of the thesis work.

**Chapter One** provides the introduction, statement of the research problem, and research objectives and methods. **Chapter Two** consists of two main sections: the first section provides the background information on CPB technology and its main components, as well as the binder hydration and reactivity of CPB, and the second section presents a literature review on previous studies that conducted OC tests to investigate the reactivity of uncemented sulphidic tailings and cemented backfills that contain sulphidic tailings. **Chapters Three to Seven** are organized into a paper-based thesis format which comprises five technical papers; therefore, each technical paper includes an introduction, sections on the materials and methods, experimental results and discussion, and a conclusion. It should be noted that because the main results of the chapters are presented as technical papers, some information will be repeated. This is because each paper is independently written (i.e., without taking into account the contents of the other papers or the rest of the document) and in accordance with the manuscript preparation instructions of the corresponding publication medium. **Chapter Eight** provides a synthesis of the results in terms of the key research objectives. Finally, **Chapter Nine** presents the summary, conclusions and recommendations for future research.

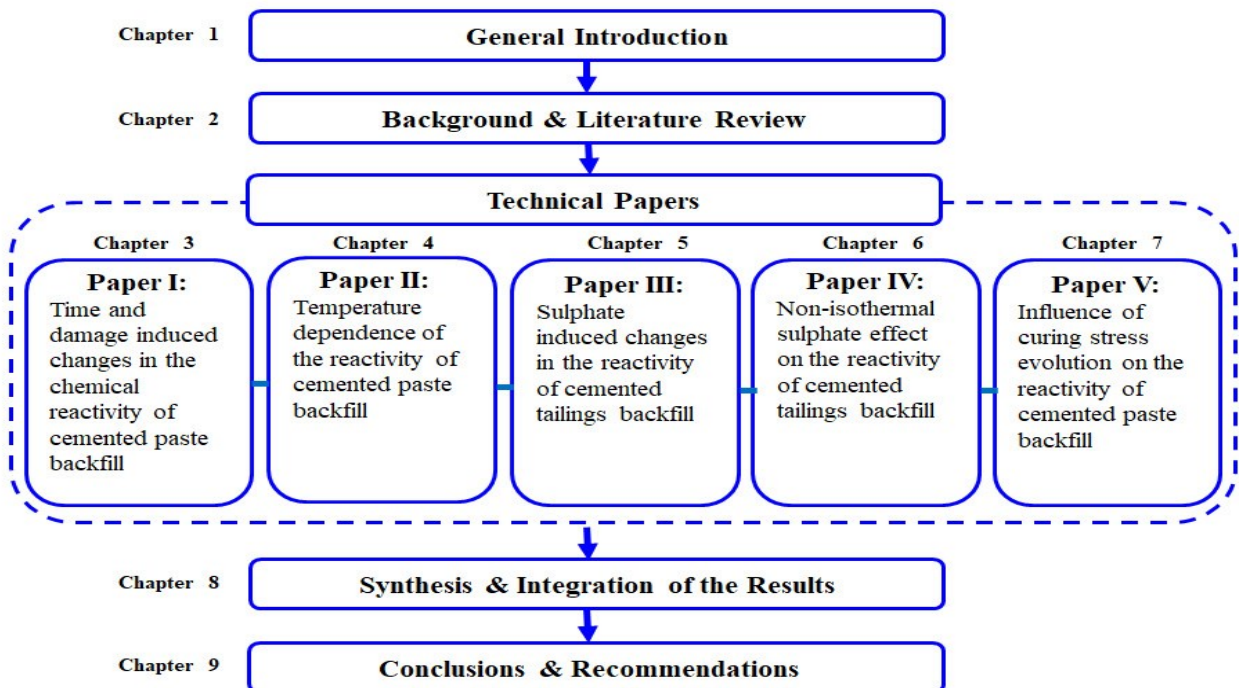


Figure 1.3. Organization of thesis

## 1.6 References

- Belem, T., & Benzaazoua, M. (2004). An overview on the use of paste backfill technology as a ground support method in cut-and-fill mines. In *Proceedings of the 5th Int. Symp. on Ground support in Mining and Underground Construction*. Villaescusa & Potvin (eds.) (pp. 637 – 650). London: Taylor & Francis Group.
- Benzaazoua, M., Bussière, B., Demers, I., Aubertin, M., Fried, É., & Blier, A. (2008). Integrated mine tailings management by combining environmental desulphurization and cemented paste backfill: Application to mine Doyon, Quebec, Canada. *Minerals Engineering*, 21(4), 330–340. <http://doi.org/10.1016/j.mineng.2007.11.012>
- Bois, D., Poirier, P., Benzaazoua, M., & Bussière, B. (2004). A feasibility study on the use of desulphurized tailings to control acid mine drainage. *36th Annual Meeting of the Canadian Mineral Processors*, 98(514), 361–380. Retrieved from [http://www.enviro-geremi.polymtl.ca/pdf/articles/CMP2004-Final version\\_LL\\_.pdf](http://www.enviro-geremi.polymtl.ca/pdf/articles/CMP2004-Final version_LL_.pdf)
- Buckby, T., Black, S., Coleman, M. L., & Hodson, M. E. (2003, February 3). Fe-sulphate-rich evaporative mineral precipitates from the Rio Tinto, southwest Spain. *Mineralogical Magazine*. <http://doi.org/10.1180/0026461036720104>  
<<http://dx.doi.org/10.1180/0026461036720104>>
- Demers, I., Bussière, B., Mbonimpa, M., & Benzaazoua, M. (2009). Oxygen diffusion and consumption in low-sulphide tailings covers. *Canadian Geotechnical Journal*, 46(4), 454–469. <http://doi.org/10.1139/T08-132>
- Dold, B. (2014). Evolution of Acid Mine Drainage Formation in Sulphidic Mine Tailings. *Minerals*, 4(3), 621–641. <http://doi.org/10.3390/min4030621>
- Elberling, B., & Nicholson, R. V. (1996). Field determination of sulphide oxidation rates in mine tailings. *Water Resources Research*, 32(6), 1773–1784. <http://doi.org/10.1029/96WR00487>
- Elberling, B., Nicholson, R. V., Reardon, E. J., & Tibble, R. (1994). Evaluation of sulphide oxidation rates: a laboratory study comparing oxygen fluxes and rates of oxidation product release. *Canadian Geotechnical Journal*, 31(3), 375–383. <http://doi.org/10.1139/t94-045>
- Fall, M., Benzaazoua, M., & Ouellet, S. (2004). Effect of tailings properties on paste backfill performance. In *Proceedings of the eighth international symposium on mining with backfill (Minefill 2004)* (pp. 193–202). China.
- Fourie, A. B. (2012). Perceived and realized benefits of paste and thickened tailings for surface deposition. *Journal of the Southern African Institute of Mining and Metallurgy*, 112(11), 919–926. Retrieved from [http://www.scielo.org.za/scielo.php?script=sci\\_arttext&pid=S0038-223X2012001100007&lng=en&nrm=iso&tlng=en](http://www.scielo.org.za/scielo.php?script=sci_arttext&pid=S0038-223X2012001100007&lng=en&nrm=iso&tlng=en)
- Kempton, H., & Atkins, D. (2009). Direct measurement of sulfide mineral oxidation rates and acid rock drainage in wall rock of open pit mines. In *Proceedings of the 8th International Conference on Acid Rock Drainage*. Skelleftea, Sweden: Swedish Association of Mines, Mineral and Metal Producers.
- Kumari, S., Udayabhanu, G., & Prasad, B. (2010). Studies on environmental impact of acid mine drainage generation and its treatment: an appraisal. *Indian Journal of Environmental Protection*, 30(11), 953–967.
- Levei, E., Frentiu, T., Ponta, M., Tanaselia, C., & Borodi, G. (2013). Characterization and assessment of potential environmental risk of tailings stored in seven impoundments in the Aries river basin, Western Romania. *Chemistry Central Journal*, 7(1), 5. <http://doi.org/10.1186/1752-153X-7-5>

- Marshall, B. (2015). *Facts and Figures 2015 of the Canadian Mining Industry*. Ottawa, Canada. Retrieved from [www.mining.ca](http://www.mining.ca)
- Mbonimpa, M., Aubertin, M., Aachib, M., & Bussière, B. (2003). Diffusion and consumption of oxygen in unsaturated cover materials. *Canadian Geotechnical Journal*, 40(5), 916–932. <http://doi.org/10.1139/t03-040>
- Mbonimpa, M., Aubertin, M., Dagenais, A. M., Bussière, B., Julien, M., & Kissiova, M. (2002). Interpretation of field tests to determine the oxygen diffusion and reaction rate coefficients of tailings and soil covers. In *The 55th Canadian Geotechnical and Joint IAH-CNC and CGS Groundwater Speciality Conferences* (pp. 147–154). Niagara Falls.
- Ohlander, B., Chatwin, T., & Alakangas, L. (2012). Management of sulphide-bearing waste, a challenge for the mining industry. *Minerals*, 2. <http://doi.org/10.3390/min2010001>
- Ouellet, S., Bussiere, B., Benzaazoua, M., Aubertin, M., Fall, M., & Belem, T. (2003). Sulphide Reactivity within cemented paste backfill: oxygen consumption test results. In *The 56th Annual Canadian Geotechnical Conference and 4th joint IAH-CNC/CGS Conference* (pp. 176–183). Winnipeg, Manitoba, Canada.
- Ouellet, S., Bussière, B., Mbonimpa, M., Benzaazoua, M., & Aubertin, M. (2006). Reactivity and mineralogical evolution of an underground mine sulphidic cemented paste backfill. *Minerals Engineering*, 19(5), 407–419. <http://doi.org/10.1016/j.mineng.2005.10.006>
- Pokharel, M. (2008). *Geotechnical and environmental response of paste tailings systems to coupled thermo-chemical loadings*. University of Ottawa. Retrieved from <http://hdl.handle.net/10393/27793>
- Statistics Canada. (2012). *Human Activity and the Environment: Waste management in Canada*. Ottawa.

## **Chapter 2: Background and Literature Review**

### **2.1 Introduction**

Backfilling is an engineering technique that uses any material or a combination of materials to fill excavations or voids generated by underground mining operations for preventing or reducing mine collapses, minimizing surface waste disposal, and improving mine production. This chapter will provide the background information on the most prevalently found types of mine backfills with a focus on cemented paste backfill (CPB) systems. Also, background information will be provided on the binder hydration process and reactivity of CPB systems as well as the main factors that may affect the reactivity. In doing so, the theoretical and technical background information will allow for a better understanding of the results and findings presented in this thesis.

### **2.2 Background Information on Mine Backfill and Cemented Paste Backfill**

#### **2.2.1 History of Mine Backfill**

The principle of backfilling is based on exploiting mine wastes to refill voids generated due to ore extraction. Backfilling has technical and environmental benefits and economical. The benefits of backfilling include enhanced stability, safety and production of mining along with reduced surface disposal of waste. Among these benefits of backfilling, the disposal of mine wastes is considered to have significant importance. Typically, backfills are made of available mine wastes mixed with a small amount of external materials (as enhancing materials), such as cement to maintain the desired characteristics of the backfill.

Historically, underground mine backfilling was developed and practiced in mines in some of the regions and countries worldwide, but especially in Australia and North America (Potvin et al., 2005). At the beginning of the nineteenth century, dry backfilling was introduced into Australian mines and then followed by Canadian mines to reduce the collapse of mines during mining operations (Potvin et al., 2005). The dry backfill consisted of filling materials such as waste rock or surface sand and gravel which was used to refill mine stopes. This method is known as the first kind of backfilling. Despite the difficulties of transportation and placement of dry backfill in underground mines, the economic benefits encouraged miners and researchers to address the challenges. Indeed, mixing water into dry fill materials was proposed for Mount Lyell Mine in Australia to solve the issue of delivery and placement of dry backfill. Then, researchers developed the concept of hydraulic backfilling. In 1933, cemented backfill was used for the first time by

mixing granulated furnace slag with pyrrhotite tailings in the Horne mine in Quebec, Canada. Using a binder agent produced cemented backfill, which is self-supporting due to the cementation process that takes place between the different components of the backfill. As a result, the addition of cement to backfill contributed to the development of new mine extraction techniques and mining methods. Furthermore, this contributed to the development of backfill technologies with a focus on cementing hydraulic backfill during the 1950s and 1960s with the addition of hydraulic binders (usually cement). The second phase of changes in backfilling technology occurred in the 1960s when North American mines began to use cemented and un-cemented rock fills. The third phase of mine backfilling started in the 1970s in industrialized countries. The substantial mining production rates in these countries generated large mine cavities which required huge masses of fill materials. This led to the search for backfill systems that would have stability yet incur a low cost. Therefore, backfill systems were developed that addressed both stability and cost. A variety of cemented backfill systems with relative stability and low cement content were developed for Canadian and Australian mines, such as the Kidd Creek mine in Ontario, Canada and Mount Isa Mines in Queensland, Australia (Potvin et al., 2005). The latter produced backfill to refill mine walls with a height of 200 m and width of 40 m. The backfill used consisted of a mixture of waste rock, quarried rock (or aggregate) and cemented tailings at a 2 to 1, ratio respectively. These successes encouraged miners and researchers to reduce the cement content in backfill in order to reduce cost. Thus, research focused on substituting cement or reducing cost by using less expensive materials such as ground furnace slag and fly ash. The results showed that the use of these materials as a substitution for cement in backfill could reduce the early strength of the backfill, but would contribute to its long term strength.

In the 1980s and 1990s, the mining industry in North American increased production by using deep extraction in addition to recovery with underground supporting pillars (Potvin et al., 2005). This led to the search for backfill with special properties such as rapid curing time and stability to support this production trend. It was clear that a faster curing time was important in backfill systems. Therefore, some mines used backfill systems that featured a fast curing time, was simple and flexible to use, and had suitable stability along with a low cost. The backfill consisted of thin cement slurry with waste rock which was mixed underground by spreading waste rock and then pouring in the cement slurry which was prepared in an underground station. In addition, research on paste backfill technology was prevalent during the 1980s. The first attempt at using a

CPB system was carried out in the early 1980s in the Bad Grund mine in Germany. This new technology proved to be promising with many benefits as opposed to the use of cemented slurry rock backfill (Potvin et al., 2005), and in the 1990s, many North American mines began to use CPB.

### **2.2.2 Prevalently Used Types of Mine Backfills**

Mine backfill systems are classified based on the type of primary fill material used, and the production and delivery methods. The type of backfill used in mines is based on the availability of the fill materials at the mine site (Potvin et al., 2005). Mine backfill systems commonly use hydraulic, rock, and paste backfills (Potvin et al., 2005). Also, these systems can be cemented or un-cemented.

#### **2.2.2.1 Hydraulic Backfill**

Hydraulic backfill is a conventional type of mine fill. Hydraulic backfilling is a commonly used method worldwide due to its simplicity and effectiveness in transporting the fill. Hydraulic backfilling can be simply described as a process that uses water to transport fill materials through pipelines into underground voids (Rantala, 2007). Thus, the name of this method is derived from how the backfill is transported (Potvin et al., 2005). Hydraulic backfill can be prepared by using several different fill materials including natural materials, such as surface sand deposits and mine wastes of crushed rock and tailings. Typically, hydraulic backfill is made of milled tailings. First, the fine fraction (particle size  $\leq 10 \mu\text{m}$ ) of milled tailings are removed through a desliming process by circulating all of the fill material into hydrocyclones which separates the fine fraction and sends them to the tailings storage facility (e.g., tailings impoundment). Then, the residual fraction of the hydraulic fill materials are mixed and flushed with water to make slurry fill materials that travel through pipelines to refill underground voids. The main function of water is to facilitate the delivery of the fill materials via pipelines to their desired destination. Water is used to quickly flush the solid particles of the fill materials which does not allow them to settle before they reach their endpoint (underground voids) (Rantala, 2007). It is clear that water is critical for hydraulic backfill to control its properties. Also, the particle size distribution of the tailings materials, in particular, the percentage of fine fraction in the total fill materials is important. Hydraulic fills can be placed without cement as it drains water and does not create hazards due to the impoundment of water. This type of fill is only used if the tailings consist of coarse particles. Recently, there is

the trend in which many mines worldwide have changed from using hydraulic backfill systems to cemented backfill systems.

### **2.2.2.2 Rock Backfill**

Rock backfilling is a technique used to manage mine wastes such as waste rocks by filling them into underground mine voids (Yao et al., 2012; Potvin et al., 2005). The fill materials used in rock backfilling are prepared before mixing by various processes, such as crushing and sieving the rocks (Yao et al., 2012). The transportation of rock backfill materials into underground voids can be done manually, or by using gravity or mechanical equipment to obtain a compressible backfill body (Yao et al., 2012). When cement is added, the backfill is called cemented rock backfill.

### **2.2.2.3 Cemented Paste Backfill**

Cemented paste backfilling is another prevalent type of backfilling used in underground mining operations. CPB technology is the focus of this study and discussed in detail in the next section.

## **2.3 Cemented Paste Backfill Technology**

Cemented paste backfill (CPB, also called cemented paste tailings (CPT) and paste backfill) technology was developed to solve the difficulties associated with hydraulic backfilling, especially the delivery and placement of the fill materials as well as the geotechnical safety issues (e.g. barricade failure, liquefaction) associated with the use of hydraulic backfill. CPB technology was introduced in the mining industry in the early 1980s at the Bad Grund mine in Germany and then this technology was implemented in North American mines in the 1990s. CPB has become the more popular method for managing milled tailings worldwide (Fall et al., 2015). It has been recently adopted by many underground mines globally due to its benefits. Implementation of CPB in underground mines offers several benefits, including reduced disposal of surface tailings, enhanced underground mine stability, safer work environment and increased mine production.

The paste in CPB is an engineered mixture typically prepared with three key ingredients: mine tailings with a solid percentage that ranges between 70% and 85%, water which can be fresh or mine processed, and a hydraulic binder (usually cement), which is between 3% and 7% by total weight of the fill paste. These components are prepared and blended in a plant commonly located at the surface of the mine. Produced paste fill is then transported by gravity, pumping and/or a combination of both to fill the desired excavated stopes which have been prepared to receive the paste fill. Figure 2.1 shows a simple schematic of a CPB system.

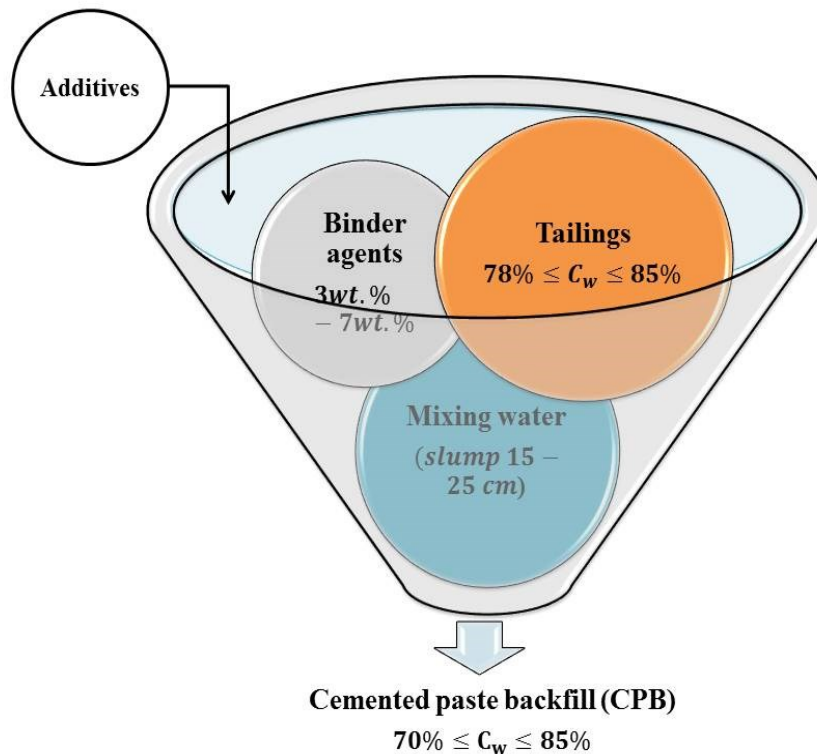


Figure 2.1. Schematic diagram of paste backfill components (Benzaazoua et al., 2002)

### 2.3.1 Main Components of CPB System

As mentioned, milled tailings, water, and a binder agent are used as the materials to prepare the paste fill. In addition, a coarse fraction is included to increase the rate of filling, and the stability and strength of the paste fill. These materials will be discussed in the following sections.

#### 2.3.1.1 Tailings

Tailings are unwanted by-product materials (e.g. silicates, oxides, hydroxides, carbonates, and sulphides) generated through a mineral concentration process (Dimitrova & Yanful, 2012; Lottermoser, 2010). Generally, mineral processing begins with crushing and grinding raw rocks into small particles typically less than 0.1 mm to facilitate separation of the desired mineral from the host rock, as shown in Figure 2.2. The term tailings is a description of the mineral processing which produces the desired minerals, which is called the “head”, and the remainder are called the “tail” (ICME/UNEP, 1998). Tailings are a mixture of fine-grained host rocks and processed effluents from mining and milling operations.

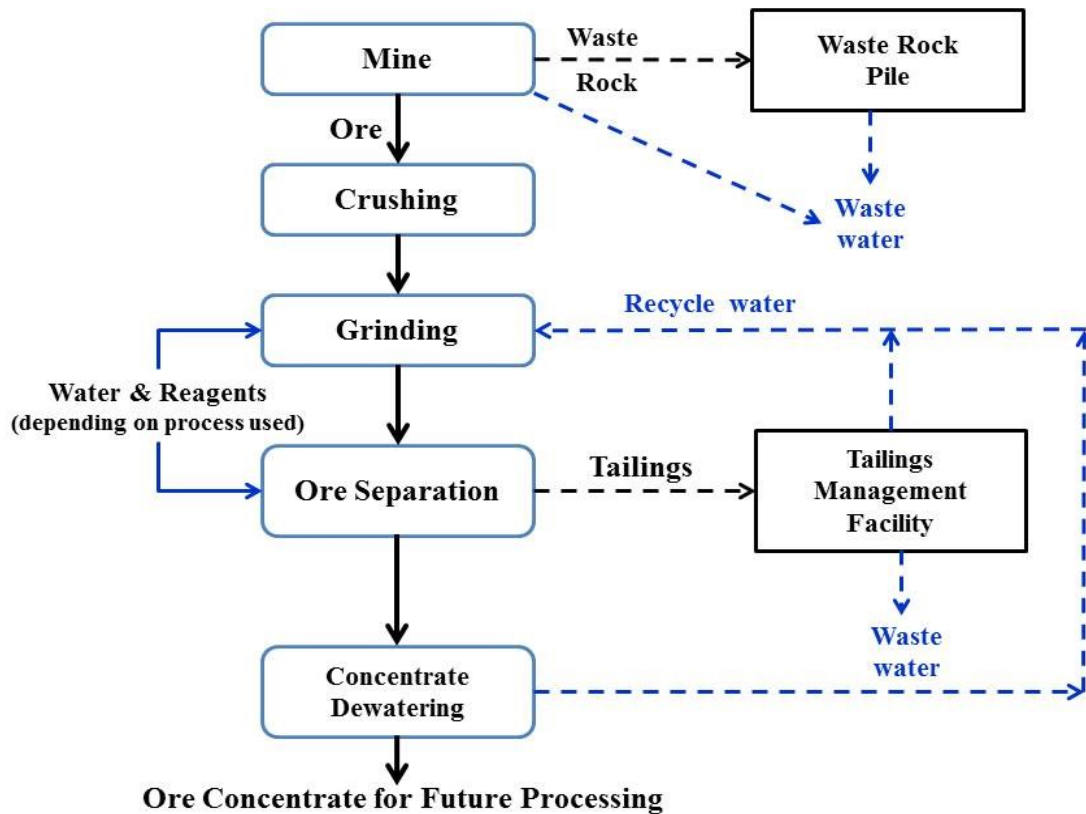


Figure 2.2. Typical activities in mine operations (Environment Canada, 2009)

The characteristics of tailings are shaped by the composition of the parent rock, mineral extraction method, and tailings materials transport and placement methods (James et al., 2003). The grain size of tailings is based on the required size of the ore for the recovery process. Usually, tailings particle size ranges from sand to silt (Rodriguez & Edeskär, 2013). Also, their grain shape is more angular than natural soil particles (Bhanbhro et al., 2013). However, tailings are the main constituent that represent typically, between 70% and 85% of the weight of the paste fill (Aldea, 2010). Therefore, their characteristics (e.g., physical, mineralogical) can play a significant role in determining the stability and performance of CPB systems with respect to the other ingredients (Kesimal et al., 2005; Fall et al., 2004). These properties are briefly discussed in the following sections.

#### 2.3.1.1.1 Physical properties

The physical properties of tailings (e.g., particle size distribution, specific gravity, porosity, specific surface area and density) play a critical role in the stability and strength of CPB and cost as well as the volume of water required. The influence of these properties on the performance of CPB systems has been studied by several researchers (e.g., Kesimal et al., 2005; Fall et al., 2004; Benzaazoua & Kongolo, 2003). The percentage of fine particles (<20 µm) in tailings is one of the main physical properties of tailings (Fall et al., 2004). Although the fine fraction in paste fill facilitates flow, it also influences the microstructure of the CPB (i.e., pore size distribution and porosity). The porosity and pore size distribution of paste fill affect the ability of CPB to drain water (Fall et al., 2004). Also, there is a proportional relationship between increasing the volume of fine particles in tailings and water demand of the paste. There is also a relatively proportional relationship between the water consumption of the hydraulic binder and tailings density in the mix. This means that when high density tailings are used, a large amount of cement is consumed in making CPB. As a result, the cost of the CPB will be higher.

#### 2.3.1.1.2 Chemical properties

The chemical properties of tailings need to be identified to ensure compatibility with the binders used in the paste mix (Aldea, 2010). The presence of sulphur in the tailings increases their density as well as enhances the strength of the paste due to the addition of more binder (Fall et al., 2004). On other hand, a high sulphur content can cause degradation of CPB because of sulphate attacks.

#### 2.3.1.1.3 Mineralogical properties

The mineralogy of tailings is considered to be one of its primary properties and affects the paste fill form because information on the mineralogy can help to determine the required solid content and water capacity of the tailings particles to form the paste fill (Potvin et al., 2005). Furthermore, the mineralogy of tailings can positively or negatively affect the final strength of CPB based on chemical reactions with itself or other components of the CPB during mixing, delivering, and the placement process.

### **2.3.1.2 Mixing Water**

The water used in the preparation of CPB could be processed or fresh water, and can consist of half the volume of CPB. Therefore, the mixing water is important and its properties need to be

evaluated before use to avoid negative impacts on the stability and strength of fill paste as well as the environment.

### **2.3.1.3 Hydraulic Binder**

The binder agent is one of main components added to increase the strength of CPB. The type of binder and the required strength of the paste fill determine the binder feed rate. The binder feed rate ranges between 2% and 6% by weight to achieve typical strength requirements (Aldea, 2010). Ordinary Portland cement (PCI) is usually used as the binder agent because it is readily available in many parts of the world (Razavi & Hassani, 2007).

## **2.3.2 CPB Operations**

### **2.3.2.1 Mixing**

The mixing process is considered to be one of the main processes in designing a CPB system. This process has a vital role in the quality of the final product (paste fill). The function of the mixing process is to blend the raw materials of the CPB, including dewatered tailings, hydraulic binder (e.g. cement), and additional water or slurry into a mixer system to produce a homogeneous paste fill that is used to refill underground voids (Potvin et al., 2005). The quantity of cement is calculated as a percentage of the total dry mass of solids. The binder is fed into the mixer through a screw conveyor and mixed with the other components. Any additional amount of cement should be well controlled because cement can comprise more than 70% of the cost of CPB. There are two types of mixing systems used in CPB plants: batch mixing and continual mixing (Potvin et al., 2005).

#### **2.3.2.1.1 Batch mixing systems**

The components of CPB are individually weighed and fed into the batch mixer. When all of the components are in the batch mixer, mixing is carried out to generate paste. Then the paste is discharged for delivery to underground mines (Potvin et al., 2005).

#### **2.3.2.1.2 Continual mixing systems**

The continual mixing system is automated. Fill materials are continuously fed into a mixer. High intensity and pugmill concrete mixers are most commonly used (Potvin et al., 2005). The mixing process is controlled by a monitoring system that ensures paste quality. Paste samples are collected

from both the batch and continuous mixers during operation. These samples are tested for strength (Potvin et al., 2005).

### **2.3.2.2 Delivery and Placement**

The delivery process transports the final paste manufactured with the mixing process to the underground stopes. The delivery system consists of boreholes, pipes, pumps, and a cleaning system. The paste fill can be transported by gravity, pumps force or a combination of both. Gravity is the first option for delivering paste fills if mine geometry permits due to the savings incurred as opposed to the use of pumps. The placement of paste fill into underground stopes is followed by the preparation of the stopes in which barricades are placed to retain the paste fill.

### **2.3.2.3 Monitoring**

Monitoring the quality of CPB begins at the paste plant and continues through delivering, placement, and after the placement of the CPB into the underground stopes. Several tests are conducted to ensure the quality of the final backfilling, including *in situ* density and strength testing (Potvin et al., 2005).

## **2.4 Background Information on Binder and its Hydration**

Binders are any material capable of holding solid particles together in a solid form under specific conditions. In general, there are two main types of binders used in construction: hydraulic and non-hydraulic. Hydraulic binders, such as Portland cement, are a type of material that sets and hardens when mixed with water as a result of a chemical reaction (hydration process). Non-hydraulic binders (e.g., lime and gypsum plaster) are a type of material that hardens without contact with water. Hydraulic binders are most commonly used, in particular, Portland cement type I (PCI, in accordance with ASTM standards). Portland cement (PC) is hydraulic cement that sets and hardens by reacting chemically with water. According to ASTM C150, PC is: “*hydraulic cement (cement that not only hardens by reacting with water but also forms a water-resistant product) produced by pulverizing clinkers consisting essentially of hydraulic calcium silicates, usually containing one or more of the forms of calcium sulfate as an inter-ground addition*”. The following section provides a brief description of the basic hydration reactions of clinker minerals as individual phases, which is necessary for the hydration of PC in general.

### 2.4.1 Portland Cement

Portland cement (PC) is a hydraulic cement. It is manufactured by crushing and mixing of defined quantities of raw materials such as limestone, clay, and shale. The mixture is burned in a rotary furnace called a kiln under extremely high temperatures up to 1500-1800°C (Baxi & Prasad, 2005). This leads to the conversion of partially molten raw materials into a combination of pellets and small balls called “clinkers” resultant of the chemical reactions. Then, the clinkers are cooled and mixed with gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) which is used to regulate the rate of the setting of the cement as well as that of other key materials (Baxi & Prasad, 2005). Finally, the mixture of clinkers and gypsum is grounded to a very fine gray powder material which is known as PC. Globally, there are several types of PC manufactured and used for different purposes. Therefore, there is no universal international standard to classify and specify these different types of PC, as different standards are used worldwide. Each standard has certain chemical and physical limits to ensure a level of consistency between cement-producing plants. For example, in Canada, PC is classified into six types under Standard A3000-03 by the Canadian Standards Association (CSA). In addition, there are six types of blended hydraulic cement (BHC) that is defined as cement that consists of PC and up to three supplementary cementing materials and blended supplementary cementing materials that contain up to three cementitious components. Table 2.1 shows both the CSA standards (previous and new) and equivalent American standards (ASTM C150 and C1157) for PC and BHC.

Table 2.1. Canadian and American standards for classification of Portland cement (PC) and blended hydraulic cement (BHC)

Canada				USA		Type description
*CSA A-3000		*CSA A-3001-03		ASTM C 150	ASTM C 1157	
PC	BHC	PC	BHC	PC	BHC	
10	10E-x	GU	GU <sup>b</sup>	I	GU	General use hydraulic cement.
20	20E-x	MS	MS <sup>b</sup>	II	MS	Moderate sulphate-resistant hydraulic cement.
20	20E-x	MH	MH <sup>b</sup>	II (MH)	MH	Moderate heat of hydration hydraulic cement.
30	30E-x	HE	HE <sup>b</sup>	III	HE	High early-strength hydraulic cement.
40	40E-x	LH	LH <sup>b</sup>	IV	LH	Low heat of hydration hydraulic cement.
50	50E-x	HS	HS <sup>b</sup>	V	HS	High sulfate-resistant hydraulic cement.

\*Previous CSA standard

<sup>a</sup> new CSA standard

(Source: CSA A3000-03)

PCI (general use (GU) cement in Canada) is the most widely used hydraulic binder for general use around the world due to the availability of its raw materials at a reasonable price. Also, it is commonly used in the mining industry for several applications, such as construction and backfilling. In backfill systems (e.g., CPB), PCI is usually used as the binder alone or partially blended with mineral admixtures, such as slag or fly ash (Yao et al., 2012). PCI (or its blends) is considered to be one of the most important ingredients in CPB systems that has a central role in determining their physical, chemical and mechanical characteristics with respect to the other ingredients (tailings and water).

#### **2.4.1.1 Chemical Composition of Portland Cement**

Typically, modern PC mainly consists of clinker plus a small quantity of gypsum (3%–7% wt.) which is used to regulate the initial setting time. Clinker is a vital ingredient which represents about 95% wt. of the PC. Typically, PC and its clinker mainly consist of four oxides: lime (CaO), silica (SiO<sub>2</sub>), alumina (Al<sub>2</sub>O<sub>3</sub>) and iron oxide (Fe<sub>2</sub>O<sub>3</sub>) in addition to the minor oxides (Klieger & Lamond, 1994), as shown in Table 2.2. These oxides at high temperatures interact with one another in the kiln to form various crystal phases. Among these phases, alite (C<sub>3</sub>S), belite (C<sub>2</sub>S), aluminate (C<sub>3</sub>A) and ferrite (C<sub>2</sub>AF) are the four main phases (Huang et al., 2014; Shetty, 2005), as provided in Table 2.3. These main phases comprise the bulk of the cement base of most PC types. Clinker is considered to be a poly-mineral material that mostly consists of silicate crystals (C<sub>3</sub>S and C<sub>2</sub>S) surrounded by an interstitial matrix that comprises aluminate and ferrite (C<sub>3</sub>A and C<sub>4</sub>AF) phases (Costa, 2015). Figure 2.3 shows a typical cement grain, and the larger C<sub>2</sub>S and C<sub>3</sub>S particles surrounded by the much smaller C<sub>3</sub>A and C<sub>4</sub>AF matrix. In addition to the main phases, there are minor phases, like periclase and alkali sulfates that may form separately or incorporated into the main clinker phases through ionic substitution due to the minor oxides found in the raw materials during the burning process in the kiln system (Telschow, 2012). The reactions of these phases during the hydration process determine the chemical, physical and mechanical properties of hardened paste. Typically, PCI consists of four clinker minerals (phases) which represent about 90-95% of its mass and some other minor constituents including calcium sulfate, alkali sulfates, free or uncombined lime (CaO) and magnesia (MgO), in addition to other minor constituents left over from the clinkering and grinding steps.

Table 2.2. Typical chemical composition of clinker and Portland cement (van Oss, 2005)

Constituent (Oxide)	Percentage by mass in clinker <sup>1</sup>	Percentage by mass in cement <sup>1,2</sup>
CaO	65	63.4
SiO <sub>2</sub>	22	20.9
Al <sub>2</sub> O <sub>3</sub>	6	5.7
Fe <sub>2</sub> O <sub>3</sub>	3	2.9
MgO	2	1.9
K <sub>2</sub> O + Na <sub>2</sub> O	0.6	0.6
Other (incl. SO <sub>3</sub> )	1.4	3.6
H <sub>2</sub> O	“nil”	1
Total	100	100

<sup>1</sup> Values shown are representative to only 2 significant figures

<sup>2</sup> Based on clinker shown plus addition of 5% gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O)

Table 2.3. Four main minerals of cement clinker

Chemical Name	Chemical Formula	Oxide Formula	CCN*	Mineral Name
Tricalcium Silicate	Ca <sub>3</sub> SiO <sub>5</sub>	3CaO.SiO <sub>2</sub>	C <sub>3</sub> S	Alite
Dicalcium Silicate	Ca <sub>2</sub> SiO <sub>4</sub>	2CaO.SiO <sub>2</sub>	C <sub>2</sub> S	Belite
Tricalcium Aluminate	Ca <sub>3</sub> Al <sub>2</sub> O <sub>6</sub>	3CaO.Al <sub>2</sub> O <sub>3</sub>	C <sub>3</sub> A	Aluminate
Tetracalcium Aluminoferrite	Ca <sub>2</sub> AlFeO <sub>5</sub>	4CaO.Al <sub>2</sub> O <sub>3</sub> .Fe <sub>2</sub> O <sub>3</sub>	C <sub>4</sub> AF	Ferrite

\*CCN: Cement Chemist Notation

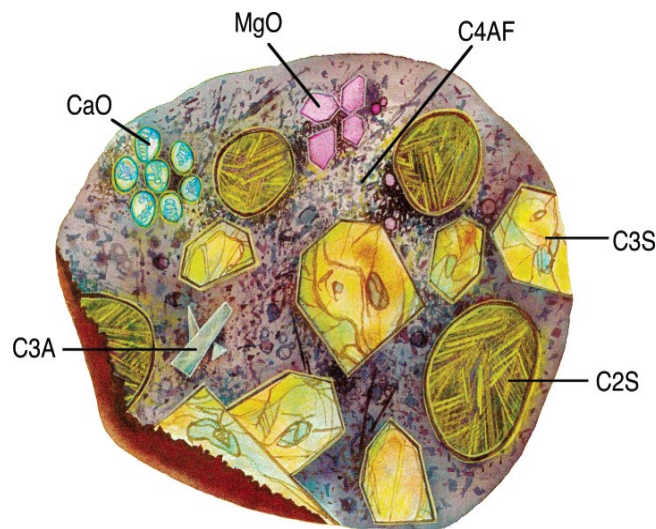


Figure 2.3. Cross-section representation of powdered cement grain (Bishop et al., 2003)

It is difficult to determine the proportion of the four main minerals in cement through direct analysis. Therefore, the approximate amount of each of these minerals can be calculated indirectly by using Bogue's equations. Bogue (1929) established a set of equations, as shown in Table 2.4, that can be used to indirectly calculate the approximate proportions of the four main types of minerals in Portland cement clinker by using the concentration of the main oxides of cement that is measured by chemical analysis (Neville, 2012; Winter, 2009). Bogue's equations were established based on the  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$  phase diagram and on the assumptions that the measured cement system is in equilibrium and that there are no secondary minerals (Costa, 2015). Figure 2.4 presents a typical composition of PCI.

Table 2.4. Bogue's equations (Costa, 2015)

Phase	Oxide content (obtained by chemical analysis)
$\text{C}_4\text{AF}$	$= 3.043 (\text{Fe}_2\text{O}_3)$
$\text{C}_3\text{A}$	$= 2.65 (\text{Al}_2\text{O}_3) - 1.692 (\text{Fe}_2\text{O}_3)$
$\text{C}_2\text{S}$	$= 3.071 (\text{CaO}) + 8.602 (\text{SiO}_2) + 5.068 (\text{Al}_2\text{O}_3) + 1.0785 (\text{Fe}_2\text{O}_3)$
$\text{C}_3\text{S}$	$= 4.071 (\text{CaO}) - 7.602 (\text{SiO}_2) - 6.718 (\text{Al}_2\text{O}_3) - 1.430 (\text{Fe}_2\text{O}_3) - 2.85 (\text{SO}_3)$

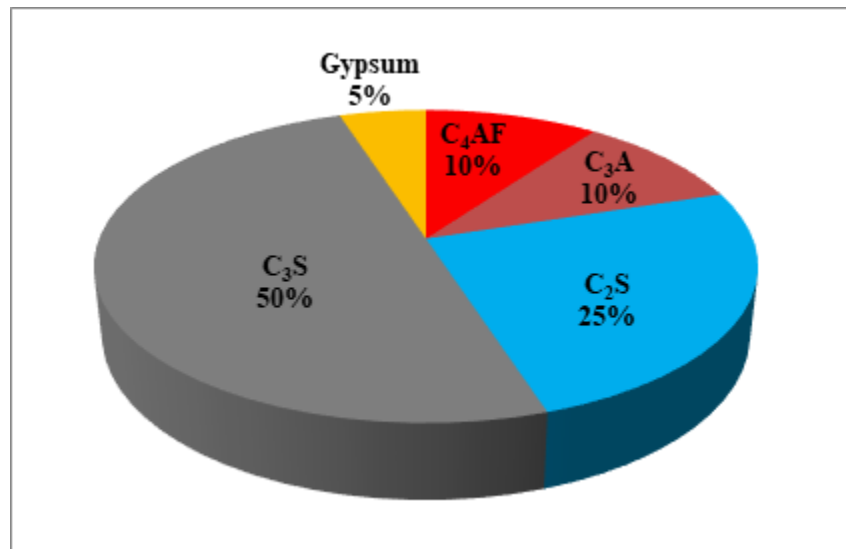


Figure 2.4. Composition of typical PCI with weight percent

## **2.4.2 Blended Cement**

Portland cement (PC) is often partially replaced with mineral admixtures (also called supplementary cementing materials (SCM)) in construction and mining applications. The motivation to use SCM materials is technically, economically and environmentally driven (Lothenbach et al., 2011). Using mineral admixtures in PC or in concrete can improve the properties of fresh and hardened cement paste (e.g., workability, strength and permeability), thus minimising material cost and energy consumption and reducing greenhouse gas footprints from cement production. For example, substituting one tonne of pure Portland cement with mineral admixtures reduces about one tonne of greenhouse gas emissions (CAC, 2016). In this research, fly ash (FA) and slag (SA) are the mineral admixtures that are used as partial replacement of PCI in paste backfill systems; therefore, they will be briefly discussed in the following sections.

### **2.4.2.1 Fly Ash**

Fly ash (FA) is also called pulverised fuel ash (PFA) and generally one of the most used types of SCMs in concrete worldwide (Lye et al., 2015; Shi & Mo, 2008). Incorporation of FA into cement and/or a concrete mix at an optimum ratio offers technical (e.g., promotes strength), environmental (e.g., reduces CO<sub>2</sub> emission) and economic (e.g., saves energy) benefits (Thomas, 2007). FA is a fine powder material that consists of mostly spherical glassy particles that are generated as a by-product of the combustion of pulverized coal in electric power generation plants (Ramezani pour, 2014), as shown in Figure 2.5. FA grains are shown in Figure 2.6. In general, FA is recognized to be a pozzolanic material that consists of a finely-divided amorphous alumino-silicate with varying amounts of calcium (Thomas, 2007). FA is classified into classes in North America based on the calcium content (CaO) in the ASTM and CSA standards (Thomas, 2007, 2013), as listed in Table 2.5. FA undergoes pozzolanic reactions with calcium hydroxide formed by the hydration of cement and water which generates cementitious products (cement gels) similar to cement. This reaction is slow and promotes the long term properties of hardened paste, such as strength in the long term by increasing the quantity of cementitious hydration products in the binder phase (calcium-silicate-hydrate (C-S-H)) and calcium-aluminate hydrate. Furthermore, some types of FA, such as Class C, have pozzolanic and cementitious properties (see Table 2.5). These types of FA can react with water in the absence of calcium hydroxide and produce hydrates (Thomas, 2007).

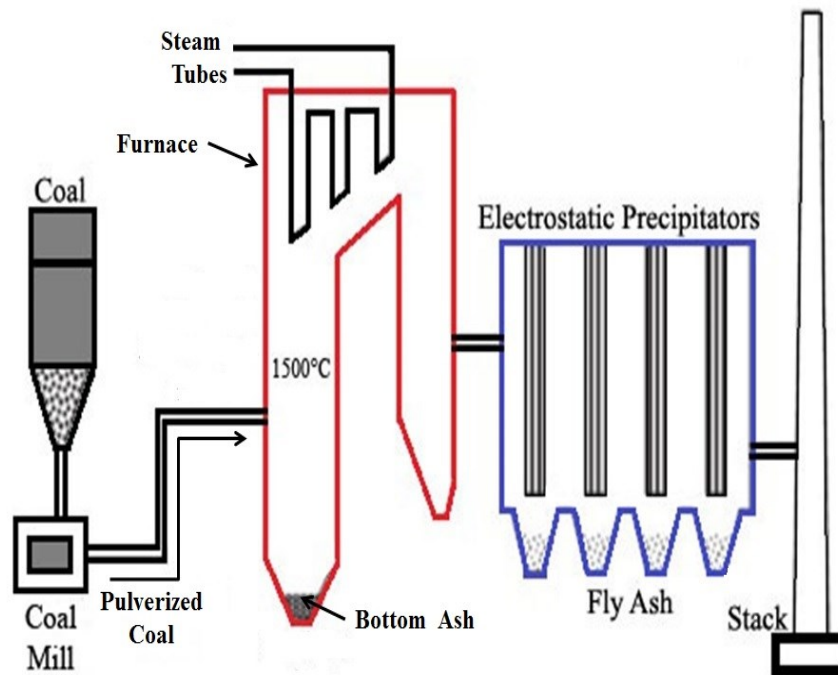


Figure 2.5. Schematic layout of production of fly ash in coal-fired electrical generating station (Thomas, 2013)

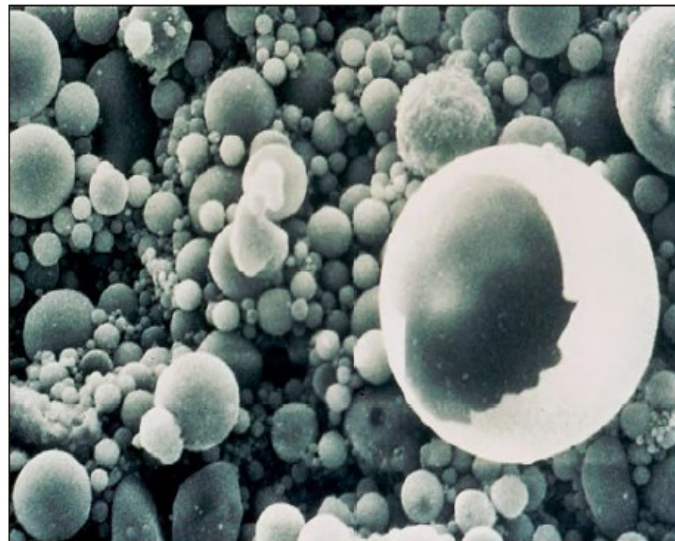


Figure 2.6. Scanning electron micrograph of fly ash particles (average particle size is about 10  $\mu\text{m}$ ) (Taylor et al., 2006)

Table 2.5. Classes of fly ash used in North America (Thomas, 2013)

Specification	Class	Description of specifications	Chemical requirements
ASTM C618	F	Fly ash normally produced from burning anthracite or bituminous coal F that meets the applicable requirements for this class as given herein. This class of fly ash has pozzolanic properties.	$\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 \geq 70\%$
	C	Fly ash normally produced from lignite or sub-bituminous coal that meets the applicable requirements for this class as given herein. This class of fly ash, in addition to having pozzolanic properties, also has some cementitious properties. Note: Some Class C FA may contain lime content greater than 10%.	$\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 \geq 50\%$
CSA A3001	F	Low-calcium fly ash	$\text{CaO} < 15\%$
	CI	Moderate-calcium fly ash	$15\% \leq \text{CaO} \leq 20\%$
	CH	High-calcium fly ash	$\text{CaO} > 20\%$

### 2.4.2.2 Slag

Blast furnace slag (BFC) is defined by ASTM C989-99 as “the non-metallic product consisting essentially of calcium silicates and other bases that is developed in a molten condition simultaneously with iron in a blast furnace”. Based on the cooling process, BFC can be typically divided into air-cooled slag (used as aggregate), expanded slag (used as lightweight aggregate) and ground granulated blast furnace slag (GGBFS) (used as SMC and blend cement), as shown in Figure 2.7.

GGBFS (or GGBS), which is sometimes simply referred to as “slag”, is commonly used as SCMs in concrete and construction applications worldwide (Thomas, 2013). GGBFS is a fine powder produced when molten slag is quenched rapidly with water jets (Brito & Saikia, 2013). Due to its hydraulic properties, GGBFS can be considered by itself a hydraulic cement that is relatively low in cost compared to PC. It can replace PC up to a much larger extent than pozzolanic materials, such as FA (Snellings et al., 2012). The physical, chemical, and mineralogical composition of slag influences its performance. The reactivity of slag is influenced by its chemical composition, glass content, fineness and particle size distribution (Bougara et al., 2010). The chemical composition of slag influences its reactivity which increases with increased contents of

alkaline, calcium, alumina, and magnesium (at least up 10% MgO) and reduced amounts of silica and magnesia (Thomas, 2013).

GGBFS can be either produced as a separate product (i.e., SCM) when it is used directly in concrete to substitute for PC or as a raw material in the manufacture of blended cements. GGBFS can be used to replace PC in concrete mixes from 30% up to 85% of the total wt. of cement, but 50% is generally used in most construction applications. A higher replacement percentage (more than 50%) is used for special applications such as in aggressive environments and to reduce the heat of hydration (Siddique & Khan, 2011).

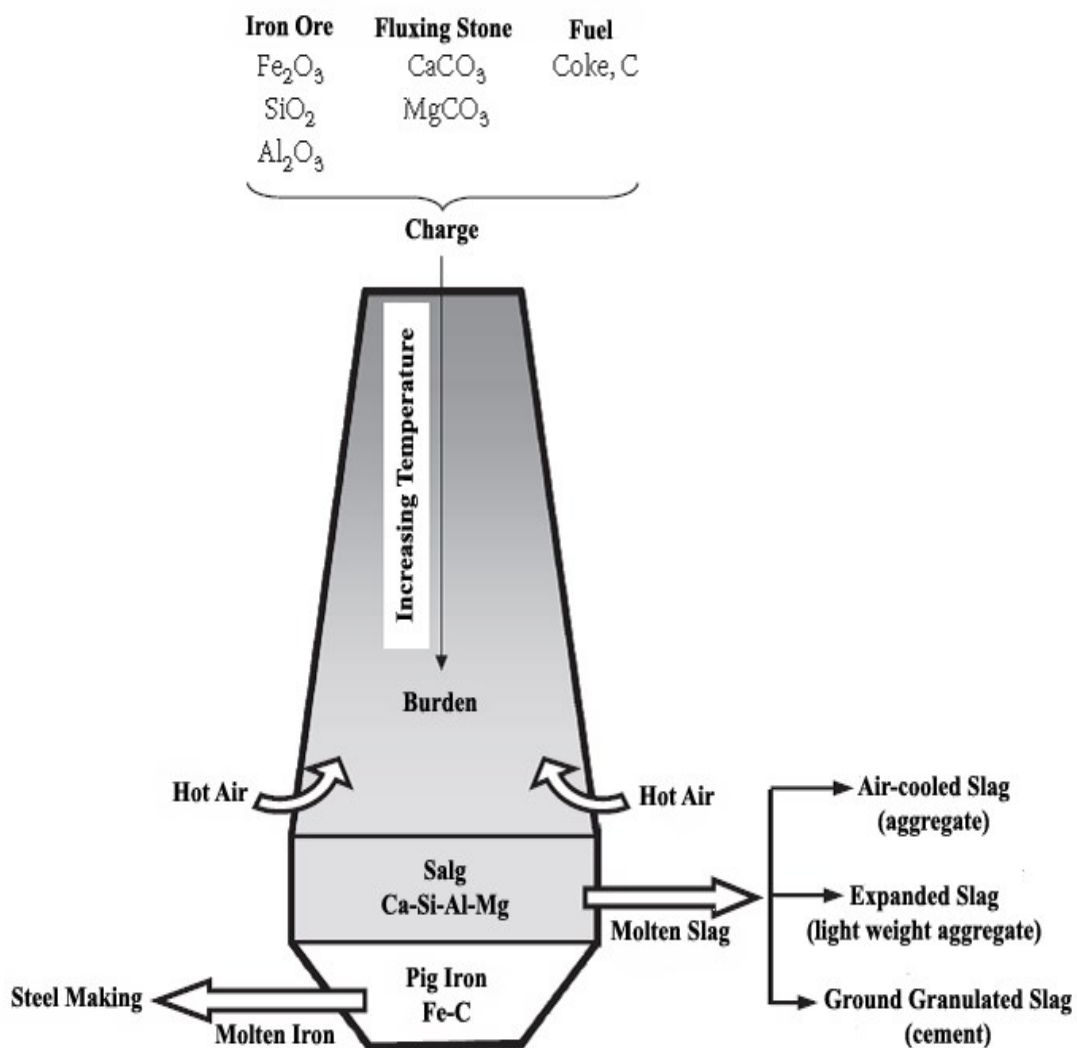


Figure 2.7. Schematic layout of iron blast furnace used to produce slag (Thomas, 2013)

### 2.4.3 Cement Hydration Process

Cement hydration is a process that occurs when hydraulic cement particles (e.g., Portland cement) come into contact with water. During this process, a set of irreversible chemical reactions and physical changes take place between the components of cement and water. Due to the hydration process, cement gains binding, setting and hardening properties. Cement hydration releases a significant amount of heat because it is an exothermic process. In the hydration process, the main components of PC react with water and generate hydration products which are responsible for the setting and hardening of concrete. Cement hydration is a continuous process that may require a long period of time depending on the availability of unhydrated cement and water. Cement hydration can be considered to have two main mechanisms, which are the dissolution and precipitation processes. Understanding the basics of hydration is important to ensuring the strength and durability of concrete or cementitious materials, recognizing and mitigating stress to prevent cracking, and appreciating the importance of good curing and construction practices (Taylor et al., 2006).

In reality, the hydration of PC is a more complex process. The process depends on the structure of the clinker particles which is determined by the raw ingredients, and the particle size and particle size distribution of the raw materials, as well as the manufacturing method. These variables shape the crystallization of the various final compounds and the porosity of the clinker grains themselves (Afshar, 1986). To understand PC hydration, researchers such Wang et al., (2012) outlined the hydration process into five stages. In these stages, the major crystalline compounds and phases of PC, including tricalcium silicate ( $C_3S$ ); dicalcium silicate ( $C_2S$ ); tricalcium aluminate ( $C_3A$ ); tetracalcium aluminoferrite ( $C_4AF$ ); and gypsum dissolve and react to form hydrate products. With the addition of water, each compound or phase in cement undergoes hydration based on the quantity and reactivity and contributes to the final hydration products. At the first contact with water, ionic species of the components of cement dissolve and interact with other species or water. There are several methods used to determine the progression of cement hydration (e.g., PC). These methods measure: (a) the amount of  $Ca(OH)_2$  in the paste; (b) the thermal changes due to hydration; (c) the specific gravity of the paste; (d) the volume of chemically combined water; and (e) the amount of unhydrated cement present (using X-ray quantitative analysis). In addition, there are indirect methods, such as the measurement of the strength of the hydrated paste. Furthermore, early reactions of the hydration process in wet pastes can be studied

by using thermogravimetric techniques and continuous X-ray diffraction scanning. Also, scanning electron microscopy (SEM) can be utilized to study the microstructure of hydrated cement paste (Neville, 2012).

### 2.4.3.1 Hydration Stages

The stages of the hydration of individual cement compounds are illustrated in Figure 2.8 (Taylor et al., 2006) which take place as a result of thermal and physical changes in the cement particles during all stages of the cement hydration. The main reactants in the hydration process are alite ( $C_3S$ ), belite ( $C_2S$ ), aluminates ( $C_3A$ ), ferrite ( $C_4AF$ ), gypsum and water. In addition, there are some minor reactants, such as alkali sulfates and free lime. The main hydration reactions for cement are summarized in Table 2.6 and schematically presented in Figure 2.9. Also, the initial hydration reactions up to the time of setting are shown in Figure 2.10.

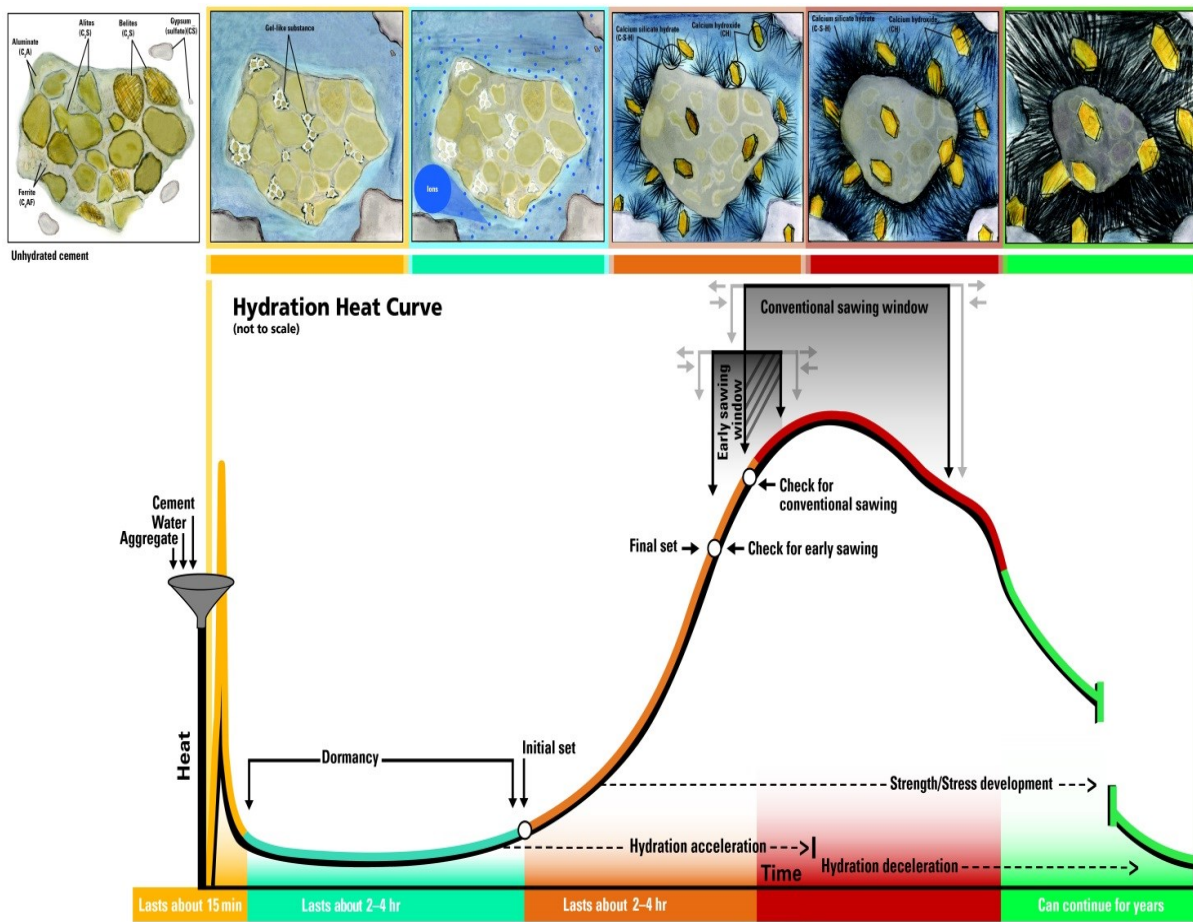


Figure 2.8. Thermal and physical changes in cement particles during all stages of cement hydration (Taylor et al., 2006)

#### 2.4.3.1.1 Stage 1: Mixing and Dissolution

Mixing and dissolution is also called the pre-induction period. This stage lasts less than 15 minutes, and generates a significant amount of heat. The short and sharp thermal peak at the beginning of the curve (Figure 2.8) is the result of the rehydration of calcium sulfate hemihydrate which is a result of the decomposition of gypsum in the grinding process and hydration of the free lime, heat of wetting, heat of solution and the initial reactions of the aluminate phases (Neville, 2012). The alkali sulphates ( $\text{Na}_2\text{SO}_4$  and  $\text{K}_2\text{SO}_4$ ) dissolve quite rapidly and free the  $\text{K}^+$ ,  $\text{Na}^+$ , and  $\text{SO}_4^{2-}$  ions in water. Also, gypsum ( $\text{CaSO}_4$ ) dissolves and dissociates into  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  ions until saturation. Tri-calcium aluminate ( $\text{C}_3\text{A}$ ) dissolves and reacts with the  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  ions (from the dissolved gypsum) to form a gel-like material called ettringite ( $\text{AF}_t$ ), which forms a surface barrier. This reaction frees heat.  $\text{C}_4\text{AF}$  also reacts to form  $\text{AF}_t \cdot \text{C}_3\text{S}$  particles which release  $\text{Ca}^{2+}$  and  $\text{OH}^-$  ions from their surface into water which then becomes a very alkaline solution. At critical concentrations,  $\text{Ca}^{2+}$  and  $\text{OH}^-$  mainly produce C-S-H ( $\text{C}_3\text{S}_2\text{H}_3$ ) gel as a layer on the surface of  $\text{C}_3\text{S}$  grains and calcium hydroxide (CH) as the crystalline phase; heat is released too. In this stage, a small fraction of  $\text{C}_3\text{S}$  hydrates, which ranges between about 2% to 10%. During this stage, a very small quantity of  $\text{C}_2\text{S}$  reacts and generates C-S-H and CH.

#### 2.4.3.1.2 Stage 2: Dormant period

The dormant period lasts about 2 to 4 hours. During this stage, the ettringite gel layer accumulates around the unhydrated grains of  $\text{C}_3\text{S}$  and  $\text{C}_2\text{S}$ , thereby limiting the access of water. Consequently, this slows down the rate of hydration rate and heat generation. Later,  $\text{C}_3\text{S}$  and  $\text{C}_2\text{S}$  begin to slowly dissolve in the water and concentrations of  $\text{Ca}^{2+}$  and  $\text{OH}^-$  increase in the solution. This stage involves little physical changes in the cement paste.

#### 2.4.3.1.3 Stage 3: Hardening

The hardening and acceleration (setting) stage lasts about 2 to 4 hours. In this stage, the hydration of  $\text{C}_3\text{S}$  is dominant. As mentioned in Stage 2, the concentration of  $\text{Ca}^{2+}$  and  $\text{OH}^-$  gradually increase in the solution until the hardening stage. This solution becomes super-saturated with these ions, C-S-H is fiber like and crystalline CH begins to produce a heat liberating chemical reaction. Then, the fibers of C-S-H network with other solids which leads to stiffening and setting of the cement paste. Therefore, this stage is considered as the early initial setting stage and marks the beginning

of hydration acceleration. During the acceleration, the heat of hydration of the cement paste increases rapidly as well the development of hardening and strength to reach the final setting.

#### 2.4.3.1.4 Stage 4: Cooling

The cooling stage takes place immediately after reaching the final setting. In this stage, the hydration products (mainly C-S-H and CH) begin to minimize the access of water to undissolved cement after the final setting. As well, the heat of hydration starts to decrease. This stage lasts for several hours.

#### 2.4.3.1.5 Stage 5: Densification

Densification is the final stage of the hydration process which can continue for years. It plays a key role in continuing the development of concrete strength and reduction of concrete permeability. As long as C<sub>3</sub>S and C<sub>2</sub>S and water are available in the concrete, the hydration process continues to form hydrate products. As hydration products continue to grow, the porosity and permeability of the concrete decreases and strength of the concrete increases.

Table 2.6. Main hydration reactions of Portland cement compound (Tennis & Jennings, 2000)

Reactants		Hydration Products	
2 (3CaO•SiO <sub>2</sub> ) Tricalcium silicate	11 H <sub>2</sub> O Water	3CaO•2SiO <sub>2</sub> •8H <sub>2</sub> O Calcium silicate hydrate (C-S-H)	3 (CaO•H <sub>2</sub> O) Calcium hydroxide (CH)
2 (2CaO•SiO <sub>2</sub> ) Dicalcium silicate	9 H <sub>2</sub> O Water	3CaO•2SiO <sub>2</sub> •8H <sub>2</sub> O Calcium silicate hydrate (C-S-H)	CaO•H <sub>2</sub> O Calcium hydroxide (CH)
3CaO•Al <sub>2</sub> O <sub>3</sub> Tricalcium aluminate	3 (CaO•SO <sub>3</sub> •2H <sub>2</sub> O) Gypsum	26 H <sub>2</sub> O Water	6CaO•Al <sub>2</sub> O <sub>3</sub> •3SO <sub>3</sub> •32H <sub>2</sub> O Ettringite (AF <sub>t</sub> )
2 (3CaO•Al <sub>2</sub> O <sub>3</sub> ) Tricalcium aluminate	6CaO•Al <sub>2</sub> O <sub>3</sub> •3SO <sub>3</sub> •32H <sub>2</sub> O Ettringite	4 H <sub>2</sub> O Water	3 (4CaO•Al <sub>2</sub> O <sub>3</sub> •SO <sub>3</sub> •12H <sub>2</sub> O) Calcium monosulfoaluminate
3CaO•Al <sub>2</sub> O <sub>3</sub> Tricalcium aluminate	CaO•H <sub>2</sub> O Calcium hydroxide (CH)	12 H <sub>2</sub> O Water	4CaO•Al <sub>2</sub> O <sub>3</sub> •13H <sub>2</sub> O Tetracalcium aluminate hydrate
4CaO•Al <sub>2</sub> O <sub>3</sub> •Fe <sub>2</sub> O <sub>3</sub> Tetracalcium aluminoferrite	10 H <sub>2</sub> O Water	2 (CaO•H <sub>2</sub> O) Calcium hydroxide	6CaO•Al <sub>2</sub> O <sub>3</sub> •Fe <sub>2</sub> O <sub>3</sub> •12H <sub>2</sub> O Calcium aluminoferrite hydrate

Note: This table lists only the primary transformations and not minor transformations. The composition of calcium silicate hydrate (C-S-H) is not stoichiometric

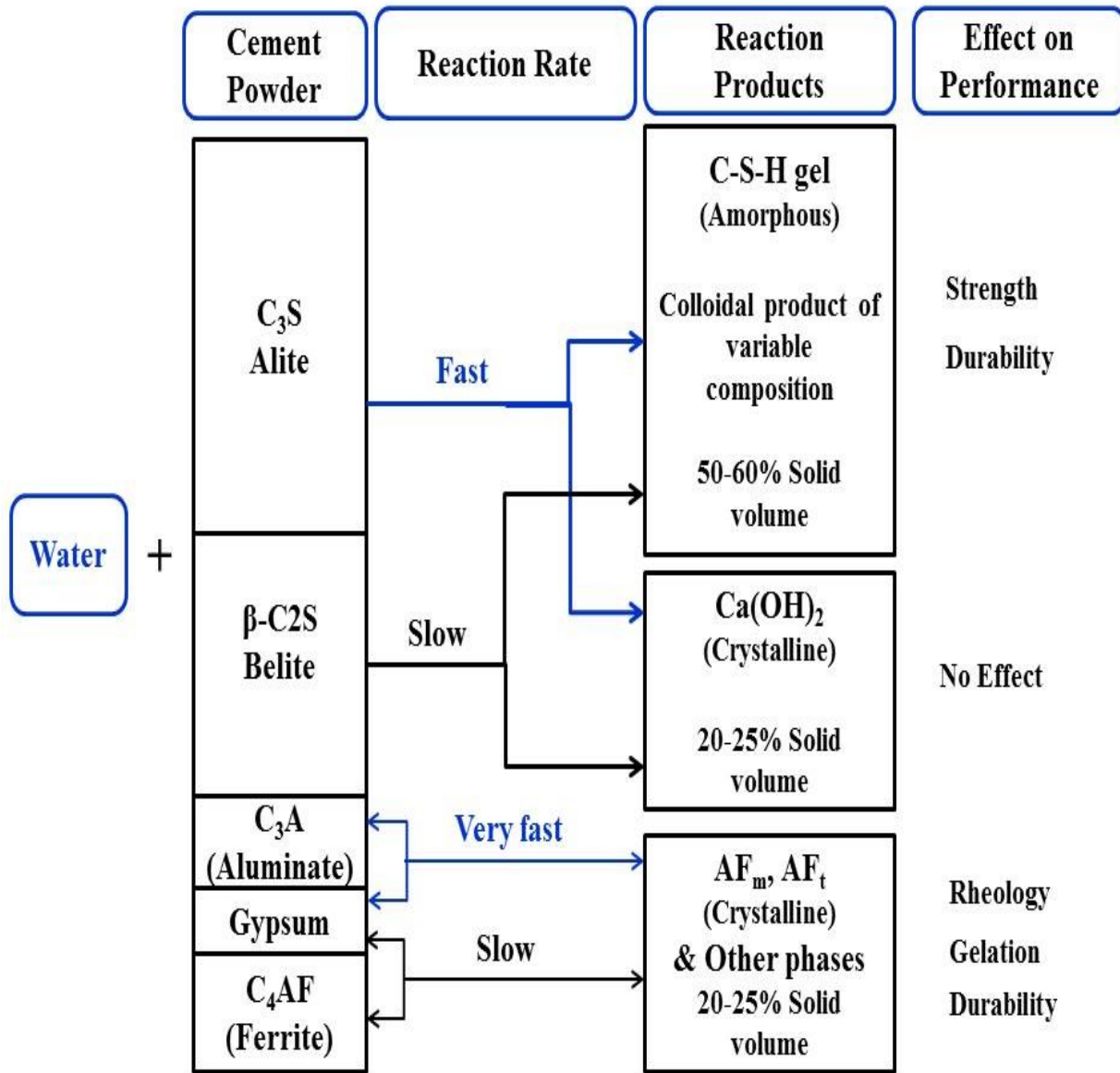


Figure 2.9. Schematic of cement-hydration reactions (Modified from SPE, 2015)

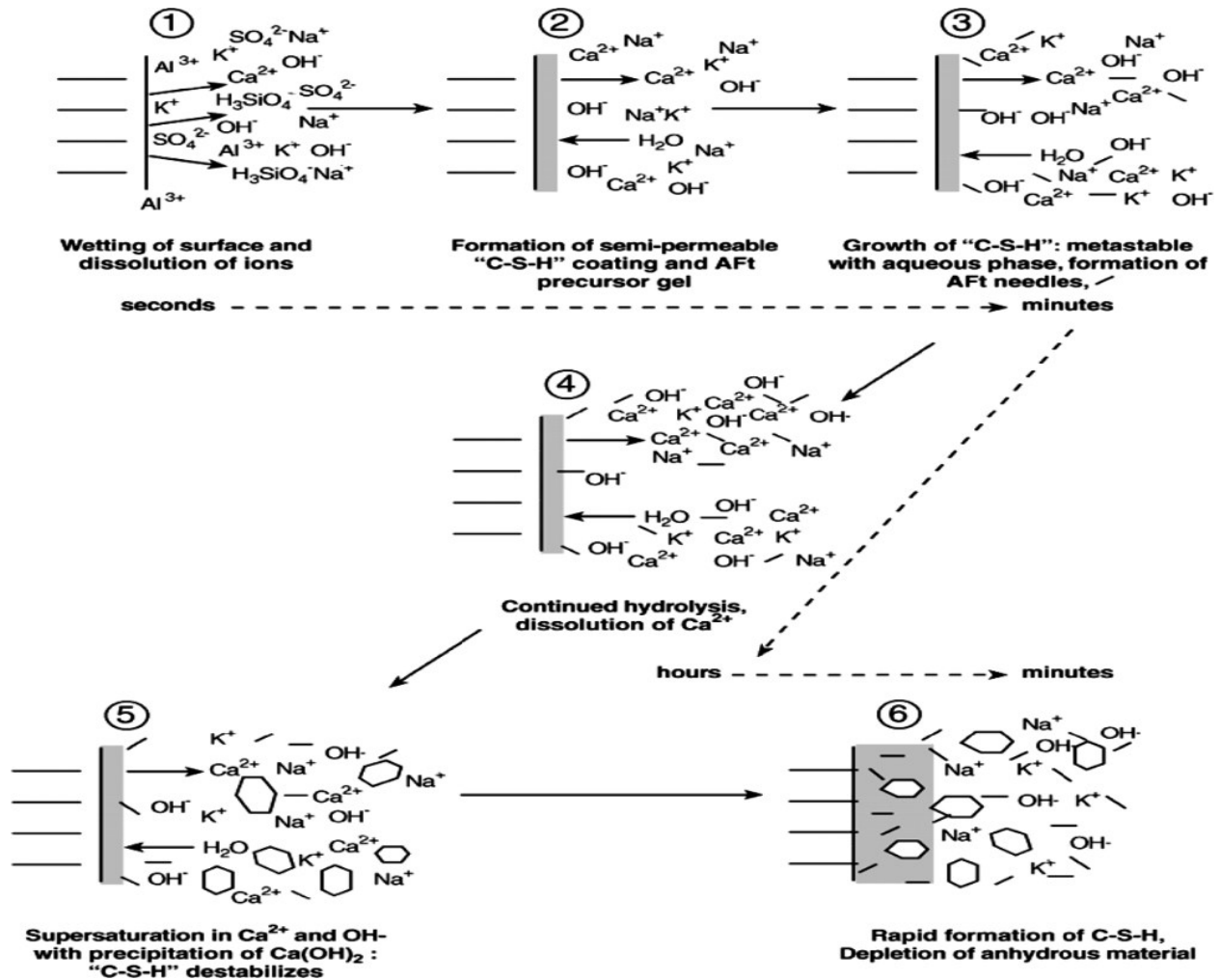


Figure 2.10. Cement hydration from mixing to setting (SPE, 2015)

## 2.4.3.2 Primary Products of Hydration Reactions

### 2.4.3.2.1 Calcium silicate hydrate

C-S-H is the main hydration product of the reaction of  $C_3S$  and  $C_2S$  with water. It is produced in a gel form. The dashes used in C-S-H indicate that the composition is indefinite.

### 2.4.3.2.2 Calcium hydroxide

CH is a secondary hydration product that is produced in the crystalline form of calcium hydroxide ( $Ca(OH)_2$ ). It has a fixed chemical composition.

#### 2.4.3.2.3 Ettringite

$AF_t$  is a hydrated product resultant of the reaction between  $C_3A$  and gypsum. It is deposited as acicular, columnar, and hexagonal crystals.

#### 2.4.3.2.4 Monosulfate

Monosulfate ( $AF_m$ ) is a calcium monosulfate aluminate hydrate. It is produced as a result of the reaction between remaining  $C_3A$  and  $AF_t$ .

As result of the hydration process, several chemical and physical changes occur in the cement paste matrix which may have vital roles in its engineering properties.

### 2.4.3.3 Pore Structure

Cement-based materials (e.g., concrete, CPB or CPT) are considered to be porous media (Tang et al., 2016). Their pore structure consists of different types and size of pores as well as voids that lead to complex microstructures (Jennings et al., 2008). The distribution of pore size as well as pore connectivity in cement-based material influence the physical, chemical and mechanical properties (Brandt, 2009; Wang et al., 2006; Aligizaki, 2005). The pores in cementitious materials significantly influence properties such as mechanical durability, and transport characteristics (Brandt, 2009; Aligizaki, 2005). Also, these pores determine the behaviour of cement materials in different environments. The hydration process of hardened cement paste matrix results in structures with many different pore sizes and pore types, which range from several nanometers to micrometers (Sant et al., 2011). The pores in the pore structure of hardened cement paste are classified in accordance with their size, from the smallest to the largest: gel, capillary and hollow-shell pores and air voids (Aligizaki, 2006). Gel pores have very small spaces - about 0.5 to 10 nm (which is only an order of magnitude larger than that of water molecules), which are found in between the C-S-H gel layers (Kumar & Bhattacharjee, 2003; Mindess et al., 2002). These pores constitute the internal porosity of the C-S-H gel phase, see Figure 2.11, which is a schematic of the structure of C-S-H at the meso- and nano-scale in white cement paste. The capillary pores in a hardened cement paste are the initially residual water-filled voids that are found between the original cement grains. Hollow-shell pores are spaces formed from the original cement boundaries and enclosed in cement gel and connected to the capillary pore system by the capillary and gel pores (Narayanan & Ramamurthy, 2000). They are considered to be third type of intrinsic pore which range from 1 to around 20  $\mu m$  in size (about the size of smaller cement grains). Finally, air

voids are “ a space in cement paste, mortar, or concrete filled with air, an entrapped air void is characteristically 1 mm (0.04 in.) or more in size and irregular in shape, and an entrained air void is typically between 10  $\mu\text{m}$  and 1 mm in diameter and spherical (or nearly so)” (American Concrete Pavement Association (ACPA)). Figure 2.12 shows the pore-size distribution in PC concrete. Among the different kinds of pores, capillary and gel pores have gained more research attention as they are studied to better understand the primary properties of hardened cementitious materials, such as durability, strength, and permeability. The quantity and distribution of these pores significantly change with progression of the hydration process (Aligizaki, 2006). Table 2.7 presents a comparison between the capillary and gel pores. There are several factors that affect the pore structure of cementitious materials, such as curing conditions, water/cement ratio, degree of hydration, and use of mineral admixtures and chemical admixtures. Also, the pore structure in hardened cement paste can be affected by chemical changes due to aggressive environments.

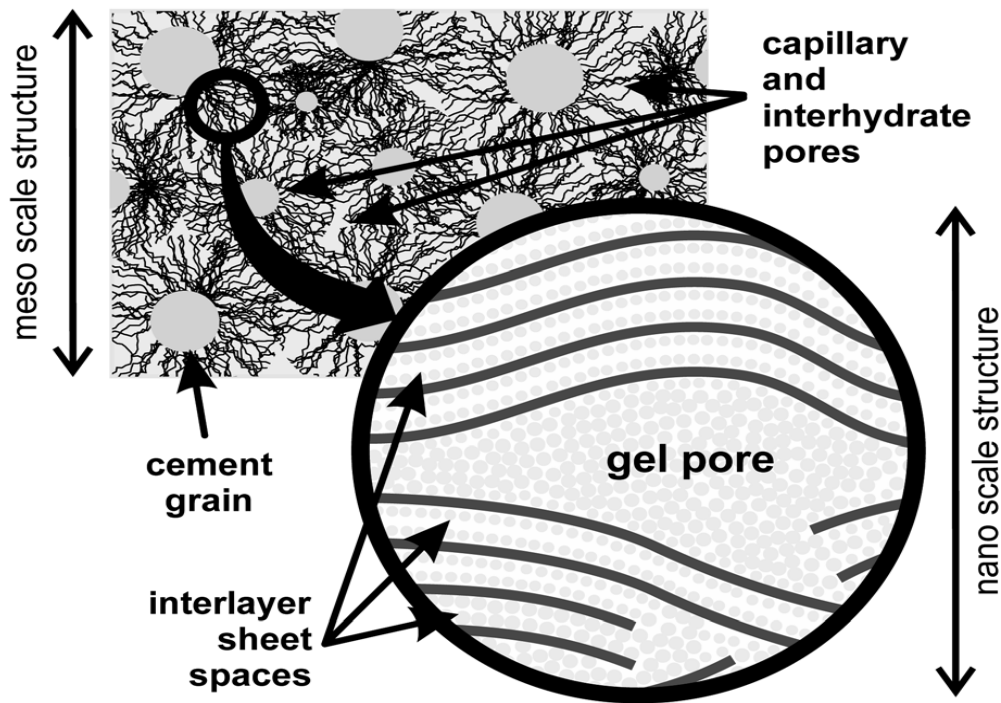


Figure 2.11. Schematic of structure of calcium-silicate-hydrate (C-S-H) at meso- and nano-scale in white cement paste (Kowalczyk et al., 2014)

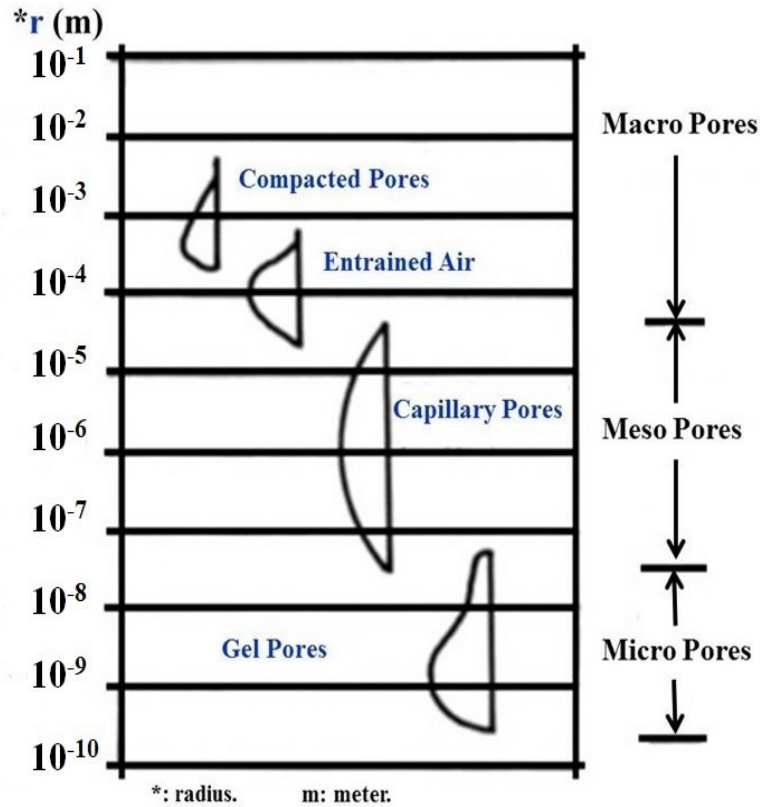


Figure 2.12. Pore-size distribution in Portland cement concrete (Brandt, 2009)

Table 2.7. Comparison of capillary and gel pores (Thomas, 2013)

Designation	Size range (nm)	Description	Role of water	Properties affected
<b>Capillary pores</b>	10,000–50	Macropores (large capillaries)	Behaves as bulk water	Largely responsible for mass transport (permeability and diffusion)
	50–10	Medium mesopores (medium capillaries)	Small surface tension forces generated	Mass transport in absence of macropores Responsible for shrinkage above 80% relative humidity
	10–2.5	Small mesopores	Large surface tension forces generated	Shrinkage between 50% and 80% relative humidity
<b>Gel pores</b>	2.5–0.5 ≤0.5	Micropores Interlayer spaces between Ca-Si sheets in C-S-H	Strongly absorbs water; no menisci form	Shrinkage at all relative humidities Creep

#### 2.4.3.3.1 Transport Properties

The transport properties of hardened cement-based material (e.g., concrete) determine its ability to allow fluids (e.g., O<sub>2</sub>, CO<sub>2</sub>, Cl<sup>-</sup>, SO<sub>4</sub><sup>-2</sup>) to move through it (Bertolini et al., 2013). This movement of fluid in concrete is controlled by four basic mechanisms: (i) capillary action inside the capillaries of cement paste, (ii) permeation due to pressure gradients, (iii) diffusion due to concentration gradients, and (iv) migration due to electrical potential gradients (Bertolini et al., 2013). The transport properties of cement paste have a significant effect on the transport characteristics of hydrated cement-based materials. This is because cement paste is the main component that is used for binding and encapsulating the aggregate particles together in hardened cement-based materials. There are several factors that can control the transport processes in concrete or cementitious material, such as its age, pore structure and environmental conditions at its surface (Bertolini et al., 2013). The transport properties of cement based material play a significant role in controlling the most common mechanisms of deterioration (e.g., sulphate attacks) as well as its durability. Thus, studies have focused on the correlation between the transport properties of cement based materials and their durability (Galle et al., 2000). In particular, permeability and diffusivity determine how fast aggressive substances penetrate into cement-based materials (Phung et al., 2013). Permeability is a property that indicates the rate of flow of a fluid through the pore structure of porous material (e.g., concrete) under a pressure gradient, whereas diffusivity indicates the movement of fluid under a concentration gradient. The permeability and diffusivity of cement-based materials are affected by parameters like cement type, water-cement ratio (w/c), curing, etc. Among these parameters, the degree of water saturation and microstructural properties mainly govern the capability of cement-based materials to transport fluids (e.g., gas or liquid). It is well known that the permeability and diffusivity of gas into cement-based material decrease with increased degree of saturation.

In CPB systems, permeability and diffusivity are the main transport processes that affect their environmental performance and durability (Fall et al., 2009). Also, these transport properties play a critical role in the reactivity of CPB systems by controlling the transport of two main agents (oxygen and water) that are necessary for beginning and continuing the oxidation of sulphide minerals that are incorporated into CPB systems. This means that permeability and diffusivity parameters influence the chemical stability of sulphidic CPB systems with respect to other factors such as the type and amount of sulphide minerals present in the system. Also, the transport

properties control the movement of solutes from the CPB matrix (i.e., leaching of CPB) as well as to the system from the surrounding environment (e.g., surface and ground water). Generally, the transport properties of any porous material are controlled by its pore structure (e.g., pore size, orientation, connectivity, and size variation). For example, the CPB matrix has coarse and highly connected pores as well as cracks which can allow and accelerate the ingress of gas and fluids (mainly oxygen and water) between the CPB structure and the surrounding environment. This can lead to an increase in the potential oxidation of the sulphide minerals found in the tailings and, thus reduce the service-life of CPB structures through sulphate attacks (Fall et al., 2009).

## **2.5 Reactivity of Mine Cemented Paste Backfill and Measurement of Reactivity**

### **2.5.1 Introduction**

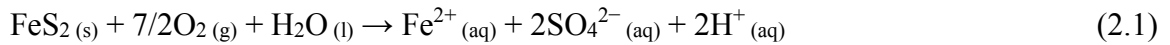
The reactivity of mine cemented paste backfill mix is related to sulphidic tailings, which are considered the predominant component. Sulphidic tailings materials are considered to be reactive waste because they contain significant amounts of sulphide minerals such as pyrite and pyrrhotite. In atmospheric conditions, such tailings materials become chemically unstable (reactive) and undergo oxidation with the formation of AMD and thus discharge heavy metals and other toxic elements (e.g., As) into the surrounding environments (Dold, 2008; Ouellet et al., 2003). The following sections provide a brief review of sulphide oxidation, the factors that may affect CPB reactivity and the methods that are used to determine reactivity.

### **2.5.2 Sulphide Oxidation**

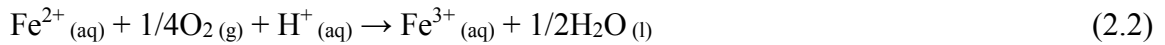
Sulphide minerals are chemically stable in ore deposits under reducing conditions where oxygen is almost completely absent like under the surface of the earth or water (Dold, 2014). These minerals then become reactive (unstable) and oxidize when exposed to atmospheric conditions ( $O_2$  and  $H_2O$ ) as a result of earthmoving processes (e.g., mining, excavation activity) (Reed & Palandri, 2006; Rosso & Vaughan, 2006; Gleisner, 2005). Among the different types of sulphide minerals, pyrite ( $FeS_2$ ) is the most common and found in several types of sedimentary, metamorphic, and igneous rocks as well as fossils. Therefore,  $FeS_2$  is commonly found in many mine wastes. It is usually used as an example to illustrate the sulphide oxidation process. Pyrite oxidation and the formation of AMD have been well documented by several studies (e.g., Nordstrom & Alpers, 1999; Nordstrom & Southam, 1997; Evangelou, 1995; Evangelou & Zhang, 1995; Lowson, 1982). It should be noted that the oxidation of  $FeS_2$  is considered to be a complex process controlled by a

combination of physical, chemical and biological processes (Dold, 2014). Also, FeS<sub>2</sub> oxidation is an exothermic process (Schoonen et al., 2000), and takes place in several steps which can be mainly summarised into three major phases: (1) oxidation of sulphur (Eq. 2.1); (2) oxidation of ferrous iron (Eq. 2.2); and (3) hydrolysis and precipitation of ferric complexes and minerals (Eq.4) (Dold, 2014). Furthermore, secondary products may be produced depending on the geochemical conditions prevalent in the site, such as the meta-stable secondary products ferrihydrite (5Fe<sub>2</sub>O<sub>3</sub>·9H<sub>2</sub>O), schwertmannite (between Fe<sub>8</sub>O<sub>8</sub>(OH)<sub>6</sub>SO<sub>4</sub> and Fe<sub>16</sub>O<sub>16</sub>(OH)<sub>10</sub>(SO<sub>4</sub>)<sub>3</sub>), and goethite (FeO(OH)). In addition, jarosite (KFe<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>), and hematite (Fe<sub>2</sub>O<sub>3</sub>) may form as more stable secondary products (Dold, 2014). The main stages of FeS<sub>2</sub> oxidation will be briefly described as follows.

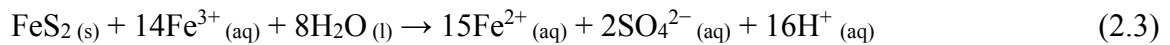
- Step (1) is the initial stage which starts the oxidation process of FeS<sub>2</sub> minerals. FeS<sub>2</sub> reacts with atmospheric elements (oxygen and water) to produce ferrous iron, sulfate and acid, as shown in Eq.2.1:



- In Step (2), the formed ferrous iron (Fe<sup>2+</sup>) in Eq.2.1 is oxidized by oxygen to produce ferric iron (Fe<sup>3+</sup>).



The rate of this reaction is significantly increased in low pH conditions by microbiological activity (e.g., *Acidithiobacillus* spp. or *Leptospirillum* spp.). As a result, the produced ferric iron (Fe<sup>3+</sup>) in Eq. 2.2 acts as the primary oxidant of FeS<sub>2</sub> in Step (3), as shown in Eq.2.3.



It should be noted that the kinetics of each reaction vary, and are controlled by conditions prevalent in the tailings. Also, sulphide oxidation is affected by several other factors, such as oxygen concentration, degree of saturation, type and content of sulphide mineral, mineralogy and the size of the pores of sulphide bearing tailings, temperature, ferrous/ferric adsorption ratio and total iron concentration, the pH and Eh of pore water and presence of certain bacteria (Bourgeot et al., 2011; Blowes et al., 2003; Saharan et al., 1995; Sasaki et al., 1995; Williamson & Rimstidt,

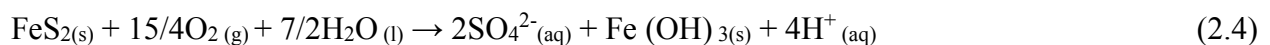
1994). Each factor can play a role in the oxidation of sulphide as well as in the generation of AMD. For example, the oxidation rate of sulphide-bearing tailings increases as their particle size decreases (Payant et al., 2012).

### **2.5.3 Factors Affecting Reactivity of CPB or Oxidation of Sulphide Minerals in CPB System**

Sulphide-bearing CPB is a complex cement composite system made of various ingredients with different ratios (e.g., sulphidic tailings, mixing water, binder, and other additives). This cementing system develops, changes and serves under various operational and environmental conditions. Thus, CPB systems are exposed to different chemical and physical processes that may originate from internal or external sources, such as binder hydration, sulphide oxidation, curing condition, etc. In addition, there are several factors that affect the reactivity of sulphidic CPB systems. These factors include availability of oxidants (mainly oxygen), content and type of sulphide mineral, exposed surface area, degree of saturation, temperature, initial sulphate content, etc.

#### **2.5.3.1 Presence of Oxidants (Oxygen) and Water**

During operations and after closure of a mine, the extent of sulphide mineral (e.g., pyrite) oxidation in the exposed surface of a CPB system is governed by the movement of air and water through and around the system. Also, this movement determines the rate at which metals or soluble secondary minerals may be released into the mine water and/or ground water after closure of the mine (MEND, 2006). Oxygen and water are the two key parameters in the oxidation of FeS<sub>2</sub>. From the overall oxidation of FeS<sub>2</sub>, it can be observed that both air (oxygen source) and water are necessary for the oxidation process (León et al., 2004), as shown in Eq. 2.4:



Thus, the amount and presence of these reactants influence the oxidation of sulphide minerals. The rate of sulphide mineral oxidation increases in tailings as the amount of available oxygen increases (Elberling et al., 1994).

#### **2.5.3.2 Sources of Oxygen**

MEND (2006) listed some of the initial sources of oxygen in CPB systems, including that a certain amount of oxygen is found in the pore spaces of paste backfill mixtures; gaps against underground

walls; fractures in the wall rock; and gaps between successive paste campaigns (joints), or incomplete fills. In addition, some of these sources can be replenished through links between adjacent stopes; exploration and underground drill holes that intercept the stopes; active mine ventilation; and oxygen contained in inflowing ground water.

### **2.5.3.3 Content and Type of Sulphide Mineral**

Mine tailings incorporated in CPB systems usually contain different amounts of sulphide minerals, but FeS<sub>2</sub> is commonly predominant (Craig & Vokes, 1993). The sulphide mineral concentration can significantly influence the reactivity of CPB systems. Each type of sulphide mineral has a different oxidation rate. In general, reactivity decreases in the order of marcasite > pyrrhotite > pyrite (e.g. Kwong & Ferguson, 1990). According to Ouellet et al. (2003), the reactivity of CPB mixtures is influenced by FeS<sub>2</sub> content. They found that as the FeS<sub>2</sub> content increases, the oxidation rate and reactivity of FeS<sub>2</sub> in CPB systems also increase.

### **2.5.3.4 Type and Contents of Binder**

Binders are one of the main components of CPB. They contribute to the strength and stability of CPB (Ercikdi et al., 2009a). The paste envelopes the tailings grains in hardened CPB. In general, PCI is commonly used alone and/or in combination with mineral admixtures (e.g., slag, FA) with different replacement amounts. As a result, the engineered properties of CPB systems depend on the type and contents of the binder as well as its chemical, mineralogical and physical characteristics. Belem et al. (2001) proposed that the addition of 5% wt. of cement to a CPB mix leads to reduced permeability and increased water retention of the CPB. Also, Ercikdi et al. (2009b) reported that adding mineral admixtures as a partial replacement of cement enhances the strength and durability of CPB systems.

### **2.5.3.5 Formation of Secondary-Oxidation Products**

It is well known that the oxidation of FeS<sub>2</sub> takes place on its grain surface (Dold, 2014; Ardejani et al., 2010; Lottermoser, 2010; Evangelou, 1995; León et al., 2004). Thus, FeS<sub>2</sub> oxidation is considered to be a surface controlled reaction (Lottermoser, 2010). In certain conditions, secondary oxidation products (e.g. ferrihyrite-type phases) may form during FeS<sub>2</sub> oxidation (Dold, 2014; León et al., 2004). These products could accumulate on the exposed surface area of sulphidic CPB structures and limit oxygen diffusion. As a result, the oxidation rate of FeS<sub>2</sub> grains will decrease, which leads to the reduced reactivity of CPB systems.

### **2.5.3.6 Exposed Surface Area**

The reactivity of CPB depends on the amount of surface area exposed to oxygen and water. As the amount of surface exposed increases, the oxidation rate of sulphide minerals also increases because there is more surface area available for interaction with the main reactants (oxygen and water) (Dold, 2014; Lottermoser, 2010).

### **2.5.3.7 Degree of Saturation of CPB**

The degree of saturation of sulphidic tailings with or without cement affects the reactivity of CPB. The reactivity of CPB systems is reduced with increased degree of saturation (Ouellet et al., 2003). This is due to the less effective oxygen diffusion coefficient which leads to reduced oxygen diffusion through the system in accordance with Fick's laws (Ouellet et al., 2003; Mbonimpa et al., 2002).

### **2.5.3.8 Temperature**

Temperature is one of the main factors that can influence the reactivity of CPB systems, and therefore deserves consideration. Temperature can impact binder hydration reactions and sulphide mineral oxidation processes, thus affecting the reactivity of CPB. However, the effect of temperature on the reactivity of CPB systems and the degree that temperature affects this reactivity are still not understood due to the lack of experimental data.

#### **2.5.3.8.1 Role of temperature in CPB operations**

Temperature is an important factor in backfill operations, and can originate from the internal or external environment. Temperature can also be classified as natural or human made. Internal sources of temperature are mainly related to the CPB itself. The cement hydration process provides a significant internal source of heat which affects the temperature. This is already discussed in the section on cement and its hydration process.

The external environmental temperature is related to the underground mining environment and mining operations. External factors that affect the temperature include the virgin rocks, blasting operations, and electrical and mechanical processes (Fall et al., 2010). The temperature of virgin rocks is governed by their depth and the geothermal gradient of the region (Sbarba, 2012). The geology and location of mines as well as thermal characteristics of the rocks affect the geothermal gradient (Sbarba, 2012; Payne & Mitra, 2008). Furthermore, the energy from blasting operations releases about 90% to 95% heat and could affect the temperature of the underground

environment (Payne & Mitra, 2008). Electrical and mechanical processes, such as hydraulic operations, are also factors that affect the temperature. They contribute to the heat load of underground mines (Sbarba, 2012; Payne & Mitra, 2008), as well as possibly affecting CPB systems. For instance, a diesel truck with 200 kW of engine power is typically utilised in Australian underground operations but releases about 400 kW of heat which add to the total heat load (Sbarba, 2012; Payne & Mitra, 2008).

### **2.5.3.9 Initial Sulphate Content**

The presence of sulphate ions ( $\text{SO}_4^{2-}$ ) in CPB mixtures can have positive or negative effects on their engineered properties. These effects are determined by the concentration of sulphate ions in the CPB mixtures. It is known that sulphate anions react with the components of hardened cement paste, mainly  $\text{C}_3\text{A}$  and portlandite (CH). As a result, some of the secondary products, mainly gypsum and ettringite minerals, form in the cement matrix. These minerals have expansive properties (swelling). The influence of these minerals depends on the sulphate concentration and the capillary pores in the hardened cement paste matrix. In paste backfill systems, the initial sulphate content varies from relatively low (<5000 ppm) to very high ( $\geq 25,000$  ppm) (Pokharel & Fall, 2010). If the initial sulphate content is high, these minerals can inhibit binder hydration and cause high internal stress inside the cement matrix which may lead to the propagation of micro cracks (Pokharel & Fall, 2010). On the other hand, less sulphate can improve the microstructure of the CPB matrix due to the refinement of pore structure and reduced transport properties. The influence of the initial sulphate content on the strength and permeability of CPB systems has already been studied by several researchers (e.g., Li & Fall, 2016; Fall & Pokharel, 2010; Pokharel & Fall, 2010; Belem & Benzaazoua, 2008; Benzaazoua et al., 2004). Sulphate ions in CPB originate from several different sources, which will be reviewed in the following section.

#### **2.5.3.9.1 Source of sulphate ions in CPB**

Sulphate ions are a polyatomic anion that consists of a sulfur atom combined chemically with four oxygen atoms. They are also known as sulfate; sulfate ions; sulphate; and sulfate anions. In inorganic chemistry, they are called sulfate by the International Union of Pure and Applied Chemistry (IUPAC). The empirical formula is  $\text{SO}_4^{2-}$  and the molecular mass is 96.06 g/mole (CTI Reviews, 2016). Sulphate is naturally found in several types of mineral salts, such as anhydrite, barite and gypsum. Also, sulphates form as a result of the oxidation of sulphide minerals. On the

other hand, sulphates are discharged as effluents from different industries, such as tanneries, pulp mills and mining. In mining operations, the presence of sulfate ions means that there is the possibility of AMD which is associated with heavy metal leaching. Furthermore, sulphate ions can lead to sulfate attacks which may cause damage in cementitious structures in mines, in particular, CPB structures. The effects of sulphate ions depend on factors such as, amount and type of sulphate present. The presence of sulphate in backfill operations is due to internal and external sources.

First, the backfill system itself contributes as an internal source of sulphate. This means that one or more of the main ingredients of CPB, including tailings, hydraulic binder agent (e.g., PC), and the mixing water (either fresh or processing water) can be a direct or indirect source of sulphates. For example, tailings represent up to 75% of the weight of a paste backfill matrix and their chemical and mineralogical compositions and physical properties can influence backfill systems. When tailings contain sulphide minerals, they are a significant source of sulphate as they are used in large quantities in backfilling. Therefore, tailings are considered to be a primary internal source of sulphate when they contain various sulphide minerals, such as  $\text{FeS}_2$  and pyrrhotite. Typically, the sulphide contents in mine tailings range between 2% to 60% (weight ratio) (Tariq & Nehdi, 2007).  $\text{FeS}_2$  is the most common mineral source of sulphide in tailings (Tariq & Nehdi, 2007; Benzaazoua et al., 2000). In the presence of water or moisture and oxygen, sulphide bearing tailings oxidise to release sulphate ions and cause AMD. These ions react with the primary components of PC or its hydration products, in particular CH and  $\text{C}_3\text{A}$  which cause expansive problems in backfilling structures (Oliveira et al., 2013). Among the internal sources of sulphate in backfill operations, tailings have attracted more attention of researchers because they represent the majority of the weight of a CPB matrix. Thus, several studies (Fall & Pokharel, 2010; Orejarena & Fall, 2010; Fall et al., 2004; Hassani et al., 2001; Benzaazoua et al., 1999) have investigated the damaging effects of sulphates by themselves or along with other parameters on the stability and strength of CPB. Indeed, Fall et al. (2004) stated that the effects of sulphate on the performance of CPB in terms of strength and cost should be measured with the increased use of CPB in underground mines worldwide. Thus, they developed a mathematical model to predict the impact of various amounts of sulphate on the performance of CPB in terms of strength and cost. They concluded that sulphate ions have a significant impact on the strength of CPB structures. Also, the influence of sulfate is based on its concentration, the chemical composition of cement and the curing time. Fall and Pokharel (2010) conducted an experimental study to investigate the coupled

effect of temperature and sulphate on the strength and mineralogical composition of CPB. They found that sulphate ions have a negative impact on the strength of CPB due to the reaction between the  $\text{SO}_4^{2-}$  ions and C–S–H, which is the main hydration product of PC. Also, they emphasised the importance of the coupled effects of temperature and sulphate on backfilling structures, so these effects should be considered in CPB design. On the other hand, external sources of sulphate ions can be the surrounding rocks and environment around paste backfill structures. The impact of these sulphates are not discussed in this research. The focus here is only on the effect of internal sulphate attacks that commonly take place in underground mines on the reactivity of CPB systems.

#### **2.5.4 Methods to Measure Reactivity of Mine Waste Materials**

The prediction of the chemical reactivity and acid mine drainage (AMD) associated with metal leaching (ML) within mine wastes is a critical aspect that helps to determine the type of rehabilitation and disposal method. There are several methods that have been developed and practiced to measure the reactivity of mine wastes as well as to predict the quality of drainage (mainly AMD and ML). Static and kinetic geochemical tests are commonly used to assess the reactivity of sulphide-bearing mine wastes such as waste rocks and tailings (Nicholson et al., 1997). Static tests are used to determine whether mine waste materials generate AMD (Bourgeot, Piccinin, & Taylor, 2011). However, they do not provide information about the rate or duration of acid generation. Furthermore, they neglect some of the key factors that affect AMD generation, such as the availability of reactive  $\text{FeS}_2$  in a rock matrix and the supply of oxygen to the reaction sites (Bourgeot et al., 2011). Therefore, kinetic geochemical tests are conducted on mine waste samples to measure the rate at which AMD is produced and its duration (Bourgeot et al., 2011). Kinetic methods, such as the use of humidity cells, column leach tests, and field-scale test piles are considered to be more advanced than static methods because they are designed to mimic the natural weathering process (Bourgeot et al., 2011). Static and kinetic tests are commonly used measurements of sulphate concentration profiles as indicators to predict AMD generation. However, the results can be underestimated or overestimated due to the precipitation of sulphate as secondary minerals (e.g., gypsum, schertmannite, jarosite) or dissolution of residual sulphate or sulphate-bearing secondary minerals (Bourgeot et al., 2011). Table 2.8 lists some of main static and kinetic tests with references for more details. In addition to these static and kinetic tests, researchers used other techniques, such as mass balance, oxygen gradient and oxygen consumption (OC) method. Mass balance and oxygen gradient are two independent methods that were used by

David and Nicholson (1995) to determine the rates of sulphide minerals (e.g., pyrrhotite) contained in tailings site at the Falconbridge mine, Ontario, Canada. Furthermore, other methods proposed or practiced to measure the reactivity of mine waste materials rely on other parameters such as oxygen gas, sulphate and ferrous. One of these methods is the oxygen consumption (OC) test, and is briefly discussed in the following section.

Table 2.8. The common static and kinetic tests used to predict reactivity and AMD

<b>Technique</b>	<b>References</b>
<b><u>Principal Static Methods</u></b>	Sobek, et al. (1978)
- Paste pH	British Columbia AMD Task Force (1989)
- Standard Acid Base Accounting	Sobek, et al. (1978)
- Modified Acid Base Accounting	Lawrence et al. (1989)
- British Columbia (B.C.) Research Initial Test	Bruynesteyn & Hackl (1982)
<b><u>Other Static Methods</u></b>	
- Net Acid Production	Lawrence, et al. (1989)
- Alkaline Production Potential/Sulphur Ratio	Caruccio, et al. (1981)
<b><u>Principal Kinetic Prediction Methods</u></b>	Caruccio, et al. (1981)
- Humidity cells	Lawrence (1990) (Sobek et al., 1978) B. C. AMD Task Force (1989)
- Columns and lysimeters	Ritcey (1989) B. C. AMD Task Force (1989)
- B. C. Research Confirmation test	Bruynesteyn & Hackl (1982)
<b><u>Other Kinetic Prediction Procedures</u></b>	Halbert, et al. (1983)
- Shake Flasks	Lawrence, et al. (1989)
- Soxhlet Extraction	Singleton & Lavkulich (1978) Sullivan & Sobek (1982)

#### 2.5.4.1 Oxygen Consumption Tests

The oxygen consumption tests are used to measure rate of oxygen consumption over time in the air chamber that created on the upper surface of sulphidic waste materials that were placed in sealed containers. Different measurement approaches were used for measuring rate of oxygen consumption such as (i) measurement of oxygen concentration using gas chromatography (Elberling, 2005; Andersen et al., 2001); (ii) direct measurement inside the vessel using electrochemical gas sensors (Bennett et al., 2005; Hollings et al., 2001; Anderson et al., 1999); (iii) measurement of pressure changes in the sealed chamber with assuming that change pressure only as result of the depletion of oxygen (Jerz & Rimstidt, 2004).

Elberling et al. (1994) and Elberling and Nicholson (1996) proposed the use of oxygen consumption (OC) testing as an indicator to determine the rate of oxidation of sulphide minerals. The principle behind OC testing is based on measuring the amount of consumed oxygen due to oxidation of sulfidic material samples in a sealed chamber during a short period of time which ranges from about 3 to 5 hours (Schmieder et al., 2012; Ouellet et al., 2003). One of the main assumptions of this test is the fact that a steady state ( $\partial C/\partial t = 0$ ) should be achieved before the reading is recorded. Therefore, it was recommended that this test is carried out in a short amount time as mentioned above. The oxidation reaction that takes place in the closed chamber is governed by the reactivity of the sulphidic material sample and the rate of diffusion of the oxygen through the sample (Demers et al., 2009). The OC test has some advantages, such as simplicity, a low cost and can be quickly implemented. Also, it can be used in either the laboratory or field. In the literature, there are several studies that have conducted OC technique to measure the reactivity of sulphidic waste materials (e.g., rock wastes and tailings) and to determine the efficiency of cover systems (e.g., Pokharel, 2008; Ouellet et al., 2006, 2003; Bussière et al., 2002; Tibble and Nicholson 1997; Elberling and Nicholson, 1996; Nicholson et al., 1995; Elberling et al., 1994)

#### 2.5.4.1.1 Calculation of the reactivity of sulphidic materials from the OC test results

The reactivity of sulphide bearing wastes (e.g., tailings) is controlled by a combination of the diffusion of oxygen and the chemical reaction rate of the sulphide oxidation. Elberling et al. (1994) modified Fick's laws and combined with kinetic reaction rate of reactive tailings to obtain the oxygen flux (reactivity),  $F(z, t)$  [ $ML^{-2}T^{-1}$ ], through reactive tailings and the corresponding concentration,  $C(z, t)$ , at position  $z$  [L] and time  $t$  [T]. This is expressed for one-dimensional diffusion by the following equation 2.5 (Nicholson et al., 1997):

$$F(z, t) = \frac{\partial C(z,t)}{\partial t} = \frac{\partial}{\partial z} \left[ D_e \frac{\partial C(z,t)}{\partial z} \right] - KC(z, t) \quad (2.5)$$

For simplicity, the Eq. 2.5 can be rewritten as

$$\frac{\partial C}{\partial t} = D_e \frac{\partial^2 C}{\partial z^2} - KC \quad (2.6)$$

The solving of the above differential equations can be used to determine the concentration profile  $C(z, t)$  and the corresponding flux by assuming the measurement conducted under steady state ( $\partial c/\partial t = 0$ ), with the initial condition  $C(z > 0, t = 0) = 0$  and boundary conditions  $C(z = 0, t > 0) = C_0$  and  $C(z = \infty, t > 0) = C_\infty = 0$ , (Mbonimpa et al., 2011). The oxygen concentration profile is then given by the following specific solution to Eq. 2.6 (Nicholson et al., 1997):

$$C(z) = C_0 \exp\left(-z \sqrt{\frac{K}{D_e}}\right) \quad (2.7)$$

The steady-state flux entering the surface of reactive tailings can then be expressed as

$$F(z = 0) = C_0 \sqrt{K D_e} = C_0 (K D_e)^{0.5} \quad (2.8)$$

where  $K$  is the first-order reaction rate coefficient for the system (tailings),  $D_e$  is the effective diffusion coefficient and  $C_0$  is the atmospheric concentration of oxygen.

According to Elberling et al. (1994), if an air chamber (sealed to the atmosphere) is placed over the tailings surface, as shown in Figure 2.13, oxygen will be consumed and the concentration will decrease in the headspace. The continuity equation (conservation mass) of the fixed air chamber over the surface of tailings can be expressed as

$$V \frac{dc}{dt} = AC(K D_e)^{0.5} \quad (2.9)$$

where  $A$  is the area of the container on the tailings, and  $V$  is the head-space volume. From the initial condition  $C = C_0$  at  $t = 0$ , integrating Eq. 2.9 yields,

$$\ln \frac{C}{C_0} = -t (K D_e)^{0.5} \frac{A}{V} \quad (2.10)$$

The slope of the plot of  $\ln C/C_0$  versus time gives the value of  $(K D_e)^{0.5}$  when  $A/V$  is known. This term is substituted into Eq. 2.8 to calculate the flux of oxygen at the surface. This method to determine sulphide oxidation rates is referred to as the oxygen-consumption method (Nicholson et al., 1997).

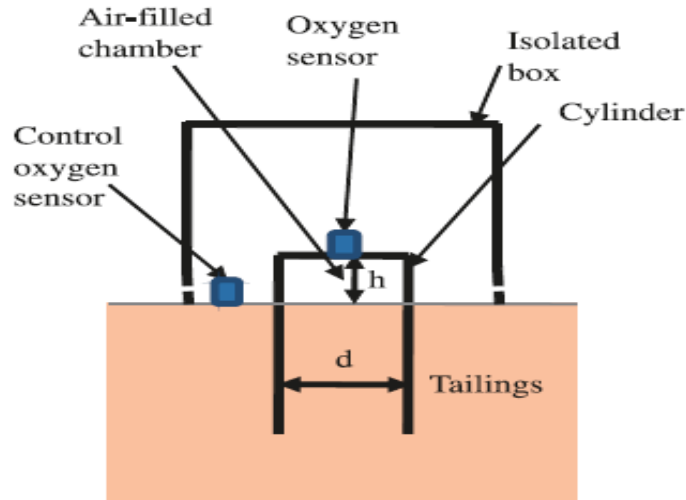
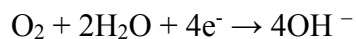


Figure 2.13. A picture of a typical OC test setup in the field (Mbonimpa et al., 2011)

#### 2.5.4.1.2 Oxygen sensor

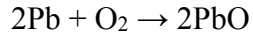
The oxygen sensor is considered a key component of the OC test. Generally there are various types of oxygen sensors, but a galvanic oxygen sensor (also called fuel-cell or electrochemical) is the most widely used types to measure oxygen concentration in the air (Hübert et al., 2015). Such type of sensor is also widely used in the OC tests for measuring the reactivity of sulphidic materials based on the oxygen consumption rate resulting of the oxidation of these materials. The galvanic oxygen sensors are an electric device consisting of three main components: a diffusion barrier, a sensing electrode (cathode) and a working electrode (anode). The function of the diffusion barrier is to control the amount of oxygen gas that enters the sensor. The cathode electrode is made of a noble metal such as gold or platinum whereas the anode is made of a base metal such as lead or zinc (Hübert et al., 2015). The both electrodes are immersed in a basic electrolyte such as a solution of potassium hydroxide or potassium acetate. As oxygen diffusing into the sensor is reduced to hydroxyl ions at the cathode (sensing electrode) (Volsko et al., 2014):



Then the Hydroxyl ions ( $\text{OH}^-$ ) in turn oxidize the lead anode (working electrode):



This yields an overall cell reaction of:



This redox reaction produces electrical signal (current) (Volsko et al., 2014). The amount of generated current is proportional to the amount of oxygen gas (the oxygen partial pressure) consumed due to the oxygen gas diffusion and the oxidation of sulphide mineral contained in waste materials. The produced current needs nothing more than a voltmeter attached to a resistor connecting the anode and the cathode to transform into a voltage (Hübert et al., 2015). Therefore, this sensor is characterised by its self-powered (no need to an external power source to operate), experimental simplicity, rapidity, detectability and low cost. Typically, the calibration of galvanic sensor is performed by measuring the sensor response in the ambient air (20.9 vol. %  $\text{O}_2$ ) and in inert gas such as nitrogen or argon (0 vol. %  $\text{O}_2$ ) (Hübert et al., 2015). Also, it can be calibrated with different standard oxygen gas concentrations (Volsko et al., 2014).

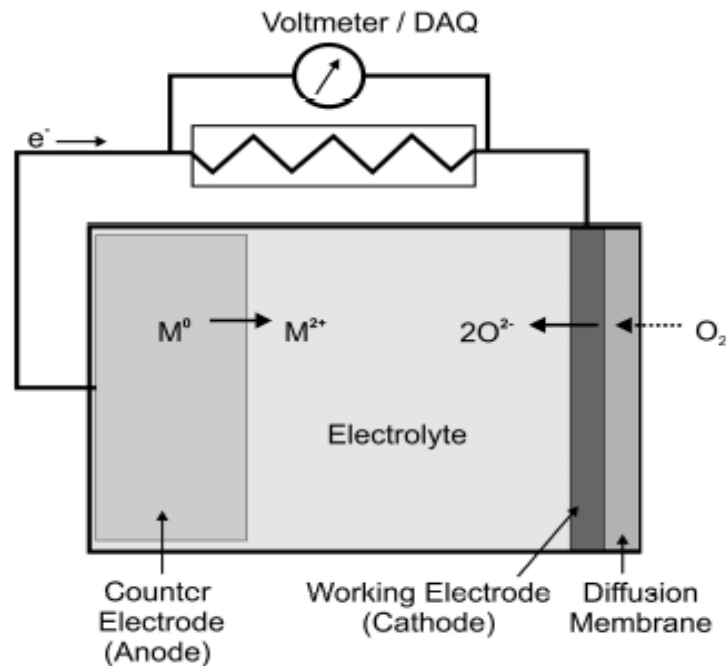


Figure 2.14. The galvanic oxygen sensor (Hübert et al., 2015)

## **2.6 Literature review on Previous Studies on Reactivity of Tailings Based Materials**

### **2.6.1 Introduction**

The reactivity of uncemented sulphidic tailings or CPB made of sulphidic tailings has been investigated in various studies to provide a better understanding of this behavior. These studies were conducted in both the laboratory and field. The purpose of this chapter is to provide a literature review on the reactivity of uncemented and cemented tailings (CPB) based materials by conducting OC tests.

### **2.6.2 Previous Studies on Reactivity of Uncemented Tailings**

Several studies have conducted OC tests in the laboratory and field to measure the reactivity of mine tailings materials (for e.g., Coulombe et al., 2012; Martin et al., 2006; Bussière et al., 2004; Bussière et al., 2002 ; Tibble and Nicholson, 1997; Elberling & Nicholson, 1996; Nicholson et al., 1995; Elberling et al., 1994a ; Elberling et al., 1994b; Mbonimpa et al., 2003; Mbonimpa et al., 2002).

Elberling et al. (1994a) developed a model that simulated the rate of  $\text{FeS}_2$  oxidation to evaluate the influence of chemical kinetics and diffusion in controlling the oxidation rate of  $\text{FeS}_2$  over time. Also, the influence of the main parameters of tailings materials, such as the effective diffusion coefficient and  $\text{FeS}_2$  mineral content, on the sensitivity of the developed model was investigated. The simulation results showed that the oxidation rate of  $\text{FeS}_2$  tailings is controlled by chemical kinetics initially at deposition and then changes with time (within the first 2-5 years) to become diffusionally controlled based on the effective diffusion coefficient of oxygen in the tailings. This means that the oxidation of  $\text{FeS}_2$  in tailings is a chemically controlled process during the initial period of deposition. The authors stated that the rate of the oxidation of  $\text{FeS}_2$  tailings depends on their composition and physical characteristics. Also, they reported that with a high degree of saturation, oxygen diffusion is significantly decreased in the tailings. They concluded that the overall rate of oxidation after a few years will be controlled by the effective diffusion coefficient of oxygen in tailings.

Elberling et al. (1994b) experimentally evaluated three techniques, namely oxygen-gradient, oxygen-consumption and sulphate-release methods which were used to measure and monitor the sulphide oxidation rates in mine tailings materials by conducting a number of column experiments.

The column experiments were carried out under controlled laboratory conditions to evaluate the sulphide oxidation rates compared to the available results of the water chemistry. The three techniques were experimentally investigated for a range of oxidation rates and covered layer schemes under different degrees of saturation with water. The experimental results of these methods were compared with the modelled results. The study recommended the use of the OC test for measuring and monitoring the reactivity of sulphide bearing tailings materials as well as evaluating the efficiency of designed cover layers for remediation schemes. The OC test is preferred over the other methods because it is simple, inexpensive, fast, unrestrictive and repeatable. The study stated that the use of fine grained covers is an effective remediation scheme to reduce the rate of sulphide oxidation if they were maintained at a high degree of saturation. Also, the authors observed the development of a zone of depleted sulphides at the upper surface of the tailings over time which led to the reduction of the oxidation rate. The modelling of the obtained results indicated that the oxidation rate of sulphides is controlled by diffusion rather than by a kinetic mechanism.

Nicholson et al. (1995) carried out a field study to monitor and measure the oxidation rates of sulphidic tailings by using the OC method. Also, they used this method to measure the efficiency of inert materials that were used to cover sulphide bearing tailings to limit their potential of generating AMD. The study reported that the *in situ* OC tests provide direct and reliable estimates of oxidation rates of sulphidic tailings. Also, they found that there is a good agreement between the measurements of OC and those of sulphate release. The field study revealed that patterns of oxygen uptake rates of sulphide minerals in tailings demonstrate consistency in time and space. In addition, they found that the age of the exposed surface area of tailings, moisture content of the upper non-sulphide layer at the surface and the depth to the water table influence the OC rates. Finally, they strongly recommended the use of the OC method to measure the oxidation rate of sulphide bearing wastes because it is quick, simple, accurate, and inexpensive. Also, it can be used in both the laboratory and field.

Elberling and Nicholson (1996) conducted a field investigation by using OC tests to measure the reactivity (OC) of sulphidic tailings (8 years, pyrrhotite mineral) at the ground surface of a mine in northeast Sudbury in Ontario, Canada. Also, carbon monoxide (CO, nonreactive) gas was used to measure the diffusivity of the tailings materials. The results of the study showed that fresh tailings have the highest reactivity whereas covered tailings have the lowest reactivity.

Furthermore, the field study results revealed that the oxidation rate of the tailings materials is governed by the oxygen diffusion rates which is supported by the diffusion flux results of CO gas. The many different OC rates at different sites on the ground surface of mines are due to the various diffusion coefficients of the tailings materials. Therefore, oxygen gas diffusion rates vary depending on the characteristics of the tailings materials (e.g., pore structure, moisture). The field results showed there is good correlation between the results of the OC test and sulphate release. The study recommended *in situ* OC tests to measure the reactivity of sulphide-bearing tailings with Fickian models to interpret their results.

Tibble and Nicholson (1997) conducted field investigations on a variety of tailings impoundments at six selected field sites by using OC testing to understand the influence of physical site characteristics, including age of tailings, moisture and sulphide contents, and the effectiveness of different cover scenarios on the OC rate of sulphide bearing tailings. The results showed that oxygen consumption testing offers a fast yet cost effective assessment method that can provide useful and critical data for a wide variety of sulphide tailings sites. In addition, the data can be used for waste management planning and evaluation of covers from test-plot to full-scale. In this study, it was observed that the sulphide and moisture content of tailings materials as well as the climatic conditions of the site can affect the consumption rate of tailings. The oxygen consumption values were measured which ranged from less than 1 to above 5,000 mol O<sup>2</sup> m<sup>-2</sup> a<sup>-1</sup>. Also, the field investigation reported that the oxygen consumption (OC) rates were observed to be significantly increased with increased sulphide content of the tailings. On the other hand, the OC rates are reduced in cooler and wetter climatic conditions, with tailings exposure time, at a higher moisture content (less effective gas diffusion coefficient) as well as depth, and the use of a properly engineered tailings cover.

Coulombe et al. (2012) performed *in situ* OC tests to assess the performance of an insulation cover with a thickness of 1.2 m that was constructed on the Xstrata Nickel Raglan Mine tailings storage facility in Quebec, Canada. They measured and evaluated the reactivity of non-covered and covered tailings to assess the efficiency of a granular insulation cover in a continuous permafrost zone. Also, they measured the temperature at various depths of the cover material and sulphide tailings. The results indicated that the reactivity of non-covered tailings reached a maximum value of 544 moles m<sup>-2</sup> year<sup>-1</sup> during August when the temperature was 12.8°C. On the other hand, the reactivity of the covered tailings was low in August and from September to the end

of October, increased to reach a maximum value of  $444 \text{ moles m}^{-2} \text{ year}^{-1}$ . In December, when the tailings temperature drops to about  $-5^{\circ}\text{C}$ , the reactivity of the tailings was reduced. The study stated that the sulphidic tailings can oxidize if not conserved from freeze-thaw cycles. Also, at subzero temperatures, the tailings may continue to oxidise.

### **2.6.3 Review of Previous Studies on Reactivity of Cemented Tailings Backfill**

Only a few studies have performed OC tests to assess reactivity or determine the rate of oxidation of tailings materials in a CPB system.

Ouellet et al. (2003) conducted OC testing in the laboratory on five synthesised tailings with 4, 12, 22, 34 and 74% wt. of  $\text{FeS}_2$  by themselves or in CPB at different degrees of saturation. CPB cylinders were prepared from the synthesised tailings mixed with 4.5% of 2 types of binders including a mixture of 50:50 PC types 10 and 50 and a mixture of PC type 10 with GGBFS and tap water. The tailings and CPB samples were placed into an OC chamber to measure their OC rates by using an oxygen sensor (GC33-200, GC Industries). The results revealed that the reactivity of tailings and CPB is significantly affected by  $\text{FeS}_2$  content and degree of saturation. Also, at degrees of water saturation less than 70%, the reactivity of CPB samples is less than that of the un-cemented tailings samples whereas at a degree of saturation of more than 70%, the reduction in the reactivity is approximately the same in both the CPB samples and tailings specimens without cement. The authors suggested that the use of CPB is a good means for disposing sulphidic tailings materials at the upper surface of mines.

Ouellet et al. (2006) used the same OC approach to determine the reactivity of a stope filled with CPB with a depth of 2150 m at Laronde mine in Quebec, Canada. The CPB consisted of highly reactive sulphidic tailings ( $\approx 53\% \text{ FeS}_2$ ) mixed with a mix of Portland cement (PC) type 10 and 50. The stope was filled in two sequences with CPB that had two binder contents of 7 wt. % and 5 wt. % respectively to construct a strong base. PC type 50 was added to resist against sulphate attacks. The results showed that there is a high rate of oxidation (mean value of  $2.4 \text{ mol O}_2/\text{m}^2/\text{day}$ ) at the beginning of the testing which then gradually decreased to  $0.2 \text{ mol O}_2/\text{m}^2/\text{day}$  after 80 days. This oxidation rate is lower than that in the laboratory tests and for tailings without a binder due to the high degree of saturation and coating on the pyrite grains. They concluded that the use of CPB with sulphidic tailings is a promising approach for disposal of underground mine waste (Ouellet et al., 2006).

Pokharel (2008) investigated the reactivity of CPB systems with artificial tailings (99.9% silica) mixed with 5 - 45% commercial FeS<sub>2</sub> mineral by weight and PCI and PCI-slag as the binders. The paste backfill samples were cured at 2°C, 20°C, 35°C and 50°C for 56 days. Furthermore, he measured the reactivity of uncemented paste tailings with 5%, 15% and 45% FeS<sub>2</sub> at different degrees of saturation (50%, 75%, 85% and 95%) and curing for 7 days. The study revealed that the reactivity of CPB systems is a function of binder type and FeS<sub>2</sub> content whereas the reactivity of uncemented paste tailings depend on both FeS<sub>2</sub> content and degree of saturation. Also, the experimental results showed that the OC (reactivity) rate decreases with time and increases with increased curing temperature. The study reported that at the earlier ages, the reactivity of CPB systems with sulphide-rich tailings as well as the potential of AMD formation is higher but decreases with increased curing time.

## **2.7 Conclusions**

The use of CPB is an alternative approach for the disposal of mine waste materials, in particular sulphide-bearing tailings which minimise the environmental, social, and economic impacts on the surrounding environments and water streams. CPB is an engineered cement-based composite made primarily with three components, namely tailings which are the primary component (often containing sulphide minerals), a small amount of binder agent (commonly PC alone or partial replacement of PC with mineral admixtures like slag or FA) and mixing water (either fresh or processing water).

From the theoretical and technical background information, it can be noted that CPB is a complex system due its ingredients. Therefore, to better understand the reactivity of sulphidic CPB systems, it is important to understand the characteristics and compositions of their main ingredients by themselves and/or in combination with other ingredients. For example, understanding the chemical and mineralogical compositions and physical properties of the binder agent used in the mixing of CPB mixtures will provide a better understanding on the influence of binder hydration on the reactivity behavior of CPB systems. Also, an understanding of the environment where CPB systems are placed and serviced allows the main factors that might affect their reactivity to be identified. These factors (e.g., curing and ambient temperatures, degree of saturation, initial sulphate content) may positively or negatively influence the reactivity of sulphide-bearing CPB systems. They can originate from the CPB itself (internal source) and/or from the surrounding environment (external sources). They can also interact with CPB systems and their components.

Therefore, investigating the influence of these main factors on reactivity will provide a better understanding of the reactivity behaviour of sulphidic CPB systems. This will provide mining engineers with useful information to design and optimise CPB mixtures with more chemical stability and durability as well as having fewer environmental impacts.

The reactivity of sulphidic tailings is a critical factor and plays an important role in their environmental behavior and durability performance. Also, it determines the proper management and remediation strategies for sulphidic tailings materials. Therefore, numerous laboratory and field studies have been conducted to understand the reactivity of sulphidic tailings to prevent and/or minimize their short- and long-term environmental, social and economic consequences on the surrounding environment. From the reviewed studies, it can be observed that only a few studies have investigated the reactivity of cemented paste tailings (CPT) or cemented paste backfill (CPB) compared to mine tailings. However, these studies have only focused on the effects of a few factors on the reactivity of CPB, such as sulphide content, curing time and temperature, and degree of saturation, whereas many other important parameters are ignored, such as ambient temperature, initial sulphate content, ageing, cracking and damage, binder type and content, addition of mineral admixtures (as partial substitutes for PCI), and curing stress. These parameters may influence the reactivity behavior of CPB systems by themselves or coupled with other parameters. There is therefore the need to understand their effects on the reactivity of CPB so as to provide essential information that would fill the research gap of previous studies. Also, a better understanding will help mining engineers to design and prepare proper CPB mixes that take into consideration the environment, durability and cost.

## 2.8 References

- Afshar, A. B. (1986). *The early hydration of cement*. Heriot-Watt University. Retrieved from <http://hdl.handle.net/10399/1059>
- Aldea, C. (2010). Paste backfill mix From concept through closure. *International Mining*, (April), 79–80.
- Aligizaki, K. K. (2006). *Pore structure of cement-based materials : Testing, Interpretation and Requirement* (1st ed.). Spon Press. Retrieved from <https://www.crcpress.com/Pore-Structure-of-Cement-Based-Materials-Testing-Interpretation-and-Requirements/Aligizaki/9780419228004>
- Baxi, C. V, & Prasad, A. (2005). *Social Responsibility Concepts and Cases: The Indian Experience*. New Delhi: Excel Books.
- Belem, T., & Benzaazoua, M. (2008). Design and Application of Underground Mine Paste Backfill Technology. *Geotechnical and Geological Engineering*, 26(2), 147–174. <http://doi.org/10.1007/s10706-007-9154-3>

- Belem, T., Bussière, B., & Benzaazoua, M. (2001). The effect of microstructural evolution on the physical properties of paste backfill. In *Proceedings of the Tailings and Mine Waste '01* (pp. 365–374). Fort Collins, Colorado, Balkema, Rotterdam.
- Benzaazoua, M., Belem, T., & Bussière, B. (2002). Chemical factors that influence the performance of mine sulphidic paste backfill. *Cement and Concrete Research*, *32*(7), 1133–1144. [http://doi.org/10.1016/S0008-8846\(02\)00752-4](http://doi.org/10.1016/S0008-8846(02)00752-4)
- Benzaazoua, M., Bussière, B., Kongolo, M., McLaughlin, J., & Marion, P. (2000). Environmental desulphurization of four Canadian mine tailings using froth flotation. *International Journal of Mineral Processing*, *60*(1), 57–74. [http://doi.org/10.1016/S0301-7516\(00\)00006-5](http://doi.org/10.1016/S0301-7516(00)00006-5)
- Benzaazoua, M., Fall, M., & Belem, T. (2004). A contribution to understanding the hardening process of cemented pastefill. *Minerals Engineering*, *17*(2), 141–152. <http://doi.org/10.1016/j.mineng.2003.10.022>
- Benzaazoua, M., & Kongolo, M. (2003). Physico-chemical properties of tailing slurries during environmental desulphurization by froth flotation. *International Journal of Mineral Processing*, *69*(1–4), 221–234. [http://doi.org/10.1016/S0301-7516\(02\)00129-1](http://doi.org/10.1016/S0301-7516(02)00129-1)
- Benzaazoua, M., Ouellet, J., Servant, S., Newman, P., & Verburg, R. (1999). Cementitious backfill with high sulfur content Physical, chemical, and mineralogical characterization. *Cement and Concrete Research*, *29*(5), 719–725. [http://doi.org/10.1016/S0008-8846\(99\)00023-X](http://doi.org/10.1016/S0008-8846(99)00023-X)
- Bertolini, L., Elsener, B., Pedferri, P., Redaelli, E., & Polder, R. B. (2013). Transport Processes in Concrete. In *Corrosion of steel in concrete : prevention, diagnosis, repair*. (2nd ed., pp. 21–48). Weinheim, Germany: Wiley-VCH Verlag GmbH & Co. KGaA. <http://doi.org/10.1002/9783527651696.ch2>
- Bhanbhro, R., Knutsson, R., Rodriguez, J., Edeskär, T., & Knutsson, S. (2013). Basic Description of Tailings from Aitik Focusing on Mechanical Behavior. *International Journal of Emerging Technology and Advanced Engineering*, *3*(12), 65–69.
- Bishop, M., Bott, S. G., & Barron, A. R. (2003). A New Mechanism for Cement Hydration Inhibition: Solid-State Chemistry of Calcium Nitrilotris(methylene)triphosphonate. *Chemistry of Materials*, *15*(16), 3074–3088. <http://doi.org/10.1021/cm0302431>
- Blowes, D. W., Ptacek, C. J., Jambor, J. L., & Weisener, C. G. (2003). The Geochemistry of Acid Mine Drainage A2 - Turekian, Heinrich D. HollandKarl K. BT - Treatise on Geochemistry. In *Treatise on Geochemistry* (pp. 149–204). Oxford: Pergamon. <http://doi.org/http://dx.doi.org/10.1016/B0-08-043751-6/09137-4>
- Bougara, A., Lynsdale, C., & Milestone, N. B. (2010). Reactivity and performance of blastfurnace slags of differing origin. *Cement and Concrete Composites*, *32*(4), 319–324. <http://doi.org/10.1016/j.cemconcomp.2009.12.002>
- Bourgeot, N., Piccinin, R., & Taylor, J. (2011). The benefits of kinetic testwork using oxygen consumption techniques and implications for the management of sulfidic materials. *Proceedings of the 7th Australian Workshop on Acid and Metalliferous Drainage*, (June), 117–129. Retrieved from [http://earthsystems.com.au/wp-content/uploads/2013/05/Bourgeot-et-al-2011\\_OxCon.pdf](http://earthsystems.com.au/wp-content/uploads/2013/05/Bourgeot-et-al-2011_OxCon.pdf)
- Brandt, A. M. (2009). *Cement-Based Composites: Materials, Mechanical Properties and Performance*. CRC Press.
- Brito, J., & Saikia, N. (2013). Construction and Demolition Waste Aggregates. In *Recycled Aggregate in Concrete: Use of Industrial, Construction and Demolition Waste* (pp. 23–80). London: Springer London. [http://doi.org/10.1007/978-1-4471-4540-0\\_3](http://doi.org/10.1007/978-1-4471-4540-0_3)
- CAC. (2016). SCMs Help Reduce Emissions. Retrieved February 7, 2017, from

- <http://www.cement.ca/en/Supplementary-Cementing-Materials.html>
- Costa, C. (2015). Hydraulic Binders. In C. M. Gonçalves & F. Margarido (Eds.), *Materials for Construction and Civil Engineering: Science, Processing, and Design* (pp. 1–52). Cham: Springer International Publishing. [http://doi.org/10.1007/978-3-319-08236-3\\_1](http://doi.org/10.1007/978-3-319-08236-3_1)
- Coulombe, V., Bussière, B., Côté, J., and Garneau, P. (2012). Performance of Insulation Covers to Control Acid Mine Drainage in Cold Environments. In *Proceedings of the 15th International Conference on Cold Regions Engineering* (pp. 789–799). Quebec City, Canada. <http://doi.org/10.1061/9780784412473.078>
- Craig, J. R., & Vokes, F. M. (1993). The metamorphism of pyrite and pyritic ores; an overview. *Mineralogical Magazine*, 57(386), 3–18. <http://doi.org/10.1180/minmag.1993.057.386.02>
- CTI Reviews. (2016). *Basic Environmental Technology, Water Supply, Waste Management and Pollution Control*. Cram101 Textbook Reviews, 2016. Retrieved from <https://pubchem.ncbi.nlm.nih.gov/compound/sulfate%0A>
- Demers, I., Bussière, B., Mbonimpa, M., & Benzaazoua, M. (2009). Oxygen diffusion and consumption in low-sulphide tailings covers. *Canadian Geotechnical Journal*, 46(4), 454–469. <http://doi.org/10.1139/T08-132>
- Dimitrova, R. S., & Yanful, E. K. (2012). Effect of drainage conditions, bed thickness, and age on the shear strength of mine tailings in a very low stress range. *Canadian Geotechnical Journal*, 49(3), 285–297. <http://doi.org/10.1139/t11-098>
- Dold, B. (2008). Sustainability in metal mining: from exploration, over processing to mine waste management. *Reviews in Environmental Science and Bio/Technology*, 7(4), 275. <http://doi.org/10.1007/s11157-008-9142-y>
- Dold, B. (2014). Submarine Tailings Disposal (STD)—A Review. *Minerals*, 4(3), 642–666. <http://doi.org/10.3390/min4030642>
- Elberling, B., Nicholson, R. V., & Scharer, J. M. (1994). A combined kinetic and diffusion model for pyrite oxidation in tailings: a change in controls with time. *Journal of Hydrology*, 157(1–4), 47–60. [http://doi.org/10.1016/0022-1694\(94\)90098-1](http://doi.org/10.1016/0022-1694(94)90098-1)
- Elberling, B., & Nicholson, R. V. (1996). Field determination of sulphide oxidation rates in mine tailings. *Water Resources Research*, 32(6), 1773–1784. <http://doi.org/10.1029/96WR00487>
- Elberling, B., Nicholson, R. V., Reardon, E. J., & Tibble, R. (1994). Evaluation of sulphide oxidation rates: a laboratory study comparing oxygen fluxes and rates of oxidation product release. *Canadian Geotechnical Journal*, 31(3), 375–383. <http://doi.org/10.1139/t94-045>
- Environment Canada. (2009). *Environmental Code of Practice for Metal Mines*. Ottawa, Canada: Environment Canada.
- Ercikdi, B., Cihangir, F., Kesimal, A., Deveci, H., & Alp, I. (2009). Utilization of industrial waste products as pozzolanic material in cemented paste backfill of high sulphide mill tailings. *Journal of Hazardous Materials*, 168(2–3), 848–856. <http://doi.org/10.1016/j.jhazmat.2009.02.100>
- Ercikdi, B., Kesimal, A., Cihangir, F., Deveci, H., & Alp, I. (2009). Cemented paste backfill of sulphide-rich tailings: Importance of binder type and dosage. *Cement and Concrete Composites*, 31(4), 268–274. <http://doi.org/10.1016/j.cemconcomp.2009.01.008>
- Evangelou, V. P. (1995). *Pyrite oxidation and its control*. Boca Raton, FL: CRC Press.
- Evangelou, V. P. (Bill), & Zhang, Y. L. (1995). A review: Pyrite oxidation mechanisms and acid mine drainage prevention. *Critical Reviews in Environmental Science and Technology*, 25(2), 141–199. <http://doi.org/10.1080/10643389509388477>
- Fall, M., Nasir, O., Cui, L., and Han, F. S. (2015). Coupled modeling of the strength development

- and distribution within cemented paste backfill structure. In *49th U.S. Rock Mechanics/Geomechanics Symposium*. San Francisco, California: American Rock Mechanics Association.
- Fall, M., Adrien, D., Célestin, J. C., Pokharel, M., & Touré, M. (2009). Saturated hydraulic conductivity of cemented paste backfill. *Minerals Engineering*, 22(15), 1307–1317. <http://doi.org/10.1016/j.mineng.2009.08.002>
- Fall, M., Benzaazoua, M., & Ouellet, S. (2004). Effect of tailings properties on paste backfill performance. In *Proceedings of the eighth international symposium on mining with backfill (Minefill 2004)* (pp. 193–202). China.
- Fall, M., Célestin, J. C., Pokharel, M., & Touré, M. (2010). A contribution to understanding the effects of curing temperature on the mechanical properties of mine cemented tailings backfill. *Engineering Geology*, 114(3–4), 397–413. <http://doi.org/10.1016/j.enggeo.2010.05.016>
- Fall, M., & Pokharel, M. (2010). Coupled effects of sulphate and temperature on the strength development of cemented tailings backfills: Portland cement-paste backfill. *Cement and Concrete Composites*, 32(10), 819–828. <http://doi.org/10.1016/j.cemconcomp.2010.08.002>
- Galle, C., Pin, M., & Daian, J. F. (2000). Gas permeability of cement based materials. Retrieved from [http://www.iaea.org/inis/collection/NCLCollectionStore/\\_Public/35/078/35078653.pdf](http://www.iaea.org/inis/collection/NCLCollectionStore/_Public/35/078/35078653.pdf)
- Gleisner, M. (2005). *Quantification of mineral weathering rates in sulfidic mine tailings under water-saturated conditions*. Stockholm University.
- Hassani, F. P., Ouellet, J., & Hossein, M. (2001). Strength development in underground high-sulphate paste backfill operation. *CIM Bulletin*, 94(1050), 57–62. Retrieved from <http://cat.inist.fr/?aModele=afficheN&cpsid=1124407>
- Huang, J., Valenzano, L., Singh, T. V., Pandey, R., & Sant, G. (2014). Influence of (Al, Fe, Mg) Impurities on Triclinic Ca<sub>3</sub>SiO<sub>5</sub>: Interpretations from DFT Calculations. *Crystal Growth & Design*, 14(5), 2158–2171. <http://doi.org/10.1021/cg401647f>
- ICME/UNEP. (1998). *Case studies on Tailings Management*. (International Council on Metals and the Environment/United Nations Environment Programme (ICME/UNEP), Ed.). UNEP/Earthprint, 1998.
- James, M., Jollette, D., Aubertin, M., & Bussière, B. (2003). An Experimental Set-up to Investigate Tailings Liquefaction and Control Measures. In *International Symposium on Major Challenges in Tailings Dams (ICOLD)* (Vol. 4711, pp. 153–164). Montreal, Qc, Canada.
- Jennings, H. M., Bullard, J. W., Thomas, J. J., Andrade, J. E., Chen, J. J., & Scherer, G. W. (2008). Characterization and Modeling of Pores and Surfaces in Cement Paste. *Journal of Advanced Concrete Technology*, 6(1), 5–29. <http://doi.org/10.3151/jact.6.5>
- Kesimal, A., Yilmaz, E., Ercikdi, B., Alp, I., & Devenci, H. (2005). Effect of properties of tailings and binder on the short-and long-term strength and stability of cemented paste backfill. *Materials Letters*, 59(28), 3703–3709. <http://doi.org/10.1016/j.matlet.2005.06.042>
- Klieger, P., & Lamond, J. F. (1994). *Significance of Tests and Properties of Concrete and Concrete-making Materials* (illustrate). ASTM International. Retrieved from <https://books.google.ca/books?id=waJhxne7K1MC>
- Kowalczyk, R. M., Gajewicz, A. M., & McDonald, P. J. (2014). The mechanism of water-isopropanol exchange in cement pastes evidenced by NMR relaxometry. *RSC Advances*, 4(40), 20709–20715. <http://doi.org/10.1039/C4RA00889H>
- Kumar, R., & Bhattacharjee, B. (2003). Porosity, pore size distribution and in situ strength of concrete. *Cement and Concrete Research*, 33(1), 155–164. [http://doi.org/10.1016/S0008-8846\(02\)00942-0](http://doi.org/10.1016/S0008-8846(02)00942-0)

- Kwong, Y. T. J., & Ferguson, K. D. (1990). Water chemistry and oxidation mineralogy at Mount Washington - Implications to acid generation and metal leaching. In *Acid Mine Drainage: Designing for Closure* (pp. 217–230). Vancouver, British Columbia: Bitech Publishers.
- León, E.A., Rate, A.W., Hinz, C., and Campbell, G. D. (2004). Weathering of Sulphide Minerals at Circum- Neutral-pH in Semi-Arid/Arid Environments: Influence of Water Content. In *SuperSoil 2004: 3rd Australian New Zealand Soils Conference* (p. 7). The Regional Institute Ltd. Retrieved from [www.regional.org.au/au/asssi/](http://www.regional.org.au/au/asssi/)
- León, E. A., Rate, A. W., Hinz, C., & Campbell, G. D. (2004). Weathering of sulphide minerals at circum-neutral-pH in semi-arid / arid environments : influence of water content. *Supersoil. 3rd Australian New Zealand Soils Conference*, (December), 5–9.
- Li, W., & Fall, M. (2016). Sulphate effect on the early age strength and self-desiccation of cemented paste backfill. *Construction and Building Materials*, 106, 296–304. <http://doi.org/10.1016/j.conbuildmat.2015.12.124>
- Lothenbach, B., Scrivener, K., & Hooton, R. D. (2011). Supplementary cementitious materials. *Cement and Concrete Research*, 41(12), 1244–1256. <http://doi.org/10.1016/j.cemconres.2010.12.001>
- Lottermoser, B. (2010). *Mine Wastes: Characterization, Treatment and Environmental Impacts*. Springer Berlin Heidelberg. <http://doi.org/10.1007/978-3-642-12419-8>
- Lowson, R. T. (1982). Aqueous oxidation of pyrite by molecular oxygen. *Chemical Reviews*, 82(5), 461–497. <http://doi.org/10.1021/cr00051a001>
- Lye, C.-Q., Dhir, R. K., & Ghataora, G. S. (2015). Carbonation resistance of fly ash concrete. *Magazine of Concrete Research*, 67(21), 1150–1178. <http://doi.org/10.1680/macr.15.00204>
- Mbonimpa, M, Aubertin, M, Aachib, M, B. (2002). *Oxygen diffusion and consumption in unsaturated cover materials*.
- MEND. (2006). Paste Backfill Geochemistry – Environmental Effects of Leaching and Weathering, (April). [http://doi.org/MEND Report 10.2](http://doi.org/MEND%20Report%2010.2)
- Mindess, S., Young, J. F., & Darwin, D. (2002). *Concrete* (2nd ed.). Upper Saddle River, NJ, USA: Pearson Education, Inc.
- Narayanan, N., & Ramamurthy, K. (2000). Microstructural investigations on aerated concrete. *Cement and Concrete Research*, 30(3), 457–464. [http://doi.org/10.1016/S0008-8846\(00\)00199-X](http://doi.org/10.1016/S0008-8846(00)00199-X)
- Neville, A. M. (2012). *Properties of Concrete* (5th ed). Prentice Hall.
- Nicholson, R. V., Elberling, B., Williams, G. (1995). A new oxygen consumption technique to provide rapid assessment of tailings reactivity in the field and the laboratory. In *Proceedings of Sudbury '95-Mining and the environment*, 3.
- Nicholson, R.V., Scharer, J.M., Anderson, M. E. (1997). *A Rapid kinetic technique for measuring the reactivity of sulfide waste rock: the oxygen consumption method*. Waterloo, ON. Retrieved from <http://mend-nedem.org/wp-content/uploads/465B.pdf>
- Nordstrom, D. K., & Alpers, C. N. (1999). Geochemistry of acid mine waters. In P. GS (Ed.), *The Environmental Geochemistry of Mineral Deposits* (pp. 133–160). Logsdon MJ: Society for Economic Geologists.
- Nordstrom, D. K., & Southam, G. (1997). Geomicrobiology of sulfide mineral oxidation. *Reviews in Mineralogy*, 35, 381–390. Retrieved from <http://pubs.er.usgs.gov/publication/70019098>
- Oliveira, I., Cavalaro, S. H. P., & Aguado, A. (2013). New Unreacted-Core Model to Predict Pyrrhotite Oxidation in Concrete Dams. *Journal of Materials in Civil Engineering*, 25(3), 372–381. [http://doi.org/10.1061/\(ASCE\)MT.1943-5533.0000531](http://doi.org/10.1061/(ASCE)MT.1943-5533.0000531)

- Orejarena, L., & Fall, M. (2010). The use of artificial neural networks to predict the effect of sulphate attack on the strength of cemented paste backfill. *Bulletin of Engineering Geology and the Environment*, 69(4), 659–670. <http://doi.org/10.1007/s10064-010-0326-7>
- Ouellet, S., Bussiere, B., Benzaazoua, M., Aubertin, M., Fall, M., & Belem, T. (2003). Sulphide Reactivity within cemented paste backfill: oxygen consumption test results. In *The 56th Annual Canadian Geotechnical Conference and 4th joint IAHCNC/CGS Conference* (pp. 176–183). Winnipeg, Manitoba, Canada.
- Ouellet, S., Bussière, B., Mbonimpa, M., Benzaazoua, M., & Aubertin, M. (2006). Reactivity and mineralogical evolution of an underground mine sulphidic cemented paste backfill. *Minerals Engineering*, 19(5), 407–419. <http://doi.org/10.1016/j.mineng.2005.10.006>
- Payant, R., Rosenblum, F., Nasset, J. E., & Finch, J. A. (2012). The self-heating of sulfides: Galvanic effects. *Minerals Engineering*, 26, 57–63. <http://doi.org/10.1016/j.mineng.2011.10.019>
- Payne, T., & Mitra, R. A. (2008). A review of heat issues in underground metalliferous mines. In *Proceedings of the 12th U.S./North American Mine Ventilation Symposium* (pp. 197–201). Reno, NV, USA: University of Nevada.
- Phung, Q. T., Maes, N., De Schutter, G., Jacques, D., & Ye, G. (2013). Determination of water permeability of cementitious materials using a controlled constant flow method. *Construction and Building Materials*, 47, 1488–1496. <http://doi.org/10.1016/j.conbuildmat.2013.06.074>
- Pokharel, M. (2008). *Geotechnical and environmental responses of paste tailings systems to coupled thermo-chemical loadings*. University of Ottawa. Retrieved from <http://hdl.handle.net/10393/27793>
- Pokharel, M., & Fall, M. (2010). Coupled Thermochemical Effects on the Strength Development of Slag-Paste Backfill Materials. *Journal of Materials in Civil Engineering*, 23(5), 511–525. [http://doi.org/10.1061/\(ASCE\)MT.1943-5533.0000192](http://doi.org/10.1061/(ASCE)MT.1943-5533.0000192)
- Potvin, Y., Thomas, E., & Fourie, A. (2005). *Handbook on mine fill*. Nedlands, Western Australia: Australian Centre for Geomechanics. Retrieved from <https://books.google.ca/books?id=oe3gAAAAMAAJ>
- Ramezaniapour, A. A. (2014). Cement Replacement Materials: Properties, Durability, Sustainability (pp. 1–46). Berlin, Heidelberg: Springer Berlin Heidelberg. [http://doi.org/10.1007/978-3-642-36721-2\\_1](http://doi.org/10.1007/978-3-642-36721-2_1)
- Rantala, P. (2007). Backfill basics. *Sudbury Mining Solutions Journal*, (June 1, 2007). Retrieved from <http://www.sudburyminingsolutions.com/backfill-basics.html>
- Razavi, S. M., & Hassani, F. (2007). Preliminary Investigation Into Gel Fill: Strength Development And Characteristics of Sand Paste Fill With Sodium Silicate. In *1st Canada-US Rock Mechanics Symposium*. Vancouver, Canada: American Rock Mechanics Association.
- Reed, M. H., & Palandri, J. (2006). Sulfide Mineral Precipitation from Hydrothermal Fluids. *Reviews in Mineralogy and Geochemistry*, 61(1), 609 LP-631. Retrieved from <http://rimg.geoscienceworld.org/content/61/1/609.abstract>
- Rodriguez, J., & Edeskär, T. (2013). Case of study on particle shape and friction angle on tailings. *Journal of Advanced Science and Engineering Research*, 3(4), 373–387. Retrieved from <https://www.sign-ific-ance.co.uk/dsr/index.php/JASER/article/view/749>
- Rosso, K. M., & Vaughan, D. J. (2006). Reactivity of Sulfide Mineral Surfaces. *Reviews in Mineralogy and Geochemistry*, 61(1), 557 LP-607. Retrieved from <http://rimg.geoscienceworld.org/content/61/1/557.abstract>

- Saharan, M. R., Gupta, K. K., Jamal, A., & Sheoran, A. S. (1995). Management of acidic effluents from tailing dams in metalliferous mines. *Mine Water and the Environment*, 14(1), 85–93. <http://doi.org/10.1007/BF02914855>
- Sant, G., Bentz, D., & Weiss, J. (2011). Capillary porosity depercolation in cement-based materials: Measurement techniques and factors which influence their interpretation. *Cement and Concrete Research*, 41(8), 854–864. <http://doi.org/10.1016/j.cemconres.2011.04.006>
- Sasaki, K., Tsunekawa, M., Ohtsuka, T., & Konno, H. (1995). Confirmation of a sulfur-rich layer on pyrite after oxidative dissolution by Fe(III) ions around pH2. *Geochimica et Cosmochimica Acta*, 59(15), 3155–3158. [http://doi.org/10.1016/0016-7037\(95\)00203-C](http://doi.org/10.1016/0016-7037(95)00203-C)
- Sbarba, H. D. (2012). *Heat recovery systems in underground mine ventilation systems and novel mine cooling systems*. Université Laval.
- Schmieder, P. J., Taylor, J. R., & Bourgeot, N. (2012). Oxygen consumption techniques to quantify acidity generation rates. In *1st International Acid and Metalliferous Drainage Workshop*. Beijing, China.
- Schoonen, M., Elsetinow, A., Borda, M., & Strongin, D. (2000). Effect of temperature and illumination on pyrite oxidation between pH 2 and 6. *Geochemical Transactions*, 1(1), 23. <http://doi.org/10.1186/1467-4866-1-23>
- Shetty, M. (2005). *Concrete Technology: Theory and Practice*. S. Chand.
- Shi, C., & Mo, Y. L. (2008). *High-Performance Construction Materials - Science and Applications*. World Scientific. World Scientific. Retrieved from [https://app.knovel.com/web/toc.v/cid:kpHPCMSA04/viewerType:toc/root\\_slug:high-performance-construction/url\\_slug:index?&issue\\_id=kpHPCMSA04](https://app.knovel.com/web/toc.v/cid:kpHPCMSA04/viewerType:toc/root_slug:high-performance-construction/url_slug:index?&issue_id=kpHPCMSA04)
- Siddique, R., & Khan, M. I. (2011). *Supplementary Cementing Materials*. Berlin: Springer. <http://doi.org/10.1007/978-3-642-17866-54>
- Snellings, R., Mertens, G., & Elsen, J. (2012). Supplementary Cementitious Materials. *Reviews in Mineralogy & Geochemistry*, 74(1), 211–278. <http://doi.org/10.2138/rmg.2012.74.6>
- SPE. (2015). Cement hydration. Retrieved January 30, 2017, from [http://petrowiki.org/Cement\\_hydration](http://petrowiki.org/Cement_hydration)
- Tang, S. W., Cai, X. H., He, Z., Zhou, W., Shao, H. Y., Li, Z. J., ... Chen, E. (2016). The review of pore structure evaluation in cementitious materials by electrical methods. *Construction and Building Materials*, 117, 273–284. <http://doi.org/10.1016/j.conbuildmat.2016.05.037>
- Tariq, A., & Nehdi, M. (2007). Developing durable paste backfill from sulphidic tailings. *Proceedings of the Institution of Civil Engineers - Waste and Resource Management*, 160(4), 155–166. <http://doi.org/10.1680/warm.2007.160.4.155>
- Taylor, P. C., Kosmatka, S. H., & Voigt, G. F. (2006). *Integrated materials and construction practices for concrete pavement: A state-of-the-practice manual*. Washington, DC. Retrieved from [http://www.cptechcenter.org/publications/imcp/imcp\\_manual.pdf](http://www.cptechcenter.org/publications/imcp/imcp_manual.pdf)
- Telschow, S. (2012). *Clinker Burning Kinetics and Mechanism: Ph.D. Thesis*. Technical University of Denmark.
- Tennis, P. D., & Jennings, H. M. (2000). A model for two types of calcium silicate hydrate in the microstructure of Portland cement pastes. *Cement and Concrete Research*, 30(6), 855–863. [http://doi.org/10.1016/S0008-8846\(00\)00257-X](http://doi.org/10.1016/S0008-8846(00)00257-X)
- Thomas, M. (2007). Optimizing the Use of Fly Ash in Concrete. *PCA*, 5420, 24.
- Thomas, M. (2013). *Supplementary Cementing Materials in Concrete*. New York: Taylor & Francis Group, LLC.
- Tibble, P.A. and Nicholson, R.V. (1997). Oxygen Consumption on Sulphide Tailings and Tailings

- Covers: Measured Rates and Applications. In *Proceedings of the 4th International Conference on Acid Rock Drainage*. (pp. 647–661). Vancouver, British-Columbia.
- van Oss, H. G. (2005). *Background facts and issues concerning cement and cement data* (Version 1.). *Open-File Report*. Retrieved from <http://pubs.er.usgs.gov/publication/ofr20051152>
- Wang, L., Yang, B., Chen, Y., Zhao, X., Chang, J., & Wang, H. (2012). Modeling early-age hydration kinetics of Portland cement using flexible neural tree. *Neural Computing and Applications*, *21*(5), 877–889. <http://doi.org/10.1007/s00521-010-0475-4>
- Wang, R., Li, X.-G., & Wang, P.-M. (2006). Influence of polymer on cement hydration in SBR-modified cement pastes. *Cement and Concrete Research*, *36*(9), 1744–1751. <http://doi.org/10.1016/j.cemconres.2006.05.020>
- Williamson, M. A., & Rimstidt, J. D. (1994). The kinetics and electrochemical rate-determining step of aqueous pyrite oxidation. *Geochimica et Cosmochimica Acta*, *58*(24), 5443–5454. [http://doi.org/10.1016/0016-7037\(94\)90241-0](http://doi.org/10.1016/0016-7037(94)90241-0)
- Winter, N. (2009). *Understanding cement: An introduction to cement production, cement hydration and deleterious processes in concrete*. WHD Microanalysis Consultants Ltd.
- Yao, Y., Cui, Z., & Wu, R. (2012). Development and Challenges on Mining Backfill Technology. *Journal of Materials Science Research*, *1*(4), 73–78. <http://doi.org/10.5539/jmsr.v1n4p73>

### **Chapter 3: Technical Paper I- Time and Damage Induced Changes in the Chemical Reactivity of Cemented Paste Backfill**

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#### **Abstract**

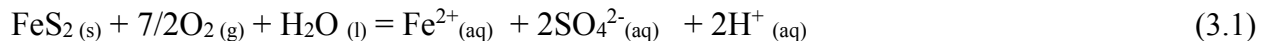
The chemical reactivity of cemented paste backfill (CPB) plays a significant role in its environmental behavior and durability. Therefore, the reactivity of sulphide bearing tailings incorporated into CPB systems should be assessed to avoid or prevent adverse potential environmental effects. The objective of this study is to therefore experimentally assess the influence of time and mechanical damage on the reactivity of CPB samples prepared with tailings that contain different pyrite contents (up to 45 wt. %). Oxygen consumption (OC) tests are conducted on undamaged and mechanically damaged CPB specimens cured at different times to study their reactivity. Furthermore, the microstructural changes of the tested CPB samples are investigated by conducting microstructural analyses (e.g., scanning electron microscopy with energy dispersive X-ray spectroscopy, mercury intrusion porosimetry, and thermogravimetry/derivative thermogravimetry). The obtained results show that the reactivity of CPB is time-dependent. The reactivity decreases as the curing time and ageing of the CPB increase. It is also found that the microstructure or pore structure of CPB significantly affects its reactivity. The encapsulation or coating of the tailings particles with cement hydration products also contributes to reducing the reactivity of CPB. It is also found that the reactivity of CPB increases as the level of damage is increased. There is therefore a relationship between increase in reactivity and level of mechanical damage.

**Keywords:** Cemented paste backfill; tailings; acid mine drainage; mine; environment

### 3.1 Introduction

The technology of using cemented paste backfill (CPB, also called pastefill) has become one of the most popular alternative methods practiced over the last two decades to manage tailings (mine waste) in Canada and many countries worldwide (Li & Fall, 2016; Ercikdi et al., 2010; Alakangas & Öhlander, 2006; Kesimal et al., 2005; Fall & Benzaazoua, 2005; Hassani & Archibald, 1998). The philosophy of the use of CPB is to return tailings materials to the underground voids (stopes) created due to mining activities (MEND, 2006).

Typically, CPB is a mixture mainly prepared with three ingredients, including mine tailings with a solid percentage that ranges between 70% and 85%, water, which is commonly fresh or mine processed water, and a hydraulic binder (usually cement), which is often between 3% to 7% by total weight of solid (Alakangas et al., 2013; Ercikdi et al., 2009). The components of CPB are generally mixed and prepared in the paste backfill plant, which is usually located on the mine surface. The CPB is then transported either by gravity and/or pumping to fill the desired underground stope (Yilmaz, 2010; Hassani & Archibald, 1998). The CPB approach is also utilized as a solidification and stabilization process. The CPB stabilization process includes the control of acid mine drainage (AMD) in the use of sulphide-bearing tailings (Yilmaz, 2010). Sulphide-bearing tailings are considered to be a key contributor to AMD which has long-term environmental impacts on surface and ground water (Tariq & Yanful, 2013; Lottermoser, 2010; Benzaazoua et al., 2008; Johnson & Hallberg, 2005; Blowes et al., 2003). AMD is considered to be one of the serious economic and environmental problems that the mining industry is facing worldwide (Lu et al., 2013; Benzaazoua et al., 2008; Johnson & Hallberg, 2005) and generated as a result of the oxidation of sulphide minerals in the mine tailings. Pyrite ( $\text{FeS}_2$ ) is one of the most common sulphide minerals and often found in the crust of the earth (Dold, 2014; Hawkins, 2014; Parmar & Singh, 2014). It is also an accessory mineral in many types of rocks (Dold, 2014; Hawkins, 2014; Parmar & Singh, 2014; Akcil & Koldas, 2006). Furthermore, pyrite is a common sulphide mineral in mine waste and main contributor to AMD (Awange & Kiema, 2013; Hudson-Edwards et al., 2011; Chugh et al., 2007). The oxidation of pyrite is a complex process, occurs in several steps and includes the formation of secondary products, such as hematite, goethite, jarosite, etc. (Dold, 2010). Generally, the oxidation of pyrite can be written in a simplified form as:



CPB technology has the potential to reduce the chemical reactivity of tailings and pollutant mobility by thickening and mixing tailings with an alkaline material, such as cement (e.g., MEND, 2006; Kesimal et al., 2005). However, despite the significant progress that has been achieved by incorporating sulphide bearing tailings into CPB systems, there are still many ambiguities, in particular, questions about its environmental behavior (Ouellet et al., 2003). During the past decade, many studies have focused on the mechanical properties of CPB (e.g., Yilmaz, 2012; Fall et al., 2010; Yilmaz, 2010; Fall et al., 2008; Kesimal et al., 2005; Elberling et al., 1994). However, few studies have highlighted the impact of chemical reactivity on the performance of CPB systems (MEND, 2006; Ouellet et al., 2003). The reactivity of sulphide bearing tailings-CPB systems could adversely affect their mechanical and environmental behaviors. The chemical reactivity of paste backfill is determined as a function of the fraction of the sulphide minerals, such as pyrite (Ouellet et al., 2003). These minerals can be oxidized by oxygen and cause serious environmental problems with financial ramifications. The extent of the oxidation process is mainly controlled by the movement of both air and water through and around the CPB structure (MEND, 2006). This movement is mainly controlled by the microstructure and transport properties of the CPB, which are influenced by several factors, such as grain size distribution of the paste backfill, degree of saturation, quantity and type of hydraulic binder, cracks, pore water chemistry of the tailings, etc. (Fall & Samb, 2009; MEND, 2006). Among these factors, damage (induces cracks) has significant effects on the transport properties of CPB and consequently, in the reactivity of paste backfill. The presence of cracks in CPB structures could influence their reactivity. The cracks facilitate the movement of air ( $O_2$ ) through the paste backfill structure, which could lead to an increase in the rate of sulphide oxidation and AMD formation. During its service life, a CPB structure can be exposed to external mechanical loads (e.g., rock wall closures, service loads, rock bursts, self-weight pressure) and/or shrinkage which may cause damage or cracking of the CPB materials (Fall et al., 2010). These loads are generally not serious enough to cause significant structural degradation of CPB structures, but with time, degradation accumulates which may lead to micro-cracking of the CPB materials, thus resulting in an increase in fluid transportability. This increase could negatively affect the environmental performance and durability (with respect to reactivity) of CPB structures by creating preferential paths for the penetration of oxygen (Fall et al., 2010).

The reactivity of sulphidic mine wastes can be measured by using direct and indirect methods, such as the sulphate release and oxygen gradient methods, and oxygen consumption (OC)

testing (Ouellet et al., 2003, 2006; Elberling & Nicholson, 1996; Elberling et al., 1994). Among these methods, OC testing is preferred not only because it is simple, low in cost and quick (Ouellet et al., 2003 and 2006), but can also be carried out in both the lab and field. OC testing was originally used in the studies of Elberling et al. (1994) and Elberling and Nicholson (1996), and then in other's several studies to determine the amount of oxidation of sulphide minerals in the laboratory and field as well as measure the reactivity of various types of tailings and mine rocks (e.g., Ouellet et al., 2006; Tibble and Nicholson, 1997; Elberling & Nicholson, 1996; Elberling et al., 1994, 1993; Bussière et al., 2002; Mbonimpa et al., 2002). However, only a few studies have been carried out to measure or assess the reactivity of CPB. For example, Ouellet et al. (2003), Fall et al. (2004) and Pokharel (2008) conducted OC tests in the laboratory on tailings with a pyrite content that ranged from 2% to 74%, separately or incorporated into CPB at different degrees of saturation. Their results revealed that the reactivity of tailings and CPB is influenced by the pyrite content and the degree of saturation. These studies concluded that at a degree of saturation under 70%, the reactivity of CPB is less than that of tailings samples without cement. Also, at higher water saturation values greater than 70%, the reduction in the reactivity is approximately the same in both the CPB samples and tailings specimens without cement. In another study, Ouellet et al. (2006) used OC testing to measure the reactivity of a stope filled with CPB at a depth of 2150 m at the LaRonde mine in Quebec, Canada. In their study, Ouellet et al. (2006) investigated CPB made of highly reactive sulphidic tailings ( $\approx 53\%$  pyrite) combined with a mixture of Portland cement Types I and V. The results showed a high rate of oxidation (mean value of  $2.4 \text{ mol O}_2/\text{m}^2/\text{day}$ ) at the beginning of the testing and then a gradual decrease to  $0.2 \text{ mol O}_2/\text{m}^2/\text{day}$  after 80 days. This oxidation rate is lower than the values obtained by the laboratory tests for tailings without binders due to a high degree of saturation. All of the referenced studies concluded that the use of CPB to manage sulphidic tailings is a promising waste disposal approach for underground mines. Despite the remarkable progress made by these studies towards a better understanding of the reactivity of CPB, none have investigated the influence of damage on the reactivity of CPB. Furthermore, the time-dependent change of the reactivity of CPB is still not well understood. Several fundamental questions remain unanswered. For example, how important is the microstructure or pore structure of CPB in its reactivity? Does the encapsulation or coating of the tailings or sulphide mineral particles in CPB systems have a significant role in their reactivity?

In this paper, we focus on investigating the influence of time and damage and the associated microstructural changes on the reactivity of CPB. The impact of the microstructure and encapsulation on the reactivity of CPB will also be assessed.

### 3.2 Materials and Experimental Program

#### 3.2.1 Materials Used

##### 3.2.1.1 Hydraulic Binder

Portland cement Type I (PCI) was used. PCI is the most common binder used in the preparation of CPB. The main physical and chemical properties of PCI are presented in Table 3.1.

Table 3.1. Main physical and chemical characteristics of binders used in study

Element (unit)	SSA (m <sup>2</sup> /g)	Gs	S (wt.%)	Ca (wt.%)	Si (wt.%)	Al (wt.%)	Mg (wt.%)	Fe (wt.%)	Si/Ca
PCI	1.32	3.15	1.5	44.9	8.4	2.4	1.6	1.9	0.2

SSA: Specific surface area

##### 3.2.1.2 Tailings

To experimentally understand the reactivity of CPB, ground silica (Sil-Co-Sil 106 manufactured by U.S. Silica Co.) and zinc tailings were used. The ground silica was used as the artificial silica tailings (ST) in the preparation of the CPB to reduce the uncertainties related to the chemical reactions of the tailings during their storage and CPB mixing. The ST are essentially made of quartz (Table 3) and mainly consist of highly pure and chemically inert silica (99.8 % of SiO<sub>2</sub>) powder with minor amounts of other components, including aluminum oxide (Al<sub>2</sub>O<sub>3</sub>; 0.05%) and iron III oxide (Fe<sub>2</sub>O<sub>3</sub>; 0.035%) (Carraro et al., 2009). Also, their grain size distribution is similar to the average grain size distribution of tailings from nine eastern Canada mines, as shown in Figure 3.1. Three different types of ST (ST-5%, ST-15% and ST-45%) were prepared by mixing the ground silica with pyrite powder at a dry weight of 5%, 15% and 45% respectively. The zinc tailings (ZT), sampled from the paste backfill plant of a mine located in eastern Canada, were used as the natural tailings. The ZT have an initial pyrite content of about 15% (Table 3.3). A specific amount of pyrite powder was also added to the zinc tailings to prepare modified ZT with 45% pyrite, which is labelled as ZT-45% in this study. The main physical and mineralogical characteristics of ST and ZT are presented in Tables 3.2 and 3.3.

Table 3.2. Main physical and chemical characteristics of binders used in study

Tailings	Gs	D <sub>10</sub> (μm)	D <sub>30</sub> (μm)	D <sub>50</sub> (μm)	D <sub>60</sub> (μm)
ST	2.71	1.9	9.0	22.5	31.5
ZT	3.34	1.6	10.9	29.9	37.8

Table 3.3. Mineralogical composition of tailings

Tailings/ Mineral (wt. %)	Quartz	Albite	Dolomite	Calcite	Chlorite	Magnetite	Pyrite	Talc	Magnesite	Pyrrhotite	Spinel	Others	Total
ST	99.8											0.2	100
ZT	11.9	1.2	5.7	2.2	18.2	11.4	15.4	16.4	7.6	3.1	3.2	3.7	100

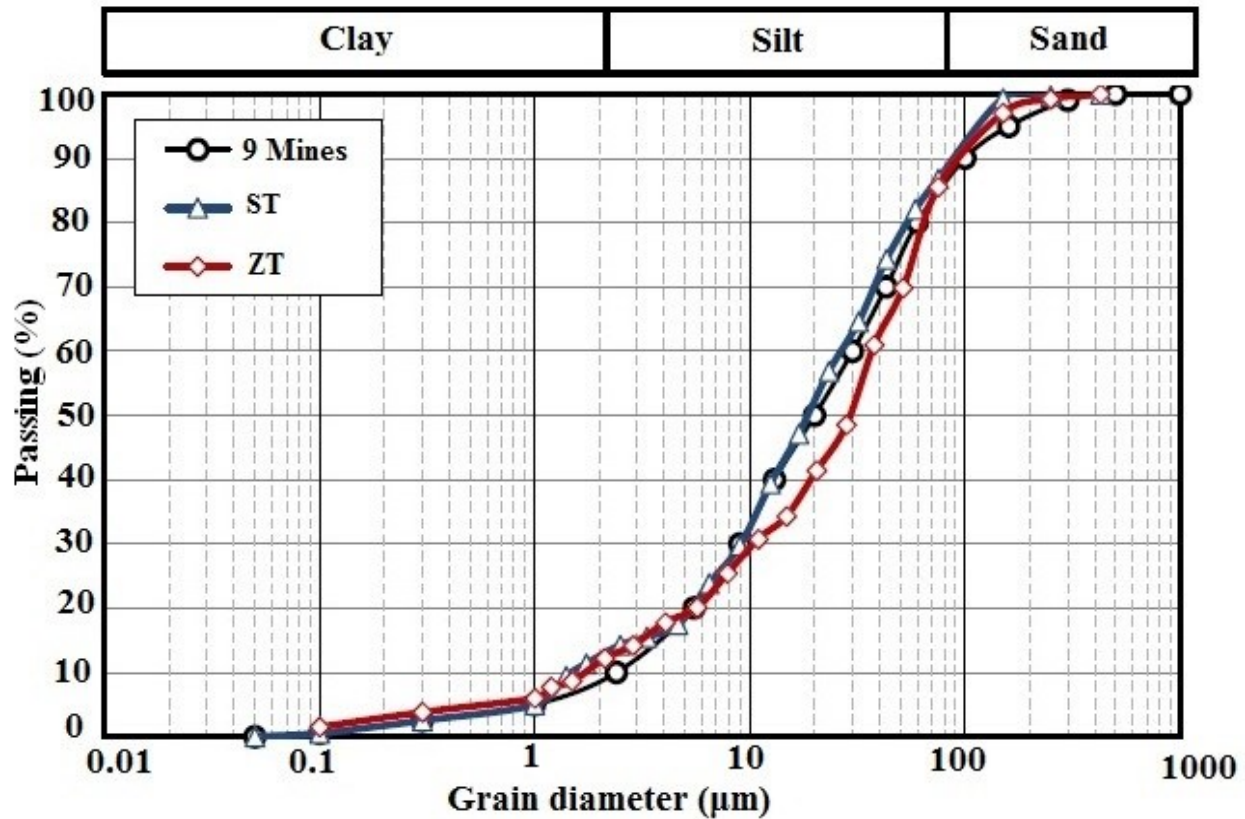


Figure 3.1. Grain size distribution of tailings used vs. average of grain size distribution of tailings from nine Canadian hard-rock metal mines

### 3.2.1.3 Mixing Water and Pyrite

Tap water was used as the mixing water. A commercial pyrite powder ( $\text{FeS}_2$ , M.W = 119.98) was blended with the ST to prepare three types of different pyrite-bearing tailings with a pyrite content

of 5, 15 and 45 wt. %. Also, the pyrite powder was mixed with ZT to prepare tailings with a pyrite content of 45% wt. %. The grain size of the pyrite powder is similar to that of pyrite minerals commonly found in natural tailings. The physical characteristics of the pyrite are presented in Table 3.4.

Table 3.4. Physical properties of pyrite (Washington Mills North Grafton, Inc.)

<b>Bulk density (g/cm<sup>3</sup>)</b>	<b>Density at 20°C (g/cm<sup>3</sup>)</b>	<b>Sp. Gravity</b>	<b>pH</b>	<b>Melting point (C°)</b>
2.35	4.7	4.6	4.0 - 6.0	1193

Sp.: specific

### 3.3 Specimen Preparation and Mix Proportions

#### 3.3.1 Preparation of CPB Samples

The CPB specimens were prepared by mixing the required quantities of pyrite-bearing ST (pyrite content of 5%, 15% and 45% wt.) or ZT (15% and 45% wt.), 4.5 wt. % of PCI and water in a double spiral mixer for seven minutes (see Table 3.5). After mixing, the slump (consistency) of the paste was measured in accordance with ASTM C143 (ASTM Standard C143/ C143M, 2012) and controlled at a slump value of 18 cm, which is the value often used for CPB preparation in many Canadian mines. Then, the CPB samples were poured into plastic cylinders with a diameter of 5 cm and a height of 10 cm. The cylinders were sealed (to avoid the evaporation of water) with wax and cured for 7, 28, 90 and 150 days in environmental chambers at a laboratory temperature of 20°C, until it was time for the testing to be carried out.

Table 3.5. CPB samples

<b>CPB Sample</b>	<b>Tailings type</b>	<b>Binder</b>	<b>Binder content (%)</b>	<b>Pyrite content (%)</b>	<b>w/c ratio</b>	<b>Curing time (days)</b>
<b>CPB-ST-5</b>	Silica Tailings	PCI	4.5	5	7.6	7, 28, 90, 150
<b>CPB-ST-15</b>	Silica Tailings	PCI	4.5	15	7.6	7, 28, 90, 150
<b>CPB-ST-45</b>	Silica Tailings	PCI	4.5	45	7.6	7, 28, 90, 150
<b>CPB-ZT-15</b>	Zinc Tailings	PCI	4.5	15.6	7.6	7, 28, 90, 150
<b>CPB-ZT-45</b>	Zinc Tailings	PCI	4.5	45	7.6	7, 28, 90, 150

#### 3.3.2 Preparation of grounded samples

To better understand the role of the microstructure (pore structure, porosity) on the reactivity of the CPB specimens, the cured samples were grounded into a homogenous fine powder (150 µm). The grinding process is intended to eliminate the effects of the microstructure. Then, OC testing was performed on those samples.

### 3.4 Testing of Specimens

#### 3.4.1 Oxygen Consumption Tests on Undamaged CPB Samples

The principle of OC testing is based on the measurement of the quantity of oxygen that is consumed through the oxidation of sulphide bearing material samples in a sealed chamber during a short period of time that ranges from about 3 to 5 hours (Schmieder et al., 2012; Fall et al., 2004; Ouellet et al., 2003; Elberling & Nicholson, 1996; Elberling et al., 1994). The primary assumption behind this test is that the steady state condition ( $\delta c / \delta t = 0$ ) will be maintained from the beginning to the end of the test. The reactivity of the CPB samples was measured by using a galvanic cell type oxygen sensor (Model GC33-200, GC Industries) to determine the oxygen consumption rate. This sensor has an accuracy of 0.1% O<sub>2</sub>. The oxygen sensor is connected to a voltmeter (Hantek 365A USB Data Logger Recorder Digital Multimeter Voltage Current PC Base) to measure and record the voltage produced by the oxidation reaction in the sealed chamber, as illustrated in Figure 3.2. This measured voltage is directly proportional to the partial pressure of oxygen in the gas phase. The OC tests were conducted on CPB samples by carefully covering the molds with an airtight lid that has an oxygen sensor attached. Each test was performed at least three times to ensure the repeatability of the results. The reactivity of the CPB samples was calculated in term of the oxygen flux ( $F_L$ ) based on the following equation proposed by Elberling et al. (1994) and Elberling & Nicholson (1996) under pseudosteady state conditions (Ouellet et al., 2006):

$$F_L = C_o (K_r D_e)^{0.5} \quad (3.2)$$

where  $K_r$  is the first-order reaction rate coefficient for sulphide mineral oxidation (e.g. pyrite),  $D_e$  is the effective diffusion coefficient and  $C_o$  is the initial concentration of oxygen. The  $(K_r D_e)$  is obtained from plotting the following equation that was proposed by Elberling et al. (1994) and Elberling & Nicholson (1996) in accordance with Fick's laws:

$$\ln (C / C_o) = - t (K_r D_e)^{0.5} (A/V) \quad (3.3)$$

where  $(K_r D_e)$  is the linear slope of the plot of  $\ln (C/C_o)$  versus time. This slope can be calculated if the volume of the gas chamber ( $V$ ) and the surface area of the exposed area of the reactive materials ( $A$ ) are known (Ouellet et al., 2006).

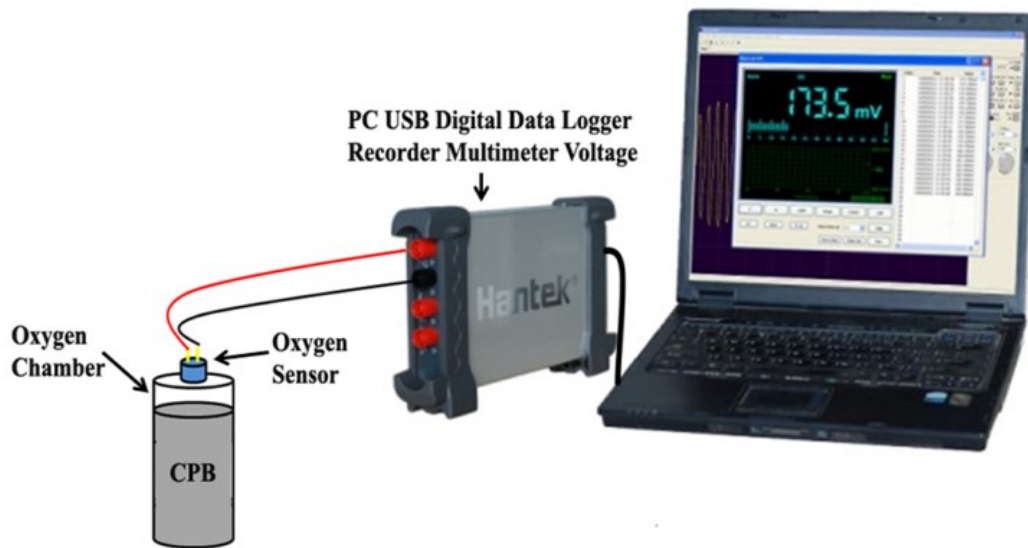


Figure 3.2. Schematic of OC test chamber with oxygen sensor

### 3.4.2 Oxygen Consumption Tests on Mechanically Damaged CPB Samples

Generally, damage can be described as processes that reflect progressive material deterioration measured through reductions in strength, stiffness, toughness, etc. (Celentano & Chaboche, 2007). Various damage models have been developed by researchers (e.g., Parviainen, 2009; Khan et al., 2007; Taher et al., 1994; Mazars & Pijaudier- Cabot, 1989; Lemaitre, 1971), but a scalar damage parameter, initially proposed by Kachanov (1958), has been widely used due to its simplicity (e.g., Ju, 1991; Choi, 1989; Lemaitre, 1971). According to the damage mechanics theory (Kachanov, 1958), the scalar damage parameter ( $d$ ) is defined from a relative ratio of the modulus of elasticity:

$$E = (1 - d) E_0 \quad (3.4)$$

where  $E_0$  and  $E$  = the initial (undamaged) and (damaged) moduli, and  $d$  is a scalar damage variable, ( $0 \leq d \leq 1$ ) (Suzuki et al., 2013; Rahman et al., 2012; Fall et al., 2009). Figure 3.3 illustrates the relationship between scalar damage and uniaxial compressive stress vs. total strain (Suzuki et al., 2013; Rahman et al., 2012; Fall et al., 2009). The  $d$  scalar variable is used to quantify the influence of micro-cracking developed in the material (Jason et al., 2004).

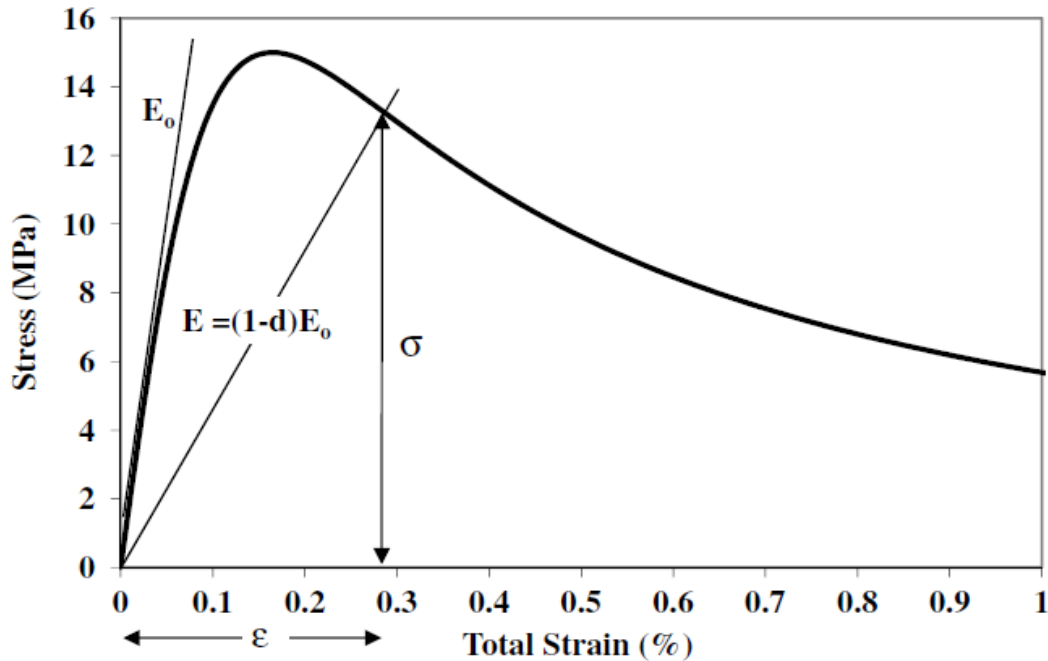


Figure 3.3. Relationship between scalar damage and uniaxial compressive stress vs. total strain (Rahman et al., 2012)

To experimentally simulate the mechanical damage of materials, several researchers have used both destructive and non-destructive techniques to induce cracking (Fall et al., 2014; Šavija & Schlangen, 2012; Chaboche, 1992). In many studies, uniaxial compressive testing, a destructive method, has been used to induce cracking in materials to study the fluid transportation throughout the materials (e.g., Wang, 2014; Djerbi Tegger et al., 2013; Zhou et al., 2011; Fall et al., 2009; Picandet et al., 2001). In this study, uniaxial compressive strength (UCS) tests in accordance with ASTM C39 are used to induce mechanically pre-damaged CPB samples with different levels of damage to evaluate its influence on the reactivity of the CPB samples. Four loading levels of 40%, 70%, 90% and 95% of the ultimate strength were used. To achieve these stress levels, a computer-controlled mechanical press (MTS 10/GL) was used. The machine has a normal loading capacity of 50 kN and equipped with an internal linear variable differential transformer (LVDT) coupled with a data acquisition system for automatically measuring and recording the axial deformation of specimens that was maintained at a rate of  $1 \text{ mm min}^{-1}$ . For each curing time, three samples were loaded to failure and then the stress–strain curves were plotted to determine 40%, 70%, 90% and 95% of the ultimate strength for each curing time. Also, the  $E$ ,  $E_0$  and  $d$  of the CPB specimens were obtained by using Equation 3. Then, the compressive stress induced onto the CPB samples

was manually interrupted before reaching the ultimate strength according to the selected percentages of ultimate strength and damage levels. The OC tests were conducted as explained above on mechanically-damaged CPB samples after each cycle of loading and unloading for each curing time. Each test was performed at least three times to ensure the repeatability of the results.

### **3.4.3 Oxygen Consumption Tests on Grounded Samples**

OC tests were performed on CPB specimens that were grounded into powder to investigate the role of the backfill microstructure (pore structure, porosity) on the reactivity of sulphide bearing tailings in CPB systems.

### **3.4.4 Microstructural Analyses**

A number of techniques were used to evaluate the microstructure of the cemented backfill samples and cemented paste, such as X-ray diffraction (XRD), scanning electron microscopy (SEM) along with energy dispersive spectroscopy (EDS), mercury intrusion porosimetry (MIP) and thermogravimetry/derivative thermogravimetry (TG/DTG) measurements. All of these techniques were utilized to investigate the influence of reactivity of CPB on its porosity, pore structure and binder hydration products as well as investigate the progress of binder hydration. Selected CPB specimens were prepared for these tests as well as hardened cement paste (HCP) specimens with a w/c ratio equal to 1 ( $w/c = 1$ ) to simulate the cement matrix of CPB. The XRD was conducted by using a Scintag XDS 2000 x-ray diffractometer on dried and grounded samples of CPB. The SEM-EDS analyses were carried out on the CPB samples by using a Hitachi S4800 field emission scanning electron microscope equipped with an Oxford Instruments 350 INCA energy-dispersive X-ray microanalysis system. The MIP tests were conducted on the CPB samples by using a Micromeritics AutoPore III 9420 mercury porosimeter. In accordance with ASTM D4404-10, the samples were dried at 50°C in the oven until mass stabilization before being subjected to MIP testing (ASTM International, 2010). The TG/DTG tests were performed on powdered and dried specimens (50°C) by using a thermogravimetric/differential thermal analyzer (TGD-9600, ULVAC). These tests were simultaneously performed on the 10 mg sample, and for reference, the HCP sample was measured with two platinum crucibles at a rate of 10°C/min from an ambient temperature up to 1000°C in flowing nitrogen (100 cm<sup>3</sup> min<sup>-1</sup>).

## 3.5 Results and Discussion

### 3.5.1 Effect of Curing Time on the Reactivity of CPB Samples

Figure 3.4 depicts the effect of curing time on the reactivity of the CPBs made of ST and ZT with various pyrite contents. The figure presents the mean and standard deviation of the reactivity of the CPB specimens. It is clear that, regardless of the tailings type and pyrite content, the reactivity of the CPB specimens decreases with increasing curing time. It can be seen that the CPB specimens at the early ages have higher reactivity values, in particular at the curing age of 7 days (oxidation rates vary between 0.2 and 5.5 mol O<sub>2</sub>/m<sup>2</sup>/day for the 7 day cured CPB samples with a pyrite content of 5% and 45%, respectively). After 7 days, the reactivity is sharply reduced until 28 days, when it begins to gradually decrease. The oxidation rate values obtained for the 150 day cured CPB samples with various pyrite contents vary approximately between 0.1 mol O<sub>2</sub>/m<sup>2</sup>/day and 0.3 mol O<sub>2</sub>/m<sup>2</sup>/day afterward. This rate is much lower than the rates reported for sulphide bearing tailings without a binder (0.8 and 5.5 mol O<sub>2</sub>/m<sup>2</sup>/day) (Ouellet et al., 2006; Elberling & Nicholson, 1996; Elberling et al., 1994, 1993). This reduction of the reactivity with time can be explained by the reduction of the porosity and refinement of the pore structure of CPB specimens with time due to the progress of the binder hydration and the associated precipitation of the hydration products, which in turn reduces the effective diffusion coefficient of oxygen (D<sub>e</sub>) (see Equations 1 and 2). Indeed, as a binder reacts with water, several changes in the microstructure of the CPB will occur due to the growth of reaction products in the form of new solids (e.g., calcium silicate hydrate (C-S-H) gel, Portlandite, ettringite). This leads to the reduction and refinement of the pore system in the CPB matrix. Also, as hydration products form, these products block the interconnected capillary pores in the CPB matrix. This argument with respect to the progress of binder hydration and the formation of more hydration products as the curing time increases is experimentally demonstrated by the results of the thermal analyses (TG/DTG) that were performed on CPB cured for 7 and 28 days, respectively, as shown in Figure 3.5. DTG enables the identification of materials that correspond to the range of the thermal decomposition of the different phases in the HCP of CPB, while TG simultaneously provides the quantity due to the thermal decomposition. Typically, the decomposition of HCP is divided into three main zones associated with rapid weight loss and major phase transformations: the first zone can be identified by a peak at the temperature range from 100°C to 200°C, thus resulting in the dehydration of ettringite, gypsum, carboaluminates and C-S-H gel. The second zone covers the range between 450°C and 500°C, thus characterizing the

decomposition of Portlandite (CH), and finally, the third zone takes place at temperatures between 650°C and 750°C thus resulting in the decomposition of the carbonate phases and calcite (CaCO<sub>3</sub>) (e.g., Fall et al., 2010; Gabrovsek et al., 2006; Alarcon-Ruiz et al., 2005; Pane & Hansen, 2005; Sha et al., 1999). Furthermore, Portlandite is a primary hydration product that can be easily identified and quantified in the TG/DTG curves, so that it can be used to assess the progress of hydration with curing time by determining the weight loss from the TG curve. From Figure 3.5, it can be noticed that the peak of the Portlandite sample cured for 28 days is higher than that of the sample cured for 7 days. In addition, there is a greater loss of weight of the 28 day cured sample. This means that there is more Portlandite in the 28 day cured sample than in the 7 day cured sample. From the TG/DTG results, it can be concluded that the 28 day cured sample has more hydration products than the 7 day cured sample.

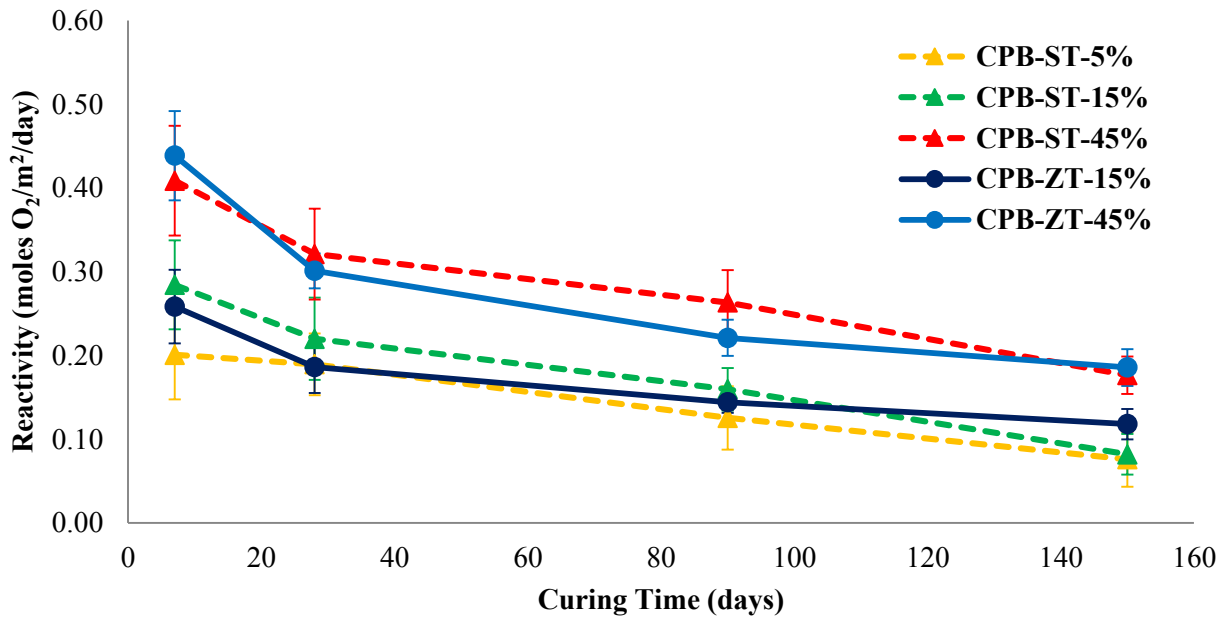


Figure 3.4. Effect of curing time on reactivity of CPB samples with various pyrite contents

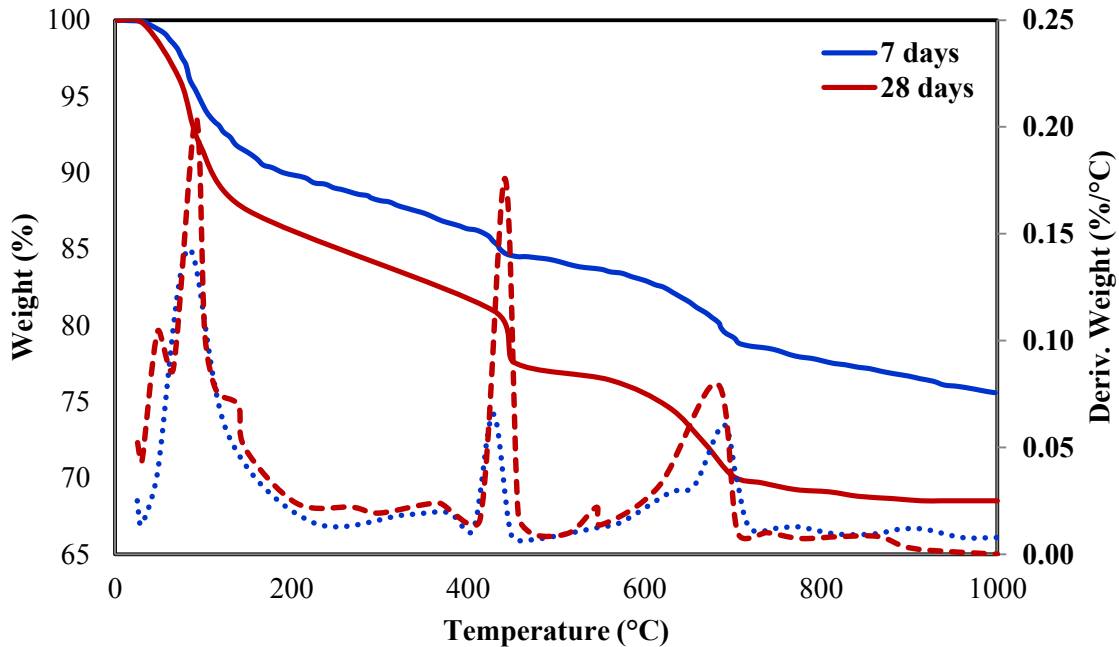


Figure 3.5. TG/DTG curves of 7 and 28 day cured samples

The argument that the microstructure becomes refined (finer pore structure, lower porosity) as binder hydration advances is in substantial agreement with the results of the MIP tests conducted on the CPB specimens cured for 7 and 28 days and presented in Figure 3.6. It is evident that the pore size distribution of the 28 day cured specimen (which contains 45% wt. of pyrite) shifts towards the left (thus indicating a smaller pore size) compared to that of the 7 day cured specimen. This indicates that the former has a finer pore structure than the latter. Furthermore, the threshold diameter value (the pore size that corresponds to the highest rate of mercury intrusion per change in pressure (Manmohan & Mehta, 1981) of the 28 day cured sample ( $0.58 \mu\text{m}$ ) is 3.1 times lower than that of the 7 day cured sample ( $1.80 \mu\text{m}$ ). In other words, the 28 day cured sample has lower fluid transportability, since the threshold diameter is a characteristic of the capillary network that connects to the surface of the cemented porous media (Manmohan & Mehta, 1981). The results of the MIP analysis presented below indicate that the fineness of the pore structure of the CPB significantly affects its reactivity and a finer pore structure is associated with lower reactivity.

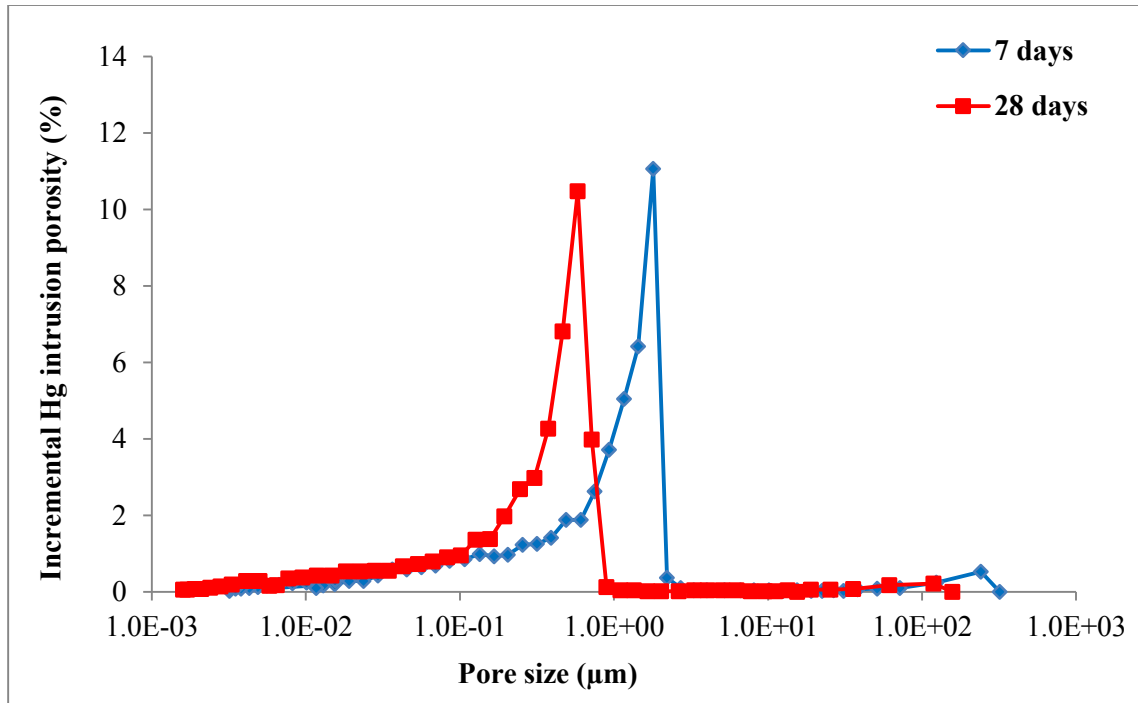


Figure 3.6. Pore size distribution curve for 7 and 28 day cured CPB samples (w/c=7.6 and 4.5% PCI)

The critical role of the microstructure (pore structure) of the CPB in terms of its reactivity is also confirmed by the results presented in Figure 3.6. This figure depicts the reactivity of the grounded or powdered samples of CPB that are cured for different times. It can be observed that the reactivity of the powdered samples of CPB follows a similar trend as that of the specimens that are not grounded. However, the reactivity values of the grounded samples (Figure 3.7) are approximately 5 to 10 times higher than those of the original CPB (Figure 3.4) for a given curing time. This significantly higher reactivity of the grounded samples of CPB is due to their loose structure which is obviously associated with a higher effective diffusion coefficient of oxygen ( $D_e$ ), and thus higher reactivity (see Equations 3.2-3.3). From Figure 3.7, it can also be observed that the reactivity of the grounded samples decreases with curing time, which can be attributed to the fact that as the curing time increases, more hydration products will form (Figure 3.5). This in turn would increase the proportion of pyrite grains coated with cement hydration products in the CPB with longer curing time. From this figure, it can be concluded that the pore structure and the coating of the pyrite with cement hydration products play significant roles in the reactivity of CPB, or in other words, in terms of the durability and environmental performance of CPB.

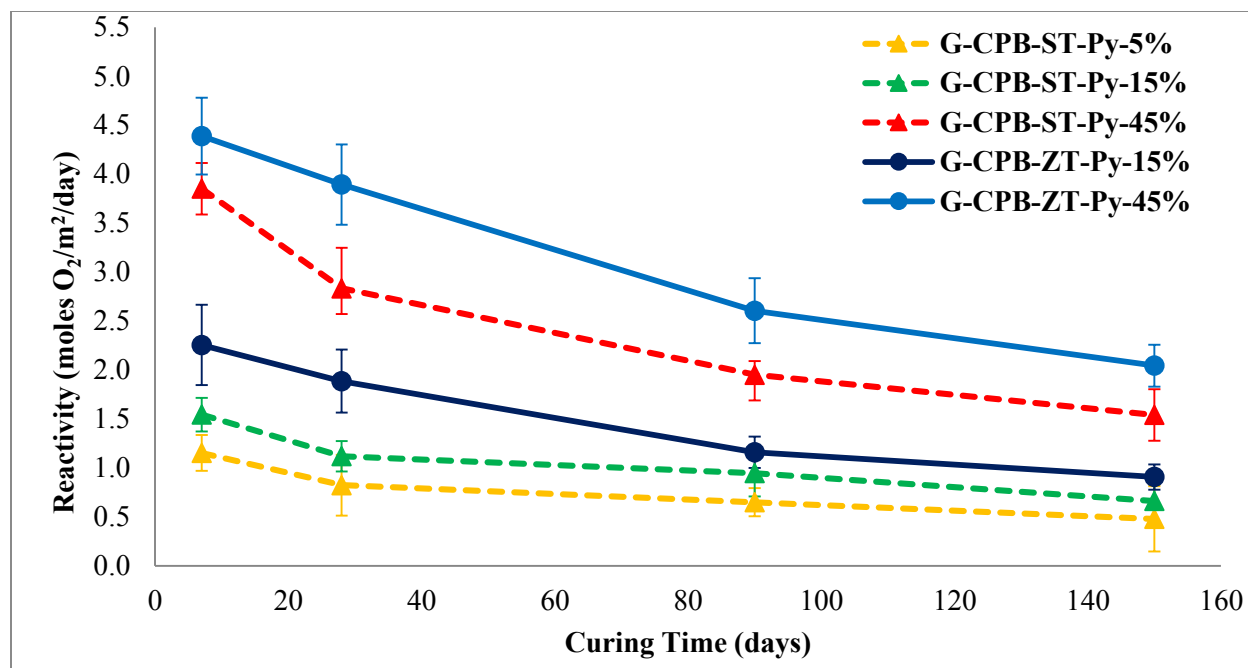


Figure 3.7. Reactivity of grounded samples of CPB cured at various times

### 3.5.2 Effect of Ageing on the Reactivity of CPB Samples

The influence of ageing on the reactivity of the CPB-ST specimens that contained 5, 15 and 45% wt. of pyrite and aged for 150 days was investigated. The results are shown in Figure 3.8. It can be seen that the reactivity of the CPB samples reduces with increased ageing time. The reduction of the reactivity is due to the combined effects of the following factors: continuous hydration, high degree of saturation and formation of a thin oxidized layer. First, the hydration of the binder in CPB systems continuously increases due to the use of a high water/cement ratio (i.e.,  $w/c=7.6$ ) in the production of CPB. As water is found in the CPB matrix, cement hydration will continue and the porosity will be reduced (Fall & Samb, 2009). Consequently, the oxidation of pyrite grains in the CPB specimens will be reduced due to limited diffusion and the consumption of oxygen. Also, the high degree of saturation of CPB is a barrier that significantly limits its oxygen ingress (Ouellet et al., 2006). Another factor that contributes to reducing the reactivity of CPB is the formation of a thin oxidized layer (i.e. hardpan layer) at the interface between the confined oxygen gas in the air chamber and the surface area of the CPB specimen, as illustrated in Figure 3.9, which is a photograph of the oxidized and unoxidized layers. This hardpan layer that forms on the CPB surface acts as a physical barrier that inhibits oxygen diffusion into the underlying CPB materials that are not oxidized (Boulet & Larocque, 1998).

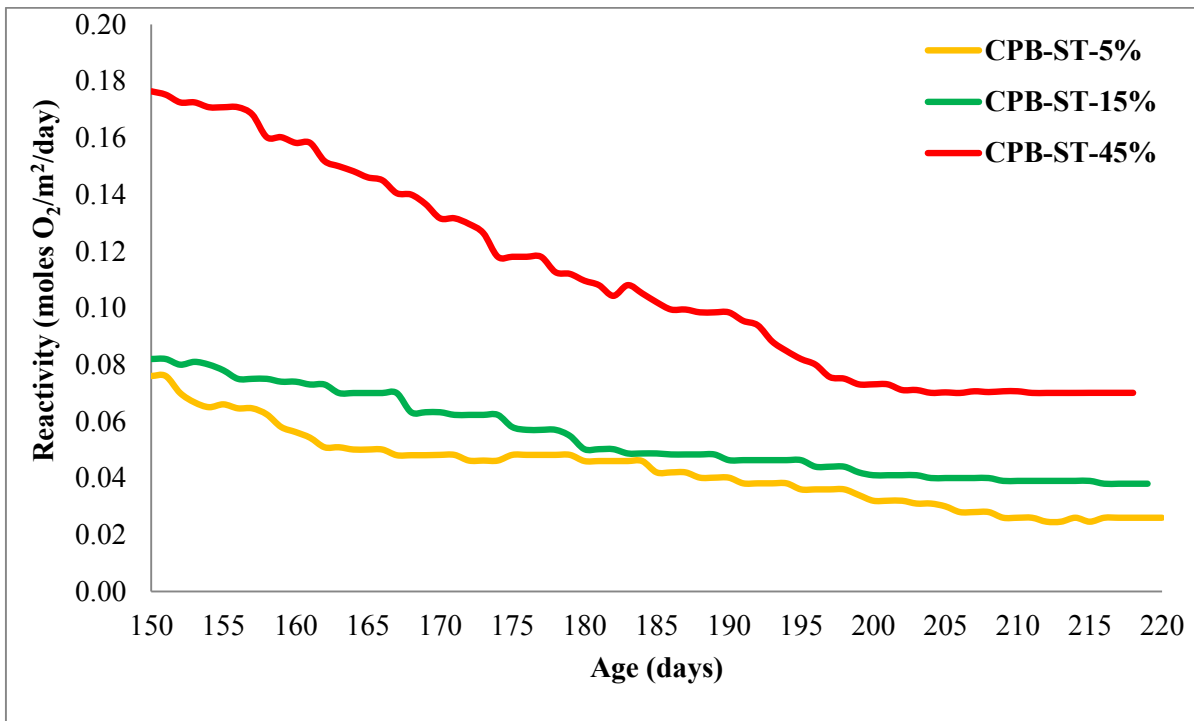


Figure 3.8. Effect of ageing on the reactivity of 150 day old CPB

To gain a better understanding of the oxidized layer (hardpan layer found at the top of the surface of the CPB specimen), it is compared with the layer that is beneath. For comparative purposes, the 150 day aged CPB specimen was vertically cut into two slices to obtain the oxidized and unoxidized (internal) layers. A visual examination along with microstructural analyses by using XRD and SEM-EDS, and a pH test were carried out on the two layers. From the visual inspection, the oxidized and unoxidized layers can be differentiated based on the colour, as shown in Figure 3.9, which is a photo of the oxidized and unoxidized layers of 150 day aged CPB specimen. It can be seen that the oxidized layer has a brownish colour due to the formation of secondary minerals generated from the oxidation of the pyrite particles, whereas the unoxidized layer is a grey colour. The pH of the paste (1:1 solid: solution ratio) as described in Sobek et al. (1978) was measured for the two layers with a 704 pH meter (Metrohm Ltd, Herisau, Switzerland) for comparison purposes. The pH tests showed that the pH of the oxidized layer is 8.78 at the laboratory temperature, whereas the unoxidized layer is 10.82. This lower pH value in the oxidized layer is related to the acid generated by the oxidation of pyrite (see Equation 3.1). Furthermore, XRD and SEM/EDS were conducted on the two layers in order to investigate their phase constitutions and microstructures, as shown in Figures 3.10 and 3.11. Figure 3.10 shows the results of the XRD

analysis of the oxidized and unoxidized layers, and quartz, pyrite and gypsum can be identified in both layers. Quartz is the dominant mineral in both layers based on the intensity of its peak, whereas there is more gypsum in the oxidized layer. The higher levels of gypsum in the oxidized layer are attributed to the additional formation of gypsum due to the reaction of the sulphate ions produced from the oxidation of pyrite with Portlandite generated by the hydration of the cement (Fall & Pokharel, 2010). Also, it can be noticed that a small quantity of ettringite and calcite is only found in the unoxidized layer. The difference in the pH of the oxidized and unoxidized layers plays a key role in the formation and stability of ettringite and calcite minerals. Both ettringite and calcite minerals are more stable in phases in alkaline environments where the pH is above 10 (Cornelis et al., 2005; Ferraris et al., 2005; Stark & Bollmann, 2000; Taylor, 1997). At a lower pH value (below 10), the ettringite phase incongruently dissolves into gypsum, amorphous calcium aluminate hydrates and aluminum hydroxide (Mötlep et al., 2007). The absence of calcite and ettringite in the oxidized layer can be explained by the dissolution of these minerals by the acid ( $H^+$  ions, see Equation 1) produced by the oxidation of the pyrite, since ettringite and calcite are not stable in acidic solutions (Dold, 2014). It should be emphasized that previous microstructural studies on the hardpan layer (e.g., Ouellet et al. (2006)) have underlined the inability of the XRD technique to clearly identify the presence of secondary minerals in the oxidized layer. This is partially attributed to the crystallographic quality of the secondary minerals precipitated (Ouellet et al., 2006). Bigham (1994) stated that these minerals are often poorly crystallized or amorphous, and thus cannot be detected by XRD analysis.

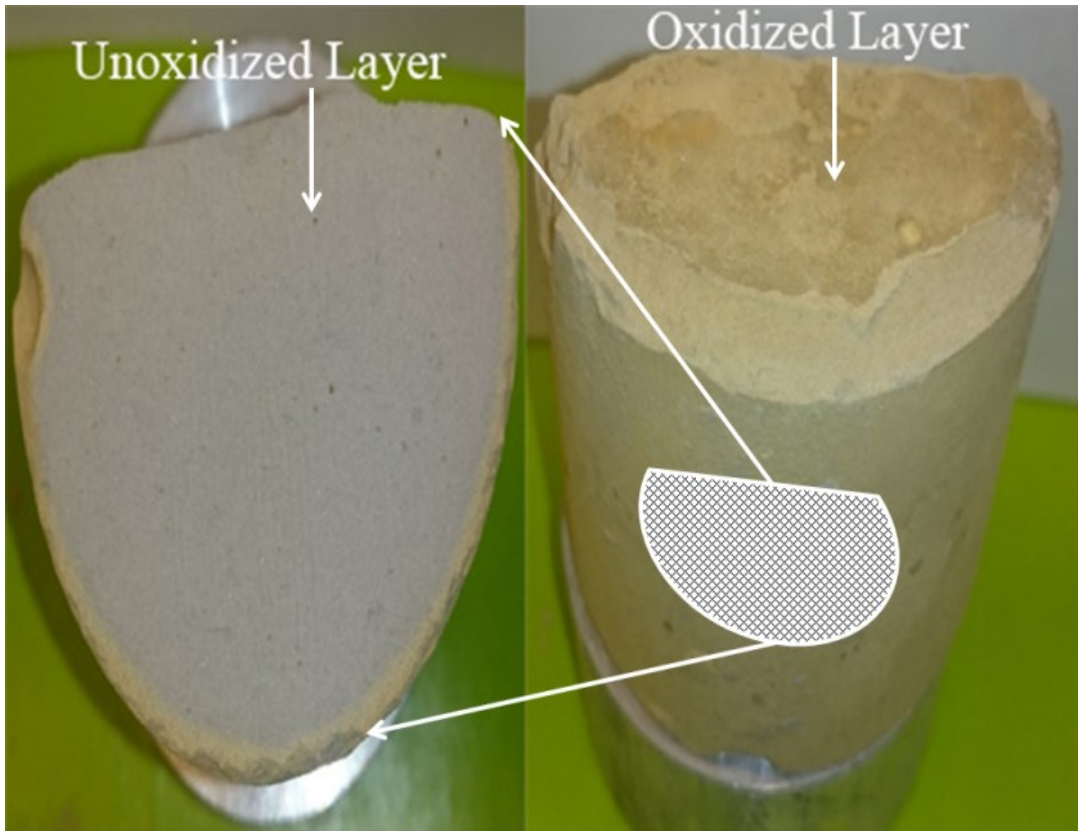
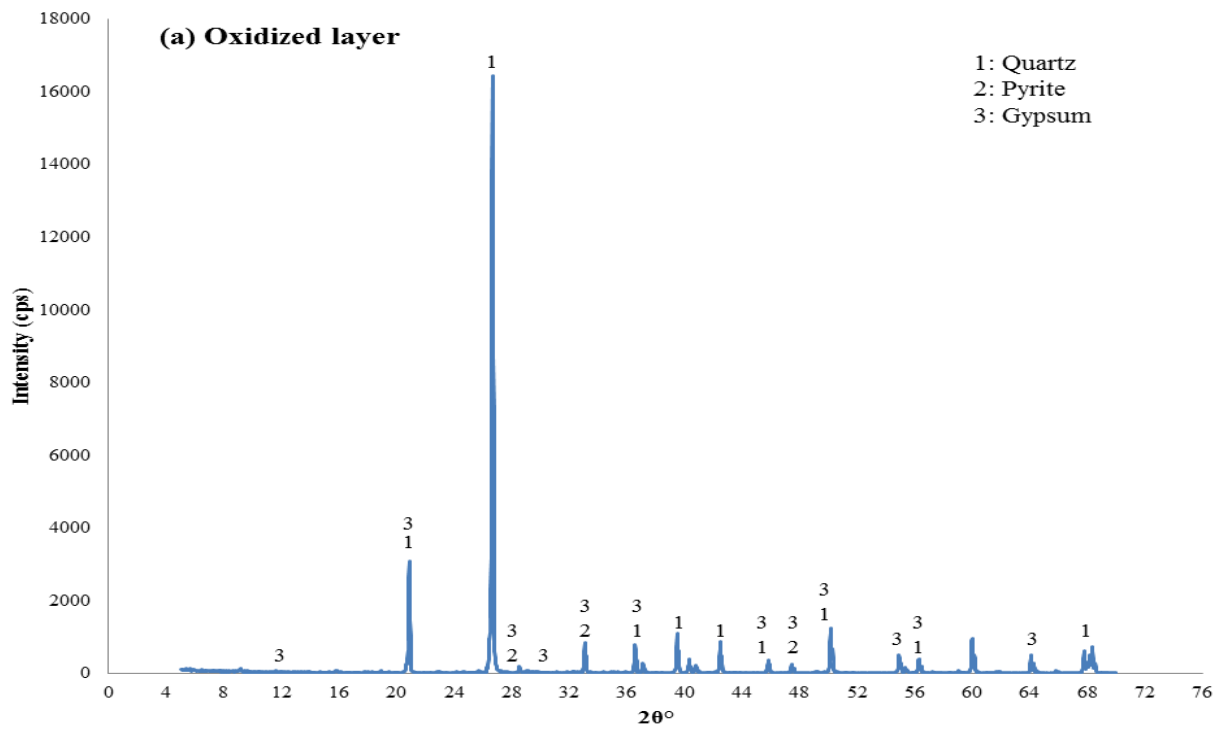


Figure 3.9. Photo of oxidized and unoxidized layers of 150 day aged CPB specimen



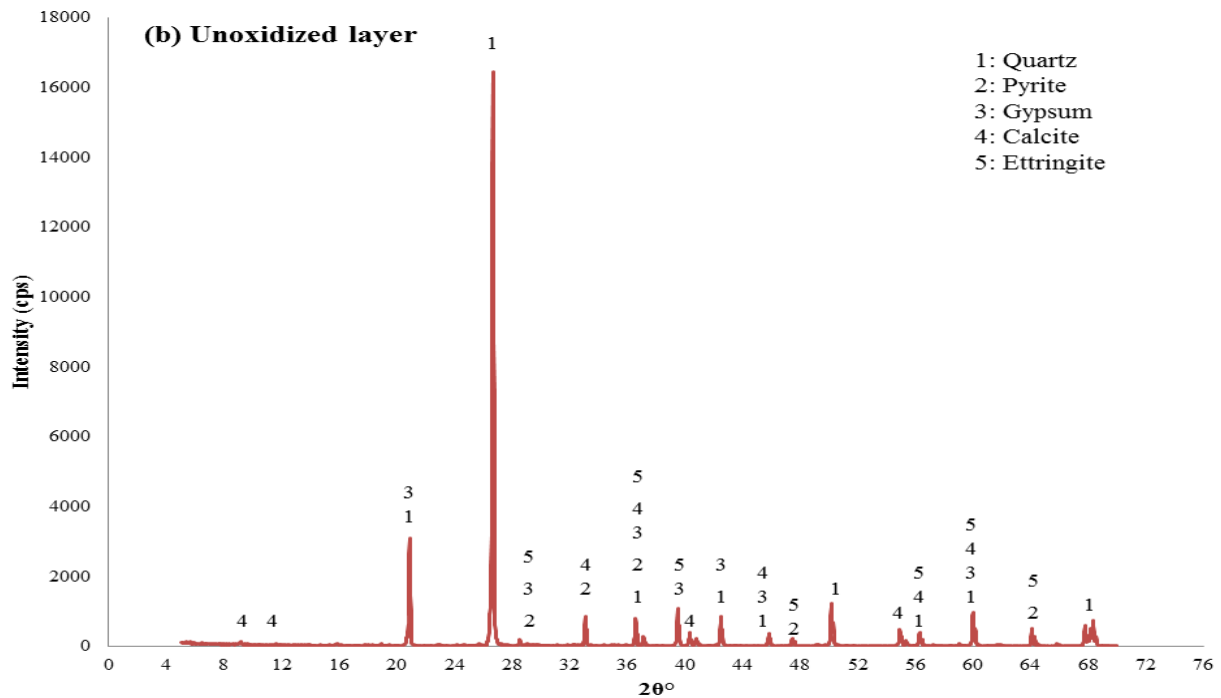


Figure 3.10. XRD diffractograms for (a) oxidized and (b) unoxidized layers of 150 day aged CPB specimen

The SEM and EDS analysis results for the two layers are shown in Figure 3.11. The SEM micrograph of the oxidized layer shows less voids and more density compared to the unoxidized layer. The EDS results show that the oxygen (O), silicon (Si), carbon (C) and calcium (Ca) are found in the oxidized layer, whereas O, Si, C, sulphur (S) and iron (Fe) are found in the unoxidized layer. From Figure 3.11a, it can be noticed that Fe, one of main element components of pyrite ( $\text{FeS}_2$ ) grains in the CPB specimen, is absent in the oxidized layer. This is an indicator that the oxidation of the pyrite grains occurred in the oxidized layer. However, Fe appears in the unoxidized layer because there is limited oxygen ingress into the layer. The EDS results are therefore in agreement with the XRD results (see Figure 3.10).

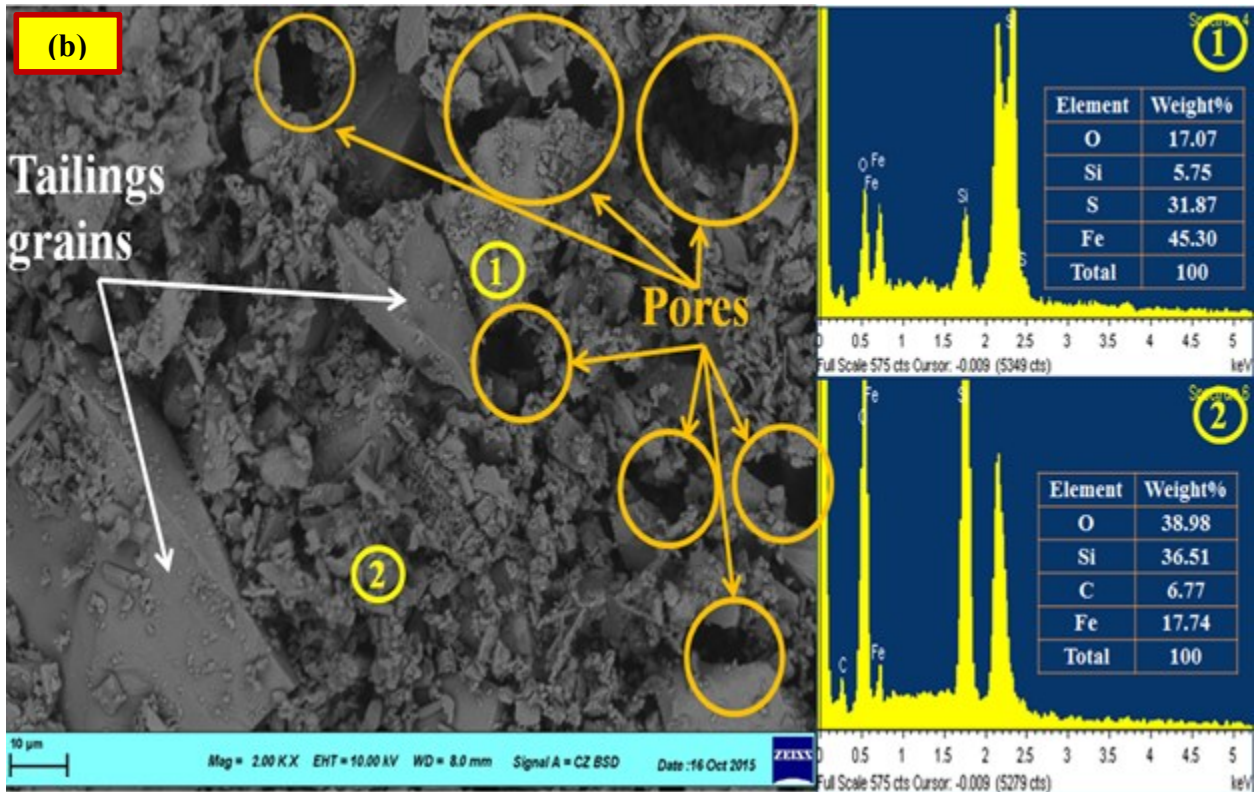
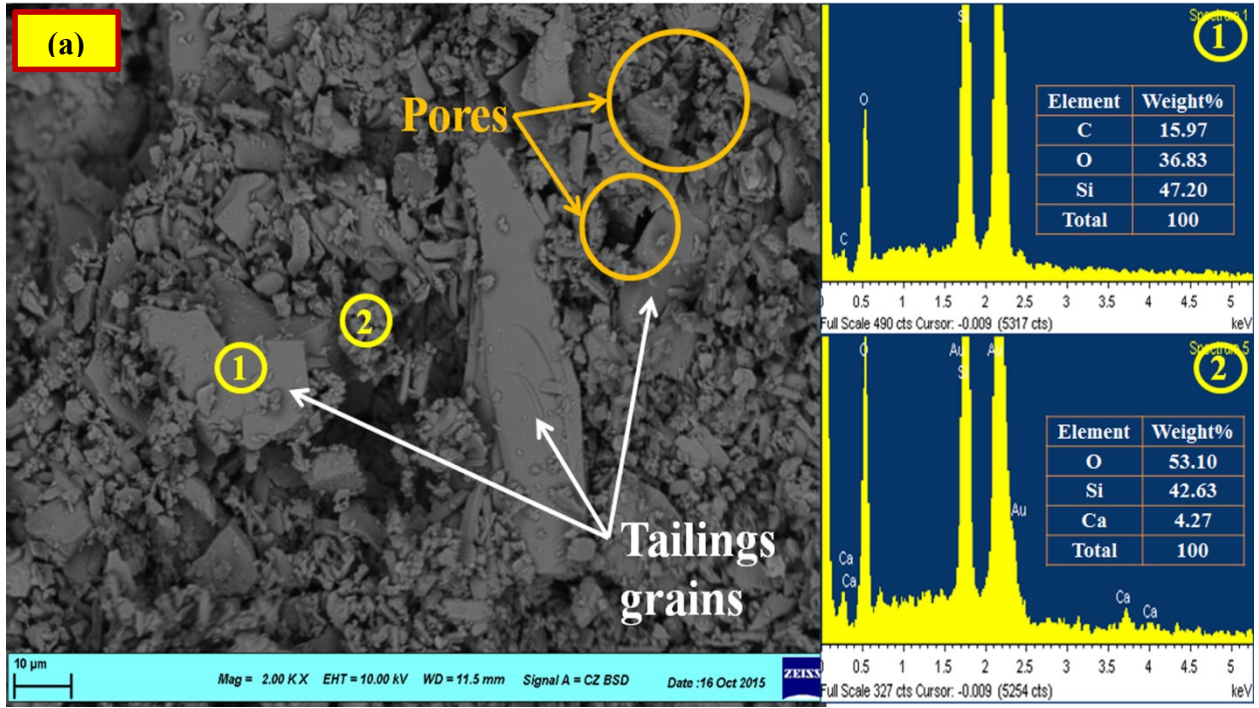


Figure 3.11. SEM micrograph and EDS spectra for (a) oxidized layer and (b) unoxidized layer of 150 day aged CPB specimen

### 3.5.3 Effect of Mechanical Damage on the Reactivity of CPB

To study the influence of mechanical damage on the reactivity of CPB, specimens aged for 150 days were subjected to various levels of damage induced by mechanical uniaxial compression (UCS). In this study, the ratio of the applied stress to the ultimate stress peak (applied stress/UCS) and scalar damage parameter ( $d$ ) are used to describe the amount of damage induced onto the CPB specimens. Also, the relative reactivity ( $r/r_0$ ) of the CPB samples is used to compare the reactivity of the damaged samples ( $r$ ) to the undamaged samples ( $r_0$ ). The results are presented in Figures 3.12 and 3.13. These figures show that the applied stress/UCS level and the mechanical damage ( $d$ ) have a significant effect on the reactivity of CPB. As the applied stress/UCS level and  $d$  increase, the reactivity of the CPB specimens increases. The rate of the increase is greater for CPB specimens with a higher pyrite content. This increase in the reactivity can be explained by the formation of cracks resultant of mechanical loading. For that reason, these cracks create preferential paths for the transport of  $O_2$  into the CPB matrix. The resulting paths will facilitate and increase the rate of oxygen diffusion into the CPB materials. Consequently, the reactivity of CPB specimens' increases due to increased oxygen diffusion and the resulting increase in the rate of pyrite oxidation in the CPB matrix.

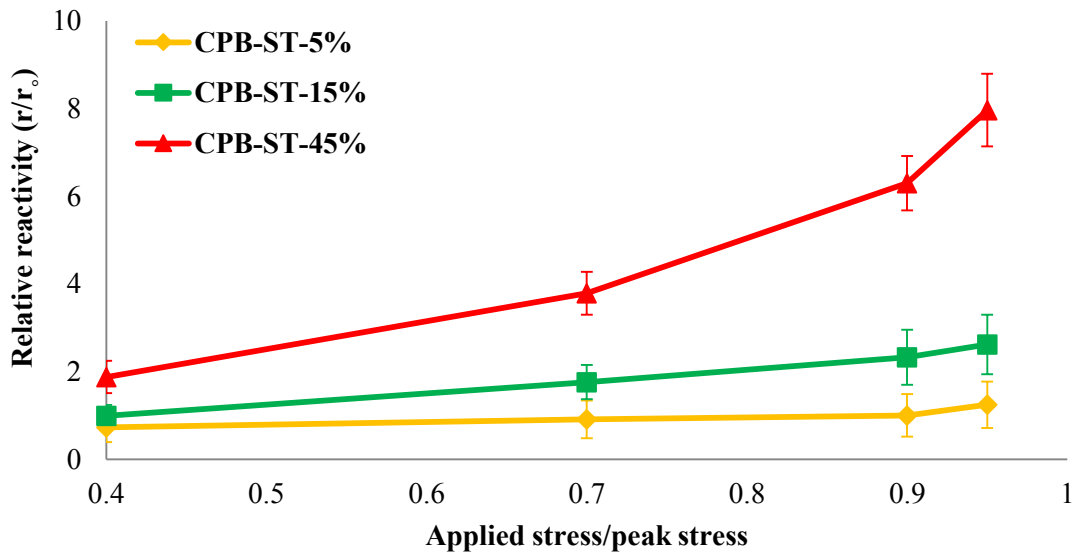


Figure 3.12. Relative reactivity ( $r/r_0$ ) of CPB samples with various pyrite contents aged for 150 days versus ratio of the applied stress to maximum peak stress

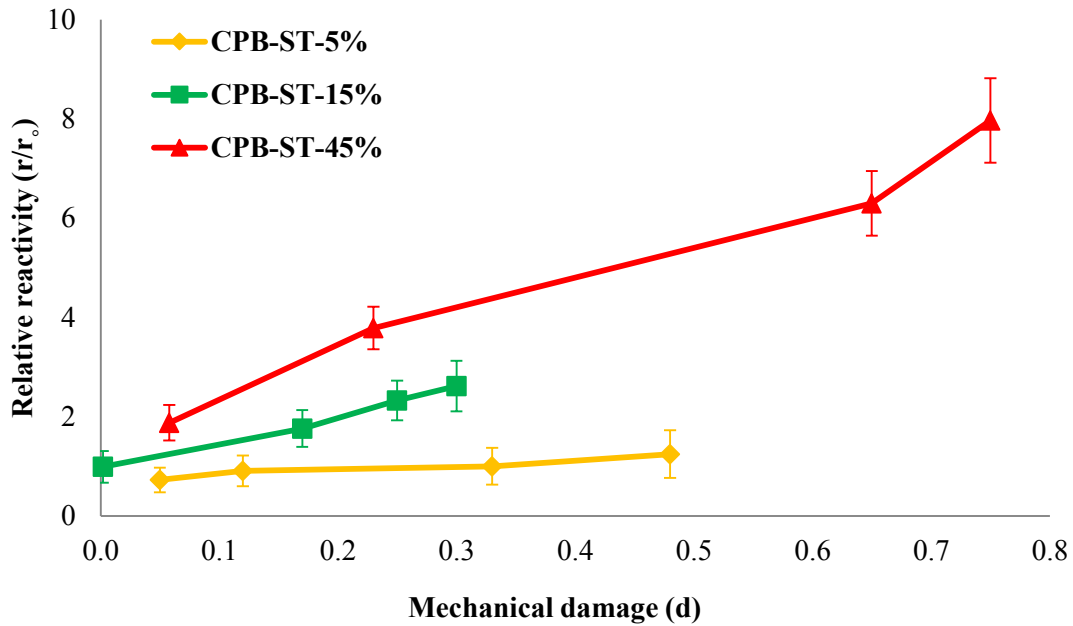


Figure 3.13. Relative reactivity ( $r/r_0$ ) of 150 day aged CPB samples with various pyrite contents versus mechanical damage (d)

### 3.6 Summary and Conclusions

In this paper, the influence of time (curing and aging), the microstructure and mechanical damage on the reactivity of CPB specimens is studied by conducting OC testing on specimens that contain artificial (ST) and natural (ZT) tailings cured at a laboratory temperature of 20°C for 7, 28, 90 and 150 days. Based on the results and discussions, the following conclusions are drawn.

- The reactivity of CPB systems is time-dependent. The reactivity decreases with curing time and the ageing of the CPB.
- The binder and its hydration products (e.g., cement) plays a key role in the reactivity of CPB.
- The microstructure or pore structure of CPB and the coating of the sulphide mineral particles with binder hydration products significantly affect the reactivity and thus its environmental behaviour.
- With time, the sulphide oxidation at the surface of CPB may form into a hardpan layer that has a positive role with respect to the reactivity and thus environmental performance of CPB systems.

- Mechanical damage can considerably increase the reactivity of CPB and thus causes negative impacts on the environmental performance of CPB structures, especially if there is a high content of pyrite. The reactivity increases with an increased damage parameter. So, mechanical damage is an important parameter that needs to be considered in the assessment of the reactivity and environmental performance of CPB.

### 3.7 References

- Akcil, A., & Koldas, S. (2006). Acid Mine Drainage (AMD): causes, treatment and case studies. *Journal of Cleaner Production*, 14(12–13), 1139–1145. <http://doi.org/10.1016/j.jclepro.2004.09.006>
- Alakangas, L., Dagli, D., & Knutsson, S. (2013). Literature Review on Potential Geochemical and Geotechnical Effects of Adopting Paste Technology under Cold Climate Conditions, 1–36. Retrieved from [http://pure.ltu.se/portal/files/43755253/Literature\\_Review\\_on\\_Potential\\_Geochemical\\_and\\_Geotechnical\\_Effects\\_of\\_Adopting\\_Paste\\_Technology\\_under\\_Cold\\_Climate\\_Conditions.pdf](http://pure.ltu.se/portal/files/43755253/Literature_Review_on_Potential_Geochemical_and_Geotechnical_Effects_of_Adopting_Paste_Technology_under_Cold_Climate_Conditions.pdf)
- Alarcon-Ruiz, L., Platret, G., Massieu, E., & Ehrlacher, A. (2005). The use of thermal analysis in assessing the effect of temperature on a cement paste. *Cement and Concrete Research*, 35(3), 609–613. <http://doi.org/10.1016/j.cemconres.2004.06.015>
- Awange, J., & Kiema, J. B. (2013). Environmental Monitoring and Management: In *Environmental Geoinformatics: Monitoring and Management* (pp. 3–16). Berlin, Heidelberg: Springer Berlin Heidelberg. [http://doi.org/10.1007/978-3-642-34085-7\\_1](http://doi.org/10.1007/978-3-642-34085-7_1)
- Benzaazoua, M., Bussière, B., Demers, I., Aubertin, M., Fried, É., & Blier, A. (2008). Integrated mine tailings management by combining environmental desulphurization and cemented paste backfill: Application to mine Doyon, Quebec, Canada. *Minerals Engineering*, 21(4), 330–340. <http://doi.org/10.1016/j.mineng.2007.11.012>
- Bigham, J. (1994). Mineralogy of ochre deposits formed by sulfide oxidation. In *The environmental geochemistry of sulfide mine-wastes* (Short Cour, pp. 103–131). Waterloo, Ontario.: Mineralogical Association of Canada.
- Blowes, D. W., Ptacek, C. J., Jambor, J. L., & Weisener, C. G. (2003). The Geochemistry of Acid Mine Drainage A2 - Turekian, Heinrich D. HollandKarl K. BT - Treatise on Geochemistry. In *Treatise on Geochemistry* (pp. 149–204). Oxford: Pergamon. <http://doi.org/http://dx.doi.org/10.1016/B0-08-043751-6/09137-4>
- Boulet, M. P., & Larocque, A. C. L. (1998). A comparative mineralogical and geochemical study of sulfide mine tailings at two sites in New Mexico, USA. *Environmental Geology*, 33(2/3), 130–142. <http://doi.org/10.1007/s002540050233>
- Bussière, B., Dagenais, A.-M., Mbonimpa, M., Aubertin, M. (2002). Modification of oxygen-consumption testing for the evaluation of oxygen barrier performance. In *Proceedings of the 55th Canadian Geotechnical Conference and 3rd Joint International Association of Hydrogeologists – Canadian National Chapter Canadian Geotechnical Society (IAH–CNC/CGS) Conferences, Ground and Water: Theory to Practice* (pp. 139–149). Niagara Falls.
- Carraro, J., Prezzi, M., & Salgado, R. (2009). Shear Strength and Stiffness of Sands Containing

- Plastic or Nonplastic Fines. *Journal of Geotechnical and Geoenvironmental Engineering*, 135(9), 1167–1178. [http://doi.org/10.1061/\(ASCE\)1090-0241\(2009\)135:9\(1167\)](http://doi.org/10.1061/(ASCE)1090-0241(2009)135:9(1167))
- Celentano, D. J., & Chaboche, J. L. (2007). Experimental and numerical characterization of damage evolution in steels. *International Journal of Plasticity*, 23(10–11), 1739–1762. <http://doi.org/10.1016/j.ijplas.2007.03.008>
- Chaboche, J.-L. (1992). Damage Induced Anisotropy: On the Difficulties Associated with the Active/Passive Unilateral Condition. *International Journal of Damage Mechanics*, 1(2), 148–171. <http://doi.org/10.1177/105678959200100201>
- Choi, K. (1989). *A Damage Mechanics Approach To The Three Dimensional Constitutive Modelling Of Ice Deformation*. MASSACHUSETTS INSTITUTE OF TECHNOLOGY.
- Chugh, Y. P., Mohanty, S., Paul Behum, J., Nawrot, W., & Bell, S. C. (2007). *Identification and Assessment of Best Management Practices in Illinois Mining Operations to Minimize Sulfate and Chloride Discharges*.
- Cornelis, G., Van Gerven, T., and Vandecasteele, C. (2005). The effect of calcium-bearing minerals on the solubility of molybdate and antimonate in alkaline wastes. In *International Conference on Engineering for Waste Treatment*. Albi, France.
- Djerbi Tegguer, A., Bonnet, S., Khelidj, A., & Baroghel-Bouny, V. (2013). Effect of uniaxial compressive loading on gas permeability and chloride diffusion coefficient of concrete and their relationship. *Cement and Concrete Research*, 52, 131–139. <http://doi.org/10.1016/j.cemconres.2013.05.013>
- Dold, B. (2010). Basic Concepts in Environmental Geochemistry of Sulfidic Mine-Waste Management. In *Waste Management* (pp. 173–198). Rijeka, Croatia: INTECH Open Access Publisher.
- Dold, B. (2014). Evolution of Acid Mine Drainage Formation in Sulphidic Mine Tailings. *Minerals*, 4(3), 621–641. <http://doi.org/10.3390/min4030621>
- Elberling, B., & Nicholson, R. V. (1996). Field determination of sulphide oxidation rates in mine tailings. *Water Resources Research*, 32(6), 1773–1784. <http://doi.org/10.1029/96WR00487>
- Elberling, B., Nicholson, R. V., & David, D. J. (1993). Field evaluation of sulphide oxidation rates. *Nordic Hydrology*, 24(5), 323–338.
- Elberling, B., Nicholson, R. V., Reardon, E. J., & Tibble, R. (1994). Evaluation of sulphide oxidation rates: a laboratory study comparing oxygen fluxes and rates of oxidation product release. *Canadian Geotechnical Journal*, 31(3), 375–383. <http://doi.org/10.1139/t94-045>
- Ercikdi, B., Cihangir, F., Kesimal, A., Deveci, H., & Alp, I. (2009). Utilization of industrial waste products as pozzolanic material in cemented paste backfill of high sulphide mill tailings. *Journal of Hazardous Materials*, 168(2–3), 848–856. <http://doi.org/10.1016/j.jhazmat.2009.02.100>
- Fall, M., Adrien, D., Célestin, J. C., Pokharel, M., & Touré, M. (2009). Saturated hydraulic conductivity of cemented paste backfill. *Minerals Engineering*, 22(15), 1307–1317. <http://doi.org/10.1016/j.mineng.2009.08.002>
- Fall, M., & Benzaazoua, M. Ouellet, S. (2004). Effect of tailings properties on paste backfill performance. In *Proceedings of the 8th International Symposia on Mining with Backfill* (pp. 193–202). Beijing, China.
- Fall, M., Benzaazoua, M., & Saa, E. G. (2008). Mix proportioning of underground cemented tailings backfill. *Tunnelling and Underground Space Technology*, 23(1), 80–90. <http://doi.org/10.1016/j.tust.2006.08.005>
- Fall, M., Célestin, J. C., Pokharel, M., & Touré, M. (2010). A contribution to understanding the

- effects of curing temperature on the mechanical properties of mine cemented tailings backfill. *Engineering Geology*, 114(3–4), 397–413. <http://doi.org/10.1016/j.enggeo.2010.05.016>
- Fall, M., Nasir, O., & Nguyen, T. S. (2014). A coupled hydro-mechanical model for simulation of gas migration in host sedimentary rocks for nuclear waste repositories. *Engineering Geology*, 176(Complete), 24–44. <http://doi.org/10.1016/j.enggeo.2014.04.003>
- Fall, M., & Pokharel, M. (2010). Coupled effects of sulphate and temperature on the strength development of cemented tailings backfills: Portland cement-paste backfill. *Cement and Concrete Composites*, 32(10), 819–828. <http://doi.org/10.1016/j.cemconcomp.2010.08.002>
- Fall, M., & Samb, S. S. (2009). Effect of high temperature on strength and microstructural properties of cemented paste backfill. *Fire Safety Journal*, 44(4), 642–651. <http://doi.org/10.1016/j.firesaf.2008.12.004>
- Gabrovsek, R., Vuk, T., & Kaucic, V. (2006). Evaluation of the hydration of portland cement containing various carbonates by means of thermal analysis. *Acta Chimica Slovenica*, 53(2), 159–165. Retrieved from <http://cat.inist.fr/?aModele=afficheN&cpsid=17897765>
- Hassani, F., & Archibald, J. H. (1998). *Mine Backfill*. CIM annual meeting.
- Hawkins, A. B. (2014). *Implications of Pyrite Oxidation for Engineering Works* (1st ed.). Springer International Publishing. <http://doi.org/10.1007/978-3-319-00221-7>
- Hudson-Edwards, K. A., Jamieson, H. E., & Lottermoser, B. G. (2011). Mine wastes: past, present, future. *Elements*, 7, 375–380. <http://doi.org/10.2113/gselements.7.6.375>
- Jason, L., Pijaudier-Cabot, G., Huerta, A., Crouch, R., & Ghavamian, S. (2004). An elastic plastic damage formulation for the behavior of concrete. In *Fracture Mechanics of Concrete Structures* (pp. 549–556).
- Johnson, D. B., & Hallberg, K. B. (2005). Acid mine drainage remediation options: a review. *The Science of the Total Environment*, 338(1–2), 3–14. <http://doi.org/10.1016/j.scitotenv.2004.09.002>
- Ju, J.-W. (1991). *Damage Mechanics of Composite Materials: Constitutive Modeling and Computational Algorithms*.
- Kachanov, L. M. (1958). Time of the rupture process under creep conditions. *Izv. Akad. Nauk. {S.S.R.} Otd. Tech. Nauk.*, 8, 26–31. Retrieved from citeulike-article-id:5466815
- Kesimal, A., Yilmaz, E., Ercikdi, B., Alp, I., & Deveci, H. (2005). Effect of properties of tailings and binder on the short-and long-term strength and stability of cemented paste backfill. *Materials Letters*, 59(28), 3703–3709. <http://doi.org/10.1016/j.matlet.2005.06.042>
- Khan, A. R., Al-Gadhib, A. H., & Baluch, M. H. (2007). Elasto-damage Model for High Strength Concrete Subjected to Multiaxial Loading. *International Journal of Damage Mechanics*, 16(3), 361–398. <http://doi.org/10.1177/1056789506065914>
- Lemaitre, J. (1971). Evaluation of Dissipation and Damage in Metal Submitted to Dynamic Loading. In *Proceedings of the First International Conference on the Mechanical Behaviour of Materials, ICM-1*. Kyoto, Japan.
- Lottermoser, B. (2010). *Mine Wastes: Characterization, Treatment and Environmental Impacts*. Springer Berlin Heidelberg. <http://doi.org/10.1007/978-3-642-12419-8>
- Lu, J., Alakangas, L., Jia, Y., & Gotthardsson, J. (2013). Evaluation of the application of dry covers over carbonate-rich sulphide tailings. *Journal of Hazardous Materials*, 244–245, 180–94. <http://doi.org/10.1016/j.jhazmat.2012.11.030>
- Manmohan, D. & Mehta, P. (1981). Influence of Pozzolanic, Slag, and Chemical Admixtures on Pore Size Distribution and Permeability of Hardened Cement Pastes. *Cement, Concrete and Aggregates*, 3(1), 63–67. <http://doi.org/10.1520/CCA10203J>

- Mazars, J., & Pijaudier- Cabot, G. (1989). Continuum Damage Theory—Application to Concrete. *Journal of Engineering Mechanics*, 115(2), 345–365. [http://doi.org/10.1061/\(ASCE\)0733-9399\(1989\)115:2\(345\)](http://doi.org/10.1061/(ASCE)0733-9399(1989)115:2(345))
- Mbonimpa, M, Aubertin, M, Achib, M, B. (2002). *Oxygen diffusion and consumption in unsaturated cover materials*.
- MEND. (2006). Paste Backfill Geochemistry – Environmental Effects of Leaching and Weathering, (April). <http://doi.org/MEND Report 10.2>
- Mõtlep, R., Kirsimäe, K., Talviste, P., Puura, E., & Jürgenson, J. (2007). MINERAL COMPOSITION OF ESTONIAN OIL SHALE SEMI-COKE SEDIMENTS. *Oil Shale*, 24(3), 405–422. Retrieved from <http://search.ebscohost.com/login.aspx?direct=true&db=bth&AN=26652091&site=ehost-live>
- Ouellet, S., Bussiere, B., Benzaazoua, M., Aubertin, M., Fall, M., & Belem, T. (2003). Sulphide Reactivity within cemented paste backfill: oxygen consumption test results. In *The 56th Annual Canadian Geotechnical Conference and 4th joint IAHCNC/CGS Conference* (pp. 176–183). Winnipeg, Manitoba, Canada.
- Ouellet, S., Bussière, B., Mbonimpa, M., Benzaazoua, M., & Aubertin, M. (2006). Reactivity and mineralogical evolution of an underground mine sulphidic cemented paste backfill. *Minerals Engineering*, 19(5), 407–419. <http://doi.org/10.1016/j.mineng.2005.10.006>
- Pane, I., & Hansen, W. (2005). Investigation of blended cement hydration by isothermal calorimetry and thermal analysis. *Cement and Concrete Research*, 35(6), 1155–1164. <http://doi.org/10.1016/j.cemconres.2004.10.027>
- Parmar, N., & Singh, A. (2014). *Bioremediation of Contaminated Sites and Aquifers*. (N. Parmar & A. Singh, Eds.). Berlin, Heidelberg: Springer-Verlag Berlin Heidelberg. [http://doi.org/10.1007/978-3-642-41837-2\\_14](http://doi.org/10.1007/978-3-642-41837-2_14)
- Parviainen, A. (2009). Tailings Mineralogy and Geochemistry at the Abandoned Haveri Au–Cu Mine, SW Finland. *Mine Water and the Environment*, 28(4), 291–304. <http://doi.org/10.1007/s10230-009-0088-2>
- Picandet, V., Khelidj, A., & Bastian, G. (2001). Effect of axial compressive damage on gas permeability of ordinary and high-performance concrete. *Cement and Concrete Research*, 31(11), 1525–1532. [http://doi.org/10.1016/S0008-8846\(01\)00546-4](http://doi.org/10.1016/S0008-8846(01)00546-4)
- Pokharel, M. (2008). *Geotechnical and environmental responses of paste tailings systems to coupled thermo-chemical loadings*. University of Ottawa. Retrieved from <http://hdl.handle.net/10393/27793>
- Rahman, M., Al-Kutti, W., Shazali, M., & Baluch, M. (2012). Simulation of Chloride Migration in Compression-Induced Damage in Concrete. *Journal of Materials in Civil Engineering*, 24(7), 789–796. [http://doi.org/10.1061/\(ASCE\)MT.1943-5533.0000458](http://doi.org/10.1061/(ASCE)MT.1943-5533.0000458)
- Šavija, B., & Schlangen, E. (2012). Chloride ingress in cracked concrete- a literature review. In C. Andrade & J. Gulikers (Eds.), *Advances in Modeling Concrete Service Life: Proceedings of 4th International RILEM PhD Workshop held in Madrid, Spain, November 19, 2010* (pp. 133–142). Dordrecht: Springer Netherlands. [http://doi.org/10.1007/978-94-007-2703-8\\_14](http://doi.org/10.1007/978-94-007-2703-8_14)
- Schmieder, P. J., Taylor, J. R., & Bourgeot, N. (2012). Oxygen consumption techniques to quantify acidity generation rates. In *1st International Acid and Metalliferous Drainage Workshop*. Beijing, China.
- Sha, W., O’Neill, E. A., & Guo, Z. (1999). Differential scanning calorimetry study of ordinary Portland cement. *Cement and Concrete Research*, 29(9), 1487–1489.

- [http://doi.org/10.1016/S0008-8846\(99\)00128-3](http://doi.org/10.1016/S0008-8846(99)00128-3)
- Sobek, A. A., Schuller, W. A., Freeman, J. R., & Smith, R. M. (1978). *Field and Laboratory Methods Applicable to Overburdens and Minesoils*. Cancinnati, Ohio. Retrieved from <http://www.osmre.gov/resources/library/ghm/FieldLab.pdf>
- Suzuki, T., Morii, T., & Kawai, T. (2013). Damage Evaluation of Concrete Structure in Disaster Areas due to the Great East Japan Earthquake. *Journal of Japan Society of Civil Engineers, Ser. F4 (Construction and Management)*, 69(2), 157–163. Retrieved from [http://dspace.lib.niigata-u.ac.jp/dspace/bitstream/10191/22579/1/65\(2\)\\_157-163.pdf](http://dspace.lib.niigata-u.ac.jp/dspace/bitstream/10191/22579/1/65(2)_157-163.pdf)
- Taher, S. E.-D. F., Baluch, M. H., & Al-Gadhib, A. H. (1994). Towards a canonical elastoplastic damage model. *Engineering Fracture Mechanics*, 48(2), 151–166. [http://doi.org/10.1016/0013-7944\(94\)90075-2](http://doi.org/10.1016/0013-7944(94)90075-2)
- Tariq, A., & Yanful, E. K. (2013). A review of binders used in cemented paste tailings for underground and surface disposal practices. *Journal of Environmental Management*, 131, 138–49. <http://doi.org/10.1016/j.jenvman.2013.09.039>
- Taylor, H. F. W. (1997). *Cement Chemistry* (2nd ed.). London: Thomas Telford Publishing. Retrieved from <http://dx.doi.org/10.1680/cc.25929>
- Tibble, P.A. and Nicholson, R.V. (1997). Oxygen Consumption on Sulphide Tailings and Tailings Covers: Measured Rates and Applications. In *Proceedings of the 4th International Conference on Acid Rock Drainage*. (pp. 647–661). Vancouver, British-Columbia.
- Wang, L. . (2014). Experimental Study on Water Absorption by Concrete Damaged by Uniaxial Loading. In J. Clek & J. Weiss (Eds.), *Proceedings of the 4th International Conference on the Durability of Concrete Structures* (pp. 198–204). West Lafayette. <http://doi.org/10.5703/1288284315402>
- Yilmaz, E. (2010). *Investigating the consolidation behavior, hydro-mechanical and micro-structural properties of cemented paste backfills using the versatile CUAPS apparatus*. University du Quebec en Abitibi-Temiscamingue (UQAT).
- Yilmaz, E. (2012). One-Dimensional Consolidation Parameters Of Cemented Paste Backfills / Parametry Jednowymiarowej Konsolidacji Podsadzki W Postaci Cementowej Pasty. *Gospodarka Surowcami Mineralnymi - Mineral Resources Management*. <http://doi.org/10.2478/v10269-012-0030-2>
- Zhou, C., Li, K., & Han, J. (2011). Characterizing the effect of compressive damage on transport properties of cracked concretes. *Materials and Structures*, 45(3), 381–392. <http://doi.org/10.1617/s11527-011-9771-4>

## **Chapter 4: Technical Paper II- Temperature Dependence of the Reactivity of Cemented Paste Backfill**

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### **Abstract**

The environmental performance of cemented paste backfill (CPB; a mixture of tailings, water and binder), which contains sulphide mineral-bearing tailings, is strongly influenced by its reactivity. However, our understanding of the reactivity of CPB under various thermal loading conditions as well as its evolution with time is limited. Hence, a laboratory investigation is conducted to study the effects of curing and mine ambient temperatures on the reactivity of CPB. The results show that the reactivity of CPB is temperature-dependent. As the curing temperature increases, the reactivity generally decreases. The reactivity is also affected by the ambient temperature. The reactivity increases as the atmospheric temperature increases. However, the extent of the effect of the temperature depends on the curing time and is generally more pronounced at the early ages. Furthermore, the presence of sulphate in the pore water of CPB can significantly affect the reactivity of CPB cured at high temperatures (50°C). The findings of this study will therefore help to better assess and predict the environmental behavior of CPB under various field thermal conditions.

**Keywords:** cemented paste backfill, tailings; reactivity, acid mine drainage, mine; temperature

## 4.1 Introduction

Historically, mining has been imperative to human and social development, and the industry will continue to make investments that meet the increasing needs of society (ICMM, 2012). Yet the mining industry generates a substantial volume of solid wastes as by-products (Lottermoser, 2010), which mainly consist of rock wastes and tailings, that can have environmentally, socially and economically long lasting and detrimental consequences (Kitula, 2006). Tailings are considered to be the largest waste by-product (Dold, 2014), and sulphide bearing tailings in particular are considered to be a serious environmental issue that the mining industry is facing worldwide (Öhlander et al., 2012).

Generally, tailings are a slurry of grounded rock and process effluents generated by mine processing plants and usually deposited into impoundments (Davies & Rice, 2001). These conventional methods of tailings storage and disposal have several environmental, geotechnical (e.g., failure of tailings dams) and economic issues for the mining industry (Dold, 2014). The management of sulphidic mine tailings is one of the greatest challenges for the mining industry worldwide (Öhlander et al., 2012) because they cause acid mine drainage (AMD) which is produced as a result of the oxidation of sulphide minerals (e.g., pyrite) found in tailings (Kumari et al., 2010). This drainage can have long-term adverse effects on the environment (Johnson & Hallberg, 2005). Therefore, the storage or disposal of tailings, in particular sulphidic mine tailings, on the surface of the ground, either in impoundments or dams, incurs the most substantial environmental liability throughout the operating and decommissioning stages of mines (Martin & Davies, 2000). The risks and consequences associated with conventional tailings impoundments, substantial operation and maintenance costs of these impoundments as well as public perception and more strict regulations on the disposal of such waste have driven the mining industry to search for alternative methods that can prevent and /or minimize the effects (Alakangas et al., 2013; Fall et al., 2009). As a result, a number of alternative techniques for the disposal or management of tailings have been developed in the recent past, such as the use of sub-aqueous techniques, application of high density thickeners, filter pressing of tailings and then stacking them (dry stacking) or mixing the tailings with cement and then pumped underground (cemented paste backfill (CBP)). Among these alternative techniques, cemented paste backfilling has been the most novel and promising technology for the management of mine tailings, including sulphide bearing tailings. Therefore, this technology has now become a commonly used method and extensively

practiced in the mining industry worldwide. The implementation of cemented paste backfilling has several advantages, such as minimizing the amount of storage tailings on the surface of mine site, increasing mining production, controlling the oxidation of sulphides and mobilisation of metals (Alakangas et al., 2013; Hassani & Archibald, 1998).

CPB is an engineered mixture that is mainly prepared from three ingredients: mine tailings (75 to 85% wt.), hydraulic binder (3-7 % wt.), and water (Alakangas et al., 2013; Fall et al., 2008). Despite the advantages of using CPB, its environmental performance is still not well understood. In particular, the role of the geochemical reactivity of CPB in terms of its environmental behavior, durability and stability is not well known. Therefore, the reactivity of CPB should be assessed before it is placed into underground mines to avoid potential environmental and economic impacts. Cemented paste backfilling should not be a method that transfers the environmental problems of mine tailings from the surface of the ground to the underground (Ouellet et al., 2006).

Most of the previous studies on CPB have focused on its mechanical properties and economic advantages (less binder consumption and cost optimization) (e.g., Ghirian & Fall, 2014; Wu et al., 2012; Nasir & Fall, 2010; Kesimal et al., 2005; Fall et al., 2004), whereas few studies have evaluated the environmental performance of CPB by investigating its geochemical reactivity.

The reactivity of sulphidic mine wastes can be measured by using direct and indirect techniques, such as the sulphate release and the oxygen gradient methods (Ouellet et al., 2006) respectively. Among these techniques, the oxygen consumption (OC) test is most preferred because it is simple, inexpensive, fast and accurate. Also, the OC test can be used to obtain both laboratory and field measurements. The OC test was first used in Elberling et al. (1994) and Elberling and Nicholson (1996). The concept is based on measuring the rate that sulphide minerals consume oxygen in a sealed vessel during their oxidation process (Ouellet et al., 2006). This technique was used in both the laboratory and field to quantify the reactivity of various acid generating tailings and mine rocks in several studies (e.g., Bussière et al., 2002; Mbonimpa et al., 2002; Martin and Davies, 2000; Tibble and Nicholson, 1997; Nicholson et al., 1995; Elberling and Nicholson, 1996; Elberling et al., 1994, 1993). However, only a few studies have attempted to measure the reactivity of CPB by using OC testing. Ouellet et al. (2006, 2003) performed OC testing to quantify the reactivity of CPB in both the laboratory and the field. Also, Fall et al. (2004) and Pokharel (2008) used the OC method on CPB samples prepared from natural and artificial tailings with different pyrite contents to investigate their reactivity. The findings of these studies

indicate that the pyrite content and degree of saturation significantly influence the reactivity of the tailings and CPB. Furthermore, all of the above studies indicated that the use of cemented paste backfilling to manage sulphide bearing tailings in underground mines could reduce their environmental impacts. However, the reactivity of CPB can be also affected by several other variables, such as the availability of oxygen, level of moisture, and range of temperature. Temperature is one of the main variables that can influence the reactivity of CPB, and CPB structures are subjected to various thermal loading conditions in the field. The temperature of CPB structures can be influenced by several different heat sources during their service life. These sources can be internal and related to CPB itself, or external and related to the mine. The main sources of internal heat include heat generated during binder hydration and the transport of paste backfill as well as oxidation sulphide minerals found in the paste backfill mixture. For example, the temperature of CPB in the stope (mine cavity) can reach 50°C due to binder hydration as observed in many field investigations on backfill (e.g., Williams et al., 2001) or modeling studies (e.g., Wu et al., 2012; Nasir and Fall, 2009). On the other hand, the external sources of heat depend on the depth of the mine and geological conditions in addition to the geographical location of the mine (Pokharel and Fall, 2010). However, our understanding of the effects of the curing and ambient temperatures on the reactivity of CPB is limited. This is because the effects of temperature on the reactivity of CPB have been mostly neglected in previous studies. Therefore, in this paper, the effects of curing and mine ambient temperatures on the reactivity of CPB have been studied and will be discussed in detail.

## 4.2 Materials and Experimental Program

### 4.2.1 Materials Used

#### 4.2.1.1 Binder

Portland cement type I (PCI) was used as the binder in the preparation of the CPB samples because in practice, it is the most commonly used binder in making paste backfill. The primary physical and chemical properties of PCI are presented in Table 4.1.

Table 4.1. Primary physical and chemical properties of PCI

Element (unit)	SSA (m <sup>2</sup> /g)	Gs	S (wt%)	Ca (wt%)	Si (wt%)	Al (wt%)	Mg (wt%)	Fe (wt%)	Si/Ca
PCI	1.32	3.15	1.5	44.9	8.4	2.4	1.6	1.9	0.2

SSA: Specific Surface Area

#### 4.2.1.2 Tailings

Three types of tailings are used in this study. The first type is called silica tailings (ST), which are a commercially available artificial tailings material that is made of ground silica (manufactured by U.S. Silica Co.). ST are characterized by a particle-size distribution (PSD) that is similar to the average grain size distribution of tailings from nine different mines in eastern Canada. ST also mainly consist of silica (99.8% SiO<sub>2</sub>) particles, which are considered to be a chemically inert material (Carraro et al., 2009). The reason for using ST was to minimize and/or control the potential chemical interactions with the other ingredients (e.g. cement) in the CPB mixture, and thus reduce the impact of uncertainty on the results and their interpretation. In addition to ST, two types of natural tailings, including gold tailings (GT) and zinc tailings (ZT) obtained from Canadian hard rock mines, were used. Tables 4.2 and 4.3 show the primary physical properties and mineral composition of the tailings used, respectively. The grain size distribution of the tailings (ST, GT and ZT) is presented in Figure 4.1.

Table 4.2. Primary physical properties of tailings

<b>Tailings</b>	<b>Gs</b>	<b>D<sub>10</sub> (µm)</b>	<b>D<sub>30</sub> (µm)</b>	<b>D<sub>50</sub> (µm)</b>	<b>D<sub>60</sub> (µm)</b>
ST	2.7	1.9	9.0	22.5	31.5
ZT	3.34	1.6	10.9	29.9	37.8
GT	2.78	1.6	10.6	29.5	37.8

Table 4.3. Mineral composition of tailings

<b>Tailings/ Mineral (wt. %)</b>	<b>Quartz</b>	<b>Albite</b>	<b>Dolomite</b>	<b>Calcite</b>	<b>Chlorite</b>	<b>Magnetite</b>	<b>Pyrite</b>	<b>Talc</b>	<b>Magnesite</b>	<b>Pyrrhotite</b>	<b>Spinel</b>	<b>Others</b>	<b>Total</b>
GT	15	32.8	15	4.2	16.1	2.4	1	7	1.8	0.3	1.8	2.6	100
ZT	11.9	1.2	5.7	2.2	18.2	11.4	15.4	16.4	7.6	3.1	3.2	3.7	100
ST	99.8	-	-	-	-	-	-	-	-	-	-	0.2	100

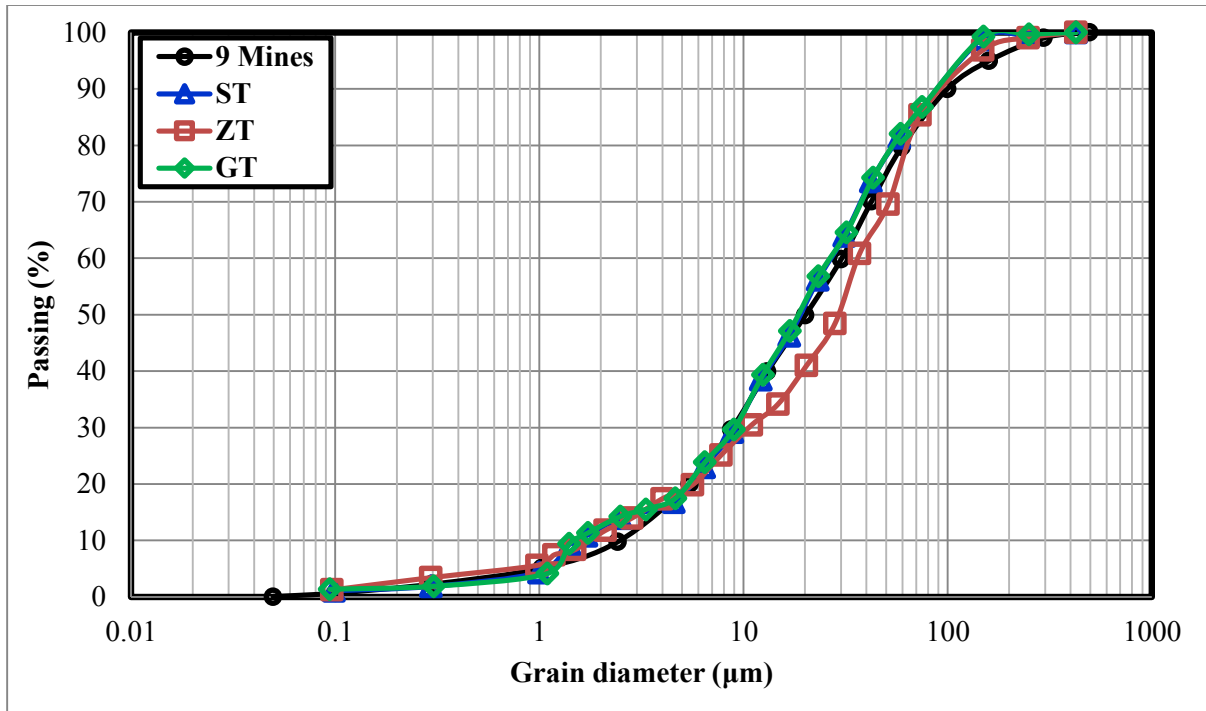


Figure 4.1. Grain size distribution of tailings (ST, ZT and GT) used and average grain size distribution of tailings from nine Canadian mines

#### 4.2.1.3 Mixing Water and Pyrite

Tap water was used as the mixing water. A commercial pyrite powder ( $\text{FeS}_2$ , M.W. = 119.98) was used to synthesize the pyrite-bearing tailings (or sulphide bearing tailings). This commercial pyrite has grains with a size similar to that of pyrite minerals commonly found in the natural tailings of hard rock mines. The pyrite-bearing tailings with a pyrite content of 5%, 15% and 45% wt. were prepared by mixing ST and GT with the appropriate amounts of pyrite powder. ZT with a pyrite content of 45% wt. was also prepared by mixing ZT and the applicable amount of pyrite. The physical properties of the pyrite are presented in Table 4.4.

Table 4.4. Physical properties of pyrite (Source: Washington Mills North Grafton, Inc.)

Bulk density (g/cm <sup>3</sup> )	Density at 20°C (g/cm <sup>3</sup> )	Specific gravity	pH	Melting point (C°)
2.35	4.7	4.6	4.0- 6.0	1193

## 4.2.2 Specimen Preparation and Mix Proportions

### 4.2.2.1 Preparation of CPB Samples

Around 400 CPB specimens (Table 4.5) were prepared by mixing the three types of tailings with a constant binder content (4.5 wt. %) and water-cement ratio ( $w/c=7.6$ ). To prepare homogenous samples, the ingredients of the CPB mixture were blended by using a mixer to reach a slump value of 18 cm, which is commonly used in preparations of CPB. The slump tests were conducted in accordance with ASTM C143-90. After the mixing process, the CPB mixtures were poured into plastic cylinders with a diameter of 5 cm and height of 10 cm. The cylinders were sealed with wax (to avoid the evaporation of water) and cured for 7, 28, 90, and 150 days in environmental chambers at various temperatures (2°C, 20°C, 35°C, and 50°C) until the time of testing.

Table 4.5. Mix composition of prepared CPB samples

CPB Sample	Binder	Binder content (%)	Tailings Type	Pyrite content (%)	w/c ratio	Curing time (days)
CPB- ST-Py-5%	PCI	4.5	ST	5	7.6	7, 28, 90, 150
CPB- ST-Py-15%	PCI	4.5	ST	15	7.6	7, 28, 90, 150
CPB- ST-Py-45%	PCI	4.5	ST	45	7.6	7, 28, 90, 150
CPB- GT-Py-5%	PCI	4.5	GT	5	7.6	7, 28, 90, 150
CPB- GT-Py-15%	PCI	4.5	GT	15	7.6	7, 28, 90, 150
CPB- GT-Py-45%	PCI	4.5	GT	45	7.6	7, 28, 90, 150
CPB- ZT-Py-15%	PCI	4.5	ZT	15	7.6	7, 28, 90, 150
CPB- ZT-Py-45%	PCI	4.5	ZT	45	7.6	7, 28, 90, 150

ST: Silica Tailings; GT: Gold Tailings; ZT: Zinc Tailings, PCI: Portland Cement I

## 4.2.3 Testing of Specimens

### 4.2.3.1 Oxygen Consumption Tests on CPB Samples Cured at Various Temperatures

The OC tests (Elberling & Nicholson, 1996; Elberling, et al., 1994) were performed at room temperature (~20°C) on the CPB samples cured at various temperatures (2°C, 20°C, 35°C, and 50°C). The principle of OC testing is based on the measurement of the quantity of consumed oxygen due to the oxidation of the sulphidic material sample in a sealed chamber during a short period of time which ranges from about 3 to 5 hours (Schmieder et al., 2012; 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 the beginning to the end of the test. The reactivity of the CPB samples was measured by using a galvanic cell type oxygen sensor (model GC33-200, GC Industries) to

estimate the rate of OC. In addition, oxygen sensors (model SO-210, Apogee Instruments, Inc.) were used to measure the reactivity at various ambient (testing) temperatures because this type of sensor has an operating range that is relatively close to the ambient temperatures (-20 to 60°C). The sensors were connected to a voltmeter (Hantek 365A USB Data Logger Recorder Digital Multimeter Voltage Current PC Base) that measured and recorded the voltage produced by the oxidation reactions in the sealed chamber. The measured voltage of the sensors is directly proportional to the partial pressure of oxygen in the gas phase. The OC tests were performed on the CPB samples by carefully covering the cylinders with an airtight lid that was equipped with an oxygen sensor, as shown in Figure 4.2. This figure illustrates the experimental setup of the OC testing. Each OC test was repeated at least four times to ensure the repeatability of the results.

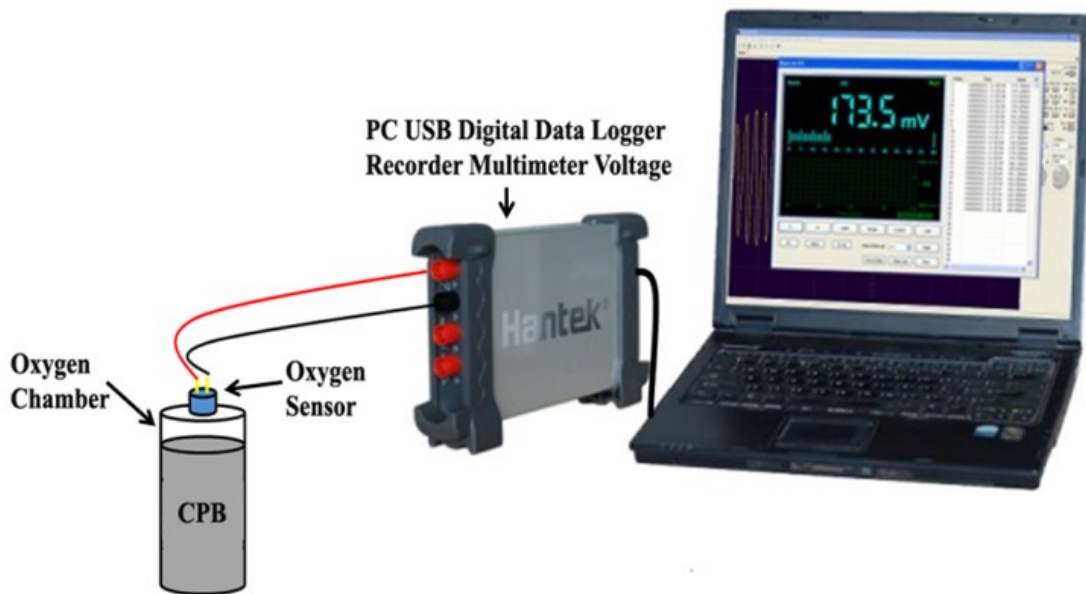


Figure 4.2. Schematic of experimental setup of OC testing

The reactivity of the CPB specimens was evaluated from the flux of oxygen ( $F_L$ ). Under pseudo steady state conditions, the  $F_L$  is determined based on the two following equations, (Eqs.4.1 and 4.2) as proposed by Elberling et al. (1994) and Elberling and Nicholson (1996):

$$F_L = C_o (K_r D_e)^{0.5} \quad (4.1)$$

where  $K_r$  is the first-order reaction rate coefficient for sulphide mineral oxidation (e.g., pyrite),  $D_e$  is the effective diffusion coefficient and  $C_o$  is the initial concentration of oxygen. The term  $(K_r D_e)$  can be obtained from the slope of plotting  $\ln (C/C_o)$  versus time based on Eq. 4.2. It can be calculated if the volume of the gas chamber ( $V$ ) and the surface area of the exposed area of the reactive materials ( $A$ ) are known (Ouellet et al., 2006).

$$\ln (C/ C_o) = - t (K_r D_e)^{0.5} (A/V) \quad (4.2)$$

#### 4.2.3.2 Oxygen Consumption Testing in Various Atmospheric Temperatures

To investigate the effect of various ambient temperatures on the reactivity of CPB specimens cured at 20°C for different curing times (7, 28, 90 and 150 days), the OC of these specimens was measured in environmental chambers with different temperatures (2°C, 20°C, 35°C, and 50°C) to simulate the different ambient temperatures of underground mines.

#### 4.2.3.3 Microstructural Analysis

For a better understanding of the influence of temperature on the reactivity and microstructure of the CPB specimens with time, a combination of various microstructural analysis techniques were adopted. These techniques allow changes that might occur in the porosity, pore structure and binder hydration products of the CPB specimens to be examined, as well as the progress of the binder hydration assessed and phases found in the specimens identified. In this study, x-ray diffraction (XRD), thermal analysis (thermogravimetry–differential thermogravimetry (TG-DTG)), and mercury intrusion porosimetry (MIP) were conducted on selected CPB specimens as well as on hardened cement paste (HCP) specimens with a high w/c ratio ( $w/c = 1$ ) to simulate the cement matrix of CPB. Prior to undergoing the microstructural analyses, the samples were prepared by using several different processes, such as cutting and drying. The samples were dried at 50°C in an oven until mass stabilization before being subjected to testing. The XRD patterns of the powdered samples were recorded with a Scintag XDS 2000 X-ray powder diffractometer with monochromatized  $\text{CuK}\alpha$  radiation ( $\lambda=1.5418 \text{ \AA}$ ). The data were collected between scattering angles ( $2\theta$ ) of 5° and 70°. The MIP tests were performed on the CPB specimens by using a Micromeritics Auto Pore III 9420 mercury porosimeter in accordance with ASTM D4404-10. The

MIP provides information on the pore size distribution in a porous material (i.e., cementitious materials). Finally, the TG-DTG tests were performed on 10 mg ( $\pm 0.5$  mg) of powdered samples (oven dried at 50°C) by using an Ulvac TGD 9600 thermal analysis system at a heating rate of 10°C/min from an ambient temperature up to 1000°C in an atmosphere of N<sub>2</sub> gas (rate of flow: 100 cm<sup>3</sup> min<sup>-1</sup>).

## 4.3 Results and Discussions

### 4.3.1 Effect of Curing Temperature on the Reactivity of CPB Samples

Figure 4.3 to 4.6 show the mean and standard deviation of the reactivity of the CPB specimens (CPB-ST, CPB-ZT and CPB-GT) cured at different temperatures (2°C, 20°C, 35°C and 50°C) and plotted as a function of curing time. Figures 4.7 to 4.9 show the influence of curing temperature on the reactivity of the CPB-ST specimens (with pyrite content of 5%, 15%, and 45%) cured for various periods of time and tested at 20°C. The results presented in Figures 4.3 to 4.9 show that in general, the reactivity of the specimens decreases with age regardless of the curing temperature and type of tailings. This reduction of the reactivity with time is due to the decrease of the porosity and refinement of the pore structure of the CPB specimens with time which is a result of the progress of binder hydration and the associated precipitation of higher amount of hydration products, which in turn, reduces the effective diffusion coefficient of oxygen ( $D_e$ ) (see Eqs. 4.1 and 4.2). This argument with respect to the precipitation of more cement hydration products as the curing time increases is fully supported by the results of the thermal analyses (TG/DTG) performed on the 7 and 28 day CPB specimens as presented in Figure 4.10. This figure depicts the TG/DTG diagrams of the 7 and 28 day CPB specimens, respectively. The first peak (DTG) or change in weight (TG) is located between 100°C and 200°C, resultant of the dehydration of the hydrates, such as calcium silicate hydrate (C-S-H), the carboaluminates, ettringite, and gypsum, while the apparition of the second peak or change in weight, which is detected at 400°C–500°C, is mainly caused by the decomposition of the calcium hydroxide (CH; Fall et al. (2010); Pane and Hansen, 2005; Zhou and Glasser, 2001)). Finally, the third peak or change in weight is observed between 650°C and 750°C, due to the decomposition of the calcite (e.g. Fall et al., 2010; Zhou and Glasser, 2001). A comparison of the TG/DTG diagrams of the 7 and 28 day CPB samples clearly indicates that the first and second peaks or changes in weight are much higher for the 28 day CPB sample, which shows that the amount of hydration products (e.g., CH, C-S-H) formed increases with longer

curing time. Furthermore, it can be noted that a higher curing temperature leads to a reduction of the reactivity of the CPB specimens with the exception of the observations made at 50°C which will be discussed later in this section. For example, the reactivity of CPB-ST-Py-5% cured at temperatures of 2°C (Figure 4.3) and 50°C (Figure 4.6) for 7, 28, 90 and 150 days is reduced by 43%, 43.2%, 40.9% and 59%, respectively. This reduction in reactivity is attributed to the improvement in the microstructure of the CPB (refinement of the pore structure) due to the acceleration in cement hydration caused by increased curing temperatures. The higher curing temperature accelerates the hydration of the cement clinker and promotes the formation of more hydrated cement products, such as C-S-H gel, portlandite (CH), and ettringite (Wang & Liu, 2011; Fall & Samb, 2009; Hearn et al., 2006; Aligizaki, 2006; Lamond and Pielert, 2006). These hydrated cement products fill the pores (in particular, the capillary pores) in the CPB matrix and around the cement grains (Fall et al., 2010). The capillary pores are a key factor that influences the transport properties (diffusion and permeability) of cement based materials (i.e., CPB). Due to the acceleration in the cement hydration from higher curing temperatures, the volume and size of the capillary pores are reduced. This leads to the improved microstructure of the CPB and a reduced oxygen diffusion coefficient (see Eqs. 4.1 and 4.2). For that reason, the reactivity of the CPB specimens will decrease due to the reduction in the oxygen diffusion which in turn decreases the oxidation rate of pyrite. The results obtained from the MIP tests, as shown in Figure 4.11, support this explanation. Figure 4.11 illustrates the differential pore size distribution of 90-day CPB-ST-Py-45% Py. specimens cured at 2°C, 20°C and 50°C. It can be observed that as the curing temperature increases, the threshold pore diameter decreases, thus indicating a refinement of the pore structure of the cementitious material. The threshold pore diameter, that is, the pore diameter related to the highest rate of mercury intrusion, has an important influence on the permeability and diffusion of cementitious materials (Fall et al., 2009).

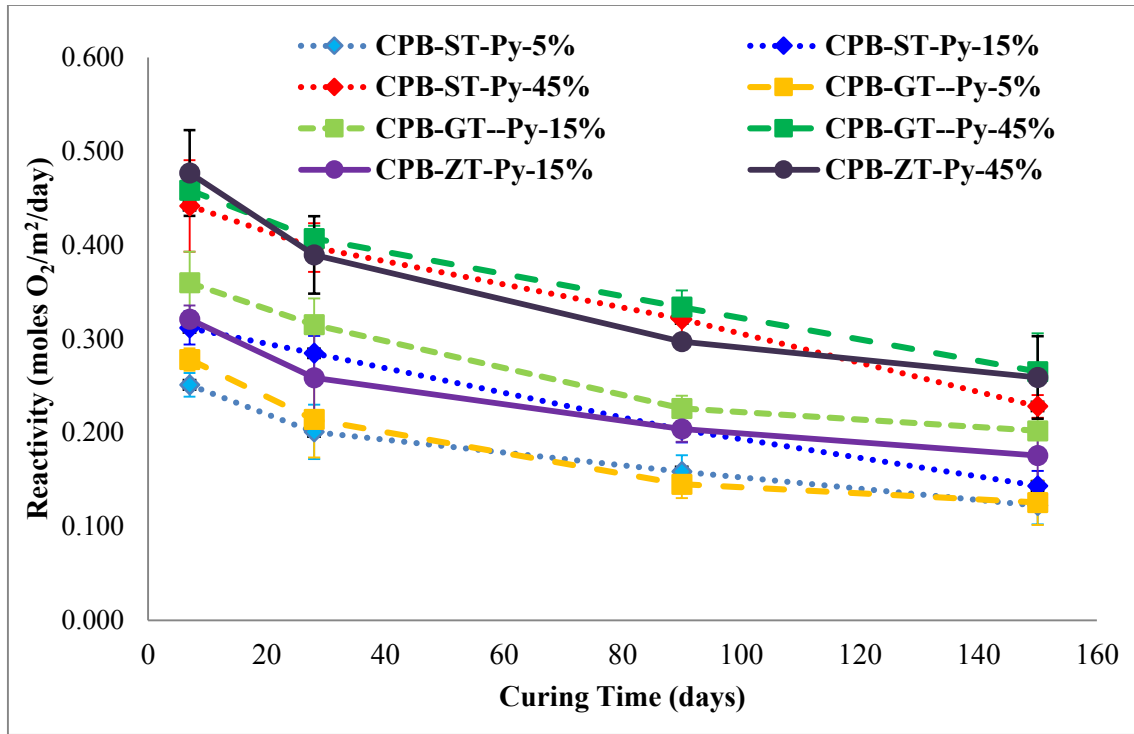


Figure 4.3. Reactivity of CPB specimens cured at 2°C for different curing times and tested at 20°C

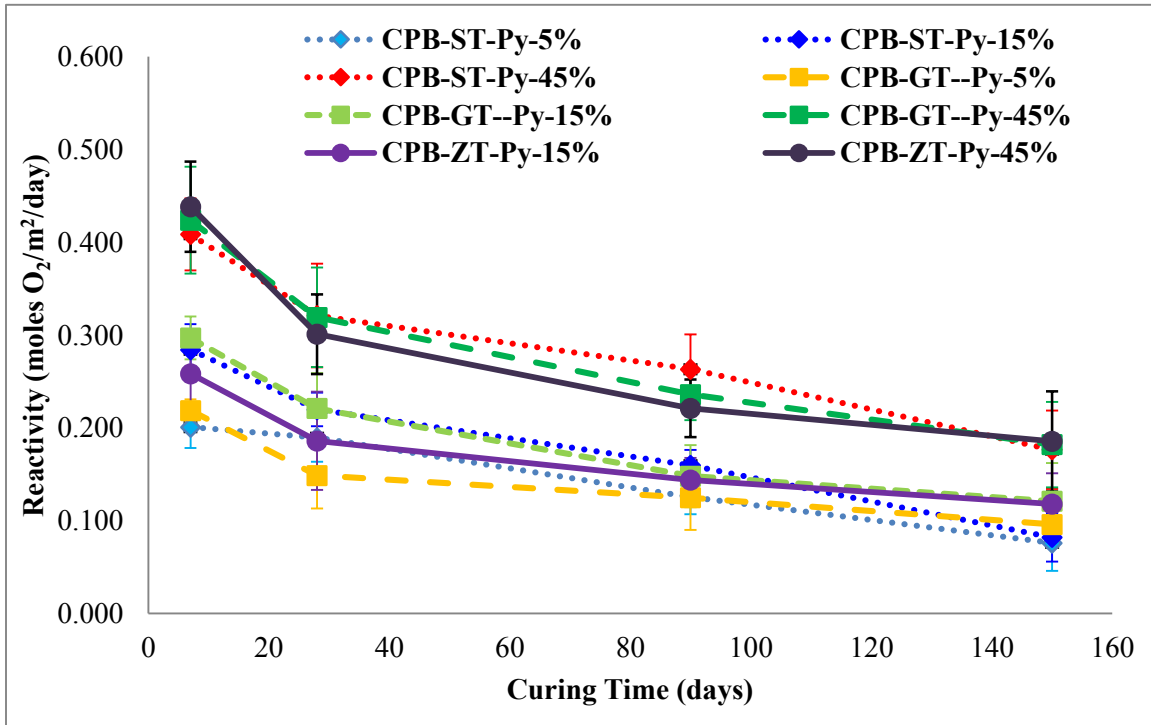


Figure 4.4. Reactivity of CPB specimens cured at 20°C for different curing times and tested at 20°C

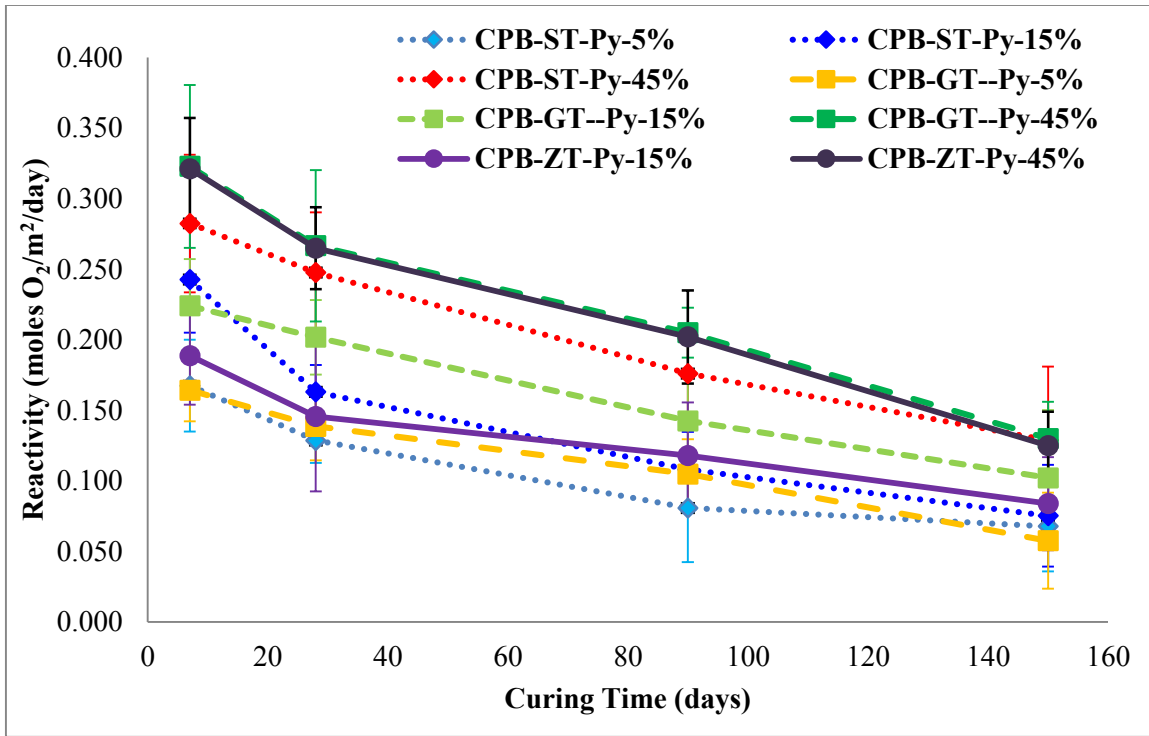


Figure 4.5. Reactivity of CPB specimens cured at 35°C for different curing times and tested at 20°C

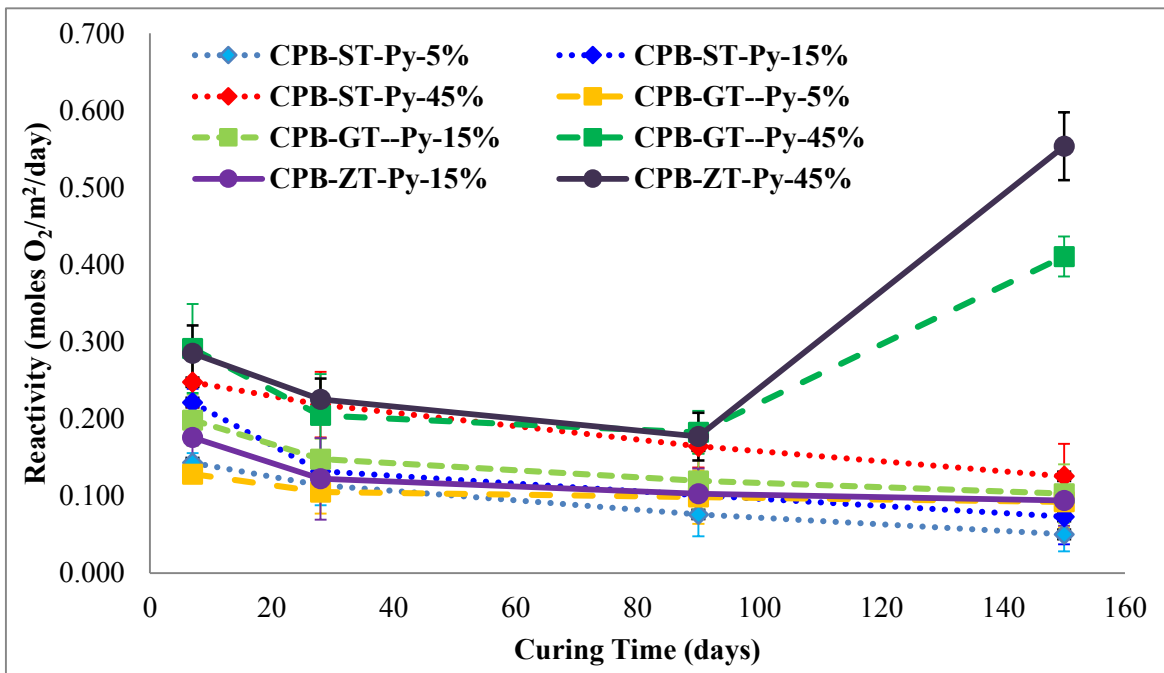


Figure 4.6. Reactivity of CPB specimens cured at 50°C for different curing times and tested at 20°C

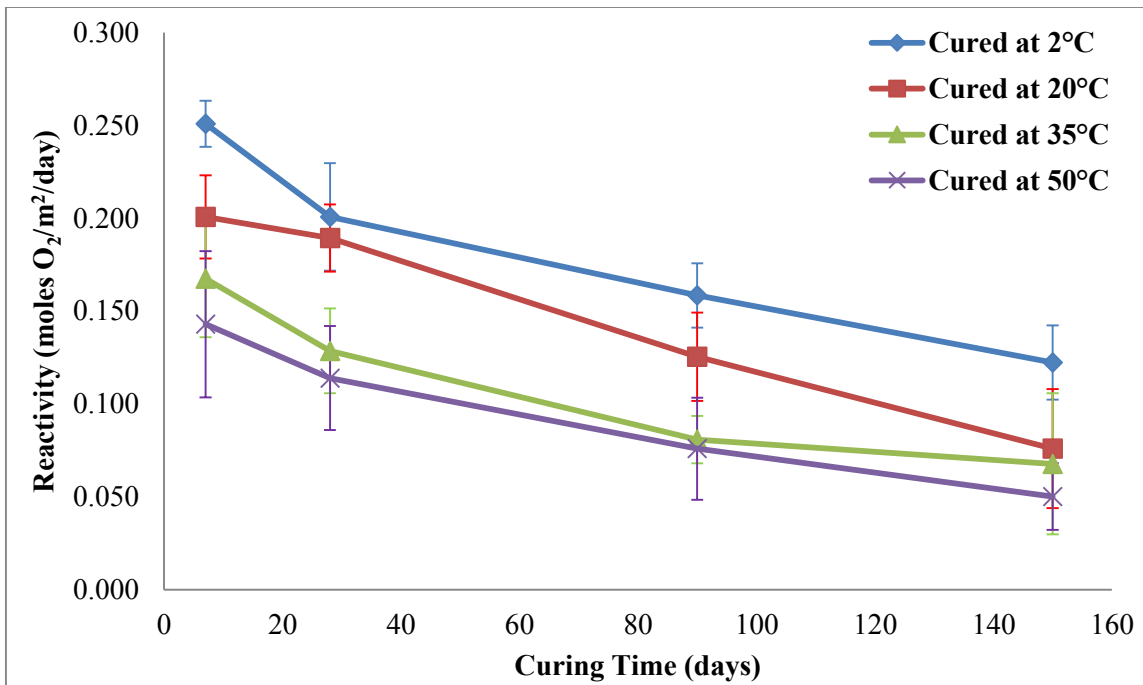


Figure 4.7. Effect of curing temperature on the reactivity of CPB-ST-Py.5% for different curing times and tested at 20°C

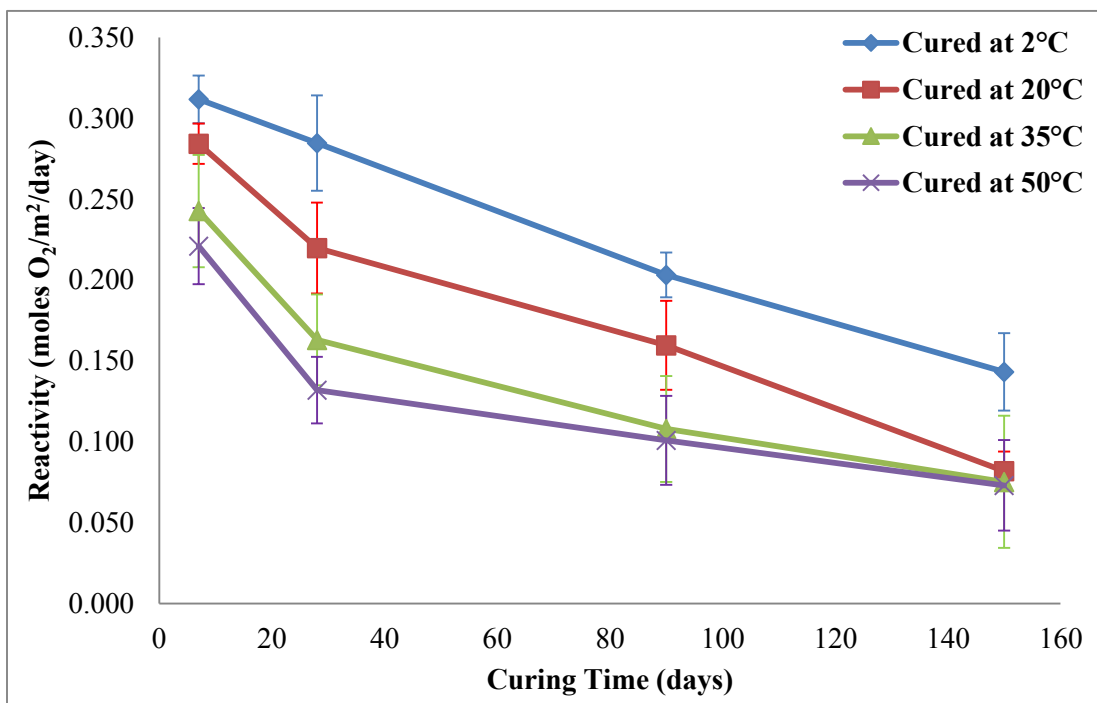


Figure 4.8. Effect of curing temperature on the reactivity of CPB-ST-Py.15% for different curing times and tested at 20°C

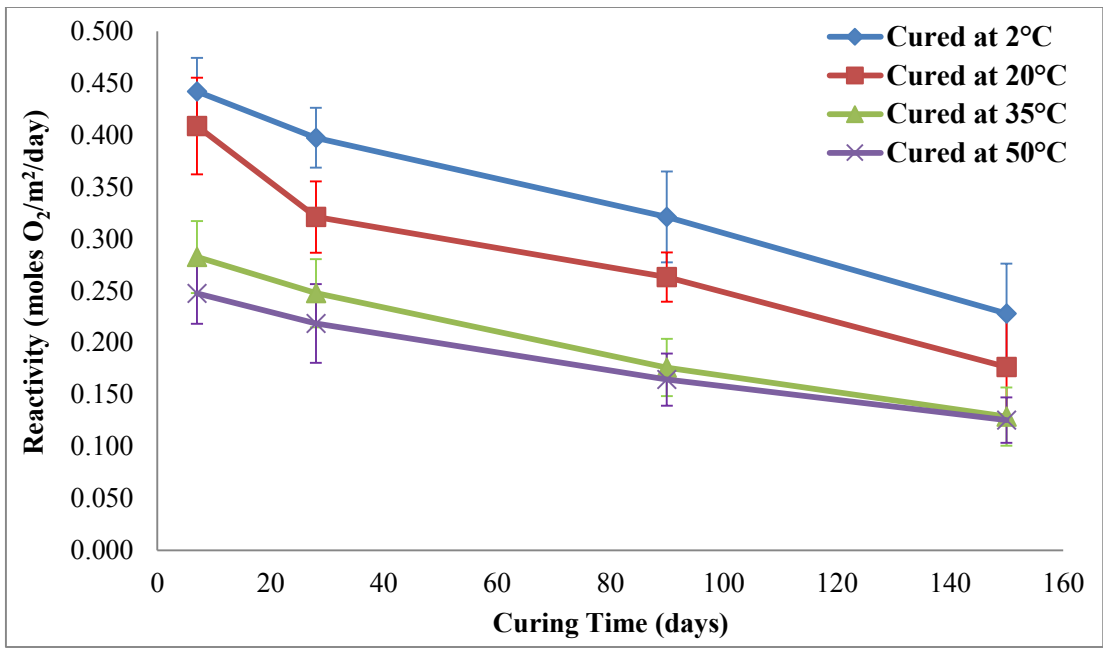


Figure 4.9. Effect of curing temperature on the reactivity of CPB-ST-Py.45% for different curing times and tested at 20°C

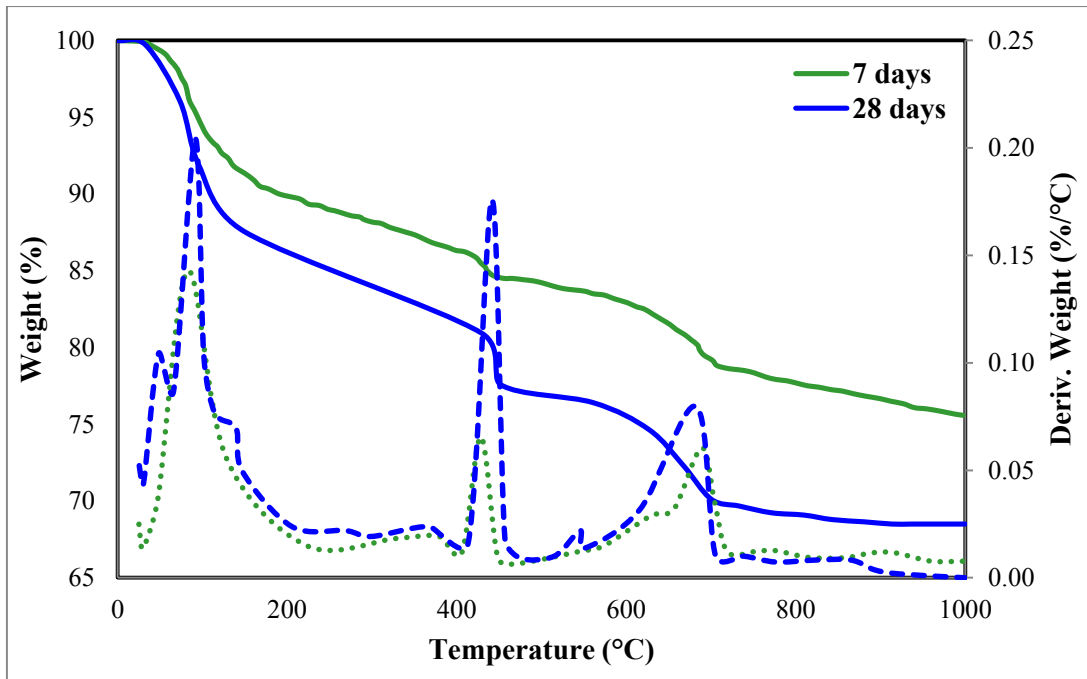


Figure 4.10. TG/DTG curves of 7 and 28 day samples

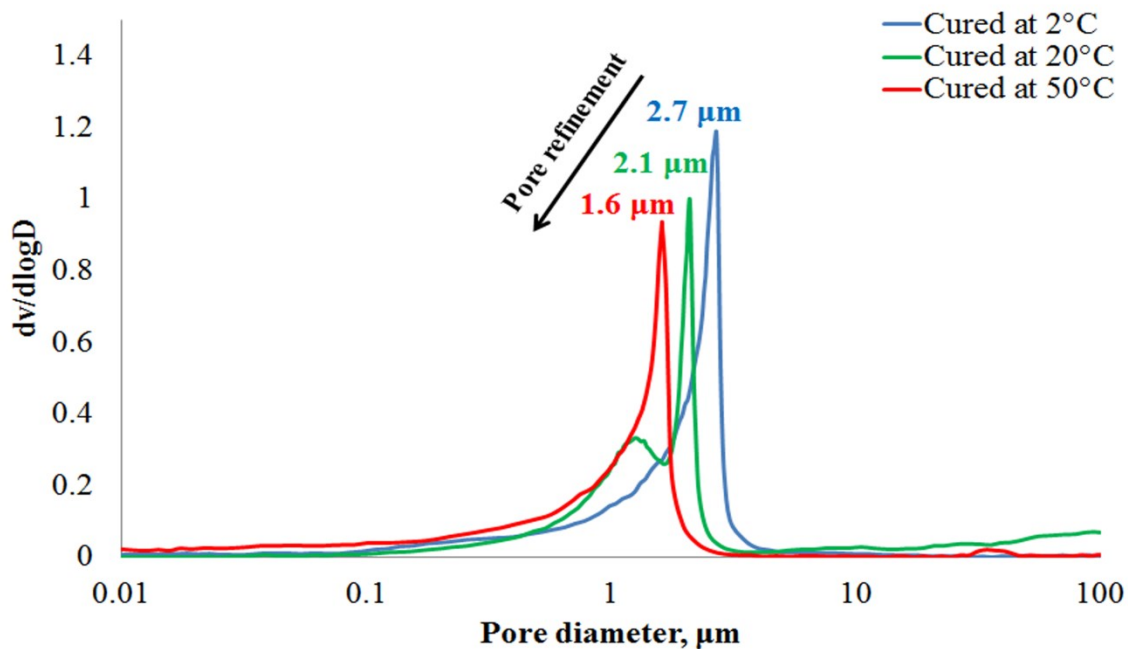


Figure 4.11. Differential pore size distribution curves of 90 day CPB specimens (w/c=7.6) cured at various temperatures (2°C, 20°C, and 50°C)

At a curing temperature of 50°C, it is obvious that the reactivity of the 150 day CPB-GT-Py. 45% and CPB-ZT-Py. 45% specimens do not follow the same trend as that of the CPB-ST-Py. 45%, as shown in Figure 4.6. The reactivity of these specimens significantly increases at 50°C. This increase cannot be explained by the coarsening of the pore structure of the CPB due to the “crossover effect” in cementitious material, a phenomenon in which the curing of CPB at excessively high temperatures results in the loss of strength (Wang and Lee, 2012; Razak and Sajedi, 2011; Sajedi and Razak, 2010; Elsageer et al., 2009; Carino, 1984) because the CPB sample made of ST does not show any increase in reactivity at a curing temperature of 50°C. However, the observed increase of the reactivity of the CPB-GT-Py.45% and CPB-ZT-Py. 45% specimens at 50°C can be attributed to the fact that these specimens have higher sulphate content (including the initial sulphate content of the pore water of GT and ZT (>5000 ppm) as well as the sulphate ions generated by the oxidation of the pyrite) than the other CPB samples with a lower pyrite content and the ST-CPB-Py. 45% sample. Previous studies (Pokharel and Fall, 2010; Barbarulo et al., 2007; Barbarulo, 2002) have demonstrated that there will be coarsening of the pore structure of CPB that contains sulphate and cured at a temperature of 50°C due to the combined effects of the following factors: (i) the adsorption of sulphate by C-S-H gel at higher temperatures, and (ii)

the destabilization of ettringite at high temperatures (since the solubility of ettringite increases with increasing temperatures (Barbarulo, 2002)). These factors lead to smaller amounts of expansive minerals available to fill the empty pores of the CPB samples with sulphate, thereby coarsening their pore structure, which in turn, increases the effective diffusion coefficient of oxygen ( $D_e$ ) (see Eqs. 4.1 and 4.2). This coarsening of the pore structure is experimentally demonstrated by the MIP results presented in Figure 4.12, which shows the pore size distribution curves of 150 day CPB-ZT-Py.45% specimens ( $w/c=7.6$ ) cured at 20°C and 50°C. From this figure, it can be observed that the pore size distribution of the sample cured at 50°C is shifting toward the right, which suggests larger pore sizes, as compared to that cured at 20°C. Furthermore, the threshold pore diameter of the CPB-ZT-Py.45% sample cured at 50°C (4.3  $\mu\text{m}$ ) is about twice that of the CPB-ZT-Py.45% sample cured at 20°C (2.6  $\mu\text{m}$ ), thus indicating coarsening of the pore structure, which is obviously associated with an increase of the oxygen effective diffusion coefficient. The aforementioned argument with respect to the smaller amount of expansive minerals (e.g. ettringite) is in substantial agreement with the results of the XRD analyses conducted on hardened cemented pastes (HCPs) with sulphate cured at 20°C (Figure 4.13a) and 50°C (Figure 4.13b), respectively. From Figure 4.13a, it can be seen that the sample that contains sulphate and cured at 20°C shows large amounts of expansive minerals due to the availability of sulphate to react with CH and tricalcium aluminate ( $C_3A$ ). However, in Figure 4.13b, the XRD result of the sample that contains sulphate and cured at 50°C shows very small amounts of expansive minerals. The peak of the CH is also high, especially at 18 degrees 2-theta. The sample that contains sulphate cured at 20°C in Figure 4.13a does not show the presence of any CH at 28.5 degrees 2-theta whereas the sample cured at 50°C contains CH. Hence, these XRD results clearly suggest that at higher curing temperatures, sulphate is absorbed by the C-S-H gel and ettringite is dissolved, which obviously result in a coarser pore structure.

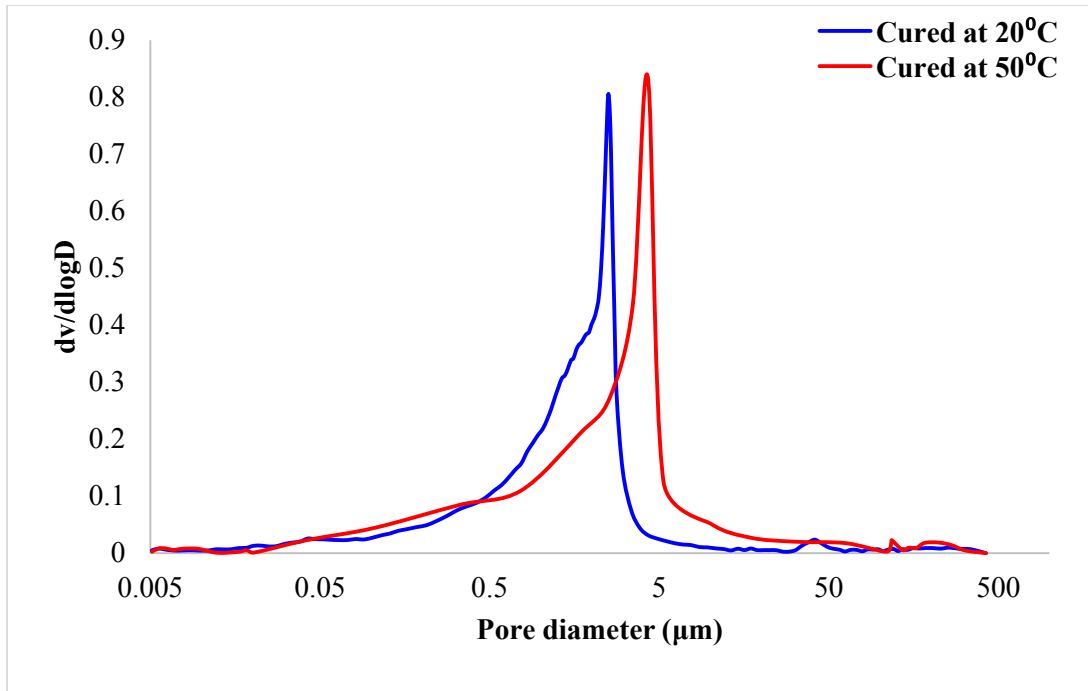
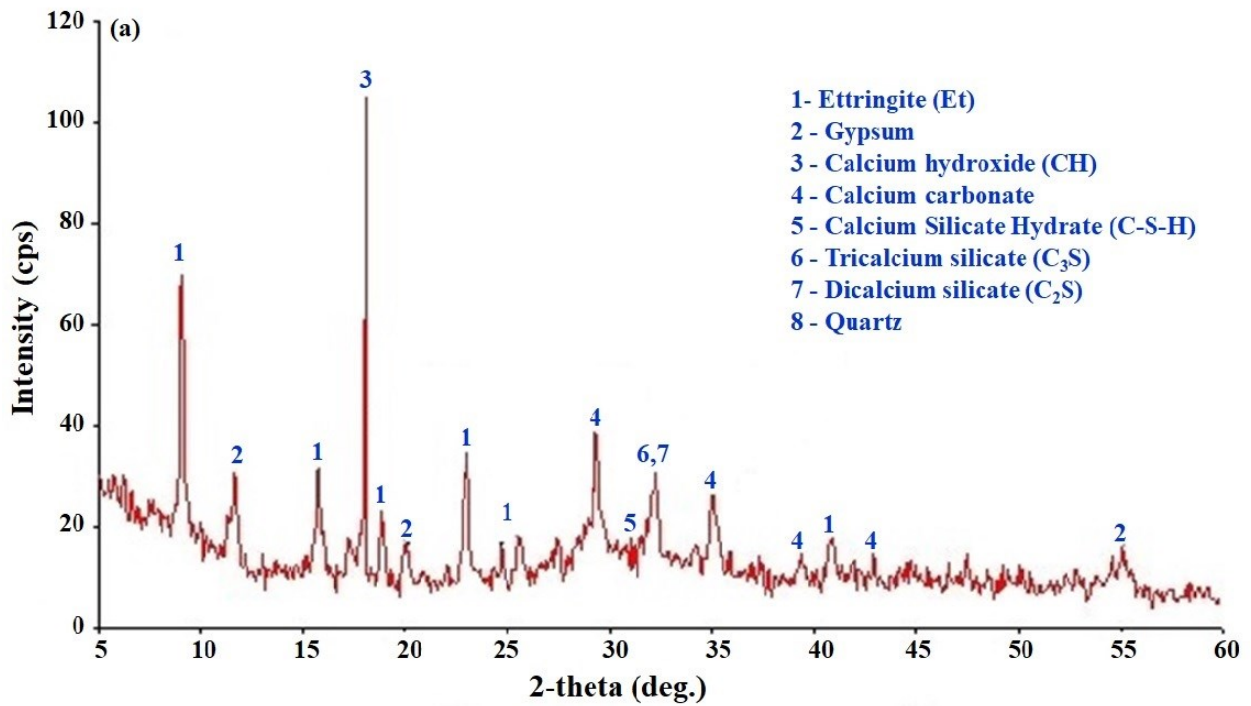


Figure 4.12. Differential pore size distribution curves of 150 day ZT-CPB-Py.45% specimens (w/c=7.6) cured at 20°C and 50°C



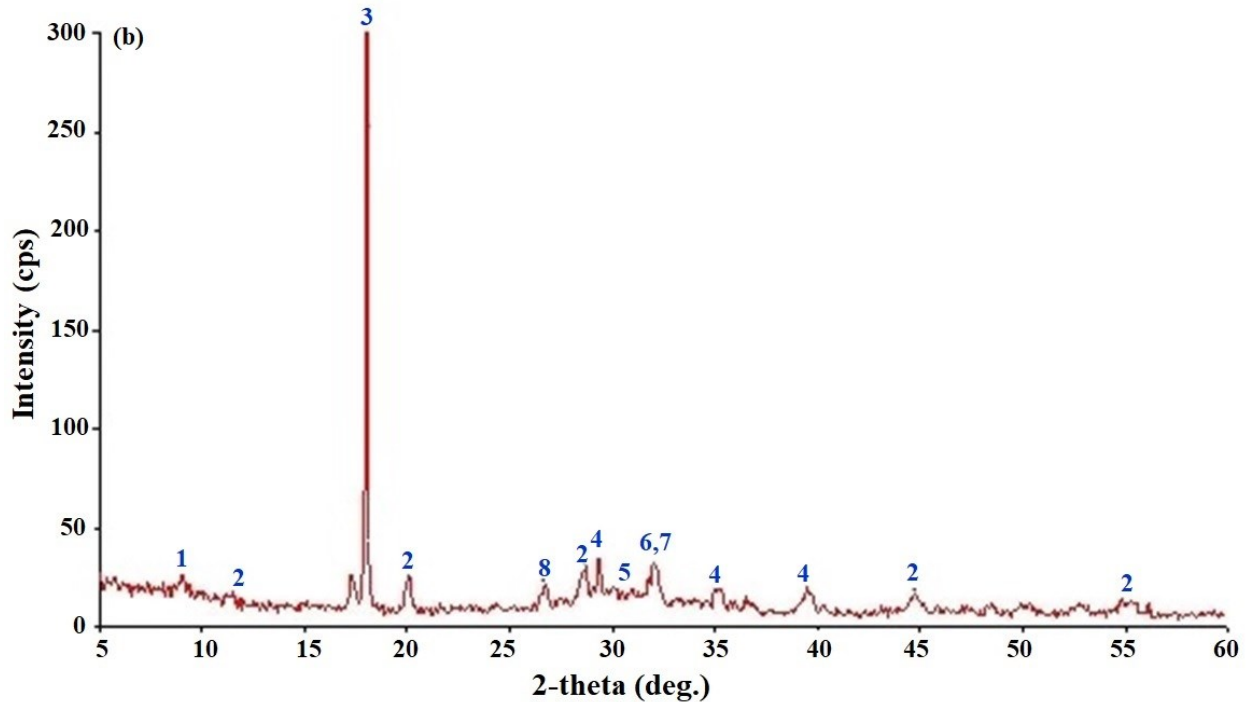


Figure 4.13. XRD result of CPB with an initial sulphate content of 25,000 ppm cured at a) 20°C and b) 50°C

#### 4.3.2 Effect of Atmospheric (Ambient) Temperature on Reactivity of CPB

Figures 4.14 to 4.17 show the influence of ambient temperatures on the reactivity of CPB-ST specimens (with pyrite content of 5%, 15%, and 45%) cured at 20°C for various curing times (7, 28, 90 and 150 days) and tested at various temperatures (2°C, 20°C, 35°C and 50°C). These figures show that the reactivity increases with increasing ambient temperatures. This increase is due to the combined effect of the two following factors: (i) the oxygen diffusion coefficient increases with increases in temperature (e.g., Dziejowski et al., 1997; Batterman et al., 1996), thus making more oxygen available on the surface of the pyrite grains for oxidation, and (ii) the oxidation rate of pyrite is temperature-dependent and increases with increasing temperatures as demonstrated by several previous studies (e.g., Meldrum et al., 2001; Evangelou, 1995; Nicholson et al., 1988). Furthermore, it can also be observed in Figures 4.14 to 4.17 that the reactivity rate of the CPB samples is a function of the temperature. For all curing times, the evolution of the reactivity rate of the CPB specimens can be described as three phases in accordance with their testing temperatures: (i) first stage (from 2°C to 20°C); (ii) second stage (from 20°C to 35°C); and (ii) third stage (from 35°C to 50°C). The reactivity gradually increases during the first stage and then

rapidly increases in the second stage. In the third stage, the increase in reactivity slightly slows down. These varying rates of reactivity are due to the fact that the oxidation rate of pyrite is strongly temperature dependent. The rate of oxidation increases as the temperature increases (Nicholson et al., 1988; Schoonen et al., 2000). The lower rates of oxygen consumption observed for temperatures  $\geq 35^{\circ}\text{C}$  are likely because at higher temperatures, the chemical rate of reaction (pyrite oxidation) substantially increases, thus resulting in the formation of a thick ferric-oxide coating that would inhibit oxygen at the pyrite surface. Ferric hydroxide production was quite obvious during the OC tests. Similar observations have been made by other researchers on pyrite materials (e.g., Schoonen et al., 2000).

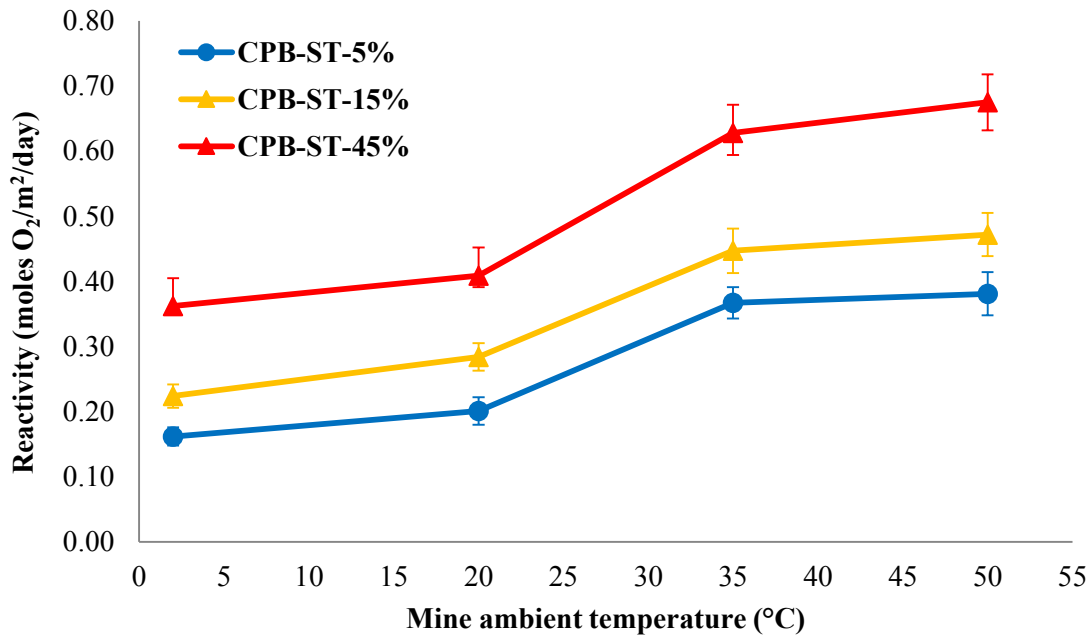


Figure 4.14. Effect of mine ambient temperatures on the reactivity of CPB-ST with 5%, 15% and 45% pyrite, cured for 7 days and tested at different temperatures

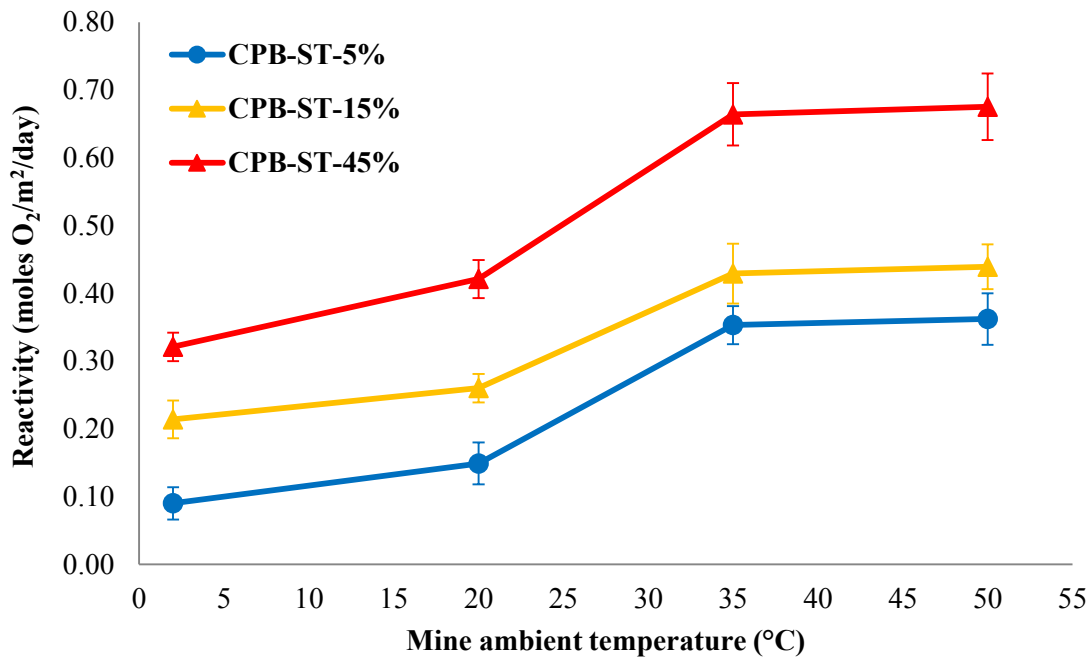


Figure 4.15. Effect of mine ambient temperatures on the reactivity of CPB-ST with 5%, 15% and 45% pyrite, cured for 28 days and tested at different temperatures

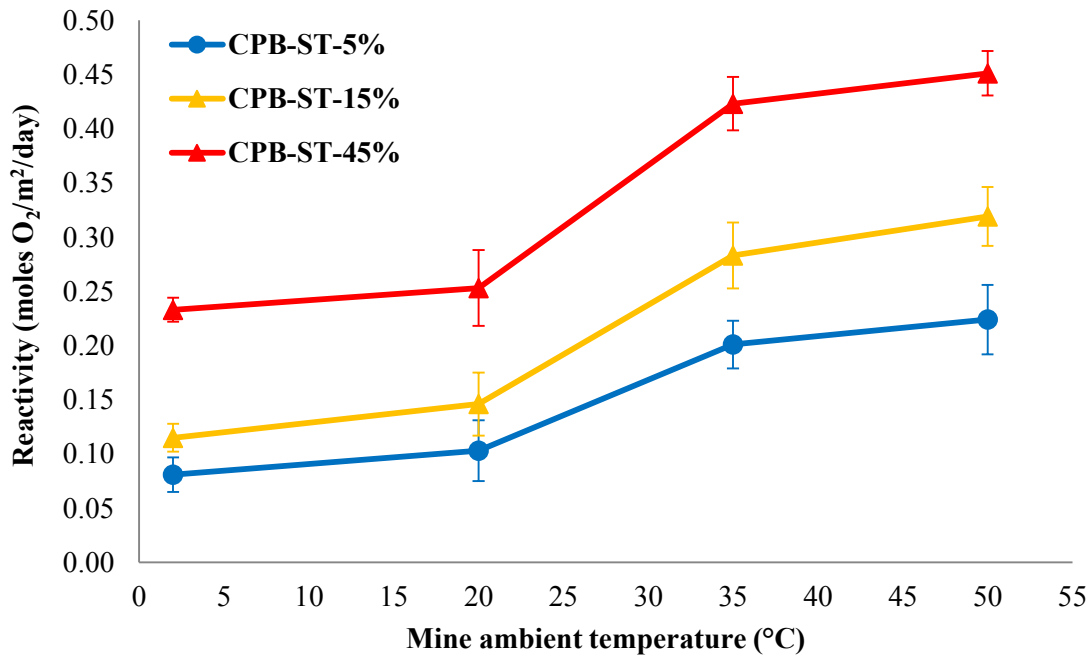


Figure 4.16. Effect of mine ambient temperatures on the reactivity of CPB-ST with 5%, 15% and 45% pyrite, cured for 90 days and tested at different temperatures

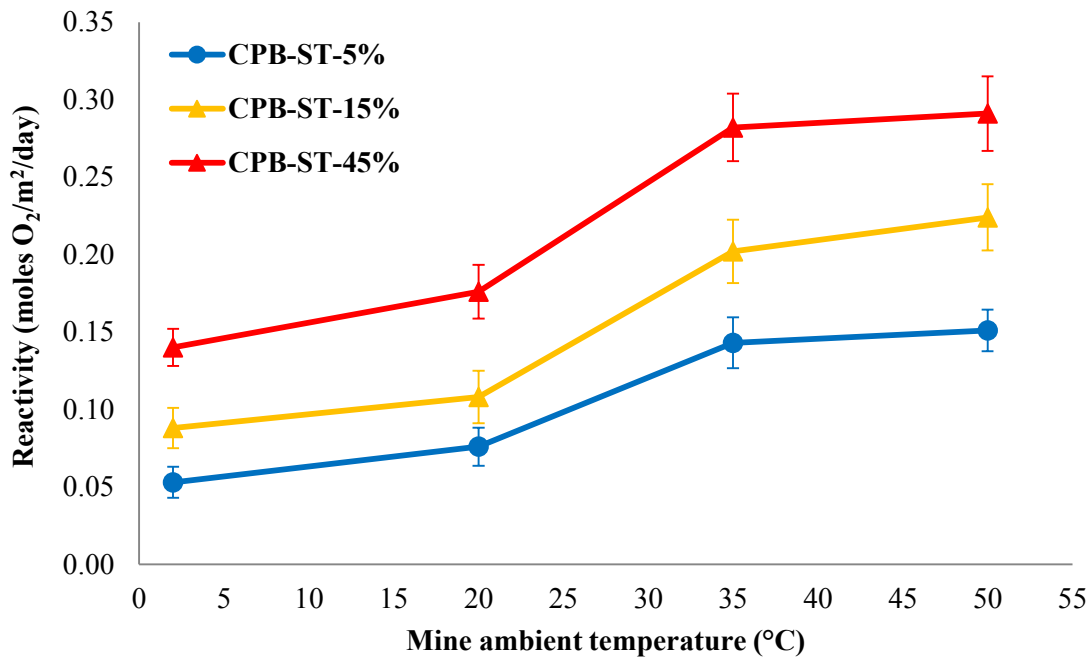


Figure 4.17. Effect of mine ambient temperatures on the reactivity of CPB-ST with 5%, 15% and 45% pyrite, cured for 150 days and tested at different temperatures

#### 4.4 Conclusions

This research is a study of the influence of curing and mine ambient temperature on the oxygen consumption or reactivity of CPB specimens prepared with three types of tailings that contain different pyrite contents and cured at different times. It is found that:

- The reactivity of CPB is influenced by both curing and ambient temperatures due to improvement change in its microstructure as well as transport properties (e.g., diffusivity),
- In general, as the curing temperature increases, the reactivity decreases. However, the presence of sulphate in the pore water of CPB can significantly increase the reactivity of CPB cured at high temperatures (50°C), and
- The reactivity increases as the ambient temperature increases. However, the extent of the effect of the temperature depends on the curing time and is generally more pronounced at the early ages.

This study has shown that temperature is a key factor that affects the reactivity of CPB systems through hydration and oxidation reactions. Temperature can affect the environmental performance and durability of CPB systems in the long term. However, despite the results found in this study, there is still the need to investigate the role of temperature coupled with other parameters (i.e.,

sulphate content, stress) on the reactivity of CPB systems. This will be the objective of further studies.

#### 4.5 References

- Alakangas, L., Dagli, D., & Knutsson, S. (2013). Literature Review on Potential Geochemical and Geotechnical Effects of Adopting Paste Technology under Cold Climate Conditions, 1–36. Retrieved from [http://pure.ltu.se/portal/files/43755253/Literature\\_Review\\_on\\_Potential\\_Geochemical\\_and\\_Geotechnical\\_Effects\\_of\\_Adopting\\_Paste\\_Technology\\_under\\_Cold\\_Climate\\_Conditions.pdf](http://pure.ltu.se/portal/files/43755253/Literature_Review_on_Potential_Geochemical_and_Geotechnical_Effects_of_Adopting_Paste_Technology_under_Cold_Climate_Conditions.pdf)
- Aligizaki, K. K. (2006). *Pore structure of cement-based materials : Testing, Interpretation and Requirement* (1st ed.). Spon Press. Retrieved from <https://www.crcpress.com/Pore-Structure-of-Cement-Based-Materials-Testing-Interpretation-and-Requirements/Aligizaki/9780419228004>
- Barbarulo, R. (2002). *Comportement des matériaux cimentaires: actions des sulfates et de la température*. Université Laval.
- Barbarulo, R., Peycelon, H., & Leclercq, S. (2007). Chemical equilibria between C–S–H and ettringite, at 20 and 85 °C. *Cement and Concrete Research*, 37(8), 1176–1181. <http://doi.org/10.1016/j.cemconres.2007.04.013>
- Batterman, S., Padmanabham, I., & Milne, P. (1996). Effective Gas-Phase Diffusion Coefficients in Soils at Varying Water Content Measured Using a One-Flow Sorbent-Based Technique. *Environmental Science & Technology*, 30(3), 770–778. <http://doi.org/10.1021/es950014i>
- Bussière, B., Dagenais, A.-M., Mbonimpa, M., Aubertin, M. (2002). Modification of oxygen-consumption testing for the evaluation of oxygen barrier performance. In *Proceedings of the 55th Canadian Geotechnical Conference and 3rd Joint International Association of Hydrogeologists – Canadian National Chapter Canadian Geotechnical Society (IAH–CNC/CGS) Conferences, Ground and Water: Theory to Practice* (pp. 139–149). Niagara Falls.
- Carino, N. (1984). The Maturity Method: Theory and Application. *Cement, Concrete and Aggregates*, 6(2), 61. <http://doi.org/10.1520/CCA10358J>
- Carraro, J., Prezzi, M., & Salgado, R. (2009). Shear Strength and Stiffness of Sands Containing Plastic or Nonplastic Fines. *Journal of Geotechnical and Geoenvironmental Engineering*, 135(9), 1167–1178. [http://doi.org/10.1061/\(ASCE\)1090-0241\(2009\)135:9\(1167\)](http://doi.org/10.1061/(ASCE)1090-0241(2009)135:9(1167))
- Davies, MP., Rice, S. (2001). An alternative to conventional tailings management–“dry stack” filtered tailings. In *Proceeding of Tailings and Mine Waste '01* (pp. 411–420). Forth Collins, Colorado: Ballema Publishing.
- Dold, B. (2014). Evolution of Acid Mine Drainage Formation in Sulphidic Mine Tailings. *Minerals*, 4(3), 621–641. <http://doi.org/10.3390/min4030621>
- Dziejowski, J. E., Rimmer, A., & Steenhuis, T. S. (1997). Preferential Movement of Oxygen in Soils? *Soil Science Society of America Journal*, 61. <http://doi.org/10.2136/sssaj1997.03615995006100060010x>
- Elberling, B., Nicholson, R. V., & Scharer, J. M. (1994). A combined kinetic and diffusion model for pyrite oxidation in tailings: a change in controls with time. *Journal of Hydrology*, 157(1–4), 47–60. [http://doi.org/10.1016/0022-1694\(94\)90098-1](http://doi.org/10.1016/0022-1694(94)90098-1)
- Elberling, B., & Nicholson, R. V. (1996). Field determination of sulphide oxidation rates in mine

- tailings. *Water Resources Research*, 32(6), 1773–1784. <http://doi.org/10.1029/96WR00487>
- Elberling, B., Nicholson, R. V., & David, D. J. (1993). Field Evaluation of Sulphide Oxidation Rates. *Hydrology Research*, 24(5), 323–338. Retrieved from <http://hr.iwaponline.com/content/24/5/323.abstract>
- Elberling, B., Nicholson, R. V., Reardon, E. J., & Tibble, R. (1994). Evaluation of sulphide oxidation rates: a laboratory study comparing oxygen fluxes and rates of oxidation product release. *Canadian Geotechnical Journal*, 31(3), 375–383. <http://doi.org/10.1139/t94-045>
- Elsageer, M. a, Millard, S. G., & Stephanie, J. (2009). Strength development of concrete containing coal fly ash under different curing temperature conditions. In *World of Coal Ash (WOCA) Conference*. Lexington, KY, USA.
- Evangelou, V. P. (1995). *Pyrite oxidation and its control*. Boca Raton, FL: CRC Press.
- Fall, M., Adrien, D., Célestin, J. C., Pokharel, M., & Touré, M. (2009). Saturated hydraulic conductivity of cemented paste backfill. *Minerals Engineering*, 22(15), 1307–1317. <http://doi.org/10.1016/j.mineng.2009.08.002>
- Fall, M., & Benzaazoua, M. Ouellet, S. (2004). Effect of tailings properties on paste backfill performance. In *Proceedings of the 8th International Symposia on Mining with Backfill* (pp. 193–202). Beijing, China.
- Fall, M., Benzaazoua, M., & Saa, E. G. (2008). Mix proportioning of underground cemented tailings backfill. *Tunnelling and Underground Space Technology*, 23(1), 80–90. <http://doi.org/10.1016/j.tust.2006.08.005>
- Fall, M., Célestin, J. C., Pokharel, M., & Touré, M. (2010). A contribution to understanding the effects of curing temperature on the mechanical properties of mine cemented tailings backfill. *Engineering Geology*, 114(3–4), 397–413. <http://doi.org/10.1016/j.enggeo.2010.05.016>
- Fall, M., & Samb, S. S. (2009). Effect of high temperature on strength and microstructural properties of cemented paste backfill. *Fire Safety Journal*, 44(4), 642–651. <http://doi.org/10.1016/j.firesaf.2008.12.004>
- Ghirian, A., & Fall, M. (2014). Coupled thermo-hydro-mechanical–chemical behaviour of cemented paste backfill in column experiments. *Engineering Geology*, 170, 11–23. <http://doi.org/10.1016/j.enggeo.2013.12.004>
- Hassani, F., & Archibald, J. H. (1998). *Mine Backfill*. CIM annual meeting.
- Hearn, N., Hooton, R. D, Nokken, M. R. (2006). Pore Structure and Permeability. In J. . Lamond, J.F., Pielert (Ed.), *Significance of Tests and Properties of Concrete and Concrete Making Materials, ASTM STP169D*.
- ICMM. (2012). Trends in the mining and metals industry. *Mining's Contribution to Sustainable Development*. London: International Council on Mining and Metals (ICMM). Retrieved from <http://www.icmm.com/document/3731%5Cnhttp://www.icmm.com/document/5423%5Cnhttp://www.icmm.com/our-work/sustainable-development-framework/10-principles%5Cnhttp://www.icmm.com/document/4441>
- Johnson, D. B., & Hallberg, K. B. (2005). Acid mine drainage remediation options: a review. *Sci Total Environ*, 338. <http://doi.org/10.1016/j.scitotenv.2004.09.002>
- Kitula, A. G. N. (2006). The environmental and socio-economic impacts of mining on local livelihoods in Tanzania: A case study of Geita District. *Journal of Cleaner Production*, 14(3–4), 405–414. <http://doi.org/10.1016/j.jclepro.2004.01.012>
- Kumari, S., Udayabhanu, G., & Prasad, B. (2010). Studies on environmental impact of acid mine

- drainage generation and its treatment: an appraisal. *Indian Journal of Environmental Protection*, 30(11), 953–967.
- Lamond, J. F., & Pielert, J. H. (2006). *Significance of tests and properties of concrete and concrete-making materials*. (C. Philadelphia, PA : ASTM, Ed.).
- Lottermoser, B. (2010). *Mine Wastes: Characterization, Treatment and Environmental Impacts*. Springer Berlin Heidelberg. <http://doi.org/10.1007/978-3-642-12419-8>
- Martin, T., & Davies, M. (2000). Trends in the stewardship of tailings dams. In *Proceedings of the Tailings and Mine Waste '00. A.A.* (pp. 393–407). Rotterdam: Balkema Publishers. <http://doi.org/10.1016/j.soildyn.2004.11.025>
- Mbonimpa, M, Aubertin, M, Aachib, M, B. (2002). *Oxygen diffusion and consumption in unsaturated cover materials*.
- Meldrum, J. L., Jamieson, H. E., & Dyke, L. D. (2001). Oxidation of mine tailings from Rankin Inlet, Nunavut, at subzero temperatures. *Canadian Geotechnical Journal*, 38(5), 957–966. <http://doi.org/10.1139/t01-028>
- Nasir, O., & Fall, M. (2009). Modeling the heat development in hydrating CPB structures. *Computers and Geotechnics*, 36(7), 1207–1218. <http://doi.org/10.1016/j.compgeo.2009.05.008>
- Nasir, O., & Fall, M. (2010). Coupling binder hydration, temperature and compressive strength development of underground cemented paste backfill at early ages. *Tunnelling and Underground Space Technology*, 25(1), 9–20. <http://doi.org/10.1016/j.tust.2009.07.008>
- Nicholson, R. V., Elberling, B., Williams, G. (1995). A new oxygen consumption technique to provide rapid assessment of tailings reactivity in the field and the laboratory. In *Proceedings of Sudbury '95-Mining and the environment*, 3.
- Nicholson, R. V., Gillham, R. W., & Reardon, E. J. (1988). Pyrite oxidation in carbonate-buffered solution: 1. Experimental kinetics. *Geochimica et Cosmochimica Acta*, 52(5), 1077–1085. [http://doi.org/10.1016/0016-7037\(88\)90262-1](http://doi.org/10.1016/0016-7037(88)90262-1)
- Öhlander, B., Chatwin, T., & Alakangas, L. (2012). Management of Sulfide-Bearing Waste, a Challenge for the Mining Industry. *Minerals*, 2(4), 1–10. <http://doi.org/10.3390/min2010001>
- Ouellet, S., Bussiere, B., Benzaazoua, M., Aubertin, M., Fall, M., & Belem, T. (2003). Sulphide Reactivity within cemented paste backfill: oxygen consumption test results. In *The 56th Annual Canadian Geotechnical Conference and 4th joint IAHR-CNC/CGS Conference* (pp. 176–183). Winnipeg, Manitoba, Canada.
- Ouellet, S., Bussière, B., Mbonimpa, M., Benzaazoua, M., & Aubertin, M. (2006). Reactivity and mineralogical evolution of an underground mine sulphidic cemented paste backfill. *Minerals Engineering*, 19(5), 407–419. <http://doi.org/10.1016/j.mineng.2005.10.006>
- Pane, I., & Hansen, W. (2005). Investigation of blended cement hydration by isothermal calorimetry and thermal analysis. *Cement and Concrete Research*, 35(6), 1155–1164. <http://doi.org/10.1016/j.cemconres.2004.10.027>
- Pokharel, M. (2008). *Geotechnical and environmental responses of paste tailings systems to coupled thermo-chemical loadings*. University of Ottawa. Retrieved from <http://hdl.handle.net/10393/27793>
- Pokharel, M., & Fall, M. (2010). Coupled Thermochemical Effects on the Strength Development of Slag-Paste Backfill Materials. *Journal of Materials in Civil Engineering*, 23(5), 511–525. [http://doi.org/10.1061/\(ASCE\)MT.1943-5533.0000192](http://doi.org/10.1061/(ASCE)MT.1943-5533.0000192)
- Razak, H. A., & Sajedi, F. (2011). The effect of heat treatment on the compressive strength of

- cement-slag mortars. *Materials & Design*, 32(8–9), 4618–4628.  
<http://doi.org/10.1016/j.matdes.2011.04.038>
- Sajedi, F., & Abdul Razak, H. (2010). Thermal activation of ordinary Portland cement–slag mortars. *Materials & Design*, 31(9), 4522–4527.  
<http://doi.org/10.1016/j.matdes.2010.04.011>
- Schmieder, P. J., Taylor, J. R., & Bourgeot, N. (2012). Oxygen consumption techniques to quantify acidity generation rates. In *1st International Acid and Metalliferous Drainage Workshop*. Beijing, China.
- Schoonen, M., Elsetinow, A., Borda, M., & Strongin, D. (2000). Effect of temperature and illumination on pyrite oxidation between pH 2 and 6. *Geochemical Transactions*, 1(1), 23.  
<http://doi.org/10.1186/1467-4866-1-23>
- Tibble, P.A. and Nicholson, R.V. (1997). Oxygen Consumption on Sulphide Tailings and Tailings Covers: Measured Rates and Applications. In *Proceedings of the 4th International Conference on Acid Rock Drainage*. (pp. 647–661). Vancouver, British-Columbia.
- Wang, P., & Liu, X. (2011). Effect of temperature on the hydration process and strength development in blends of Portland cement and activated coal gangue or fly ash. *Journal of Zhejiang University SCIENCE A*, 12(2), 162–170. <http://doi.org/10.1631/jzus.A1000385>
- Wang, X.-Y., & Lee, H.-S. (2012). Evaluation of the mechanical properties of concrete considering the effects of temperature and aging. *Construction and Building Materials*, 29, 581–590. <http://doi.org/10.1016/j.conbuildmat.2011.11.001>
- Williams, T. J., Denton, D. K., & Larson, M. K. (2001). *Geomechanics of reinforced cemented backfill in an underhand stope at the Lucky Friday Mine, Mullan, Idaho*. Columbia Parkway Cincinnati, OH. Retrieved from <http://stacks.cdc.gov/view/cdc/8322/>
- Wu, D., Fall, M., & Cai, S. (2012). Coupled Modeling of Temperature Distribution and Evolution in Cemented Tailings Backfill Structures that Contain Mineral Admixtures. *Geotechnical and Geological Engineering*, 30(4), 935–961. <http://doi.org/10.1007/s10706-012-9518-1>
- Zhou, Q., & Glasser, F. P. (2001). Thermal stability and decomposition mechanisms of ettringite at <120°C. *Cement and Concrete Research*, 31(9), 1333–1339.  
[http://doi.org/10.1016/S0008-8846\(01\)00558-0](http://doi.org/10.1016/S0008-8846(01)00558-0)

## **Chapter 5: Technical Paper III- Sulphate Induced Changes in the Reactivity of Cemented Tailings Backfill**

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### **Abstract**

The reactivity of cemented paste tailings (CPT) that contains sulphide mineral-bearing tailings is a key parameter that can influence its environmental performance and durability. This reactivity can be influenced by several factors, such as the initial sulphate content of CPT. In this paper, the effect of initial sulphate content of CPT on its reactivity is experimentally investigated by conducting oxygen consumption (OC) tests on CPT specimens. Microstructural tests were also conducted on CPT specimens to better understand the mechanisms responsible for the change in CPT reactivity. These specimens were prepared by mixing defined amounts of pyritic tailings (45% wt.), various proportions of Portland cement Type I alone or partially replaced with different types and amounts of mineral admixtures, and mixing water with various sulphate concentrations (0, 5,000, 15,000 and 25,000 ppm). The samples were cured for 150 days at room temperature. The results obtained show that, regardless of the type of binders, the reactivity of CPT specimens increases with increasing the concentrations of sulphate with exception at 5000 ppm. Also, a partial substitution of Portland cement type I by minerals admixtures, such as granulated blast furnace slag and fly ash, reduces their chemical reactivity. Regardless of the initial sulphate content, increasing the amount of the cement content and /or replacement level of cement by mineral admixtures leads to reduce the reactivity value of the paste.

**Keywords:** Cemented paste backfill- Reactivity - Sulphate- Oxygen consumption-Tailings.

## 5.1 Introduction

Mining is an important economic activity in Canada as well as in many parts of the world. In 2014, the mining industry added a value of \$57 billion to the Canadian Gross Domestic Product (Marshall, 2015). On the other hand, mining industry is considered the largest solid waste producer in Canada and in many countries over the world. Among mine wastes, tailings are fine grain residual materials produced with huge volume yearly as a byproduct of mining activities. This type of mine waste is generally disposed and stored in Tailings Storage Facility (TSF) at the upper surface of mine sites. It is commonly disposed and stored in slurry form which consists of a mixture of fine ground rock and processing water and chemical agents. Such type of management of a large volume of tailings has economic, social and environmental consequences in long term (Gleisner, 2005). Furthermore, the management of mine tailings is one of the main challenges the mining industry is facing worldwide. Moreover, tailings management will become more complex challenge if they contain chemically reactive minerals, such as sulphide minerals (commonly pyrite). These sulphide minerals incorporated in tailings are chemically unstable in the presence of air (oxygen) and water because they oxidize to form a highly acidic, sulfate-rich solution, which is called acid mine drainage (AMD) (Buckby et al., 2003). The generated acid solution can increase the acidity of the surrounding streams (e.g., ground and surface water). Furthermore, it has ability to solubilize and mobilize heavy trace metals containing in tailings into surrounding streams and soil. This can cause serious degradation of the quality of the surface and groundwater as well as used land. Pyrite ( $\text{FeS}_2$ ) is the most common sulphide minerals found in mining waste (Lottermoser, 2010; Moncur et al., 2009). The oxidation of pyrite mineral is exothermic and a very complex process, including several reactions and intermediate steps. In general, it is written as the following equation (Bigham and Nordstrom, 2000):



Commonly, sulphide-rich tailings are stored under water in tailing disposal impoundment and/ or covered by inert materials such as soil. The principle of the above disposal methods is based on isolation of sulphide bearing tailing from direct contact with oxygen and water (triggers agents). As a result, the formation of AMD will be prevented or minimized to acceptable levels. The implementations of these traditional disposal methods have some environmental and economic

issues (Bowker and Chambers, 2015). In addition, due to more stringent environmental legislations, these issues have driven miners and researchers to search for alternative disposal and storage techniques in terms of cost-effective, environmental and sustainable manner. As a result, several methods have been proposed and practiced over the world to manage reactive mine wastes (e.g., sulphidic tailings). Among these alternative disposal methods, cemented paste tailings (CPT) appears to be appropriate technology for managing sulphidic tailings in a more environmental-friendly manner. It has several advantages over traditional and alternative methods, such as reduction of surface storage, improving mine production and reducing environmental impacts. Due to the multi-advantages of CPT technology, it has been widely and increasingly used in many underground mines around the world, such as in North America, Australia, China, and Turkey.

The CPT can simply be described as a cementitious material that consists mainly of three ingredients, namely thickening tailings (dominant; solid percentage commonly between 75 to 85%), binder (3-7% by dry mass of tailings, often) that can be Portland cement alone or partially replaced with mineral admixtures, and mixing water which could be either fresh water or processing water. The fresh CPT mixture is transported by gravity and/or pumping to fill the desired mined voids (stopes) in the underground mine. This fluidic mixture will solidify with time and gain the required strength (mainly due to the progress of binder hydration) to stand like a “concrete” structure in underground mine.

Environmental and durability are two important aspects in the design of CPT structures. This environmental performance and durability of CPT is strongly influenced by the ability of the sulphide minerals (pyrite) to oxidize (chemically react with  $O_2$ ) within the CPT system. This chemical reaction could lead to the generation of sulphate ions and acidity, and thus to a degradation of CPT by sulphate attack and to a formation of AMD (Tariq and Yanful, 2013; Fall et al., 2005). Therefore, the measurement of the chemical reactivity (with respect to  $O_2$ ) of the CPT can be a good indicator for understanding the environmental performance of sulphidic CPT system with respect to the generation of AMD.

Hence, there are several direct and indirect methods proposed and conducted to determine the reactivity of mine wastes or CPT, such as the sulphate release and oxygen gradient methods, and oxygen consumption (OC) testing (Ouellet, et al., 2006, 2003; Elberling and Nicholson, 1996; Elberling et al., 1994). Among these methods, OC is considered as a direct technique that can be used to measure the reactivity of sulphidic mine wastes by measuring rate of oxygen consumption

through oxidation of sulphide minerals. Also, OC test overcomes the drawbacks (commonly overestimation) of other methods, such as column leach tests and humidity cells (Schmieder et al., 2012). OC tests were used in several previous studies to assess the oxidation rate of sulphide minerals (e.g., pyrite) and the reactivity of sulphide mineral-bearing tailings based materials alone and/or incorporated in cemented paste backfill mixtures (e.g., Aldhafeeri, Fall et al., 2016; Aldhafeeri and Fall, 2016; Fall and Pokharel, 2010; Pokharel, 2008; Ouellet et al., 2006, 2003; Fall et al., 2004).

During the last decades, the majority of studies performed on CPT have mainly focused on the mechanical properties and behaviour of the CPT (e.g., Ghirian and Fall, 2016; Koohestani et al., 2016; Yilmaz et al., 2014; Fall et al., 2007). On the other hand, a few studies have investigated the reactivity of the CPT system by performing OC tests (e.g., Aldhafeeri et al., 2016; Aldhafeeri and Fall, 2016; Pokharel, 2008; Ouellet et al., 2003; Fall et al., 2004). These studies have examined the influence of a few factors on the CPT reactivity that include sulphide (commonly pyrite) content, moisture content and temperature. They concluded that the reactivity of CPT system increases with an increase of its sulphide content and decreases with an increase of its moisture content. Aldhafeeri et al. (2016) also indicated that the reactivity of CPB is temperature dependent. However, despite these positive findings, there are still other important factors that can significantly affect the reactivity of CPT system, and thus its environmental and durability performance. One of these key factors is the initial sulphate content of the CPT. Frequently, CPTs contain various amounts of sulphate ions. The sulphate ions can originate from different sources, such as pre-oxidized sulphidic tailings that are used in CPT mix, the residual mineral processing water in the thickened tailings, gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) or anhydrite ( $\text{CaSO}_4$ ) that are added within small portion to cement clinker to act as setting regulator, and the mixing water that is either mine processing and fresh water (Li and Fall, 2016; Fall and Pokharel, 2010). The concentrations of sulphates ions that are present in paste backfill system vary from relatively low (<5000 ppm) to very high ( $\geq 25,000$  ppm) (Fall and Pokharel, 2010). However, no study has investigated the effect of the initial sulphate of CPT on its reactivity. Most of the previous studies on the influence of initial sulphate on the CPT have focused only on the effect of initial sulphate content on the mechanical properties (i.e., strength) of the paste backfill structures in short- and long-term. Therefore, the main objective of this research is to experimentally study the effect of initial sulphate content on the reactivity of mature sulphidic-CPT specimens by conducting OC tests. In

addition to OC tests, microstructural analyses are performed on selected specimens to gain better understanding of the microstructural changes induced by initial sulphate content and their impact on the reactivity of CPT.

## 5.2 Experimental Programs

### 5.2.1 Materials

#### 5.2.1.1 Tailings

Pure silica powder (SIL-CO-SIL 106, manufactured by U.S. Silica Co.), which is essentially made of quartz (99.8 wt. %), was chosen to be used as basic artificial tailings (ST) in all of the CPT specimens in this work to eliminate the uncertainties related to natural tailings. Indeed, besides sulphide minerals, natural tailings contain other reactive minerals that interact with the cement hydration and thus affect the reliability of the results obtained and their interpretation. Also, quartz is one of the main minerals found in Canadian hard rock mine tailings. Silica powder is characterized by chemical inertness and its grain size distribution corresponds to the average of particle size distribution of nine eastern Canadian mines, as shown in Figure 5.1. Table 5.1 shows the primary physical properties of the tailings used.

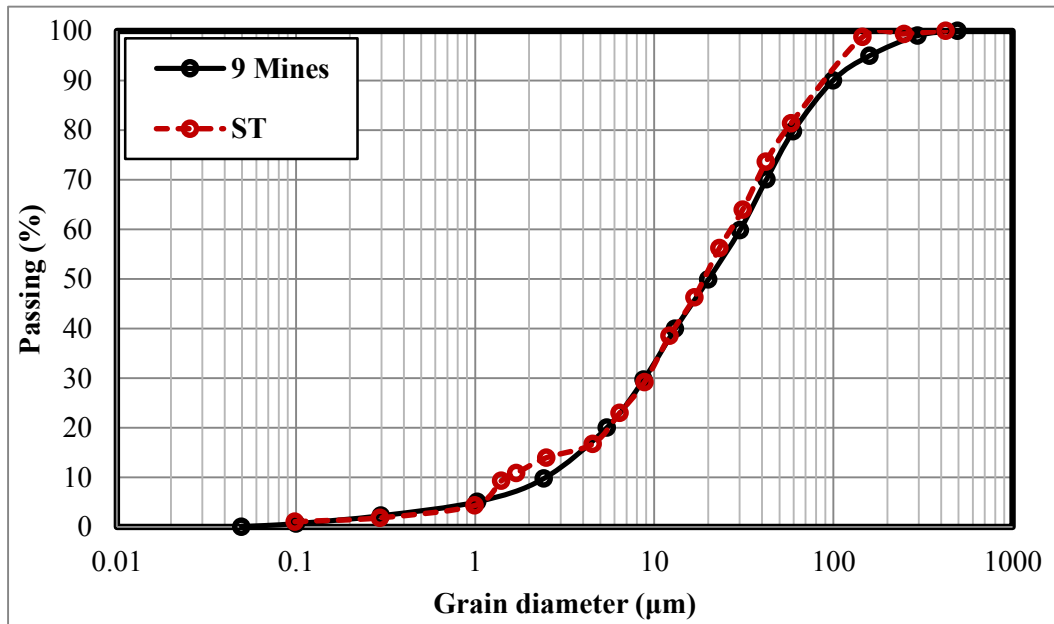


Figure 5.1. Grain size distribution of the tailings (ST) used and the average grain size distribution of tailings from 9 eastern Canadian mines

Table 5.1. Primary physical properties of the tailings used

Tailings	Gs	D <sub>10</sub> (μm)	D <sub>30</sub> (μm)	D <sub>50</sub> (μm)	D <sub>60</sub> (μm)
ST	2.7	1.9	9.0	22.5	31.5

### 5.2.1.2 Pyrite

To prepare pyrite-bearing tailings, the tailings were mixed with a specific amount (45% wt.) of a commercial pyrite powder (FeS<sub>2</sub>, M.W. = 119.98, Washington Mills North Grafton, Inc.). This pyrite powder has the same particle size as the pyrite minerals commonly found in natural tailings. The physical characteristics of the used pyrite powder are presented in Table 5.2. The prepared pyrite bearing tailings (ST-45% wt. of Pyrite) were then used for the preparation of the CPT specimens.

Table 5.2. Physical properties of pyrite (Source: Washington Mills North Grafton, Inc.)

Bulk density (g/cm <sup>3</sup> )	Density at 20°C (g/cm <sup>3</sup> )	Specific gravity	pH	Melting point (°C)
2.35	4.7	4.6	4.0- 6.0	1193

### 5.2.1.3 Binders used

Portland cement type I (PC) was used as basic binder agent in CPT mixes. In addition to PC, two mineral admixtures, namely granulated blast furnace slag (SA) and Fly ash type C (FA) were used as partial replacement of PC with 25%, 50% and 75% of its total weight. These blend binders were identified as PF for a mix of PC with FA and PS for a mix of PC with SA. The chemical properties of PC, SA and FA are presented in Table 5.3.

Table 5.3. Chemical properties of the cement and mineral admixtures used

Binder	MgO (wt. %)	CaO (wt. %)	SiO <sub>2</sub> (wt. %)	Al <sub>2</sub> O <sub>3</sub> (wt. %)	Fe <sub>2</sub> O <sub>3</sub> (wt. %)	SO <sub>3</sub> (wt. %)	Relative density
PC	2.65	62.82	18.03	4.53	2.7	3.82	3.1
SA	10.98	41.14	34.23	9.54	-	3.87	3.3
FA (Class C)	5.58	21.47	38.06	19.45	5.33	2.7	2.6

#### **5.2.1.4 Mixing Water**

Distilled water (DW) was used as basic mixing water to prepare all of the CPT specimens. To study the influence of the initial sulphate content, mixing waters with various concentrations of sulphate (0, 5000, 15,000 and 25,000 ppm) were prepared by mixing defined amounts of sulphate salt (Ferrous Sulphate Heptahydrate,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , F.W. = 278.01, Fisher Chemical Inc.) powder with a specific volume of DW. Ferrous sulphate was chosen because it is a most common sulphate type found in cemented backfills (Fall and Pokharel, 2010).

### **5.2.2 Sample Preparation**

#### **5.2.2.1 Mix Proportions**

Over 100 CPT specimens were prepared using selected amount of ST containing 45 wt % of pyrite mineral, three types of binder with different binder content (3, 4.5 and 6 %) and DW. The water to binder ratio (w/b) was maintained at 7.6 in this work. All specimens were mixed by small food mixer for 7 minutes until obtaining homogenous CPT material with a slump value of 18 cm (according to the slump test). The slump tests were performed in accordance with ASTM C143-90. The above mixing formula was chosen because it is often used for CPT in Canadian underground mines. The CPT pastes were poured into curing cylinders (PVC moulds of 10 cm in height and 5 cm in diameter). During the pouring of the pastes, moulds were manually vibrated to remove any air. Finally, they were closed by their plastic covers sealed with plastic tape to prevent the evaporation of water and cured in environmental room at temperature ( $22 \pm 1^\circ\text{C}$ ) for a period of 150 days.

The experimental work was divided into three parts to study: (i) effect of initial sulphate content on the reactivity of CPT made of various types of binder, (ii) combined effect of binder content and sulphate on the reactivity of CPT made of various types of binder (initial sulphate content = 25000 ppm), and (iii) combined effect of the proportion of mineral admixtures and sulphate on the reactivity of CPT made of various types of binder (initial sulphate content = 25000 ppm). Tables 5.4 to 5.6 present the CPT mixes for each experimental part. Furthermore, for microstructural analysis, over 20 binder paste specimens (w/c =1; to simulate the high water content of CPT) were prepared for each part of the experimental work at the same conditions and curing time.

Table 5.4. Mix design of the prepared CPT samples to study the effect of initial sulphate content

<b>CPT Sample</b>	<b>Binder</b>	<b>Blending ratio (%)</b>	<b>Binder content (%)</b>	<b>Tailings Type</b>	<b>Pyrite content (%)</b>	<b>w/c ratio</b>	<b>[Sulphate] (ppm)</b>	<b>Curing time (Day)</b>
PC-CPT-0	PC	-	4.5	ST	45%	7.6	0	150
PC-CPT-5	PC	-	4.5	ST	45%	7.6	5,000	150
PC-CPT-15	PC	-	4.5	ST	45%	7.6	15,000	150
PC-CPT--25	PC	-	4.5	ST	45%	7.6	25,000	150
PS-CPT-0	PC:SA	50:50	4.5	ST	45%	7.6	0	150
PS-CPT-5	PC:SA	50:50	4.5	ST	45%	7.6	5,000	150
PS-CPT-15	PC:SA	50:50	4.5	ST	45%	7.6	15,000	150
PS-CPT--25	PC:SA	50:50	4.5	ST	45%	7.6	25,000	150
PF-CPT-0	PC:FA	50:50	4.5	ST	45%	7.6	0	150
PF-CPT-5	PC:FA	50:50	4.5	ST	45%	7.6	5,000	150
PF-CPT-15	PC:FA	50:50	4.5	ST	45%	7.6	15,000	150
PF-CPT--25	PC:FA	50:50	4.5	ST	45%	7.6	25,000	150

SA: Slag; FA: Fly ash (Class C); PC: Portland cement type I; PS: mix of Portland cement type I and Slag; PF: mix of Portland cement type I and Slag

Table 5.5. Mix design of the prepared CPT samples to study the effect of binder content and sulphate

<b>CPT Sample</b>	<b>Binder</b>	<b>Blending ratio (%)</b>	<b>Binder content (%)</b>	<b>Tailings Type</b>	<b>Pyrite content (%)</b>	<b>w/c ratio</b>	<b>[Sulphate] (ppm)</b>	<b>Curing time (Day)</b>
PC-CPT-3%	PC	-	3.0	ST	45%	7.6	25,000	150
PC-CPT-6%	PC	-	6.0	ST	45%	7.6	25,000	150
PS-CPT-3%	PS	50:50	3.0	ST	45%	7.6	25,000	150
PS -CPT-6%	PS	50:50	6.0	ST	45%	7.6	25,000	150
PF-CPT-3%	PF	50:50	3.0	ST	45%	7.6	25,000	150
PF -CPT-6%	PF	50:50	6.0	ST	45%	7.6	25,000	150

Table 5.6. Mix design of the prepared CPT samples to study the effect of blending ratio and sulphate

<b>CPT Sample</b>	<b>Binder</b>	<b>Blending ratio (%)</b>	<b>Binder content (%)</b>	<b>Tailings Type</b>	<b>Pyrite content (%)</b>	<b>w/c ratio</b>	<b>[Sulphate] (ppm)</b>	<b>Curing time (Day)</b>
PS-CPT-75	PC:SA	25:75	4.5	ST	45%	7.6	25,000	150
PS-CPT-25	PC:SA	75:25	4.5	ST	45%	7.6	25,000	150
PF-CPT-75	PC:FA	25:75	4.5	ST	45%	7.6	25,000	150
PF -CPT-25	PC:FA	75:25	4.5	ST	45%	7.6	25,000	150

## 5.3 Testing of Specimens

### 5.3.1 Oxygen Consumption Tests

The OC method, proposed by Elberling et al. (1994), is a measurement of the depletion rate of oxygen in a reservoir with a fixed volume by considering time (Pokharel, 2008; MEND, 2006). The theory behind the OC test originates from the diffusion of oxygen and consumption of oxygen by sulphide minerals for oxidation. The main assumption behind this test is that the steady state condition ( $\delta C/\delta t = 0$ ) will be maintained from the beginning to the end of the test (Pokharel, 2008). In research by Pokharel (2008), who used the same test, he applied a monitoring method, which was purposed by Elberling and Nicholson (1996), to monitor the oxygen concentration in a sealed chamber that contained an oxygen sensor for every 5 minutes to over 120 minutes. The OC test was conducted in the lab by digging a 2 cm oxygen chamber in the cylinder before the beginning of the test (Pokharel, 2008). The same approach is used in the present study. The type of sensor that is applied in this test to measure the oxygen concentration is the GC33-200 manufactured by GC Industries in California. This oxygen sensor was connected to the voltmeter and the number of voltage recorded was directly proportional to the partial pressure of oxygen in the gas phase (Pokharel, 2008). To initiate the testing, the oxygen sensor was carefully fixed onto the lid of the cylinder above the active materials.

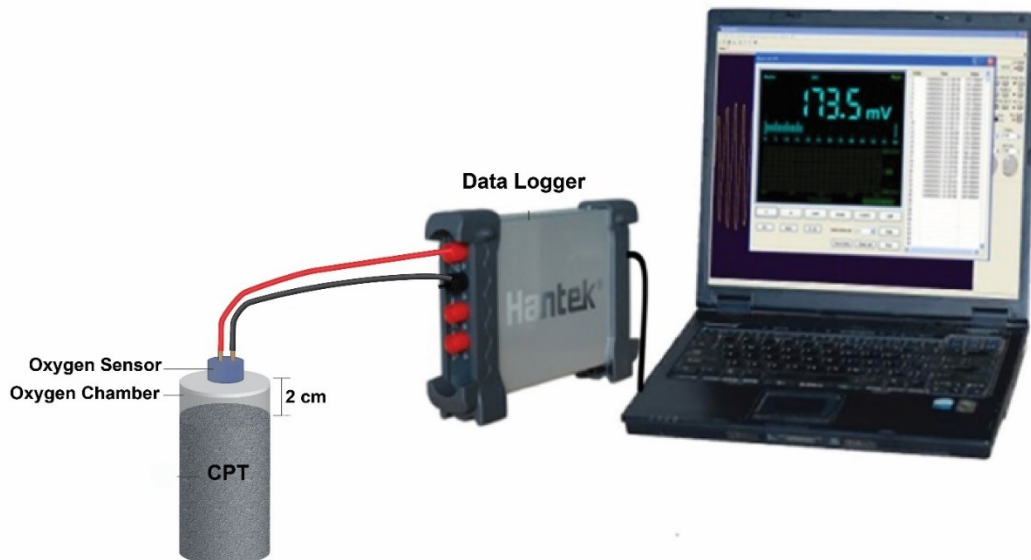


Figure 5.2. Schematic of experimental setup of OC testing

The reactivity of CPT specimens can be calculated by measuring the flux of oxygen ( $F_L$ ) through the specimens. The oxygen  $F_L$  is calculated by the two following equations, (Eqs. 5.1 and 5.2), which were proposed by Elberling et al. (1994) and Elberling and Nicholson (1996):

$$F_L = C_o (K_r D_e)^{0.5} \quad (5.1)$$

where  $K_r$  is the first-order reaction rate coefficient for sulphide mineral oxidation (e.g., pyrite),  $D_e$  is the effective diffusion coefficient and  $C_o$  is the initial concentration of oxygen. The term  $(K_r D_e)$  can be obtained from the slope of plotting  $\ln(C/C_o)$  versus time based on Eq. 5.2. It can be calculated if the volume of the gas chamber ( $V$ ) and the surface area of the exposed area of the reactive materials ( $A$ ) are known (Ouellet et al., 2006).

$$\ln(C/C_o) = -t (K_r D_e)^{0.5} (A/V) \quad (5.2)$$

### 5.3.2 Microstructural Analyses

In this study, various types of microstructural analysis techniques were used to evaluate the influence of initial sulphate content on the microstructure of the CPT specimens, such as pore structure and binder hydration progress and products. X-ray diffraction (XRD) and thermal analysis (TG/DTG) were used to identify and characterize the mineralogical composition of selected CPT and hardened cemented paste (hcp) specimens with various sulphate contents cured at room temperature for 150 days. Also, Mercury Intrusion Porosimetry (MIP), which is an analytical technique that is widely used to characterize the pore structure of cementitious materials, was used. The influence of initial sulphate content on the microstructure or pore structure of the CPT specimens was also investigated by using Scanning Electron Microscopy (SEM). The specimens were firstly dried at 50°C in a vacuum oven to remove the free water before they were subjected to microstructural analyses. The XRD tests were conducted by using a Scintag XDS-2000 diffractometer, which is a multi-purpose powder diffractometer with KEVEX Peltier Cooled Silicon Detector. The SEM investigation was conducted in a Hitachi S4800 field emission scanning electron microscope. The MIP tests were conducted on the CPB samples by using a Micromeritics AutoPore III 9420 mercury porosimeter according to ASTM D4404-10. The thermal analyses were conducted by using a simultaneous thermogravimetric analyzer and

differential scanning calorimeter (SDT) from TA Instruments, which enabled the simultaneous registration of changes in weight, heat flow and transition in temperature of the sample.

## **5.4 Results and Discussions**

### **5.4.1 Effect of Initial Sulphate Content on the Reactivity of CPT Made of Various Types of Binder**

Figure 5.3 shows the mean and standard deviation of the reactivity values of sulphidic-CPT (45wt. % pyrite) specimens made from three binder types (PC, PS and PF) and with various initial sulphate contents (0, 5000, 15,000 and 25,000 ppm). From this figure, it can be seen that the reactivity of all CPT specimens generally increases with an increase in their initial sulphate content regardless of the binder type (except for samples with 5,000 ppm initial sulphate content; will be discussed later). This increase in the reactivity can be attributed to the disruptive effect of sulphate ( $\text{SO}_4^{2-}$ ) ions on CPT specimens. The  $\text{SO}_4^{2-}$  ions react with cement hydration products, such as calcium hydroxide (Portlandite, CH) and with the components of the cement clinker, tri-calcium aluminate ( $\text{C}_3\text{A}$ ), in the CPT system (Pokharel and Fall, 2013). This reaction can have negative effect on the microstructure (e.g., pore structure, porosity) of CPT, such as coarsening of the pore structure and presence of micro-cracks in the cemented matrix of CPT as demonstrated by several previous studies on internal sulphate attack on CPT (e.g., Pokharel and Fall, 2013; Fall et al., 2009; Pokharel, 2008; Ouellet et al., 2006; Benzaazoua et al., 2002, 1999). A coarsening of the pore structure and/or the presence of micro-cracks is obviously associated with an increase of the  $\text{O}_2$  diffusion into the CPT specimen and thus greater reactivity (see Eq. 5.1). This negative effect on the microstructure results from the combined effects of two main mechanism or factors: (i) the sulphate-induced inhibition of binder hydration reactions, which leads to coarser pore structure of the CPT specimen due to the formation of lower amount of binder hydration products (Pokharel and Fall, 2011; Fall and Pokharel, 2010; Kesimal et al., 2004; Benzaazoua et al., 2002; Ouellet et al., 1998); (ii) and the formation of excessive amount of secondary expansive minerals (e.g., ettringite and gypsum) that induce internal stresses that can physically damage the CPT matrix and thus lead to the generation of micro-cracks (Hurdowski, 2014; Bonakdar and Mobasher, 2010; Fall and Pokharel, 2010). This argument with respect to the inhibition of the binder hydration by high sulphate content (25,000 ppm) agrees well with the X-ray analysis results of the 150 days old 25,000 ppm cemented paste samples for the different types of binder studied (PCI, PS, PF), presented in Figure 5.4. The results show the presence of unreacted clinker phases,  $\text{C}_3\text{S}$  and  $\text{C}_2\text{S}$ ,

in the 25,000 ppm CPT specimen regardless of the type of binder. These clinker phases were not observed in the the X-ray analysis results of the 150 days old cemented paste sample with low sulphate content (5,000 ppm) presented in Figure 5.5. The aforementioned coarsening of the pore structure of CPT that results from the sulphate-induced inhibition of the binder hydration is experimentally supported by the results of pore structure analysis (MIP) presented in Figure 5.6. This figure shows the MIP test results for PC-CPT samples with no sulphate and 25,000 ppm of sulphate content, respectively. It can be seen that the pore size distribution of the 25,000 ppm-CPT is coarser than that of the specimen with 0 ppm sulphate content. Furthermore, the threshold diameter (the pore size corresponding to the highest rate of mercury intrusion per change in pressure, (Manmohan and Mehta, 1981)) value of the 25,000 ppm-CPT (1.8  $\mu\text{m}$ ) is higher than that of the CPT without sulphate (1.6  $\mu\text{m}$ ). In other words, this means that the 25,000 ppm CPT has higher fluid transportability, since the threshold diameter is characteristic of a capillary network connected to the surface of the cemented porous media (Manmohan and Mehta, 1981). Moreover, SEM observations in Figure 5.7 of highly sulphated CPT samples, published elsewhere (Fall et al., 2009), fully supports the assumption mentioned above with respect to the destructive effect (formation of micro-cracks) by the expansive minerals (ettringite, gypsum) on the cemented matrix of CPT. Figure 5.7 clearly shows that secondary gypsum minerals that fill the pores of CPT have physically damaged the CPT. Also, the figure shows a number of cracks in the sulphated specimen. These cracks may provide preferential paths for ingress of  $\text{O}_2$  and thus lead to increase of the reactivity. However, from Figure 5.3 it can be seen that the reactivity of specimens with 5,000 ppm sulphate content slightly decreased compared with other sulphated specimens and even with sulphate-free specimens. This positive phenomenon can be attributed to the formation of appropriate amount (not excessive) of expensive minerals, such as ettringite and gypsum, within the capillary pores in 5,000 ppm-CPT matrix without applying excessive pressure on the pore of the matrix. This will reduce the porosity of specimens through reducing connected capillary pores and refining capillary pores (Li and Fall, 2016; Pokharel and Fall, 2013; Ouellet et al., 2007, 2006; Fall et al., 2005; Benzaazoua et al., 2002). Consequently, it reduces the diffusion coefficient of specimen and diminishes ingress of oxygen into the specimen, thereby reducing the reactivity of specimen. A comparative analysis of the XRD results presented in Figures 5.4a and 5.5 confirms a lower proportion of ettringite and gypsum has formed in the 5,000 ppm CPT samples than in the 25,000 ppm CPT. This refining of the pore structure of CPT induced by low sulphate content has

been observed and reported by several previous studies on sulphated CPT (e.g., Li and Fall, 2016; Pokharel and Fall, 2013; Ouellet et al., 2007; Fall and Benzaazoua, 2005; Benzaazoua et al., 2004).

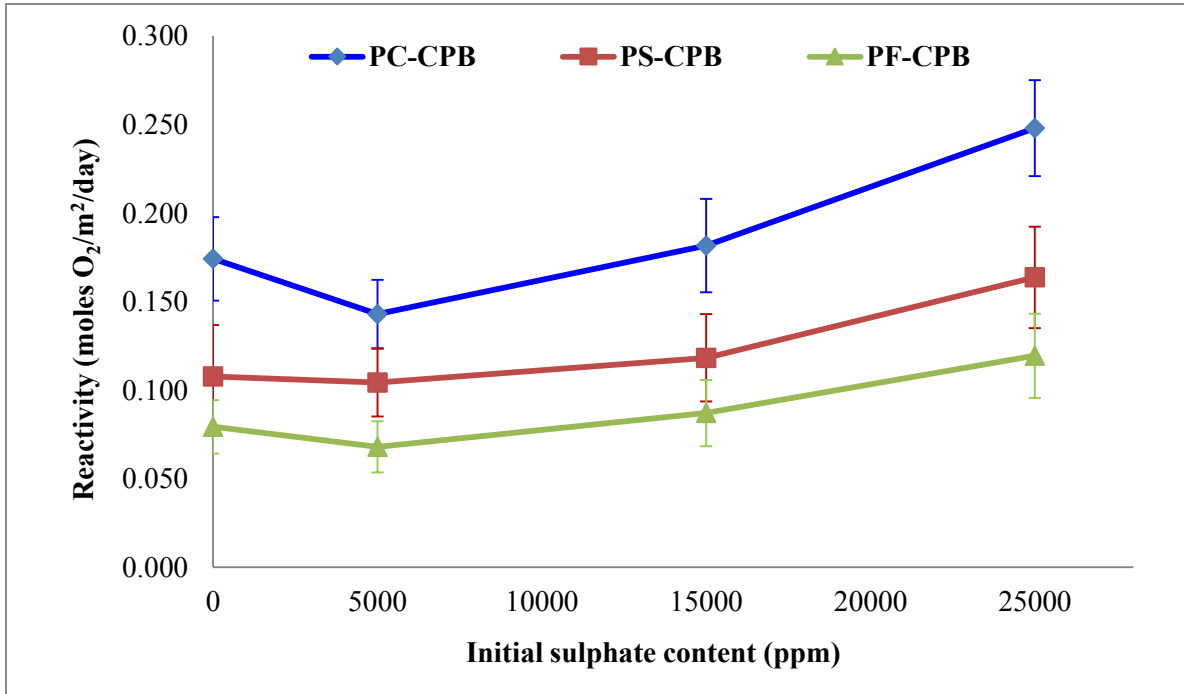
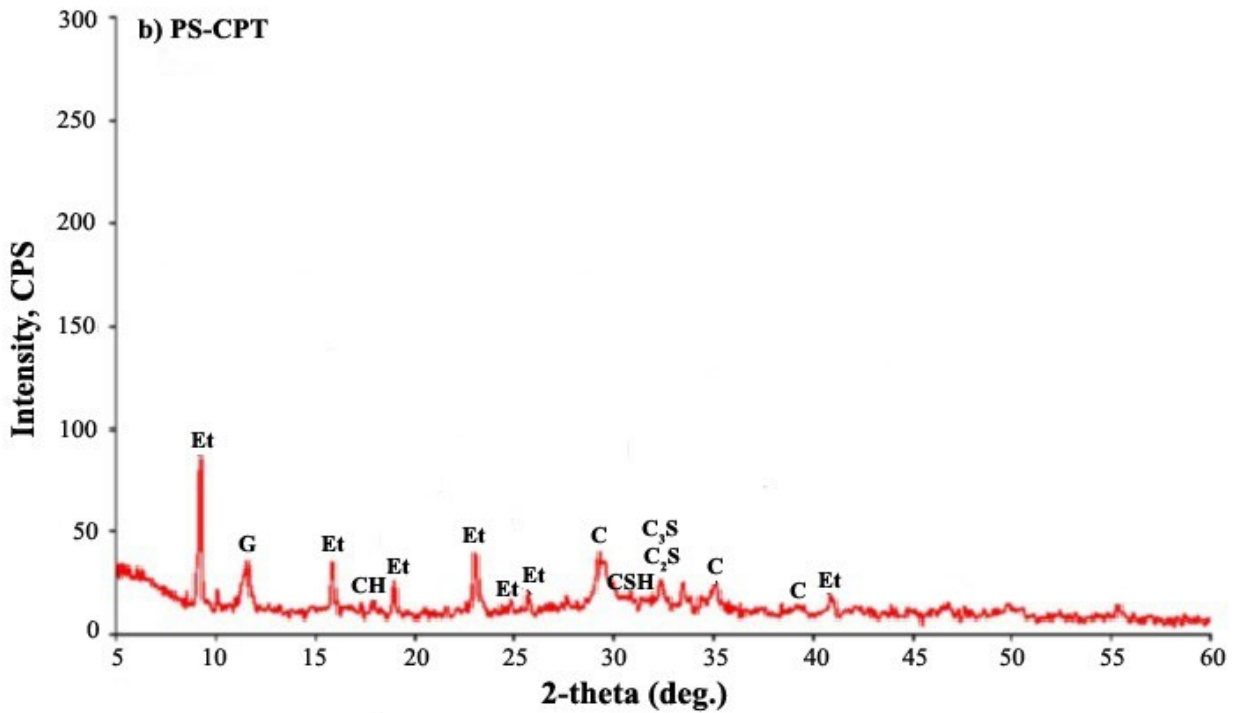
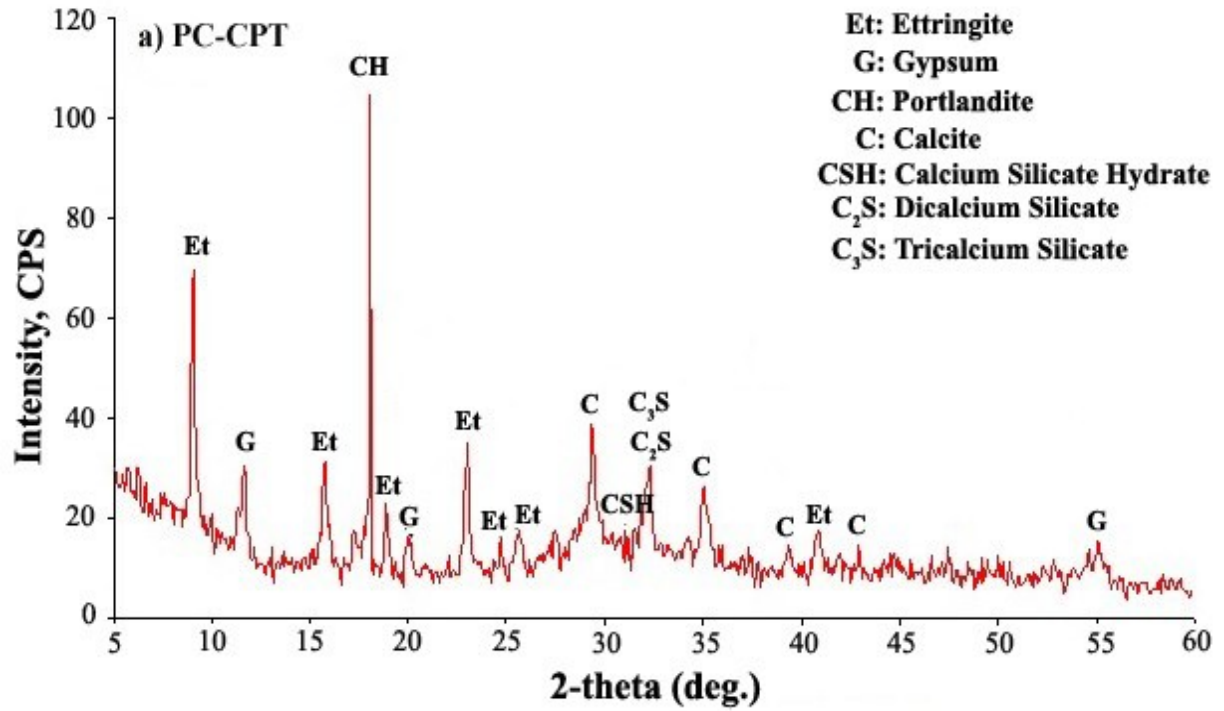


Figure 5.3. Effect of initial sulphate content on the reactivity of CPT made of various types of binder



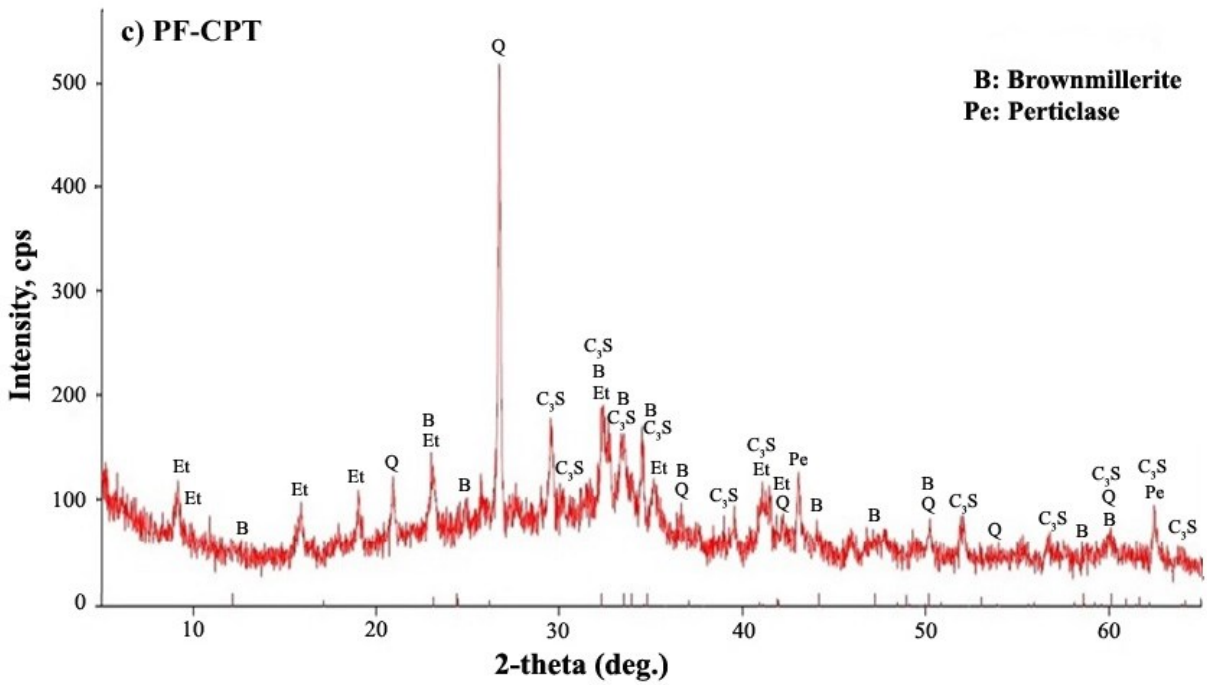


Figure 5.4. XRD result 150-day age PC- paste specimens with an initial sulphate content of 25,000 ppm: a) PC-CPT; b) PS-CPT; c) PF-CPT

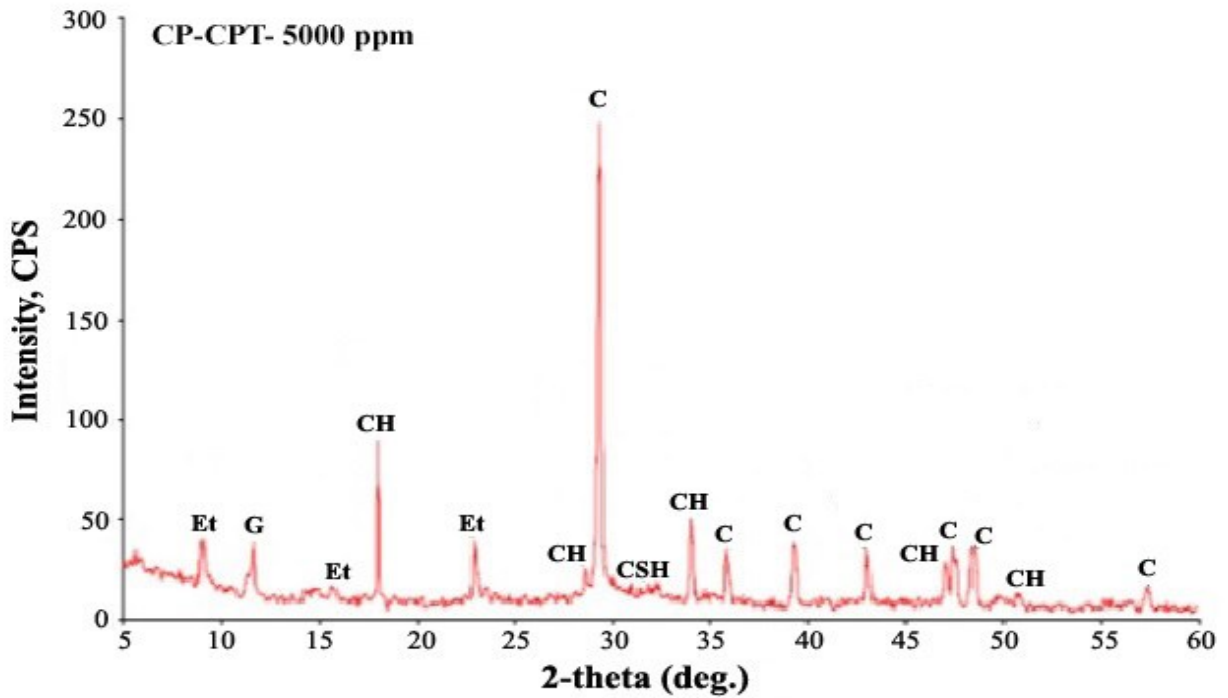


Figure 5.5. XRD result 150-day age PC-paste specimens with an initial sulphate content of 5000 ppm

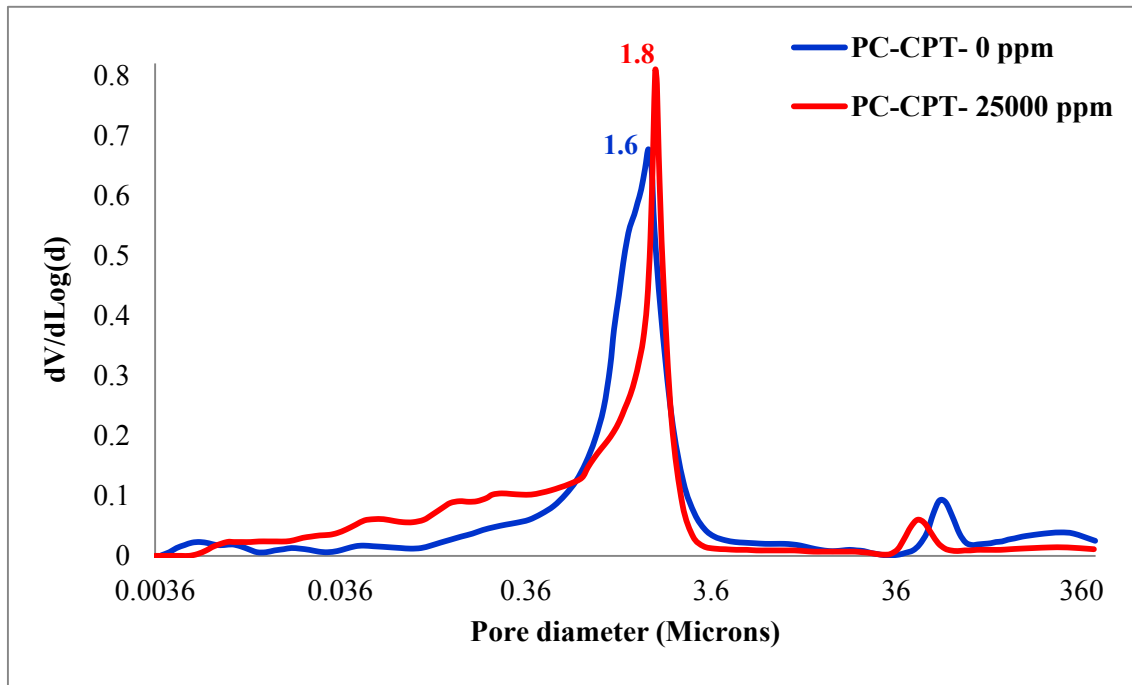


Figure 5.6. Pore size distribution of 150-day old CPT samples with 0 ppm and 25,000 ppm initial sulphate content

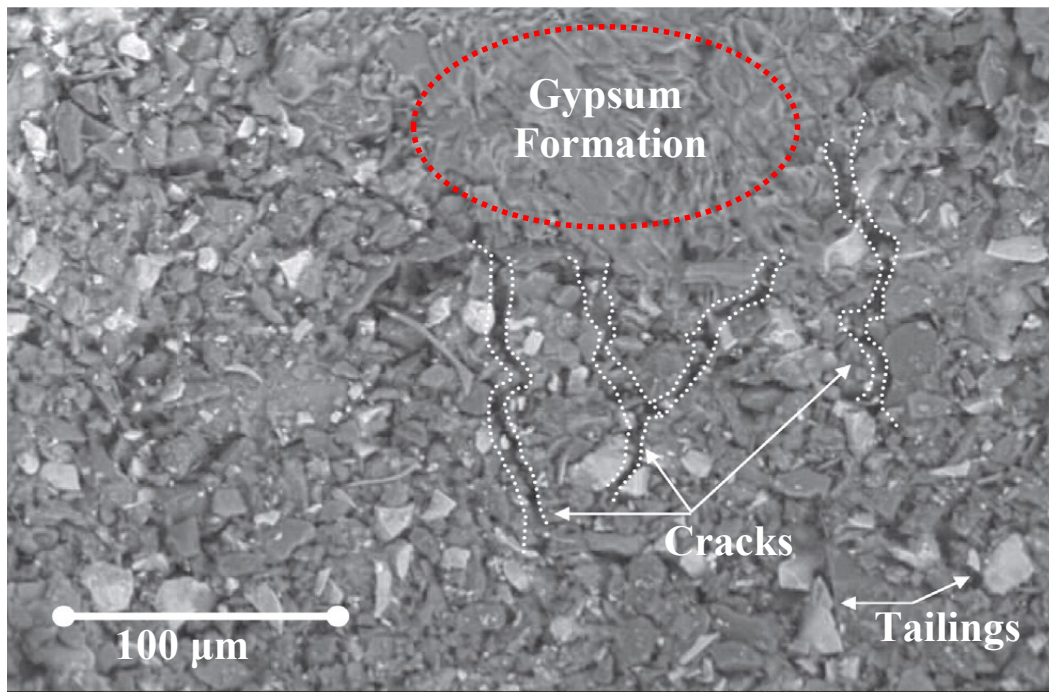


Figure 5.7. SEM micrograph of the CPT specimen cured with 25000 ppm sulphate content for 150 days at 20°C

Moreover, one can observe in Figure 5.3 that PS-CPT and PF-CPT specimens exhibited the same reactivity trend as that made from PC alone but with lower values. For instance, the reactivity of the PS-CPT specimens with an initial sulphate content of 5,000, 15,000 and 25,000 ppm is reduced by 38, 27, 35, and 34 % compared the reactivity of the PC-CPT specimens with the same initial sulphate content , respectively. It can be seen that the PF-based CPT specimens have the lowest reactivity values as compared with other specimens. This significant reduction in reactivity of PS- and PF-CPT specimens as compared to those made from PC alone is related to two main reasons. The first reason is the high degree of saturation of CPT due to lower water consumption of the hydration of the blended binder (Ayub et al., 2013; Thomas, 2013; Boukendakdji et al., 2012). As a result of the high degree of saturation, the oxygen diffusion rates through water-filled pore spaces in the specimen matrix decreases due to the fact that the diffusion rate of oxygen through the water media is slower about 1, 0000 times than through air media (Mbonimpa et al., 2002; Brix and Schierup, 1990). This argument is supported by the results of the degree saturation of mature CPT specimens made of various binders, constant 4.5 binder content and  $w/c = 7.6$ , as shown in Figure 5.8. The Figure 5.8 presents the degrees of saturation of 150-day old CPT specimens made of various binder types. From the figure, it can be observed that PS- and PF-CPT specimens exhibit higher degree of saturation than those made of PC alone. The micro-filler effect of SA and FA (Siddique and Khan, 2011; Şahmaran et al., 2009; Termkhajornkit et al., 2006; Isaia et al., 2004) is the second reason that could have provided the CPT with blended binders finer pore structure, which is obviously associated with lower effective diffusion coefficient of oxygen ( $D_e$ , see Eq. 5.1). This argument with respect to the micro-filler effect induced pore refinement is in agreement with the SEM images of the CPT with different binders presented in Figure 5.9. The figure presents the SEM observations of CPT containing various binder types cured with high initial sulphate content. These images show that the blend cement based CPT specimens possess more refined and denser microstructure than that those made of PC alone. In addition to SEM observations, TG/DTG curves for 150-day old PC, PS and PF pastes of CPT cured with 25,000 ppm of initial sulphate content show in Figure 5.10. The DTG curve represents the temperature at which thermal decompositions of various hydrated phases occur in hardened cement paste, whereas DTG simultaneously reflects the weight loss as a result of these decompositions. It has been reported that the thermal decomposition of cement pastes took place in three key stages: (a) dehydration of water molecules in hydrates such as C-S-H, carboaluminates, ettringite, and gypsum occurred

within the range from room temperature to 200°C; (b) dehydroxylation of calcium hydroxide ( $\text{Ca}(\text{OH})_2$ , also called portlandite, (CH)) in the range of 410 – 550°C; and (c) decarbonation of calcium carbonate ( $\text{CaCO}_3$ ) at 680 – 750°C (Li and Fall, 2016; He et al., 2014; Gomes et al., 2005; Hewlett, 2004; Ramachandran et al., 2002; Taylor, 1997). From these curves, one can be seen two distinct exothermic peaks. The first peak appeared between 50 to 125°C can be related to the dehydration of hydrates (e.g., C-S-H and ettringite), whereas the second peak located between 400 and 435°C can be attributed mainly to the dehydroxylation of portlandite. The decomposition peaks of calcium carbonate at 680–750°C cannot be easily observed in the DTG curves. This is due to the intensity of peaks decrease as hydration proceeds (Dweck et al., 2000). Also, it can be noted that PC-CPT specimen has a higher peak and weight loss at 400 – 450°C related to decomposition of portlandite than that containing blended cement. The PF-CPT has the lowest peak and weight loss. The thermal analysis results indicate that the addition of mineral admixtures (e.g., FA and SA) as a partial replacement cement leads to less expensive minerals (e.g., gypsum) would be formed within the CPT matrix. This means the potential of CPT to be damaged (formation of micro-cracks) by excessive pressure of gypsum will be less in CPT made of blended cements.

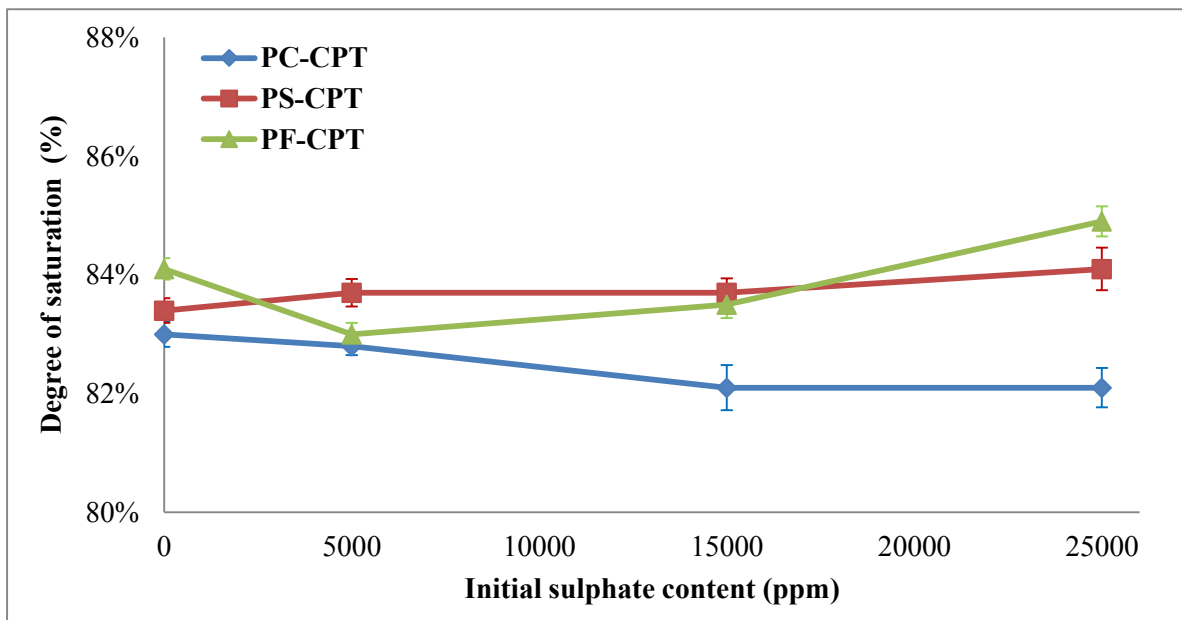
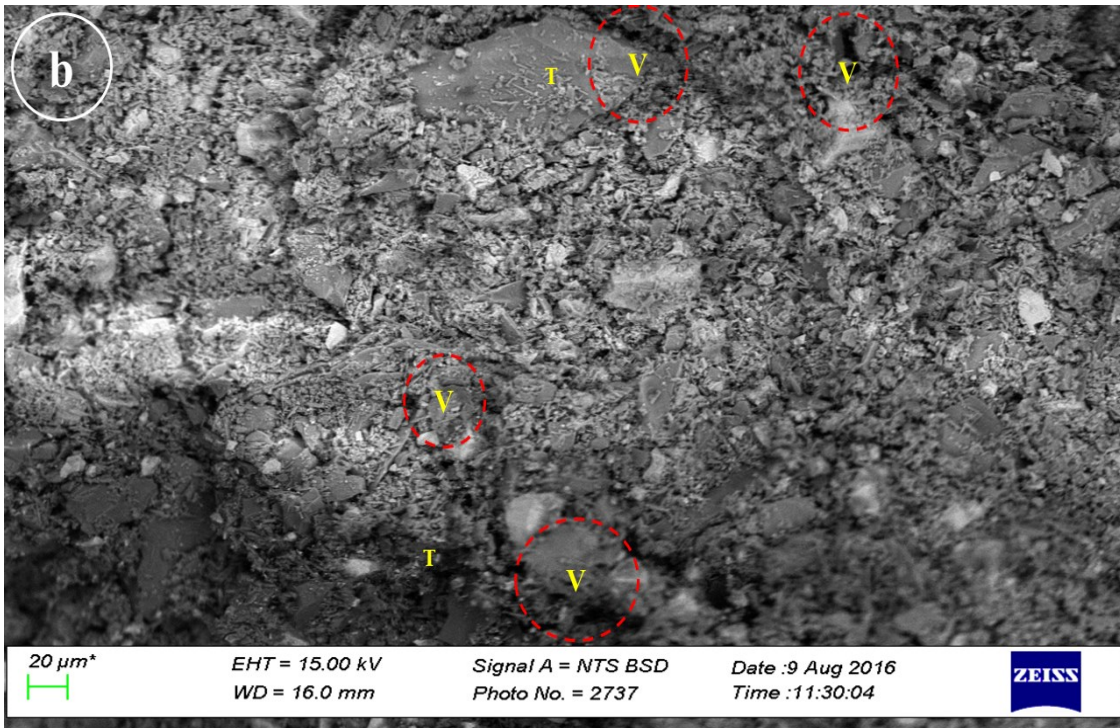
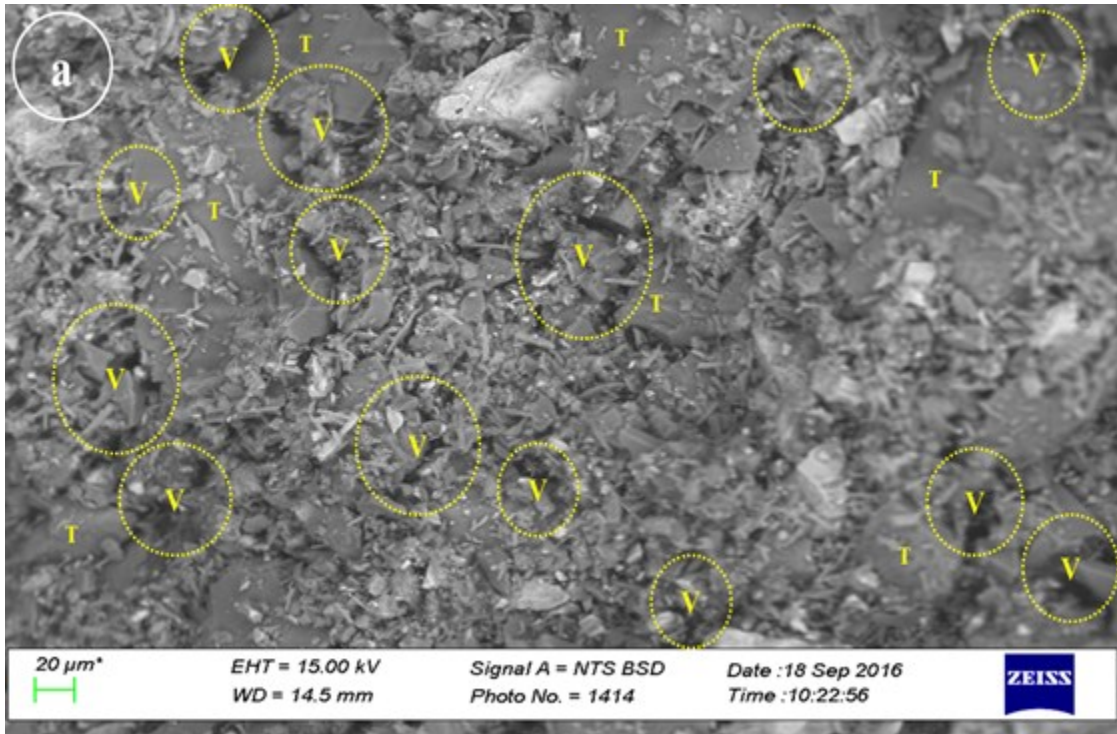


Figure 5.8. The degree of saturation of 150-day old CPT samples with different type of cements (PC, PS and PF)



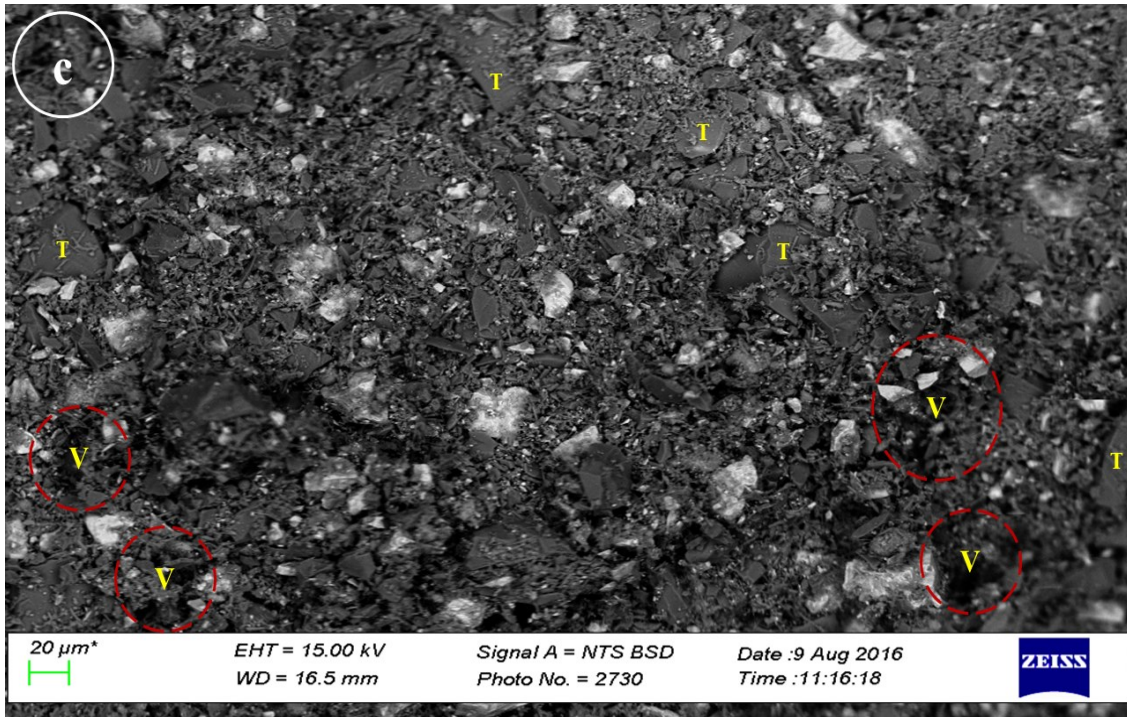


Figure 5.9. The SEM micrographs of 150-day old CPT samples with different type of cements cured with 25,000 ppm sulphate content: a) CP-CPT; b) PS-CPT and c) PF-CPT (T: Tailings, V: Void)

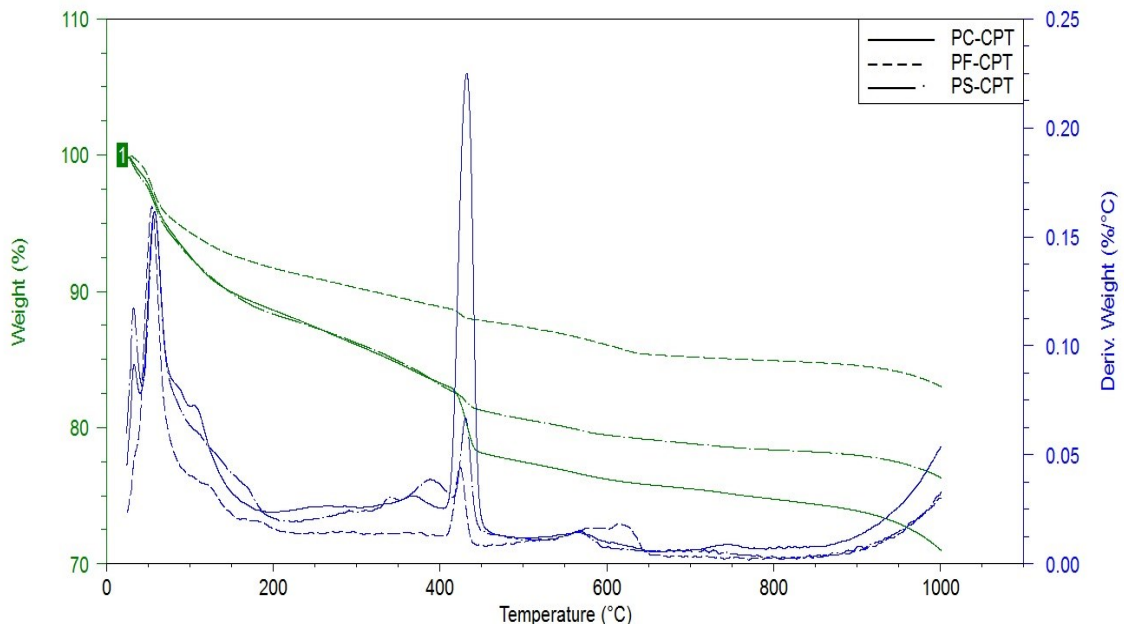


Figure 5.10. TG / DTG curves for 150-day old PC, PS and PF pastes of CPT cured with 25,000 ppm of initial sulphate content

### 5.4.2 Effect of Binder Content and Sulphate on the Reactivity of CPT Made of Various Types of Binder

Figure 5.11 shows the average of three reading with standard deviations of reactivity CPT specimens cured with various types (PC, PS and PF) and contents (3%, 4.5 and 6%) of binder and with a constant sulphate content (25,000 ppm) for 150 days. It can be seen from the figure, that as expected, the reactivity of specimens decrease, as the binder content increases, regardless of the binder type. This decline trend in reactivity of PC-CPT specimens can be explained by the higher binder content induced increase of the hydration products that fill the capillary pores specimen matrix and leading to decrease the porosity and refine pore structure (Fall et al., 2010; Fall et al., 2008; Godbout et al., 2007; Ouellet et al., 2006, 2003). As a result, this will lead to minimize the oxygen diffusion rate through the samples as well as its reactivity.

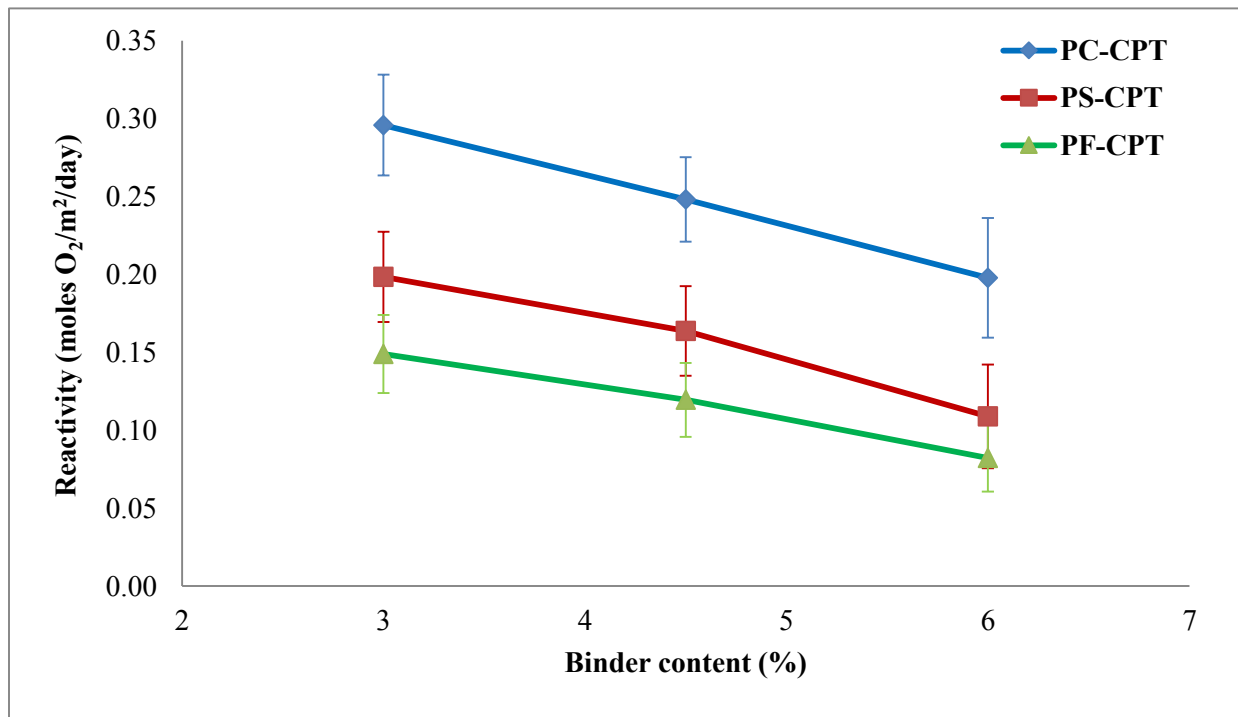


Figure 5.11. Effect of binder content and sulphate on the reactivity of CPT made of various types of binder (initial sulphate content = 25000 ppm)

### **5.4.3 Effect of the Proportion of Mineral Admixtures and Sulphate on the Reactivity of CPT Made of Various Types of Binder**

Figure 5.12 shows the histogram of the reactivity results of CPT specimens made with various proportions of mineral admixtures namely SA and FA cured with constant initial sulphate content 25,000 ppm. It can be observed from the figure that the reactivity of CPT specimens decreased with increasing amount of mineral admixture. This is due to the positive role of addition of mineral admixtures as a partial substitution to PC on the microstructure of CPT systems. As mentioned in the previous sections, the addition of mineral admixtures as a partial replacement to the PC in CPT system leads to increase the degree of saturation of CPT specimens and enhance microstructure due to micro-filler effect. As expected, increasing the level of replacement of PC with SA and or FA leads to lower the reactivity of CPT system due mainly to lower water consumption of the hydration of the blended binder. This behavior is supported by results of the degree of saturation of PS- and PF-CPT specimens, as shown in Figure 5.13. This figure presents the degree of saturation for 150-day old CPT samples with different SA and FA replacement ratios by PC cement. From the figure, one can be noted that as level of replacement increases, the degree of saturation of CPT samples increases. Furthermore, from the visual comparison of the upper surfaces of PS- and PF-CPT specimens, it can be noted that at high replacement levels (75%), CPT specimens have free amount of water at their upper surfaces, as shown in Figure 5.14. The figure shows a comparison of two photos of the upper surfaces of 150 days old SA:PC-CPT (25:75) and SA:PC-CPT (75:25) specimens. From the figure, it is clearly demonstrated that the upper surface of CPT specimen with high replacement level SA (75%) having free amount of water comparing to that with low partial substitution (25%). This causes higher degree of saturation and leading to lower O<sub>2</sub> diffusion as well as less reactivity. The FA based samples show a higher degree of saturation due to its fineness and spherical particles shape compared to those contain SA. At high replacement levels, FA can act as water reducing agent (Mehta, 2004).

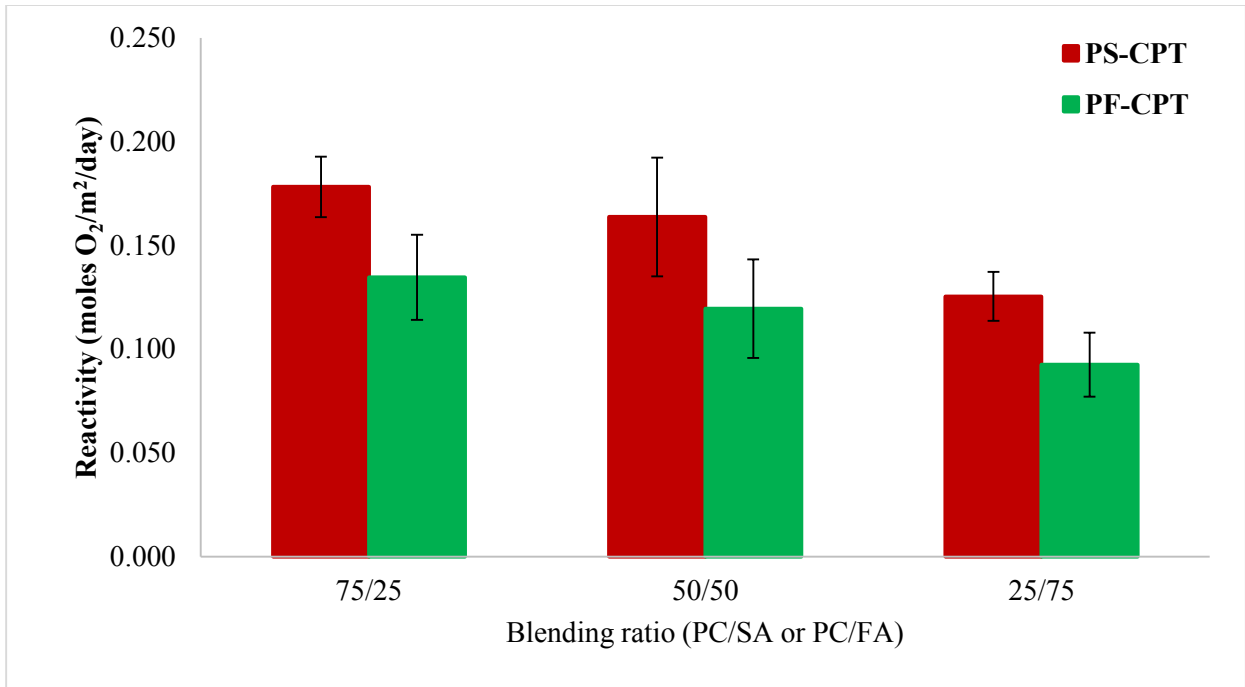


Figure 5.12. Effect of the proportion of mineral admixtures and sulphate on the reactivity of CPT made of various types of binder (initial sulphate content = 25000 ppm)

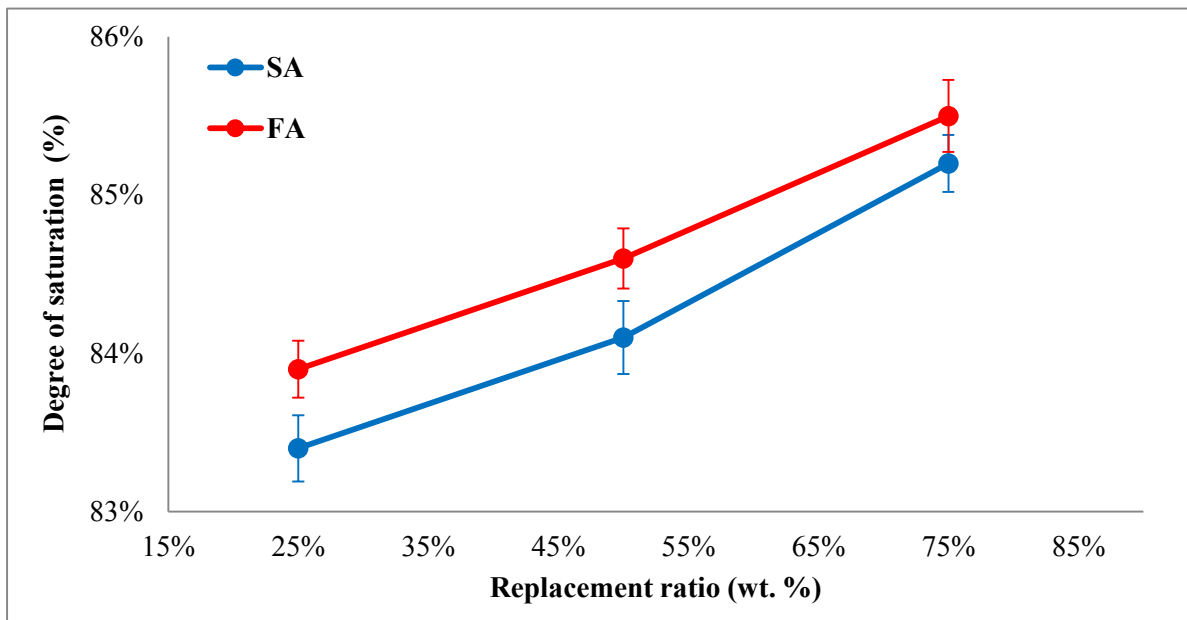


Figure 5.13. The degree of saturation for 150-day old CPT samples with different SA and FA replacement ratios by PC cement



**(a) SA(25%):PC(75%)-CPT specimen.**



**(b) SA(75%):PC(25%)-CPT specimen.**

Figure 5.14. Two Photos show the upper surface of 150-day old CPT samples with different SA replacement ratios by PC cement

### 5.5 Summary and Conclusions

This paper presents the results of the experimental works that investigate the influence of various initial sulphate contents on the reactivity of the CPT specimens made with different types and contents of binders as well as partial replacement with mineral admixtures (slag and fly ash) and cured at laboratory conditions for 150 days. Based on these results, the following main conclusions can be drawn:

- Generally, the reactivity of CPT specimens increases with increasing initial sulphate concentrations with exception of 5,000 ppm specimens that have a slight decrease.
- Initial sulphate content can play beneficial or detrimental role on the reactivity of CPT specimens. If the sulphate concentrations are relatively low, they can reduce the reactivity due to refinement pore structure of specimens of the studied CPT by filling their capillary pores with appropriate amounts of secondary expensive minerals (ettringite and gypsum) that do not generate effective internal stresses. Above this level of sulphate content, the specimens may be exposed to detrimental effects that are dependent upon the concentration of sulphate.

- Addition of mineral admixtures (e.g., slag and fly ash) as a partial replacing based cement (PC) in the CPT mixtures will enhance their resistance to sulphate attack as well as reduce their chemical reactivity (with respect to oxygen) compared with those containing PC alone.
- Increased binder content can enhance the microstructure of sulphidic CPT system as well sulphate resistance and thus can lead to lower its reactivity.

## 5.6 References

- Aldhafeeri, Z., & Fall, M. (2016). Time and damage induced changes in the chemical reactivity of cemented paste backfill. *Journal of Environmental Chemical Engineering*, 4(4), 4038–4049. <http://doi.org/10.1016/j.jece.2016.09.006>
- Aldhafeeri, Z., Fall, M., Pokharel, M., & Pouramini, Z. (2016). Temperature dependence of the reactivity of cemented paste backfill. *Applied Geochemistry*, 72, 10–19. <http://doi.org/10.1016/j.apgeochem.2016.06.005>
- Ayub, T., Shafiq, N., Khan, S., & Nuruddin, M. (2013). Durability of Concrete with Different Mineral Admixtures: A Review. *International Journal of Civil, Architectural, Structural and Construction Engineering*, 7(8), 273–284. Retrieved from <http://www.waset.org/publications/9996810>
- Benzaazoua, M., Belem, T., & Bussi re, B. (2002). Chemical factors that influence the performance of mine sulphidic paste backfill. *Cement and Concrete Research*, 32(7), 1133–1144. [http://doi.org/10.1016/S0008-8846\(02\)00752-4](http://doi.org/10.1016/S0008-8846(02)00752-4)
- Benzaazoua, M., Fall, M., & Belem, T. (2004). A contribution to understanding the hardening process of cemented pastefill. *Minerals Engineering*, 17(2), 141–152. <http://doi.org/10.1016/j.mineng.2003.10.022>
- Benzaazoua, M., Ouellet, J., Servant, S., Newman, P., & Verburg, R. (1999). Cementitious backfill with high sulfur content Physical, chemical, and mineralogical characterization. *Cement and Concrete Research*, 29(5), 719–725. [http://doi.org/10.1016/S0008-8846\(99\)00023-X](http://doi.org/10.1016/S0008-8846(99)00023-X)
- Bigham, J. M., & Nordstrom, D. K. (2000). Iron and Aluminum Hydroxysulfates from Acid Sulfate Waters. *Reviews in Mineralogy and Geochemistry*, 40(1), 351–403. Retrieved from <http://rim.g.geoscienceworld.org/content/40/1/351.abstract>
- Bonakdar, A., & Mobasher, B. (2010). Multi-parameter study of external sulfate attack in blended cement materials. *Construction and Building Materials*, 24(1), 61–70. <http://doi.org/10.1016/j.conbuildmat.2009.08.009>
- Boukendakdji, O., Kadri, E.-H., & Kenai, S. (2012). Effects of granulated blast furnace slag and superplasticizer type on the fresh properties and compressive strength of self-compacting concrete. *Cement and Concrete Composites*, 34(4), 583–590. <http://doi.org/10.1016/j.cemconcomp.2011.08.013>
- Bowker, L. N., & Chambers, D. M. (2015). *The risk, public liability & economics of tailings storage facility failures*. Retrieved from [https://www.earthworksaction.org/files/pubs-others/BowkerChambers-RiskPublicLiability\\_EconomicsOfTailingsStorageFacilityFailures-23Jul15.pdf](https://www.earthworksaction.org/files/pubs-others/BowkerChambers-RiskPublicLiability_EconomicsOfTailingsStorageFacilityFailures-23Jul15.pdf)
- Brix, H., & Schierup, H.-H. (1990). Soil oxygenation in constructed reed beds: the role of

- macrophyte and soil-atmosphere interface oxygen transport. In *Constructed Wetlands in Water Pollution Control* (pp. 53–66). Elsevier. <http://doi.org/10.1016/B978-0-08-040784-5.50010-3>
- Buckby, T., Black, S., Coleman, M. L., & Hodson, M. E. (2003, February 3). Fe-sulphate-rich evaporative mineral precipitates from the Rio Tinto, southwest Spain. *Mineralogical Magazine*. <http://doi.org/10.1180/0026461036720104>  
<<http://dx.doi.org/10.1180/0026461036720104>>
- Dweck, J., Buchler, P. M., Coelho, A. C. V., & Cartledge, F. K. (2000). Hydration of a Portland cement blended with calcium carbonate. *Thermochimica Acta*, 346(1–2), 105–113. [http://doi.org/10.1016/S0040-6031\(99\)00369-X](http://doi.org/10.1016/S0040-6031(99)00369-X)
- Elberling, B., & Nicholson, R. V. (1996). Field determination of sulphide oxidation rates in mine tailings. *Water Resources Research*, 32(6), 1773–1784. <http://doi.org/10.1029/96WR00487>
- Elberling, B., Nicholson, R. V., Reardon, E. J., & Tibble, R. (1994). Evaluation of sulphide oxidation rates: a laboratory study comparing oxygen fluxes and rates of oxidation product release. *Canadian Geotechnical Journal*, 31(3), 375–383. <http://doi.org/10.1139/t94-045>
- Fall, M., Adrien, D., Célestin, J. C., Pokharel, M., & Touré, M. (2009). Saturated hydraulic conductivity of cemented paste backfill. *Minerals Engineering*, 22(15), 1307–1317. <http://doi.org/10.1016/j.mineng.2009.08.002>
- Fall, M., Belem, T., Samb, S., & Benzaazoua, M. (2007). Experimental characterization of the stress-strain behaviour of cemented paste backfill in compression. *Journal of Materials Science*, 42(11), 3914–3922. <http://doi.org/10.1007/s10853-006-0403-2>
- Fall, M., Benzaazoua, M., & Ouellet, S. (2004). Effect of tailings properties on paste backfill performance. In *Proceedings of the eighth international symposium on mining with backfill (Minefill 2004)* (pp. 193–202). China.
- Fall, M., Benzaazoua, M., & Ouellet, S. (2005). Experimental characterization of the influence of tailings fineness and density on the quality of cemented paste backfill. *Minerals Engineering*, 18(1), 41–44. <http://doi.org/10.1016/j.mineng.2004.05.012>
- Fall, M., Benzaazoua, M., & Saa, E. G. (2008). Mix proportioning of underground cemented tailings backfill. *Tunnelling and Underground Space Technology*, 23(1), 80–90. <http://doi.org/10.1016/j.tust.2006.08.005>
- Fall, M., Célestin, J. C., Pokharel, M., & Touré, M. (2010). A contribution to understanding the effects of curing temperature on the mechanical properties of mine cemented tailings backfill. *Engineering Geology*, 114(3–4), 397–413. <http://doi.org/10.1016/j.enggeo.2010.05.016>
- Fall, M., & Pokharel, M. (2010). Coupled effects of sulphate and temperature on the strength development of cemented tailings backfills: Portland cement-paste backfill. *Cement and Concrete Composites*, 32(10), 819–828. <http://doi.org/10.1016/j.cemconcomp.2010.08.002>
- Ghirian, A., & Fall, M. (2016). Strength evolution and deformation behaviour of cemented paste backfill at early ages: Effect of curing stress, filling strategy and drainage. *International Journal of Mining Science and Technology*. <http://doi.org/10.1016/j.ijmst.2016.05.039>
- Gleisner, M. (2005). *Quantification of mineral weathering rates in sulfidic mine tailings under water-saturated conditions*. Stockholm University.
- Godbout, J., Bussière, B., Aubertin, M., & Belem, T. (2007). Evolution of cemented past backfill saturated hydraulic conductivity at early curing time. In *Proceedings of the OttawaGeo2007* (pp. 2230–2230). Retrieved from <http://www.polymtl.ca/envirogeremi/pdf/articles/CGS2007095.pdf>

- Gomes, C., Ferreira, O., & Fernandes, M. (2005). Influence of vinyl acetate-versatic vinylester copolymer on the microstructural characteristics of cement pastes. *Materials Research*, 8(1), 51–56. <http://doi.org/10.1590/S1516-14392005000100010>
- He, X., Miao, C., Wu, Y., Cao, X., & Liu, D. (2014). Thermal Reaction Kinetics of Fly Ash Cement Paste at the Age of 28 Days. *Applied Mechanics and Materials*, 668–669, 91–94. <http://doi.org/10.4028/www.scientific.net/AMM.668-669.91>
- Hewlett, P. C. (2004). *Lea's Chemistry of Cement and Concrete* (4th ed.). Butterworth-Heinemann.
- Isaia, G. ., Gastaldini, A. L. ., & Moraes, R. (2004). Physical and pozzolanic action of mineral additions on the mechanical strength of high-performance concrete. *Cement and Concrete Composites*, 25(1), 69–76. [http://doi.org/10.1016/S0958-9465\(01\)00057-9](http://doi.org/10.1016/S0958-9465(01)00057-9)
- Kesimal, A., Yilmaz, E., & Ercikdi, B. (2004). Evaluation of paste backfill mixtures consisting of sulphide-rich mill tailings and varying cement contents. *Cement and Concrete Research*, 34(10), 1817–1822. <http://doi.org/10.1016/j.cemconres.2004.01.018>
- Koohestani, B., Belem, T., Koubaa, A., & Bussière, B. (2016). Experimental investigation into the compressive strength development of cemented paste backfill containing Nano-silica. *Cement and Concrete Composites*, 72, 180–189. <http://doi.org/10.1016/j.cemconcomp.2016.06.016>
- Li, W., & Fall, M. (2016). Sulphate effect on the early age strength and self-desiccation of cemented paste backfill. *Construction and Building Materials*, 106, 296–304. <http://doi.org/10.1016/j.conbuildmat.2015.12.124>
- Lottermoser, B. (2010). *Mine Wastes: Characterization, Treatment and Environmental Impacts*. Springer Berlin Heidelberg. <http://doi.org/10.1007/978-3-642-12419-8>
- Manmohan, D. & Mehta, P. (1981). Influence of Pozzolanic, Slag, and Chemical Admixtures on Pore Size Distribution and Permeability of Hardened Cement Pastes. *Cement, Concrete and Aggregates*, 3(1), 63–67. <http://doi.org/10.1520/CCA10203J>
- Marshall, B. (2015). Facts and figures of the Canadian mining industry: F&F 2015. *Mining Association of Canada*.
- Mbonimpa, M, Aubertin, M, Aachib, M, B. (2002). *Oxygen diffusion and consumption in unsaturated cover materials*.
- Mehta, P. K. (2004). High-performance, high-volume fly ash concrete for sustainable development. In *Proceedings of the International Workshop on Sustainable Development and Concrete Technology* (pp. 3–14). Beijing, China: Iowa State University, Ames.
- Moncur, M. C., Jambor, J. L., Ptacek, C. J., & Blowes, D. W. (2009). Mine drainage from the weathering of sulfide minerals and magnetite. *Applied Geochemistry*, 24(12), 2362–2373. <http://doi.org/10.1016/j.apgeochem.2009.09.013>
- Ouellet, J., Benzaazoua, M., & Servant, S. (1998). Mechanical, mineralogical and chemical characterization of a paste backfill. In *Proceedings of the 4th International Conference on Tailings and Mine Waste, A.A.* (pp. 139–146). Balkema, Rotterdam, The Netherlands.
- Ouellet, S., Bussiere, B., Benzaazoua, M., Aubertin, M., Fall, M., & Belem, T. (2003). Sulphide Reactivity within cemented paste backfill: oxygen consumption test results. In *The 56th Annual Canadian Geotechnical Conference and 4th joint IAHCNC/CGS Conference* (pp. 176–183). Winnipeg, Manitoba, Canada.
- Ouellet, S., Bussière, B., Mbonimpa, M., Benzaazoua, M., & Aubertin, M. (2006). Reactivity and mineralogical evolution of an underground mine sulphidic cemented paste backfill. *Minerals Engineering*, 19(5), 407–419. <http://doi.org/10.1016/j.mineng.2005.10.006>

- Pokharel, M. (2008). *Geotechnical and environmental responses of paste tailings systems to coupled thermo-chemical loadings*. University of Ottawa. Retrieved from <http://hdl.handle.net/10393/27793>
- Pokharel, M., & Fall, M. (2011). Coupled Thermochemical Effects on the Strength Development of Slag-Paste Backfill Materials. *Journal of Materials in Civil Engineering*, 23(5), 511–525. [http://doi.org/10.1061/\(ASCE\)MT.1943-5533.0000192](http://doi.org/10.1061/(ASCE)MT.1943-5533.0000192)
- Pokharel, M., & Fall, M. (2013). Combined influence of sulphate and temperature on the saturated hydraulic conductivity of hardened cemented paste backfill. *Cement and Concrete Composites*, 38, 21–28. <http://doi.org/10.1016/j.cemconcomp.2013.03.015>
- Ramachandran, V. S., Paroli, R. M., Beaudoin, J. J., & Delgado, A. H. (2002). Formation and Hydration of Cement and Cement Compounds. In *Handbook of Thermal Analysis of Construction Materials* (pp. 71–142). Elsevier. <http://doi.org/10.1016/B978-081551487-9.50005-0>
- Şahmaran, M., Yaman, İ., & Tokyay, M. (2009). Transport and mechanical properties of self consolidating concrete with high volume fly ash. *Cement and Concrete Composites*, 31(2), 99–106. <http://doi.org/10.1016/j.cemconcomp.2008.12.003>
- Schmieder, P. J., Taylor, J. R., & Bourgeot, N. (2012). Oxygen consumption techniques to quantify acidity generation rates. In *1st International Acid and Metalliferous Drainage Workshop*. Beijing, China.
- Siddique, R., & Khan, M. I. (2011). *Supplementary Cementing Materials*. Berlin: Springer. <http://doi.org/10.1007/978-3-642-17866-54>
- Tariq, A., & Yanful, E. K. (2013). A review of binders used in cemented paste tailings for underground and surface disposal practices. *Journal of Environmental Management*, 131, 138–49. <http://doi.org/10.1016/j.jenvman.2013.09.039>
- Taylor, H. F. W. (1997). *Cement chemistry* (2nd editio). Thomas Telford Publishing. <http://doi.org/10.1680/cc.25929>
- Termkhajornkit, P., Nawa, T., & Kurumisawa, K. (2006). Effect of water curing conditions on the hydration degree and compressive strengths of fly ash–cement paste. *Cement and Concrete Composites*, 28(9), 781–789. <http://doi.org/10.1016/j.cemconcomp.2006.05.018>
- Thomas, M. (2013). *Supplementary Cementing Materials in Concrete*. New York: Taylor & Francis Group, LLC.
- Yılmaz, T., Ercikdi, B., Karaman, K., & Külekçi, G. (2014). Assessment of strength properties of cemented paste backfill by ultrasonic pulse velocity test. *Ultrasonics*. <http://doi.org/10.1016/j.ultras.2014.02.012>

## **Chapter 6: Technical Paper IV- Non-Isothermal Sulphate Effect on the Reactivity of Cemented Tailings Backfill**

Submitted: Aldhafeeri, Z. and Fall M. 'Non-Isothermal Sulphate Effect on the Reactivity of Cemented Tailings Backfill'.

### **Abstract**

The reactivity of sulphidic cemented paste tailings (CPT) is an indicator which can be used to assess their environmental performance and durability. However, the reactivity is influenced by several factors either alone or in combination with other factors, such as temperature, curing time, and initial sulphate content. In this paper, the combined effect of the initial sulphate content and curing temperature on the reactivity of CPT is experimentally investigated with oxygen consumption (OC) tests. Microstructural analyses (x-ray diffraction (XRD) and scanning electron microscopy (SEM)) of the CPT samples are also performed to understand the impact of the microstructure of the CPT samples on their reactivity. The results of the experiments show that regardless of the binder type, the reactivity of the CPT system is significantly dependent on the curing temperature and initial sulfate content and their interaction. As curing temperature and sulphate concentration increase, the reactivity increases (except for the CPT samples with 5,000 ppm of sulphate). Also, the results show that the CPT sample with high contents of sulphate (25,000 ppm) and cured at 50°C has the highest reactivity regardless of the type of binder. The addition of mineral admixtures as a partial substitute for Portland cement also has a significant role in reducing the reactivity as compared to samples made only with Portland cement.

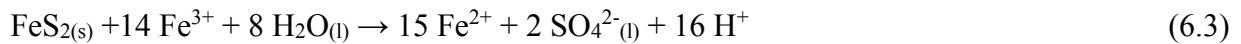
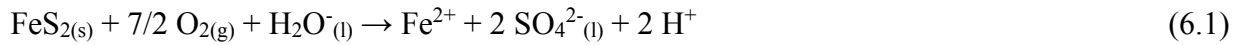
**Keywords:** cemented paste backfill, tailings; reactivity, acid mine drainage, sulphate; temperature

## 6.1 Introduction

As the world's population increases in size, the global demand for mining products (minerals and metals) also increases, and projected to increase by about 25% between 2000 and 2050 (Kesler, 2007). To meet this demand, lower grade ores and deeper deposits are beginning to be mined due to significant advancements in mining technologies. This development in the mining industry has several challenges. One of the greatest challenges is the management of mine wastes, in particular tailings, that are generated yearly in large volume. Tailings are a by-product waste disposed in the slurry form that consists of processing water, finely grounded rock and mineral waste products. Generally, they are disposed and stored in conventional tailings storage facilities, such as dams, embankments and other types of surface impoundments (Obermeyer & Alexieva, 2011; Blight, 2009). These conventional methods have many economic, technical and environmental issues. Therefore, several alternative tailings management methods have been proposed and practiced by mining engineers and researchers, such as thickening tailings and using cement paste in tailings (Edraki et al., 2014; Bussière, 2007).

Among all of these methods, the use of cemented paste tailings (CPT) (also called cemented paste backfill (CPB)) has become a widely practiced method for managing tailings worldwide (Fall et al. 2010). CPT are an engineered composite made of tailings (75-85% solid by weight), low quantities of hydraulic binders (generally 3-7% by total dry paste weight) and a high proportion of water (typically 25%) (Fall et al., 2010; Coussy et al., 2012). Its main function is to fill the voids (openings) left by ore extracting processes to achieve the desired ground support and stability in the underground mining environment (Fall et al. 2010). Furthermore, the implementation of CPT offers numerous economic, technical, social, and environmental benefits compared to the conventional methods (Tariq and Yanful, 2013). These advantages include enhancing mine production, reducing the large amounts of tailings that are disposed at the surface of the mine, and minimizing environmental liabilities (Öhlander et al., 2012; Yilmaz, 2011). Furthermore, CPT can be used to safely dispose sulphide bearing tailings (Bois et al., 2005) that are considered to be one of the most environmentally devastating mine wastes. As a result, their disposal is a key environmental challenge that the global mining industry needs to address (Aldhafeeri et al., 2016; Huang et al., 2011). This is due to the chemical reactivity of sulphide bearing tailings so that if exposed to atmospheric weathering (mainly water and oxygen), react with oxygen and water, and oxidize to form acid mine drainage (AMD) (Kumari et al., 2010).

AMD is considered to be a devastating environmental problem that all mines face worldwide due to the leaching of heavy metals into the environment, and therefore the pollution of the surrounding environments, such as the surface and groundwater (Dold, 2014). AMD is produced as a result of the oxidation of sulphide minerals (usually pyrite (FeS<sub>2</sub>) which are commonly associated with mine wastes (Dold, 2014; Kumari et al., 2010). The oxidation of pyrite occurs through a number of steps (Bois et al., 2005), as described in the following reactions:



Since there is no standard method for measuring or assessing the reactivity of sulphidic tailings and CPT, a variety of different techniques have been practiced, such as sulphate (SO<sub>4</sub><sup>2-</sup>) release, O<sub>2</sub> gradient and O<sub>2</sub> consumption tests (Martin et al., 2006). Among them, oxygen consumption (OC) testing is preferred because it is inexpensive, simple, accurate and quick (Aldhafeeri et al., 2016). The OC test measures the reduction of oxygen gas concentration in a sealed air chamber placed at the top of a PVC cylinder from diffusion and sulphide oxidation reactions (Mbonimpa et al., 2011).

There are a very limited number of studies that have investigated the reactivity of CPT systems by using OC testing (Aldhafeeri and Fall, 2017, 2016; Aldhafeeri et al., 2016; Ouellet et al., 2006., 2003; Fall et al., 2004). They investigated some of the factors that affect the reactivity of CPT systems, such as sulphide and water content and curing temperature. Despite the important findings of these studies, they have mostly focused on the effect of one influential factor (e.g., temperature) on the reactivity of CPT systems. For a better understanding of the reactivity of CPT systems, the coupled effects of these factors should be investigated. In CPT systems, sulphate and temperature commonly have coupled effects. Therefore, a number of studies have investigated their effects on the mechanical behaviour of CPT systems (e.g., Li and Fall, 2016; Ghirian and Fall, 2014; Pokharel and Fall, 2013; Pokharel, 2008). To the best of the knowledge of the author, a similar study has not been conducted to date on the reactivity of CPT. Therefore, the main

objectives of this paper is to experimentally investigate the coupled effects of curing temperature and initial sulphate content on the reactivity of CPT systems.

## 6.2 Experimental Program

### 6.2.1 Materials

#### 6.2.1.1 Tailings

Silica tailings (ST), which are a synthetic material and essentially consist of pure silica powder (99.9 wt. % SiO<sub>2</sub>) (SIL-CO-SIL 106, manufactured by U.S. Silica Co.), were used as the tailings material. ST are characterized by a chemical inertness and grain size distribution similar to the average particle size distribution of natural tailings from 9 mines in eastern Canada (Carraro et al., 2009), as illustrated in Figure 6.1. In this work, the use of ST instead of natural tailings enables more precise control over the mineralogical and chemical compositions, and thus reduces the uncertainties associated with the use of natural tailings. The ST are blended with the desired quantity of pyrite (45 wt. %) to make sulphide bearing tailings. The sulphidic-ST were used as the basic tailings for all of the CPT samples.

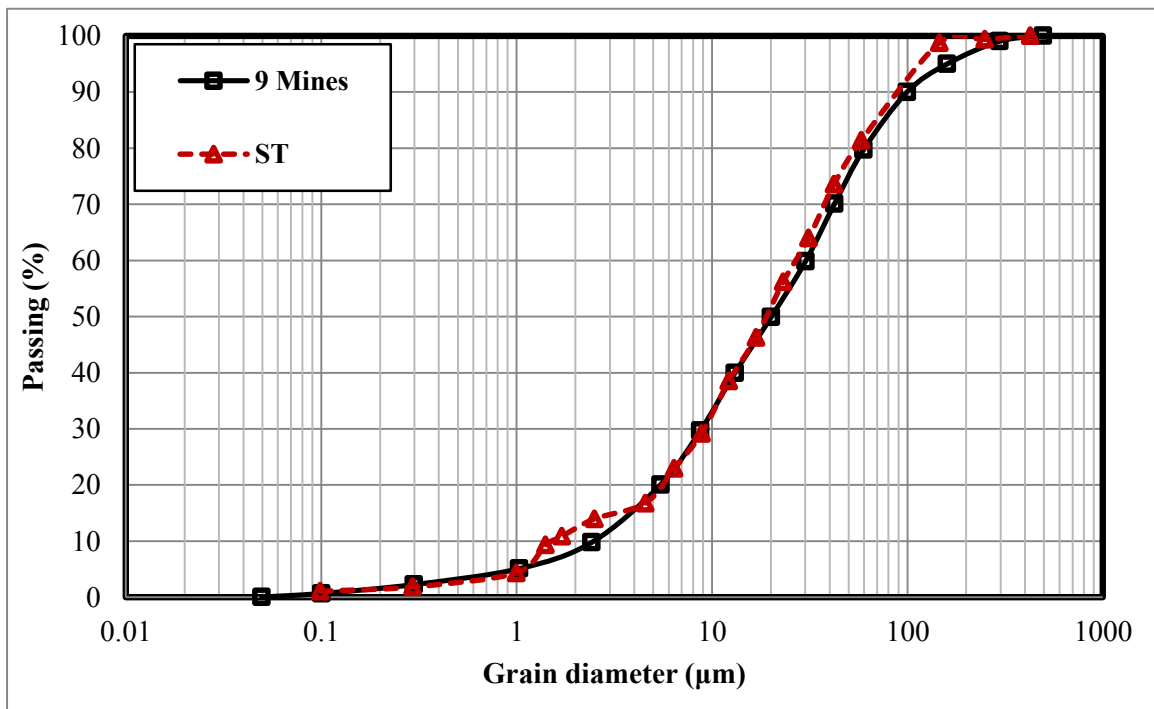


Figure 6.1. Grain size distribution of tailings (ST) used and the average grain size distribution of tailings from 9 mines in eastern Canada

### 6.2.1.2 Pyrite

A commercial pyrite powder ( $\text{FeS}_2$ , M.W. = 119.98, Washington Mills North Grafton, Inc.) was mixed for the desired amount of pyrite mineral (45 wt. %) for creating the sulphidic –ST. The grain size of the pyrite powder is similar to that of natural pyrite minerals found in natural tailings. The physical properties of the commercial pyrite powder are presented in Table 6.1.

Table 6.1. Physical properties of pyrite (Washington Mills North Grafton Inc., 2017)

Bulk density (g/cm <sup>3</sup> )	Density at 20°C (g/cm <sup>3</sup> )	Specific gravity	pH	Melting point (°C)
2.35	4.7	4.6	4.0- 6.0	1193

### 6.2.1.3 Binders

Portland cement type I (PCI) was used as the binder agent in the CPT mixes. In addition, two blended cements were prepared by replacing 50 wt. % of the PC with mineral admixtures, namely, ground granulated blast furnace slag (SA) and Type C fly ash (FA). In this work, the PC: SA (50:50) binder is denoted with PS, whereas PC: FA (50:50) is denoted with PF. Table 6.2 presents the main physical and chemical properties of the PC, SA and FA.

Table 6.2. Chemical properties of binders and mineral admixtures used

Binder	MgO (wt. %)	CaO (wt. %)	SiO <sub>2</sub> (wt. %)	Al <sub>2</sub> O <sub>3</sub> (wt. %)	Fe <sub>2</sub> O <sub>3</sub> (wt. %)	SO <sub>3</sub> (wt. %)	Relative density
PC	2.65	62.82	18.03	4.53	2.7	3.82	3.1
SA	10.98	41.14	34.23	9.54	-	3.87	3.3
FA (Class C)	5.58	21.47	38.06	19.45	5.33	2.7	2.6

### 6.2.1.4 Mixing Water

For the preparation of the CPT samples, distilled water (DW) was used as the basic mixing water. Also, DW was used as the solvent to prepare solutions with different initial sulphate contents (0, 5,000, 15,000 and 25,000 ppm) to examine their influence on CPT reactivity. Different sulphate concentrations were made by dissolving desired amounts of sulphate salt (ferrous sulphate heptahydrate,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , F.W. = 278.01, Fisher Chemical Inc.) powder with a specific volume of DW.

## 6.2.2 Sample Preparation

### 6.2.2.1 Mix Proportion

One hundred and twenty (120) CPT samples were prepared by mixing a selected amount of sulphidic-ST and three types of binder with 4.5% wt PC and water-to-binder ratio (w/b) of 7.6, as shown in Figure 6.3. Furthermore, they were mixed with water at various sulphate concentrations as shown in Table 3. All of the CPT mixes were mixed with a small food mixer for 7 minutes to achieve homogeneity with a slump of 18 cm in accordance with the slump test as provided in ASTM C143-90. The CPT mixes were then poured into PVC cylinders that are 5 cm in diameter and 10 cm in height for curing. During the pouring of the paste, the moulds were manually tapped against a hard surface to remove any trapped air. The cylinders were sealed with their plastic covers and then plastic tape to prevent the evaporation of water. Finally, they were cured in an environmental room at various temperatures (20°C, 35°C and 50°C) for 150 days. In addition to the CPT samples, 20 binder paste (binder and water only) samples (w/b=1; to simulate the high water content of CPT) were prepared for microstructural analysis in the same conditions and with the same curing times.

Table 6.3. CPT mixture designs

CPT Sample	Binder	Blending ratio	Binder content (wt. %)	Tailings Type	Pyrite content (wt. %)	w/b ratio	Sulphate (ppm)	Curing time (days)
PC-CPT- 0	PC	-	4.5	ST	45	7.6	0	150
PC-CPT- 5	PC	-	4.5	ST	45	7.6	5,000	150
PC-CPT-15	PC	-	4.5	ST	45	7.6	15,000	150
PC-CPT- 25	PC	-	4.5	ST	45	7.6	25,000	150
PS-CPT- 0	PC/SA	50:50	4.5	ST	45	7.6	0	150
PS-CPT- 5	PC/SA	50:50	4.5	ST	45	7.6	5,000	150
PS-CPT-15	PC/SA	50:50	4.5	ST	45	7.6	15,000	150
PS-CPT- 25	PC/SA	50:50	4.5	ST	45	7.6	25,000	150
PF-CPT- 0	PC/FA	50:50	4.5	ST	45	7.6	0	150
PF-CPT- 5	PC/FA	50:50	4.5	ST	45	7.6	5,000	150
PF-CPT-15	PC/FA	50:50	4.5	ST	45	7.6	15,000	150
PF-CPT- 25	PC/FA	50:50	4.5	ST	45	7.6	25,000	150

PC: Portland cement; SA: Slag; FA: Fly Ash

## 6.2.3 Testing of Samples

### 6.2.3.1 Oxygen Consumption Tests

To measure the reactivity of sulphide bearing mine wastes, Elberling et al. (1994) and Elberling and Nicholson (1996) suggested OC testing (Pokharel, 2008). The OC test measures the reduction

of oxygen gas concentration in a sealed air chamber placed at the top of a PVC cylinder as a result of oxygen diffusion and reactivity of waste materials (sulphide oxidation reaction) (Mbonimpa et al., 2011), as illustrated in Figure 6.2. The oxygen ingress for the tested material (e.g. CPT) depends on its effective diffusion ( $D_e$ ) and reactivity rate coefficients ( $K_r$ ) (Mbonimpa et al., 2011). Under a steady state condition ( $\delta C/\delta t = 0$ ), the reactivity of the CPT sample can be determined by using OC testing (Pokharel, 2008). The reactivity of CPT can be determined in terms of the flux of oxygen ( $F_L$ ), which is expressed in moles of  $O_2/m^2/year$  or moles of  $O_2/m^2/day$ . The  $F_L$  can be calculated by using two equations (Eqs.6.5 and 6.6) which were proposed in Elberling et al. (1994) and Elberling and Nicholson (1996), as follows:

$$F_L = C_o (K_r D_e)^{0.5} \quad (6.5)$$

where  $K_r$  is the first-order reaction rate coefficient for sulphide mineral oxidation (e.g., pyrite),  $D_e$  is the effective diffusion coefficient and  $C_o$  is the initial concentration of oxygen. The term  $(K_r D_e)$  can be obtained from the slope of plotting  $\ln (C/C_o)$  versus time based on Eq. 6.6. It can be calculated if the volume of the gas chamber ( $V$ ) and the surface area of the exposed area of the reactive materials ( $A$ ) are known (Aldhafeeri et al., 2016).

$$\ln (C/ C_o) = - t (K_r D_e)^{0.5} (A/V) \quad (6.6)$$

Eq. 6.5 is only valid for short-duration tests since the steady-state condition ( $\delta C/\delta t = 0$ ) is assumed to occur before and during the tests (Mbonimpa et al., 2011).

In this work, OC testing is performed on mature CPT samples in the laboratory to measure their reactivity. Prior to the testing, the headspace was created by removing 2 cm of the CPT material from the top of the PVC cylinders. Then, the cylinders were closed by using an airtight lid with an oxygen sensor (Oxygen galvanic cell type, GC33-200 manufactured by GC Industries in California) attached. Finally, the sensor was connected to a voltmeter (Hantek 365A USB Data Logger Recorder Digital Multimeter Voltage Current PC Base) to measure and record the voltage produced by the oxidation reaction with time in the sealed chamber. This voltage is directly proportional to the partial pressure of oxygen in the gas phase. The OC tests were performed in

triplicate on each CPT sample. The reactivity of the CPT samples was calculated by using the equations mentioned earlier.

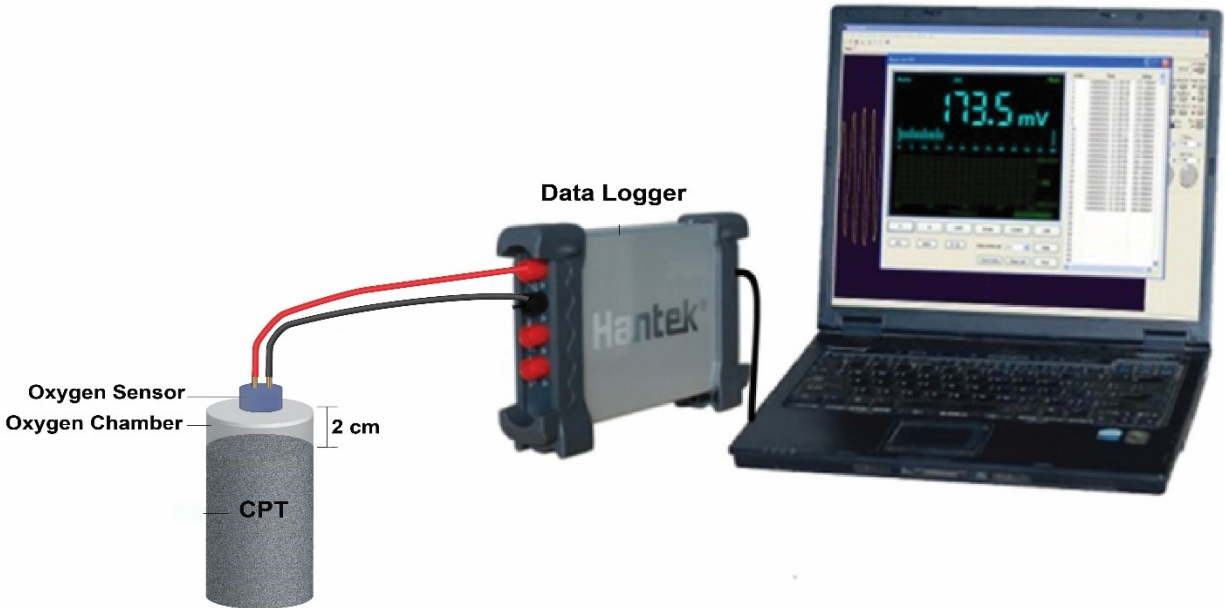


Figure 6.2. Schematic of experimental setup of OC testing

### 6.2.3.2 Microstructural Analyses

In this work, x-ray diffraction (XRD) and scanning electron microscopy (SEM) were performed on selected 150-day CPT samples and their hardened cement pastes ( $w/c = 1$ ). These two techniques provide more clarity on the coupled effects of curing temperature and initial sulphate content on the reactivity and microstructure of the CPT samples. They can provide valuable information about the porosity, pore structure and binder hydration products of the samples. XRD was performed with a Scintag XDS 2000 powder diffractometer at 40 kV and 44 mA for  $\text{Cu K}\alpha$  X-ray radiation ( $\lambda = 1.541836 \text{ \AA}$ ) between  $4$  and  $65^\circ$  ( $2\theta$ ) with a scanning speed of  $1^\circ/\text{min}$  and step size of  $0.02^\circ$ . The SEM was conducted with a Hitachi S4800 field emission scanning electron microscope.

## 6.3 Results and Discussion

### 6.3.1 Coupled Effect of Sulphate and Temperature on Reactivity of PC-CPT

Figure 6.3 shows the reactivity results of 150-day PC-CPT samples with different initial sulphate contents at various curing temperatures. The reactivity values are presented in terms of the oxygen flux (moles  $O^2/m^2/day$ ) and calculated as the mean of three OC measurements with standard deviation. From this figure, it can be seen that the coupled effects of sulphate and temperature on the reactivity of each sample can be primarily viewed in three parts based on the sulphate concentration: (i) Part I: from zero to 5000 ppm of sulphate; (ii) Part II: from more than 5000 to 15000 ppm of sulphate and (iii) Part III: greater than 15,000 ppm of sulphate.

In Part I, regardless of the curing temperature, the reactivity is slightly reduced from zero to 5000 ppm of sulphate. This decline can be attributed to the positive impact of the sulphate on the microstructure of the PC-CPT samples. In this sulphate concentration range, the sulphate ions react with the cement hydration products and produce an adequate amount of secondary expansive minerals (e.g., ettringite and gypsum) in the empty capillary pores of the matrix of the samples which leads to the refinement of their pore structure (Fall and Pokharel, 2010). This results in smaller effective coefficients of oxygen diffusion ( $D_e$ ) of the PC-CPT sample (see Eq. 6.5), which in turn can significantly reduce the rate of oxygen diffusion across its pore matrix. This results in less oxidation of the sulphide minerals in the CPT sample, and therefore reduced reactivity.

The above argument is consistent with that in previous studies on the effects of sulphate on CPT systems (see for e.g., Li and Fall, 2016; Pokharel and Fall, 2013; Fall and Benzaazoua, 2005). These studies have reported that low concentrations of sulphate ( $\leq 5000$  ppm) can have a positive effect on CPT systems. Furthermore, this argument is supported experimentally and confirmed by the XRD tests (Figure 6.4) and the results of the saturated hydraulic conductivity (Figure 6.5) tests on PC-paste sample with 5000 ppm of sulphate. Figure 6.4 presents the XRD pattern of the mature PC-paste sample with 5000 ppm of sulphate which shows the absence of tri- and di-calcium silicate ( $C_3S$  and  $C_2S$ , respectively) peaks. This indicates the almost complete hydration of the binder and verifies that 5000 ppm of sulphate does not inhibit the hydration of cement. Also, the XRD result shows that the formation of secondary expansive minerals (ettringite and gypsum). This leads to the refinement of the pore network and blocking of the interconnected pores (reduction in permeability) in the CPT matrix. This refinement is shown in a graph in Figure 6.5, which presents the results of permeability tests conducted by Pokharel (2008) on 150 day CPT

samples with initial sulphate contents of 0, 5000, 15,000 and 25,000 ppm and cured at 50°C. From the figure, it can be observed that the CPT sample with 5000 ppm of sulphate shows the lowest permeability compared to the other samples due to refinement of its pore structure. This explains for its low reactivity. On the other hand, it can be observed from Figure 6.3 that, in Part I, the reactivity decreases with increases in the curing temperature. This can be attributed to the accelerated hydration reaction of the cement due to a higher curing temperature. As the curing temperature increases, more hydration products (mainly tricalcium silicate hydrate (C-S-H) and portlandite/calcium hydroxide (CH)) are formed (Lothenbach et al., 2007). Therefore, the sulphate ions react with more portlandite and produce more gypsum minerals which fill the empty capillary pores in the matrix of the sample and thus leads to reduced porosity. Based on these observations, the coupled effects of the initial sulphate content and curing temperature in Part I have a role in reducing the reactivity of the CPT samples. Low concentrations of sulphate and the temperatures can mean positive changes in the microstructure of the samples which leads to reduced oxygen diffusion through the samples and thus a lower reactivity.

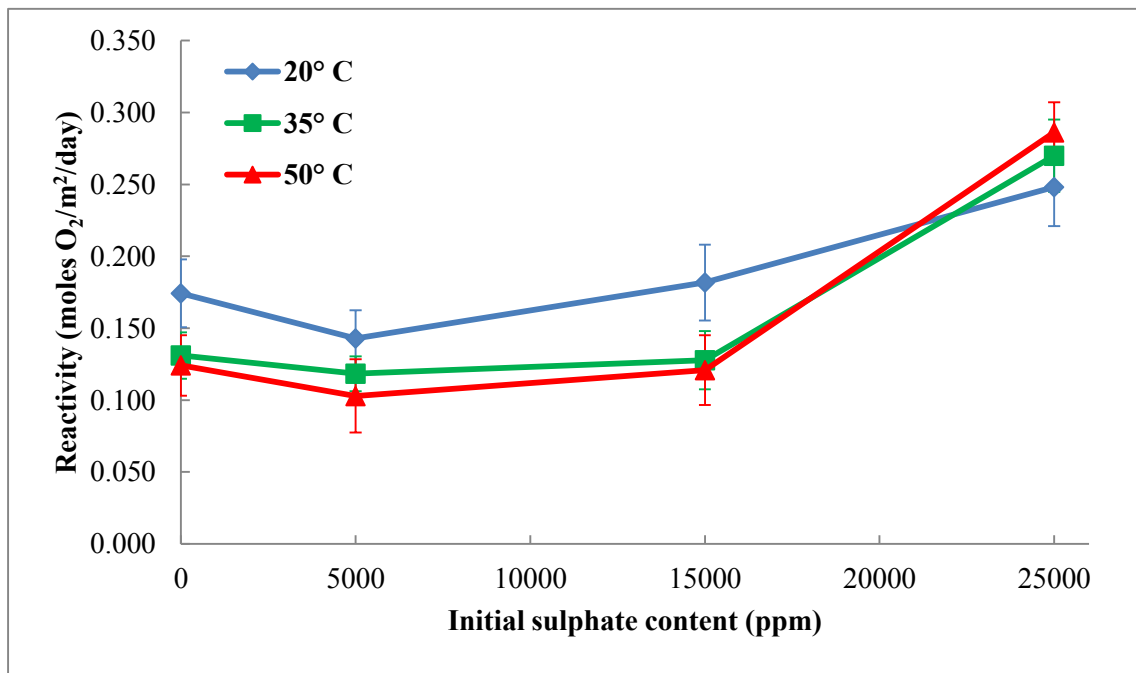


Figure 6.3. Combined effects of initial sulphate content and curing temperature on reactivity of PC-CPT samples

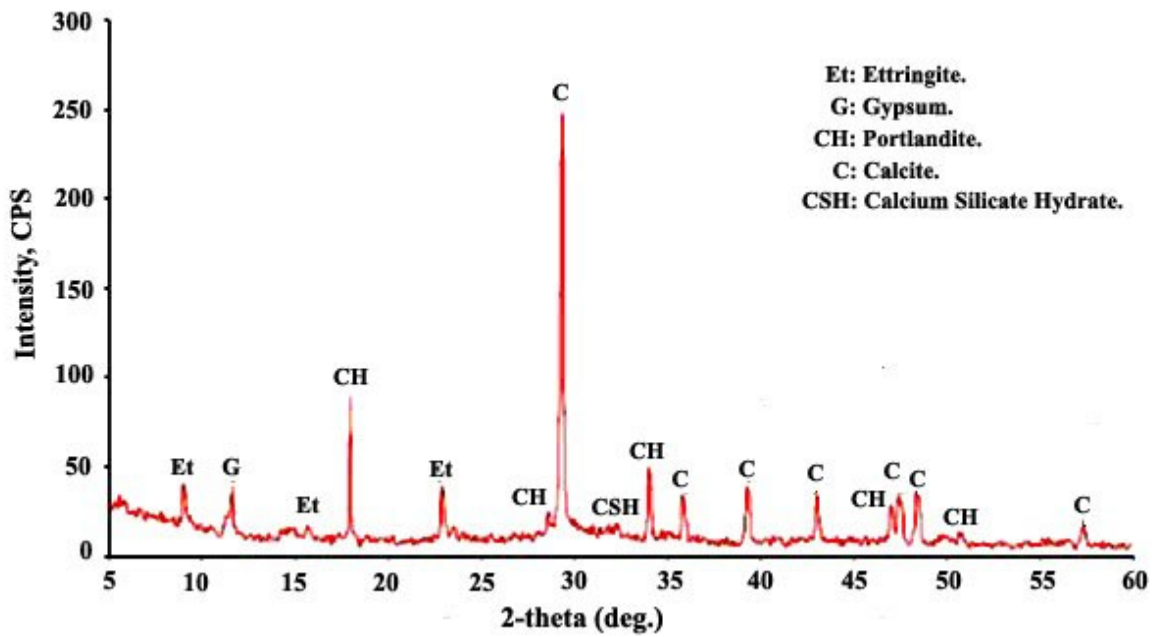


Figure 6.4. XRD pattern of PC-paste with 5000 ppm of sulphate cured at 20 °C for 150 days

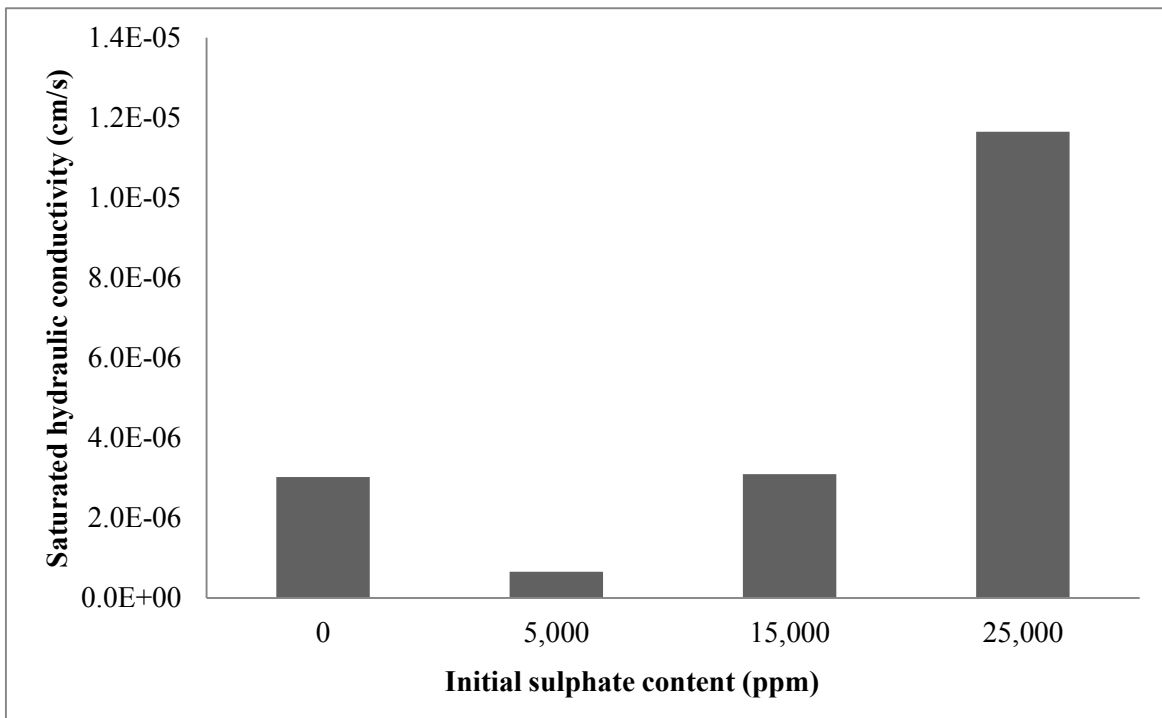


Figure 6.5. Effect of initial sulphate content on saturated hydraulic conductivity of 150 day PC-CPT samples cured at 50°C (Fall & Pokharel, 2010)

In Part II, the reactivity gradually increases with increased initial sulphate concentration at each curing temperature. Despite the positive contribution of a higher curing temperature in increasing the binder hydration rate, increasing the amount of sulphate ions results in greater inhibition of the hydration of the cement binder of the CPT sample (Pokharel and Fall, 2013), and thus leads to the coarsening of the pore structure of the samples with a high sulphate content. This concurs with the results of previous studies on the cemented paste in CPT which show that a high sulphate content strongly inhibits the early hydration of aluminates ( $C_3A$ ; e.g., Fall and Pokharel, 2010) as well as the result of studies on conventional concrete (Tzouvalas et al., 2004). This coarsening of the pore structure is obviously associated with an increase in the reactivity.

Finally, in Part III, the reactivity increases rapidly with increases in both the sulphate concentration and curing temperature. This increase in reactivity can be attributed to the changes in the pore structure of hardened cement pastes caused by the coupled effects of sulphate and temperature. As the curing temperature and sulphate content are increased, a greater amount of sulphate will be absorbed by the C–S–H gel. As a result, the formation of expansive minerals (gypsum or ettringite) in the matrix of the sample will be reduced as compared to curing that is carried out at 20°C (Fall et al., 2010). Also, a high curing temperature negatively affects the stability of ettringite and could lead to its dissolution, thus resulting in the coarsening of the pore structure of the samples. The combined effects of the above mechanisms result in higher oxygen diffusion coefficients of the CPT samples (see Eq 6.5). Consequently, these effects lead to an increase in the rate of the oxygen diffusion as well as consumption of the sulphate, which explain for the high reactivity values. This explanation is in agreement with the obtained results of the XRD and permeability tests. The inhibition of cement hydration by sulphate ions is validated by the XRD results of 150-day PC-paste with 0 ppm and 25,000 ppm of sulphate cured at 50°C, as shown in Figure 6.6. By comparing the XRD patterns of these samples, the presence of cement clinker phases ( $C_3S$  and  $C_2S$ ) in the XRD pattern of the 25,000 ppm sample (Figure 6.6b) which indicates inhibition of cement hydration due to a high sulphate content can be observed. On the other hand, these two clinker phases are not found in the XRD pattern of the control sample (0 ppm of sulphate) (Figure 6.6a) which indicates that cement hydration is almost completed. Also, it can be observed that the low amount of ettringite in the PC-paste sample with 25,000 ppm of sulphate cured at 50°C compared to the PC-paste sample with 0 ppm of sulphate which is also cured at 50°C confirms the dissolution effect of higher curing temperatures on ettringite which

leads to the coarsening of the pore structure. The coarsening effect is supported by the permeability tests (Figure 6.5). It can be seen from Figure 6.5 that the 25,000 ppm sample has the highest permeability value, which indicates the coarsening of the pore structure.

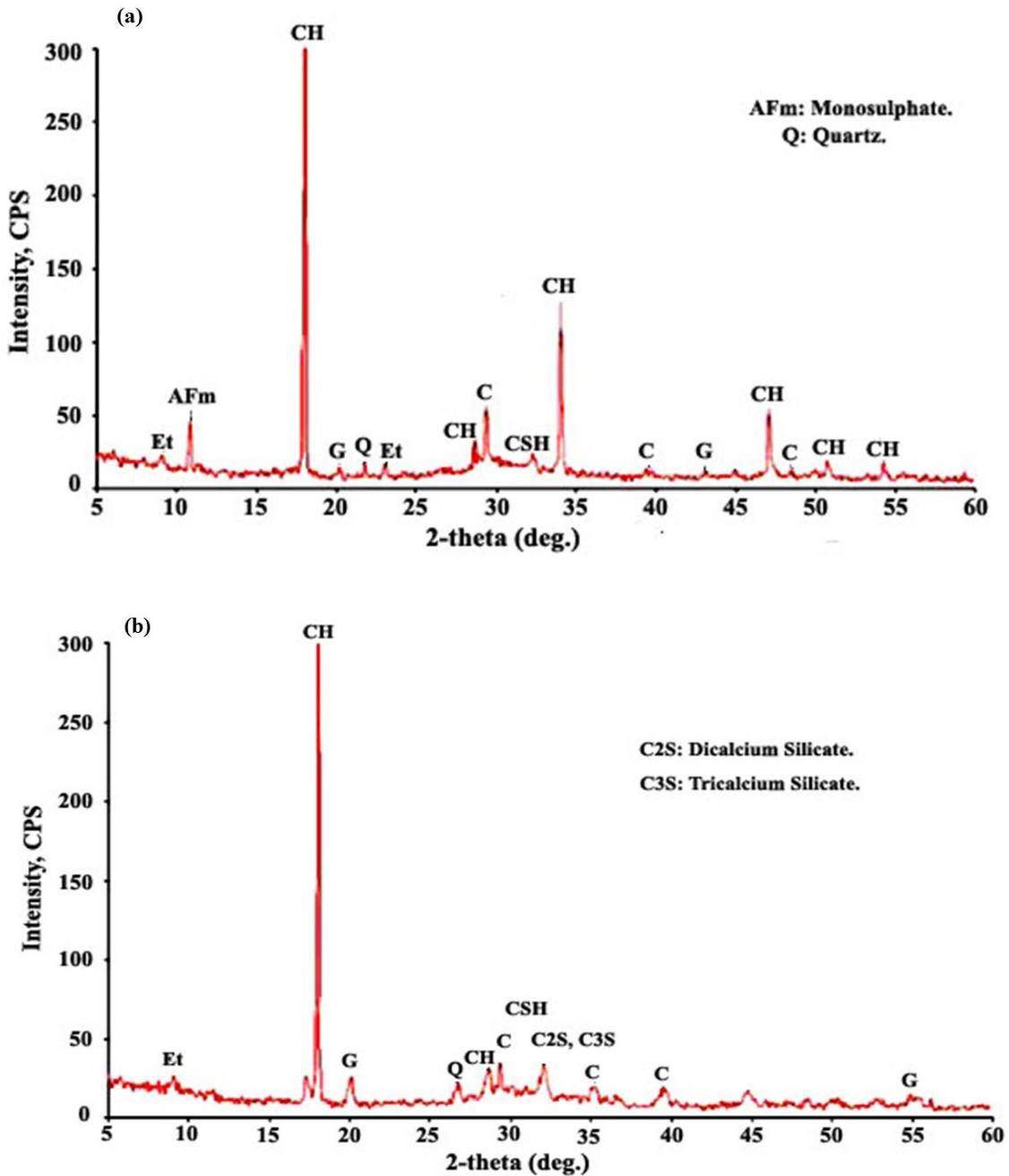


Figure 6.6. XRD patterns of PC-paste of mature CPT with (a) 0 ppm and (b) 25,000 ppm of sulphate cured at 50°C

### 6.3.2 Coupled Effects of Sulphate and Temperature on Reactivity of Blended Cement

Figures 6.7 and 6.8 show the combined effects of initial sulphate content and curing temperature on the reactivity of mature CPT specimens made of two types of blended cement, PS (50/50 PC/SA) and PF (50/50 PC/FA), respectively. It can be observed that the reactivity of the PS-CPT and PF-CPT samples follow a similar trend of those that contain only PC but with lower values. These low reactivity values can be explained by the positive role of the addition of mineral admixtures, namely SA and FA, as a partial substitute for PC in the CPT samples (except for the 25,000 ppm sample cured at 50°C). As compared to PC, blended cements like PS and PF require less water to hydrate and produce cementitious material (CPT) of the same workability. This is due to dilution and the microfiller effects of blended cements (Rashad, 2015; Ayub et al., 2013; Boukendakdji et al., 2012; Snellings et al., 2012; Şahmaran et al., 2009). In addition, cement paste backfill requires large volumes of water for transporting the paste to the mine stope compared to the use of concrete (Drebenstedt and Singhal, 2014; Clark et al., 1995). The combined effects of these factors lead to increases in the amount of free water in the matrices of the PS- and PF-based CPT samples and thus increase the water content and degree of saturation of the samples (Aldhafeeri and Fall, 2017). As a result, the high degree of saturation acts like a barrier that limits oxygen diffusion through the samples and explains for their low reactivity values compared to the samples that contain only PC.

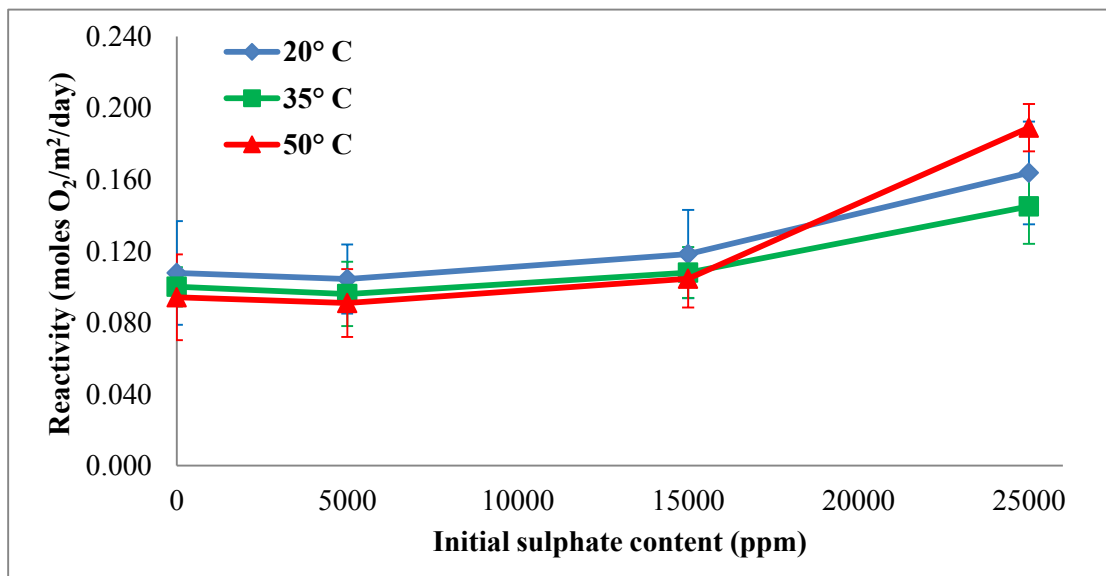


Figure 6.7. Combined effect of initial sulphate content and curing temperature on reactivity of 150-day PS-CPT samples

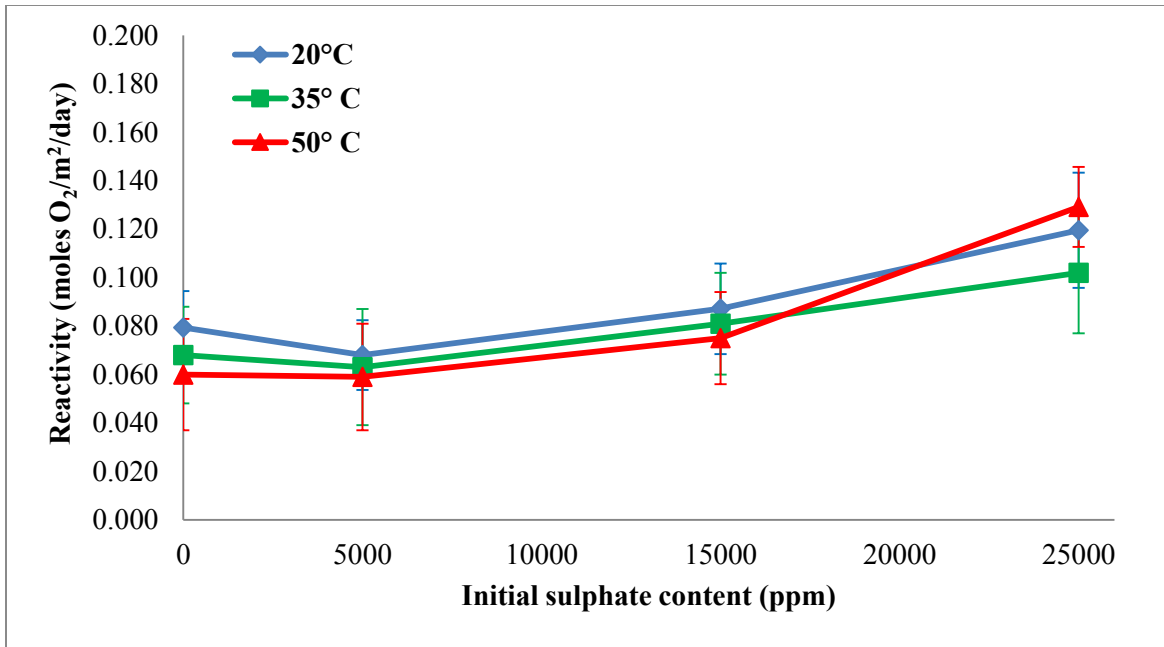


Figure 6.8. Combined effect of initial sulphate content and curing temperature on reactivity of PF-CPT samples

The above explanation is supported by the measurements of the degrees of saturation for mature CPT samples with different types of binders (PC, PS and PF), as shown in Figure 6.9, which shows variation in the degrees of saturation. In this figure, the PF-CPT sample has the highest degree of saturation as compared to the others, thus explaining for its lower reactivity. With respect to the other factors (e.g., pore structure, porosity, and binder type), the degree of saturation is a key factor that controls the oxygen diffusion rate through the CPT samples. This is due to the fact that the diffusion of gases (e.g., oxygen) in the water phase is about ten thousand-folds less than in the gas phase (Farver, 2010; Yanful, 1993). Furthermore, the results of the XRD analyses concur with the fact that higher curing temperatures reduce the reactivity of CPT with no sulphate or a low sulphate content, as shown in Figure 6.10. Figures. 6.10(a) and 6.10(b) show the results of the XRD performed on 150-day PS-CPT without sulphate cured at 20°C and 35°C, respectively. Portlandite (mineral name of CH) is one of the main hydration products which dominate the properties of cement paste, and therefore can be used to determine the hydration rate of cement. By comparing the intensity of CH at 18 degrees 2-theta in these figures, it can be observed that the sample cured at 35°C has a higher intensity (around 95 CPS), than that of the sample cured at 20°C (75 CPS). This high intensity (CH peak) indicates that the sample cured at 35°C produces more hydration products as compared to the sample cured at 20°C. This is mainly due to the fact that there are

more hydration products due to a higher curing temperature (Fall et al. 2010). Therefore, a higher curing temperature leads to the refinement of the pore structure and densification of the sample matrix which enhance its transportability. Consequently, the rate that oxygen diffuses through the sample is reduced and thus reduces the reactivity.

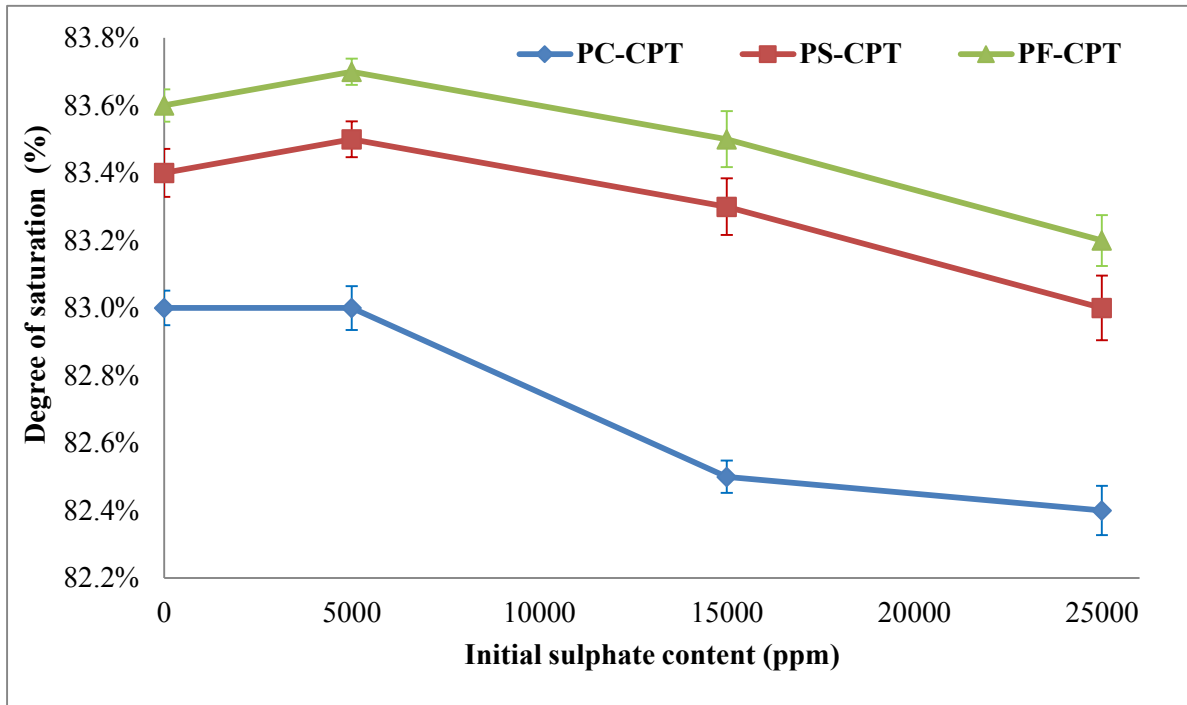
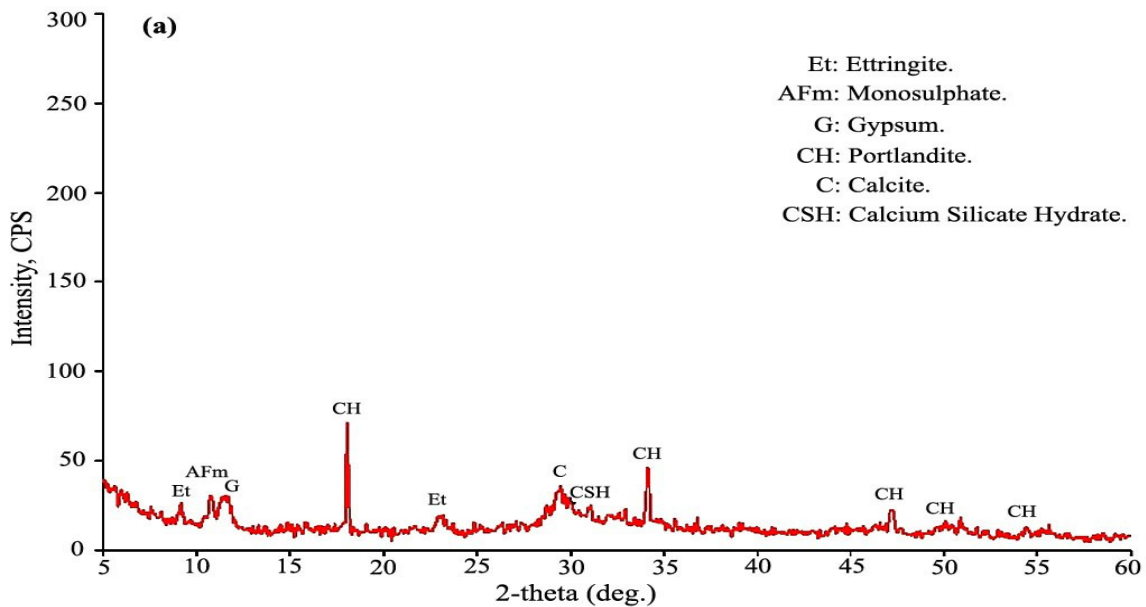


Figure 6.9. Degree of saturation of 150-day CPT samples with different types of binder



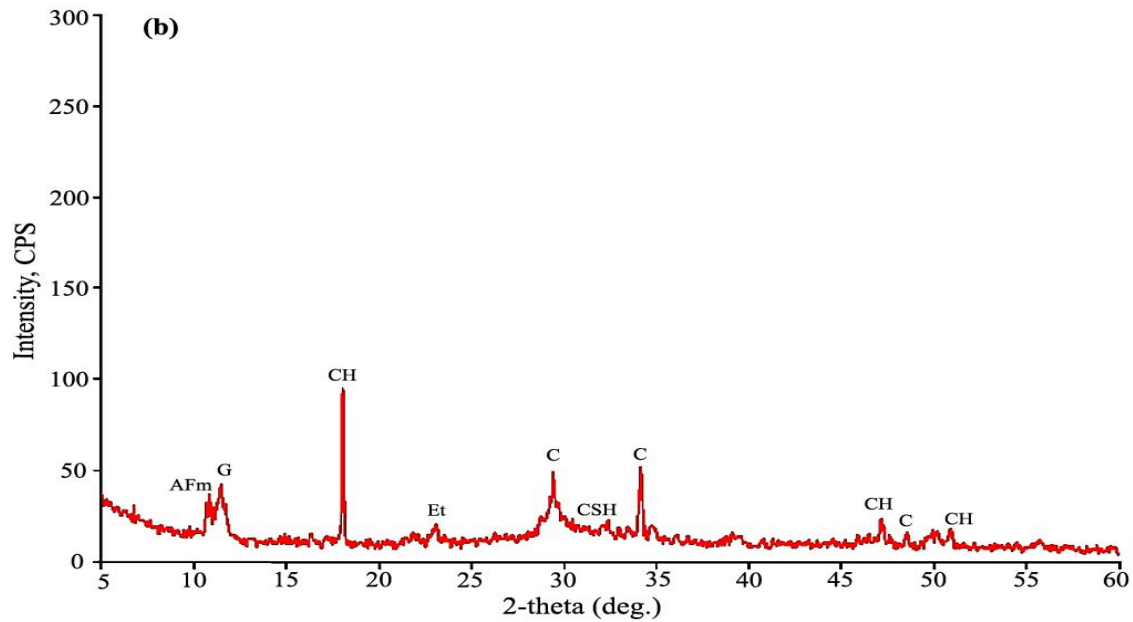


Figure 6.10. Results of XRD of PS-CPT with 0 ppm of sulphate cured at (a) 20°C, and (b) 35°C for 150 days

Also, Figures 6.7 and 6.8 show that the reactivity of the 25,000 ppm samples cured at 50°C is significantly higher than that of the 5,000 and 15,000 ppm samples. This could be attributed to the combined effects of a few processes, namely, (i) the dissolution of ettringite crystals with increases in the curing temperature thus leading to coarsening of the pore structure (Lee et al., 2003; Fall and Pokharel, 2010); (ii) the inhibition of cement hydration; and (iii) the formation of hydration rims around SA and/or FA particles as a result of the high temperature thus leading to delays in any subsequent hydration reactions. All of these processes are resultant of increases in sulphate and temperature. This conclusion is fully supported by the results of the observations made by using a scanning electron microscopy on mature PF-CPT samples that contain 0 ppm and 25,000 ppm sulphate and cured at 50°C, as shown in Figure 6.11. The figure is a comparison of the SEM micrographs of the PF-CPT samples that contain 0 ppm (Figure 6.11a) and 25,000 ppm (Figure 6.11b) of sulphate and cured for 150 days at 50°C. It can be seen that the sample with an initial sulphate content of 25,000 ppm has more voids as sulphate is an inhibitor of cement hydration and temperature causes the dissolution of ettringite. These can result in the formation of preferential pathways for the ingress of O<sub>2</sub> and thus lead to high levels of reactivity. Furthermore, the saturated hydraulic conductivity (permeability) results of the PS-CPT samples with various sulphate concentrations and cured for 150 days at 50°C are presented in Figure 6.12, which clearly

shows that the CPT sample with an initial sulphate content of 25,000 ppm has a higher permeability which explains for its high reactivity.

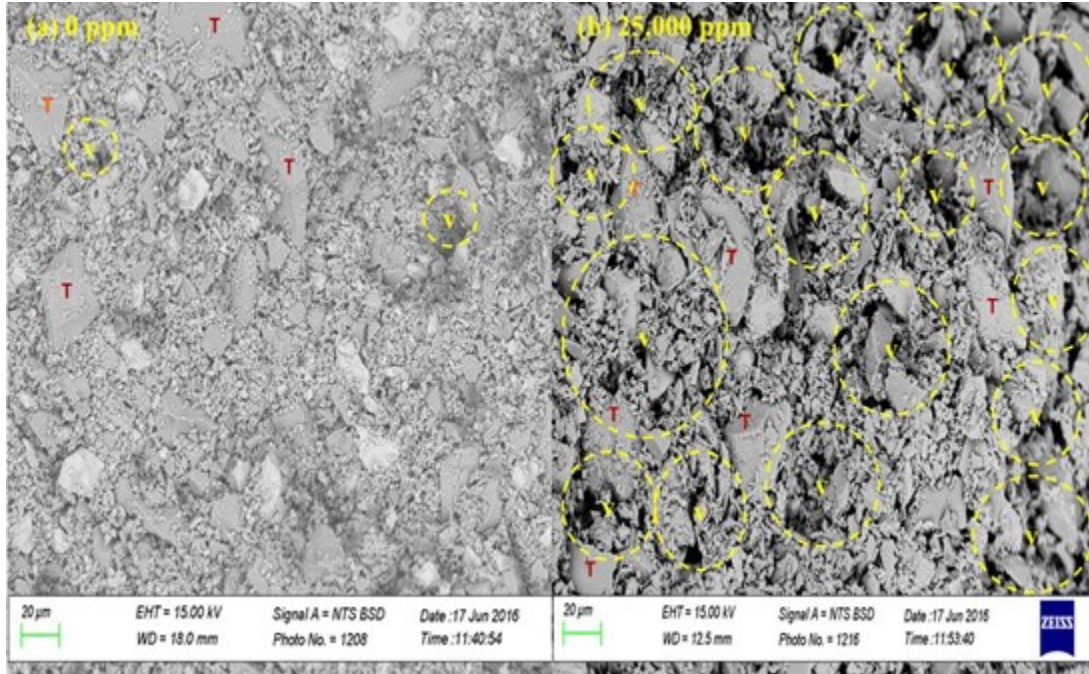


Figure 6.11. SEM micrographs of (a) mature PF-CPT samples with 0 ppm of sulphate and (b) mature PF-CPT samples with 25,000 ppm of sulphate, cured at 50°C [T: Tailings; V:Void]

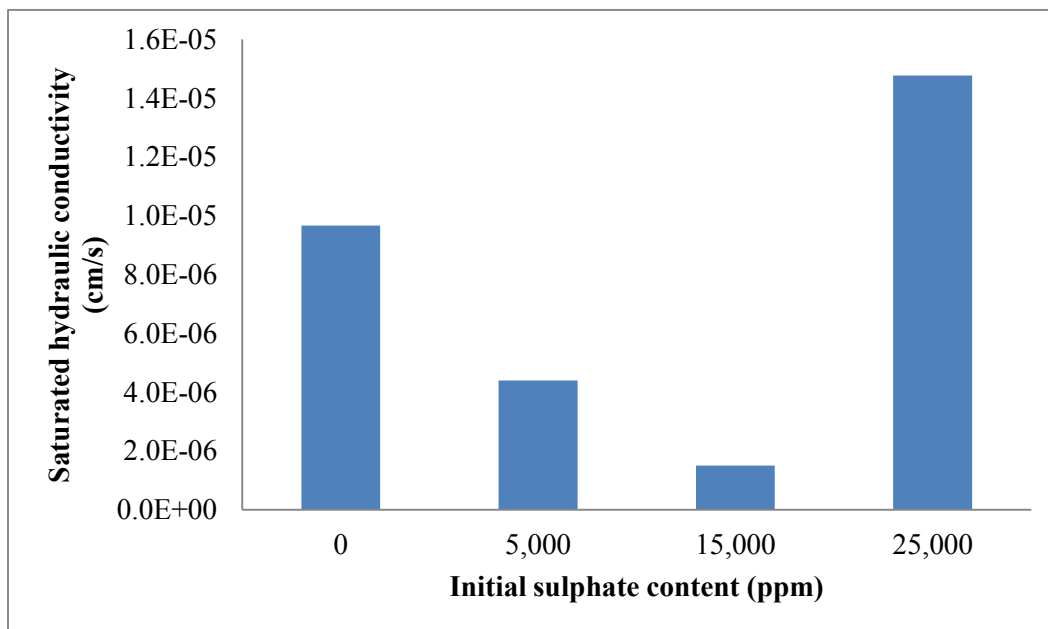


Figure 6.12. Effect of initial sulphate content on saturated hydraulic conductivity of 150-day PS-CPT samples cured at 50°C (Mukesh Pokharel & Fall, 2011)

## 6.4 Summary and Conclusion

The combined effect of the initial sulphate concentration and curing temperature on the reactivity of a CPT system has been experimentally studied by conducting OC tests as well as microstructural analysis. The CPT samples are made of three types of binders (PC, PS and PF) with 0 ppm, 5,000 ppm, 15,000 ppm and 25,000 ppm of sulphate. The samples are cured at 20°C, 35°C and 50°C for 150 days. The main conclusions that can be drawn from the experimental work are as follows.

- The coupled effects of the initial sulphate content and curing temperature have significant impacts on the reactivity of CPT samples. This impact can be negative (increased reactivity) or positive (reduced reactivity).
- Regardless of the type of binder used, the reactivity of the studied CPT systems increases with both higher curing temperature and more sulphate content for CPT with sulphate contents higher than 5000 ppm.
- The partial substitution of PC with mineral admixtures (e.g., slag and fly ash) leads to an increase in the degree of saturation of the CPT samples, which reduces their reactivity.

## 6.5 References

- Aldhafeeri, Z., & Fall, M. (2017). Sulphate induced changes in the reactivity of cemented tailings backfill. *International Journal of Mineral Processing*, 166. <https://doi.org/10.1016/j.minpro.2017.06.007>
- Aldhafeeri, Z., Fall, M., Pokharel, M., & Pouramini, Z. (2016). Temperature dependence of the reactivity of cemented paste backfill. *Applied Geochemistry*, 72, 10–19. <https://doi.org/10.1016/j.apgeochem.2016.06.005>
- Ayub, T., Shafiq, N., Khan, S., & Nuruddin, M. (2013). Durability of Concrete with Different Mineral Admixtures: A Review. *International Journal of Civil, Architectural, Structural and Construction Engineering*, 7(8), 273–284. Retrieved from <http://www.waset.org/publications/9996810>
- Belem, T., & Benzaazoua, M. (2004). An overview on the use of paste backfill technology as a ground support method in cut-and-fill mines. In *Proceedings of the 5th Int. Symp. on Ground support in Mining and Underground Construction*. Villaescusa & Potvin (eds.) (pp. 637 – 650). London: Tayler & Francis Group.
- Blight, G. (2009). *Geotechnical Engineering for Mine Waste Storage Facilities*. CRC Press. Retrieved from <https://books.google.ca/books?id=OdFp3wKyxJoC>
- Bois, D., Benzaazoua, M., Bussiere, B., Kongolo, M. and Poirier, P. (2005). A feasibility study on the use of desulphurized tailings to control acid mine drainage. *CIM Bulletin*, 98(1087).
- Boukendakdji, O., Kadri, E.-H., & Kenai, S. (2012). Effects of granulated blast furnace slag and superplasticizer type on the fresh properties and compressive strength of self-compacting concrete. *Cement and Concrete Composites*, 34(4), 583–590. <https://doi.org/10.1016/j.cemconcomp.2011.08.013>

- Bussière, B. (2007). Colloquium 2004: Hydrogeotechnical properties of hard rock tailings from metal mines and emerging geoenvironmental disposal approaches. *Canadian Geotechnical Journal*, 44(9), 1019–1052. <https://doi.org/10.1139/T07-040>
- Carraro, J., Prezzi, M., & Salgado, R. (2009). Shear Strength and Stiffness of Sands Containing Plastic or Nonplastic Fines. *Journal of Geotechnical and Geoenvironmental Engineering*, 135(9), 1167–1178. [https://doi.org/10.1061/\(ASCE\)1090-0241\(2009\)135:9\(1167\)](https://doi.org/10.1061/(ASCE)1090-0241(2009)135:9(1167))
- Clark, C. C., Vickery, J. D., & Backer, R. R. (1995). Transport of total tailings paste backfill: results of full-scale pipe test loop pumping tests.
- Coussy, S., Benzaazoua, M., Blanc, D., Moszkowicz, P., & Bussière, B. (2012). Assessment of arsenic immobilization in synthetically prepared cemented paste backfill specimens. *Journal of Environmental Management*, 93(1), 10–21. <https://doi.org/10.1016/j.jenvman.2011.08.015>
- Dold, B. (2014). Evolution of Acid Mine Drainage Formation in Sulphidic Mine Tailings. *Minerals*, 4(3), 621–641. <https://doi.org/10.3390/min4030621>
- Drebenstedt, C. and, & Singhal, R. (2014). *Mine Planning and Equipment Selection*. (C. Drebenstedt & R. Singhal, Eds.). Cham: Springer International Publishing. <https://doi.org/10.1007/978-3-319-02678-7>
- Edraki, M., Baumgartl, T., Manlapig, E., Bradshaw, D., Franks, D. M., & Moran, C. J. (2014). Designing mine tailings for better environmental, social and economic outcomes: a review of alternative approaches. *Journal of Cleaner Production*, 84, 411–420. <https://doi.org/http://dx.doi.org/10.1016/j.jclepro.2014.04.079>
- Elberling, B., Nicholson, R. V., & Scharer, J. M. (1994). A combined kinetic and diffusion model for pyrite oxidation in tailings: a change in controls with time. *Journal of Hydrology*, 157(1–4), 47–60. [https://doi.org/10.1016/0022-1694\(94\)90098-1](https://doi.org/10.1016/0022-1694(94)90098-1)
- Elberling, B., & Nicholson, R. V. (1996). Field determination of sulphide oxidation rates in mine tailings. *Water Resources Research*, 32(6), 1773–1784. <https://doi.org/10.1029/96WR00487>
- Elberling, B., Nicholson, R. V., Reardon, E. J., & Tibble, R. (1994). Evaluation of sulphide oxidation rates: a laboratory study comparing oxygen fluxes and rates of oxidation product release. *Canadian Geotechnical Journal*, 31(3), 375–383. <https://doi.org/10.1139/t94-045>
- Fall, M., & Benzaazoua, M. (2005). Modeling the effect of sulphate on strength development of paste backfill and binder mixture optimization. *Cement and Concrete Research*, 35(2), 301–314. <https://doi.org/10.1016/j.cemconres.2004.05.020>
- Fall, M., Benzaazoua, M., & Ouellet, S. (2004). Effect of tailings properties on paste backfill performance. In *Proceedings of the eighth international symposium on mining with backfill (Minefill 2004)* (pp. 193–202). China.
- Fall, M., Célestin, J. C., Pokharel, M., & Touré, M. (2010). A contribution to understanding the effects of curing temperature on the mechanical properties of mine cemented tailings backfill. *Engineering Geology*, 114(3–4), 397–413. <https://doi.org/10.1016/j.enggeo.2010.05.016>
- Fall, M., & Pokharel, M. (2010). Coupled effects of sulphate and temperature on the strength development of cemented tailings backfills: Portland cement-paste backfill. *Cement and Concrete Composites*, 32(10), 819–828. <https://doi.org/10.1016/j.cemconcomp.2010.08.002>
- Farver, J. R. (2010). Oxygen and Hydrogen Diffusion in Minerals. *Reviews in Mineralogy and Geochemistry*, 72(1), 447 LP-507. Retrieved from <http://ring.geoscienceworld.org/content/72/1/447.abstract>
- Ghirian, A., & Fall, M. (2014). Coupled thermo-hydro-mechanical–chemical behaviour of

- cemented paste backfill in column experiments. *Engineering Geology*, 170, 11–23.  
<https://doi.org/10.1016/j.enggeo.2013.12.004>
- Huang, L.-N., Zhou, W.-H., Hallberg, K. B., Wan, C.-Y., Li, J., & Shu, W.-S. (2011). Spatial and Temporal Analysis of the Microbial Community in the Tailings of a Pb-Zn Mine Generating Acidic Drainage. *Applied and Environmental Microbiology*, 77(15), 5540–5544. <https://doi.org/10.1128/AEM.02458-10>
- Kesler, S. . (2007). Mineral supply and demand into the 21st century. In *Proceedings, Workshop on Deposit Modeling, Mineral Resource Assessment, and Sustainable Development* (pp. 55–62). U.S. Geological Survey Circular 1294. Retrieved from <http://pubs.usgs.gov/circ/2007/1294/reports/paper9.pdf>
- Kumari, S., Udayabhanu, G., & Prasad, B. (2010). Studies on environmental impact of acid mine drainage generation and its treatment: an appraisal. *Indian Journal of Environmental Protection*, 30(11), 953–967.
- Lee, H., Cody, R., Cody, A., & Spry, P. (2003). Reduction of Concrete Expansion by Ettringite Using Crystallization Inhibition Techniques. *Environmental & Engineering Geoscience*, 9(4), 313–326. Retrieved from <http://eeg.geoscienceworld.org/content/9/4/313.abstract>
- Li, W., & Fall, M. (2016). Sulphate effect on the early age strength and self-desiccation of cemented paste backfill. *Construction and Building Materials*, 106, 296–304.  
<https://doi.org/10.1016/j.conbuildmat.2015.12.124>
- Lothenbach, B., Winnefeld, F., Alder, C., Wieland, E., & Lunk, P. (2007). Effect of temperature on the pore solution, microstructure and hydration products of Portland cement pastes. *Cement and Concrete Research*, 37(4), 483–491.  
<https://doi.org/10.1016/j.cemconres.2006.11.016>
- Martin, V., Aubertin, M., Bussière, B., Mbonimpa, M., Dagenais, A. M., & Gosselin, M. (2006). Measurement of oxygen consumption and diffusion in exposed and covered reactive mine tailings. In *The Proceedings of 7th ICARD* (pp. 1156–1169). St. Louis MO, USA.
- Mbonimpa, M., Aubertin, M., & Bussière, B. (2011). Oxygen consumption test to evaluate the diffusive flux into reactive tailings: interpretation and numerical assessment. *Canadian Geotechnical Journal*, 48(6), 878–890. <https://doi.org/10.1139/t11-015>
- Obermeyer, J., & Alexieva, T. (2011). Design, Construction and Operation of a Large Centerline Tailing Storage Facility with High Rate of Rise. In *Proceedings Tailings and Mine Waste*.
- Öhlander, B., Chatwin, T., & Alakangas, L. (2012). Management of Sulfide-Bearing Waste, a Challenge for the Mining Industry. *Minerals*, 2(4), 1–10.  
<https://doi.org/10.3390/min2010001>
- Ouellet, S., Bussiere, B., Benzaazoua, M., Aubertin, M., Fall, M., & Belem, T. (2003). Sulphide Reactivity within cemented paste backfill: oxygen consumption test results. In *The 56th Annual Canadian Geotechnical Conference and 4th joint IAH-CNC/CGS Conference* (pp. 176–183). Winnipeg, Manitoba, Canada.
- Ouellet, S., Bussière, B., Mbonimpa, M., Benzaazoua, M., & Aubertin, M. (2006). Reactivity and mineralogical evolution of an underground mine sulphidic cemented paste backfill. *Minerals Engineering*, 19(5), 407–419. <https://doi.org/10.1016/j.mineng.2005.10.006>
- Pokharel, M. (2008). Geotechnical and environmental response of paste tailings systems to coupled thermo-chemical loadings. University of Ottawa. Retrieved from <http://hdl.handle.net/10393/27793>
- Pokharel, M., & Fall, M. (2011). Coupled Thermochemical Effects on the Strength Development of Slag-Paste Backfill Materials. *Journal of Materials in Civil Engineering*, 23(5), 511–525.

[https://doi.org/10.1061/\(ASCE\)MT.1943-5533.0000192](https://doi.org/10.1061/(ASCE)MT.1943-5533.0000192)

- Pokharel, M., & Fall, M. (2013). Combined influence of sulphate and temperature on the saturated hydraulic conductivity of hardened cemented paste backfill. *Cement and Concrete Composites*, 38, 21–28. <https://doi.org/10.1016/j.cemconcomp.2013.03.015>
- Rashad, A. M. (2015). A brief on high-volume Class F fly ash as cement replacement – A guide for Civil Engineer. *International Journal of Sustainable Built Environment*, 4(2), 278–306. <https://doi.org/10.1016/j.ijbsbe.2015.10.002>
- Şahmaran, M., Yaman, İ., & Tokyay, M. (2009). Transport and mechanical properties of self consolidating concrete with high volume fly ash. *Cement and Concrete Composites*, 31(2), 99–106. <https://doi.org/10.1016/j.cemconcomp.2008.12.003>
- Snellings, R., Mertens, G., & Elsen, J. (2012). Supplementary Cementitious Materials. *Reviews in Mineralogy & Geochemistry*, 74(1), 211–278. <https://doi.org/10.2138/rmg.2012.74.6>
- Tariq, A., & Yanful, E. K. (2013). A review of binders used in cemented paste tailings for underground and surface disposal practices. *Journal of Environmental Management*, 131, 138–49. <https://doi.org/10.1016/j.jenvman.2013.09.039>
- Tzouvalas, G., Rantis, G., & Tsimas, S. (2004). Alternative calcium-sulfate-bearing materials as cement retarders: Part II. FGD gypsum. *Cement and Concrete Research*, 34(11), 2119–2125. <https://doi.org/10.1016/j.cemconres.2004.03.021>
- Yanful, E. K. (1993). Oxygen diffusion through soil covers on sulphidic mine tailings. *Journal of Geotechnical Engineering*, 119(8), 1207–1228.
- Yilmaz, E. (2011). Advances in reducing large volumes of environmentally harmful mine waste rocks and tailings. *Gospodarka Surowcami Mineralnymi*, 27(2), 89–112.

## **Chapter 7: Technical Paper V- Effects of Curing Stress on Reactivity of Cemented Paste Backfill**

Submitted: Aldhafeeri, Z. and Fall, M. 'Effects of Curing Stress on Reactivity of Cemented Paste Backfill'.

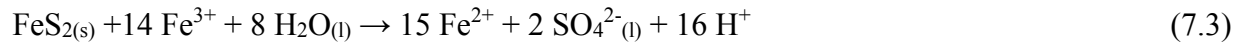
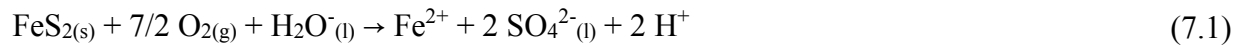
### **Abstract**

Cemented paste backfilling is a relatively new technology that is widely applied worldwide by many companies that are involved in underground mining. The method enables the disposal of sulphide-bearing tailings, which are considered to be one of the most significant contributors to environmental and economic challenges faced by the mining industry. The chemical reactivity of sulphidic tailings by themselves or incorporated into a cemented paste backfill (CPB) mixture is a key factor that affects the environmental behaviour of CPB. Chemical reactivity can be measured by oxygen consumption (OC) testing, and the measured reactivity helps to assess the environmental behaviour and durability of CPB systems. There are numerous internal and external factors that can influence the reactivity behaviour of a CPB mixture during its mixing, placement and operation life-time. The investigation of these factors can provide a better understanding of the reactivity behaviour of CPB systems. One of the most important factors is the curing stress and its effects on CPB. The main objective of this paper is to therefore study the effect of curing stress on the reactivity of CPB when cured at room temperature in both drained and undrained conditions for different curing times by conducting OC testing. The results of this study show that the reactivity of undrained CPB samples at room temperature decreases with increases in curing time and curing stress. Furthermore, the drained condition has a significant influence on the reactivity of CPB in comparison to the undrained condition. This reduction in reactivity is attributed to a smaller effective diffusion coefficient ( $D_e$ ) of oxygen in the surface of the CPB samples over time as a result of the progression of cement hydration and the consolidation induced by the applied curing stress. It can be concluded that the curing stress has a significant influence on the reactivity of CPB systems, and should be considered when assessing the reactivity of CPB.

**Keywords:** Cemented paste backfill; curing stress; tailings; mine; acid mine drainage

## 7.1 Introduction

Cemented paste backfilling has become a widely adopted technology for managing tailings in modern mining operations worldwide (Kermani et al., 2015; Huang et al., 2011; Thottarath, 2010; Belem et al., 2000). Cemented paste backfilling is an alternative tailings disposal method that has a number of technical and environmental advantages over conventional methods. One of these advantages is controlling the chemical reactivity of sulphidic tailings by limiting the molecular diffusion of atmospheric oxygen (Yilmaz and Fall, 2017; Tariq and Yanful, 2013; Rankine and Sivakugan, 2007; Tariq and Nehdi, 2007). It is well known that sulphidic tailings have the potential to form acid mine drainage (AMD) when exposed to atmospheric oxygen and water (Dold, 2014; Lottermoser, 2010; Akcil and Koldas, 2006). Pyrite ( $\text{FeS}_2$ ) is a dominant sulphide mineral commonly found in mine wastes (Lottermoser, 2010). The oxidation of pyrite is a complex process that involves a series of oxidation-reduction and hydrolysis reactions and formation of complex products (Dold, 2014; Lottermoser, 2010; Kimble, 2004; Norton et al., 1990). The following equations show that there is oxidation in the pyrite mineral (Bois et al., 2005):



The above reactions produce AMD, and the produced acid can reduce the pH of nearby water bodies (Kumari et al., 2010). Also, the acid can dissolve toxic metals and metalloids (e.g., arsenic) from the surrounding materials and leach them into the environment (Johnson and Hallberg, 2005). Consequently, this can cause serious economic, environmental, and social problems that may last for years or decades (Naidoo, 2016). Sulphidic tailings are commonly stored underwater and/or covered with inert materials (e.g., soil) to prevent them from direct contact with the atmospheric oxygen (thereby reducing oxygen availability) (Ripley and Redmann, 1995). Such conventional methods have negative environmental impacts related to physical stability, leaching, and water and soil quality (Moncur et al., 2015; Rankin, 2011).

Over the past few decades, the mining industry has been developing and applying several alternative methods (e.g., use of paste and dry-stack tailings, and cemented paste backfilling) for managing tailings (mainly sulphidic tailings) to avoid future liability (Öhlander et al., 2012; Mular et al., 2002). Among these methods, cemented paste backfilling has become a more widespread technology in many mines worldwide (Fall et al., 2015; Tariq and Yanful, 2013; Belem and Benzaazoua, 2004). Cemented paste backfill (CPB) is an engineered composite that consists of three main ingredients: tailings (70 - 85% solids by weight), hydraulic binder (typically 3 - 7 wt%), and mixing water that can be either fresh or processed (Benzaazoua et al., 2002). This mixture is typically prepared in a CPB plant at the mine surface and pumped by gravity or electrical pumps to fill voids (stopes) created by mining excavation.

The chemical reactivity of sulphidic tailings alone or incorporated with cement paste (i.e., CPB) can be used as an index property to assess its ability to cause AMD; in other words, its environmental behaviour and durability performance. Several methods have been used to measure and evaluate the reactivity of tailings with and without cement paste, such as sulphate release, oxygen gradient, and oxygen consumption (OC) tests. The OC test is considered a preferred approach amongst other methods because it is simple, quick, accurate and low in cost. Furthermore, it can be used in both the laboratory and the field.

CPB is exposed to various internal and external factors during mixing, placement, and application which affect its properties. These factors can positively and/or negatively influence the reactivity of CPB individually or combined with other factors, and an investigation of these factors can provide a better understanding of the reactivity of CPB systems. The influence of some of these factors, such as sulphide content, temperature, degree of saturation, and initial sulphate content, both individually and combined, on the reactivity of CPB has been studied by several researchers through OC testing (e.g., Aldhafeeri and Fall, 2017; Aldhafeeri et al., 2016; Aldhafeeri and Fall, 2016; Pokharel, 2008; Ouellet et al., 2003, 2006). Despite the contributions of these studies, there are other relevant factors that have not been investigated, such as the influence of curing stress. Curing stress is considered to be one of the most important factors that affect CPB properties (Ghirian & Fall, 2016b; Yilmaz et al., 2014). It is known that the curing conditions of CPB samples in the laboratory are significantly different from those in the field (Fahey et al., 2011). This difference is partly due to the fact that in the field, a CPB system is cured under different conditions of stress, such as backfill overburden pressure, filling strategy (e.g., filling rate

and sequence), plug filling methods, and drainage conditions. Such curing conditions can affect the properties of a CPB system and its environmental behaviour and durability performance. Furthermore, they may influence the short- and long-term reactivities of CPB systems. Therefore, curing stress is a key factor that should be investigated for a better understanding of the reactivity of CPB systems. However, there have been no experimental studies to date that investigate the effects of curing stress on the reactivity of CPB. Hence, the main objective of this study is to experimentally investigate the influence of curing stress on the reactivity of CPB.

## 7.2 Experimental Program

### 7.2.1 Materials

#### 7.2.1.1 Tailings

A pure silica powder (99.9 wt.% silicon dioxide ( $\text{SiO}_2$ ) called SIL-CO-SIL 106 (ground silica) which is manufactured by U.S. Silica Co. is used as the artificial silica tailings (ST) in this work. ST are characterized by chemical inertness and a grain size distribution similar to the average particle size distribution of tailings from 9 mines in eastern Canada, as illustrated in Figure 7.1. The use of ST allows uncertainties otherwise associated with the use of natural tailings to be greatly reduced in the results.

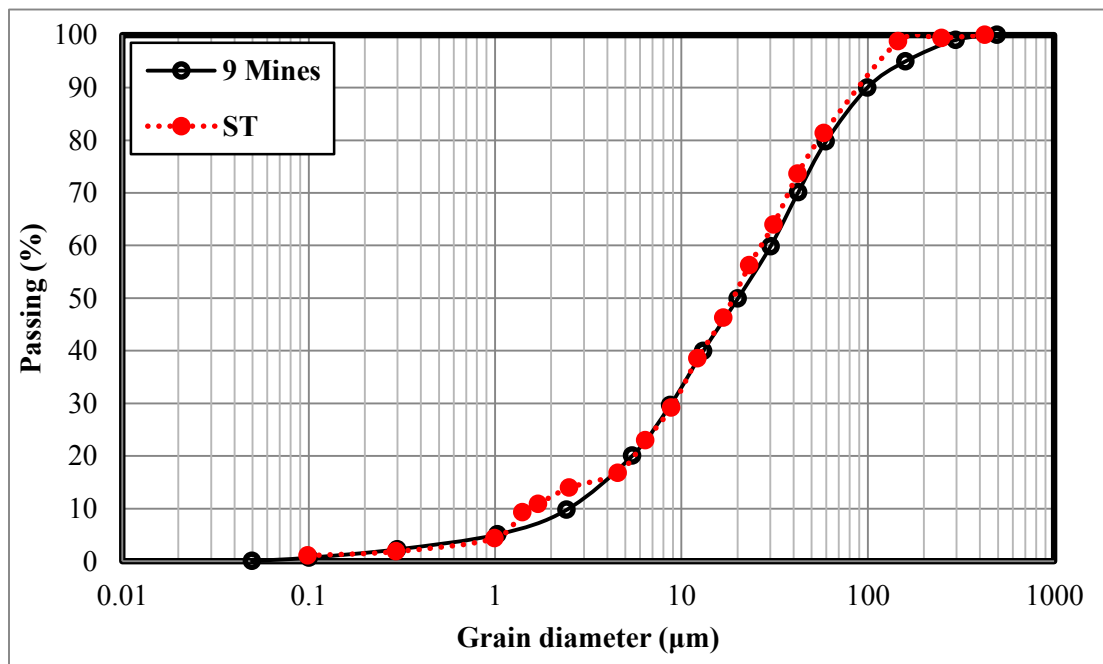


Figure 7.1. Grain size distribution of tailings (ST) used, and average grain size distribution of tailings from 9 mines in eastern Canada

### 7.2.1.2 Pyrite

A commercial pyrite powder ( $\text{FeS}_2$ , M.W. = 119.98, Washington Mills North Grafton, Inc.) was mixed with a defined amount of ST to create tailings that contained 45 wt% of sulphide mineral. Its grain size is similar to that of natural pyrite minerals found in natural tailings. The physical properties of the commercial pyrite powder are presented in Table 7.1. To mix the tailings with 45 wt% of pyrite mineral (ST-45%), the required quantity of pyrite powder was added to the ST powder and mixed dry in a clean bowl until the mixture had a uniform colour.

Table 7.1. Physical properties of pyrite used (Source: Washington Mills North Grafton, Inc.)

Bulk density ( $\text{g/cm}^3$ )	Density at 20°C ( $\text{g/cm}^3$ )	Specific gravity	pH	Melting point (°C)
2.35	4.7	4.6	4.0- 6.0	1193

### 7.2.1.3 Hydraulic Binder

Portland Cement Type I (PCI) was used for the preparation of the CPB samples, as it is the most common type of binder used in CPB plants. The main physical and chemical properties of PCI are presented in Table 7.2.

Table 7.2. Chemical properties of binder used

Binder	MgO (wt%)	CaO (wt%)	SiO <sub>2</sub> (wt%)	Al <sub>2</sub> O <sub>3</sub> (wt%)	Fe <sub>2</sub> O <sub>3</sub> (wt%)	SO <sub>3</sub> (wt%)	Relative density
PCI	2.65	62.82	18.03	4.53	2.7	3.82	3.1

## 7.2.2 Sample Preparation

### 7.2.2.1 Mix Proportion

The CPB samples were made by mixing selected quantities of pyritic-ST with 4.5% PC and distilled water at a water-to-binder ratio (w/b) of 7.6, as shown in Table 7.3. All of the CPB mixtures were mixed in a small food mixer for 7 minutes in order to achieve homogenous mixes with a slump of 18 cm in accordance with the slump test described in ASTM C143-90. The CPB mixes were then poured into polyvinyl chloride (PVC) cylinders with a diameter of 10 cm and height of 20 cm for curing. During the paste-pouring, the moulds were manually tapped against a

hard surface to remove any trapped air. Then, the cylinders were placed inside pressure cells under different curing stresses for various curing times (7, 28, and 90 days) at room temperature. The pressure cell is an apparatus developed at the University of Ottawa by Ghirian and Fall (2013), as illustrated in Figure 7.2, and its function is to mimic the different stress conditions on the CPB samples that are similar to those found in the field. These stresses could be generated by gradual filling (with varying sequences and different rates of filling) and the self-weight pressure of mine paste backfill. The apparatus is composed of a Perspex (acrylic plastic) cylinder with a diameter of 101.6 mm (4 inches) and height of 304.8 mm (12 inches), with an axial piston on the top of the cylinder. The piston is pressed down onto the CPB sample by using high-pressure air supplied by an air system in the laboratory. In this work, 600 kPa is the maximum air pressure used, which is considered the maximum allowable laboratory working pressure, and equivalent to a backfill mass with a height of about 30 to 35 m, if there is no arching effect (Ghirian and Fall, 2013). The pressure cell is a controllable apparatus that can simulate, at the laboratory scale, various curing conditions that approximate underground mine stope conditions. A number of pressure regulators and gauges are used which apply different air pressures onto each sample. In order to evaluate and better understand the effects of curing stress conditions on the reactivity of CPB, various loading conditions and different curing scenarios were applied to the samples as explained below.

Table 7.3. Mix compositions of the prepared CPB samples

<b>CPB Sample</b>	<b>Binder</b>	<b>Binder content (%)</b>	<b>Tailings type</b>	<b>Pyrite content (%)</b>	<b>w/c ratio</b>	<b>Curing time (Days)</b>
<b>ST-PC-CPB-45</b>	PCI	4.5	ST	45%	7.6	7, 28, 90

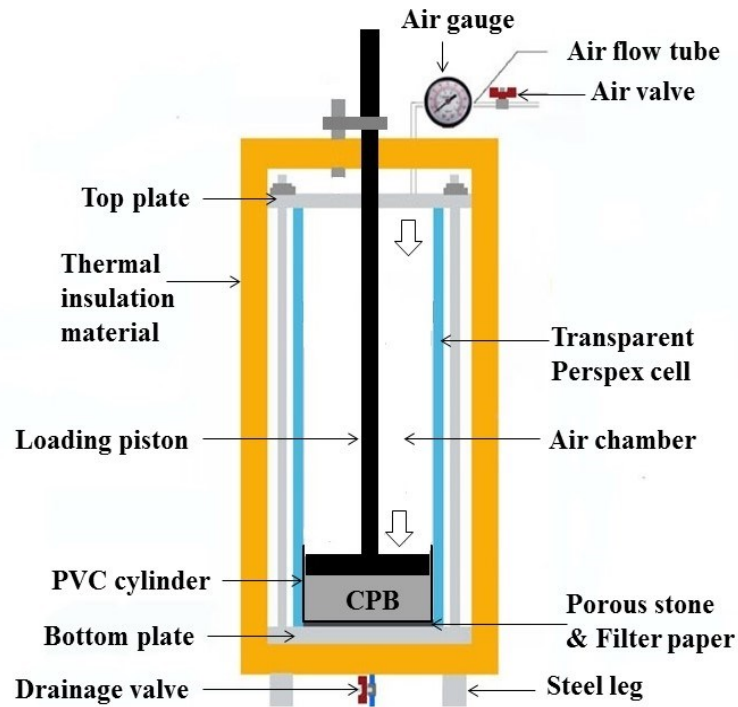


Figure 7.2. Schematic diagram of pressure cell apparatus (Ghirian and Fall, 2013)

### 7.2.2.2 Simulated Scenarios

In this study, four different scenarios are experimentally tested by using pressure cells to assess and better understand the effects of curing stress on the reactivity of CPB systems. These scenarios include the following.

**Scenario One:** investigates the effects of curing stress increases on the reactivity of the CPB system in undrained conditions. Three different stress levels (Cases A, B, and C) were studied. The cases simulate the curing stresses to which the undrained CPB will be subjected at different stope depths and in the absence of the arching effect, as illustrated in Figure 7.3. In Case A (control), the CPB sample is cured without stress, whereas in Cases B and C, the applied pressure is gradually increased in the first 12 h (i.e., every 3 h) and up to 150 kPa in order to simulate a more realistic self-weight pressure of the sample during the early ages of curing. Then, the pressure is increased every 24 h up to 600 kPa for Case B as illustrated in Figure 7.4.

**Scenario Two:** investigates the influence of rate of filling of CPB on the reactivity of the CPB system by using three different filling rates (0.31 m/h, 0.62 m/h, and 0.155 m/h), as illustrated in Figure 7.5.

**Scenario Three:** assesses the influence of plugs and their curing time on the reactivity of the CPB system. Three different cases with a constant filling rate were studied, namely: no plug (continuous filling); a plug cured for 1 day; and a plug cured for 3 days, as illustrated in Figure 7.6.

**Scenario Four:** investigates the influence of curing stress and drainage conditions (i.e., drained vs. undrained) on the reactivity of CPB. Two different drainage conditions (i.e., drained and undrained) with a filling rate of 0.31 m/h are applied as shown in Figure 7.7.

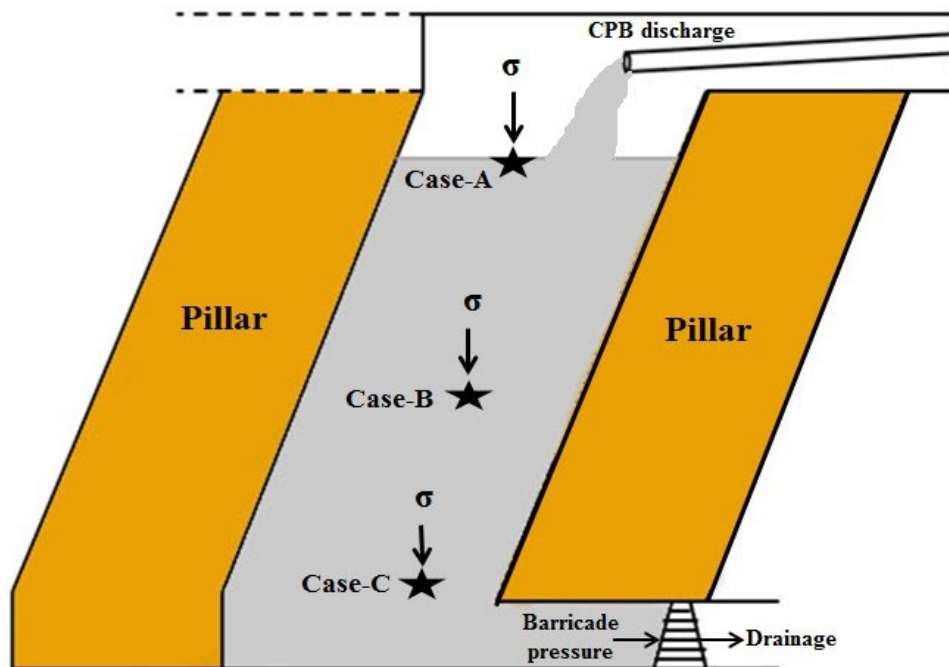


Figure 7.3. Schematic diagram of Cases A, B, and C for CPB stope

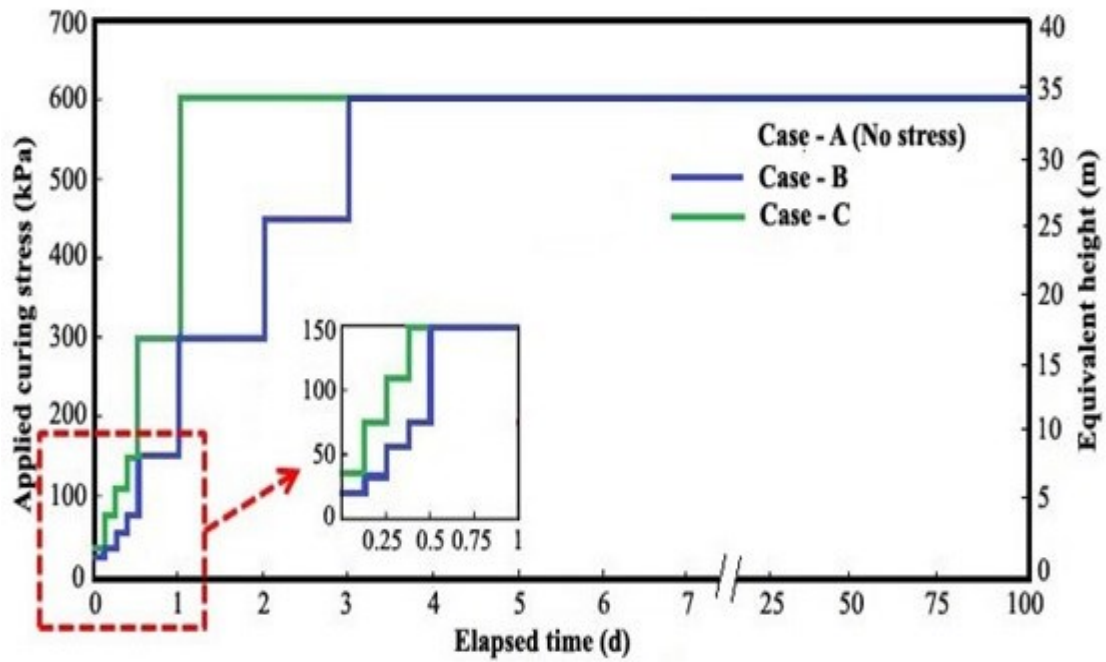


Figure 7.4. Load application for Scenario One: effect of incremental stress increase on the reactivity of CPB

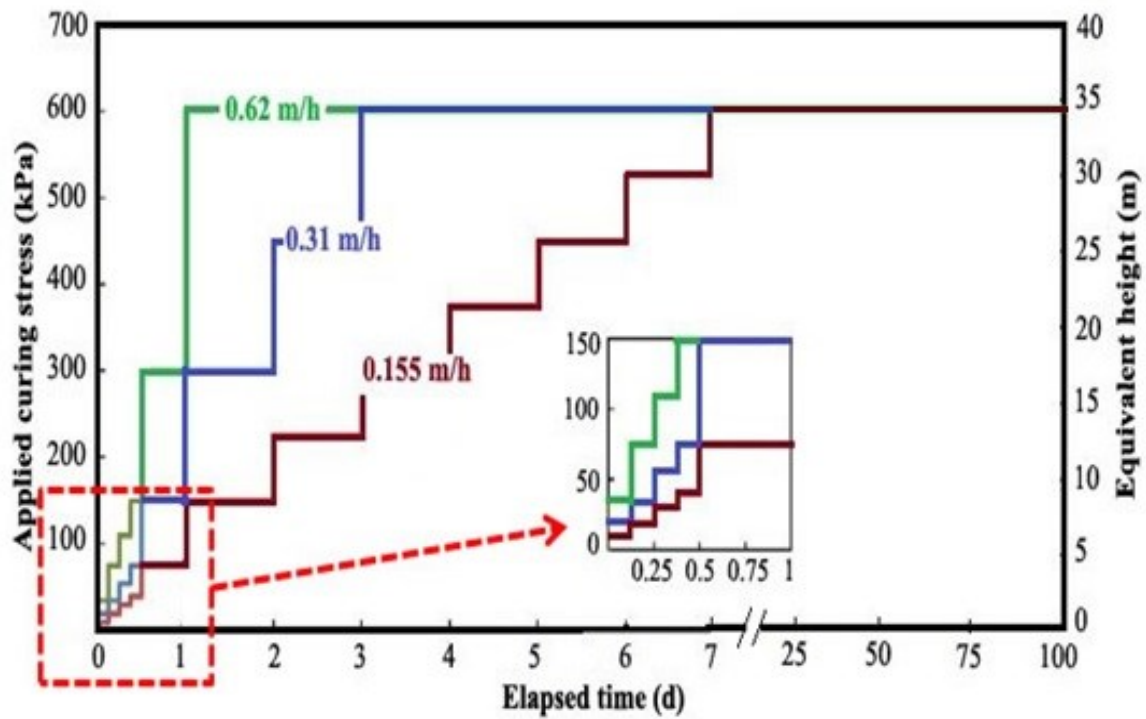


Figure 7.5. Load application for Scenario Two: effect of rate of filling on reactivity of CPB

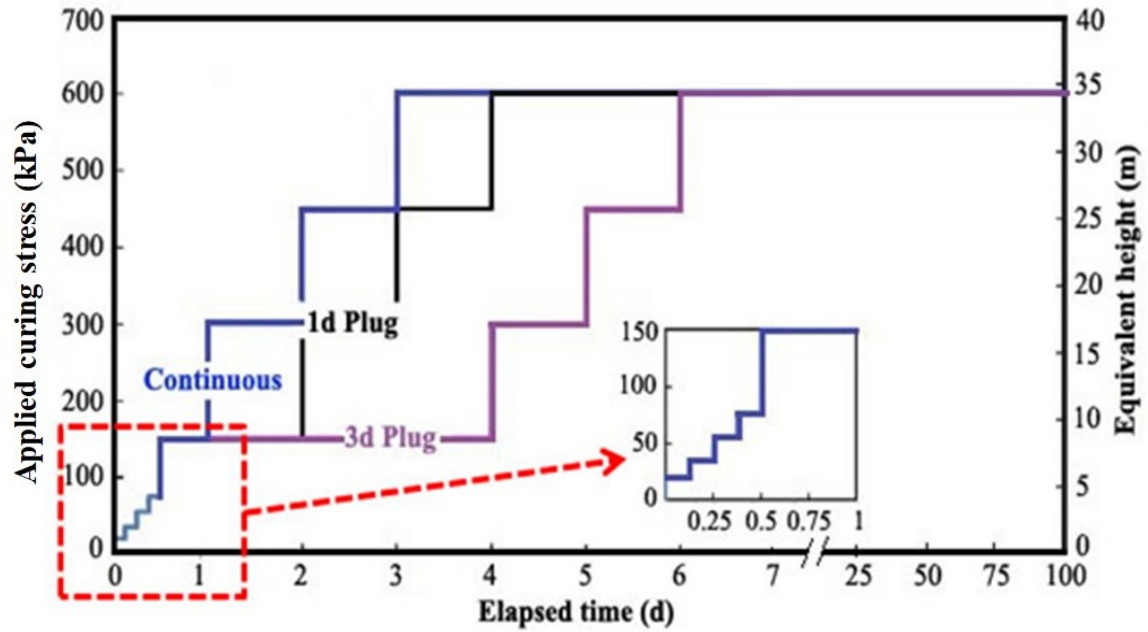


Figure 7.6. Load application for Scenario Three: effect of plug on reactivity of CPB

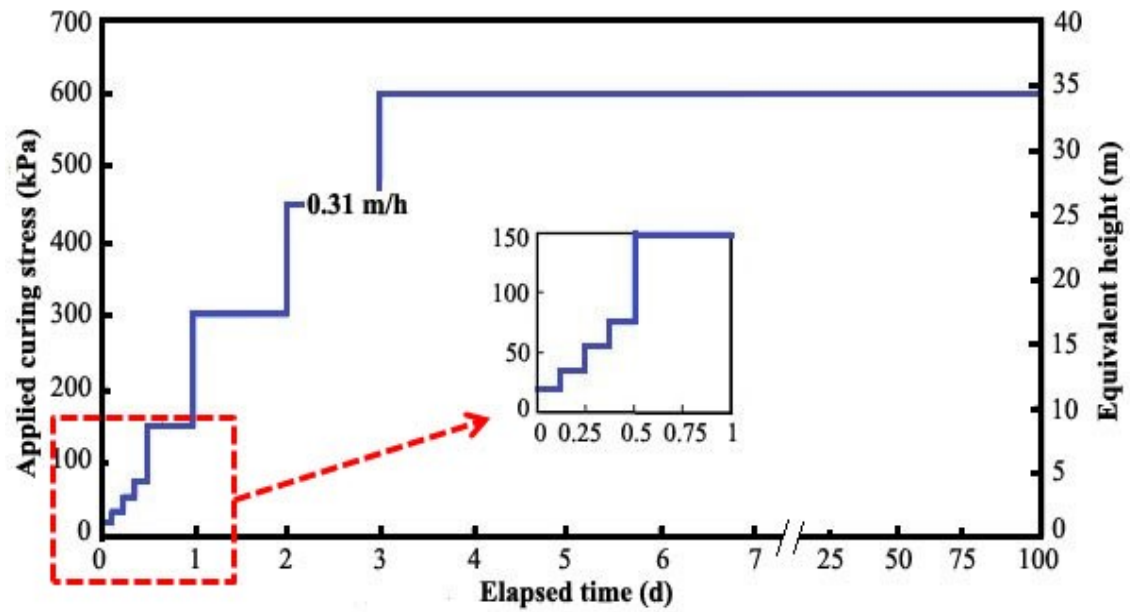


Figure 7.7. Load application for Scenario Four: effect of curing stress and drainage conditions (drained vs. undrained) on reactivity of CPB

## 7.2.3 Testing Program

### 7.2.3.1 Oxygen Consumption Test

The OC test proposed and developed by Elberling et al. (1994) and Elberling and Nicholson (1996) was used to evaluate the reactivity of sulphide-bearing mine wastes (mainly tailings) by measuring their rate of consumption of airborne oxygen (Aldhafeeri and Fall, 2016; Mbonimpa et al., 2011). It is known that oxygen flux into mine tailings is mostly affected by diffusion. The OC test is therefore used to measure the depletion of oxygen. A headspace of 2 cm is left at the surface of the CPB sample in the sealed PVC cylinder. The depletion of oxygen is due to oxygen diffusion and the reactivity of the sulphide-bearing waste materials (Mbonimpa et al., 2011). To describe this loss of oxygen, Elberling et al. (1994) used Fick's Laws, and solved Fick's second law for describing oxygen diffusion through reactive tailings for a first-order reaction under a steady state condition ( $\delta C/\delta t = 0$ ). As a result, Fick's second law was modified to measure reactivity in terms of the flux of oxygen ( $F_L$ ) through the tailings surface.  $F_L$  (reactivity) is expressed in moles of  $O_2/m^2/year$  or moles of  $O_2/m^2/day$ , as shown in Eq. 7.5.

$$F_L = C_o (K_r D_e)^{0.5} \quad (7.5)$$

where  $K_r$  is the first-order reaction rate coefficient for the sulphide mineral oxidation (e.g., pyrite),  $D_e$  is the effective diffusion coefficient, and  $C_o$  is the initial concentration of oxygen. The term  $(K_r D_e)$  can be obtained from the slope of plotting  $\ln(C/C_o)$  versus time based on Eq. 7.6. It can be calculated if the volume of the gas chamber ( $V$ ) and the surface area of the exposed area of the reactive materials ( $A$ ) are known (Aldhafeeri and Fall, 2016).

$$\ln(C/C_o) = -t (K_r D_e)^{0.5} (A/V) \quad (7.6)$$

Equation 7.6 is only valid for short-duration tests (i.e., about 3 hours) since the steady-state condition ( $\delta C/\delta t = 0$ ) is assumed to occur before and during the tests (Mbonimpa et al., 2011). Several previous studies have conducted OC tests to assess the reactivity of tailings (e.g., Schmieder et al., 2012; Martin et al., 2006; Ouellet et al., 2003; Mbonimpa et al., 2002; Elberling and Nicholson, 1996; Elberling et al., 1994), whereas only a few studies have evaluated the reactivity of CPB (e.g., Aldhafeeri and Fall, 2016; Aldhafeeri et al., 2016; Pokharel, 2008; Ouellet

et al., 2006). Furthermore, OC testing is used to evaluate the efficiency of cover systems that are used to prevent the exposure of sulphidic tailings to atmospheric conditions in order to reduce or counter any environmental impacts or economic repercussions (e.g., Dagenais et al., 2012; Mbonimpa et al., 2003, 2011; Martin et al., 2006).

In this work, OC testing was performed on CPB samples cured under various stress conditions and different curing times (7, 28, and 90 days) in the laboratory to determine their reactivity. Each OC test was repeated at least three times to ensure the repeatability of the results. Prior to the testing, the headspace was created by removing 2 cm of the CPB material from the top of the PVC cylinders. Then, the cylinders were closed with airtight lids equipped with an oxygen sensor (model SO-210, Apogee Instruments). Finally, the sensor was connected to a voltmeter (Hantek 365A USB Data Logger Recorder Digital Multimeter Voltage Current PC Base) to measure and record the voltage produced by the oxidation reaction over time in the sealed chamber. The voltage is directly proportional to the partial pressure of oxygen in the gas phase. The experimental setup of the OC test is shown in Figure 7.8. OC testing was performed on each CPB sample, and its reactivity was calculated by using Eqs. 7.5 and 7.6.

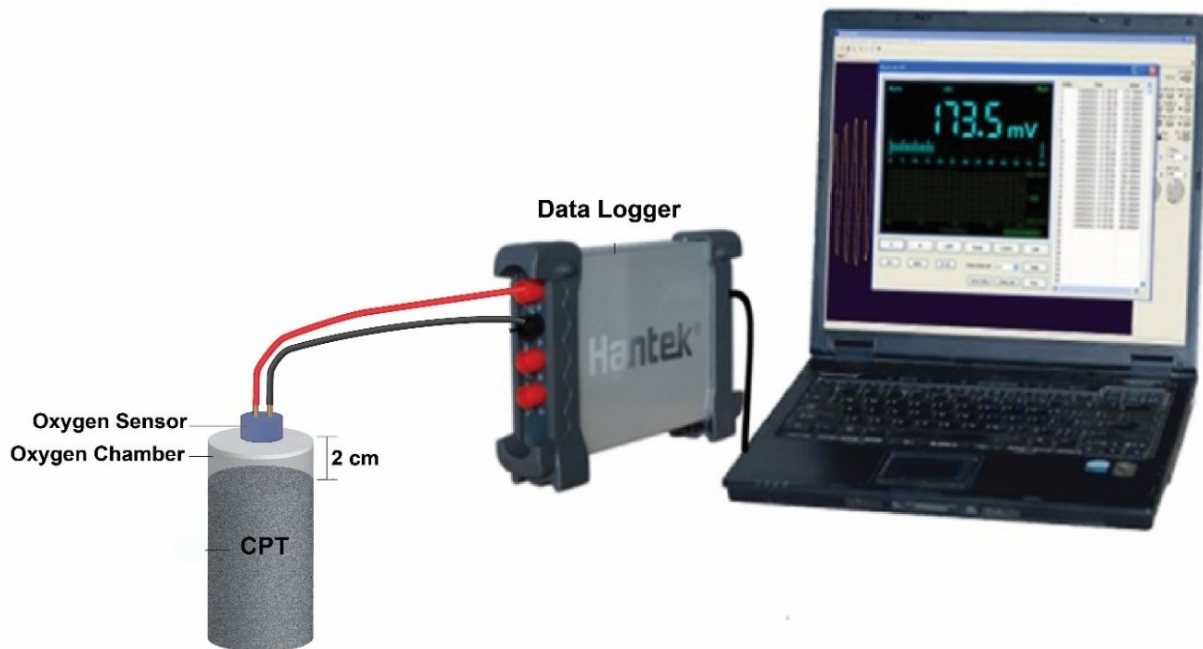


Figure 7.8. Schematic of experimental setup for OC testing

### 7.2.3.2 Microstructural Analysis

Aside from the OC tests, mercury intrusion porosimetry (MIP), thermogravimetric (TG) and derivative thermogravimetric (DTG) tests were also implemented to investigate the microstructural changes in the matrices of the CPB samples. These tests provide valuable information about the porosity, pore structure, hydration products, progression of hydration, etc. In the MIP analyses, a Micromeritics Auto Pore III 9420 mercury porosimeter was used in accordance with ASTM D4404-10. The MIP test provides information on the pore size distribution in a porous material (i.e., cementitious materials). The TG-DTG tests were performed on 10 mg ( $\pm 0.5$  mg) of powdered specimens by using a thermogravimetric analyzer (Ulvac, TGD-9600) with a heating rate of  $10^{\circ}\text{C}/\text{min}$  from room temperature to  $1000^{\circ}\text{C}$  in an atmosphere of  $\text{N}_2$  gas at a flow rate of  $100 \text{ cm}^3 \text{ min}^{-1}$ .

## 7.3 Results and Discussion

### 7.3.1 Effects of Incremental Stress Increases on Reactivity of CPB

Figure 7.9 shows the mean reactivity values (based on three repeated measurements) and error bars (which represent one standard deviation) of undrained CPB samples subjected to curing stress (Cases B and C) and without curing stress (Case A) for different curing times (7, 28, and 90 days). From this figure, it can be observed that regardless of the amount of curing stress, the reactivity of the CPB samples decreases with increased curing time. This reduced reactivity is due to the progression of cement hydration with a longer curing time. As cement hydration progresses, more hydration products, such as calcium silicate hydrate (C-S-H), calcium hydroxide (CH), and ettringite are produced, as demonstrated in several previous studies (El-Diadamony et al., 2016; Pang et al., 2013; Hewlett, 2003). These products fill and/or block the pores in the CPB matrix, which leads to a finer pore size and reduced porosity. Consequently, this reduces the effective oxygen diffusion coefficient ( $D_e$ ) of the CPB specimen (Kurdowski, 2014). It is known that oxygen ingress in porous materials (e.g., CPB) is governed by their  $D_e$  (Aachib et al., 2004), and therefore, as the  $D_e$  decreases, the oxygen flux through the surface of the sample is reduced, which leads to lower reactivity (see Eq. 7.5). This pore refinement and porosity reduction is fully demonstrated experimentally from the results of the MIP tests performed on 7-day- and 28-day-CPB, as shown in Figure 7.10.

Figure 7.10 presents the MIP results on the effects of curing time on the CPB samples cured under stress for 7 and 28 days. It can be seen that the pore size distribution of the 28-day sample tends towards a smaller pore size compared to the 7-day sample, see Figure 7.10a. This indicates that the former has a finer pore structure than the latter. Furthermore, a comparison of the threshold pore diameter of these samples can be used to assess their pore refinement, as shown in Figure 7.10b. The threshold pore diameter is defined as the largest pore diameter at which significant pore intrusion is detected (Manmohan and Mehta, 1981). It can be observed in Figure 7.10a that the 28-day sample has a smaller pore size compared to the 7-day sample. The pore size has a critical role in the transport properties of cementitious materials (e.g., CPB) because it is part of the capillary network that connects the pores to the surface of the matrix of cementitious material (Promentilla et al., 2009; Aligizaki, 2006). The 28-day CPB sample has lower fluid transportability (e.g. O<sub>2</sub>), which can explain for its low reactivity as compared to the 7-day sample.

Also, it can also be observed in Figure 7.9 that as the incremental stress during curing increases, the reactivity of the CPB samples significantly decreases compared to those cured without stress (Case A). This decreasing trend in reactivity can be attributed to limited oxygen ingress by diffusion in the CPB samples due to the effect of incremental stress. Increasing the incremental stress leads to reduced porosity and a finer pore structure of the CPB sample. The reduction in porosity and the finer pore structure are mainly due to the increased packing density of the CPB ingredients (Yilmaz, 2017) and stress-induced acceleration of the cement hydration process (Cui and Fall, 2016; Ghirian and Fall, 2016a). The discussed effects of the curing stress result in a smaller diffusion coefficient ( $D_e$ ) of the CPB samples. Thus, the diffusion and consumption of the molecular oxygen of the CPB samples decrease, which results in lower reactivity values. The argument with respect to the effect of pressure on cement hydration is consistent with the results of the thermal analyses (TG-DTG) presented in Figure 7.11. This figure shows the TG-DTG results for the hardened cemented paste (HCP) of the CPB samples cured under stress for 7 days. The TG curve simultaneously provides the temperature, composition, and quantity of material lost due to thermal decomposition, whereas the DTG curve shows the materials that correspond to the range of the thermal decomposition in the different phases of the HCP. Typically in DTG curves, the decomposition of HCP shows three exothermic peaks at different temperatures: the first exothermic peak occurs in the temperature range of 100°C to 200°C, thus resulting in the dehydration of ettringite, gypsum, carboaluminates and C-S-H gel; the

second peak is in the range of 450°C to 500°C and related to the decomposition of Portlandite; and finally, the third peak occurs between 650°C and 750°C, thus resulting in the decomposition of the carbonate phases and calcite ( $\text{CaCO}_3$ ) (e.g., Fall et al., 2010; Gabrovsek et al., 2006; Pane and Hansen, 2005; Alarcon-Ruiz et al., 2005; Sha et al., 1999). CH is one of main hydration products commonly used to evaluate the increase in hydration with curing time by determining the weight loss from the TG curve. It can be observed in Figure 7.11 that the peak of the CH of the CPB sample cured under stress is slightly higher than that of the sample cured without stress. This means that the sample cured under stress produces more hydration products. Similar observations with respect to the effect of curing stress on cement hydration were made by Ghirian and Fall (2016).

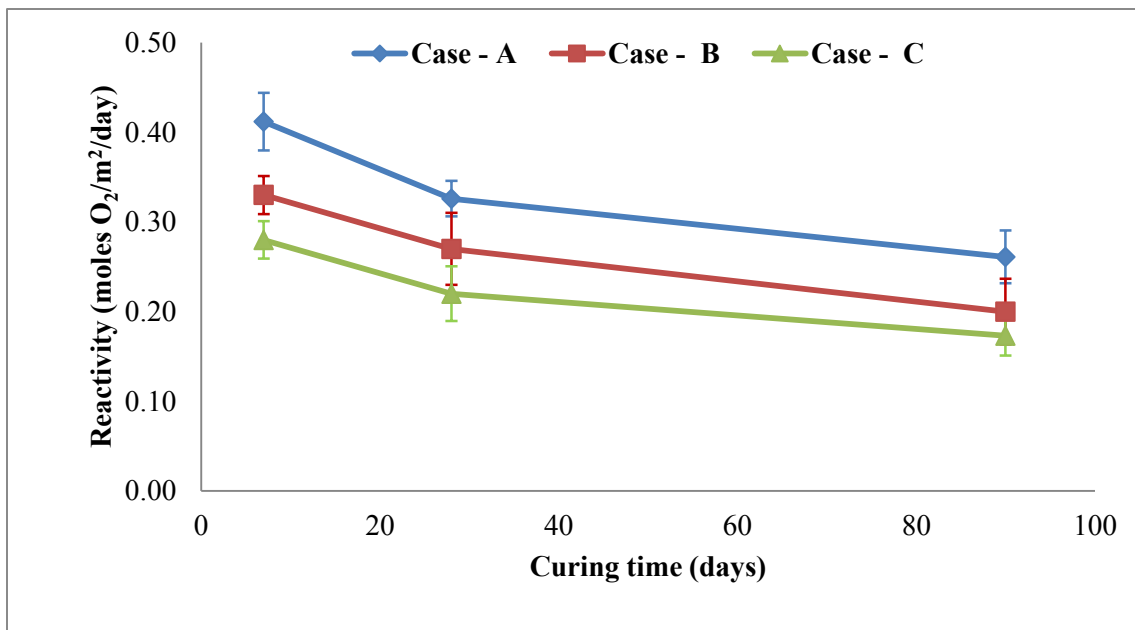


Figure 7.9. Effect of curing stress on reactivity of undrained CPB samples

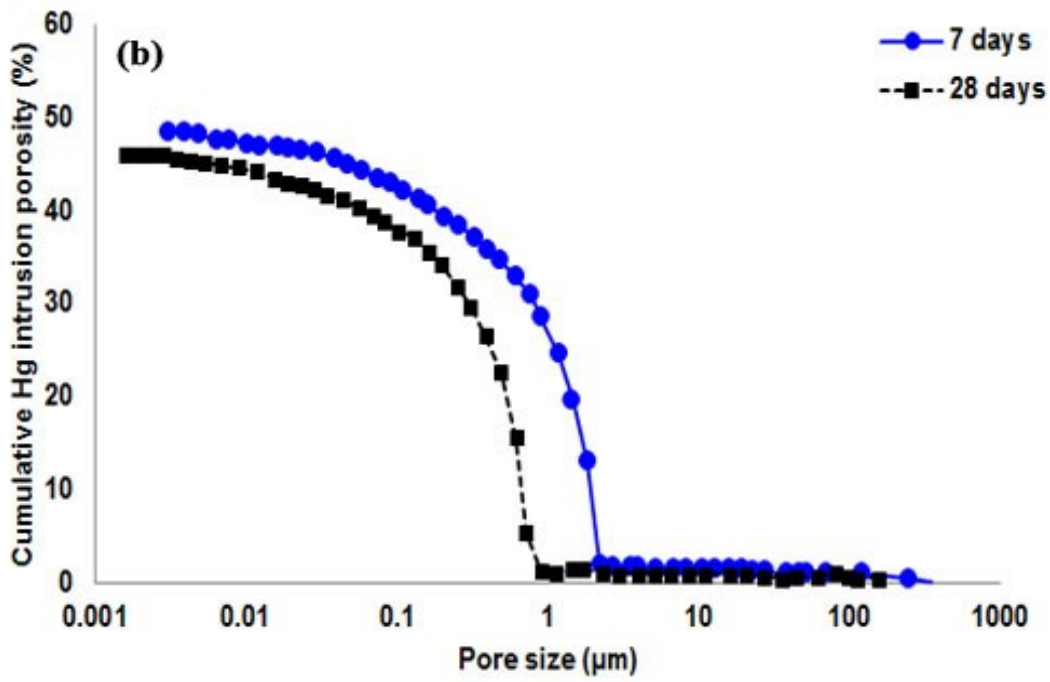
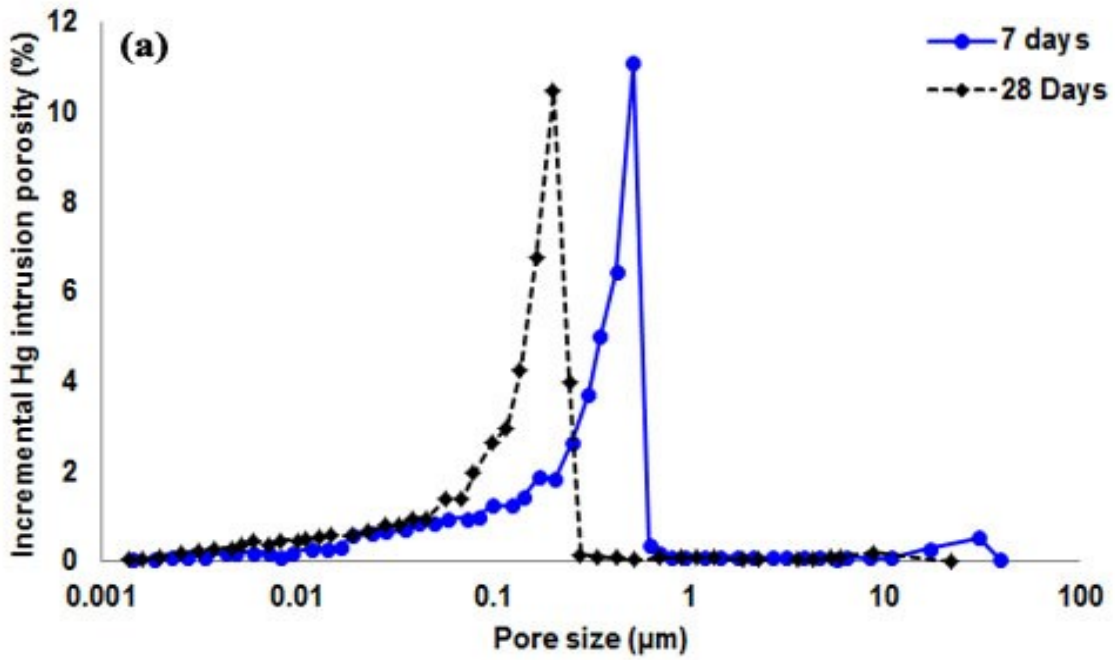


Figure 7.10. Effect of curing time in MIP tests: a) pore size distribution and b) porosity of CPB

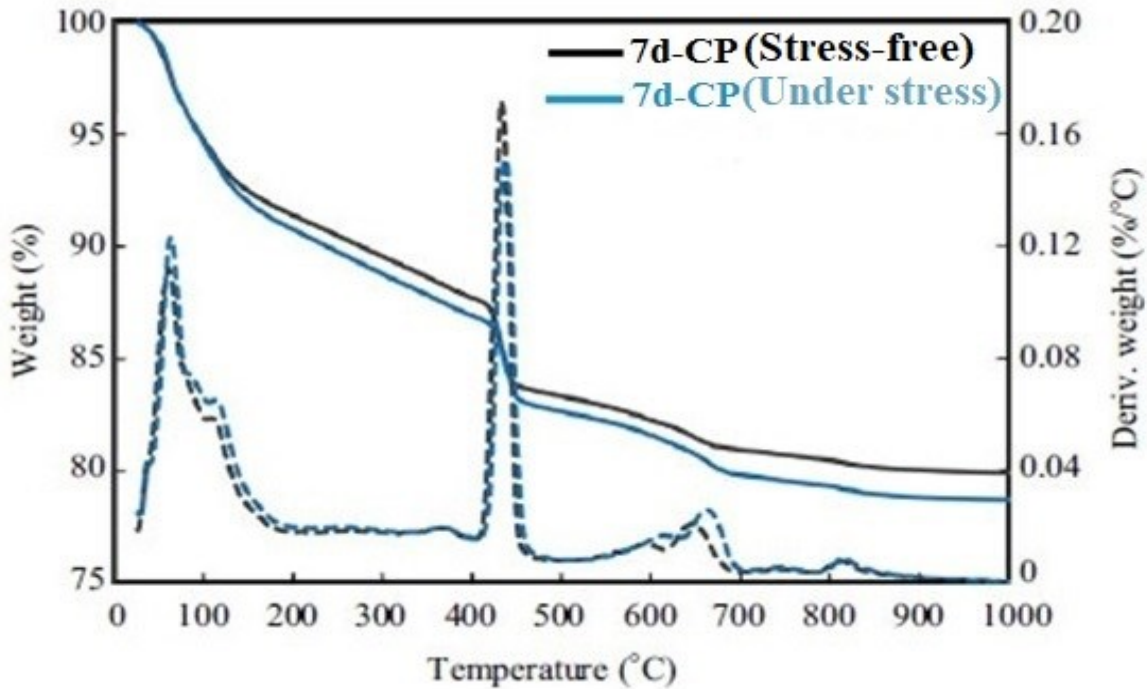


Figure 7.11. TG-DTG analysis of hardened cement paste cured under stress and without stress for 7 days

### 7.3.2 Effects of Rate of Filling of CPB on its Reactivity

The results of the effect of the rate of filling on the reactivity of undrained CPB samples are presented in Figure 7.12. The figure shows the mean reactivity values (based on three separate measurements) and the error bar (which represents one standard deviation) of undrained CPB samples cured under different rates of filling. It can be observed that the CPB reactivity values decrease with an increased rate of filling. This reduction in reactivity is due to a smaller effective oxygen diffusion coefficient ( $D_e$ ) of the CPB samples as a result of decreased porosity and refined pore structure caused by increasing the rate of filling, particularly for shorter curing times. This is supported by the conclusions of a number of previous studies which indicated that the curing stress or rate has a significant impact on the CPB microstructure (i.e., porosity and pore size distribution) (e.g., Yilmaz, 2017; Cui and Fall, 2016; Ghirian and Fall, 2016a, 2016b; Yilmaz et al., 2015).

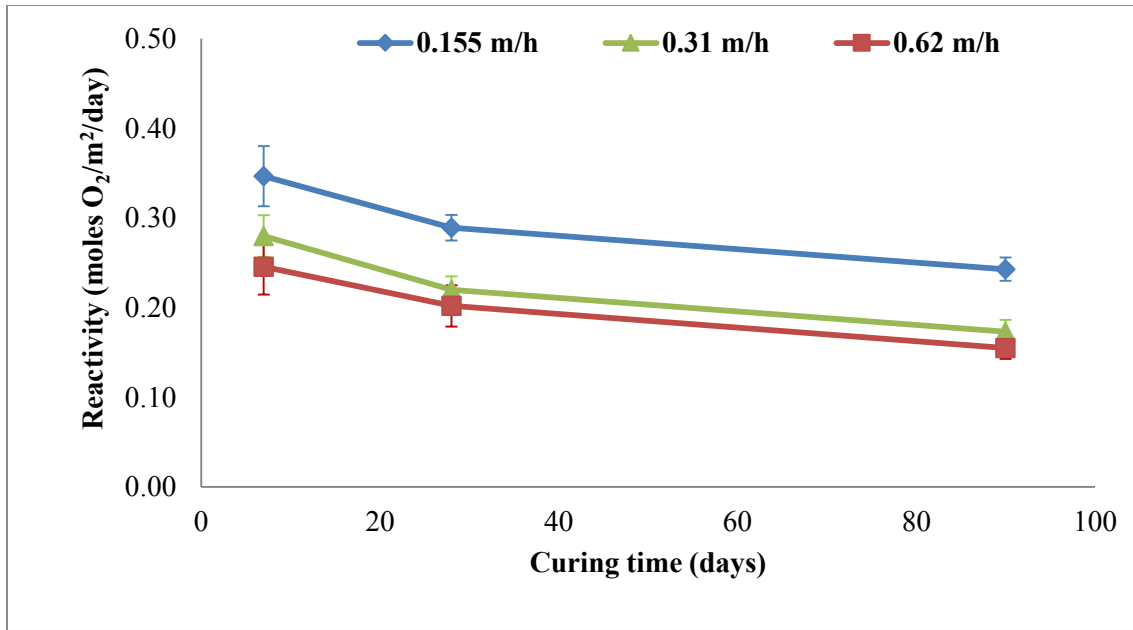


Figure 7.12. Effect of rate of filling on reactivity of undrained CPB samples

### 7.3.3 Effects of Plugs on Reactivity of CPB

Figure 7.13 shows the results of the reactivity of undrained CPB samples with a rate of filling of 0.31 m/h with a continuous pour (no plug) or a stage-pour procedure for different curing times. From this figure, it can be seen that regardless whether the filling sequence is continuous or takes place in stages, the reactivity decreases with curing time due to the acceleration in cement hydration as explained previously (Alhafaeri and Fall, 2016; MEND, 2006). Also, it can be observed that as the rest time (for plug filling) increases, the reactivity decreases with curing time. It can be seen from Figure 7.13 that a longer plug curing time results in the lowest reactivity as compared to continuous filling and a short rest time. This reduction in reactivity is attributed to more cement hydration products with time. This behaviour has been observed and reported in many previous studies (e.g., Cui & Fall, 2016; Ghirian & Fall, 2016; Yilmaz et al., 2015; Yumlu, 2008; Helinski et al., 2007). A longer rest time (with plug filling) can enhance the microstructure of the CPB samples and result in smaller effective oxygen diffusion coefficients. Consequently, the reactivity of the CPB samples is reduced as result of limiting the amount of oxygen ingress through their surface.

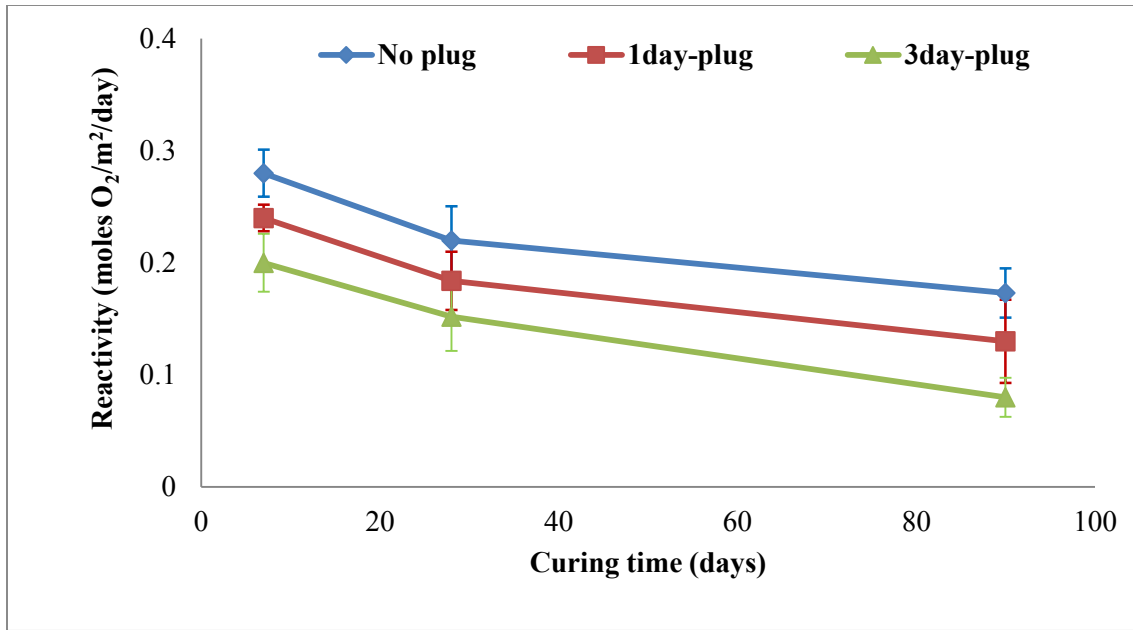


Figure 7.13. Effect of plug on reactivity of undrained CPB samples cured for different times

#### 7.3.4 Influence of Drainage on Reactivity of CPB Cured Under Stress

The influence of drainage conditions (i.e., undrained to fully drained) on the reactivity of CPB samples subjected to curing stress at a constant filling rate (0.31 m/h) over time is shown in Figure 7.14. From this figure, it can be observed that the reactivity of the drained CPB sample is lower than the undrained sample. This reduction in the reactivity of the CPB sample in a drained condition is attributed to its self-weight consolidation process during vertical curing stress. This leads to the generation of higher effective stress, thereby leading to pore refinement and porosity reduction. The latter results in a smaller effective oxygen diffusion coefficient. The above explanation is supported by the results of MIP tests conducted by Ghirian and Fall (2016b) on CPB samples cured under stress and without stress in drained and undrained conditions for 7 days, as illustrated in Figure 7.15. From this figure, it can be seen that drained samples subjected to curing stress has a finer pore structure compared to the undrained samples cured under stress and without stress. As a result, the drained CPB sample has a smaller oxygen effective diffusion coefficient ( $D_e$ ), thus resulting in a low reactivity value. The influence of drainage on the properties (e.g., mechanical) of CPB subjected to curing stress has been investigated in a number of studies (e.g., Yilmaz, 2017; Cui and Fall, 2016; Ghirian and Fall, 2016a,b; Yilmaz et al., 2015). These studies

have reported that the porosity reduction in drained CPB samples cured under vertical stress is due to the effects of effective stress and drainage conditions, and supported by MIP and thermal tests.

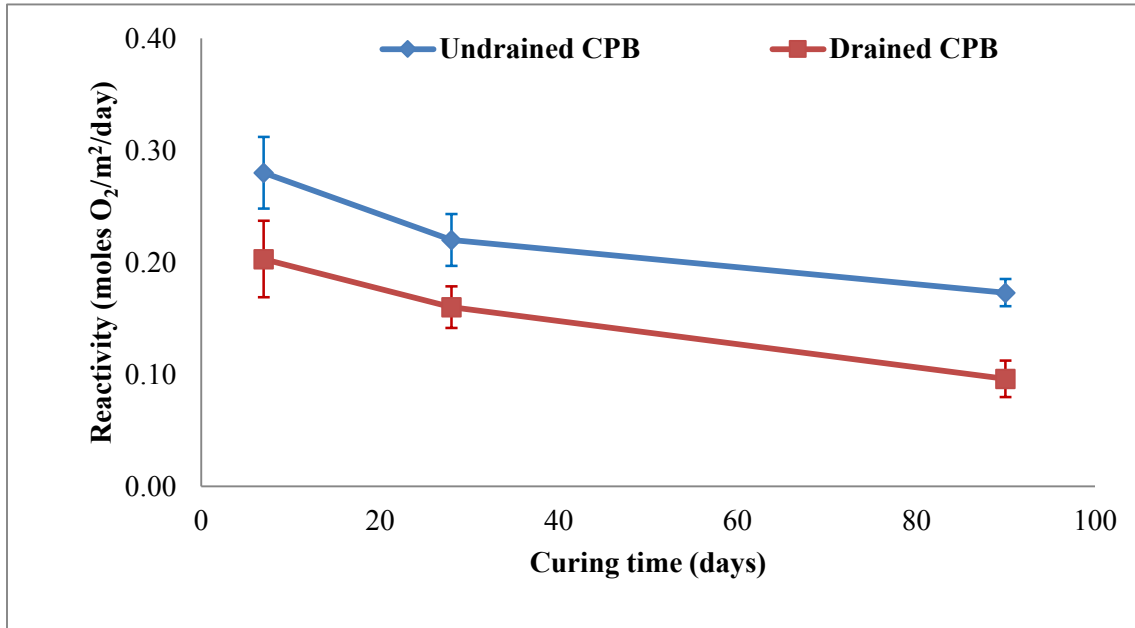


Figure 7.14. Influence of draining on reactivity of CPB samples subjected to curing stress for different curing times

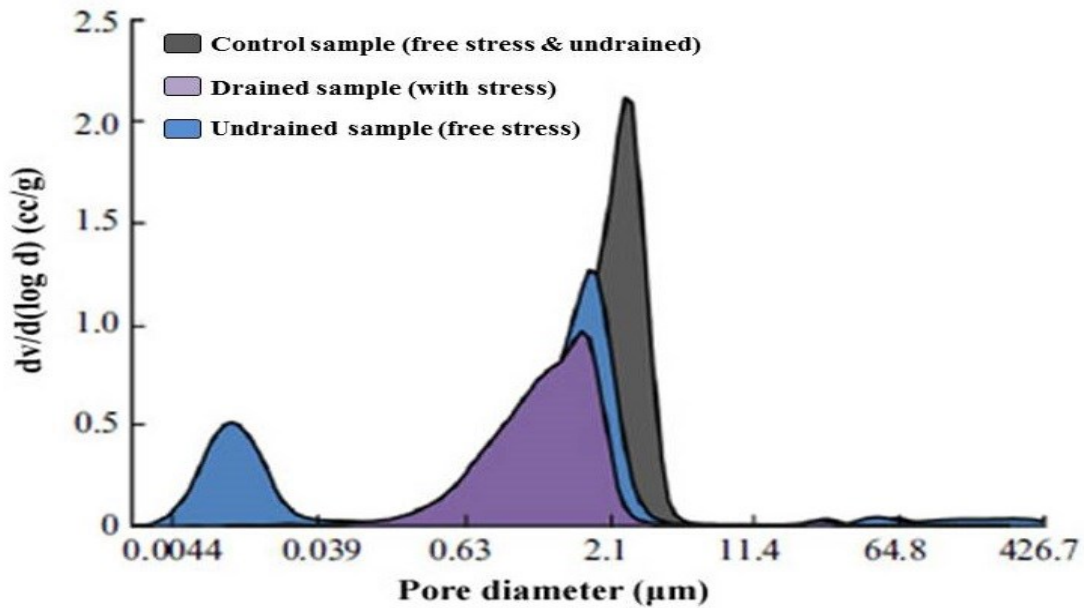


Figure 7.15. Effect of drainage conditions on pore size distribution of CPB samples filled at 0.31 m/h and cured under stress and without stress for 7 days (Ghirian and Fall, 2016a)

## 7.4 Summary and Conclusion

In this paper, the effects of incremental stress increases during curing, filling strategy (i.e., rate and sequence), and drainage conditions on the reactivity of CPB systems for various curing times have been investigated. Various scenarios have been applied to simulate the stress states of CPB stope conditions in the field by using a pressure cell device in the laboratory. The results indicate that the reactivity of an undrained CPB system decreases with increased curing time and vertical curing stress. The lower reactivity is due to a smaller effective diffusion coefficient ( $D_e$ ) of oxygen on the surface of CPB samples over time as a result of accelerated cement hydration and consolidation from vertical curing stress. Furthermore, the drained condition has a significant influence on the reactivity of CPB as compared to the undrained condition. It can be therefore concluded that curing stress is an important factor with a significant role in the reactivity of CPB systems and should be considered in assessments of the reactivity of CPB.

## 7.5 References

- Aachib, M., Mbonimpa, M., & Aubertin, M. (2004). Measurement and Prediction of the Oxygen Diffusion Coefficient in Unsaturated Media, with Applications to Soil Covers. *Water, Air, and Soil Pollution*, 156(1), 163–193.  
<https://doi.org/10.1023/B:WATE.0000036803.84061.e5>
- Akcil, A., & Koldas, S. (2006). Acid Mine Drainage (AMD): causes, treatment and case studies. *Journal of Cleaner Production*, 14(12–13), 1139–1145.  
<https://doi.org/10.1016/j.jclepro.2004.09.006>
- Alarcon-Ruiz, L., Platret, G., Massieu, E., & Ehlacher, A. (2005). The use of thermal analysis in assessing the effect of temperature on a cement paste. *Cement and Concrete Research*, 35(3), 609–613. <https://doi.org/10.1016/j.cemconres.2004.06.015>
- Aldhafeeri, Z., & Fall, M. (2016). Time and damage induced changes in the chemical reactivity of cemented paste backfill. *Journal of Environmental Chemical Engineering*, 4(4), 4038–4049. <https://doi.org/10.1016/j.jece.2016.09.006>
- Aldhafeeri, Z., & Fall, M. (2016). Time and damage induced changes in the chemical reactivity of cemented paste backfill. *Journal of Environmental Chemical Engineering*, 4(4).  
<https://doi.org/10.1016/j.jece.2016.09.006>
- Aldhafeeri, Z., & Fall, M. (2017). Sulphate induced changes in the reactivity of cemented tailings backfill. *International Journal of Mineral Processing*, 166.  
<https://doi.org/10.1016/j.minpro.2017.06.007>
- Aldhafeeri, Z., Fall, M., Pokharel, M., & Pouramini, Z. (2016). Temperature dependence of the reactivity of cemented paste backfill. *Applied Geochemistry*, 72, 10–19.  
<https://doi.org/10.1016/j.apgeochem.2016.06.005>
- Aligizaki, K. K. (2006). *Pore Structure of Cement-Based Materials: Testing, Interpretation and Requirements*. Abingdon England: CRC Press. Retrieved from  
<https://books.google.com/books?id=P-DGDRfAk8MC&pgis=1>

- Belem, T., Benzaazoua, M., & Bussière, B. (2000). Mechanical behaviour of cemented paste backfill. In *InProc. of 53rd Canadian Geotechnical Conference, Montreal* (pp. 373–380).
- Belem, T., & Benzaazoua, M. (2004). An overview on the use of paste backfill technology as a ground support method in cut-and-fill mines. In *Proceedings of the 5th Int. Symp. on Ground support in Mining and Underground Construction. Villaescusa & Potvin (eds.)* (pp. 637 – 650). London: Tayler & Francis Group.
- Benzaazoua, M., Belem, T., & Bussière, B. (2002). Chemical factors that influence the performance of mine sulphidic paste backfill. *Cement and Concrete Research*, 32(7), 1133–1144. [https://doi.org/10.1016/S0008-8846\(02\)00752-4](https://doi.org/10.1016/S0008-8846(02)00752-4)
- Bois, D., Benzaazoua, M., Bussiere, B., Kongolo, M. and Poirier, P. (2005). A feasibility study on the use of desulphurized tailings to control acid mine drainage. *CIM Bulletin*, 98(1087).
- Cui, L., & Fall, M. (2016). Mechanical and thermal properties of cemented tailings materials at early ages: Influence of initial temperature, curing stress and drainage conditions. *Construction and Building Materials*, 125, 553–563. <https://doi.org/http://dx.doi.org/10.1016/j.conbuildmat.2016.08.080>
- Dagenais, A., Mbonimpa, M., Bussière, B., & Aubertin, M. (2012). A Modified Oxygen Consumption Test to Evaluate Gas Flux through Oxygen Barrier Cover Systems. *Geotechnical Testing Journal*, 35(1), 103621. <https://doi.org/10.1520/GTJ103621>
- Dold, B. (2014). Evolution of Acid Mine Drainage Formation in Sulphidic Mine Tailings. *Minerals*, 4(3), 621–641. <https://doi.org/10.3390/min4030621>
- El-Diadamony, H., Amer, A. A., Sökkary, T. M., & El-Hoseny, S. (2016). Hydration and characteristics of metakaolin pozzolanic cement pastes. *HBRC Journal*. <https://doi.org/http://dx.doi.org/10.1016/j.hbrcej.2015.05.005>
- Elberling, B., & Nicholson, R. V. (1996). Field determination of sulphide oxidation rates in mine tailings. *Water Resources Research*, 32(6), 1773–1784. <https://doi.org/10.1029/96WR00487>
- Elberling, B., Nicholson, R. V, Reardon, E. J., & Tibble, R. (1994). Evaluation of sulphide oxidation rates: a laboratory study comparing oxygen fluxes and rates of oxidation product release. *Canadian Geotechnical Journal*, 31(3), 375–383. <https://doi.org/10.1139/t94-045>
- Fahey, M., Helinski, M., & Fourie, A. (2011). Development of Specimen Curing Procedures that Account for the Influence of Effective Stress During Curing on the Strength of Cemented Mine Backfill. *Geotechnical and Geological Engineering*, 29(5), 709–723. <https://doi.org/10.1007/s10706-011-9412-2>
- Fall, M., Célestin, J. C., Pokharel, M., & Touré, M. (2010). A contribution to understanding the effects of curing temperature on the mechanical properties of mine cemented tailings backfill. *Engineering Geology*, 114(3–4), 397–413. <https://doi.org/10.1016/j.enggeo.2010.05.016>
- Gabrovsek, R., Vuk, T., & Kaucic, V. (2006). Evaluation of the hydration of portland cement containing various carbonates by means of thermal analysis. *Acta Chimica Slovenica*, 53(2), 159–165. Retrieved from <http://cat.inist.fr/?aModele=afficheN&cpsid=17897765>
- Ghirian, A., & Fall, M. (2013). Coupled thermo-hydro-mechanical–chemical behaviour of cemented paste backfill in column experiments. Part I: Physical, hydraulic and thermal processes and characteristics. *Engineering Geology*, 164, 195–207. <https://doi.org/10.1016/j.enggeo.2013.01.015>
- Ghirian, A., & Fall, M. (2016a). Long-term coupled behaviour of cemented paste backfill in load cell experiments. *Geomechanics and Geoengineering*, 11(4), 237–251. <https://doi.org/10.1080/17486025.2016.1145256>

- Ghirian, A., & Fall, M. (2016b). Strength evolution and deformation behaviour of cemented paste backfill at early ages: Effect of curing stress, filling strategy and drainage. *International Journal of Mining Science and Technology*.  
<https://doi.org/10.1016/j.ijmst.2016.05.039>
- Helinski, M., Fourie, A., Fahey, M., & Ismail, M. (2007). Assessment of the self-desiccation process in cemented mine backfills. *Canadian Geotechnical Journal*, 44(10), 1148–1156.  
<https://doi.org/10.1139/T07-051>
- Hewlett, P. (2003). *Lea's Chemistry of Cement and Concrete* (4th ed.). Oxford: Butterworth-Heinemann. <https://doi.org/10.1016/B978-075066256-7/50028-X>
- Johnson, D. B., & Hallberg, K. B. (2005). Acid mine drainage remediation options: a review. *Sci Total Environ*, 338. <https://doi.org/10.1016/j.scitotenv.2004.09.002>
- Kermani, M., Hassani, F. P., Aflaki, E., Benzaazoua, M., & Nokken, M. (2015). Evaluation of the effect of sodium silicate addition to mine backfill, Gelfill – Part 1. *Journal of Rock Mechanics and Geotechnical Engineering*, 7(3), 266–272.  
<https://doi.org/http://dx.doi.org/10.1016/j.jrmge.2015.03.006>
- Kimble, J. (2004). *Cryosols*. (J. M. Kimble, Ed.) (1st ed.). Berlin, Heidelberg: Springer Berlin Heidelberg. <https://doi.org/10.1007/978-3-662-06429-0>
- Kumari, S., Udayabhanu, G., & Prasad, B. (2010). Studies on environmental impact of acid mine drainage generation and its treatment: an appraisal. *Indian Journal of Environmental Protection*, 30(11), 953–967.
- Kurdowski, W. (2014). The Properties of Cement Paste. In *Cement and Concrete Chemistry* (pp. 279–368). Dordrecht: Springer Netherlands. [https://doi.org/10.1007/978-94-007-7945-7\\_5](https://doi.org/10.1007/978-94-007-7945-7_5)
- Lottermoser, B. (2010). *Mine Wastes: Characterization, Treatment and Environmental Impacts*. Springer Berlin Heidelberg. <https://doi.org/10.1007/978-3-642-12419-8>
- Manmohan, D. & Mehta, P. (1981). Influence of Pozzolanic, Slag, and Chemical Admixtures on Pore Size Distribution and Permeability of Hardened Cement Pastes. *Cement, Concrete and Aggregates*, 3(1), 63–67. <https://doi.org/10.1520/CCA10203J>
- Martin, V., Aubertin, M., Bussière, B., Mbonimpa, M., Dagenais, A., & Gosselin, M. (2006). MEASUREMENT OF OXYGEN CONSUMPTION AND DIFFUSION IN EXPOSED AND COVERED REACTIVE MINE TAILINGS. In *The 7th International Conference on Acid Rock Drainage (ICARD)* (Vol. 2006, pp. 1156–1169). the American Society of Mining and Reclamation (ASMR). <https://doi.org/10.21000/JASMR06021156>
- Mbonimpa, M., Aubertin, M., & Bussière, B. (2011). Oxygen consumption test to evaluate the diffusive flux into reactive tailings: interpretation and numerical assessment. *Canadian Geotechnical Journal*, 48(6), 878–890. <https://doi.org/10.1139/t11-015>
- Mbonimpa, M., Aubertin, M., Dagenais, A. M., Bussière, B., Julien, M., & Kissiova, M. (2002). Interpretation of field tests to determine the oxygen diffusion and reaction rate coefficients of tailings and soil covers. In *The 55th Canadian Geotechnical and Joint IAHR-CNC and CGS Groundwater Speciality Conferences* (pp. 147–154). Niagara Falls.
- MbonimpaMamert, AubertinMichel, & BussièreBruno. (2011). Oxygen consumption test to evaluate the diffusive flux into reactive tailings: interpretation and numerical assessment. *Canadian Geotechnical Journal*, 48(6), 878–890. <https://doi.org/10.1139/t11-015>
- MEND. (2006). *Paste Backfill Geochemistry – Environmental Effects of Leaching and Weathering*. Vancouver, British Columbia, Canada. <http://mend-nedem.org/mend-report/paste-backfill-geochemistry-and-environmental-effects-of-leaching-and-weathering/>
- Moncur, M. C., Ptacek, C. J., Blowes, D. W., Lindsay, M. B., & Jambor, J. L. (2015). Long-

- term mineralogical and geochemical evolution of sulfide mine tailings under a shallow water cover. *Applied Geochemistry*, 57, 178–193.  
<https://doi.org/10.1016/j.apgeochem.2015.01.012>
- Mular, A. L., Halbe, D. N., & Barratt, D. J. (2002). *Mineral Processing Plant Design, Practice, and Control Proceedings*. SME.
- Naidoo, S. (2016). *Acid Mine Drainage in South Africa: Development Actors, Policy Impacts, and Broader Implications*.
- Norton, S. A., Lindberg, S. E., & Page, A. L. (1990). *Acidic Precipitation*. (S. A. Norton, S. E. Lindberg, & A. L. Page, Eds.) (Vol. 4). New York, NY: Springer New York.  
<https://doi.org/10.1007/978-1-4612-4456-1>
- Ouellet, S., Bussiere, B., Benzaazoua, M., Aubertin, M., Fall, M., & Belem, T. (2003). Sulphide Reactivity within cemented paste backfill: oxygen consumption test results. In *The 56th Annual Canadian Geotechnical Conference and 4th joint IAH-CNC/CGS Conference* (pp. 176–183). Winnipeg, Manitoba, Canada.
- Ouellet, S., Bussière, B., Mbonimpa, M., Benzaazoua, M., & Aubertin, M. (2006). Reactivity and mineralogical evolution of an underground mine sulphidic cemented paste backfill. *Minerals Engineering*, 19(5), 407–419. <https://doi.org/10.1016/j.mineng.2005.10.006>
- Pane, I., & Hansen, W. (2005). Investigation of blended cement hydration by isothermal calorimetry and thermal analysis. *Cement and Concrete Research*, 35(6), 1155–1164.  
<https://doi.org/10.1016/j.cemconres.2004.10.027>
- Pang, X., Bentz, D. P., Meyer, C., Funkhouser, G. P., & Darbe, R. (2013). A comparison study of Portland cement hydration kinetics as measured by chemical shrinkage and isothermal calorimetry. *Cement and Concrete Composites*, 39, 23–32.  
<https://doi.org/10.1016/j.cemconcomp.2013.03.007>
- Pokharel, M. (2008). *Geotechnical and environmental response of paste tailings systems to coupled thermo-chemical loadings*. University of Ottawa. Retrieved from <http://hdl.handle.net/10393/27793>
- Pokharel, M. (2008). *Geotechnical and environmental responses of paste tailings systems to coupled thermo-chemical loadings*. University of Ottawa. Retrieved from <http://hdl.handle.net/10393/27793>
- Promentilla, M. A. B., Sugiyama, T., Hitomi, T., & Takeda, N. (2009). Quantification of tortuosity in hardened cement pastes using synchrotron-based X-ray computed microtomography. *Cement and Concrete Research*, 39(6), 548–557.  
<https://doi.org/http://dx.doi.org/10.1016/j.cemconres.2009.03.005>
- Rankine, R. M., & Sivakugan, N. (2007). Geotechnical properties of cemented paste backfill from Cannington Mine, Australia. *Geotechnical and Geological Engineering*, 25(4), 383–393. <https://doi.org/10.1007/s10706-006-9104-5>
- Ripley, E. A., & Redmann, R. E. (1995). *Environmental Effects of Mining*. CRC Press.
- Schmieder, P. J., Taylor, J. R., & Bourgeot, N. (2012). Oxygen consumption techniques to quantify acidity generation rates. In *1st International Acid and Metalliferous Drainage Workshop*. Beijing, China.
- Sha, W., O'Neill, E. A., & Guo, Z. (1999). Differential scanning calorimetry study of ordinary Portland cement. *Cement and Concrete Research*, 29(9), 1487–1489.  
[https://doi.org/10.1016/S0008-8846\(99\)00128-3](https://doi.org/10.1016/S0008-8846(99)00128-3)
- Tariq, A., & Nehdi, M. (2007). Developing durable paste backfill from sulphidic tailings. *Proceedings of the Institution of Civil Engineers - Waste and Resource Management*,

- 160(4), 155–166. <https://doi.org/10.1680/warm.2007.160.4.155>
- Tariq, A., & Yanful, E. K. (2013). A review of binders used in cemented paste tailings for underground and surface disposal practices. *Journal of Environmental Management*, 131, 138–49. <https://doi.org/10.1016/j.jenvman.2013.09.039>
- Thottarath, S. (2010). *Electromagnetic characterization of cemented paste backfill in the field and laboratory*. University of Toronto.
- Yilmaz, E. (2017). Stope depth effect on field behaviour and performance of cemented paste backfills. *International Journal of Mining, Reclamation and Environment*, 1–24. <https://doi.org/10.1080/17480930.2017.1285858>
- Yilmaz, E., Belem, T., & Benzaazoua, M. (2014). Effects of curing and stress conditions on hydromechanical, geotechnical and geochemical properties of cemented paste backfill. *Engineering Geology*, 168, 23–37. <https://doi.org/10.1016/j.enggeo.2013.10.024>
- Yilmaz, E., Belem, T., Bussière, B., Mbonimpa, M., & Benzaazoua, M. (2015). Curing time effect on consolidation behaviour of cemented paste backfill containing different cement types and contents. *Construction and Building Materials*, 75, 99–111. <https://doi.org/http://dx.doi.org/10.1016/j.conbuildmat.2014.11.008>
- Yilmaz, E., & Fall, M. (2017). Introduction to Paste Tailings Management. In E. Yilmaz & M. Fall (Eds.), *Paste Tailings Management* (pp. 1–5). Cham: Springer International Publishing. [https://doi.org/10.1007/978-3-319-39682-8\\_1](https://doi.org/10.1007/978-3-319-39682-8_1)
- Yumlu, M. (2008). Barricade pressure monitoring in paste backfill. *Gospodarka Surowcami Mineralnymi - Mineral Resources Management*, 24(4/3), 233–244.

## Chapter 8: Synthesis and Integration of Results

### 8.1 Introduction

The goal of this chapter is to synthesize and integrate the results of the five technical papers presented in the previous chapters. Each of these papers has investigated one or more of the factors that affect the reactivity of CPB systems, as shown in Table 8.1. The table presents a summary of the influential factors investigated and the main tests conducted in each technical paper.

Table 8.1. Main factors investigated and tests conducted

Process		T		H	M		C				Tests	
Technical paper	Chapter	Curing Temp.	Atmospheric Temp.	Degree of saturation	Curing stress	Mechanical damage	Progress of cement hydration	Pyrite content	Sulphate content	Mineral admixtures	Oxygen consumption test	Microstructural investigation
1	3			√		√	√	√			√	XRD; SEM; MIP; TG-DTG
2	4	√	√	√			√	√			√	XRD; MIP; TG-DTG
3	5			√			√	√	√	√	√	XRD; SEM; MIP; TG-DTG
4	6	√		√			√	√	√	√	√	XRD; SEM;
5	7			√	√		√				√	MIP; TG-DTG

XRD: X-ray diffraction; SEM: Scanning electron microscopy; MIP: Mercury intrusion porosimetry; TG-DTG: Thermogravimetry-derivative thermogravimetry; M: Mechanical; T: Thermal; H: Hydraulic; and C: Chemical

This chapter provides an overview of the main factors that affect the reactivity of CPB systems. The results will be summarized as follows:

- i. Mechanical processes
  - Curing stress
  - Mechanical damage
- ii. Thermal processes
  - Curing temperature
  - Atmospheric temperature

- iii. Hydraulic process
  - Degree of saturation
- iv. Chemical processes
  - Progression of cement hydration
  - Pyrite content
  - Sulphate content
  - Addition of mineral admixtures

Finally, the reactivity results of the CPB in this study will be compared with those of CPB and tailings from other studies.

### 8.2 Multiphysics Processes in CPB Systems

During mixing and placement, and their service life, CPB systems are exposed to thermal, hydraulic, mechanical, and chemical (THMC) processes or factors that affect their reactivity, as shown in Figures 8.1 and 8.2. Figure 8.1 illustrates the main processes that affect the reactivity of CPB systems, whereas Figure 8.2 illustrates the processes and factors in CPB-backfilled stopes in underground mines.

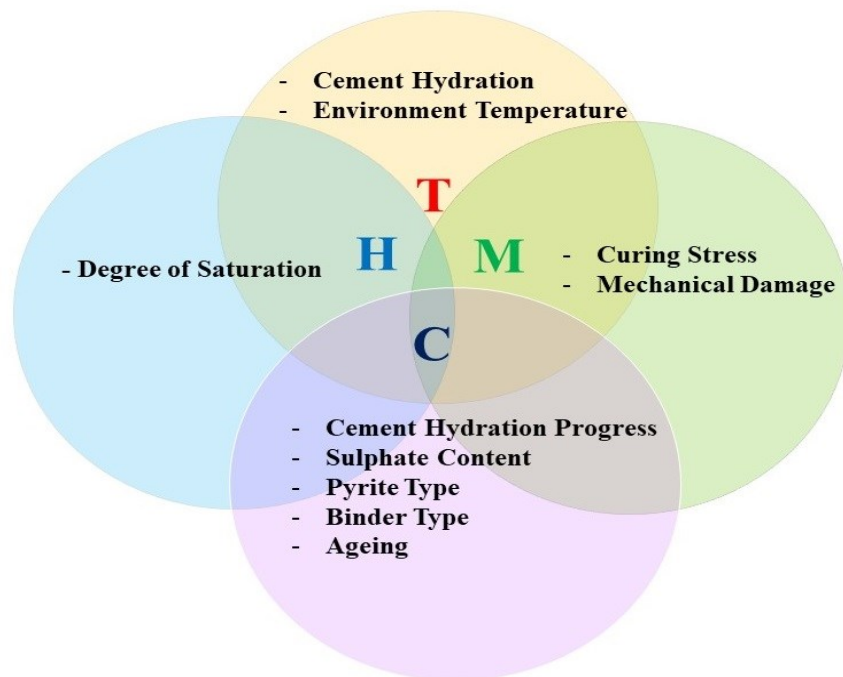


Figure 8.1. Main thermal, hydraulic, mechanical, and chemical (THMC) processes that affect reactivity of CPB systems, and their interactions

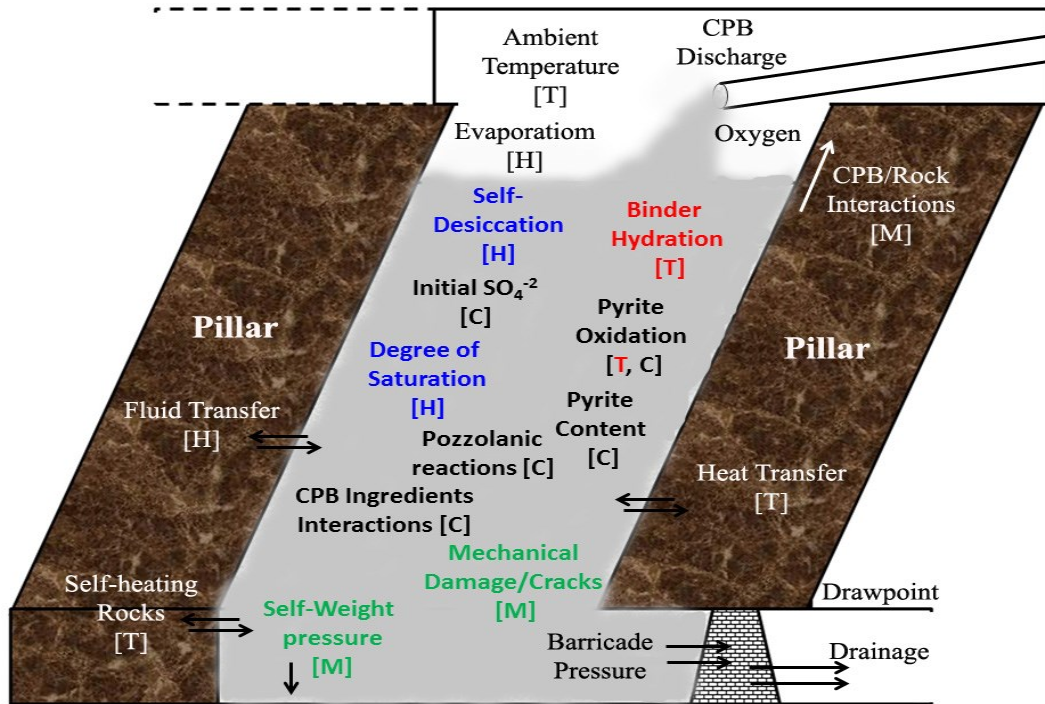


Figure 8.2. Schematic diagram of various THMC processes in a CPB stope (static condition)

### 8.3 Effect of Multiphysics Processes on Reactivity of CPB Systems

#### 8.3.1 Mechanical Processes

##### 8.3.1.1 Curing Stress

Curing stress is an external factor that results from self-weight loading conditions. This factor can significantly affect the properties of a CPB mixture as well as its reactivity. The effect of curing stress on CPB reactivity has been experimentally investigated by using a pressure cell device to simulate various loading conditions under different curing scenarios. The results indicate that as the curing stress increases, the reactivity of the CPB decreases. This lower reactivity can be explained by the combined effects of increased packing density of the tailings grains and acceleration of binder hydration in the CPB matrix when cured in undrained conditions for shorter periods of time and under a higher curing stress. Consequently, the oxygen diffusion coefficient of CPB is smaller, which results in less oxygen ingress and low reactivity. Also, the reactivity is significantly reduced in the drained condition as compared to the undrained condition because there is drainage of excess pore water from the CPB mixture in the early ages due to the application of higher stress during curing. This leads to a reduction in the porosity and pore size of the CPB.

As a result, the oxygen diffusion coefficient of the CPB is smaller, thus leading to much lower oxygen ingress and reactivity.

### **8.3.1.2 Mechanical Damage**

Cemented backfilled stopes can be subjected to various external mechanical loads, such as rock wall closures, service loads, rock bursts, and self-weight pressure. These loads can cause micro-cracks and their propagation in CPB structures which affect their transport properties (e.g., diffusivity and permeability) as well as reactivity. The effects of mechanical damage on the reactivity of pre-damaged CPB samples are experimentally studied in this thesis by conducting OC tests. Different levels of damage (40%, 70%, 90%, and 95% of the ultimate strength) are induced onto mature CPB samples with unconfined compressive stress (UCS) in order to simulate the different damage scenarios. The results show that the reactivity of the CPB samples significantly increases with more damage. This increase in reactivity is due to the micro-cracks that are caused by the mechanical loading which affect the transport and diffusion properties of the CPB samples.

### **8.3.2 Thermal Processes**

CPB systems are usually exposed to several different types of thermal processes, as shown in Figure 8.2. These processes are classified into two types based on their source: internal and external. The internal thermal processes, such as heat generated by exothermic binder hydration and pyrite oxidation reactions, originate from the CPB system itself, whereas the external processes, such as heat transfer from adjacent rocks and ambient underground mine temperature, are related to the surrounding environment. In this research, the influence of the two main thermal factors on CPB reactivity is experimentally investigated.

#### **8.3.2.1 Curing Temperature**

Curing temperature is one of the most important thermal factors that affect the properties of CPB structures, including reactivity. This thermal factor results from different thermal processes; in particular, binder hydration. The effect of curing temperature on the reactivity of CPB samples was studied by conducting a series of experiments, and the results of the experiments showed that reactivity decreases with increased curing temperatures and curing time. As the curing temperature and time increase, the diffusivity of CPB decreases due to acceleration of cement hydration (more

C-S-H gel and ettringite). Consequently, the rate that oxygen diffuses into the CPB matrix is reduced, which in turn, causes the pyrite oxidation process to slow down.

### **8.3.2.2 Atmospheric Temperature**

In the underground mine environment, the atmospheric temperature depends on various parameters such as the geographic location, depth, strata composition, and seasonal temperature. The effect of the ambient mine temperature on the measured reactivity of CPB samples cured at 20°C was investigated by simulating different temperature scenarios (i.e., 2°C to 50°C). The experimental results indicated that as the ambient temperature increases, the reactivity also increases. This is attributed to the combined effect of the two following factors: (i) a larger oxygen diffusion coefficient (as molecules move more rapidly) with increases in temperature, thus making more oxygen available on the surface of the pyrite grains for oxidation; and (ii) the temperature-dependence of the oxidation of pyrite which increases with higher temperatures.

### **8.3.3 Hydraulic Processes**

#### **8.3.3.1 Degree of Saturation**

The degree of saturation of CPB in a filled stope varies over time and with height, and is also dependent on the binder hydration as well as evaporation. The effect of saturation on the diffusion of oxygen into CPB samples was analyzed before and after conducting the OC tests, and the results showed that the reactivity of CPB strongly depends on its degree of saturation. As the degree of saturation increases, the reactivity of the CPB sample decreases (Figure 8.5). This is due to the fact that the diffusion of oxygen into air-filled pores is approximately 10,000 times faster than in water-filled pores (Neira et al., 2015). Furthermore, it was observed that when saturation exceeds 85%, reactivity is significantly reduced. Figure 8.3 presents a comparison between the different degrees of saturation in this study and the results from Ouellet et al. (2003).

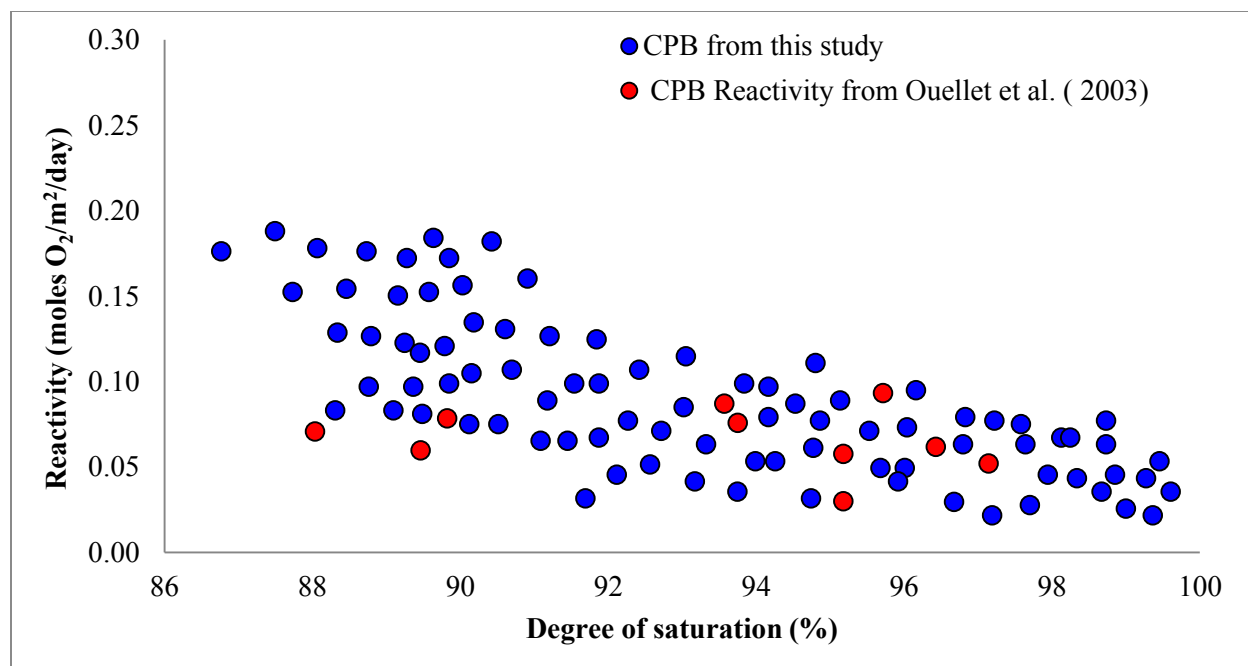


Figure 8.3. Relationship between degree of saturation and reactivity of CPB

### 8.3.4 Chemical Processes

#### 8.3.4.1 Progression of Cement Hydration

The progression of cement hydration over time affects the properties of CPB, including its reactivity. The progression of cement hydration was studied for the CPB samples and hardened cement pastes in this thesis by performing microstructural analyses such as XRD, MIP, SEM, and GT-DTG testing. The results showed that the progression of cement hydration with time gradually reduces the reactivity of CPB, as shown in Figure 8.4. The progression of the cement hydration produces more hydration products in the CPB matrix, which leads to a reduction in the porosity and increased pore refinement in the CPB. This will reduce the rate of oxygen diffusion as well as the reactivity. Furthermore, the results showed that the cement hydration process is affected by several other factors, including curing time, temperature and stress; binder type, chemical composition and content; the chemical, physical and mineralogical characteristics of the tailings (e.g., pyritic content); and composition of the mixing water (e.g., initial sulphate content). For example, higher curing temperatures as well as curing stress (e.g., self-weight) lead to more hydration products. On the other hand, high pyrite or initial sulphate content in CPB causes an increase in reactivity.

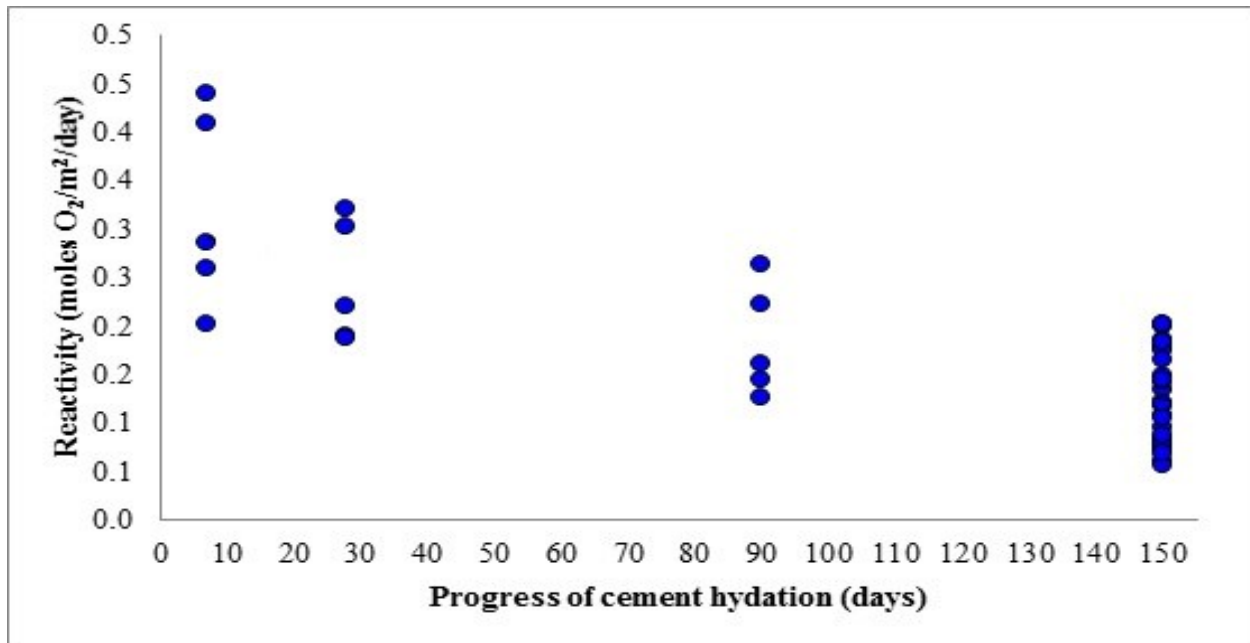


Figure 8.4. Effect of progression of cement hydration on CPB reactivity

#### 8.3.4.2 Pyrite Content

Pyrite ( $\text{FeS}_2$ ) is the most common form of iron sulphide in the Earth's crust, and therefore frequently found in mine waste (i.e., tailings). Pyrite is commonly found in polymetallic ore deposits, and chemically stable if not exposed to oxygen or oxidizing conditions. However, when exposed to oxidizing conditions in mines, pyrite oxidizes to form acid mine drainage (AMD). The sulphide content of tailings is influenced by several factors, such as the type of ores being mined and mineral processing. The sulphide content in CPB mixtures is determined by the concentration of sulphidic tailings that are used in the mixes.

The pyrite (i.e., sulphide) content of tailings is also considered to primarily affect the reactivity of CPB systems. The extent that the pyrite content affects reactivity is experimentally studied in this thesis by preparing CPB samples with different pyrite contents (up to 45 wt%) and then the reactivity of the CPB samples was determined by OC testing followed by an examination of the microstructure. It was found that as the pyrite content increases, the reactivity of the CPB samples also increases because more pyrite increases oxygen consumption in the oxidation process in CPB systems, thus leading to greater reactivity.

### 8.3.4.3 Initial Sulphate Content

In CPB systems, sulphate ions ( $\text{SO}_4^{2-}$ ) are commonly found in various concentrations. The concentration of  $\text{SO}_4^{2-}$  ions varies from relatively low ( $\leq 5000$  ppm) to very high ( $\geq 25,000$  ppm). These sulphate ions usually originate from internal sources in CPB systems, including the pre-oxidized sulphidic tailings used in CPB mixtures, processing water that contain residual minerals in thickened tailings, or minerals like gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) or anhydrite ( $\text{CaSO}_4$ ), which are added in small amounts to the cement clinker as a setting regulator, or from the mixing water, which could be either mine processing water or fresh water.

The effects of the initial sulphate content on the reactivity of CPB at different curing temperatures, as well as with different amounts of pyrite and types of binder for different curing times were experimentally investigated. The results showed that high sulphate content has significantly negative effects on the reactivity of the CPB samples. Reactivity increases with more sulphate, except for a sulphate content of 5000 ppm. This can be attributed to the detrimental impact of the initial sulphate content on the microstructure (e.g., pore structure and porosity) of CPB. The sulphate ions attack the cement hydration products (e.g., calcium hydroxide (CH)), and thus leads to coarsening of the pore structure and the presence of micro-cracks in the CPB matrix. Subsequently, this leads to larger oxygen diffusion coefficients in CPB systems and the oxidation of more sulphide tailings particles, and finally, the reactivity of the CPB systems increases.

### 8.3.4.4 Mineral Admixtures

Mineral admixtures (e.g., fly ash, silica fume and slag) are commonly used as a partial substitute for Portland cement to reduce costs, as Portland cement makes up about 75% of the total cost of CPB operations. The effect of this substitution on CPB reactivity was studied by conducting a number of laboratory experiments, and the results indicated that the reactivity of the CPB samples decreases when some of the cement is replaced with fly ash or slag as compared to samples that only use cement. This can be attributed to the increased saturation of the CPB mixtures when the cement is partially replaced with mineral admixtures (e.g., fly ash or slag). Such mineral admixtures consume less water for hydration in comparison to cement alone. In addition to the high degree of saturation, these minerals have a micro-filler effect that leads to the refinement of the CPB pore structure. The above effects can lead to smaller diffusion coefficients for CPB as well as lower reactivity. Also, it was found that as the proportion of these minerals increases, the reactivity values decrease, and as more of these mineral admixtures are used in CPB in lieu of

cement, the oxygen diffusion rates decrease due to high degrees of saturation and greater pore refinement.

#### 8.4 Comparison of Reactivity of CPB with that of Tailings without Cement

Figure 8.5 presents a comparison of the reactivity values obtained from this study with those of previous studies on CPB and tailings. It can be observed that the reactivity of the CPB samples is significantly lower than that of the tailings without cement (i.e., non-cemented tailings). This is due to the critical role of the hydraulic binder in preventing the reactive materials (e.g., pyritic tailings) from direct contact with mainly atmospheric oxygen and moisture. In particular, binder hydration is a chemical process which is considered vital to CPB technology as it greatly affects the physical and chemical properties of CPB, such as reactivity, strength, and permeability. Also, the results of this study are within the field reactivity range for CPB samples as observed by Ouellet et al. (2006).

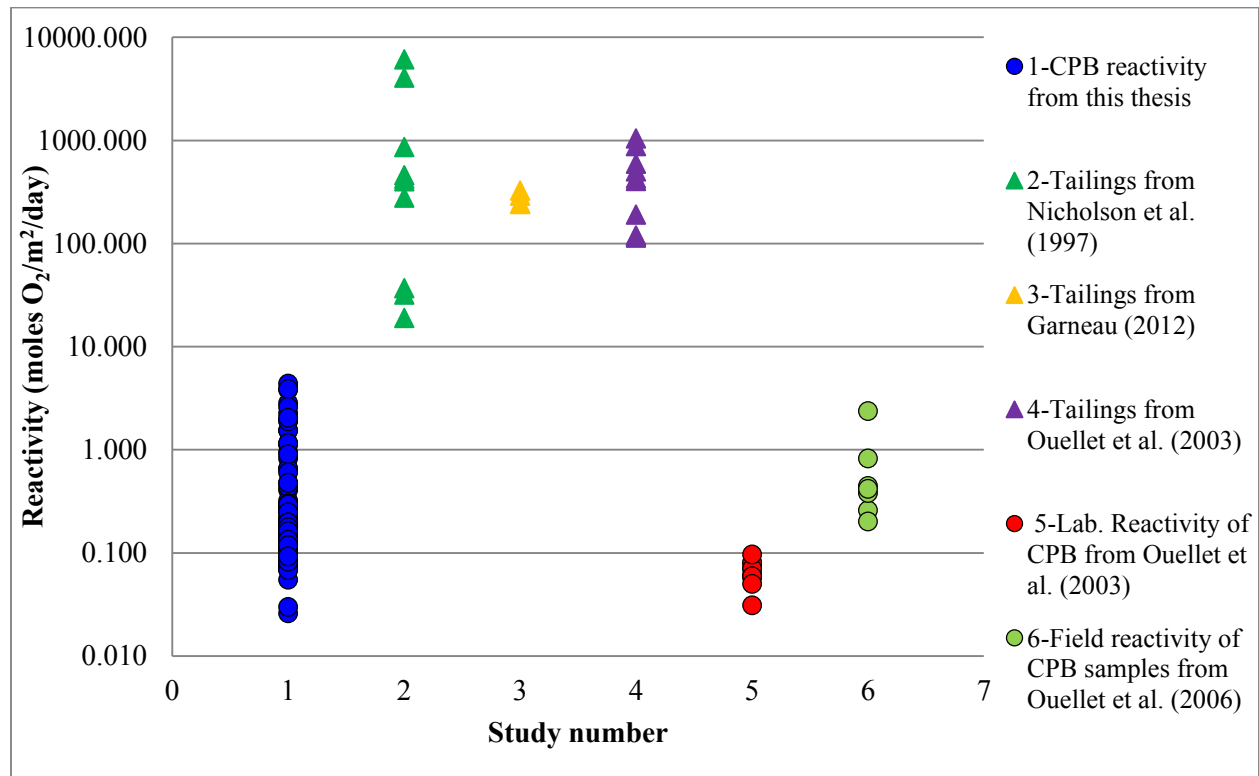


Figure 8.5. Comparison of reactivity of CPB with that of tailings without cement (Garneau, 2012; Nicholson et al., 1997; Ouellet et al., 2003; Ouellet, Bussière et al., 2006)

## 8.5 References

- Garneau, P. (2012). Oxygen Consumption in a Northern Canada Tailings Storage Facility. Royal Roads University, Victoria, British-Columbia, Canada.
- Neira, J., Ortiz, M., Morales, L., & Acevedo, E. (2015). Oxygen diffusion in soils: Understanding the factors and processes needed for modeling. *Chilean Journal of Agricultural Research*, 75, 35–44. <https://doi.org/10.4067/S0718-58392015000300005>
- Nicholson, R. V., Tibble, P., & Williams, S. (1997). A survey of in situ oxygen concentrations rates on sulphide tailings: Investigation on exposed and covered tailings. Vancouver, Ontario, Canada.
- Ouellet, S., Bussiere, B., Benzaazoua, M., Aubertin, M., Fall, M., & Belem, T. (2003). Sulphide Reactivity within cemented paste backfill: oxygen consumption test results. In *The 56th Annual Canadian Geotechnical Conference and 4th joint IAH-CNC/CGS Conference* (pp. 176–183). Winnipeg, Manitoba, Canada.
- Ouellet, S., Bussière, B., Mbonimpa, M., Benzaazoua, M., & Aubertin, M. (2006). Reactivity and mineralogical evolution of an underground mine sulphidic cemented paste backfill. *Minerals Engineering*, 19(5), 407–419. <https://doi.org/10.1016/j.mineng.2005.10.006>

## Chapter 9: Conclusion and Recommendations

### 9.1 Conclusion

The following conclusions are drawn from this study:

- The reactivity of CPB systems is governed by the independent or coupled effects of thermal, hydraulic, mechanical and chemical (THMC) processes (e.g., curing stress, temperature and time, pyrite and sulphate contents, progression of cement hydration and addition of mineral admixtures as a partial substitute for cement). These factors play a significant role in the reactivity of CPB systems.
- Increased curing time, temperature and stress, binder content, dosage of mineral admixtures and degree of saturation of CPB systems lead to reduction in its reactivity values. This can be attributed to their significant role in the improvement and enhancement of the microstructure of CPB systems, therefore leading to a smaller effective diffusion coefficient as well as lower rate of oxygen diffusion. On the other hand, more pyrite and sulphate can lead to increased reactivity of CPB systems.
- The progression of cement hydration is a critical factor that can affect the reactivity values of CPB.
- The partial substitution of cement with mineral admixtures results in reduced reactivity in CPB and lowers the cost. These minerals can enhance the microstructure of the CPB matrix due to the pozzolanic, dilution and filler effects.

### 9.2 Recommendations For Future Studies

The following recommendations are made for further studies.

- In the future, more work needs to be done on OC testing to determine the reactivity of CPB in the field for a better understanding of the factors discussed in this thesis, such as:
  - ✓ the effect of the quality of the mixing water (i.e. salinity, heavy metal contents),
  - ✓ the effect of the pore water chemistry,
  - ✓ the coupled effects of temperature, curing stress and sulphate,
  - ✓ the effect of carbonation of CPB on its reactivity, and
  - ✓ the effect of the hardpan layer (precipitation of principal secondary minerals, such as hematite and gypsum) on oxygen diffusivity of CPB as well as its reactivity
- Further investigations of the coupled THMC effects on the reactivity of CPB are recommended.
- The experimental results obtained in this study can be used to carry out theoretical modelling of the coupled THMC processes. The validation process is a very important step for better

understanding of the effects of different processes on the reactivity of CPB systems for predicting its reactivity under different environmental conditions in the long-term.