UNIVERSITÉ DU QUÉBEC EN ABITIBI-TÉMISCAMINGUE

ÉVALUATION DES PROPRIÉTÉS DES REMBLAIS EN PÂTE CIMENTÉS INCORPORANT DIFFÉRENTS TYPES D'ADJUVANTS ORGANIQUES ET INORGANIQUES

THÈSE

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UNIVERSITÉ DU QUÉBEC EN ABITIBI-TÉMISCAMINGUE

INVESTIGATION INTO THE PROPERTIES OF CEMENTED PASTE BACKFILL BY INCORPORATION OF DIFFERENT ORGANIC AND INORGANIC ADMIXTURES

THESIS

PRESENTED

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS

FOR THE DEGREE OF DOCTOR OF PHYLOSOPHY IN ENVIRONMENTAL SCIENCES

BY
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Suite aux activités minières, des résidus (produits à partir du traitement du minerai) et des roches stériles (produits à partir du développement) sont générés. Les minéraux extraits ne représentent qu'une petite fraction de l'ensemble du gisement dont l’essentiel se transforme en résidus. Près de la moitié des résidus générés sont pompés dans des aires d’entreposage des résidus (parcs à résidus), mais l’autre moitié de ces résidus peut généralement être placée dans les vides miniers souterrains ou les chantiers desquels le minerai a été extrait sous forme de remblai (méthode de minage chambre et remblais). L’entreposage des rejets miniers en surface nécessite une grande attention en raison de l'existence éventuelle de matières dangereuses comme les métaux lourds, métalloïdes, et des produits chimiques. Cependant, toute gestion efficace des rejets miniers devrait limiter leurs impacts environnementaux potentiels. Dans le cas des résidus chimiquement réactifs, par exemple, l'oxydation des minéraux sulfurés produit le drainage minier acide (DMA) qui peut affecter les écosystèmes.

Parmi les types de remblai minier possibles il existe le remblai en pâte cimenté (RPC) qui est fait à base des résidus miniers. Comme technique efficace de gestion des résidus miniers, le RPC permet de minimiser les impacts environnementaux en réduisant leur quantité à stocker en surface tout en jouant le rôle de support secondaire des terrains. Le RPC est ainsi constitué de résidus filtrés (72-85% en poids des grains solides), de l'eau (15-28%), et d’un agent de liant tel que le ciment Portland ou composé de ciment et de pouzzolanes (2-8% en poids de la masse sèche des résidus). Le RPC est mis en place dans les vides miniers souterrains par pompage ou par gravité. L’augmentation de la demande mondiale en métaux a entraîné l’augmentation de la production minière et par conséquent la quantité de rejets à stocker. Puisque l'ajout d'un liant (par exemple, ciment Portland) fait partie de la gestion des résidus sous la forme de RPC, plus de cycles de remblayage résulteront à une demande plus élevée de la consommation en liant. Dans ce cas, les compagnies

minières doivent dépenser des millions de dollars chaque année pour acheter des liants requis pour les opérations de remblayage. Par conséquent, toute petite réduction de la consommation en liant pourra générer des milliers de dollars d'économie pour les sociétés minières. Ainsi, l'évaluation de la substitution partielle de liant par d'autres produits ou la réduction de l'utilisation de liant est toujours souhaitable.

L'objectif de cette recherche doctorale est d'étudier trois différents types de mélanges (les sciures de bois, les nanoparticules, et les poudres de polymères ré-dispersibles) capables d'améliorer les différentes propriétés des RPCs en présence de l'agent liant. Les critères d'utilisation de ces adjuvants dans le RPC sont les suivants : être peu coûteux et abondant (cas des sciures de bois), être efficace pour affecter l'hydratation et augmenter le développement de la résistance des matériaux cimentaires (cas des nanoparticules), influencer l'hydratation du ciment en formant un film polymérique dans les matériaux cimentaires (cas des poudres de polymères). Généralement, le prix unitaire du ciment est inférieur aux prix des nanoparticules et des poudres de polymères. Par conséquent, l'ajout de ces adjuvants dans les RPCs doit être considéré à grande échelle non seulement comme substitut de liant, mais aussi au niveau des coûts d'opération.

Cette thèse de doctorat comprend trois articles, dont deux articles déjà publiés dans deux revues spécialisées (*Construction and Building Materials* et *Cement and Concrete Composites* de Elsevier), et un troisième bientôt soumis à la revue canadienne de génie civil. Le premier article a étudié l'influence des charges de fibres de bois sur les propriétés mécaniques et la microstructure du RPC. Cet article s'est appuyé sur une étude de laboratoire en utilisant des résidus non sulfurés de la mine Casa Berardi, Québec, Canada. Les différentes formulations de RPC ont été préparées par ajout des charges de 12,5 et 14,5% de fibres de bois et les éprouvettes fabriquées ont subi des essais de compression uniaxiale et une analyse de la microstructure. L'ajout de sciures de bois d'érable a légèrement diminué le développement de la

résistance à court-terme du RPC (quantifiée par la résistance en compression uniaxiale notée UCS), mais a amélioré cette résistance à plus long terme. Le deuxième article a étudié l'influence des nanoparticules colloïdales et des superplastifiants sur la résistance mécanique et la microstructure du RPC durci en utilisant également des résidus de Casa Berardi. L'influence des nanoparticules et de superplastifiant a été étudiée sur les phases hydratées du liant et de la variation de l’UCS. L'ajout de nanoparticules et de superplastifiant a essentiellement favorisé l’accélération du durcissement du RPC en améliorant sa résistance mécanique. Le troisième article a étudié l'influence des poudres de polymères ré-dispersibles sur les propriétés mécaniques et la microstructure du RPC en utilisant respectivement des résidus miniers sulfurés et non sulfurés des mines LaRonde et Goldex (Québec, Canada). La poudre du polymère Ethylène-vinyl acétate de Vinylester (EVA/VE) a été utilisée comme source unique de poudres de polymères dans cet article. L'ajout d'EVA/VE a principalement retardé le durcissement du RPC en changeant l'évolution des phases minérales formées à un âge précoce d'hydratation.

Mots-clés : Résidus miniers, Adjuvants, Remblai en pâte cimenté (RPC), Nanoparticules, Superplasticizer, Sciures de bois, Poudre de polymère, Durcissement, Résistance en compression uniaxiale, Microstructure.

ABSTRACT

Tailings produced from ore processing and waste rock coming from mining development are the results of mining activities. The recovered minerals represent only a small fraction of the entire orebody and a significant part of extracted orebody converts to the tailings. Most of the produced tailings are pumped to tailings storage facilities (surface tailings ponds), but part of these tailings can also be placed into the underground mine voids or stopes from which the ore was extracted (mine backfills). Storage of mine wastes requires significant attention due to the possible existence of hazardous materials such as heavy metals, metalloids, and chemical additives. Any effective waste management should restrict the potential environmental impacts of that mine wastes. In the case of chemically reactive tailings for example, oxidation of sulfidic minerals produces acid mine drainage (AMD) that can affect both the surface run-off water and underground water systems.

As an efficient underground mining operation and mine waste management, cemented paste backfill (CPB) minimizes the environmental impacts by decreasing the amount of waste storage from the surface and acts as a secondary ground support. CPB consists of filtered mill tailings (72 – 85 wt% solids), water (15 – 28%), and a binding agent such as Portland cement or a blend of cement and pozzolanic materials (2 – 8 wt% by dry mass of tailings). Up to 50% of total produced tailings stream can be delivered to underground mine voids through the pumping or gravity. Upraising the mining activities because of high demands of ore minerals increases the rate of waste production and waste cycling storage. Since the addition of a binder (e.g., Portland cement) is part of waste management in CPB, higher backfilling cycles results in higher demand of binder consumption. In this case, mining companies have to spend millions of dollars annually to purchase required binder(s) for the backfilling operations. Hence, a small reduction in binder consumption will bring thousands of

dollars saving for the mining companies, thus investigation in this case of binder replacement or binder usage reduction is always reasonable.

The objective of this Ph.D. research is to investigate three different types of admixtures (wood fillers, nanoparticles, and redispersible polymer powders) to affect different properties of CPB because of binder consumption. Motivations for using such admixtures in CPB are being inexpensive and abundant (for wood fillers), being efficient to affect the hydration and increase the strength development of cementitious materials (for nanoparticles), influencing the cement hydration while forming a polymer film in cementitious materials (for polymer powders). Generally, the unit price of cement is lesser than nanoparticles and polymer, hence the addition of such admixtures should be considered in large CPB plant scale including operational costs not simply as the binder replacement.

This Ph.D. thesis comprises of three papers including one published journal paper, one submitted journal paper with minor correction, and one journal article submitted (under review). The first paper investigates the influence of wood fillers on mechanical and microstructural properties of CPB. This article was arranged based on a laboratory experiment using non-sulfidic tailings from Casa Berardi mine, Quebec, Canada. Different CPB formulations were prepared by addition of 12.5 and 14.5% wood fillers and underwent mechanical and microstructural analyses The addition of wood particles decreased the early strength development of CPB (estimated by uniaxial compressive strength development or UCS), but at later ages of hydration some positive influence of wood fillers on UCS values was observed. The second paper investigates the influence of colloidal nanoparticles and superplasticizer on mechanical and mineralogical properties of hardened CPB using similar tailings to the first article. The influence of nanoparticles and superplasticizer were investigated on minerals produced from the binder hydration and UCS development. The addition of nanoparticles and superplasticizer mainly accelerated the hydration of binder by

improving the early strength development of CPB. The third paper investigated the influence of redispersible polymer powders on the mechanical, microstructural, and mineralogical properties of CPB using both sulfidic and non-sulfidic tailings from LaRonde and Goldex mine tailings respectively (Quebec, Canada). Ethylene-vinyl acetate of vinyl ester (EVA/VE) was used as the single source of polymer powders in this article. The addition of EVA/VE mainly postponed the hydration of binder and changed the mineralogical evolution of minerals at early ages of hydration.

Keywords: Mine tailings, Admixtures, Cemented paste backfill, Nanoparticles, Superplasticizer, Wood fillers, Polymer powder, Hydration, Curing, Uniaxial compressive strength, Microstructure.

CHAPTER 1

GENERAL INTRODUCTION

1.1 Problem statement

Mining activities produce a significant amount of solid waste materials which can be divided in two main categories including (i) mine tailings, originating from ore processing plant, and (ii) waste rock, producing from the recovery of ore body (Ledin and Pedersen, 1996). Since mine wastes may contain different hazardous substances such as heavy metals, metalloids, and chemical additives, their storage requires a significant amount of efforts and consideration (Yilmaz, 2010). An effective waste management system should restrict the potential environmental impacts especially if the source of waste being chemically reactive to the air and water. For instance, mining wastes containing sulfide minerals may oxidize and produce acid mine drainage (AMD) affecting both the surface run-off water and underground water systems (MEND, 2012).

While the recovered minerals represent only a small fraction of the entire ore body, a significant part of extracted ore body converts to tailings (Lottermoser, 2010). Most of the produced tailings are pumped to tailings storage facilities (surface tailings ponds), but part of these tailings can be placed into the underground mine voids or stopes from which the ore was extracted (mine backfills). Also, appreciable proportion of water can be removed from the tailings to produce high-density slurry or paste tailings prior to discharge for paste technologies (Yilmaz, 2011). As an efficient underground mining operation and mine waste management, the most commonly used mine backfills can be divided into three main categories including rock fill (RF), hydraulic fill (HF), and cemented paste backfill (CPB) (Hassani and Archibald, 1998). The use of tailings in backfilling method minimizes the environmental footprints by decreasing the amount of waste storage from the surface. In the case of tailings containing sulfide minerals, CPB is also advantageous due to the mixing of tailings with alkaline binders and low oxygen availability condition; even after mine closure at permanent flooding condition the release of acidity and metals from sulfidic mine tailings will certainly be decreased. In addition, the use of CPB for ground support is another advantage for mining operations; in this case, the dependency of the mine to extracted ore for ground support will be lessened and the recovery of the leftover ore pillars will be increased (MEND, 2006).

Upraising the mining activities because of high demands of ore minerals increases the rate of waste production; hence, the waste cycling storage will also be increased. Since the addition of a binder (e.g., Portland cement) is part of waste management in CPB, higher backfilling cycles result in higher demand of binder consumption. Apart from operational costs, mining companies have to spend millions of dollars annually to purchase required binder(s) for the backfilling operations. A small reduction in binder consumption will bring thousands of dollars saving for the mining companies, thus investigation in this case is always legitimate. Since mining companies consume a considerable amount of cement, any reduction in the usage of cement is also beneficial for the environment (lesser amount of cement will be produced and therefore lesser amount of carbon dioxide will be released since cement manufacturers has a main role in this case) (Worrell et al., 2001). In light of binder consumption challenge, working on any innovative solution that can meet the CPB operation requirements in an environmental manner is essential. This idea will be supported by consistently increasing environmental standards and mine closure requirements. Since CPB partially consists of binder, to some extent can be compared with other cementitious materials such as mortar. Therefore, the addition of any admixture in CPB might be examined in cementitious materials in advance (i.e., gelfill as an alkali activator admixture) (Kermani et al.. 2011).

In this Ph.D. thesis, three different admixtures including wood fillers, chemical nanotechnology (silane), and redispersible polymer powders are used. Such admixtures are not new in cement-based materials whereas are quietly unused in the case of CPB. The use of wood fillers/fibres in cementitious materials is common to produce wood cement composites (Wolfe and Gjinolli, 1996; Bouguerra et al., 1999; Boustingorry et al., 2005; Sudin and Swamy. 2006; Sierra-Beltran, 2011). Being inexpensive and abundant are the main reasons of using wood fillers in cementitious materials (Sudin and Swamy, 2006; Taj et al., 2007). Uses of nanotechnology including prepared chemical or mechanical nano-particles are growing rapidly in many applications such as cementitious materials. Structural manipulation of cementitious materials at the scale of nano is extensively efficient since hydration of Portland cement produces calcium silicate hydrate (C-S-H), which is a nano-structured material. In fact, addition of nanoparticles in cement-based materials can affect the structure of C-S-H; this is essential because C-S-H is the main reason of strength development (Ji, 2005; Kong et al., 2012). Polymer-based admixtures are also another class of high technology materials that are used in cement-based materials (Chandra and Flodin, 1987; Khayat. 1998). The addition of polymer admixtures in cementitious materials can change the hydration of cement in addition to the formation of a polymer film across the material as a possible reinforcement agent (Ohama, 1995; Mailvaganam and Rixom, 2002; Silva and Monteiro, 2006).

Apart from being innovative admixtures in CPB, financial justifications should be reasonable to add high technology admixtures in CPB (nanotechnology and polymer powders in this case). It should be reminded that one of the main aims of working with such admixtures is to reduce the binder consumption in CPB whereas the unit price of cement is lesser than that mentioned high technology admixtures. Hence, the addition of such admixtures should be considered in large CPB plant scale not simply as binder replacement. Moreover, a precise evaluation in whole backfilling process (i.e., operational costs) is required to justify the use of high technology admixtures, but this Ph.D. thesis just concentrated on the influence of mentioned admixtures on the mechanical, chemical, and microstructural properties of CPB.

1.2 Cemented paste backfill

As an efficient underground mining operation, cemented paste backfill (CPB) minimizes the environmental impacts by decreasing the amount of waste storage on the surface and acting as a secondary ground support. CPB consists of filtered mill tailings (72 – 85 wt% solids), water (15 – 28%), and a binding agent such as Portland cement or a blend of cement and pozzolanic materials (2 – 8 wt% by dry mass of tailings). Up to 50% of total produced tailings stream can be delivered to underground mine voids through the pumping or gravity (Belem and Benzaazoua, 2004; Coussy et al.. 2011; Koohestani et al., 2013). Depending on the type of binding agent, mineralogy of the tailings and curing time, uniaxial compressive strength (UCS) of CPB varies between 0.2 and 4 MPa (Belem and Benzaazoua, 2004, 2008; Yilmaz et al., 2009; Yilmaz et al.. 2011; Yılmaz et al., 2014). Many are the factors that can affect the low strength of CPB such as small amount and source of used binder, excessive amount of water, mineralogy of the tailings, particle size distribution, and source of additional water (Benzaazoua et al., 2002).

Basically, the available amount of water in CPB is in excess for the hydration of a binder (water/cement ≥ 3), but in order to make the mixture flowable through the pipelines, CPB should have sufficient amount of water (Belem et al., 2010). Basically, slump height measurement is a technique that gives the information regarding the flowability of the paste; a slump height between 15-25 cm (or 6-10 inches) is required for proper transportation of CPB to underground spaces via gravity or pumping (Clark et al., 1995). It is also noticeable that if the used tailings in CPB mixture contains 15 wt% fine particles (with 20 μm minimum size) they can act as a lubricant while preventing the plug in the pipelines during delivery (Landriault et al., 1997). Basically, grain size distribution (GSD) of tailings can be divided into three main categories including coarse (15-35 wt% < 20 μm), medium (35-60 wt% < 20 μm), and fine (60-90 wt% < 20 μm). As the amount of fine particles increases, the water retention ability of the CPB mixture rises whereas the strength decreases (Yilmaz, 2010).

It is essential that the chemical composition of mine tailings be analyzed since some minerals may bring different issues for the paste backfill plant. For example, oxidation of pyrite and pyrrhotite produce sulfate ions that may result in sulfate attack followed by short- or long-term strength deterioration (Benzaazoua et al., 1999). Such interactions between produced sulfate ions and the products of hydration mainly form secondary minerals including ettringite (AFt), gypsum, and monosulfoaluminate (AFm). Such produced new sources of minerals are highly expansive and can generate high internal pressures inside the mine voids resulting in the CPB's failure or strength deterioration (Klein and Simon, 2006).

Moreover, spontaneous oxidation of the tailings containing high amount of pyrrhotite may result in self-heating and excessive heat generation. This phenomenon may cause in mine fires, producing toxic gas (e.g. SO_2) while deplete the oxygen availability, generating acid mine drainage and even mine closure (Zarassi and Hassani, 2011).

1.3 Addition of admixtures

An admixture is defined as “a material other than water, aggregates, hydraulic cement, and fiber reinforcement used as an ingredient for cementitious materials, and added to the batch immediately before or during the mixing process” (ACI, 2010). In general, admixtures can be divided in two main categories including chemical and mineral admixtures. Addition of admixtures can control and change the configuration, structure, technical and technological properties and economic preferences of cement-based materials (Ramachandran, 1996; Rahman et al., 2014).

A chemical admixture basically is soluble in water and either is a water-reducing agent or a retardant or an accelerator or a combination of which. Those kinds of chemical admixtures that accelerate the hydration of cement by shortening the initial and final setting time are called accelerators. Using accelerators mainly increase the early strength development of cementitious materials. Most of the accelerators (i.e., calcium chloride, $CaCl_2$) react with calcium hydroxide (product of hydration, CH) and produce the higher amount of calcium silicate hydrate (C-S-H). Retardants, on the other hand, are organic or inorganic substances used to extend the workability of the cementitious mixture from the time of mixing to the time of placement. Some examples of retardants include the salts of hydroxycarboxylic acids, esters of cellulose, derivatives of melamine and naphthalene, carbohydrate sulfates, and unrefined salts of lignosulfonates. Water reducing admixtures are those that provide high flowability in lesser water to cement ratio (w/c regulator). In fact, the water to cement ratio in the range 0.2 - 0.23 is sufficient for the hydration of cement, but the proper flowability is achievable at w/c 0.7 to 0.8. Water reducing agents are surface-active substances and have plasticization influence on cementitious materials. For example, plasticizers and superplasticizers are prone to decrease the water surface tension and release the hydrated cement grains while adsorbing at the surface of cement solid phases (Ramachandran, 1996; Ohama, 1998; Roussel, 2011; Rahman et al., 2014).

A mineral admixture is a pozzolanic or hydraulic material other than Portland cement while contributing additional mineral oxides into the cementitious material; the term "mineral admixture" clarifies the mineral source of admixture in nature. Mineral admixtures can be divided in three main groups including physically active, physically and chemically active, and chemically active (Caldarone, 2008; Rakhimova and Rakhimov, 2012; Rahman et al., 2014; Rakhimova and Rakhimov, 2014). Quartz sand with the surface area 200 m^2/kg is an example of physically active mineral admixture. It acts as a nucleation agent for the growth of hydration products. Grinded quartz sand up to 300-1000 m^2/kg fineness is an example of physically and chemically active mineral admixtures. This type of admixture chemically participates in the hydration process forming binding agents while some elements act merely as physical filler. Silica fume with 2000 m^2/kg specific surface area is an example of chemically active mineral filler. It entirely reacts with the production of hydration to form extra binder. Mineral admixtures at the scale of nano with the approximate specific surface of 10000-100000 m^2/kg have the highest specific surface energy (~1 MJ/kg) (Rahman et al.. 2014; Rakhimova and Rakhimov, 2014).

Addition of admixtures into the cemented paste backfill is a solution that can change the total specifications and economical concerns of mining industries that spend millions of dollars for cement. Among chemical and mineral admixtures, in the case of paste backfill, mineral admixtures including silica fume (SF), ground granulated blast furnace slag (GGBFS) and fly ash (FA), are mainly examined (also called supplementary cementitious materials, SCMs). Slag, fly ash, and silica fume are by-products of iron production, coal combustion, and production of metallic silicon or ferrosilicon alloys respectively. Since no specific clinkering is used for the production of such materials, they can be used as a valuable source of cement replacement resulting in carbon dioxide reduction from the production of cement. In addition, use of such mineral admixtures presents a proper solution for the use of by-products from other industries. Moreover, the total costs of the used binder may be reduced because it is expected that such mineral admixtures being less expensive in comparison to Portland cement (the price of slag however fluctuates at the same or higher level of Portland cement) (Chung, 2002, Lothenbach et al., 2011; Snellings et al., 2012).

Silica fume (SF) exclusively consists of very fine amorphous SiO_2 and thus has a reasonably high pozzolanic influence. The reactivity of SF in cementitious materials depends upon the particle size and the dispersion of silica particles in the mixture. The reactivity of SF is higher than that of slag or fly ash due to the smaller particle size, but it shows a slow reaction with the hydration products (portlandite CH) especially during the first hours of hydration. As the pH of pore solution increases the reaction of SF accelerates (Bapat, 2012; Snellings et al., 2012). It is reported that the addition of silica fume in cemented paste backfill was more efficient for the strength development at later ages of hydration and it delay the hydration at early ages. In addition, increase in the amount of silica fume seems to worsen this situation although the resistance to sulfate attack improves (Ercikdi et al., 2009).

Similar to silica fume, fly ash (FA) improves the performance of cementitious materials in long-term. ASTM C618 classifies fly ash in two types including class F and class C. Class F fly ash originates from burning anthracite or bituminous coal and the sum (% wt) of silica (SiO_2), alumina (Al_2O_3), and iron oxide (Fe_2O_3) must be at least 70% with less than 10% CaO. The crystalline minerals in class F fly ash are unreactive, but this type of FA has pozzolanic influence. Class C fly ash is produced from burning of lignite or sub-bituminous coal and has at least 50% of the sum of silica (SiO_2), alumina (Al_2O_3), and iron oxide (Fe_2O_3) and between 10% and 30% CaO. All the minerals in class C fly ash are reactive hence, this class of fly ash has both pozzolanic influence and cementitious properties. The hydration of cementitious material when containing FA will be delayed and early age strength development is weak whereas sulfate attack resistance and strength development at later ages of hydration will be improved (for class F fly ash) in comparison to Portland cement (Bijen, 1996; Li and Zhao, 2003; Ercikdi et al., 2009; Lothenbach et al., 2011).

The reactivity of slag among other mineral admixtures depends on the silica content since SiO_2 is reactive in slag and is responsible for the reaction with portlandite (CH) to produce secondary calcium silicate hydrate (C-S-H, pozzolanic effect). In comparison to fly ash, slag has higher CaO and lesser Al_2O_3 and shows a faster reaction in cementitious materials. The pH dependency of slag reaction in cement-based materials indicates that any reduction in cement content postpones the reactivity of slag. However, during the first hours of hydration the amount of portlandite present in the mixture containing slag-cement blend is similar or higher even from a mixture containing Portland cement only because of faster clinker reaction as a consequence of filler. It is reported that the addition of slag retarded the setting time of cement and increased the carbonation rate (Bijen, 1996; Li and Zhao, 2003; Ercikdi et al., 2009; Lothenbach et al., 2011; Bapat, 2012; Rakhimova and Rakhimov, 2012; Snellings et al., 2012; Rahman et al., 2014; Rakhimova and Rakhimov, 2014).

As it was discussed, all the most experienced admixtures in cemented paste backfill (slag, fly ash, and silica fume) postpone the hydration of cement. Hence, the early strength development of CPB using such mineral admixtures is very low. Generally, ordinary Portland cement as a single binder provides better early strength development, but it also is so sensitive to sulfate attack since being calcium rich binder. In the case of mixed binders, the formulation of a binder with less than 5% content may not provide enough compressive strength of paste backfill (Ercikdi et al., 2009). Moreover, insufficient early strength of CPB containing blended binder can bring different issues for mining operations. Hence, the early strength development in paste backfill is quite important aspect that should be considered. For example, if the filled stope with CPB did not cure properly, it may be necessary for mining activities and operations (i.e., blasting) to be performed enough far from the filled stope in order to prevent some possible failure or collapse such as liquefaction. Moreover, for safety reasons it may be necessary for workers and machineries to work in other parts of mines far from filled stopes.

In addition, in the case of highly acidic condition, the addition of such sulfate attack resisting mineral admixtures to the Portland cement will not guarantee the hydration fulfillment and strength development at later ages of hydration while we expect such mineral admixtures to provide sufficient strength at that period of time (Bijen, 1996).

As a result, it is not the only concern to reduce the binder costs by addition of some by-products from other industries. Although, it is correct that the cost of binder is decreased, at the same time different technical problems are arisen that may cost much more than the saving amount of money from binder expenses. Hence, the financial calculations should be estimated in large scale. In the best case, a combination of binder and admixtures at small amount with the capability to provide proper early strength development and being sulfate attack resistant is preferable. However, this combination may not necessarily provide the cheaper price in comparison to Portland cement while may be reasonable if we look at the backfill plant scale.

There are not a lot of investigations in this field that attempted to experiment the new admixtures for the improvement in the properties of fresh and hardened CPB; possibly since being waste management and since looking for cheaper material than Portland cement. Sodium silicate for instance is one of the main used admixtures in the case of paste backfill (Kermani et al., 2011). This Ph.D. thesis however attempts to use different types of admixture including high technology admixtures (silane and polymer powder) and cheap admixtures (wood fillers) as possible cement replacement and mechanical properties improvement. It is also noticeable that wood filler in fact is not an admixture and basically plays the role of aggregate, but the way it is used in this thesis was as an admixture (used at small amount and as a complementary material) to affect the water availability of the paste backfill. Silane admixture has a silicon atom at the core of its molecule and is a high technology admixture that can influence the properties of CPB considerably. Indeed, since the silicon part of silane molecule is in the scale of nano and hence has a high specific surface and is highly reactive (chemically). Polymer powders are also well known organic admixtures that can improve the consistency of the fresh mixture while also improving the mechanical strength. The main criteria to specify such admixtures were to affect the water content and early strength development of paste backfill. It is also crucial that the addition of such admixtures should not influence the consistency of fresh mixture negatively resulting in difficulties of the mixture transportation into the underground spaces.

It has to be noticed that sometimes a single admixture may not fulfill all the expectations in paste backfill (mechanical strength and consistency), thus a combination of different admixtures should also be considered. For example, addition of superplasticizer not only facilitates the dispersion of nanoparticles but also improves the consistency of the mixture by reducing the water demand of the paste. In this case, multiple targets are achievable and different problems in paste backfill may be addressed.

In light of the above-mentioned statements, the main originality of this Ph.D. work is to use some new admixtures that have never been used in CPB. In addition:

1- Most of researchers worked on CPB long-term strength development and very little on its early age strength development.

2- Improving the early age strength development of CPB may change the design of paste backfill and the backfilling operation.

3- Up to now, most of the mineral additives used in CPB (e.g., fly ash, slag, etc.) have retarding effect on strength development. So, addition of a new admixtures to overcome this issue is advantageous.

4- The benefit of binder replacement is real if the CPB can harden as early as possible due to the acceleration influence of the used admixture. In this case, CPB reaches the maximum strength (UCS) in a short period regardless of binder content without the need of using high early type Portland cement.

1.4 Research objectives and hypothesis

The main objective of this doctoral thesis is to improve the early age strength development of CPB (3-28 days) by using organic and inorganic admixtures including wood fillers, nano-silica, and polymer powders. Indeed, increasing the early age strength development of CPB will facilitate the backfilling operation by continuous filling. CPB's early age strength improvement can occur through the acceleration influence of used admixture. At the same time, it aimed at decreasing the required amount of water for the target flowability of CPB (measured via slump height). In this case, the preparation of CPB materials will be more convenient. Also, the addition of these admixtures should help reducing the paste backfilling costs by partial replacement of cement. Finally, it will be helpful of finding new possibilities for the use of other industries by-products in mining industries.. The ultimate goal of using the proposed admixture as the binder replacement is to reduce the binder cost. Some specific objectives of this Ph.D. study are:

1) The beneficial use of wood fillers as the binding agent replacement for improving the CPB mid- and long-term strength development.

2) The influence of nano-silica addition as the binder replacement and its influence on CPB early age and long-term strength development.

3) The effect of a polymer powder addition as the binder replacement and its influence on CPB early age strength development.

In this thesis, three different organic and inorganic admixtures including lignocellulosic fillers, nano-silica and redispersible polymers were assessed. The selection criteria of such admixtures are: ease of use, availability, being inexpensive, being applicable in cementitious materials, and being effective although it is difficult to meet all these criteria for a single admixture.

This doctorate thesis is done based on the lab experiment using different types of mine tailings including sulfidic and non-sulfidic tailings. To achieve the specific objectives and goals of this study, the following steps are pursued.

A) A literature reviews on different admixtures used in this thesis. The aim of this review is to bring some knowledge to the readers regarding the types of different admixtures including their structure, category, and so on.

B) Investigation into the influence of different admixtures on hardened CPB early age strength development and presenting the most effective formulation, which can also facilitate the filling process (in terms of slump value).

C) Investigation into the microstructural changes of hardened CPB incorporating different types of admixture using scanning electron microscopy (SEM) and mercury intrusion porosimetry (MIP). The aim was to observe the influence of used admixtures on the microstructure of hardened CPB.

D) Monitoring the influence of different admixtures on the consistency of the fresh CPB by using slump height measurement. The aim was to understand the positive or negative influence of used admixtures on the consistency of CPB.

E) Investigation into the possible binder reduction by using different admixtures. The aim was to reduce the total costs regarding the binder usage.

The main hypothesis of this Ph.D. research is that organic and inorganic admixtures can positively affect the binder hydration or CPB hardening process by improving their compressive strength, especially at early age curing times. It is also assumed that the binder replacement by the admixtures can reduce the binder consumption resulting in lesser carbon dioxide release and money saving (financially and environmentally beneficial). It is believed that the addition of small amount of used admixtures including wood fillers, nano-silica, and polymer powders (in comparison to the amount of binder used) can satisfy the target expectations.

Some specific hypotheses of this thesis are:

1) If the wood fillers can absorb a significant amount of water in CPB (in comparison to their initial mass), their addition may improve the hydration process by reducing the water to cement ratio. In addition, wood fillers may act as the reinforcement fillers in CPB matrix.

2) The water drainage (due to self-weight consolidation) in CPB-filled stopes can be reduced by wood filler addition.

3) Nano-silica can accelerate the hydration process and improve the compressive strength by pozzolanic reaction and pore volume filling.

4) Addition of superplasticizer will improve the dispersion of nano-silica and hence will boost the strength development of CPB. In addition, it reduces the water usage of CPB for a given target slump height.

5) The polymer powder addition to CPB would possibly alter the flowability and decrease the water-to-cement ratio of the CPB.

6) The formation of polymer film in CPB (because of hydrolysis and chemical reaction with water and hydrated cement) could also improve the compressive strength (UCS) and decrease the binder consumption in the CPB.

1.5 Thesis outline

This doctorate thesis is based on three written journal papers (two of them are already published, and one is ready to be submitted). This thesis is prepared in six chapters; the first chapter presents the general introduction about the research including the background, objectives, materials in use, and the logics behind the work.

The second chapter is a literature review, which is allocated to bring some knowledge to the readers regarding the used admixtures in this Ph.D. research.

The third chapter presents a published paper entitled *"Experimental investigation of mechanical and microstructural properties of cemented paste backfill containing maple-wood filler"* in Construction and Building Materials, an Elsevier journal. This section describes the use of wood fillers in cemented paste backfill.

The fourth chapter presents a published journal paper entitled *"Experimental investigation into the compressive strength development of cemented paste backfill containing Nano-silica"* in Cement and Concrete Composites, an Elsevier journal. This chapter discovers the positive influence of nano-silica in CPB.

The fifth chapter is assigned based on the use of redispersible polymer in CPB. This chapter is written based on a prepared journal paper to be submitted (possibly in Composite Part A – Applied Science and Manufacturing).

The sixth chapter is a summary and general conclusion followed by the appendices.

The first appendix is the published conference paper in GeoMontreal 2013 conference in Canada and the second appendix is allocated to the work of using organosilanes as a complementary admixture for nano silica in CPB.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter presents a short review of some general concepts regarding the use of different admixtures in composites such as cementitious materials. Thereafter, all the used materials in this research namely cemented paste backfill, wood fillers, redispersible polymers, and nano-silica will be described and discussed. It is attempted to explore the used materials in this thesis briefly and comprehensively.

2.2 Composite materials

Composites are composed of two or more distinct constituent materials or phases, with properties that are noticeably different from the constituent properties. Composite materials consist of one or more discontinuous phases called reinforcement embedded in a continuous phase called the matrix. The thermos-mechanical properties of the reinforcement and matrix phases, the orientation and distribution of the reinforcement phase, and the interfacial properties between the phases dictate the ultimate properties and performance of the composite material (Nielsen and Landel, 1994).

Composite materials are typically classified by their matrix type and/or by their reinforcement form. A composite material may be classified according to the matrix type as polymer-matrix composites (PMC), metal-matrix composites (MMC), and ceramic-matrix composite (CMC) composites. In some sources cementitious composites are considered as a different class of composite materials (Chung, 2010). Based on the form of the reinforcement phase, different classifications of composite materials are proposed in the literature including particulates, flakes, whiskers-short fibres, and long continuous fibres. In some cases a very thin coating is typically applied to the fibre surfaces to minimize fibre damage and increase the level of adhesion between the fibre and the matrix (Kessler, 2004).

2.3 Cement-based materials

As a pulverized fine powder, cement converts into a strong binder when mixed with water while ordinary Portland cement (OPC) is the best well-known hydraulic cement (products are stable in aqueous system). Cement is the most widely used solid on earth with the production of approximately over 3 billion tons per year. Calcium and silica, the major abundance natural constituents of cement are responsible for its current low price (~200 $/tone). Unfortunately, the production of cement is also responsible for approximately 5–10% of the global carbon dioxide emissions (Pacheco-Torgal et al., 2013).

As mentioned, cement is basically calcium silicate, where the SiO_4 tetrahedron is the fundamental building material. The hardening process of a cement base composite, which occurs as an exothermic reaction known as hydration, does not require heat or pressure. In cementitious composites water enters the cement crystals and forms a gel that is a hydrate, particularly calcium silicate hydrate (abbreviated C-S-H, with the average chemical formula $3CaO.2SiO_2.3H_2O$). The most widely used civil structural material (concrete) is an example of cement-matrix composites (cement-matrix composite with a fine aggregate-sand, a coarse aggregate-gravel, and optionally other additives-admixtures). When the coarse aggregate is absent, the composite is known as a mortar, which is used in masonry and for filling cracks. When both coarse and fine aggregates are absent, the material is known as cement paste (Claus, 2008). Controlled low strength materials (CLSM) could also be categorized as the cementitious materials consisting of cement, water, additives (fly ash, slag...), and uncommon aggregates such as mineral processing tailings (Bouzalakos et al., 2008).

Through the thermal processing about 1450°C on a mixture composing of limestone and clay, or other materials of similar bulk composition while being sufficient reactive, clinker nodules are produced. The OPC is produced after cooling and pulverizing of clinker (< 150 μm) by addition of calcium sulfate. Table 2.1 represents the main crystalline phases in OPC (Itul, 2010).

Table 2.1- Major crystalline phases in Portland cement (Itul, 2010)

Pure phase	Name	Simplified notation	Impure phase	Proportion by weight
$3CaOSiO_2$	Tricalcium silicate	C_3S	Alite	60-65%
$2CaOSiO_2$	Dicalcium silicate	C_2S	Belite	10-20%
$3CaOAl_2O_3$	Tricalcium aluminate	C_3A	Celite	8-12%
$4CaOAl_2O_3Fe_2O_3$	Tetracalcium ferroaluminate	C_4AF		8-10%

The production of cement is intensively energy consuming while is responsible for 5% of global greenhouse emission (Gartner, 2004; Sierra-Beltran, 2011) hence possible replacement of cement with some supplementary cementitious materials (SCM) such as coal combustion fly ash, blast furnace slag, silica fume could be beneficial for the environment. SCM materials can also bring some additional benefits in cementitious systems such as mechanical strength improvement (Itul, 2010).

As an exothermic reaction, hydration of Portland cement is more complex to be described through the individual composition reaction. As a matter of fact, it consists of a series of reactions between individual clinker minerals; calcium sulfates and water. Combination of cement with water dissolves the calcium sulfate (dehydrated) and most of the alkali sulfates. Dissolved calcium sulfates in fact control the hydration of C_3A whereas the absence of calcium sulfates results in rapid hydration of C_3A and release of heat (Hewlett, 2003; Newman and Choo, 2003). Fig. 2.1 illustrates the heat evolution of cement paste while hydration of cement paste is shown in Fig. 2.2.

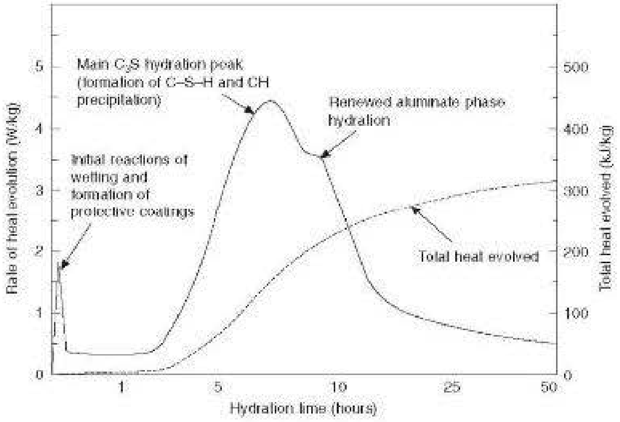


Figure 2.1- Heat of hydration of a cement paste

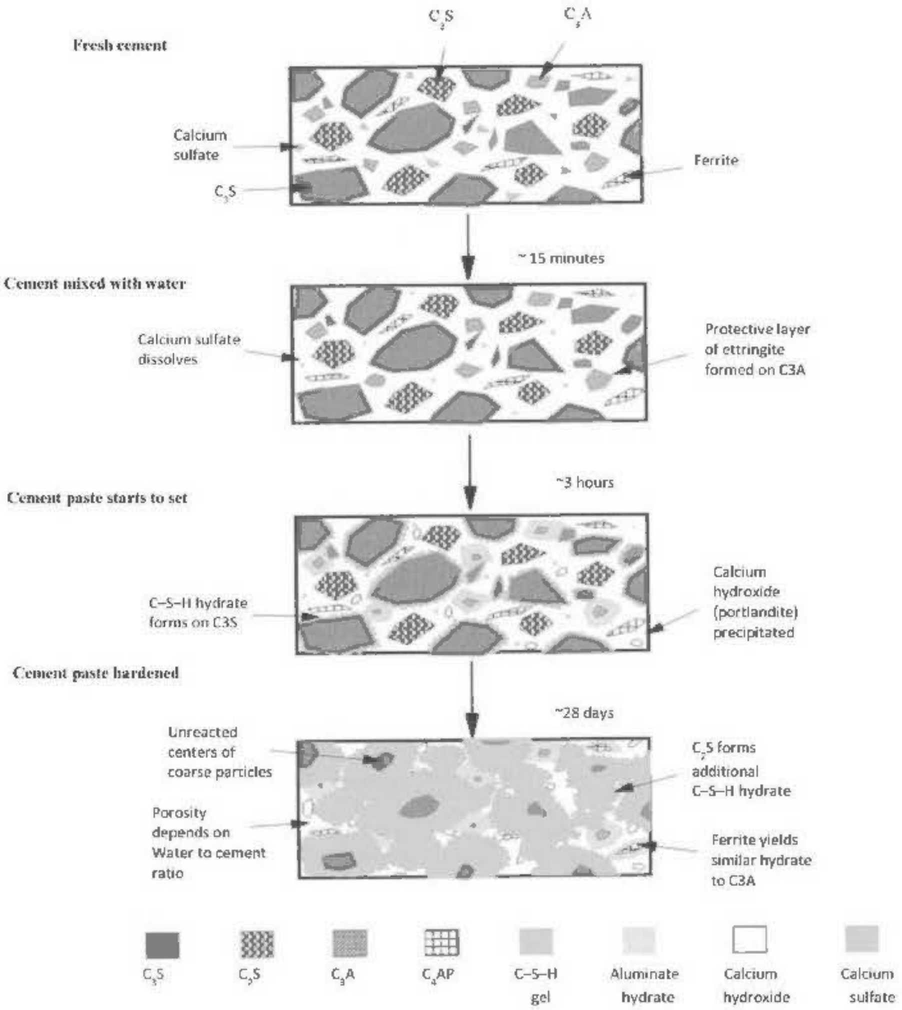


Figure 2.2- Simplified illustration of hydration of cement paste (Newman and Choo, 2003)

Finely grounded cement with a high C_3S content (>60%) and a high C_3A content (>10%) generally has the highest heat of hydration during the first 48 hours. It can be expected that a typical Portland cement cured at 20 °C reaches its maximum hydration (~90%) by 28 days. Cement fineness and the proportion of coarse particles in cement have a critical role in the extent of hydration and long-term strength development. Cement grains which are coarser than ~30 microns will probably never fully hydrate (Newman and Choo, 2003).

As a very low crystalline material with amorphous structure, calcium silicate hydrate (C-S-H) is the main production of cement hydration (50-70%) and directly forms on the surface of cement particles. It can be characterized with the Ca/Si ratio and can be tolerated from 1.2 to 2.3 but it can be dropped to 0.41. It is generally accepted that the C-S-H is a nano-structure compound and thus is the major strength provider. Depending on the Ca/Si ratio, the structure of C-S-H can be close to tobermorite, jennite, and bermorite (Taylor, 1997; Richardson, 1999; Yu, et al. 1999; Itul, 2010; Li, 2011).

As the second main product of hydration of Portland cement (~25%), calcium hydroxide (CH) or Portlandite has a crystalline structure and can be easily observed by the optical microscopy (Hewlett, 2003). Even though a minimum amount of CH is necessary to keep the alkalinity of cementitious materials, increase in the amount of CH elevates the alkalinity and makes the cementitious materials unstable (Stefanovic et al., 2007). High amount of CH may be leached due to the high solubility, or may be resulted in carbonation while reacting with CO_2, or may chemically interact with alkali aggregates due to the high PH value, or may resulted in sulfate attack due to the reaction with sulfate ions (Li, 2011).

Depending on the amounts of C_3A and ferrite phase, and based on the degree of hydration, the hydrated calcium aluminate (AFm) or monosulfoaluminate and ettringite (AFt) or calcium-sulfoaluminate-hydrate can be present in some amounts in the products of hydration.

As a needle-shape crystal with large volume expansion, ettringite forms on the surface of the particles of C_3A thus acting as a diffusion barrier while slowing down the hydration of C_3A. If ettringite forms before the paste has hardened, it will contribute to the early strength development but if it forms after the hardening of paste while the precipitated minerals occupied most of free spaces, it will make its space by breaking the hardened hydrated products resulting in the formation of cracks. Ettringite is stable at a temperature less than 60 °C when there is adequate amount of sulfate available. When AFm is brought into the contact with a new source of sulfate ions, ettringite can be formed again. In maximum degree of hydration of Portland cement, the amount of AFt is decreased whereas the amount of AFm is increased (Hewlett, 2003; Matschei, et al., 2007; Li, 2011).

2.4 Fibre reinforced composite materials

Fibre-reinforced composite materials consist of fibres of high strength and modulus embedded in or bonded to a matrix with distinct interfaces (boundaries) between them. In this form, both fibres and matrix retain their physical and chemical identities, yet they produce a combination of properties that cannot be achieved with either of the constituents acting alone. In general, fibres are the principal load-carrying members, while the surrounding matrix keeps them in the desired location and orientation, acts as a load transfer medium between them, and protects them from environmental damages due to elevated temperatures and humidity, for example. Thus, even though the fibres provide reinforcement for the matrix, the latter also serves a number of useful functions in a fibre reinforced composite material. Fibres can be classified in different categories including glass fibres, carbon fibres, aramid fibres, natural fibres, boron fibres, and ceramic fibres (Mallick, 2008).

Fibre-reinforced cementitious materials (FRC) are cement-based composites incorporated with fibre, mainly short and discontinuous fibres. Use of fibres in cementitious materials basically address two major issues including low tensile strength and low energy consumption capacity. Hence, the influence of fibre reinforced cementitious materials can be evaluated through the shrinkage crack control and changes in mechanical properties. Generally, fibre type, fibre volume ratio (ratio of the fibre volume/total volume), matrix variation, and processing methods are the major variables that affect the effectiveness of fibre reinforced cementitious materials (Li, 2011).

2.5 Tailings

As a particulate suspension containing undesired minerals such as silicates, oxides, carbonates, hydroxides, and sulfides, tailings are generated from mineral processing plant after size reduction and separation of valuable minerals. While the recovered ore minerals represent only a small fraction of the entire ore mass, a significant part of extracted mine materials converts to the tailings. Most of the produced tailings are pumped to tailings impoundments, but it is also possible to thicken the tailings by removing a significant part of the water to produce a high-density slurry or paste. The thickened tailings provide a number of advantages such as occupying a smaller space for damping, possibility of using the recovered water in mine site, decreasing the risk of water run-off from tailings dams and reduce the possibility of tailings dam failures (Lottermoser, 2010).

2.6 Mine backfill

Consisting from waste rock or dewatered tailings residues and frequently mixed with cement to achieve moderate strength, mine backfill can be delivered to underground mine voids (stopes) in different ways such as pumping and/or gravity or as dense slurry or paste through boreholes and pipelines. Backfill serves a number of functions in underground mines such as maintaining the stability and reducing the risk of ground failure especially if the cementitious binders are also added (Grice, 2014). By delivering a significant proportion of produced tailings stream (up to fifty percent) from surface to underground mine spaces, some advantageous are also provided to the environment; for instance, a filled mine stope can encapsulate the acid-generating tailings in backfill plant and can act as a virtual impermeable cell (Benzaazoua et al., 2004; Coussy et al., 2011; Koohestani et al., 2013; Grice, 2014).

William Wayment patented Cemented paste backfill (United States Patent 4101333, 1978) in May 1977. In this patent cemented paste backfill (CPB) is described as "A method of backfilling in underground mine operations by a mill tailings slurry which is dewatered to provide a material with a controlled water content to permit the dewatered material to be used as a backfill without requiring any substantial dewatering after placement and which material can, when desired, be mixed with selected quantities of cement to provide a mortar for backfilling or surface covering" (Wayment, 1978).

CPB consists of filtered (dewatered) mill tailings (72 – 85 wt% solids), water (15 – 28%), and a binding agent such as Portland cements or combination of cement and pozzolanic materials (2 – 8 wt% by dry mass of tailings) (Benzaazoua et al., 2004; Coussy et al., 2011; Koohestani et al., 2013). Depending on the type of binding agent, mineralogy of tailings and curing time, uniaxial compressive strength (UCS) of CPB varies between 0.2 and 4 MPa (Belem and Benzaazoua, 2004, 2008; Yilmaz et al., 2009; Yilmaz et al., 2011; Yılmaz et al., 2014). Mainly, compressive strength of CPB is considered more importantly as in many cases 1 MPa compressive strength is reported for 28 days of curing time (Hassani et al., 2007; Razavi, 2007; Yilmaz et al., 2009; Kermani et al., 2011; Yilmaz et al., 2011; Yılmaz et al., 2014). However, the required compressive strength depends on mining method and the function of CPB in mine as some researchers suggested that in cut and fill mining method compressive strength less than 1 MPa is sufficient for 28 days (Hassani and Archibald, 1998, Kermani, 2012). Since the CPB should be delivered to underground mine voids *via* gravity or pumping, it should have proper fluidity; therefore, additional water will be added to CPB to maintain its flowability and workability at an acceptable range, reportedly 6 to 10 inches of standard slump consistency measurement satisfies the purpose (Belem and Benzaazoua, 2008). In light of this, the available water generally exceeds the amount of water that a binder requires for hydration (water/cement ≥ 3) (Belem et al., 2010).

2.7 Natural fibres/fillers additives

Natural fibres/fillers are generally classified in the literature as being derived from plant, animal or mineral sources. All of the plants fibres are composed of cellulose while animal fibres consist of proteins (hair, silk, and wool). Plant fibres include bast (stem) fibres, leaf or hard fibres, seed, fruit, wood, cereal straw, and other grass fibres. Mineral fibres are naturally occurring fibres such as asbestos (Chand and Fahim, 2008). Another general term used for natural fibres is lignocellulosic fibres but it is a term meaning lignin and cellulose- containing' and some fibres such as cotton have little or no lignin (Pickering, 2008).

Wood is derived from shrubs and trees. It is a heterogeneous, hygroscopic, cellular and anisotropic solid material composed of cellulose (40–50%) and hemicellulose (15–25%) held together by lignin (15–30%). It is commonly classified as either softwood (e.g. pine) or hardwood (e.g. oak). Softwood species comprise wood cells, mostly of one kind, tracheid, that make the material more uniform in structure than hardwoods. There are no vessels (pores) in softwood. Hardwoods are more or less filled with vessels (Chand and Fahim, 2008). The fibres obtained from softwood are longer (3-5 mm average) with diameters of 45 μm for earlywood and 13 μm for latewood while hardwood fibres are generally shorter (1 mm average) and thinner (20 μm average). In addition, the cell wall of hardwood is basically thicker and stiffer than softwood (Sierra-Beltran, 2011).

Wood-fillers usually come from two different sources round wood (debarked wood, logging residues and thinning) and industrial wood residues (sawdust, shavings, offcuts and slabs) (Xu et al., 2008). It has to be notified that the properties of natural fibre compositions (i.e. the cell wall) can be different up to 100% different in comparison to the properties of fibre itself due to the latter consists of an assembly of fibre cells grouped together in different microstructures (Bentur and Mindess, 2006).

The main components of natural fibres are cellulose, hemicellulose, lignin, pectin, and waxes (Cristaldi et al., 2010). Cellulose is a natural polymer consisting of D-anhydro glucose ($C_6H_{11}O_5$) repeating units joined by 1,4-**β**-D –glycosidic linkages at C_1 and C_4 position. Each repeating unit contains three hydroxyl groups (Fig. 2.3). These hydroxyl groups and their ability to hydrogen bond play a major role in directing the crystalline packing and also govern the physical properties of cellulose. Cellulose is resistant to strong alkali but is easily hydrolyzed by acid to water-soluble sugars. Cellulose is relatively resistant to oxidizing agents like hydrogen peroxide (John and Thomas, 2008).

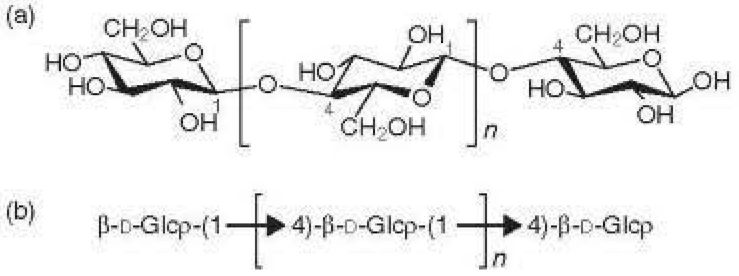


Figure 2.3- Fundamental structure of cellulose (a) Sterochemical (b) Abbreviated (Stokke et al., 2013)

Hemicellulose includes a group of polysaccharides composed of a combination of 5 to 6 carbon ring sugars. In comparison to cellulose, hemicellulose contains several different sugar units and exhibits a considerable degree of chain branching containing pendant side groups giving rise to its non-crystalline nature. The degree of polymerization of native cellulose is 10–100 times higher than that of hemicellulose. Being absolutely hydrophilic, soluble in alkali, and easily hydrolyzed in acids, hemicellulose forms the supportive matrix for cellulose microfibrils (John and Thomas, 2008). Fig. 2.4 shows the structure of hemicellulose found in softwood consisting primarily of galactoglucomannan and arabinoglucuronoxylan. Glucomannan consists of a partially acetylated linear backbone of glucopyranose and mannopyranose (Fig. 2.4a) and the backbone of arabinoglucuronoxylan is comprised of unacetylated xylopyranose (Fig. 2.4b) (Stokke et al., 2013).

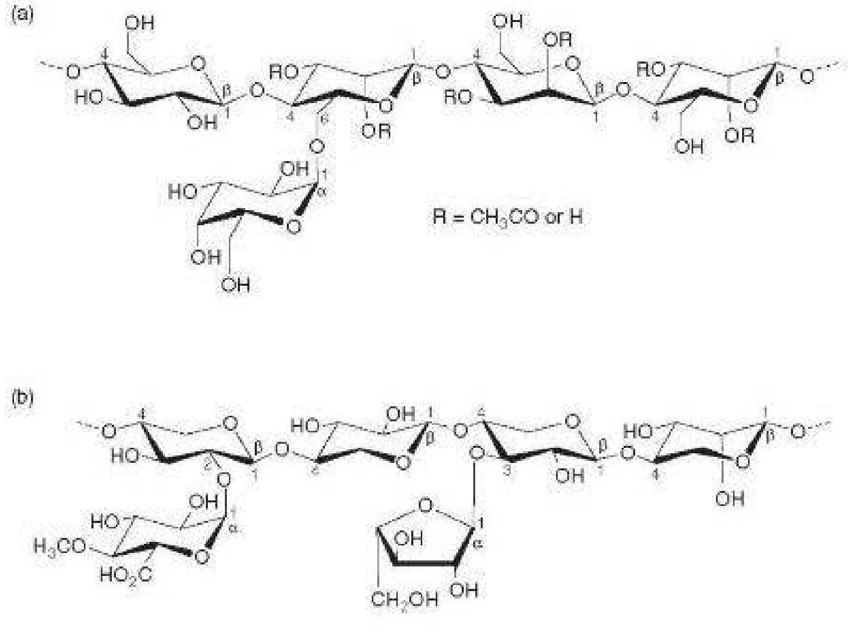


Figure 2.4-Structure of major hemicellulose found in softwood trees (Stokke et al., 2013)

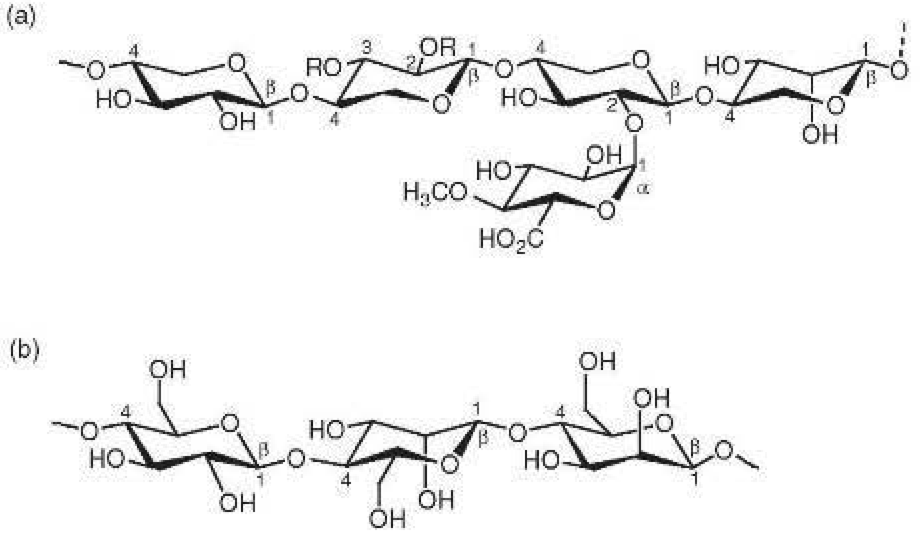


Figure 2.5- Structure of major hemicellulose found in hardwood trees (Stokke et al., 2013)

Glucuronoxylan and glucomanna mainly consist the hemicellulose of hardwood trees. The xylan backbone is similar to that in softwoods, but has considerably fewer and more evenly distributed uronic acid side groups (Figure 2.5). The xylan backbone contains about 3.5–7 acetyl groups per 10 xylose units. Hardwood glucomannan is unsubstituted and is not acetylated (Stokke et al., 2013). Fig. 2.5 shows the structure of hemicellulose found in hardwood trees consisting of glucuronoxylan Fig. 2.5a and glucomannan Fig. 2.5b.

As the flexibility provider to the plants, pectins are carbohydrate oligomers akin to the hemicellulose. The amount of pectins in the wood basically is less than 10 percent while hemicellulose and pectins are the components of dietary fibre. Hemicellulose and possibly pectins have the negative role in the context of composite materials since being sensitive to the temperature, absorbing the moisture, and easily degrading by heat (Stokke et al., 2013).

Being totally amorphous and hydrophobic in nature, lignin basically is insoluble in most solvents and cannot broken down to monomeric units. Lignin is the compound that gives the plant its rigidity. Containing hydroxyl and carbonyl groups, lignin is a three-dimensional copolymer with high molecular weight. Lignin has a complex molecule consisting of three precursors, p-coumaryl, coniferyl, and sinapyl alcohol (Fig. 2.6). From such oligomers, the building blocks of lignin are composed namely p-hydroxyphenyl, guaiacyl, and syringyl phenylpropanoid units (Stokke et al., 2013).

The main difficulty in lignin chemistry is that no method has been established being possible to isolate lignin in its native state from the fibre. It is not hydrolyzed by acids, but soluble in hot alkali, readily oxidized, and easily condensable with phenol (John and Thomas, 2008).

Extractives are other nonstructural organic molecules such as pectins, proteins, tannins, waxes, aromatics, and low-molecular-weight carbohydrates, which exist in the plant cell wall. Extractives may be extracted or removed from the plant cell wall due to solubility in water and/or organic solvents. In the case of composite materials extractives have a crucial role by affecting the adhesive bonding between fibre and matrix through the chemical interaction (John and Thomas, 2008; Stokke et al., 2013). All the chemical components are formed through the photosynthesis of sugar in the leaves (Sierra-Beltran, 2011).

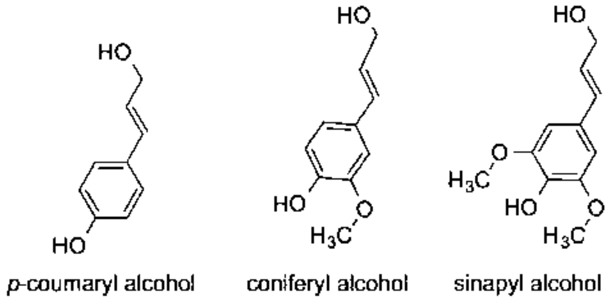


Figure 2.6- Oligomers of lignin (Stokke et al., 2013)

Much of the research on the use of natural fibres is motivated by the ready availability and low costs of such fibres (Bentur and Mindess, 2007). Overall, whenever there is a need of high mechanical properties as well as low weight to reinforce polymeric matrix, the use of natural fibres is feasible. Although tensile strength and Young modulus of natural fibres are lower than some other fibres, their lower density could bring a higher specific strength and stiffness in comparison to other fibres especially if weight reduction is essential and high load-bearing capability is not necessary (Wollerdorfer and Bader, 1998, Wambua, Ivens et al. 2003, Duflou, Deng et al. 2012). In addition, natural fibres have good capabilities in waste management due to their biodegradability.

The required amount of energy per produced amount of natural fibres is another advantage. Energy consumption of flax fibre for example, (including activation, harvesting and fibre preparation) is only 9.55 MJ/kg while this energy for glass fibre is 54.7 MJ/kg (Joshi et al., 2004).

2.8 Natural fibres/fillers in cementitious materials

The main problems of natural fibres using in cementitious materials are low elastic modulus, high water absorption, susceptibility to fungal and insect attack, lack of durability in the alkaline environment, and containing a wide range of carbohydrates (Sobral et al., 1990). Natural fibres have the capability to mineralize inside the alkaline environment due to the migration of calcium hydroxide to the fibre lumen, middle lamella and cell walls (Miller, 2005; Sudin and Swamy, 2006; Mohr et al., 2007). Presence of sugar acid, sugars, and lignosulfonates form an impermeable layer (e.g. flaky calcium silicate hydrate) around the non-hydrated cement grains resulting in the delay of setting time in the hydration of cement and increase in the amount of extractives content increase the non-hydrated cement grains as well (Frybort et al., 2008). Hence, natural fibre cementitious composites may undergo a reduction in strength and toughness as a result of weakening of the fibres (Toledo Filho et al., 2003). Such inhibitory substances (extractives) also decrease the maximum temperature of hydration thus temperature of hydration can be used as a compatibility indicator between wood fibres and cement (Frybort et al., 2008). It is mentioned that the lignin-content of the natural fibres may also affect hydration of cementitious composites (Cabrera and Nwaubani, 1990; Atadana, 2010) thus some additives such as $CaCl_2$ and $MgCl_2$ are often used (between 1 to 5 percent) to accelerate the hydration of cement and counteract the retarding effect of inhibitors like phenolic compounds and free carbohydrates (Cabrera and Nwaubani, 1990). It is believed that the bond between the wood fibre and cement may be chemical, physical, or a combination of both and chemical bonds are thought to be hydrogen bonds and/or hydroxide bridges (Coutts and Kightly, 1984). Wood fibres are relatively short and inflexible, but are usually strong and perform better during long aging in cement environment (Bentur and Mindess, 2006). In many cases researchers strived to prevent the compatibility problems of natural fibres and cementitious materials by performing different modifications on natural fibres (Ghavami, 1995; Bilba et al., 2003, Arsene et al., 2007, Bilba and Arsene, 2008). Addition of natural fibres to cementitious materials also increases the surface area and thus decreases the workability of the mixture (Frybort et al., 2008). Due to the hygroscopic properties and in comparison to pure cementitious composite, wood fibres keep the cementitious materials wet for a longer period (Sierra-Beltran, 2011).

2.9 Polymer additives in cementitious materials

Despite the extensive use, cementitious materials could have some downsides such as delayed hardening, low tensile strength, large drying shrinkage, and low chemical resistance. To get over of such difficulties, addition of polymeric admixtures in cementitious materials can be an advantage. Modification of cementitious materials with polymers provides a homogenized monolithic co-matrix through the combination of organic polymer matrix and cement gel matrix. Such a co-matrix binds aggregates in between and the properties of cementitious materials are defined based on such a co-matrix. Modification of cementitious materials using polymers admixtures is prepared through the mixing process of a dispersed, powder, or liquid form of a polymer or monomer in fresh cementitious mixture basically at a dosage of 5–20% by weight of cement. By interaction with hydrating cement, polymers influence the setting, bleeding, workability, and mechanical properties of cementitious materials (Ramachandran, 1996; Mailvaganam and Rixom, 2002; Czarnecki, 2005). Some common disadvantages associated with the use of polymers with cement including susceptibility to moisture and deterioration while exposing to weathering and reduction in the final density of the material by increase in the amount of trapped air while mixing resulting in porosity enhancement (Riley and Razl, 1974; Ohama, 1998; Anagnostopoulos, 2005). Addition of polymers in fresh cementitious materials may also cause additional stickiness between the components of the mixture (Miller, 2005).

Different kinds of the polymer-modified cementitious materials including latex, redispersible polymer powder, water-soluble polymer, liquid resin, and monomers modifiers are produced; among them latex by far is the most widely used cement modifier. In the modified systems with latexes, redispersible polymer powders, and water-soluble polymers, formation of a film or membrane occurs. In the systems modified with the liquid resins and monomers, water induces the hydration of the cement and the polymerization of the liquid resins or monomers (Ohama, 1995; Ramachandran, 1996; Kardon, 1997). Fig. 2.7 shows the different polymer admixtures usable in cementitious materials.

As an emulsion containing fine polymer particles and non-polymeric constituents in water, latex is a stable dispersion of micro-particles in an aqueous medium. The properties of the latex form of the polymer or copolymer are very dependent on how the various constituents are put together. Latex basically forms with polymerization of a monomer such as vinyl acetate, if necessary a co-monomer i.e. vinyl ester, a surfactant, and water. The used monomer in polymerization determines the properties (i.e. flexibility, hardness) of final product. As non-ionic polymer particles are the most functional with cementitious materials, surfactants can charge the polymer particles during the polymerization reaction positively (cationic), negatively (anionic), or no charge (non-ionic) (Decker and Moussa, 1990; Cheremisinoff and Cheremisinoff, 1993; Moussa and Decker, 1993; Ohama, 1998; Miller, 2005; Lamond and Pielert, 2006; Van Krevelen and Te Nijenhuis, 2009; Doran and Cather, 2013).

Fig. 2.8 shows the process of latex film formation. Polymer particles join together as water is either removed or evaporated or chemically consumed through the hydration of cement. Polymer molecules subsequently combine and deform while the final shape and product of polymer (film) is produced (Jenni et al., 2005; Jenni et al., 2006; Winnefeld, Kaufmann et al., 2012). Addition of latex improves the workability of cement-based materials while decreases a significant amount of water for a given slump. This effect originates from the presence of polymer particles accompanying with air and dispersing effect of the surfactant emulsifiers resulting in ball-bearing effect. In comparison to normal mixes and in regards to the type of polymer and polymer-cement ratio, the setting time of latex modified cementitious materials can be inhibited due to the presence of surfactants. The tendency of the mixture to bleed or segregate is diminished due to the hydrophilic colloidal properties of the latex, water reduction, and entertained air (Mailvaganam and Rixom, 2002).

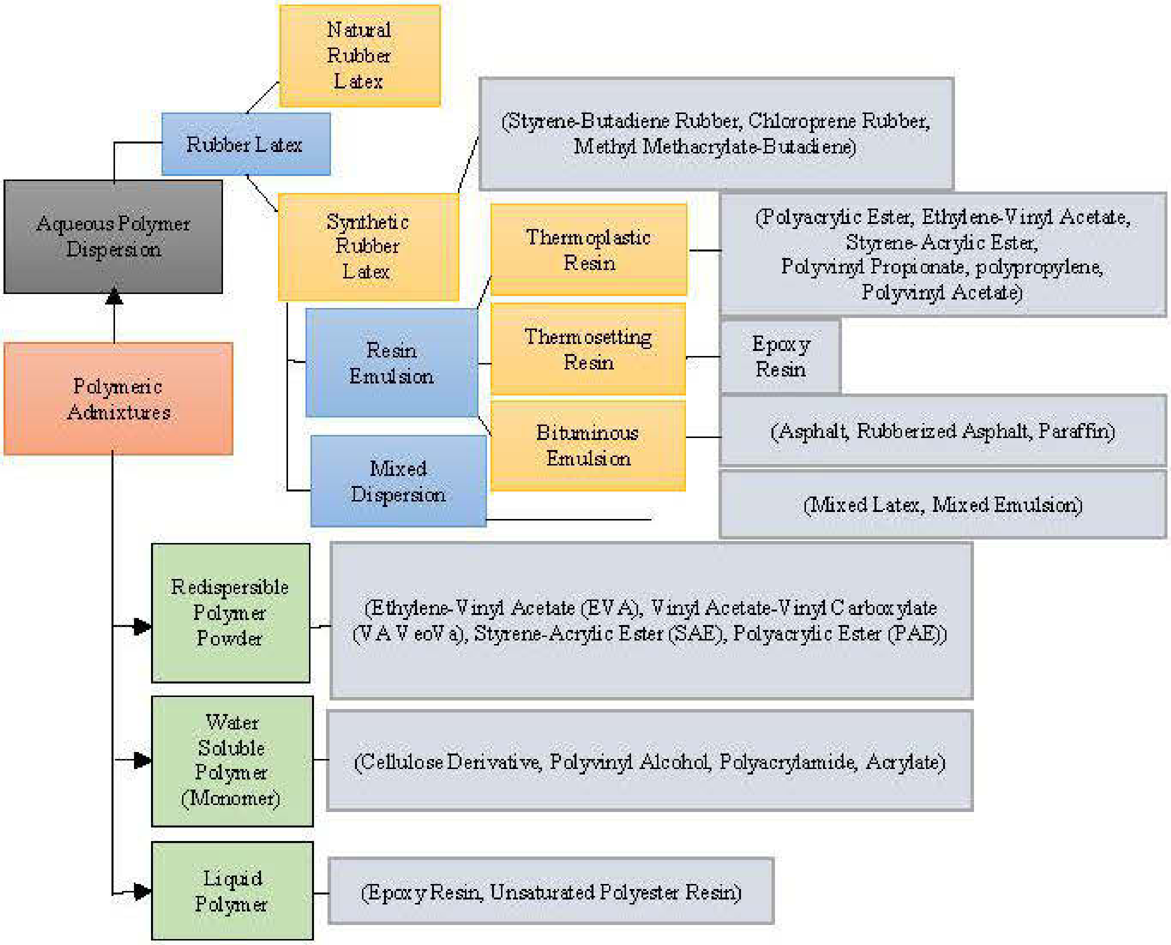


Figure 2.7- Classification of polymeric admixtures (Ohama, 1997)

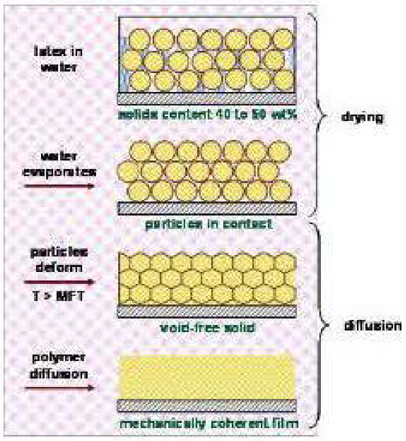


Figure 2.8- Latex film formation (Winnik, 2016)

Both hydration of cement and formation of polymer film regulate the modification of latex in cementitious materials. The hydration of cement in fact precedes the polymer formation and at the final stage a co-matrix phase is formed by both cement and polymer film formation processes (Sperry et al., 1981; Mailvaganam and Rixom, 2002; Kaeding and Maass, 2003; Miller, 2005; ACI, 2010).

Solid forms of latex are called redispersible polymer powders and the modification of cementitious materials with redispersible polymer powders is as latex modification. Preparation of redispersible polymer powders from latexes involves the pressurized or non-pressurized procedure following by spray drying. Since latex is water-based emulsion, produced redispersible polymer powders are free of solvents and all the redispersible polymer powders are thermoplastic in nature. The majority of which are vinyl acetate co-polymers while the secondary monomer could be ethylene, styrene, vinyl ester, and so on. Utilizing such polymers in cementitious materials involves the addition of powders to dry admixtures containing cement followed by the addition of water (Riley and Razl, 1974; Ohama, 1995; Ramachandran, 1996; Kardon, 1997; Ohama, 1998; Schulze and Killermann, 2001; Mailvaganam and Rixom, 2002; Jenni et al., 2005; Miller, 2005; Jenni et al., 2006; Winnefeld et al., 2012). Addition of such polymers may have more influence on flexural and tensile strength in comparison to compressive strength; in addition, an improved workability is achievable in fresh mixture hence the water demand may be deceased for maintaining the same consistency (Chandra and Flodin, 1987; Schneider et al., 1993; Miller, 2005; Page and Page, 2007).

Use of vinyl acetate monomer or polyvinyl acetate within the cementitious materials is well-known (Schneider et al., 1993; Ohama, 1997; Fowler, 1999; Schulze and Killermann, 2001; Silva et al., 2002; Silva and Monteiro, 2006; Van Krevelen and Te Nijenhuis, 2009). Vinyl acetate is an active monomer and in the presence of a catalyst synthesizes (Yates et al., 1999; Miller, 2005). Structure of vinyl acetate ($C_4H_6O_2$) is shown in Fig. 2.9. As a thermoplastic agent, vinyl acetate consists of a carbon-carbon double bond with an acetic acid functional group on one of the carbons. Vinyl acetate is used for different purposes including adhesiveness and bonding improvement (Yeo, 1996; Zhang et al., 2005).

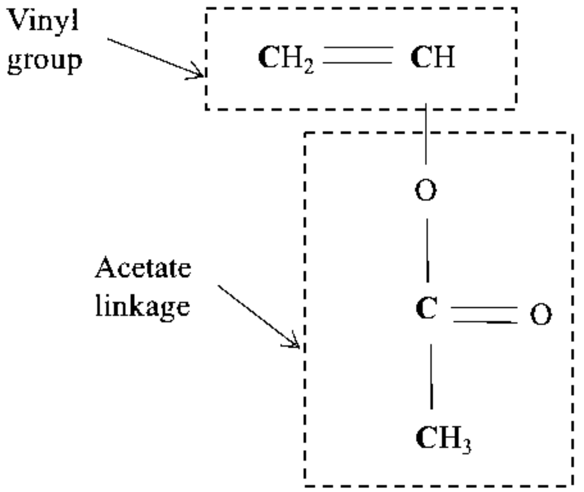
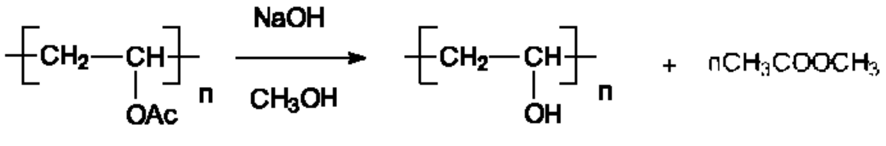


Figure 2.9- Structure of vinyl acetate

However, in the presence of moisture and specifically in alkaline conditions vinyl acetate hydrolyzes and converts to acetic acid and vinyl alcohol. Fig. 2.10 shows the reaction of polyvinyl acetate (PVA) in alkaline solution in the presence of methanol (Kricheldorf et al., 2010).



$$-\!\left[CH_2-\underset{OAc}{CH}\right]_n- \xrightarrow[CH_3OH]{NaOH} -\!\left[CH_2-\underset{OH}{CH}\right]_n- \quad + \quad nCH_3COOCH_3$$

Figure 2.10- Conversion of polyvinyl acetate in alkaline solution with methanol

In cementitious materials on the other hand, hydrolysis of vinyl acetate occurs in the presence of water and calcium hydroxide (portlandite) as one of the main products of cement hydration. In this case, acetate anion (CH_3COO) releases and combines with Ca^{2+} ions and calcium acetate ($Ca(CH_3COO)$) is produced in addition to polyvinyl alcohol. Calcium acetate is an organic salt while polyvinyl alcohol is water soluble (Silva et al., 2002). The formation of calcium acetate is also possible due to the attack of acetic acid (CH_3COOH) to calcium hydroxide particles (Sasaoka et al., 1998). Due to the low price of PVA, its consumption in applicable composites as the adhesion and or bonding improvement is recommendable specifically if the surrounding area remains dry (Miller, 2005).

Even though the chemical structure of ethylene (C_2H_4 or $CH_2=CH_2$) is very simple, a broad family with a variety of properties originates from it because of its capability to crosslink with other polymers (Biron, 2012). Ethylene is a hydrophobic monomer and its polymerization with vinyl acetate decreases the tendency of acetic group to undergo the hydrolysis. This is significantly important in cementitious materials because of exposing to the moisture (Miller, 2005). In addition, incorporation of vinyl acetate to ethylene chain improves its flexibility and toughness because of low-density of polyethylene (Bard et al., 2004).

The chemical structure and usage of vinyl ester is similar to vinyl acetate but it is more expensive because of being difficult to prepare (Kricheldorf et al., 2010; McLennan et al., 2010). Vinyl esters are a family of thermosetting resins having the superior toughness and corrosion resistance to organic solvents and water (Strong, 2008). Moreover, addition of vinyl esters of carboxylic acids to vinyl acetate can improve the stiffness while improving the plasticizing effect of final co-polymer. Among vinyl esters that are used with vinyl acetate, vinyl ester of versatic acid (VeoVa) has attracted the most interests (Blackley, 1997; Sidney Goodman, 1998; Gomes and Ferreira, 2005). Versatic acid is tertiary carboxylic acid wherein one alkyl group is methyl and two other alkyl groups are linear (Jacobs et al., 1985, Weissermel and Arpe, 2008).

In contrast to linear polymers, backbone polymers have connected side chains in a regular manner. The structure of backbone polymers if drawn with all side chains looks like a comb (Roussel, 2011). Fig. 2.11 represents the structure of a comb polymer with an anionic backbone attached with side chains.

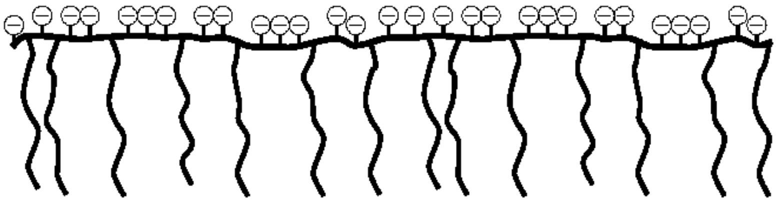
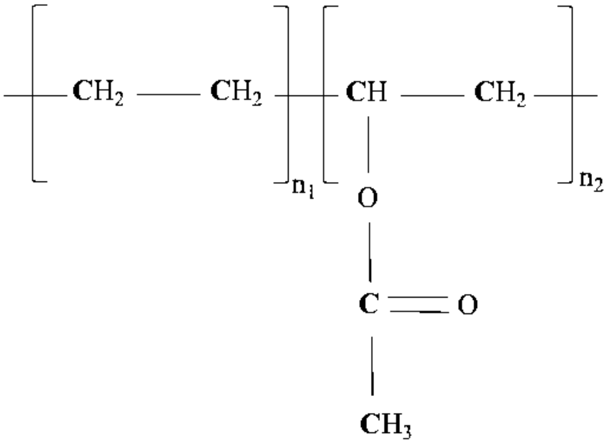


Figure 2.11- Comb polymer with anionic backbone (Roussel, 2011)

Among backbone polymers, ethylene-vinyl acetate (EVA) is the most frequently used one (Mildenberg et al., 2008). Fig. 2.12 displays the structure of ethylene-vinyl acetate, which originates from the polymerization of ethylene and vinyl acetate.



$$-\left[CH_2-CH_2\right]_{n_1}-\left[\underset{\underset{\underset{\underset{CH_3}{|}}{C=O}}{|}}{\underset{O}{\underset{|}{CH}}}-CH_2\right]_{n_2}-$$

Figure 2.12- Typical structure of ethylene-vinyl acetate (EVA) (Harper and Petrie, 2003)

It is reported that the redispersible powder form of EVA decreased the degree of bond adhesion in addition to permeability reduction of the modified cementitious materials (Miller, 2005). Wacker Company provided a redispersible copolymer (terpolymer) of ethylene-vinyl acetate/vinyl ester for improvement of workability and adhesion in cementitious materials, but the source of vinyl ester is not mentioned if it is originated from carboxylic or versatic acids for example. However, since this product improves the workability of cementitious materials it might be carboxylic base acid family such as versatic acid. This product is used in this research to evaluate its influence in cemented paste backfill. The properties of such backbone copolymers basically depend on the core polymer level (vinyl acetate in this case), the crystallinity, branching level, molecular weight and polarity (Biron, 2012).

2.10 Nanotechnology

Approximately, more than one decade now the term nano-materials received ample interests and particles with the size less than 100 nm (1 nm= 10^{-9} m) referred as nanoparticles (Sepeur 2008). Preparation of nanoparticles could be achieved either through the high milling energy (Sobolev and Gutiérrez, 2005) or chemical synthesis (Lee and Kriven, 2005). Nanotechnology includes the productions and applications of physical, chemical, and biological systems at the scale of atom or molecule to the sub-micron dimension in addition to the integration of nano-structures into larger systems (Bhushan, 2010). Different terms in the field of nanotechnology are common including top-down approach (establishment of smaller device by using larger compositions (e.g. microprocessors)), bottom-up approach (arrangement of smaller component into more complex assemblies (e.g. DNA)), and nano-science or nanotechnology as the general term, which asserts the study of materials at nanoscale (Scrivener, 2009; Sanchez and Sobolev, 2010).

Chemical nanotechnology is production of systems, materials or components in the range of atomic or molecular dimensions through the chemical synthesis with nanoscale measurements between 1 nm and 100 nm. Integration of agglomerate-free nanoparticles or corresponding dispersions as an additive for coating purposes, in order to maintain multi-functional surfaces, is an example of chemical nanotechnology; this is considered as the colloid chemistry. Different functionalities such as mechanical, electrical, magnetic, optical, chemical, and biological are attainable or improvable through the use of nanoparticles and/or in nanostructure solids, this is more perceivable due to the similar behavior of nanoparticles and atoms (Sepeur, 2008). Fig. 2.13 illustrates the concepts of bottom-up and top-down in the field of nanotechnology.

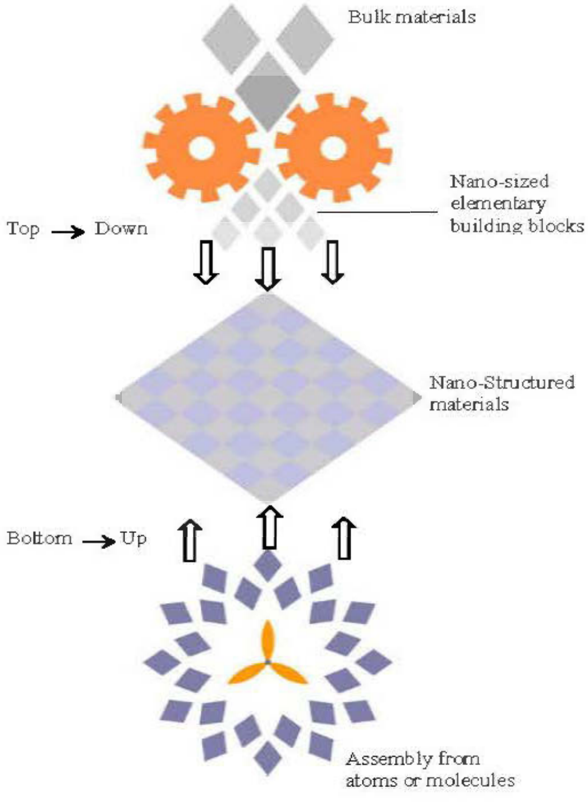


Figure 2.13- Top-down and bottom-up approaches (Sanchez and Sobolev, 2010)

2.11 Silane technology

As a coupling agent or adhesion promoter, silane is a monomeric silicon-based molecule containing four constituents. The electropositive nature of the silicon atom causes specific atoms or groups to link to silicon atom directly and make it reactive and inorganic rather than organic. A silane is called organo-functional (organosilane) if an organic group is attached to the silicon molecule directly or through the alkyne, arylene, or other types of organic bridges to establish organic reactivity. The organic group is either reactive (amino, epoxy, methacrylate, etc.) or unreactive (methyl, butyl, octyl, phenyl, etc.).

Silane substituents such as chlorine, amine, methoxy, acetoxy, or hydroxyl, are reactive with inorganic materials containing hydroxyl groups such as minerals. The advantage of organosilane is the bonding development-establishment of an organic molecule to an inorganic particle, surface, or substrate; in fact, organosilanes act in the interphase region like bonding or bridging agent (Mittal, 2007; Hermanson, 2010; Ebnesajjad and Ebnesajjad, 2013). A typical structure of an organofunctional silane is shown in Fig. 2.14 and interphase mechanism of organosilanes is illustrated in Fig. 2.15.

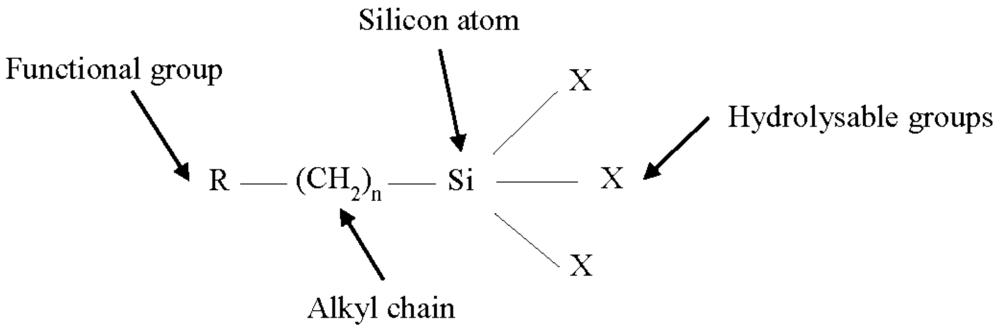


Figure 2.14- Typical structure of organofunctional silane (Hermanson, 2010)

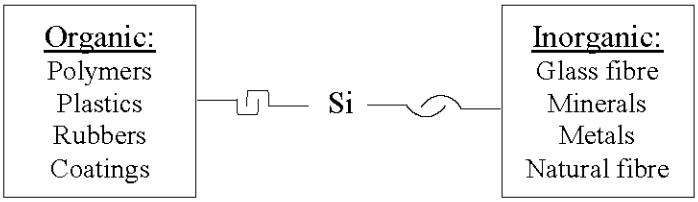


Figure 2.15- Dual reactivity of organosilanes (Ebnesajjad and Ebnesajjad, 2013)

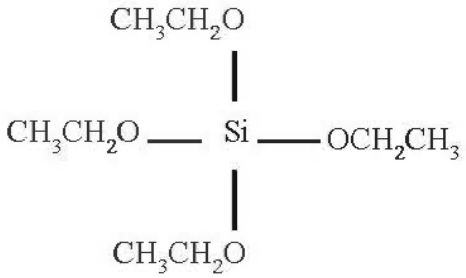
Sol is a liquid containing dispersed non-settled and/or non-agglomerated solid colloidal particles ($\sim 1 - 1000$ nm) in which the gravitational forces are negligible and the interactions of particles are dominated by short-range forces such as van der Waals attractions or surface charges (Iler, 1955; Brinker and Scherer, 1990; Bergna, 1994; Livage, 1997; Caruso, 2006). Hydrosol (aquasol) and organosol are the sols in which their liquids are water and organic solvents respectively. If the colloidal dispersion of particles is in a gas it is called aerosol (Bergna, 1994, Bergna and Roberts, 2005).

Gel is a continuous solid form made from colloidal particles enclosing a continuous liquid phase; if the gel is dried under normal condition, it is called xerogel. Aerogel, as the specific form of xerogel, is made through the drying process (autoclave) of a wet gel above the critical temperature of liquid (minimize the shrinkage of aerogel). Cryogels are powders are obtained by freeze-drying of a sol (Bergna, 1994; Bergna and Roberts, 2005).

The precursors for the preparation of a colloid consist of a metal or metalloid elements encompassed by ligands (alkoxides mostly). An alkyl is a ligand when one hydrogen (proton) is removed from an alkane molecule, for example, methyl (CH_3^-) is an alkyl produced from methane (CH_4). Addition of a hydroxyl (OH) group to an alkyl molecule forms an alcohol such as methyl alcohol (CH_3OH or methanol). When a proton is removed from the hydroxyl of alcohol, the most used ligand (alkoxides) for the preparation of precursor is prepared (e.g. methoxy (CH_3O^-)). If a metal or metalloid is attached to an alkoxy, metal alkoxides, as a group of metalorganic compounds, is established. Meal alkoxides are the most broadly used precursors in sol-gel process since they easily react with water (hydrolysis). It should be notified that metalorganic compounds are different with organometallic compounds, which have direct metal-carbon bond (Brinker and Scherer, 1990; Niederberger and Pinna, 2009).

The aqueous sol-gel process defines as the conversion of a precursor solution into an inorganic solid via inorganic polymerization in the presence of water; this process involves the hydrolysis (attachment of hydroxyl ion to the metal atom) and condensation (liberate of small molecules e.g. water or alcohol). Further condensation and hydrolysis can continue to create a large metal containing molecules through the polymerization (Brinker and Scherer, 1990; Kickelbick, 2007; Niederberger and Pinna, 2009).

The most widely used metal-alkoxide is tetraethyl-orthosilicate (TEOS) or tetraethoxysilane (Brinker and Scherer, 1990; Kickelbick, 2007; Sepeur, 2008; Niederberger and Pinna, 2009). Fig. 2.16 shows the structure of tetraethyl-orthosilicate. Equation 1 shows the hydrolysis of TEOS through the addition of water. If the hydrolysis occurs completely, the results of this reaction include four unstable silanols and four molecules of ethyl alcohol in which evaporates. Equations 2 and 3 illustrate different possibilities of partial condensation of silanols to siloxane bonds ($R=CH_3CH_2$). Through the polymerization, equations 2 and 3 continue to react (hydrolysis-condensation) to build a large silicon containing molecules (macromolecule). Generally, polymerization occurs on three stages including polymerization of monomer and formation of particle, growth of particle, particle linkages into chains and then networks and finally thickening of networks and formation of the gel (Brinker and Scherer, 1990; Sepeur, 2008).



$$CH_3CH_2O-\underset{\underset{CH_3CH_2O}{|}}{\overset{\overset{CH_3CH_2O}{|}}{Si}}-OCH_2CH_3$$

Figure 2.16- Structure of tetraethyl-orthosilicate (Battersby et al., 2002)

$$Si(OR)_4 + 4H_2O \rightarrow Si(OH)_4 + 4ROH \qquad (1)$$

$$(OR)_3Si\text{-}OH + OH\text{-}Si(OR)_3 \rightarrow (OR)_3Si\text{-}O\text{-}Si(OR)_3 + H_2O \qquad (2)$$

$$(OR)_3Si\text{-}OR + OH\text{-}Si(OR)_3 \rightarrow (OR)_3Si\text{-}O\text{-}Si(OR)_3 + ROH \qquad (3)$$

The condensed form of TEOS forms a pure nano-SiO_2 (within the size range of 1-100 nm) network without organic modification. However, hydrolysis and condensation reactions of TEOS or metal alkoxides are strongly pH dependent. It is specified that the pH range between 0 and 2 show higher rate of hydrolysis in comparison to the rate of condensation (high hydrolysis-low condensation), whereas under alkaline condition (pH>7) the rate of condensation becomes higher than that of hydrolysis. That is, after slow formation of hydrolyzates in alkaline condition, the condensation starts rapidly, whereby incomplete hydrolyzates crosslink through the polysiloxane units (Brinker and Scherer, 1990; Arkles, 2004; Arkles and Pan, 2006; Sepeur, 2008; Sobolev et al., 2009; Abel, 2011). Fig. 2.17 shows the hydrolysis-condensation rate of a typical silane at different pH.

Changes in the pH values of a sol play a critical role in the formation of nanoparticles from alkoxides, but there are some other variables that have a role in this case including type of solvent, type and chain length of the alkoxide function (e.g. methyl,

ethyl), concentration of agent, temperature, type and concentration of the catalyst, rate of evaporation, and available water (Brinker and Scherer, 1990; Sepeur, 2008).

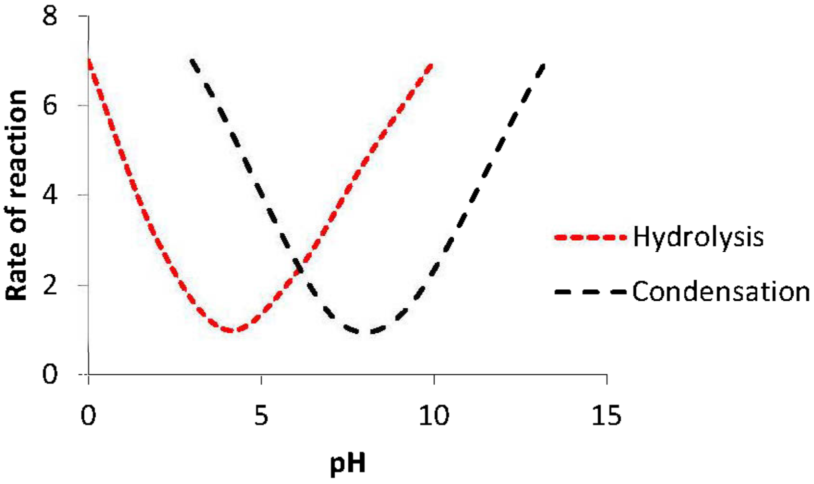


Figure 2.17- Hydrolysis and condensation rate of a typical silane (Brinker and Scherer, 1990; Arkles, 2004; Itul, 2010)

2.12 Nano-material additives in cementitious materials

Introduction of nanotechnology in cementitious materials has the potential to address multiple challenges including carbon dioxide emission; poor crack resistance, long curing procedure, tensile strength, water absorption, ductility and etc. (Spotlight, 2012). Polymeric admixtures influence the nano-scale behavior of cementitious materials by changing the interaction forces between cement particles and nano sized molecules, hence in some sense, such chemical admixtures could be considered as nanotechnology in cementitious materials (Garboczi, 2009). Interaction between products of hydrated cement, admixtures and nano-fillers modify the cement reactions while creating new surfaces, layers and products within cementitious materials (Scrivener, 2009).

From nanotechnology point of view, since hierarchical structure of hardened cement starts from sub-millimeter dimension and then converts to nanometer, it can be considered as a nano-material (Soni, 2014). Figure 2.18 illustrates the specific surface area and particle size of cementitious materials. Calcium silicate hydrate (C-S-H) for example, as the main product of cement hydration is a nanostructure material. The structure of C-S-H consists of thin solid layers separated by gel pores filled with interlayer and adsorbed water. Moisture movement through the structure of C-S-H results in shrinkage and consequent cracking (Birgisson et al., 2012). Structure of C-S-H consists of well-defined nano-pores that can be treated as a partially saturated drained granular material. Analyses regarding the drying shrinkage and mechanical strength development of C-S-H declare the possible roles of capillary water, disjoining water, and surface water (Garboczi, 2009; Jennings, 2009). Figure 2.19 displays a schematic structure of C-S-H in hydrated Portland cement.

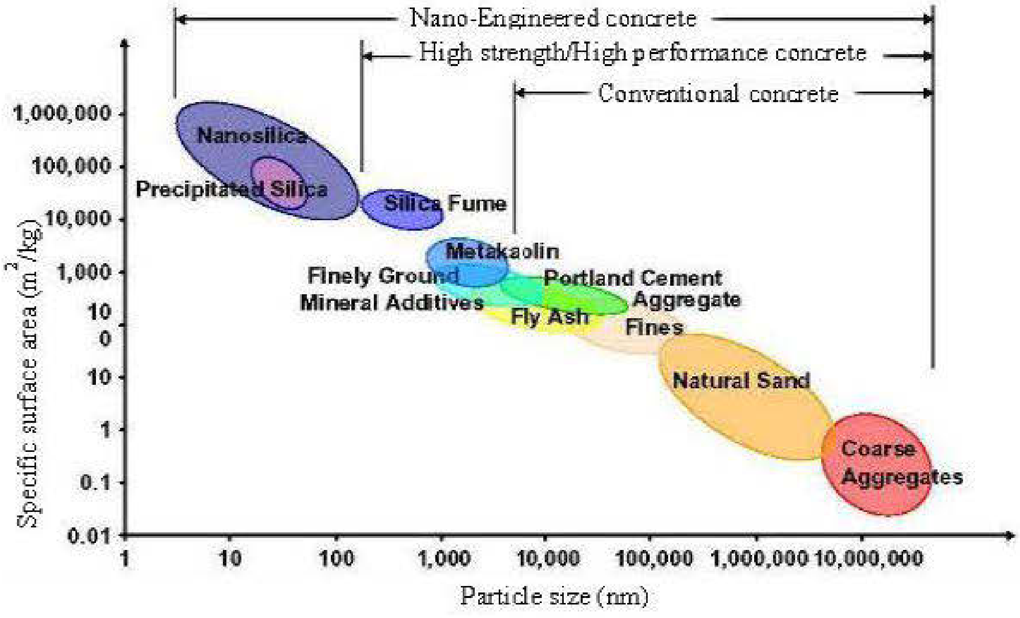


Figure 2.18- Particle size and specific surface area related to cementitious materials and concrete (Sanchez and Sobolev, 2010)

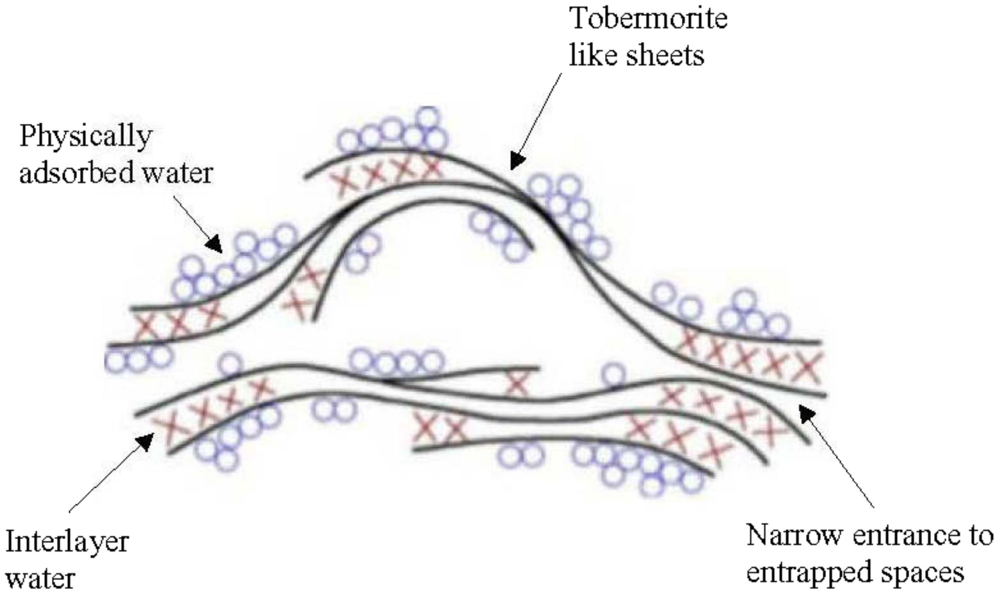


Figure 2.19- Simplified physical model of C-S-H in hydrated Portland cement (Raki et al., 2010; Soni, 2014)

Regarding the structure of C-S-H, any changes in the silicate and calcium ions upon the removal of water may be responsible for the variations of mechanical behavior (Raki et al., 2009). Figure 2.20 shows the structure of tobermorite mineral similar to C-S-H. Appropriate organic polymers may bond and reinforce the C-S-H at the nano-scale through the grafting to the defected sites of the silicate chains where thetrahedra is missing (Fig. 2.21) (Garboczi ,2009; Raki et al., 2009).

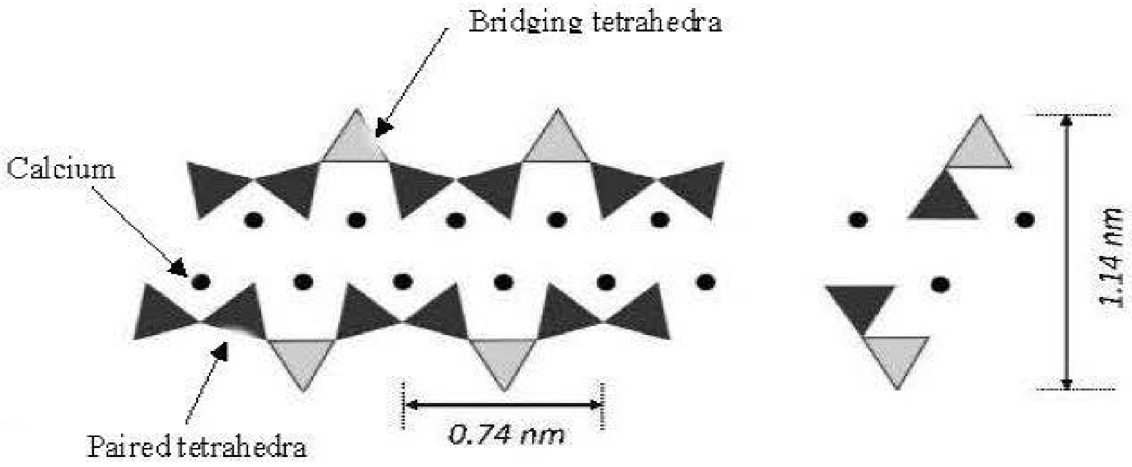


Figure 2.20- The schematic molecular structure of a single sheet of tobermorite (Raki et al., 2010)

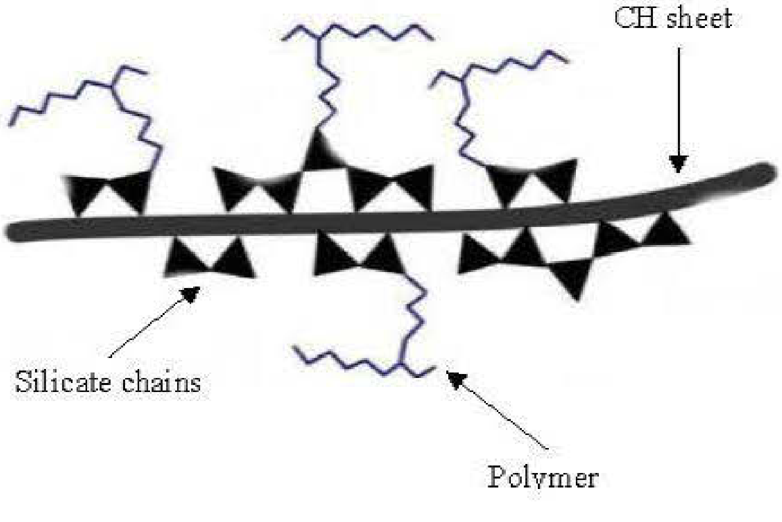


Figure 2.21- The schematic of backbone polymer groups grafted to silicon sites (Raki et al., 2010)

Addition of nano-size additives in the forms of solid particles or nano-size molecules (colloidal) can influence liquid/solid phases or liquid-solid interface (Garboczi, 2009). However, dispersion of nano-particles in the form of colloidal is more effective in comparison to the solid nano-particles (Gaitero et al., 2010). Among different nano-materials, nano-silica is the most used nano-material in cementitious materials possibly due to the cost and effectiveness (Sobolev et al., 2009; Choolaei et al., 2012; Pourjavadi et al., 2012; Hou et al., 2013; Singh et al., 2013; Zapata et al., 2013). Nano-particles have the capability to fill the nano-pores of C-S-H and reduce the total porosity resulting in reinforcement of cement-based materials (Gaitero et al., 2010, Birgisson et al., 2012), but that is not the only potential expecting from nano-materials. Addition of colloidal nano-silica (CNS) accelerates the dissolution of C_3S resulting in the rapid formation of C-S-H; it can also react with calcium hydroxide as the second product of cement hydration to generate additional amount of C-S-H gel through the pozzolanic reaction.

Both of acceleration in the hydration and reaction with calcium hydroxide are influenced by particle size and proper dispersion of nano-particles in the cementitious material (Sobolev and Gutiérrez, 2005; Sobolev et al., 2009; Sanchez and Sobolev, 2010; Birgisson et al., 2012, Singh et al., 2013). Pozzolanic reaction occurs through the attack and attachment of OH^- ions of any pozzolanic material (e.g. calcium hydroxide) on the SiO_2 or Al_2O_3-SiO_2 framework. Through the pozzolanic reaction free lime content of cement-based material is reduced while the amounts of silica and alumina are increased (Taylor, 1997; Hewlett, 2003; Gaitero et al., 2008; Gaitero et al., 2010). However, since the addition of nano-silica makes the structure of C-S-H more compact and dense, pozzolanic reaction of nano-silica may be marginal (Birgisson et al., 2012).

Nano-particles are extremely susceptible to agglomeration hence addition of a superplasticizer can help the dispersion of which within the cementitious matrix (Senff et al., 2009; Senff et al., 2010; Berra et al., 2012; Kong et al., 2012; Heikal et al., 2013; Hou et al., 2013; Kong et al., 2013). Superplasticizers are water-reducing agents that are often used in cementitious materials as dispersive agent as well. There is a general agreement that superplasticizer molecules adsorb on the surface of hydrating cement grains during the initial hydration process and release the trapped water by van der Waals forces (Mollah et al., 2000; Zapata et al., 2013). Superplasticizers do not have negative effect on the strength development when added to cementitious materials for workability improvement. In some cases, a substantial increase in compressive strength may occur (Mailvaganam and Rixom, 2002).

Early generation of superplasticizers were based on natural products (lignosulfonates or sulfonated melamine or naphthalene formaldehyde) therefore there was little control on the basic chemical structure. However, in recent years, introduction of polycarboxylate ether-based superplasticizer (PCE) established a new generation of anionic comb like polymer with backbone and side branches. The performance of this new generation of superplasticizer can be modified by manipulation of backbone chains and side branches (Scrivener, 2009). Adsorption of PCE to cement grains is mediated by carboxylate groups while dispersing effect of PCE originates from repulsion effect of long ether-group chains (Ren et al., 2014).

Only few basic structural units are utilized to form PCE polymers but a number of different formulations are developed. Methacrylic acid and maleic acid are the main monomers consisting the backbone while polyethylene oxide is used as the chain sides in a majority of PCEs (Roussel, 2011). Fig. 2.22 illustrates the structure of PCE containing copolymer of acrylic acid, polyethylene oxide, mono-vinyl ether, and maleic acid. When combined with nano-silica, PCE improves the dispersion of nano-particles resulting in mechanical strength development of cementitious materials significantly at early ages of hydration (Sobolev et al., 2009).

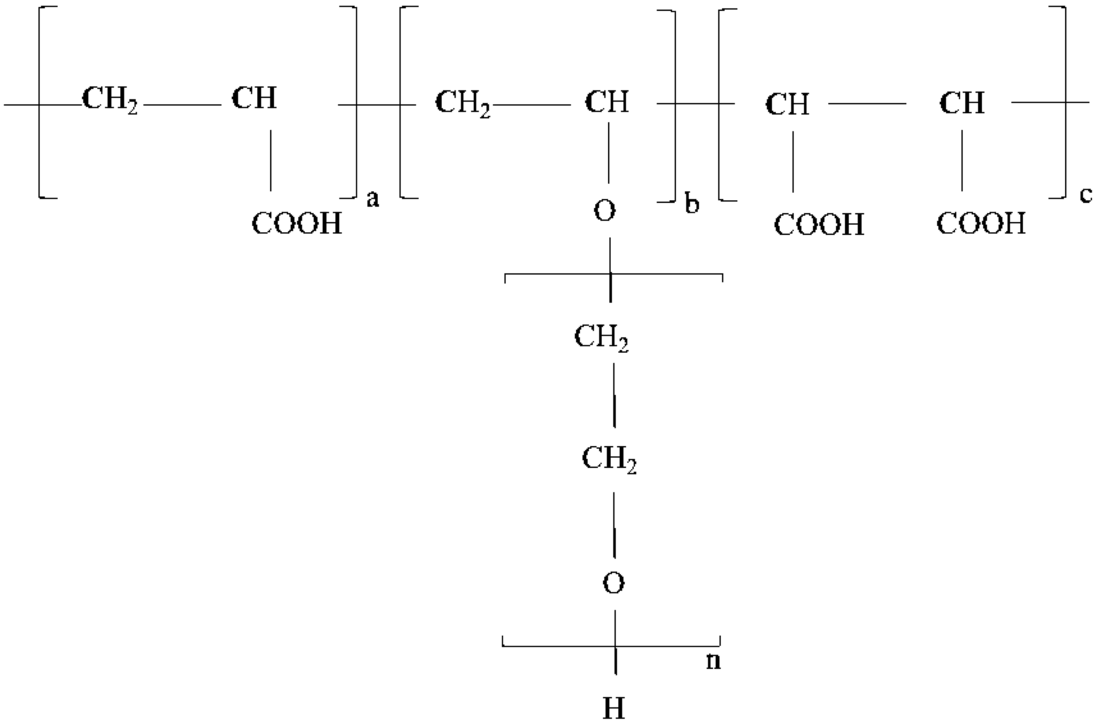


Figure 2.22- PCE based on copolymer of acrylic acid, polyethylene oxide, mono-vinyl ether, and maleic acid (Roussel, 2011)

2.13 Conclusion

The aim of this chapter was to provide a brief review regarding the use of proposed admixtures in this Ph.D. thesis. All of the discussed admixtures in this thesis were assessed in cementitious materials but not in cemented paste backfill. Since mining sectors are massive cement consumers, any investigation in this case is legitimate. Each of discussed admixtures/additives/fillers in this chapter has specific influence (not necessarily similar) on cementitious materials that we are going to discuss in upcoming chapters.

CHAPTER 3

EXPERIMENTAL INVESTIGATION ON MECHANICAL AND MICROSTRUCTURAL PROPERTIES OF CEMENTED PASTE BACKFILL CONTAINING MAPLE WOOD FILLERS

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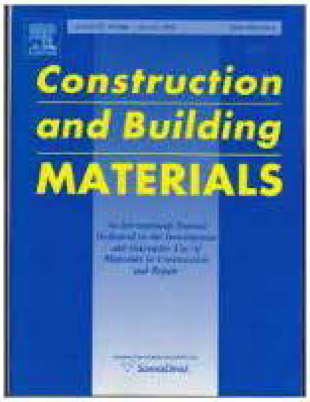

3.0 Foreword

This chapter presents an experimental investigation on the capability of wood fillers to be used as a reinforcement agent and or binder replacement in cemented paste backfill. This is linked with the binder cost reduction and early age strength development objectives of this Ph.D. thesis. In fact, wood fillers are inexpensive, broadly available, easy to process, and biodegradable materials, hence are a legitimate source of fillers in different applications. The main original aim of using wood fillers with CPB was to combine two different wastes from different industrial sectors for reciprocal benefit. Since wood industries produce a considerable amount of waste in different forms, it would be beneficial to find some new storage places or usage for such wastes. Wood fillers are used in the mining industry for mine water treatment and in cementitious materials as a filler, but they have never been used in cemented paste backfill. Wood fillers have the capability to absorb a considerable amount of water in comparison to their original mass and since the amount of water in CPB is high, it is assumed that the use of wood fillers may improve the hardening process by absorbing part of water within the CPB. Thus, this chapter is going to examine and discuss all of the above-mentioned points. The lab work, sample preparation, data collection and interpretation all are performed by Babak Koohestani. Dr. Ahmed Koubaa mainly conducted this research especially in the case of wood filler characterization. Dr. Tikou Belem proposed different formulations based on the wood filler addition in CPB and controlled the data. Dr. Bruno Bussiere made some comments and suggestions.

3.0 Résumé

Cette étude expérimentale examine l'influence de l'ajout de sciures de bois d'érable sur les propriétés mécaniques et la microstructure du remblai en pâte cimenté (RPC). Les propriétés mécaniques de RPC sont déterminées par les tests de résistance à la compression uniaxiale (UCS) et les changements de la microstructure sont évalués par la porosimétrie par intrusion de mercure (PIM) et l'analyse par la microscopie électronique à balayage (MEB). Les résultats obtenus à partir de cette étude ont indiqué le rôle positif de l'ajout de 12,5% de sciures de bois d'érable (en % massique de liant) sur le développement de la résistance des RPCs à des âges d'hydratation compris entre 14 et 91 jours. Cependant, lorsque la quantité de sciures de bois d'érable a été augmentée à 14,5%, l'amélioration de la résistance a diminuée. Les analyses PIM et MEB ont également montré que l'addition de charges de sciures de bois a rendu le RPC moins poreux et plus compacte, en augmentant la quantité de minéraux formés à partir de l'hydratation du liant. Le rôle positif des sciures de bois d'érable sur le RPC a été principalement associé avec les proportions plus élevées de liant (≥ 5%) et à moyen-terme et long terme (≥ 56 jours).

Mots-clés: Résidus miniers; Renforts de sciures de bois d'érable; Agent liant; Remblai en pâte cimenté; Résistance en compression uniaxiale; Porosité; MEB.

3.0 Abstract

This experimental study investigates the influence of maple-wood sawdust addition on the mechanical and microstructural properties of cemented paste backfill (CPB). Mechanical properties of CPB were determined by uniaxial compressive strength (UCS) tests and microstructural changes were evaluated by mercury intrusion porosimetry (MIP) and scanning electron microscopy (SEM) analysis. Results indicate that the addition of 12.5% maple-wood sawdust (by dry mass of binder) improves the strength development of CPB specimens at later hydration age (91 curing days). However, at a higher maple-wood sawdust content of 14.5%, the UCS showed lower improvement. Moreover, MIP and SEM analysis results revealed that the 12.5% wood filler addition made the CPB material less porous and more compact by increasing the mineral content formed by cement hydration. The positive influence of maple-wood sawdust on CPB was associated with higher binder content (≥ 5%) and mid- to long-term curing times (≥ 56 days).

Keywords: Mine tailings; Maple wood sawdust; Binder; Cemented paste backfill; Compressive strength; MIP; Porosity; SEM.

3.1 Introduction

The use of cemented paste backfill (CPB) is an innovative mine tailings management method that can reduce the tailings stream from surface storage to extracted underground mine stopes by up to 50%. Furthermore, CPB can also be used as secondary ground support (Benzaazoua et al., 2004; Koohestani et al., 2013). CPB is made of mill tailings (68–77%) generated by the mineral processing plant, water (15–30%), and a binding agent (2–8%) such as Portland cement or blends of cement and mineral additives such as lime, pulverized fly ash, ground granulated blast furnace slag, or silica fume (Benzaazoua et al., 2004; Coussy et al., 2011). The binding agent provides the CPB with undrained cohesive strength, which is commonly evaluated by the uniaxial compressive strength (UCS ~ 0.2 to 4 MPa) (Belem and Benzaazoua, 2008; Yilmaz et al., 2009, 2011). The prepared CPB mixture should have appropriate flowability for delivery to mine stopes, either by gravity or pumping. Generally, a slump height equal to or greater than 180 mm (≥ 7 inches) provides adequate fluidity (Clark et al., 1995). In this case, the available water content in the CPB largely exceeds what is required for binder (e.g., Portland cement) hydration (water-to-binder ratio ≥ 3) (Belem and Benzaazoua, 2008; Belem et al., 2010; Yin et al., 2012; Yılmaz et al., 2014).

Wood fillers usually consist of cellulose (40–50%), hemicellulose (15–25%), lignin (15–30%), pectin, and waxes (Vaickelionis and Vaickelioniene, 2006; Kumar et al., 2009; Cristaldi et al., 2010). They are generally obtained from two sources: residues from round wood (debarked wood, logging residues after thinning) and from industrial wood (sawdust, shavings, offcuts, and slabs) (Mahin, 1991; Xu et al., 2008). Whereas cellulose is insoluble in water, organic solvents, and alkaline solutions, hemicellulose is soluble in alkaline condition, and even in water. Lignin, the most complex naturally occurring polymer, remains stable under the influence of various organic solvents, alkaline solutions, and water. Extractives, on the other hand, are the non-polymeric components of wood that are dissolvable in organic solvents and water (Horvath, 2006; Vaickelionis and Vaickelioniene, 2006; Kumar et al., 2009). It has been reported that sugar concentrations (originating from hemicellulose), even at low amounts (0.03–0.15 wt.%), retard the initial setting time and strength of cementitious materials (Janusa et al., 2000). In fact, tricalcium aluminate (C_3A), being the fastest reacting cement component, is responsible for the initial setting time of hydration, but the presence of organic compounds alters the C_3A reaction. In addition, extractives contained in wood fillers may be adsorbed on the calcium hydroxide nuclei, thereby retarding the hydration of tricalcium silicate (C_3S) (Young, 1972; Bentz et al., 1994). In cement-based materials, wood fillers act through different mechanisms, including chemical interaction with hydration processes, adsorption on cement particle surfaces, alteration of the surface tension of water (affecting the rheology of the mixture), and addition of specific chemicals to the mixture (Govin et al., 2006; Hein et al., 2009; Tonoli et al., 2009; Koohestani et al., 2013). The main advantages of wood filler addition to cementitious materials and composites are that they are inexpensive, abundant, environmentally friendly, and easy to process (Sudin and Swamy, 2006; Taj et al., 2007). In addition, they reduce the setting time of cement hydration (Savastano Jr et al., 2000; Sedan et al., 2008) and improve the mechanical properties, including flexural strength, toughness, impact resistance (Wolfe and Gjinolli, 1996; Soroushian et al., 2012), and compressive and tensile strength (Gong et al., 2004; Poornima and Sivaraja, 2012). However, they come with certain disadvantages, including low modulus of elasticity, deterioration and mineralization in alkaline conditions (Sobral, 2004; Sudin and Swamy, 2006; Ardanuy et al., 2011), dimensional instability, high variability of physical and mechanical properties (Yu et al., 2006; Cristaldi et al., 2010), and inconsistent reinforcement (Wambua et al., 2003). Although some authors have proposed various treatments for natural and wood fillers to reduce potential problems within cementitious materials (Ghavami, 1995; Bilba et al., 2003, Toledo Filho et al., 2003;

Bilba and Arsene, 2008), these treatments are not feasible for paste backfill due to the additional waste management cost. Furthermore, the incompatibility of some wood species with cementitious materials means that the compatibility of each wood species must be assessed individually (Karade, 2010).

In cement-based materials, the use of blended binders (e.g., a blend of general use Portland cement – GU and ground granulated blast furnace slag – GBFS) can reduce the potential negative influence of wood filler. The effectiveness of slag cement binder in cementitious materials, especially at later hydration ages, has been reported in several studies (Belem et al., 2000; Benzaazoua et al., 2002; Benzaazoua, Fall et al., 2004; Belem and Benzaazoua, 2008). In addition, the use of slag in cementitious materials containing wood filler can prevent the retarding influence of sugars (from hemicellulose) and extractives. In fact, because slag has a higher specific surface area compared to that of cement (Li and Zhao, 2003; Toutanji et al., 2004), it adsorbs primarily the extractives and water-soluble sugars released from the wood filler (Vaickelionis and Vaickelioniene, 2006). Furthermore, the combination of Portland cement and slag can decrease the pore size distribution in CPB specimens (Belem et al., 2001; Ouellet et al., 2007, Kermani et al., 2011).

To our knowledge, no studies to date have addressed the influence of wood fillers on the properties of CPB, hence the motivation for this study. Because CPB has substantial water content, and because wood fillers can absorb large amounts of water (compared to their initial weight) (Bouguerra et al., 1999; Espert et al., 2004), the authors believe that wood filler addition to CPB materials can improve the hydration process by reducing the water-to-binder ratio. In addition, water drainage due to self-weight consolidation in CPB-filled stopes can be reduced by wood filler addition (Yilmaz et al., 2015). However, it should be mentioned that the addition of powdered wood filler would increase the water absorption and decrease the water uptake time (Horisawa et al., 1999; Koohestani et al., 2013). Moreover, when the shape and size of wood filler grains are similar to those of the tailings grains, the wood filler dispersion within the CPB matrix would be more homogeneous. Consequently, when the CPB is under load, forces could be transferred throughout the material more uniformly (Ashori, 2008). Therefore, powdered wood fillers (sawdust) were used in this study. The influence of wood fillers on different properties of CPB are assessed and discussed in terms of UCS, slump height, mercury intrusion porosimetry (MIP), and scanning electron microscopy (SEM) results.

3.2 Materials and methods

3.2.1 Mine tailings and maple-wood sawdust

The Casa Berardi mine (Hecla Mining Company gold mine), located in the Northwest region of Québec (Canada), provided all the tailings for this study. Tailings were collected from the ore processing plant and stored in barrels. After transfer to the lab, the tailings barrels were homogenized. Different tailings samples were then taken for X-ray diffractometry (XRD) analysis (mineralogy), grain size distribution determination, and inductively coupled plasma-atomic emission spectrometer (ICP-AES) analysis (chemical composition), as explained elsewhere (Deschamps et al., 2008, Coussy et al., 2011). The specific gravity of tailings G_s was determined to be 2.715 using a helium pycnometer (AccuPyc 1330, Micrometrics). Fig. 3.1 shows the grain size distribution and Table 3.1 presents the chemical and mineralogical compositions (ICP-AES and XRD analyses) of the mine tailings.

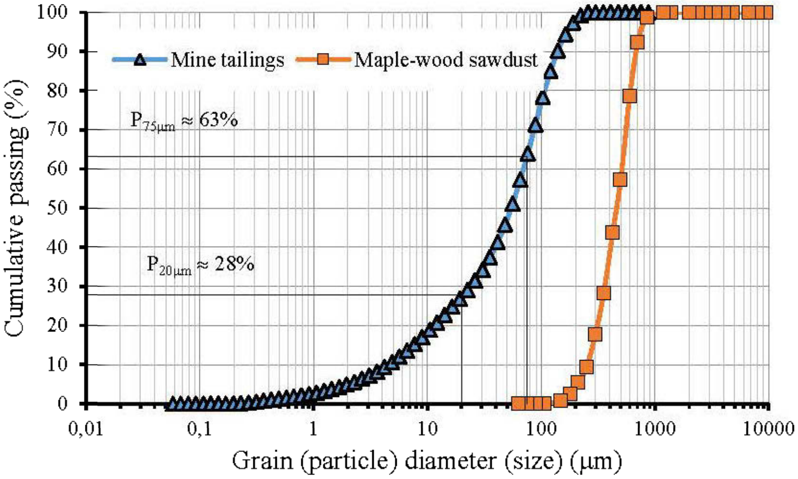

Figure 3.1- Cumulative grain and particle size distribution curves for the Casa Berardi mine tailings and maple-wood sawdust (fillers)

Table 3.1- ICP-AES analysis and XRD quantification of Casa Berardi mine tailings

ICP-AES analysis (%)		XRD quantification (%)	
Element	Tailings	Minerals	Tailings
Al	1.7	Quartz	86.6
As	0.21	Muscovite	4.49
Ca	0.75	Albite	5.41
Fe	1.8	Pyrite	1.04
K	0.56	Ankerite	2.46
Na	0.34		
S	0.84		

Maple is a hardwood species. The maple-wood sawdust used in this study was purchased from P.W.I. Industries. The average specific gravity of the cell walls of wood filler made from maple wood is approximately 1.5 (Ding et al., 2008), with a specific surface area of 1.1 m^2/g. The particle size distribution of maple-wood sawdust is shown in Fig. 3.1. The chemical and elemental compositions of maple-wood sawdust are presented in Table 3.2 and Table 3.3 (Rowell, 2012).

Table 3.2- Chemical composition of maple wood sawdust (Rowell, 2012)

Cellulose (%)	Lignin (%)	Pectin (%)	Ash (%)	Hemicellulose (%)	Methoxyl (%)	Acetyl (%)
42-47	23.3	1.9	0.2-0.5	30.4	7.25	3.2-3.8

Table 3.3- Main elemental composition of maple wood sawdust (Rowell, 2012)

Ca (ppt)	K (ppt)	Mg (ppt)	P (ppt)	Mn (ppt)	Fe (ppm)	Cu (ppm)	Zn (ppm)	Na (ppm)	Cl (ppm)
0.8	0.7	0.12	0.03	0.07	11	5	29	5	18

The addition of 12% natural filler (by dry mass of cement) has been proposed in different studies as an effective amount to improve various properties of cementitious materials (Savastano Jr et al., 2000). Hence, in this study, 12.5% and 14.5% maple-wood sawdust filler in CPB (by dry mass of binder) are examined.

3.2.2 Binder types and mixing water

As mentioned above, the use of a blended binder is preferable in cementitious materials containing wood filler. Hence, a binder consisting of a blend of 20% general use Portland cement (GU) and 80% ground granulated blast furnace slag (Slag) was prepared for use in this study (GU/Slag@20/80). The mineralogical composition and the relevant physical properties of the binder (GU and Slag) are presented in Tables 3.4 and 3.5. The effective grain size (D_{10}) and the mean grain size (D_{50}) of the GU and Slag are presented in Table 3.5. Potable municipal water (tap water) was used to prepare all mixtures.

Table 3.4- Mineralogical compositions of cement and slag (%)

Minerals	Portland cement	Slag
SiO_2	20.25	33.8
Al_2O_3	5.04	13.4
Fe_2O_3	3.16	1.8
CaO	63.61	41.7
MgO	4.56	7.4

Table 3.5- Physical characterizations of used binders

Binder	Specific gravity	Specific surface (m^2/g)	Particle size distribution	
			D_{10}	D_{50}
Portland cement	3.14	1.1	0.6	14.11
Slag	2.9	2.75	0.54	7.25

3.2.3 Preparation of cemented paste backfill

To prepare the CPB specimens, three different binder contents (B_W = mass of binder/mass of dry tailings) of 2, 4.5, and 7% were tested with three formulations: a control CPB (without wood filler) and CPB containing 12.5% and 14.5% maple-wood sawdust by dry mass of binder (CWF specimens). Table 3.6 presents the mix proportioning for all prepared CPB specimens. CPB specimens were prepared by adding the prepared binder–wood filler mixture to the tailings in a Hobart mixer while tap water was slowly added to obtain a target slump height of ~180 mm (7 inches). A total of nine mixtures and 108 triplicate specimens were prepared and poured into cylindrical plastic moulds of 50.8 mm diameter and 101.6 mm height (2 inches diameter and 4 inches height), capped, and left in a humidity chamber at 23 °C and ≥ 90% relative humidity for four curing times (14, 28, 56, and 91 days).

Table 3.6- CPB mixture formulations and characteristics

Formulation	Binder content (%)	Wood filler content (%)	Curing time (day)	Slump (mm)
Control	2, 4.5, 7	0	14, 28, 56, 91	~180
*CWF-12.5	2, 4.5, 7	12.5	14, 28, 56, 91	~180
CWF-14.5	2, 4.5, 7	14.5	14, 28, 56, 91	~180

*CWF: Containing wood fibres

3.2.4 Experimental methods

The consistency of the CPB mixtures was determined by slump height measurement using a standard slump cone. To determine the influence of maple-wood sawdust on

CPB consistency, a control mixture (without wood filler) was prepared at approximately 180 mm slump height, corresponding to 74.1% solid mass concentration. Then, two new distinctive CPB mixtures containing 12.5% and 14.5% wood filler contents were prepared, and slump height of each was again measured (Table 6).

Uniaxial compressive strength (UCS) is a frequently used strength index to evaluate the strength performance of CPB (Belem and Benzaazoua, 2008; Yilmaz et al., 2011; Yılmaz et al., 2014). Compressive strength measurements were performed according to ASTM D 2166-91 using a computer-controlled mechanical press (MTS 10/GL) having a normal loading capacity of 50 kN, with tests performed at a displacement rate of 1 mm/min. The shape factor (height-to-diameter ratio) of CPB specimens was 2. After each curing time, UCS was determined for three specimens (triplicate) and only the average value was considered.

Mercury intrusion porosimetry (MIP) is a widely used method for microstructural analysis of cementitious materials (Cook and Hover, 1993). However, this method has certain limitations that should be considered (Diamond, 2000). In this study, MIP was used to assess the impact of wood fillers on the microstructure of hardened CPBs, including pore size and volume. It is generally agreed that material strength is a function of shape, void volume fraction, and void distribution (O'Farrell et al., 2001), which are related to binder hydration and hydration product (minerals) formation (e.g., calcium silicate hydrate or C-S-H). Hence, binder content and curing time are the two main influential factors on the total porosity and porous network of cement-based materials (Aligizaki, 2005; Alonso et al., 2012). The influence of hydration on minerals formation in paste backfill is discussed elsewhere (Belem et al., 2001). In the present study, an Autopore III 9420 series porosimeter (Micrometrics) was used for MIP analysis. This apparatus generates a maximum pressure of 414 MPa and can measure mesopores as small as 0.003 µm in diameter.

Prior to MIP testing, CPB samples were oven-dried and then cut into small pellets of approximately 10 mm diameter. Sample preparation and MIP testing are described in detail elsewhere (Ouellet et al., 2007).

Scanning electron microscopy (SEM) analysis was used to observe the influence of maple-wood filler on microstructural changes in the CPB specimens. SEM also allows direct observation of the interface between the wood filler and CPB matrix. The SEM observations were performed using a Hitachi S3500-N scanning electron microscope with an accelerating voltage of 20 keV and a current emission of approximately 110 μA. Oven-dried specimens were cut and initially left untouched. They were subsequently carbon-coated for SEM observation. SEM observations were performed on the control specimen and CWF specimen containing 12.5% wood filler (CWF-12.5) and 7% binder content after 91 days curing time. The SEM analysis procedure is explained elsewhere (Belem et al., 2001; Deschamps et al., 2008).

3.3 Results and discussion

3.3.1 Compression test results

Uniaxial compression tests were performed on the specimens at 14, 28, 56, and 91 curing days. Fig. 3.2 shows the variation in UCS as a function of binder content for the control specimens and the specimens containing 12.5% and 14.5% wood filler (CWF-12.5 and CWF-14.5). Figs. 3.2a-3.2d show that the addition of 2% GU/Slag binder (with or without wood filler) resulted in UCS values ranging from 250 to 500 kPa for a curing period of 14 to 91 days only, whereas the addition of 4.5% binder content produced noticeable differences in UCS values.

After 14 curing days (Fig. 3.2a), increasing the binder content from 2% to 4.5% did not significantly improve the UCS for specimens containing wood filler compared to control specimens. However, when the binder content was increased to 7%, the UCS values for the CWF-12.5 specimens improved by 12% over the UCS for control specimens, as did the UCS values for the CWF-14.5 specimens. Notably, at 14 curing days, the UCS improvement rate for control specimens was more progressive when the binder content was increased from 2% to 4.5%. However, when the binder content was increased from 2% to 7%, the UCS improvement rate changed more or less linearly for the specimens containing wood filler. After 28 days (Fig. 3.2b), the control specimens with 4.5% binder content continued to show higher UCS values, but when the binder content was increased to 7%, UCS values for all specimens were more or less similar. The strength improvement rate for the specimens containing wood filler improved after 56 curing days (Fig. 3.2c). The UCS values for the specimens containing 4.5% binder were almost similar, but the increase in binder content to 7% improved the UCS values up to 9% for the CWF-12.5 specimens. After 91 curing days (Fig. 3.2d), the UCS values for both of the specimens containing 12.5% and 14.5% wood filler with 4.5% and 7% binder content, were higher than those for the control specimens (17% improvement was achieved for CWF-12.5 with 4.5% binder content).

The UCS results indicate that the addition of maple-wood sawdust improved the compressive strength of CPB by less than 20% in the best case. The addition of 12.5% maple-wood filler was more effective for UCS development (compared to 14.5% wood filler content), especially after 56 curing days. Table 3.7 presents the percentage of UCS improvement for the CWF-12.5 and CWF-14.5 specimens at 56 and 91 curing days compared to control specimens.

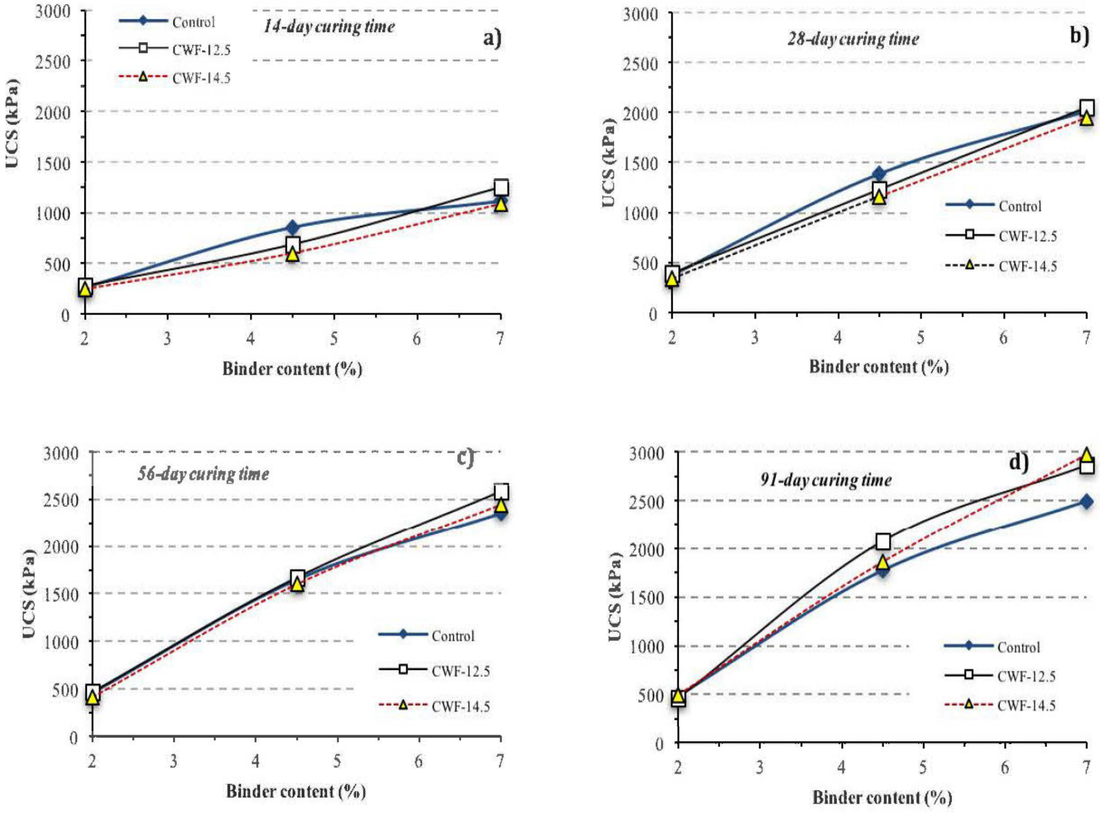

Figure 3.2- UCS variations as a function of binder/wood filler contents and curing time

Table 3.7- Percentage of UCS improvement for CPB specimens

CPB mixture formulation	Maple sawdust content	UCS improvement (%) of CPBs compared to control sample			
		56-day curing time		91-day curing time	
		4.5% binder	7% binder	4.5% binder	7% binder
CWF-12.5	12.5%	~0%	10%	17%	15%
CWF-14.5	14.5%	~0%	4%	5%	19%

It can be concluded from the UCS data that the addition of wood filler retarded the binder hydration and reduced the early strength development of CPBs (Fig. 3.2a and Fig. 3.2b) consequent to extractive release from the wood fillers (Boustingorry et al., 2005). It is known that the high specific surface area of wood fillers (BET specific surface area of 1100 m^2/kg) makes them highly reactive in cementitious materials, resulting in rapid release of extractives after contact with water. Therefore, the positive influence of wood filler on the mechanical strength development of CPB occurred only after the extractives were released from the sawdust.

For each CPB formulation and for each curing time, three standard deviations of UCS (in kPa) values were calculated for the three binder contents used:

- *For control specimens*: ±20–110 (14-day); ±6–53 (28-day); ±12–58 (56-day); ±13–124 (91-day).
- *For CWF-12.5 formulations*: ±14–37 (14-day); ±23–92 (28-day); ±28–159 (56-day); ±68–172 (91-day).
- *For CWF-14.5 formulations*: ±17–25 (14-day); ±13–39 (28-day); ±16–48 (56-day); ±6–104 (91-day).

3.3.2 MIP test results

Table 3.8 presents the quantitative results of the MIP analysis and Fig. 3.3 shows the changes in pore size as a function of intrusion volume for the control, CWF-12.5, and CWF-14.5 specimens with 2, 4.5, and 7% binder content at 91 curing days. As shown in Fig. 3.3, when the binder content was increased from 2% to 7%, the average pore diameter (d_{av}) for all specimens decreased, indicating the dependency of pore size on binder content (Ouellet et al., 2007). The influence of maple-wood sawdust on average pore size change is not evident in the specimens containing 2% and 4.5% binder (Figs. 3.3a, 3.3b), whereas it becomes apparent at 7% binder content (Fig. 3.3c). Figs. 3.3a to 3.3c and Table 3.8 indicate that d_{av} for the control specimens decreased from approximately 1.8 to 0.9 μm, whereas d_{av} for the CWF-12.5 and CWF-14.5 specimens decreased from 1.8 to 0.72 μm and from 2.02 to 0.59 μm, respectively. In addition, the increased binder content produced a new source of pores with average diameter less than 0.2 μm (Figs. 3.3a, 3.3b, 3.3c), due to the formation of additional binder hydration products (filling the larger pores and forming smaller pores). The total porosity of the specimens containing wood filler is approximately 5% less than that of the control specimens (Table 3.8).

Table 3.8- Quantitative results from MIP experiments

CPB mixtures formulation	Binder content (%)	Wood filler content (%)	Curing time (day)	Total MIP porosity (%)	Average pore diameter (μm)	Volume of pores (mL/g)
Control	2, 4.5, 7	0	91	39.7-39.9	0.9-1.8	0.029-0.038
CWF-12.5	2, 4.5, 7	12.5	91	33.8-34.8	0.72-1.8	0.029-0.046
CWF-14.5	2, 4.5, 7	14.5	91	34.8-37.1	0.59-2.02	0.022-0.041

It is noteworthy that sawdust is a porous material, with porosity that can exceed 80% (Horisawa et al., 1999). However, the porosity of the wood particles was not considered in the MIP assessment due to the small amounts added (>1% of the total solid concentration).

The total porosity of the CPB specimens containing wood filler is lower than that of the control specimens at later hydration ages (Fig. 3.3, Table 3.8), a result that is in a good agreement with the UCS results. The MIP results also indicate that the pore size for CWF-14.5 specimens was smaller than that for CWF-12.5 specimens, but more importantly, total porosity was higher (Table 3.8). This difference is also in good agreement with the UCS results (higher UCS values for CWF-12.5 specimens). Therefore, it can be concluded that 12.5% wood filler addition is more effective in densifying the CPB structure compared to 14.5% wood filler addition.

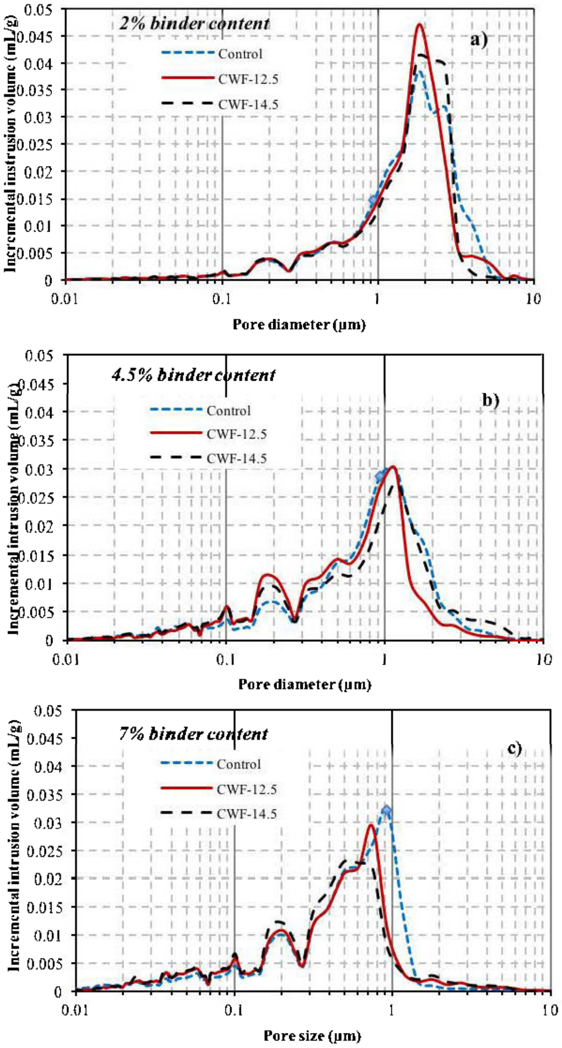

Figure 3.3-Pore size distribution of CPBs at 91 days with a) 2%, b) 4.5% and c) 7% binder content

3.3.3 SEM observations

The SEM micrographs of control and CWF-12.5 specimens are shown in Fig. 3.4. Figs. 3.4a and 3.4b respectively show tailings grains and a wood particle within the CPB matrix. Both the tailings grains and wood particle are well placed in the cementitious matrix and surrounded by the hydration products. Zooming in on Figs. 3.4a and 3.4b (from 100 µm to 20 µm), Figs. 3.4c and 3.4d provide more detailed views of the concentration of hydration products on the surface of a tailings grain and the wood particle, showing that the hydration products are not trapped on the smooth surface of the tailings (Fig. 3.4c), in contrast to the wood particle surface (Fig. 3.4d).

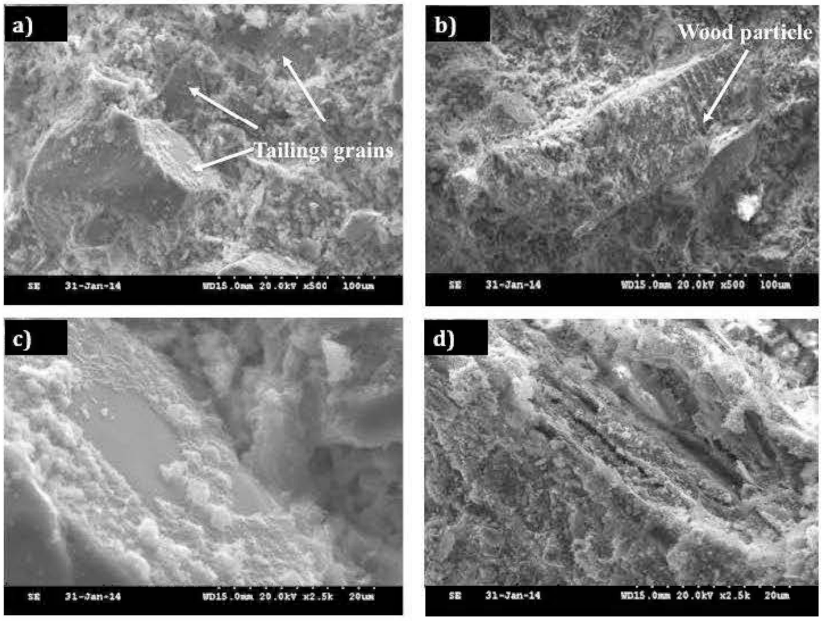

Figure 3.4-SEM micrographs of control sample (a, c) and CWF-12.5 (b, d)

Fig. 3.5 shows SEM micrographs revealing the concentration of calcium ions at the surface of a wood filler particle and a tailings grain within the CPB matrix. Fig. 3.5a and Fig. 3.5b show a tailings grain and the surface of a wood particle, respectively, and Fig. 3.5c and Fig. 3.5d show the distribution of calcium in Fig. 3.5a and Fig. 3.5b. The black area in Fig. 3.5c indicates that the calcium ions were unable to concentrate at the tailings surface (the tailings grain is unable to entrap the calcium). In contrast, the wood particle has entrapped the calcium ions at the surface (white spots in Fig. 3.5d). In fact, due to the high ability of pectins to entrap hydration products on the wood filler surface, new bonds are formed between the wood filler and the cementitious matrix. Furthermore, when calcium is trapped at the wood filler surface, the amount of silica in the pore solution increases due to the lower availability of calcium for reaction (Sedan et al., 2007, 2008). This could explain the UCS improvement observed in this study.

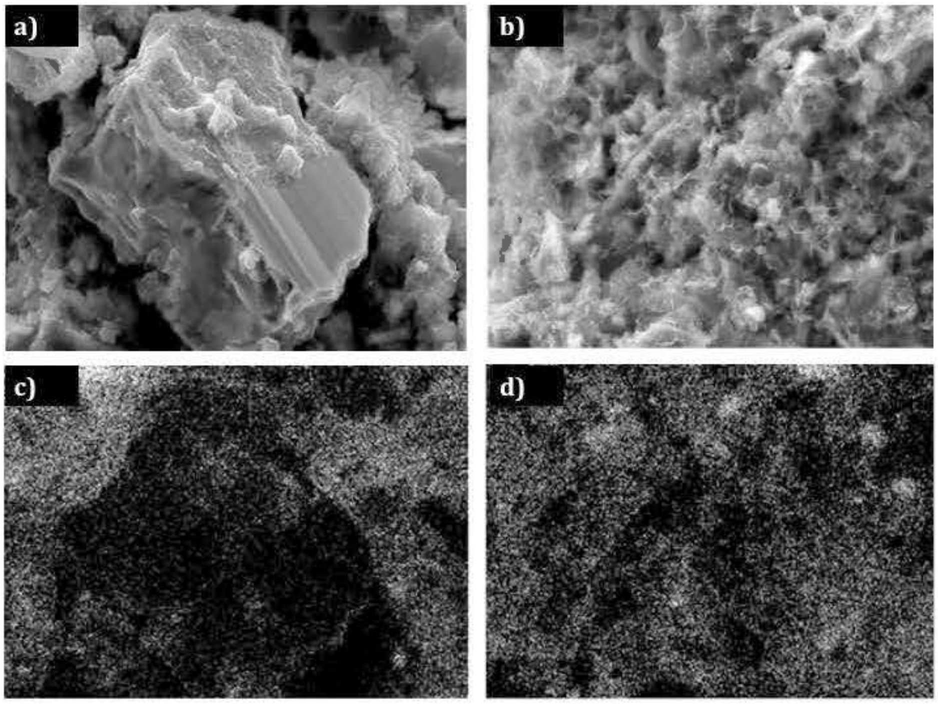

Figure 3.5- Micrographs of a) a grain of tailings in CPB b) a particle of wood in CPB, c) calcium distribution on Fig.a, and d) calcium distribution on Fig.b

Although the wood particles can bond mechanically (i.e., interlock) with the cementitious matrix, the amount of wood filler used in this study accounted for less than 1% of the total solid concentration. Hence, the mechanical bonding would not considerably improve the strength of the CPB. Moreover, interlocking is a low energy bonding mechanism compared to chemical bonding between the pectins and formed products of hydration, and would therefore have negligible (Frybort et al., 2008).

3.4 Conclusions

The main results of this study are summarized as follows:

- The addition of maple-wood sawdust did not negatively affect the consistency of CPB specimens (slump measurements in Table 3.6), which can be attributed to the amount and type of wood sawdust used. However, further studies are needed to determine the effects of different types and contents of wood filler on the consistency of cementitious materials.
- The addition of wood filler negatively influenced the early strength development of CPB specimens: wood fillers were more effective in improving strength development at later hydration ages. Of the two maple-wood filler contents used in this study, 12.5% (based on binder mass) was more effective in improving CPB strength. However, further studies are needed to examine the influence of different types and contents of wood filler on CPB strength.
- The addition of wood filler decreased the total porosity of the CPBs in all cases, but did not improve the mechanical strength accordingly: because the wood fillers occupied a certain amount of space within the cementitious matrix, the total porosity was decreased.
- Because wood is a porous material, the estimated total porosity of the CPBs could have been affected by the addition of wood filler. However, the addition of small amounts of wood filler would have a negligible effect on the estimated total porosity of the CPBs.
- The influence of wood filler on hydration retardation was due to the release of extractives from the wood filler at early curing ages. The positive reinforcing influence of wood filler occurred only after the release of extractives, at later hydration ages.
- SEM micrographs revealed the ability of pectins to entrap calcium at the wood filler surface, resulting in the formation of new bonds and improved mechanical strength at later hydration ages.

CHAPTER 4

EXPERIMENTAL INVESTIGATION INTO THE COMPRESSIVE STRENGTH DEVELOPMENT OF CEMENTED PASTE BACKFILL CONTAINING NANO-SILICA

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4.0 Foreword

This chapter presents an experimental investigation on the capacity of nano-silica as an admixture to reduce the binder consumption and improve the early age strength development of cemented paste backfill. Here this is linked with the binder cost reduction and early age strength development objectives of this Ph.D. thesis. After discovering the incapability of wood fillers to improve the early age strength development of CPB in the chapter 3, colloidal nano-silica as a high-technology admixture was used in this chapter 4 to affect the strength development and binder consumption in CPB. It is assumed that nano-silica, as a high pozzolanic material, can accelerate the hydration process, thus the amount of binder usage can be reduced. It is attempted to reduce the binder consumption due to the acceleration influence of nano-silica by considering the highest strength gain of CPB in a short period (3 to 28 days). It is more important since most of the used mineral additives in CPB have the retardation influence (e.g., fly ash, slag, etc.) and the addition of nano-silica may compensate this retardation effect in the mixed binders. In this case, the backfilling process may be accomplished in one filling process (continuous filling) resulting in time and cost savings. However, using such high-technology admixtures in the mine site requires a precise financial assessment to be applicable in large-scale. The lab work, sample preparation, data collection and interpretation of this study all are performed and prepared by Babak Koohestani. Dr. Tikou Belem chiefly conducted this study by proposing different mixture preparation while controlling the necessary and pertinent data to enrich this work. Dr. Ahmed Koubaa and Bruno Bussiere made some suggestions and comments while they both controlled the accuracy of the collected data. All of the professors read this article in order to improve the consistency and accuracy.

4.0 Résumé

Cet article étudie l'influence de l'addition de nano-silice (NS) sur la consistance et le développement de la résistance à la compression du remblai en pâte cimenté (RPC). Le Tétraéthyle Orthosilicate (TEOS) a été utilisé comme le précurseur de nano-silice avec le super plastifiant polycarboxylate à base d'éther (PCS). Deux types de liants (ciment Portland et Slag-ciment) et différentes quantités de TEOS (0,7 - 14% en masse de liant) avec et sans PCS ont été évaluées pour 3, 7, 14, et 28 jours de temps de cure. Les tests de compression uniaxiale pour la détermination de la résistance à la compression uniaxiale (UCS), la mesure de l'affaissement, les variations de la teneur en eau gravimétrique, et l'analyse thermogravimétrique différentielle (DTG) ont été utilisés pour évaluer l'influence de NS et d'adjuvants (TEOS-PCS) sur les performances du RPC. Les résultats de cette étude expérimentale montrent que l'addition d'environ 5% de TEOS ainsi que 0,5% de PCS (en masse de liant) fournit les meilleures résistances à la compression qui pouvaient également être anticipées à travers une plus grande quantité de silicate de calcium hydratés (S-C-H) sur les courbes ATD/ATG. Il est également à noter que l'influence positive de NS est plus évidente lorsque la quantité de liant a été diminuée. L'addition de PCS au RPC contenant NS a amélioré à la fois la consistance du mélange et le développement de la résistance à la compression du RPC.

Mots-clés: Nano-silice; Tétraéthyle orthosilicate; Remblai en pâte cimenté; Superplastifiant; Polycarboxylate; Résistance à la compression uniaxiale; Agent liant.

4.0 Abstract

This paper investigates the influence of Nano-silica (NS) addition on the consistency and compressive strength development of cemented paste backfill (CPB). Tetraethyl-Orthosilicate (TEOS) was used as the precursor of Nano-silica along with ether-based Polycarboxylate superplasticizer (PCS). Two binder types (Portland cement and Slag-cement) and different amounts of TEOS (0.7-14% by mass of binder) with and without PCS are examined for 3, 7, 14, and 28 days curing time. Uniaxial compression tests for unconfined compressive strength (UCS) determination, slump height measurement, changes in gravimetric water content, and differential thermogravimetric analysis (DTG) are used to assess the influence of NS and admixtures (TEOS-PCS) on CPB performance. The results of this experimental study indicate that the addition of approximately 5% TEOS along with 0.5% PCS (by mass of binder) provide the best compressive strengths that can also be anticipated through the higher amount of calcium silicate hydrate (C-S-H) on DTG curves. It is also noticeable that the positive influence of NS is more evident when the amount of binder was decreased. The addition of PCS to CPB containing NS improved both the consistency of the mixture and the compressive strength development of CPB.

Keywords: Nano-Silica; Tetraethyl-Orthosilicate; Cemented paste backfill; Polycarboxylate superplasticizer; Compressive strength; Binding agent;

4.1 Introduction

Nowadays, use of nanoparticles in different applications interests many researchers due to the enhanced performance and sustainable features (Sobolev and Gutiérrez, 2005; Stefanidou and Papayianni, 2012). Even though different nanoparticles such as Nano-silica (NS), Nano-titanium, carbon nanotubes, and Nano-alumina exist, use of Nano-silica has reportedly been more extensive in cementitious materials (Sobolev et al., 2009; Choolaei et al., 2012; Pourjavadi et al., 2012; Hou et al., 2013; Singh et al., 2013; Zapata et al., 2013).

As a highly pure pozzolanic material with high specific surface, NS affects the cementitious materials by accelerating the hydration and pore volume filling (Hou et al., 2013; Singh et al., 2013) and reaches the maximum pozzolanic effect after three days of curing (Abd El Aleem et al., 2014). Because of pozzolanic effect and due to the molecular reactivity with hydroxides, NS reacts with calcium hydroxide (CH) crystals to form calcium silicate hydrate (C-S-H) gel; hence, the amount of CH crystals reduces at early ages of hydration (Ji, 2005; Qing et al., 2006; Qing et al., 2007; Tobón et al., 2012). The effectiveness of NS to react with calcium hydroxide is due to its molecular reactivity with hydroxide groups (OH) on the surface of cement or other hydroxide minerals produced from cement hydration (Vieira et al., 2004). By filling the Nano-pores of C-S-H and gaps between the aggregates and cement particles, NS improves the solidification and compactness (Ji, 2005; Kong et al., 2013) while it also decreases the water bleeding and segregation of cementitious materials by improving the cohesiveness at early ages (Senff et al., 2009; Flores-Vivian et al., 2013). However, nanoparticles are extremely susceptible to agglomeration, which is resulting in weaknesses of cementitious materials. Thus, use of any complementary materials (admixtures) such as superplasticizer improves the dispersion of nanoparticles in cementitious materials (Ji, 2005; Senff et al., 2009; Sobolev et al., 2009; Senff et al., 2010; Berra et al., 2012; Kong et al., 2012; Flores-

Vivian et al., 2013; Heikal et al., 2013; Hou et al., 2013; Kong et al., 2013). Superplasticizer adsorbs to the cement particles and releases the trapped water by causing electrostatic-electrostatic/repulsive forces (such forces are generally ascribed to van der Waals forces). This phenomenon improves the workability of the mixture while facilitating the dispersion of nanoparticles through the mixture as well (Zapata et al., 2013).

Tetraethyl-Orthosilicate (TEOS) and Tetramethyl-Orthosilicate (TMOS) are the mostly used precursors for producing Nano-silica in cementitious materials (Sobolev et al., 2006). Growth of nanoparticles by using such precursors basically occurs through the sol-gel process in which a precursor solution (sol) hydrolyzes and converts into an inorganic solid (silica gel) *via* inorganic polymerization (condensation) (Gill and Ballesteros, 2000). Chemical reaction that produce Nano-silica (silica gel) from TEOS precursor is illustrated in Fig. 4.1 (Battersby et al., 2002).

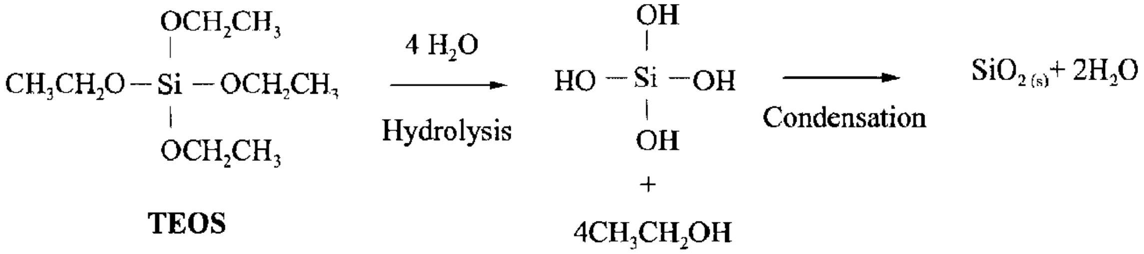

Figure 4.1- Chemical reaction scheme of Tetraethyl-Orthosilicate (TEOS)

As an innovative mine tailings management technology, cemented paste backfill (CPB) can return up to 50% of the total produced tailings stream to underground mine stopes. Tailings are generated from mineral processing plant after the recovery of valuable parts of minerals such as metals. The aim of backfilling is to act as a secondary ground support while minimizing the environmental impact by reducing the amount of waste storage from the surface (Benzaazoua et al., 2004; Coussy et al., 2011;, Koohestani et al., 2013). CPB consists of dewatered mill tailings (72 – 85 wt% solid content and corresponding water content of 38-18%), and a binding agent such as Portland cement or a combination of cement and pozzolanic materials (2–10 wt% by dry mass of tailings) (Benzaazoua et al., 2004; Coussy et al., 2011; Koohestani et al., 2013). Depending on the type of binding agent, mineralogy of the tailings and curing time, unconfined compressive strength (UCS) of CPB varies between 0.2 and 4 MPa (Belem and Benzaazoua, 2008; Yilmaz et al., 2011; Yılmaz et al., 2014). It has been shown that any increase in the amount of binder in CPB, elevates the UCS values almost linearly (Belem and Benzaazoua, 2008). In addition, the self-weight consolidation of CPB because of water drainage and/or bleeding (in backfilled stope) can increase or improve the UCS value. Since CPB is delivered from the surface of a mine to the underground stopes (by gravity or pumping), it should have a proper fluidity/consistency (estimated through slump height measurement using Abrams cone) (Belem et al., 2010). In order to reach the targeted fluidity for CPB's pipeline transport, additional water is often added to the mixture, hence the availability of water become very high (water/binder ≥ 3), which is not ideal for hardening.

To our knowledge, there is no published data regarding the influence of produced NS from TEOS on the properties of cemented paste backfill. Thus, this study attempts to highlight the benefits of NS as a pozzolanic material, especially when mixed with superplasticizer. The authors strongly believe this combination can solve multiple problems in the case of paste backfill. Indeed, Nano-silica can improve the compressive strength of CPB, specifically at early ages of hydration while the addition of superplasticizer can also reduce the water consumption of this material. Hardening and strength development of CPB at early ages of curing can allow continuous backfilling and hence a possible reduction in binder consumption. Consequently, this can reduce the backfilling operating costs of a mine where the filling process is carried out in two different stages (a plug fill and a residual fill). A plug-fill of few meters' height (containing more than 5% binder) is first poured into the open stope followed by the residual fill pouring (containing less than 5% binder). Most of the time the plug-fill is left at rest between 2 and 5 days prior to the residual filling in order to avoid excess pressure on the barricade (backfill retaining structure); this fact emphasizes the importance CPB's early strength development. The backfilling procedure accounts for 10-20% of the total operating cost of a mine from which the binder cost represents up to 75-80% of that cost (Grice, 1998) while the binder cost is approximately $ 1.40/wt% binder/metric ton of CPB (Belem. et al., 2013).

In this study, the influence of Nano-silica (NS) and Polycarboxylate superplasticizer (PCS) was assessed through the compressive strength development and slump height changes. Differential thermogravimetric analysis (DTG) is also performed to understand the effect of admixtures on the evolution of binder hydration products (such as calcium hydroxide CH and calcium silicate hydrate C-S-H) (Ji, 2005; Gaitero et al., 2008; Tobón et al., 2012) because DTG analysis is a valid method for observing CH and C-S-H phase changes (Vieira et al., 2004; Pane and Hansen, 2005; Qing et al., 2006).

4.2 Materials and methods

4.2.1 Tailings characteristics

Tailings used in this study were sampled from the Casa Berardi Mine (CBM, Hecla Mining Company, a gold mine) located in North-West Quebec (Canada). Fig. 4.2 presents the cumulative grain size distribution curve determined using a Malvern® Mastersizer S2000 laser particle size analyzer. From this figure, the fine ($d < 75$ µm) grains content ($P_{75\mu m}$) of the tailings is about 90% while the ultra-fine ($d < 20$ µm) grains content ($P_{20\mu m}$) is about 60% and making these tailings a fine size class tailings

(Landriault et al., 1995). The mineralogy of the CBM tailings was determined by X-Ray diffraction (XRD) analysis using Bruker AXS Advance D8 diffractometer. The chemical composition of CBM tailings was analyzed by spectroscopy using Perkin-Elmer ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectroscopy) Optima 3000 DV. Table 4.1 summarizes the results of analysis. The procedure of tailings preparation, XRD and ICP-AES analyses are explained elsewhere (Deschamps et al., 2008; Coussy et al., 2011). Specific gravity G_s of CBM tailings was determined to be 2.715 using helium pycnometer (AccuPyc 1330 from Micrometrics®) in accordance with ASTM C128 standard.

Table 4.1- Chemical and mineralogical compositions of Casa Berardi mine tailings

Chemical composition (ICP-AES)		Mineralogy (XRD quantification)	
Element	wt%	Mineral	wt%
Al	1.7	Quartz	86.6
As	0.21	Muscovite	4.49
Ca	0.75	Albite	5.41
Fe	1.8	Pyrite	1.04
K	0.56	Ankerite	2.46
Na	0.34		
S	0.84		

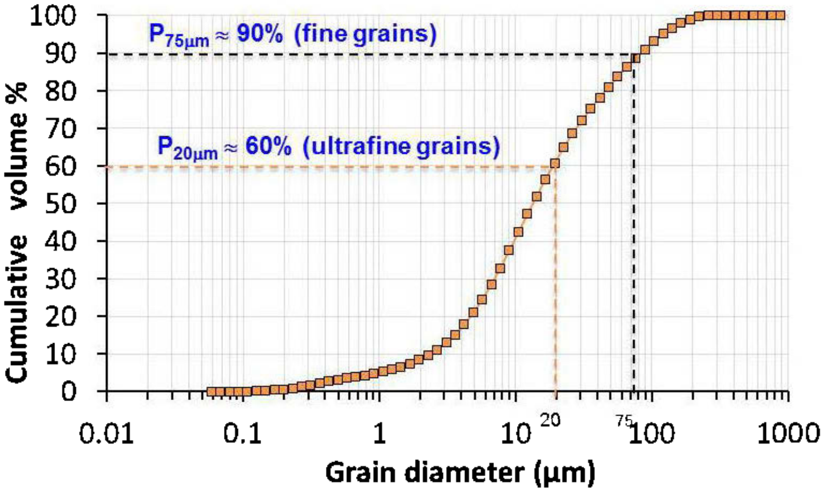

Figure 4.2- Cumulative grain size distribution curve of Casa Berardi Mine (CBM) tailings

4.2.2 Admixtures

Two types of admixture were used in this study including Tetraethyl-Orthosilicate (TEOS), as the precursor for the production of Nano-silica, and Polycarboxylate ether-based superplasticizer (PCS). Since TEOS is in the form of colloid, it may also improve the dispersion of nanoparticles in CPB (Thomas et al., 2009). TEOS was purchased from Dow Corning Inc. under the trade name XIAMETER® OFS-6697 silane. The specifications of TEOS are presented in Table 4.2. PCS in this study was purchased from BASF Inc. under the trade name PS-1466; its specifications are presented in Table 4.3.

Table 4.2- Tetraethyl-Orthosilicate (TEOS) properties

Active ingredient (%)	Chloride content (ppm)	Specific gravity (-)	SiO_2 content (%)	Kinematic viscosity (mm^2/S)
>99	<10	0.93	28.7	0.72

Table 4.3-Polycarboxylate superplasticizer (PCS) properties

Density (gr/cm^3)	pH	Color	Chemical base
1.104 – 1.116	5.7 – 6.5	Brown	Polycarboxylate condensate

4.2.3 Types of binding agents and mixing water

Two types of binder including general use Portland cement (GU) and a blend of 20% GU and 80% ground granulated blast furnace Slag (GU/Slag@20/80) were used in this study. The main oxide composition of the binders used is given in Table 4.4. These binding agents were provided by Lafarge North America Inc. In addition, potable municipal water (tap water) was used for the mixtures preparation.

Table 4.4- Mineralogical compositions of the binder types used

Oxide	Cement GU (wt%)	Slag (wt%)	20%GU/80%Slag (wt%)
SiO_2	20.25	33.8	31.1
Al_2O_3	5.04	13.4	11.7
Fe_2O_3	3.16	1.8	2.1
CaO	63.61	41.7	46.1
MgO	4.56	7.4	6.8

4.2.4 Paste backfill mixture preparation

The preparation of the paste backfill mixtures was accomplished in two stages (phase I and phase II). The aim of phase I is to find the most effective amount of TEOS that develops the highest UCS value. In addition, the influence of PCS on the chosen amount of TEOS is also investigated in phase I. In phase II the efficient amount of TEOS from phase I along with the PCS were examined while the type and amount of binder were varied. The aim of phase II is to understand the influence of TEOS/PCS combination on different types and amounts of used binder.

For the phase I of the experiment, 0.7 to 14% of TEOS (by the mass of binder) were added to CPB mixtures containing a fixed 4.5% (by dry mass of tailings) of GU/Slag@20/80 binder in order to determine which amount of TEOS can develop the highest UCS value. Thus, 7 formulations and 84 triplicate samples were prepared (Table 4.5) and poured into the cylindrical plastic molds (50.8 mm diameter and 101.6 mm height) then sealed and left in a humidity chamber for four curing times (3, 7, 14 and 28 days) at 23°C and 90% relative humidity.

Preparation of the control mixtures was started with the mix of tailings and binder for 5 minutes while tap water was slowly added until the mixture approximately reaches the slump height of about 7 inches (72.1% of solid concentration). The preparation of

CPB specimens containing admixture is similar to the control specimens (without admixture), but on the third minute the admixtures (TEOS/PCS) were also added to the mixture and the mixing process continued for another 2 minutes, then the targeted slump height was measured again to observe the influence of TEOS on the CPB consistency.

Table 4.5- Formulations of prepared CPB mixtures (Phases I & II)

Formulation	Binder content (%)	Binder type	TEOS, PCS content (%)	Curing time (day)	Slump height (inch)
GU/Slag (control)	4.5	GU/Slag	0	3, 7, 14, 28	7.1
TEOS1	4.5	GU/Slag	0.71	3, 7, 14, 28	6.8
TEOS2	4.5	GU/Slag	1.43	3, 7, 14, 28	6.8
TEOS3	4.5	GU/Slag	2.85	3, 7, 14, 28	7.1
TEOS4	4.5	GU/Slag	5.7	3, 7, 14, 28	6.8
TEOS5	4.5	GU/Slag	8.3	3, 7, 14, 28	6.8
TEOS6	4.5	GU/Slag	14.19	3, 7, 14, 28	6.7
TEOS4/PCS	4.5	GU/Slag	5.7, 0.5	3, 7, 14, 28	7.1
GU3 (control)	3	GU	0	3, 7, 14, 28	6.9
TEOS/PCS-GU3	3	GU	5.7, 0.5	3, 7, 14, 28	6.8
GU7 (control)	7	GU	0	3, 7, 14, 28	6.8
TEOS/PCS-GU7	7	GU	5.7, 0.5	3, 7, 14, 28	7

In order to observe the influence of superplasticizer on CPBs containing TEOS, an additional formulation (TEOS4/PCS) containing 0.5% PCS (by mass of binder) and 5.7% TEOS (optimal amount in terms of highest UCS values) was also prepared and poured into cylindrical plastic molds (Table 4.5). In fact, the addition of 0.1 to 1 percent superplasticizer (by the mass of binder) is suggested in different studies (Sobolev et al., 2009; Heikal et al., 2013); hence in this study however, 0.5% superplasticizer was selected as the average value in this range. It is anticipated that any improvement in the dispersion of nano-silica can boost the compressive strength of CPBs. However, for a given fixed slump height the CPB specimens containing

PCS will have a lesser amount of water, which will in turn increase the UCS values as well.

In the Phase II of this experimental program the binder type was changed to general use Portland cement (GU). Thus, new CPB formulations containing 5.7% TEOS and 0.5% PCS were prepared with 3% and 7% GU binder. All the protocols of the mixture preparation are similar to that of Phase I and 72 specimens (including control specimens) were prepared (Table 4.5).

4.2.5 Experimental methods

The consistency of CPBs was evaluated through the slump height measurement using a standard Abrams cone in accordance with ASTM C-143 standard. The targeted slump height was 7 inches and a slump height of 6.9±0.1 inches was achieved (see Table 4.5). The unconfined compressive strength (UCS) of CPB specimens was determined by uniaxial compression tests according to ASTM D 2166-91 using a computer-controlled mechanical press (MTS 10/GL) having a normal loading capacity of 50 kN and at a vertical displacement rate of 1 mm/min. The shape factor (height-to-diameter ratio) of the CPB specimens was 2. After each curing time, three specimens (triplicate) underwent the UCS determination and only the average value was considered.

Since TEOS reacts with water (Niederberger and Pinna, 2009) and PCS is also a water reducing agent (Dubey and Kumar, 2013), the determination of the gravimetric water content W(%) of fresh CPB is beneficial to understand the water requirement of the mixtures containing admixtures for achieving the target slump (6.9±0.1 inches). In order to hit the target slump height of ~7 inches, depending on the influence of admixtures (TEOS/PCS) and the type of binder used, lesser amounts of water (3 to

4%) were added to the mixtures. The gravimetric method (Smith 2000) was used to evaluate the free water content of hardened CPBs by oven-drying the specimens at 60°C for three days. The calculated free water content at 3 days (= mass of water/mass of dried specimen) for phases II CPB specimens are given in Table 4.6. It is also noticeable that the hydration of cement will be in process when the specimens are in the oven, but this kind of error occurs in all the specimens, hence is negligible.

The determination of water content of hardened CPBs is used to calculate the water/cement ratio *w/c* (= mass of water/mass of dry cement or binder) which will help understanding the effect of admixtures addition on the compressive strength development with curing time. The water/cement ratio can also be calculated from the calculated gravimetric water content *W*(%) as follows:

$$\frac{w}{c}=\frac{W(\%)}{100}\left(1+\frac{100}{B_w(\%)}\right) \tag{1}$$

where $B_W(\%)$ is the binder content (= mass of binder/dry mass of tailings) in the CPB.

Differential thermogravimetric analysis (DTG) was performed using the SDT Q600 apparatus in an inert nitrogen atmosphere at a rate of 20°C/min up to 1000°C. Prior to DTG analysis, samples were oven-dried at 60°C for three days to remove any free water.

4.3 Results

4.3.1 Compressive strength evaluation

As can be seen from Fig. 4.3, except for 3 days of curing time, 5.7% TEOS content (TEOS4 formulation) improved the compressive strength of CPBs more effectively.

At 3 days of curing time, the UCS values of control, TEOS1, TEOS2, and TEOS3 specimens were less than 90 kPa and all of which deformed plastically under the load. At the same period, TEOS4, TEOS5, and TEOS6 specimens developed approximately similar UCS values (UCS≥125 kPa). It can be concluded that at 3 days of curing time there is no meaningful difference between the strength development of specimens as a consequence of imperfect hydration when the slag-cement (20% of cement GU and 80% of slag) was used. Between 7 days to 28 days of the curing time, the UCS improvement with TEOS4 formulation became more appreciable in comparison to other formulations, but it is similar to TEOS5 formulation. Therefore, 5.7% TEOS (TEOS4) was selected as optimal formulation. Addition of 1 to 5% (by mass of binder) TEOS admixture in cementitious materials is proposed in different studies (Ji, 2005; Qing et al., 2007; Senff et al., 2009, Abd El Aleem et al., 2014), hence the preferred amount of TEOS in this study (5.7%) is not far from the literature. As previously mentioned, NS is highly capable of agglomeration; hence, higher loaded amount of NS in cementitious materials will increase the agglomeration possibility. This phenomenon may explain the UCS reduction with the TEOS6 (14.18%) formulation specimens, but further investigation is required in this case. When compared with control specimen, as shown in Fig. 4.3, the addition of 5.7% TEOS increased the UCS values from 6 to 706% between the period of 3 to 28 days; the maximum and minimum UCS improvement were achieved at 7 and 28 days of curing respectively. This implicates that the addition of TEOS was efficient to nullify the retarding influence of slag in cement/slag binder. The range of standard deviations for control and TEOS4 specimens from 3 to 28 curing days varied from 7.59 to 67.1 and 7.25 to 101.05 respectively.

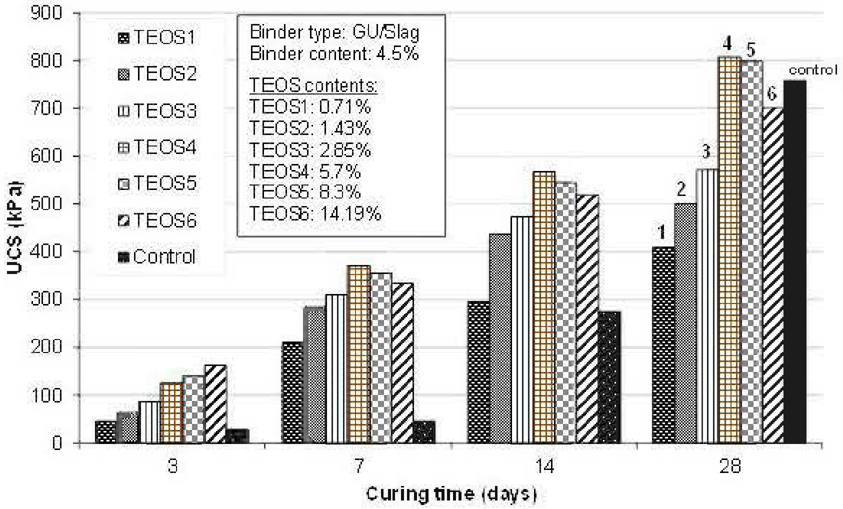

Figure 4.3- Influence of TEOS on UCS values, Phase I-Part 1

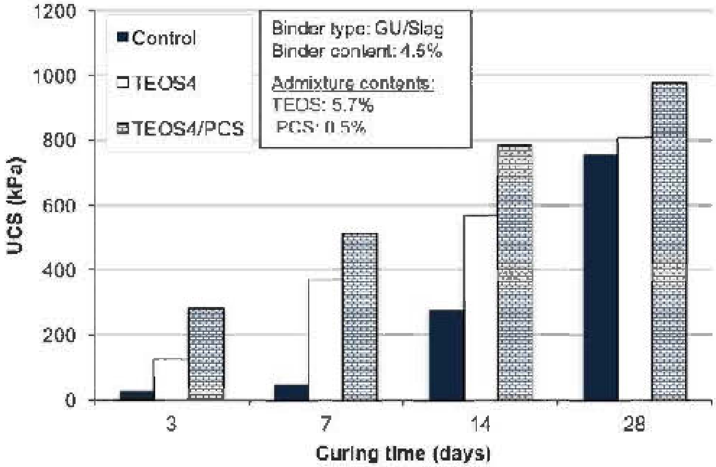

Figure 4.4-Influence of TEOS and PCS admixtures on UCS values, Phase I-Part 2

Fig. 4.4 highlights the positive influence of PCS on UCS improvement with TEOS4/PCS formulation specimens at all the curing times in comparison to the control and TEOS4 formulation specimens. In comparison to the TEOS4 formulation specimens, the UCS value of the TEOS4/PCS formulation specimens was increased up to 125% at 3 days and 21% at 28 days, but in comparison with control specimens this improvement was between 29% (28 days) to 1009% (7 days). That is, the addition of PCS to TEOS increased the strength gain of CPB specimens to the higher levels. The standard deviations for TEOS4/PCS specimen from 3 to 28 curing days varied from 27.93 to 120.77.

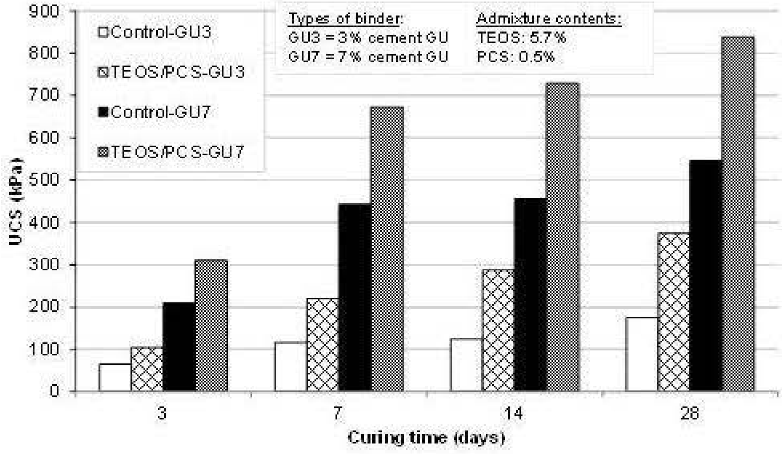

Figure 4.5- Influence of TEOS and PCS admixtures on UCS values, Phase II

The UCS results from Phase II were plotted in Fig. 4.5. As can be observed from Fig. 4.5, the UCS improvement with TEOS/PCS-GU3 formulation with respect to Control-GU3 is approximately 60% strength gain at 3 days of curing. At 28 days of curing time, this strength gain raised up to 114%. The UCS gain with TEOS/PCS-GU7 formulation was approximately 48% compared to the Control-GU7 specimen while this strength gains slightly increased to approximately 53% at 3 days and 28 days of curing time, respectively (Fig. 4.6). Based on Fig. 4.6, the rate of UCS improvement of the specimens with 3% GU binder content is higher than that of the specimens containing 7% GU binder. In fact, by increasing the binder content from 3% to 7% (more than double) less strength gain was observed. This indicates the higher effectiveness of TEOS/PCS formulation on UCS development at lower amount of GU binder, specifically at early ages of curing (from 3 to 14 days). From Fig. 4.6 it can be seen that the highest strength gains of 130% and 60% were observed at 14 days curing time for specimens containing 3% and 7% binder, respectively. More investigations regarding the influence of admixtures in paste backfill mixtures with sulphide-rich tailings is required. In addition, the influence of PCS alone on the UCS improvement of CPBs is beneficial to be investigated.

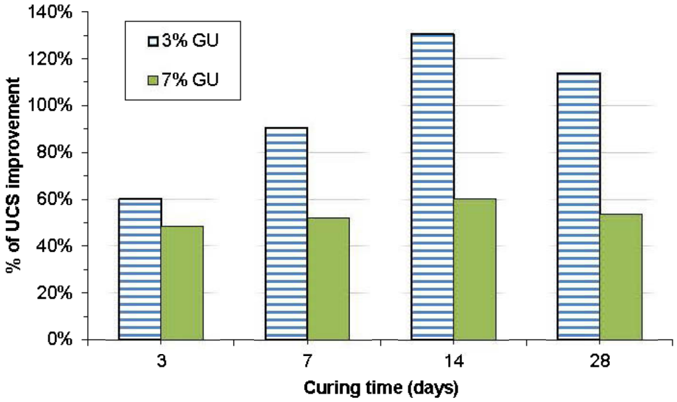

Figure 4.6- Improvement in UCS values (%) of CPB specimens from Phase II

4.3.2 Water content calculation

The quantified free water content of fresh and hardened CPB formulations from Phase II are listed in Table 4.6. TEOS/PCS-GU3 formulation water content was reduced by 1.8% at 3 days of curing compared to the initial water content (fresh state) of the mixture whereas the water content of GU3 formulation (control) at the same conditions did not change noticeably. This implies the progressive and less pronounce hardening process in the TEOS/PCS-GU3 formulation specimens compared to the control specimens, that resulted in higher UCS values of the specimens (ability of NS to form higher amount of C-S-H) (Björnström et al., 2004). The water content of TEOS/PCS-GU7 formulation specimens was reduced by 4.6% at 3 days of curing compared to the initial water content of the mixture, but this reduction was by 2.5% for GU7 formulation (control) at the same conditions. This can also be associated with likely rapid hardening process of the specimens containing Nano-silica and superplasticizer at 3 days. From Table 4.6 it can also be noted that the water content reduction of all formulation specimens compared to the control specimens is in the range 1.2% – 3.2% from 3 to 28 days of curing times.

However, the rate of these changes is approximately similar between all the specimens. The highest reduction in water content occurred from the time just after the mixture preparation to 3 days of curing. Table 4.6 represents the calculated corresponding solid mass concentration for different CPB formulations (C_w(%) [= 100*(1+0.01*W(%))$^{-1}$]). As can be seen from Table 4.6, for the mixtures containing 3% GU binder, the solid mass concentration C_w(%) was increased between 1% (control) and 3% (TEOS/PCS formulation), whereas for the formulation containing 7% GU binder C_w(%) was increased between 3% (control) and 4% (TEOS/PCS formulation). This fact also implicates the dependency of UCS values on solid concentration for a given slump height (higher C_w(%) will lead to the higher UCS value).

Table 4.6- Water content and solid mass concentration of Phase II CPB specimens

Formulation	Water content W(%) and corresponding solid mass concentration C_w(%) of CPB specimens									
	0-day		3-day		7-day		14-day		28-day	
	W(%)	C_w(%)	W(%)	C_w(%)	W(%)	C_w(%)	W(%)	C_w(%)	W(%)	C_w(%)
GU3	37.7	73	37.7	73	37.7	73	36.0	74	35.6	74
TEOS/PCS/GU3	34.6	74	34.6	75	31.8	76	30.2	77	30.0	77
GU7	38.3	72	38.3	74	33.3	75.	32.7	75	32.6	75
TEOS/PCS/GU7	34.6	74	34.6	77	30.1	77	29.9	77	29.0	78

4.3.3 DTG results

Since significant differences of UCS values and water contents mostly occurred at 3 days of curing, DTG analyses were performed on all the specimens from Phase II at 3 days. The aim of the DTG analysis was to understand the influence of admixtures on the evolution of CH and C-S-H at early strength development of CPB. Based on different studies through the literature, thermal decomposition of C-S-H and CH occurs between 90-200°C (Villain et al., 2007; Heikal et al., 2013) and 440-550°C (Sha et al., 1999; Vieira et al., 2004; Pane and Hansen, 2005) respectively. Figs. 4.7a &4.7b show roughly marginal weight loss difference between the temperatures 440°C and 550°C regarding the CH content changes. Hence, no significant change between the CH content of the CPB specimens could be observed because of NS reaction. However, there is a significant weight loss (especially with the sample containing 7% GU binder) between the temperatures 80°C to 120°C (Figs. 4.7a &4.7b), representing the C-S-H content of the CPBs.

4.4 Discussion

In this study, superplasticizer was used to improve the dispersion of NS and binder particles in CPB (by causing electrostatic-electrostatic/repulsive forces) and it is obvious that any decrease in the amount of water in CPB could increase the UCS values. Table 4.7 presents the water-to-cement ratio (*w/c)* for the CPB formulations. As it is well known, any reduction in the amount of *w/c can increase* the compressive strength in cementitious material. Table 4.7 shows that the *w/c* of the CPB formulations containing 7% GU is lesser than half of the *w/c* of CPB formulations containing 3% cement. This can explain the additional amount of C-S-H in the TEOS/PCS-GU7 formulation specimen that is as twice as the C-S-H amount in control-GU7 (Fig. 4.7b).

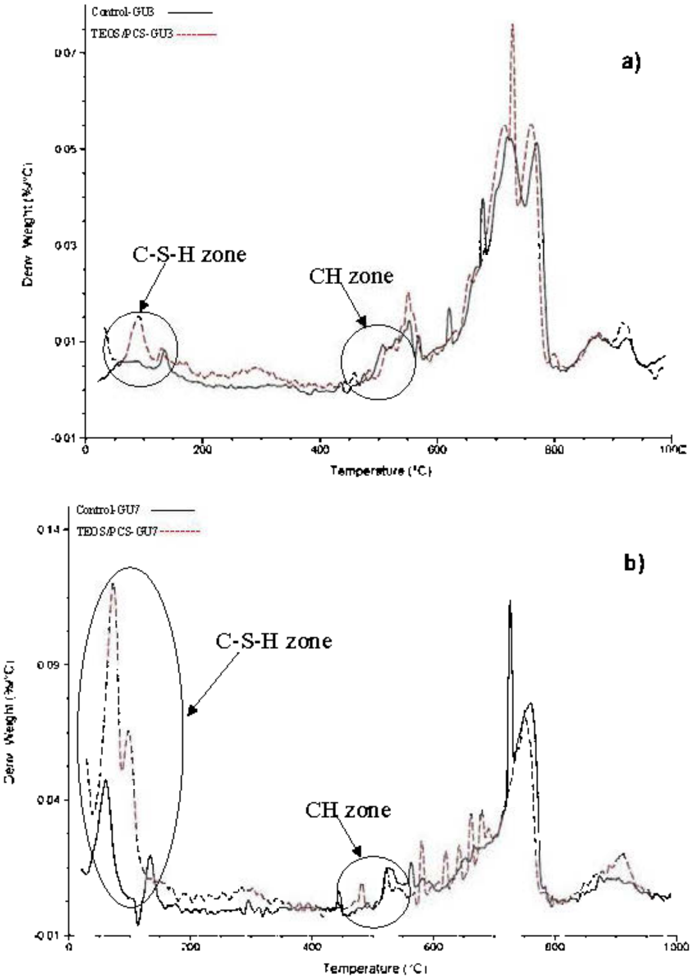

Figure 4.7- DTG curves of CPBs at 3 days of curing: a) 3% and b) 7% (binder GU)

In addition, for a given amount of binder, the *w/c* difference between control and TEOS/PCS formulations is more noticeable for 3% binder (change between 1.1 and 2) than that of 7% GU binder (change between 0.4 and 0.9) (Table 4.7). The higher *w/c* differences between the formulations containing 3% GU binder formulations (GU3 and TEOS/PCS-GU3) partly explain the higher strength development at this range. Moreover, it can be asserted that the produced Nano-silica (silica gel) from the hydrolysis of TEOS chemically bounded and filled the Nano-pores of C-S-H (Geffers et al., 2015) resulting in additional availability of calcium silicate hydrate. In fact, Nano-silica is not simply a filler but also an activator for the hydration of binder (Li et al., 2004).

As shown in Fig. 4.1, hydrolysis of TEOS releases four molecules of ethanol as the reaction byproduct, but since in this study the amount of TEOS used was very small (0.12% solid mass concentration for TEOS-GU3 and 0.27% for TEOS-GU7 formulations), the influence of ethanol on the hydration of binder was disregarded. The influence of alcohols on the hydration of cement-based materials is discussed in different studies (Muhua and Roy, 1987; Edmonds and Majumdar, 1989; Singh and Rai, 2001).

Table 4.7- Water-to-cement ratio (*w/c*) of Phase II CPB formulations

Formulation	Water-to-cement ratio *w/c*				
	0 day	3 days	7 days	14 days	28 days
GU3	12.9	12.9	12.9	12.4	12.2
TEOS/PCS-GU3	11.9	11.3	10.9	10.4	10.3
GU7	5.9	5.5	5.1	5.0	5.0
TEOS/PCS-GU7	5.3	4.6	4.6	4.6	4.4

Due to the high specific surface area and high purity of Nano-silica, pozzolanic influence of NS may dominate the pozzolanic effect of Slag in GU/Slag binder (rapid consumption of calcium hydroxide by NS at early ages of hydration) (Hou et al., 2013). Yet, even pozzolanic effect of Slag in control specimens was ineffective for the first week while UCS values of control specimens were less than 100 kPa (Fig. 4.4). Thus, Slag-cement requires more time to be effective as a pozzolanic material, but NS has already consumed parts of CH and in later ages of hydration, there may not be enough calcium hydroxide available to be consumed by Slag. Hence, unreacted amounts of Slag may be detectable at later ages of the hydration (Hou et al., 2013). Overall, utilization of blended binders having two different pozzolanic materials requires more in depth investigation. By comparison between Fig. 4.4 and Fig. 4.5, it can be concluded that the combination of Portland cement and Slag was inefficient to develop the UCS of the control sample for the first week (Fig. 4.4) whereas the use of lesser amount of GU binder was more efficient at the same period (UCS value of control sample containing 3% GU is higher than that of specimen containing 4.5% GU/Slag at 7 days). This implies that the pozzolanic influence of Slag is inefficient at the short period. Even so, by changing the source of tailings (varying mineralogy and/or grain size distribution), the pozzolanic influence of GU/Slag binder will probably be changed, specifically with sulphide-rich tailings. More investigation is needed in this regard.

4.5 Conclusion

This study showed the positive effect of TEOS/PCS admixtures on compressive strength development and microstructural evolution of CPB specimens. It was observed that the addition of TEOS slightly reduces the slump height of CPB in most cases (TEOS1-TEOS6). However, the addition of PCS not only improved the slump height of the CPB containing Nano-silica (TEOS/PCS) as the slump height of control specimens (GU/Slag), but also improved the UCS values. Furthermore, since the addition of superplasticizer (PCS) decreased the water requirement of the mixtures for the target slump height, the amount of delivered tailings per unit volume of CPB was increased (increase in solid mass concentration). For example, the solid mass concentration increased by 2% when 0.5% of PCS was added to the mixture containing 5.7% of TEOS and 7% of GU binder.

The influence of Nano-silica on CPB mixtures with different binder types (GU and GU/Slag) was not similar, but in both cases, UCS improvement was observed. Nano-silica is a high pozzolanic material that can react with the produced CH from the hydration of cement, but in this study we did not observe a noticeable difference in CH content of the prepared formulations. Hence, the main reason of UCS improvement can be attributed to the hydration acceleration, pore volume filling, and bonding influence of nano-silica (silica gel) with C-S-H because of decreased water-to-cement ratio. The additional amount of C-S-H hardens the CPB 3 days after the filling that can also help decrease the horizontal pressure on the barricade. Moreover, since the addition of Nano-silica and superplasticizer increases the UCS values, it is possible to replace a partial amount of binder with the admixtures without affecting the flow and transport properties of the CPB.

CHAPTER 5

INFLUENCE OF POLYMER POWDER ON PROPERTIES OF CEMENTED PASTE BACKFILL

To be submitted in Canadian Journal of Civil Engineering

Babak Koohestani, Bruno Bussière, Tikou Belem, Ahmed Koubaa

5.0 Foreword

This chapter presents an experimental investigation on the capability of polymer powders to be used as an admixture in cemented paste backfill for binder consumption reduction and early age strength development. This is linked with the binder cost reduction and early strength development objectives of this Ph.D. thesis. After discovering the inefficiency of wood fillers and efficiency of nano-silica to improve the early age strength development of CPB in the previous chapters (3 and 4), Ethylene-vinyl Acetate/vinyl ester powder was used as the third admixture in the chapter 5. The fact was to find another potential admixture (in addition to nano-silica) for CPB to provide the same properties. Since polymer powers are in the form of solid, the pertinent storage and safety is higher over the colloidal nano-silica. Moreover, the addition of such powdery polymers to CPB is more convenient and flexible. Vinyl acetate (monomer) has excellent adhesion properties and it is routinely used as an adhesive and surface coating agent with different substrates (e.g., metal, porcelain, wood and paper, etc.). When copolymerized with different monomers (e.g., ethylene, vinyl ester, etc.) the properties of vinyl acetate will be improved. Polymeric materials are high-technology admixtures and the use of them require a precise financial assessment in large-scale to be feasible in mine site. The main hypothesis of using polymeric admixture was the establishment of a polymeric film in CPB resulting in strength development and possible binder usage reduction (similar to resin). However, the addition of polymeric admixture may also interact with the hydrated binder and change the whole microstructure of CPB. All of the concerns regarding the use of polymer powder will be discussed and investigated in this chapter. The lab work, data collection and interpretation all are performed and prepared by Babak Koohestani. Dr. Bruno Bussiere chiefly conducted this work by asking for specific analyses and formulations. Dr. Tikou Belem and Ahmed Koubaa made some suggestions and comments to this work. All the professors read this article for the accuracy and consistency improvement.

5.0 Résumé

Cette étude examine l'influence de l'éthylène-acétate de vinyle/ester de vinyle de l'acide versatique (EVA/VE) sous forme de poudre de polymère redispersable sur les propriétés mécaniques, chimiques, et sur la microstructure du remblai en pâte cimenté (RPC). Pour se faire, différentes quantités de poudre de polymère EVA/VE (7,5 à 20% de la masse du ciment) ont été utilisées pour la préparation des composites à base de CPB. Les propriétés mécaniques telles que la résistance mécanique en compression uniaxiale a été caractérisée. Également, les propriétés structurales, les propriétés chimiques et la porosité des composites RPC ont été caractérisées respectivement à l'aide de la microscopie électronique à balayage (MEB), l'analyse thermogravimétrique différentielle (ATG/ATD) et des tests de porosimétrie par intrusion de mercure (PIM).

Les résultats indiquent que l'ajout de polymères EVA/VE a entrainé une légère modification des propriétés mécaniques, microstructurales et chimiques des RPCs. Toutefois, l'hydratation du ciment a été considérablement diminuée par l'ajout des polymères EVA/VE. En fait, ces derniers ont empêché l'apparition des phases de silicates de calcium hydratés (S-C-H) et aussi ont permis de réduire la quantité de S-C-H à un âge précoce d'hydratation. Les résultats de PIM obtenus montrent également que la teneur en polymère n'a pas influencé la porosité du RPC.

Mots-clés: Polymère redispersable; Remblai en pâte cimenté; Éthylène acétate de vinyle/ester de vinyle; Analyse thermogravimétrique différentielle (ATD); Résistance à la compression uniaxiale (UCS); Microscopie électronique à balayage (MEB); Porosimétrie par instrusion de mercure (PIM).

5.0 Abstract

This study investigates the influence of ethylene-vinyl acetate/vinyl ester of versatic acid (EVA/VE), a redispersible polymer powder, on the mechanical, chemical, and microstructural properties of cemented paste backfill (CPB). CPB mixtures were prepared with different contents of added EVA/VE (7.5 to 20 wt% of cement mass). In order to assess the influence of EVA/VE on the consistency of the fresh CPB mixtures, slump height was measured using a small Abram's cone. Uniaxial compressive strength (UCS) testing was conducted to determine the influence of polymer powder addition on the mechanical strength development of CPBs, and mercury intrusion porosimetry (MIP), scanning electron microscopy (SEM), and differential thermogravimetric analysis (DTG) were used to determine the influence of polymer powder addition on the microstructure and mineralogy of hardened CPBs. The results showed a minor influence of EVA/VE on the mechanical, microstructural, and chemical properties of CPBs. The main effect of polymer powder addition was to delay cement hydration by preventing the production of calcium hydroxide and reducing the amount of calcium silicate hydrate at early hydration ages. Of the different polymer powder proportions used in this study, the addition of 15% EVA/VE (based on the mass of binder) was more effective in improving UCS values. However, the MIP results indicated that polymer content did not significantly influence CPB porosity.

Keywords: Redispersible polymer; Cemented paste backfill; Ethylene vinyl acetate/vinyl ester; Differential thermogravimetric analysis (DTG); Mercury intrusion porosimetry (MIP), Uniaxial compressive strength (UCS); Scanning electron microscopy (SEM).

5.1 Introduction

Polymer admixtures are added to cementitious materials in order to improve certain material properties. The polymers or monomers are incorporated into the fresh cementitious mixture, typically at a dosage of 5–20% by weight of cement. As they interact with the hydrating cement, polymers can influence the setting time, bleeding, workability, and mechanical properties of cementitious materials (Ramachandran, 1996; Mailvaganam and Rixom, 2002; Czarnecki, 2005). The types of polymers used in cementitious materials can be divided into three main categories: dispersible in water (latex), redispersible powder, and water-dispersible or water-soluble liquid (Chandra and Flodin, 1987; Khayat, 1998; Kaeding and Maass, 2003). In this study, only ethylene-vinyl acetate/vinyl ester of versatic acid, a redispersible polymer, is used.

Redispersible polymer powders consist of two or more monomers, derived from elastomeric or thermoplastic polymers, that form a continuous film as they interact with hydration products (Ohama, 1995; Mailvaganam and Rixom, 2002; Silva and Monteiro, 2006). Although the addition of a redispersible polymer can delay cement hydration, the polymer film that forms around the cement particles can reinforce the cementitious material (Brandt, 2009), for instance, by improving adhesion, tensile, and flexural strength (Justnes and Flodin, 1987; Page and Page, 2007). Redispersible polymer powders are chemically stable and freely dispersible in water or mixtures. Their particle size typically varies from 0.05 to 5 μm (Mailvaganam and Rixom, 2002). It should be noted that the formation of minerals during cement hydration creates capillary pores (0.0005–0.5 μm in diameter) in the matrix. The polymer films are unable to fill capillary pores of this size. Instead, they fill the larger (i.e., > 0.02 μm) and more spherical voids, for a potential decrease in the final porosity of the cementitious material (Miller, 2005).

A thermoplastic monomer with the formula $C_4H_6O_2$, vinyl acetate has excellent adhesive properties, and the addition of various copolymers such as ethylene or vinyl ester improves its flexibility and hydrophobicity (Miller, 2005). The copolymerization of vinyl ester (as a thermosetting polymer) and vinyl acetate improves the overall bonding and adhesion (Aggarwal et al., 2007) of vinyl acetate (Domone and Illston, 2010; Fangueiro, 2011). Fig. 5.1a and Fig. 5.1b show the structure of vinyl acetate and vinyl ester monomer, respectively.

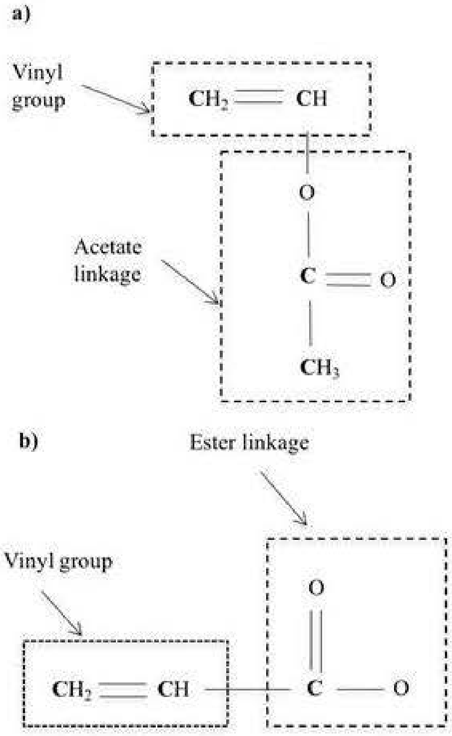

Figure 5.1- Structure of vinyl acetate (a) and vinyl ester (b) (Chandra and Rustgi, 1998; Strong, 2008)

Vinyl ester of versatic acid (VeoVa) has been the most widely investigated polymer for copolymerization with vinyl acetate (Blackley, 1997; Sidney Goodman, 1998; Gomes and Ferreira, 2005). Versatic acid is a tertiary carboxylic acid wherein one alkyl group is methyl and the two other alkyl groups are linear (Jacobs et al., 1985; Weissermel and Arpe, 2008). Fig. 5.2 shows the structure of vinyl ester of versatic acid, where the total number of carbon atoms in the three groups is eight (X+Y+Z=8). Ethylene, with the simple formulation C_2H_4 or $CH_2{=}CH_2$, is a hydrophobic monomer: its copolymerization with vinyl acetate decreases the tendency of the acetic group to undergo hydrolysis (Miller, 2005; Biron, 2012). Fig. 5.3 shows the proposed structure of ethylene-vinyl acetate/vinyl ester of versatic acid (EVA/VE).

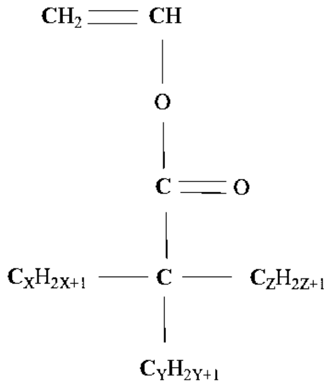

Figure 5.2- Typical structure of vinyl ester of versatic acid (Blackley, 1997; McLennan et al., 2010)

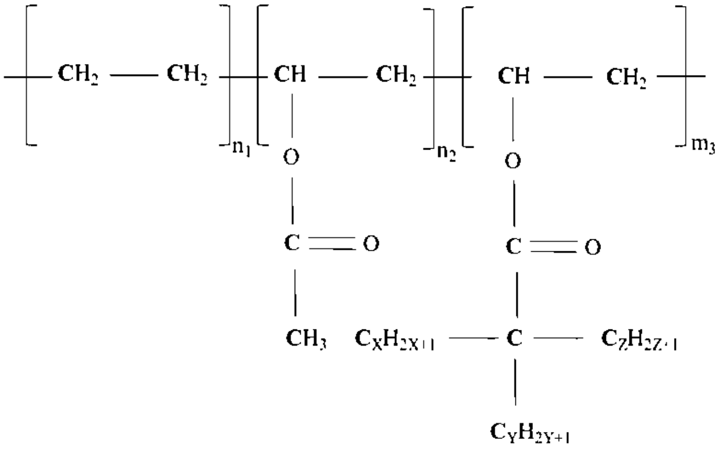

Figure 5.3- Proposed structure of ethylene-vinyl acetate/vinyl ester of versatic acid

Unlike linear polymers (e.g., polyethylene), the side chains of backbone polymers are connected in a regular manner. When all the side chains are represented, the structure of a backbone polymer resembles a comb (Roussel, 2011). Of the backbone polymers, ethylene-vinyl acetate (EVA) is the most frequently used (Mildenberg et al., 2008). The properties of backbone copolymers depend primarily on the polymer's core structure as well as its crystallinity, branch configuration, molecular weight, and polarity (Biron, 2012). In the presence of water, the acetate group of vinyl acetate undergoes alkaline hydrolysis as it interacts with Ca++ ions from dicalcium silicate (C_2S) and tricalcium silicate (C_3S), thereby forming an organic salt (calcium acetate). This decreases the amount of calcium hydroxide (CH) in the cementitious mixture, which consequently delays cement hydration, especially at early ages (Gomes and Ferreira, 2005; Gomes et al., 2005; Betioli et al., 2009). EVA/VE is a water-soluble polymer that improves material workability by adding air to the mixture. In addition, polymer powders improve the dispersion of cement particles by acting as surfactants (i.e., reducing surface tension) via repulsive and electrostatic forces (Kardon, 1997; Ohama, 1998; Hall and Minton, 2003). Moreover, the expansion of hydrolyzed polymer powders within the cementitious material can negatively affect consolidation (Kaeding and Maass, 2003).

The use of cemented paste backfill (CPB) is an innovative mine tailings management technology that can return half of the tailings stream produced from a mineral processing plant to the underground stopes and voids, thereby providing secondary ground support and minimizing the environmental impact by reducing surface waste storage (Benzaazoua et al., 2004; Koohestani et al., 2013). CPB consists of filtered mill tailings (75–85 wt% solids), water (15–28%), and a binding agent such as cement (2–10 wt% of the dry mass of tailings) (Benzaazoua et al., 2004; Coussy et al., 2011; Koohestani et al., 2013). Hardened CPB generally has low uniaxial compressive strength (UCS ~ 0.2–4 MPa), depending on the type of binding agents, the tailings grain size distribution, and the mineralogy of the tailings (Belem and Benzaazoua, 2008; Yilmaz et al., 2009; Yilmaz et al., 2011; Yılmaz et al., 2014).

Because they are delivered by pumping or gravity, CPB materials should have adequate consistency so as not to block or stick in the pipeline. Water may therefore be added to the CPB to make it sufficiently flowable. However, water addition increases the water-to-cement ratio, which negatively influences the mechanical strength of CPB (typically water/cement ≥ 3) (Belem et al., 2010).

To our knowledge, no studies to date have investigated the use of polymer-based admixtures in CPB. Hence, this study provides an investigation of the potential benefits of adding redispersible polymer powder to CPB. The main hypothesis is that polymer addition would alter the flowability and decreases the water-to-cement ratio of the CPB. The formation of polymer film in CPB could also improve the mechanical strength (UCS) and decrease the binder consumption of the CPB, resulting in lower operational costs. However, the addition of polymer powder could also delay cement hydration and decrease the mechanical strength. To evaluate the potential influences of polymer powder (EVA/VE) on CPB an experimental laboratory study was conducted on two mine tailings with different mineralogical compositions. The influence of EVA/VE on early strength development (0–28 curing days) of CPB was assessed by UCS tests. The influence of EVA/VE on mineralogical changes (using thermogravimetric testing) and microstructural changes (using mercury intrusion porosimetry and scanning electron microscopy analyses) of CPBs are also investigated.

5.2 Materials and methods

5.2.1 Materials

Two different types of tailings were used in this study: sulfidic (G_s=3.7) and non-sulfidic (G_s=2.6), obtained respectively from the Laronde and Goldex mine backfill processing facilities (Agnico Eagle, Quebec, Canada). The aim was to investigate the influence of polymer powder on the properties of CPB prepared with different tailings having different mineral compositions. Fig. 5.4 shows the particle size distributions of the tailings, estimated using a laser particle size analyzer (Malvern Mastersizer). The significance of particle size distribution is explained in the literature (Verkerk and Marcus, 1988). As shown in Fig. 5.4, the two tailings have a very similar grain size distribution, which is typical for Canadian hard rock mining operations (Bussière, 2007). The proportion of particles smaller than 80 μm ranges from 60 to 80%, D10 ranging from 5 to 6.8 μm and CU (=D60/D10) from 14 to 16.

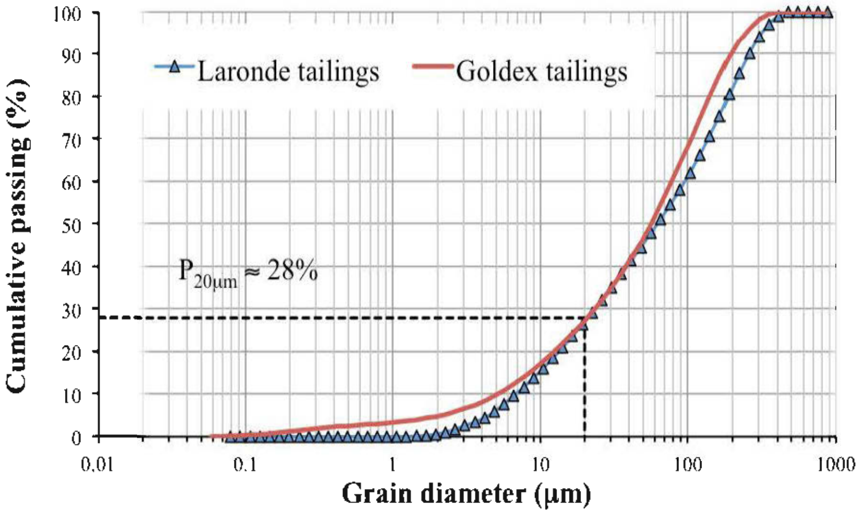

Figure 5.4- Particle size distribution (cumulative) of Laronde tailings and Goldex tailings

Table 5.1 presents the results of the XRD and ICP-AES analyses of the Laronde and Goldex tailings. Both tailings are composed largely of silicate-based minerals, including quartz, chlorite, and (for the Goldex tailings) albite. The Laronde tailings have higher pyrite content (26%) than the Goldex tailings (<1%). The mineralogical analysis results for both materials correlate well with the chemical analysis results obtained by ICP-AES.

Table 5.1-ICP-AES analysis and XRD quantifications of Laronde and Goldex tailings

ICP-AES analysis (%)			XRD quantification (%)		
Element	Laronde tailings	Goldex tailings	Minerals	Laronde tailings	Goldex tailings
Al	4.5	7.7	Quartz	46	18
Mg	0.36	1.4	Muscovite	9	8
Ca	0.75	3.4	Gypsum	3	-
Fe	17.9	2.2	Pyrite	26	0.7
Ti	0.03	0.04	Chlorite	8	8
Zn	0.22	-	Paragonite	6	-
S	13.8	0.2	Calcite	-	8
K	0.6	0.5	Albite	-	55
Na	0.1	3.6			

The redispersible polymer powder EVA/VE was obtained from Wacker Polymers Company under the brand name Vinnapas 7034. The specifications are presented in Table 5.2.

Table 5.2- Specifications of EVA/VE

Solid content %	Ash content %	Bulk density gr/cm^3	Particle size µm
99-100	<10	0.44-0.54	0.7-7

Lafarge Inc. provided the ordinary Portland cement general use (GU) used as the binder in this study. Table 5.3 presents the XRD analysis results and the physical properties of the Portland cement. As shown in Table 5.3, the main mineral component of the Portland cement is tricalcium silicate (C_3S). Typically, Portland cement also contains mainly tetracalcium aluminoferrite (C_4AF), dicalcium silicate (C_2S), and tricalcium aluminate (C_3A) (Scrivener et al., 2004; Woodson, 2011). In addition, potable municipal water (tap water) was used to prepare all the mixtures.

Table 5.3- Mineralogical composition and physical properties of the Portland cement

Physical specification	Specific gravity		Specific surface (m^2/g)			Particle size distribution		
						D_{10}	D_{50}	
	3.15		1.1			0.6	14.11	
Minerals	C_3S	C_2S	C_3A	C_4AF	Quartz	Calcite	Gypsum	Lime
(%)	56.8	9.5	3.8	13.5	1.2	4.6	1.2	1.5

5.2.2 Mixture preparation and test methods

In this study, 4.5% GU cement (based on dry mass of tailings) was used for all CPB mixtures. The amount of added polymer (7.5–20%) was calculated based on the weight of binder: different amounts of polymer powder were tested to determine the most effective polymer content. Prior to mixture preparation, EVA/VE was added to the binder and mixed. The tailings were then mixed with the polymer-containing binder (polymeric) for five minutes using a kitchen aid mixer while tap water was slowly added to reach a solid concentration of approximately 72.9% to 76%, providing 37.2% to 31.6% water content (to reach a 74–84 mm slump height using a mini-slump cone). CPB flowability measured by a slump height ranging from 150 to 250 mm (using a standard Abrams slump cone) has been reported as suitable for delivery from a mine surface to underground stopes by gravity or pumping (Clark et al., 1995). However, because a mini-slump cone (i.e., half the height of a standard Abrams slump cone) was used in this study, it is assumed that the measured slump height of fresh CPB would be approximately half the height of the slump measured with a standard slump cone. Slump height was measured according to ASTM WK27311 and Chinese standard GB 8077, as explained elsewhere (Li and Xiao, 2005). Table 5.4 presents the CPB mixtures used in this experimental study and their respective consistency (slump height) after five minutes of mixing.

All specimens were prepared at three curing times: 3, 7, and 28 days. For each mixture, triplicate specimens were prepared including specimens without polymer powder (control) and specimens containing polymer powder (polymeric CPBs). Specimens were prepared and poured into cylindrical polyvinyl molds (50.8 mm diameter and 101.6 mm height), then sealed and left to cure in a humidity chamber at 23 °C and 90% relative humidity.

Table 5.4- CPBs Formulations and Characteristics-Binder GU

Formulation	Binder content %	Polymer content %	Curing time (days)	Solid content %	Slump (mm)
*LA-Control	4.5	0	3, 7, 28	72.9	~74
**GOL-Control	4.5	0	3, 7, 28	76	~84
LA-7.5% Pol	4.5	7.5	3, 7, 28	72.9	~74
GOL-7.5% Pol	4.5	7.5	3, 7, 28	76	~84
LA-15% Pol	4.5	15	3, 7, 28	72.9	~74
GOL-15% Pol	4.5	15	3, 7, 28	76	~84
LA-20% Pol	4.5	20	3, 7, 28	72.9	~74
GOL-20% Pol	4.5	20	3, 7, 28	76	~84

*LA: Laronde tailings, **GOL: Goldex tailings

5.2.3 UCS analysis and water content estimation

The mechanical strength of the CPB specimens (CPBs) was measured using UCS tests (ASTM standard D 2166-91). The shape factor (height-to-diameter ratio) for the specimens was 2, and a computer-controlled mechanical press (MTS10/GL) with a normal loading capacity of 50kN and a displacement rate of 1 mm/min was used. The mean value of each set of triplicate specimens was selected as the overall outcome.

Because both the binder and polymer powder react with water due to the hydration and hydrolysis, the gravimetric method was used to evaluate the free water content (= mass of water/mass of dried specimen). Because the binder type and content used for the two different CPBs (prepared with Goldex and Laronde tailings) was similar, it was assumed that the change in the gravimetric water content of CPBs is attributable mainly to the hydrolysis of polymer powder. Hence, CPB prepared with Laronde tailings) underwent the water content estimation only and compared with control. The specimens were oven-dried (60 °C for three days) (ASTM D2216 – 10) at each curing time to detect differences in water consumption for the specimens with and without polymer addition.

5.2.4 Thermogravimetric analysis

Differential thermogravimetric analysis (DTG) was used to observe changes in the mineral content within the cementitious materials, including the minerals formed from cement hydration, such as calcium hydroxide (CH), portlandite, and calcium silicate hydrate (C-S-H) (Vieira et al., 2004; Gomes and Ferreira, 2005; Gomes et al., 2005; Pane and Hansen, 2005; Betioli et al., 2009). It is known that C-S-H gel (as the primary strength-developing phase) and calcium hydroxide are the main products of cement hydration in CPB (Stepkowska et al., 2005; Ouellet et al., 2006; Camilleri, 2008), and thermal analysis can identify their presence in CPB samples. In the present study, DTG analysis was applied more specifically to observe the polymer influence on the formation of CH and C-S-H, using an SDT Q600 simultaneous thermal analyzer (TA Instruments) in an inert nitrogen atmosphere at a rate of 20 C°/ min up to 1000 C°. Oven-dried specimens (60 °C for three days) were used for the DTG analysis.

5.2.5 Mercury intrusion porosimetry (MIP)

Mercury intrusion porosimetry (MIP) is an effective method for microstructural analysis of cement-based materials (Cook and Hover, 1993). It is generally accepted that the strength of materials is a function of the shape, quantity, and distribution of the voids (O'Farrell et al., 2001). The porosity configuration of cementitious materials depends mainly on the amount of binder (which affects the amount of hydration products) and the curing time (which affects hydration completeness) (Aligizaki, 2005; Alonso et al., 2012). In the case of CPB, MIP testing is frequently used to characterize the pore distribution (Belem et al., 2001; Ouellet et al., 2004; Ouellet et al., 2007; Benzaazoua et al., 2008; Yilmaz et al., 2011).

An Autopore III 9420 machine (Micrometrics) with the ability to generate a maximum pressure of 414 MPa (60,000 psi), corresponding to a theoretical pore diameter of 0.003 µm, was used for the MIP analysis. The analysis was performed in two steps: at low pressure and high pressure. In the low-pressure step, the available gases were first evacuated and the specimen holder was then filled with mercury at pressure ranging from 7 to 345 kPa. In the high-pressure step, the pressure was raised from 345 kPa to 414 MPa. The entire MIP procedure took 8 h to complete. The mercury stem volume was set at 25% to 90% of the total stem volume and the contact angle and surface tension were set at 130° and 485 dyn/cm (manufacturer's recommendation).

In this study, MIP analysis was performed to assess the influence of polymer powder addition on microstructural changes (pore size and total porosity) in polymeric CPBs at early hydration age (3 days) compared with controls. For the MIP analysis, oven-dried CPB specimens were cut into small pellets of approximately 1 cm in diameter. Specimen preparation and MIP test procedures for CPB specimens are described in detail elsewhere (Ouellet et al., 2007).

5.2.6 Scanning electron microscopy

In addition, scanning electron microscopy (SEM) analysis was performed to observe the influence of added polymer powder on the microstructure and morphology of CPBs. SEM combined with X-mapping allows direct observation of the polymer influence on CPB structure and morphology. A Hitachi S-3500N scanning electron microscope with accelerating voltage at 20 keV and current emission at 110 µA was used. Oven-dried specimens were broken up and left untouched. They were subsequently carbon-coated prior to SEM observation. This procedure is described in detail elsewhere (Belem et al., 2001;, Deschamps et al., 2008).

5.3 Results and discussion

5.3.1 Compressive strength results

The uniaxial compressive strength (UCS) results and the error bars representing significant standard deviations for the different formulations at different curing times are shown in Fig. 5.5. For the LaRonde tailings, the specimens containing 15% polymer (LA-15% Pol) show the greatest improvement in UCS (20% improvement at 3 days and 13% at 28 days over the control specimens. The UCS values for all specimens (except for LA-20% Pol) changed similarly at 3 curing days (120 kPa≤UCS≤180 kPa), indicating that up to 15% polymer addition did not noticeably change the early strength development of CPBs containing sulfidic tailings. However, when the polymer content was increased to 20%, the early strength values of CPBs decreased to values less than 100 kPa, indicating that this amount of polymer powder delayed the hydration process more noticeably. The UCS values at 7 curing days were also more or less similar across all specimens (340 kPa ≤ UCS ≤ 432 kPa). The LA-15% Pol specimen shows the highest UCS value (at 7 days) of all the specimens, along with some improvement (~80 kPa). The differences in UCS between the specimens become more evident when the hydration process took up to 28 days (430 kPa≤UCS≤735 kPa). At 28 curing days, the UCS for the LA-15% Pol [specimen is approximately 90 kPa higher than that for the control specimen. Hence, it can be concluded that the addition of 15% polymer was slightly beneficial for the strength development of the CPBs prepared with sulfidic tailings. The maximum and minimum standard deviations at 3, 7, and 28 days' curing varied from 12.2 to 28.3, 31.19 to 42.95, and 22.71 to 71.51, respectively (Fig. 5.5a).

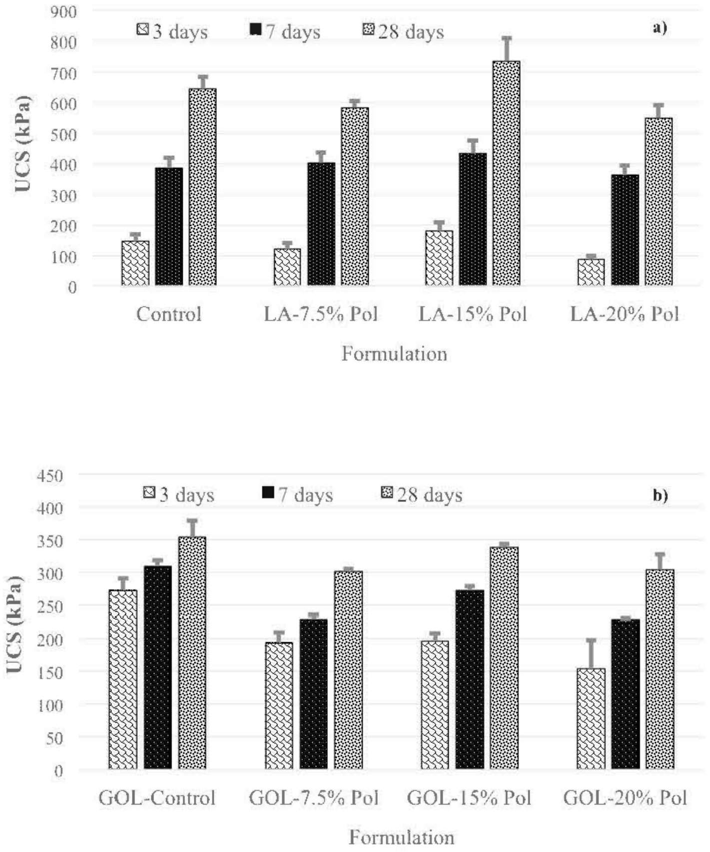

Figure 5.5- UCS variations of CPB specimens prepared with a) Laronde and b) Goldex tailings

Fig. 5.5b shows the UCS values for the CPBs prepared with Goldex (low sulfide) tailings. The addition of polymer powder at any amount (7.5–20%) decreased the UCS values of CPB specimens at 3 curing days compared to controls (approximately 75–120 kPa). The highest retarding influence is observed with 20% polymer addition, in good agreement with the results for the Laronde tailings. At 7 curing days, the UCS values for the polymeric specimens remain lower than those for controls (approximately 35–80 kPa), except for the specimen with 15% polymer addition, which shows some improvement over the 7.5% and 20% formulations. The UCS values for the control specimens at 28 days are higher than those for the polymeric specimens (by approximately 15–50 kPa), but this difference is less than that observed for 3 and 7 curing days. Whereas various studies have found a negative influence of polymers on the compressive strength development of cementitious materials (Kardon, 1997; Chung, 2004; Miller, 2005), other studies have found a positive influence (Afridi, Ohama et al. 2003, Aggarwal et al., 2007). The maximum and minimum standard deviations for the results on Goldex tailings at 3, 7, and 28 days' curing varied from 12.38 to 42.47, 1.59 to 9.1, and 4.4 to 25.45, respectively (Fig. 5.5b).

In summary, the UCS results show some differences in the influence of polymers on the CPBs composed of different tailings. However, for both tailings, 15% polymer addition had a stronger influence on the strength development of CPBs compared to the other polymeric formulations. It is also apparent that polymer powder has a more positive influence on the strength development of sulfidic tailings compared to non-sulfidic tailings (and especially at 15% polymer content).

5.3.2 Quantification of water content

Gravimetric water content was measured on CPBs prepared with Laronde tailings to determine whether polymer powder has an impact on the CPB water phase. For these measurements, CPB mixtures were prepared at 72.9% solid concentration (corresponding slump height 74 mm and 37.2% water content). The results showed that EVA/VE copolymer addition had no influence on the slump height of mixtures when prepared with similar tailings at the same solid concentration (Table 5.4).

Table 5.5 shows that the maximum water loss takes place from the time of mixture preparation up to 3 curing days (~10%). The calculated water content changes across all formulations from 3 to 28 curing days were approximately similar, and can be considered negligible (~2%). This indicates that the chemical reactions associated with polymer hydrolysis and Portland cement hydration took place mainly in the first three days. In addition, the minor difference in water content across specimens suggests that the water contained within the CPBs stabilized due to self-weight consolidation up to 3 days (Yilmaz et al., 2009). In most cases, small amounts of water accumulated at the surface of the CPBs when they were in the plastic molds (due to the bleeding influence), and this water was removed from the specimens when they were removed from the molds.

Table 5.5- Water content of CPBs prepared with Laronde tailings

Formulation	Water content %		
	3 days	7 days	28 days
LA-Control	28	26	26
LA-7.5% Pol	25	27	26
LA-15% Pol	26	28	26
LA-20% Pol	25	26	28

5.3.3 DTG results

Differential thermogravimetric analysis was performed on CPB specimens prepared with Goldex tailings (GOL-Control and GOL-15% Pol) at 3 and 28 curing days (Fig. 5.6). The Goldex tailings were used for this part of the study because of having less complex mineralogy (small sulfide content), which would produce fewer background interactions between the tailings and cementitious mineral responses. Fig. 5.6 shows four major peaks within the temperature ranges 90 to 95, 320 to 445, 609 to 775, and 750 to 775 °C. Generally, a peak within the 90 to 95 °C range represents dehydration of the C-S-H phase (loss of bonded water) (Alarcon-Ruiz et al., 2005; Ouellet et al., 2006; Cizer, 2009; Heikal et al., 2013). The second major peak within the 320 to 445 °C range is generally attributed to the decomposition of portlandite (Kamel et al., 1972; Swamy et al., 1979; Swamy and Prasad, 1981; Jorgensen and Moyle, 1982; Blgham et al., 1990; Hu et al., 2006; Masset et al., 2006). The third and fourth major peaks at 609 °C and from 750 to 775 °C can represent the decomposition of albite, chlorite, and carbonate-based minerals (present in the Goldex tailings, as shown in Fig. 5.6a) (Cheyrezy et al., 1995; Gualtieri and Tartaglia, 2000; Alarcon-Ruiz et al., 2005; Makó, 2007; Ion et al., 2010; Feng et al., 2012). Because the aim of the DTG analysis was to observe the variation in cementitious minerals (mainly C-S-H and CH), we did not consider the peaks at 609 or from 750 to 775 °C.

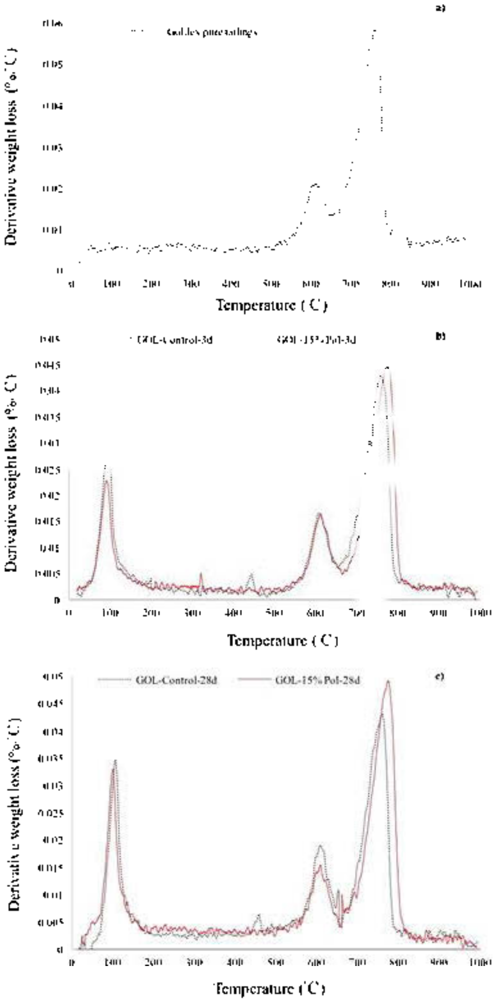

Figure 5.6- DTG curves of a) Goldex pure tailings and CPB specimens prepared with Goldex tailings at b) 3 days and c) 28 days

Fig. 5.6a shows higher derivative weight loss associated with C-S-H in the control specimen compared to the specimen with 15% polymer content (decreasing from 0.022 to 0.031), indicating more C-S-H in controls. The formation of portlandite in the control specimen appeared at approximately 440 °C. It appears that the portlandite that was formed in the specimen containing 15% polymer was replaced (at least in part) by calcium acetate ($Ca(CH_3COO)_2$), which was formed as an organic salt at 321 °C. Calcium acetate originates from the reaction of vinyl acetate with Ca++ ions during the hydration of C_2S and C_3S (Gomes et al., 2005; Low, 2014; Kang et al., 2015). This mechanism can explain the retarding influence of polymer powder on cement hydration at early ages (Gomes et al., 2005; Kang et al., 2015).

At 28 curing days, the difference in weight loss related to C-S-H between control and polymeric specimens becomes more or less similar (~0.034), which could explain why the UCS results are relatively similar. No more CH was observed in the polymeric specimen at 28 days, whereas small amounts are observed in controls. The peak C-S-H content (related to strength gaining) in the polymeric specimens was higher than that for controls (15% for GOL-Control and 45% for GOL-15% Pol specimens for 3–28 curing days), indicating a stronger retarding influence of polymer on hydration at early ages (3 days or less).

5.3.4 MIP results

MIP analysis was performed on specimens prepared with Goldex tailings at 3 curing days to observe the retarding influence of polymer powder on the pore distribution of CPB at early hydration ages. Table 5.6 presents the quantitative results at early age and Fig. 5.7 presents the pore size changes as a function of cumulative intrusion porosity for the tested specimens. Pore size distribution was characterized by total porosity (η), threshold diameter (d_{th}) and critical pore diameter (d_{cr}). The threshold diameter represents the smallest diameter of pores that are geometrically continuous, and d_{cr} represents the maximum continuous pore diameter, corresponding to the steepest slope of the cumulative porosity curve. Theoretically, these parameters are influenced by curing time and the generated hydration products: the more strength generated, the lower the values (Ouellet et al., 2007; Yilmaz et al.. 2011). Because pore sizes smaller than 0.3 μm have been associated with CPB mechanical strength (Ouellet et al., 2007), this parameter (proportion of pores greater or less than 0.3 μm) was also investigated.

Table 5.6- Quantitative results from MIP experiment at 3 days

CPB mixtures formulation	Binder content (%)	Critical pore diameter (μm)	Threshold diameter (μm)	Total porosity (%)	Porosity ≥0.3 μm	Porosity <0.3 μm
GOL-Control	4.5	1.79	2.71	42.83	35.63	7.2
GOL-15% Pol	4.5	1.81	3.31	44.98	36.18	8.77

Table 5.6 shows that the polymeric specimens have approximately 2% higher total porosity (η_{tot}) compared to controls, which can explain the lower UCS values, as found elsewhere (Ouellet et al., 2007). Accordingly, polymer powder addition increased both the threshold and critical pore diameter, indicating a coarser pore size distribution for the polymeric samples, due, at least in part, to lower generation of hydration products in these samples. Values for pore sizes <0.3 μm and ≥0.3 μm in controls are 1.57% and 0.55% less than those for the polymeric specimens, respectively. This indicates that the finer porosity associated with cementitious products is less determinant for strength development in the polymeric samples. The MIP results obtained at early age (3 days) are in a good agreement with those obtained with the DTG apparatus.

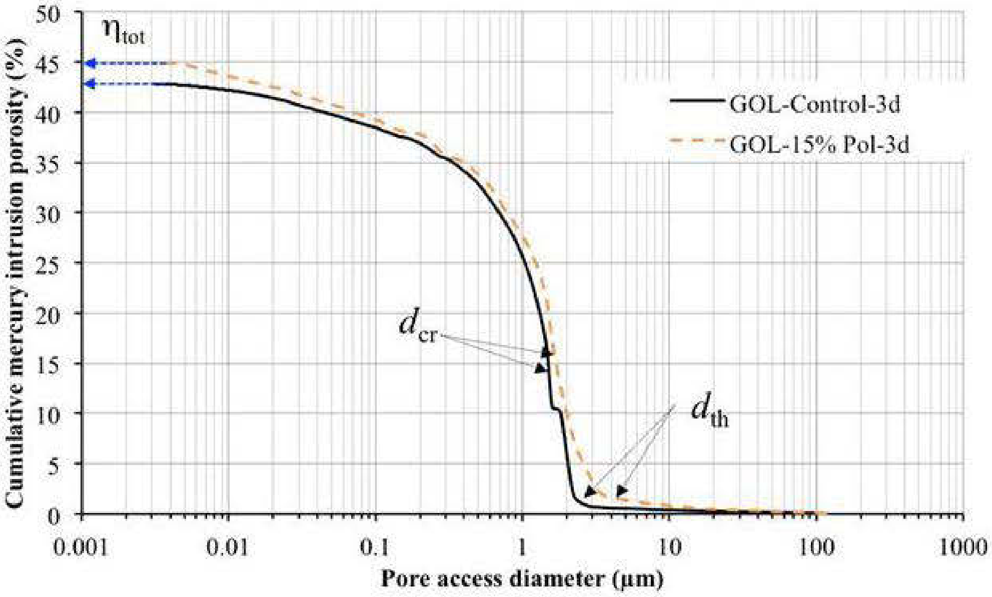

Figure 5.7- Pore size distribution curves of CPBs prepared with Goldex tailings

5.3.5 SEM results

SEM analysis was used on LA-Control and LA-15% Pol specimens (because this polymeric specimen obtained the largest UCS difference compared to control) to observe differences between the morphological and structural properties of the CPBs due to polymer addition. Similar to the UCS, MIP, and DTG results, the SEM images confirm some minor differences between control and polymeric specimens, although the SEM micrograph of the LA-15% Pol specimen at 28 days shows a slightly more compact structure (see Figs. 5.8a, 5.8b). The minor improvement in the structure of the polymeric specimen may be attributed to the improved grain adhesion resulting from the polymeric film formed within the CPB matrix (Khayat, 1998; Jenni et al., 2005). The hydrated minerals are well distributed and they encapsulate the tailings grains (Figs. 5.8c and 5.8d). Zooming on Fig. 5.8c and Fig. 5.8d (from 100 µm to 30 µm), some minor improvements can be observed in terms of hydrated mineral formation (see Fig. 5.8f and Fig. 5.8e).

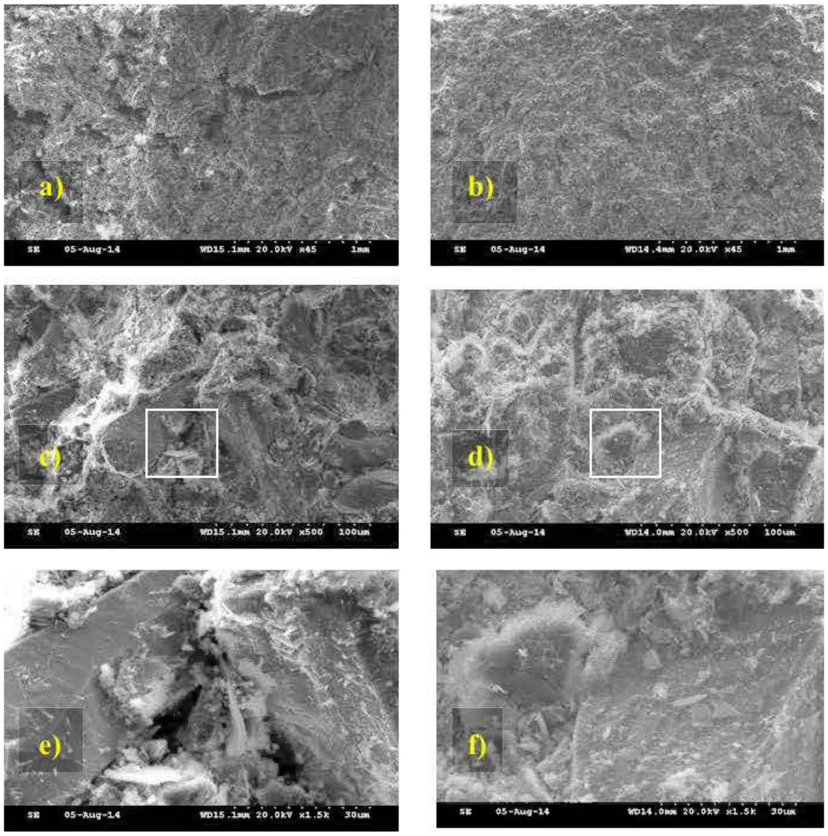

Figure 5.8- SEM images of LA-Control (a, c, e) and LA-15% Pol samples (b, d, f)

5.4 Conclusion

The results of this study demonstrate that the addition of EVA/VE polymer powder as an admixture did not noticeably influence the performance of cemented paste backfill (CPB). Moreover, the addition of polymer powder can delay cement hydration and reduce the early strength development of CPBs. The DTG analysis results indicated that the production of calcium hydroxide (CH), one of the main hydration products in CPBs, was prevented by the addition of polymer powder. Instead of CH, an organic salt (calcium acetate) was formed, probably due to the reactions of Portland cement phases (C_2S, C_3S) with vinyl acetate, which delayed the hardening process of CPB at early ages. When the polymer powder content was increased to 20%, the retarding influence was stronger at early ages. In addition, according to the UCS results, the chemical interactions between the polymer powder and the different tailings differed slightly. The UCS results indicated that polymer addition has a stronger impact on sulfidic tailings, but the explanation for this behavior remains unclear. Further studies are required to explore the chemical interactions that may take place between polymer powders and hydrated cement in the presence of different tailings. Of the different polymer contents, the addition of 15% EVA/VE polymer powder was more effective in improving the strength development of CPBs. Moreover, at later hydration ages, the positive influence of polymer powder became more evident. Further studies are needed to better understand the influence of polymer addition on the strength development of CPBs at later ages (≥28 days).

Finally, it is worth mentioning that, based on the results, the addition of EVA/VE does not influence the slump height of CPB mixtures, and a constant amount of water was consumed to reach the same slump height as that for control specimens. The main changes in water content were observed from the time of mixture preparation up to 3 days of curing, which could be attributed to the self-weight consolidation of CPB (release of water as bleeding). Furthermore, the water content changed only slightly (2%) across the different specimens during 3 to 28 curing days.

GENERAL CONCLUSION AND DISCUSSION

Due to the environmental and governmental restrictions, mining companies cannot store all the produced tailings at the surface in tailings ponds. Hence, apart from the operational expenses, cemented paste backfill (CPB) as an innovative mine tailings management could bring different advantages to the environment in comparison to the surface disposal. For example, reducing the mine reclamation, decreasing the release of acid mine drainage (AMD) originating from sulfide-rich mine tailings, and functioning as the secondary ground and mine stabilization system.

Due to the different operational and economic concerns regarding CPB material preparation and method including the high availability of water (~ 30%) and binder costs, any investigation into the new materials (admixtures) to overcome such concerns is legitimate. Since CPB is a method of waste management, the addition of expensive materials (e.g. nano-silica) even if being efficient, requires an accurate financial estimation. In order to have such estimations, all the operational and financial factors regarding backfilling plant should be considered (including direct and indirect costs). For example, if the addition of an admixture can reduce the water consumption while it can also decrease the binder consumption of CPB, on each cycle of backfilling, the CPB materials contains higher solid concentration of tailings. Hence, it may be possible to deliver some additional amount of tailings per cycle of backfilling while reducing the amount of performed work per unit of delivered material. Moreover, if the addition of an admixture results in rapid hardening of CPB (early strength development), the filling process of mine stope can be fulfilled continuously (as previously mentioned it performs in two steps including plug fill and residual fill). In addition, rapid hardening of CPB enables the miners to work and even perform new operations (e.g. blasting) around the filled stope(s) whereas in many cases it is necessary to work in other sites far from filled stopes letting the CPB materials gaining the sufficient strength. Rapid hardening of CPB in filled stopes will also decrease the pressure on the barricade since becoming a self-supportive material in a short period. This fact can also influence the design of barricade resulting in possible cost reduction. Indeed, financial estimation regarding the use of an admixture in CPB is not simply to calculate the price of admixture and compare it with the price of cement (direct costs as binder replacement). Since Portland cement by itself is not an expensive material (~200$/Ton), other than that of some wastes or by-products from other industries (e.g. sludge from paper and pulp industry, pulverized fly ash from coal combustion and etc.), it is very difficult to find a replacement for such an inexpensive material. In fact, since mine companies have to use a considerable amount of binder per year, the total cost of binder becomes so high and any small reduction in binder usage can save a considerable amount of money. The addition of cheap materials or by-products from other industries even if reduces the direct costs of binder used, will not necessarily provide either the required mechanical strength or acceptable flow consistency or both. Furthermore, the addition of large volume of such by-products in the CPB, even if improve some of their properties, may decrease the amount of delivered tailings into the stopes. Therefore, in the long term, mining companies may need to perform additional filling cycles to compensate this deficiency (indirect influence). It may be justified that the addition of a new source of waste material to the CPB is legitimate because it decreases the amount of waste storage from the surface, but CPB is already designed for this purpose while the consequences of each waste storage for the environment is not necessarily similar. Hence, the addition of a new material (admixture) in CPB should be scrutinized in large scale rather than simply comparing the direct prices of binder and admixture in use. In the best case, any admixture at small amount that can reduce the water and binder consumption, and improve the consistency of CPB is preferable.

In light of all the above-mentioned statements, this Ph.D. research examined three different additives including wood fillers, nano-silica, and polymer powders to improve and change the microstructure of CPB. The wood fillers used in this Ph.D. are considered as by-products from wood industry while nano-silica and polymer powders are considered as the commercial high-technology materials. The addition of wood fillers to CPB had some benefits to improve the compressive strength development (UCS) of CPB at later curing ages. This is interesting because wood fillers are abundant and cheap materials and can be added to the CPB mixture easily. The addition of nano-silica had an immerse influence on the microstructure change of CPB especially when used with superplasticizer. The combination of nano-silica and superplasticizer resolved multiple concerns in the case of paste backfill including early age strength development, hardening acceleration, and water consumption reduction. Addition of nano-silica with the binders containing pozzolanic materials (e.g., slag) was more beneficial since nullifying the retarding influence of such pozzolanic materials. Hence, the binder cost can be reduced (by addition of a considerable pozzolanic materials) while the target strength development can also be achieved. Addition of polymer powders did not influence the compressive strength development of CPBs containing non-sulfidic tailings. However, some compressive strength improvement was achieved with the CPBs prepared with sulfidic tailings although this achievement was not considerable in comparison to the nano-silica. Overall, the influence of both polymer powders and wood fillers were more or less similar whereas the influence of nano-silica was more effective over them.

The influence of used admixtures on mechanical strength development of CPBs was assessed through the compression test (UCS) for all the CPB mixtures. For better understanding of achieved results, some additional chemical and microstructural analyses were performed (based on the best achieved results from compression test section). In light of this, obtained results can be asserted as follows:

- Addition of 12.5 to 14.5% maple wood filler did not change the CPB's consistency (assessed via slump test) even when the amount of binder was increased up to 7%. However, as will be shown in the appendix, change in the source of wood fillers from hardwood to softwood (black spruce sawdust) changed and thickened the CPB at fresh state. Thus, different wood species have various influences over the consistency changes. It would be worthy to specify the influence of different wood species on fresh state of CPB in future trends to find the most compatible wood filler in the fresh state of cementitious materials.

- Approximately 20% UCS improvement was achieved for the CPB's containing maple wood filler at later hydration ages (91 days). However, at early ages, addition of wood fillers had negative influence on CPB's UCS achievements as a consequence of hydration delay caused by wood extractive. UCS improvement at later hydration ages can be attributed to the calcium entrapment ability of the wood fillers to establish new bonds in CPB matrix. However, more investigation is needed in the case of calcium entrapment by wood fillers especially with different wood species. For example, assessment of calcium ions in the CPB's pore water can bring more clarity to the calcium entrapment ability of wood fillers.

- Based on obtained results from this thesis, the addition of colloidal nano silica resolved the problem of early strength development especially when used with polycarboxylate superplasticizer. When the combination of TEOS/PCS was used along with the cement-slag binder, the retarding influence of slag on hydration was nullified. At 7 days of hydration, the maximum UCS improvement (~1000%) was achieved in comparison to control specimen. However, when the source of binder was changed to only cement, this improvement dropped to ~130%, which indicates the retarding influence of slag and effectiveness of proposed admixture for early strength development of CPBs containing pozzolanic materials. In this case, it would be feasible to reduce the binder price by addition of pozzolanic materials and to reduce the binder content by addition of second admixture TEOS/PCS (due to the higher effectiveness on lesser binder contents). Addition of PCS also reduced the water requirement of CPB for a specific slump height, which made the CPB materials to be prepared more conveniently.

- For better clarity, it would be interesting to use the PCS as the single admixture in CPB to differentiate the influence of each admixture separately.

- The obtained DTG results showed that the addition of nano silica increased the amount of calcium silicate hydrate (C-S-H) in the CPB mixture. Since the amount of formed CH in CPB was not considerable, the pozzolanic influence of proposed admixture was disregarded. However, more investigation is needed regarding the lacking formation of CH in CPB. The observed improvement in the amount of C-S-H can be attributed to the filling and chemically bonding influence of TEOS, in addition to the additional produce of silica gel. It would be quite interesting to investigate the influence of pure silica gel and solid form of nano silica in CPB to compare with the obtained colloidal nano silica results.

- An on-site experiment and accurate financial assessment is necessary for the validation of TEOS/PCS admixture on the real field.

- The influence of ethylene-vinyl acetate/vinyl ester (EVA/VE) admixture on CPBs was dependent on the type of tailings. Addition of 15% EVA/VE improved the UCS values of CPBs prepared with sulfidic tailings (LaRonde) from 18 to 27%. However, when the source of tailings was changed to non-sulfidic (Goldex), the polymer powder postponed the cement hydration and decreased the UCS values from 3 to 27%. Addition of EVA/VE made the fresh state of CPB mixture more homogeneous by entertaining the additional air to the mixture, although it did not influence the total consistency of the CPB.

- Since different factors such as chemistry of the existing minerals in the tailings, particle size distribution and so on influence the configuration of CPBs, it is recommendable such admixtures to be used with an inert material such as pure silica to control the exact influence of them.

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APPENDIX A

ADDITION OF DIFFERENT NATURAL AND BY-PRODUCT ADDITIVES IN CEMENTED PASTE BACKFILL

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A.1 Introduction

Cemented paste backfill (CPB) is an innovative tailings management solution that returns more than half of the produced mine tailings to the underground stopes (Benzaazoua et al., 2004). CPB is composed of filtered mill tailings (75 – 85 wt% solids) generated during mineral processing, mixed with mixing water and binding agent (2–10 wt% of dry mass of tailings) which can be Portland cements or blends of cement and mineral additives such as lime, pulverized fly ash, ground granulated blast furnace slag, and silica fume. The role of the binder is to develop cohesion within the CPB materials so the filled stope becomes self-supportive. The uniaxial compressive strength (UCS) of cemented paste backfill changes typically between 0.2 MPa and 4 MPa depending on the binder type and proportion, the mineralogy and size of tailings, and curing time (Belem and Benzaazoua, 2008).

From a geotechnical point of view, CPB is more similar to controlled low-strength material (CLSM) except that its targeted mechanical strength is optimized rather than being controlled (Belem et al., 2010). CLSM, also called 'flowable fill', is composed of water, Portland cement, pozzolanic materials (e.g. fly ash) and fine/coarse aggregates (e.g. sand). After hardening CSLM solidifies and becomes suitable for filling applications (Bouzalakos et al., 2008). Some differences between CPB and CLSM are slump height (152–254 mm for CPB and ≥ 254 mm for CLSM), water/cement ratio w/c (≥ 3 for CPB and ≤ 3 for CLSM) and upper limit strength of 8 MPa for CLSM and ≤ 5 MPa for CPB (Belem et al., 2010). In addition, CSLM is standardized (ACI, 1994) and has a lower limit strength of 1.4 MPa (200 psi) at 28 days curing time, unlike the CPB which is neither standardized nor has a lower limit strength. Moreover, while the sulfate attack is a phenomenon in CPB containing sulfide rich tailings, that is not the case in CLSM (Belem et al., 2010).

The use of fibres/fillers to strengthen different composite materials, which are much weaker in tension than in compression, goes back to ancient times (Bentur and Mindess, 2007). Fibres can be classified in different categories including glass fibres, carbon fibres, aramid fibres, natural fibres, boron fibres, and ceramic fibres (Mallick, 2008). Basically, fibres/fillers act in a number of mechanisms through the cementitious materials such as chemical interaction with hydration process, adsorption onto cement particle surfaces, modification of surface tension of the water, modification of the rheology of the mixture and introduction of special chemicals into the hardened cementitious matrices (Newman and Choo, 2003).

To reinforce cementitious materials, natural fibres/fillers are attractive because of being abundant. Also, reuse of natural fibres as the reinforcing agents in cementitious materials can lead directly to energy savings, conservation of scarce resources and reduction in environmental pollution (Sudin and Swamy, 2006). Natural fibres are generally classified in the literature as being derived from plant, animal or mineral sources. All plant fibres are composed of cellulose while animal fibres consist of proteins (hair, silk, and wool). Plant fibres can be derived from different parts of a plant such as the base (stem), leaf, seed, fruit, cereal, and straw or different sources such as wood fibres or grass fibres. Mineral fibres are naturally occurring fibres such as asbestos (Chand and Fahim, 2008).

Another general term used for natural fibres is lignocellulose fibres (Pickering, 2008). Wood fibres usually obtains from two different sources including round wood (debarked wood, logging residues and thinning) and industrial wood residues (sawdust, shavings, offcuts and slabs) (Xu et al., 2008). These fibres are relatively short and rigid, but are usually strong and effective during long ageing in the cementitious materials (Bentur and Mindess, 1990). Basically, wood is composed of cellulose (40-50%), lignin (16-33%), hemicelluloses (15-25%), and extractives (5-10%) from cellular structure (Coutts and Warden, 1990).

There are a number of studies which investigated the effects of adding different natural fibres to cementitious composites (Coutts and Campbell, 1979; Coutts and Kightly, 1984; Coutts and Warden, 1990; Blankenhorn et al., 2001; Bilba et al., 2003; Coutts, 2005; Ghavami, 2005; Lima et al., 2008; Joaquim et al., 2009; Pacheco-Torgal and Jalali, 2011). However, none of which investigated the influence of natural fibres additives on CPBs. There are some reasons to add natural fibres to CPB materials including possible binder replacement, reducing environmental pollution by putting another source of waste (lignocellulose fillers) to underground stopes, and mechanical strength improvement. Since CPB should be pumped to underground mine stopes via pumping or gravity it should contain enough water. Hence, apart from the residual water contained in the filtered tailings, it's always necessary to add extra water for the mixing and transport processes. The total amount of water is in excess regarding the amount of water needed for cement hydration thus has a negative effect on the strength development of CPB.

Since being hydrophilic materials containing hydroxyl group (Azwa et al., 2013), natural fibres/fillers can absorb/retain water within the CPB mixture which will in turn change the binder hydration process. While in some composite materials (e.g. wood plastic) the hydrophilic nature of natural fibres is a negative point, in the case of CPB it may influence the properties of material positively. The aim of this study is to investigate the possibility of lignocellulose fillers (sawdust, powdered bark, and paper sludge) as the reinforcing and water collecting in CPB resulting in possible mechanical strength improvement.

A.2 Materials and methods

All the materials used in this research including natural fillers (black spruce sawdust, black spruce powdered bark, and paper and pulp sludge), filtered mill tailings, mixing water (tap water) and a blended binder (ordinary Portland cement and slag). The mains analyses performed in this research including uniaxial compressive strength (UCS) and natural fillers sensitivity to water.

A.2.1 Natural fillers and tailings

Three sources of natural fillers were used in this study including powdered black spruce bark, deinked pulp and paper sludge and black spruce sawdust. The procedure of fillers preparation includes laboratory drying at 100°C for 24 hours followed by homogenization and powdering in a hammer mill up to 0.2 mm (for black spruce bark and black spruce wood fillers). It is assumed that the similarity between fillers size and tailings grains brings more homogeneity in final CPB mixture. Sludge, on the other hand, originates from mechanical processing in paper and pulp industry and it is already in the powdered form.

Black spruce bark extractives are by-product of lumber production (Ngueho Yemele et al., 2008) that is supplied by Tembec Inc. sawmill at La Sarre, Quebec. The bark extractives were taken directly from the debarking units in each mill. Black spruce sawdust is also by-product of Tembec Inc. sawmill from the same origin of black spruce bark. Paper sludge used in this study was deinked paper sludge obtained from a recycling paper mill of Cascades group, Kingsey Falls in Quebec. It should be noted that in fact paper sludge is not a natural fibre/filler by itself but it mainly consists of cellulose, lignin, hemicellulose and substantial amounts of ash. Table A.1 and Table A.2 present the physical properties and chemical compositions of used fillers in this study.

Table A.1- Physical properties of used fillers

Filler type	Relative density of cell wall	Specific surface area (m^2/g)
Powdered bark	1.45	0.28
Sawdust	1.48	1.1
Deinked paper sludge	1.98	0.17

Table A.2- Chemical compositions of used fillers

Fibre type	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Ash (%)
Bark	26.8	43.1*	25.1	1.8
Wood fibre	51.1	20.6	27.3	1
Paper sludge	46	8.5	13.8	51.1

*Includes hemicellulose and partially cellulose (holocellulose)

The tailings used in this study were obtained from Perseverance Mine in Mattagami (Xstrata Zinc) in Quebec. The relative density and specific surface of used tailings were calculated 3.65 and 5.27 m^2/g respectively. Table A.3 summarizes the elemental analysis (ICP test) properties and Table A.4 shows the physical characterizations of used tailings in this study.

Table A.3- Elemental compositions of tailings

Elemental composition	Amount (% w/w)
Al	2.06
As	0.009
Ba	0.001
Ca	0.419
Cd	0.002
Co	0.017
Cr	0.001
Cu	0.061
Fe	38.8
Mg	4.07
Mn	0.076
Ni	0.001
Pb	0.025
Ti	0.079
Zn	0.766
S	17.9

Table A.4- Particle size distribution of used tailings

Parameters	Value	Units
Cu = D60/D10	9.36	(-)
Cc = $D30^2/(D60*D10)$	1.08	(-)
U = (D90-D10)/D50	4.15	(-)
D10	3.23	(μm)
D20	6.37	(μm)
D30	10.29	(μm)
D40	15.42	(μm)
D50	21.92	(μm)
D60	30.24	(μm)
D70	41.36	(μm)
D80	57.78	(μm)
D90	94.18	(μm)
%fines (d<20μm)	48	%

A.2.2 Binding agent and mixing water

The binder type used is a blend of 20% general use Portland cement (GU) and 80% blast furnace slag provided by Lafarge. This combination of binder for CPB is asserted as an effective formulation in different studies (Belem, Benzaazoua et al. 2000, Benzaazoua, Belem et al. 2002, Benzaazoua, Fall et al. 2004, Belem and Benzaazoua 2008). Different binder contents are calculated based on dry mass of tailings. Tap water was used for the preparation of all the mixtures.

A.2.3 Natural fillers sensitivity to water

Since lignocellulose based fillers have the capability to absorb the water, and since the water availability in CPB mixture is high, it is essential that the water absorption of fillers be calculated. By decreasing the size of lignocellulose fillers, the capability of water absorption becomes more predominant because of increase in the specific surface of fillers (Govin 2004).

In order to monitor the role of water absorption of maple wood sawdust, screens with different mesh sizes (0.7-8) were used. Accumulated wood particles in eleven sizes then were immersed in water for 24 hours while the mass of particles was recorded before and after submersion.

A.2.4 Mix proportioning and CPB mixture preparation

CPB mixtures were prepared by mixing lignocellulose fillers, tailings, binder, and tap water together. For each set of specimens, a control sample (without filler) was also prepared for comparison. Afterwards, prepared CPBs are poured in plastic molds (50.8 mm diameter and 101.6 mm height) and left in a humidity chamber for two curing times (14 and 28 days) at 23°C and 90% relative humidity.

The amount of filler content was calculated based on i) 10% binder replacement (only for maple sawdust formulation), ii) 12% of binder content. The binder contents (mass of binder/mass of dry tailings) were 1, 2, 4.5 and 7 wt%. The solid mass concentration (mass of solid/total mass) of the mixtures varies between 73% and 82%. It should be noted that there is an approximate relationship between the solid concentration and the CPB consistency measured through the slump height. Table A.5 summarized the experimental program.

Table A.5- Experimental program specifications

Filler type	Filler content	Binder content	Solid content	Curing time (day)
Sawdust	0, 10	1, 2, 4.5, 7	82	14, 28
Bark	0, 12	2, 4.5, 7	75	28
Sludge	0, 12	2, 4.5, 7	73	28

A.2.5 CPB consistency measurements

In order to understand the influence of different admixtures on the flowability (consistency) of CPBs, slump height measurement was calculated by using a small Abrams cone. The steel slump cone was placed on a solid, impermeable, level base and filled with the fresh CPB in three steps (layer). On each step by using a steel rod, the placed CPB in the cone homogenizes with thuds. The third layer should fill the cone entirely and represents the top of the CPB. Then, the filled cone carefully lifts up, leaving a heap of CPB that settles or 'slumps' slightly. The upturned slump cone was placed on the base to act as a reference, and the difference in level between its top and the top of the CPB was measured and recorded to the nearest 5 mm to give the slump of the CPB (Fig. A.1).

The slump was generally found to increase proportionally with the water content of CPB mixture, and thus expects to be inversely related to CPB strength. The slump height measurement was used to monitor the change in CPB consistency due to lignocellulose fibres addition.

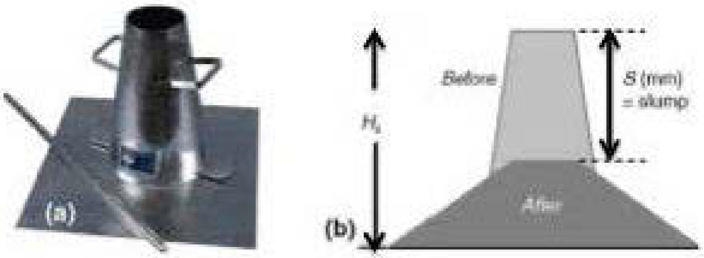


Figure A.1- a) slump cone mold, b) schematic view of the slump test
(from Belem and Benzaazoua, 2008)

A.2.6 Uniaxial compression tests

A low capacity universal mechanical press MTS 10/GL with a maximum loading capacity of 50 kN with a minimum deformation rate is 0.0001 mm/min and displacement rate of 1 mm/min is used in this study to evaluate the uniaxial compressive strength (UCS) of specimens at each curing time. In UCS analysis, any CPB sample placed between two platens of the machine while applying an axial force upon the sample break. The stress corresponding to the force at failure is the uniaxial compressive strength. A pressure cell measures the applied force to the sample while a magnetic induction displacement sensor measures the displacement. The accuracy of the force measurement is about 1%. The shape factor (height-to-diameter ratio) of the CPB specimens was 2.

A.3 Results and discussion

A.3.1 Sawdust water retention capacities

Table A.6 displays the water absorption capability of the wood fillers in different sizes while Fig. A.2 illustrates the graphical changes of Table A.6. As can be seen from Fig. A.2, as the size of wood particle increases, the amount of water retention is reduced. In fact, as the size of wood chips increases, bundles of fibres are joined together and the process of water absorption become more difficult and requires more time. Hence, at 24 hours that the wood particles are immersed in water, wood particles with lesser size absorbed higher amount of water.

Table A.6- Water absorption of wood fillers (24 hours)

Sieve opening (mm)	Mass of dry fillers (g)	Mass of saturated fillers (g)	Water content
8	6.62	14.7	122%
6.7	3.93	8.8	124%
4.75	10.49	24.2	131%
4	10.39	25.2	143%
3.35	10.08	27.2	170%
2.8	10.94	29.9	173%
2.36	7.73	21.2	174%
2	10.07	28.2	180%
1.4	17.54	52	196%
0.7	5.27	17.8	238%
Sawdust < 0.7	11.75	54.3	362%

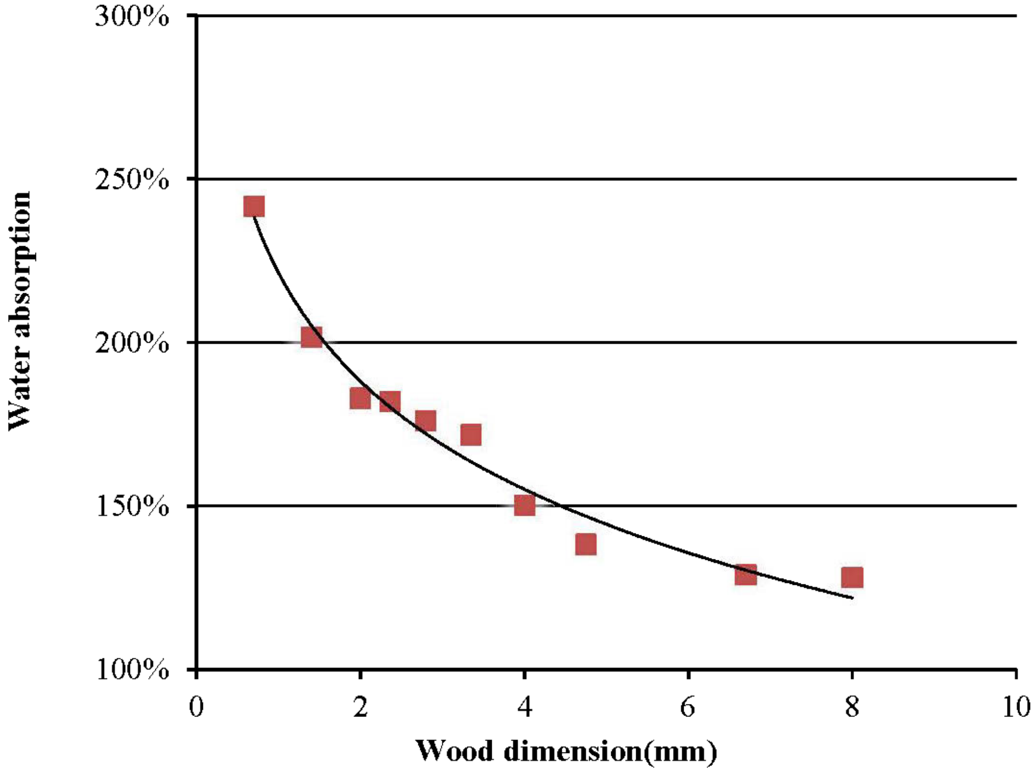


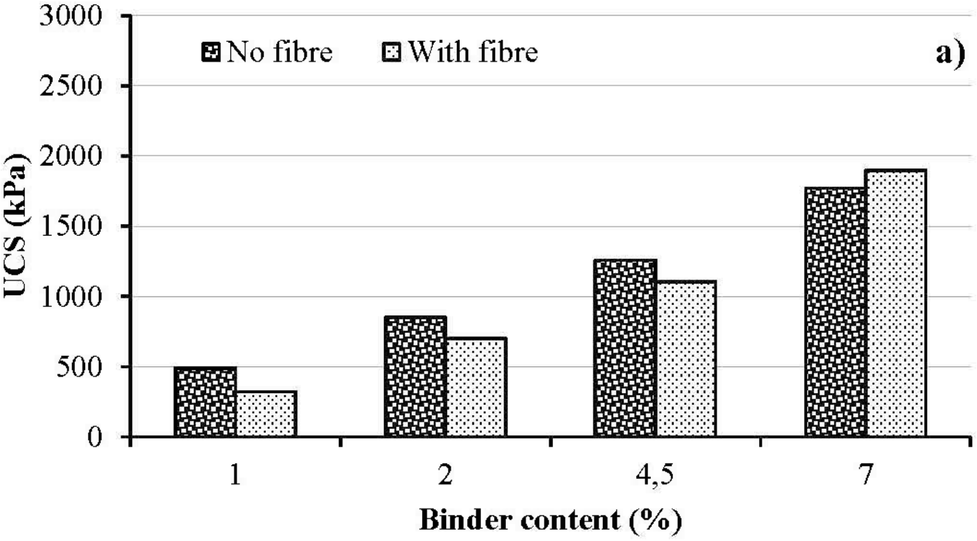
Figure A.2- Water absorption capability of wood particles

It should also be mentioned that the amount of water retention for other materials including bark and sludge is not as high as wood fibres (sawdust). For the same size of sawdust (less than 0.7 mm) and same mass (11.75 g), the mass of saturated bark increased up to 37 gr (215% water retention) while the mass of sludge materials increased up to 35.4 g (201% water retention). Bark and sludge are more hydrophobic materials in comparison to wood fibres due to a higher phenolic content in bark and high ash content of sludge. Based on the Fig. A.2, if water absorption is the main reason of lignocellulose fillers addition to CPB, the minimum size is desirable.

A.3.2 Reinforcement influence of maple sawdust

Figure A.3 shows the reinforcement influence of maple sawdust on CPBs at different binder contents and curing times (14, 28 days) in comparison to control samples.

As can be seen from Figures A.3a and A.3b, UCS values of samples with 7% binder at 28 days curing time is approximately 20% higher than that of control specimen. However, UCS values of specimens containing 1% binder is 29% lesser than that of control sample. As the amount of binder increases to 7%, the difference between UCS values of becomes more similar (7 to 9% difference) while in 7% binder content the UCS values of specimen containing maple sawdust becomes higher. It can be asserted that the addition of maple sawdust as an admixture to CPB (as a binder replacement) had negative effect for the binder contents less than 6%. This negative effect can be attributed to the incompatibility of cement hydration and sawdust while reducing the binder content will highlight the role of incompatibility.



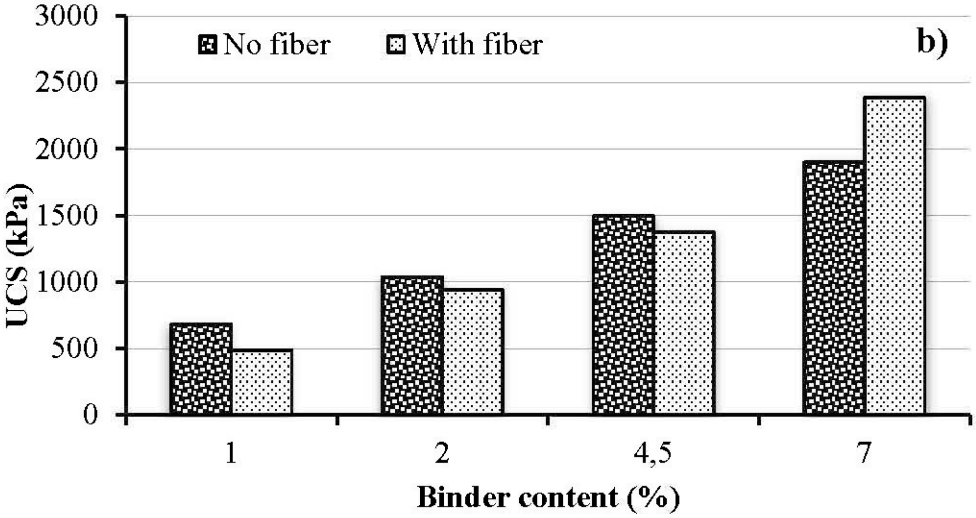


Figure A.3- UCS values of CPBs containing maple sawdust-a) 14 days b) 28 days

A.3.3 Reinforcement influence of paper sludge

Figure A.4 displays the influence of 11% addition paper sludge on UCS values of CPB specimens at 28 days of curing. In contrast to previous section, the addition of paper sludge was not as a binder replacement.

As can be seen from Fig. A.4, the positive influence of paper sludge addition to CPB appears at the binder content higher than 4.5%. The UCS improvement of CPBs containing paper sludge was more predominant at 7 % binder content (12 %). The difference in UCS changes between control samples and samples with paper sludge are less noticeable in comparison to sawdust reinforced CPB.

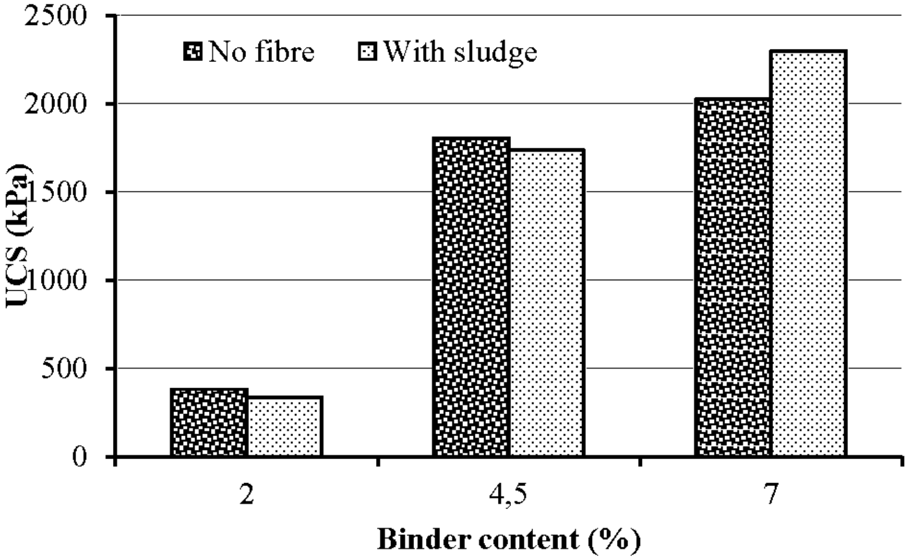


Figure A.4- UCS values of CPBs containing paper sludge-28 days

A.3.4 Reinforcement influence of powdered bark

Influence of powdered bark addition on CPB is illustrated in Fig. A.5. As can be seen from Fig. A.5, the UCS value of CPB containing bark at 4.5 % binder content is approximately higher than that of control samples (or similar). The amount of UCS improvement with a 4.5-wt% binder content was 6% while this improvement was 18% with a 7 wt% binder content.

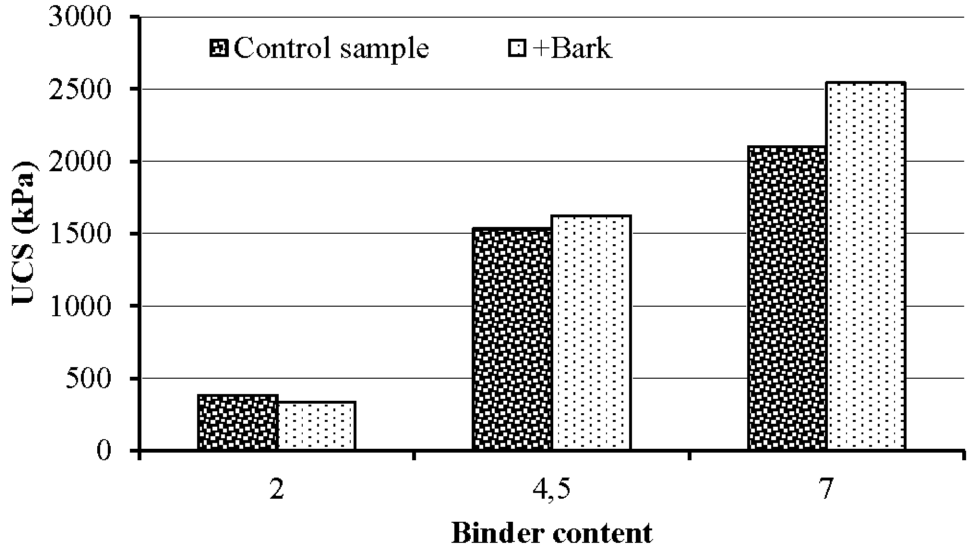


Figure A.5- UCS values of CPBs containing powdered bark-28 days

A.3.5 Effect of maple sawdust on CPB fluidity

The changes in slump height between control and specimens containing maple sawdust are shown in Fig. A.6. As can be seen from Fig. A.6, the addition of 11% sawdust thickened the CPB (drop in slump height) and this thickening becomes more evident by the addition of binder up to 7% (slump drops between 5 to 23%).

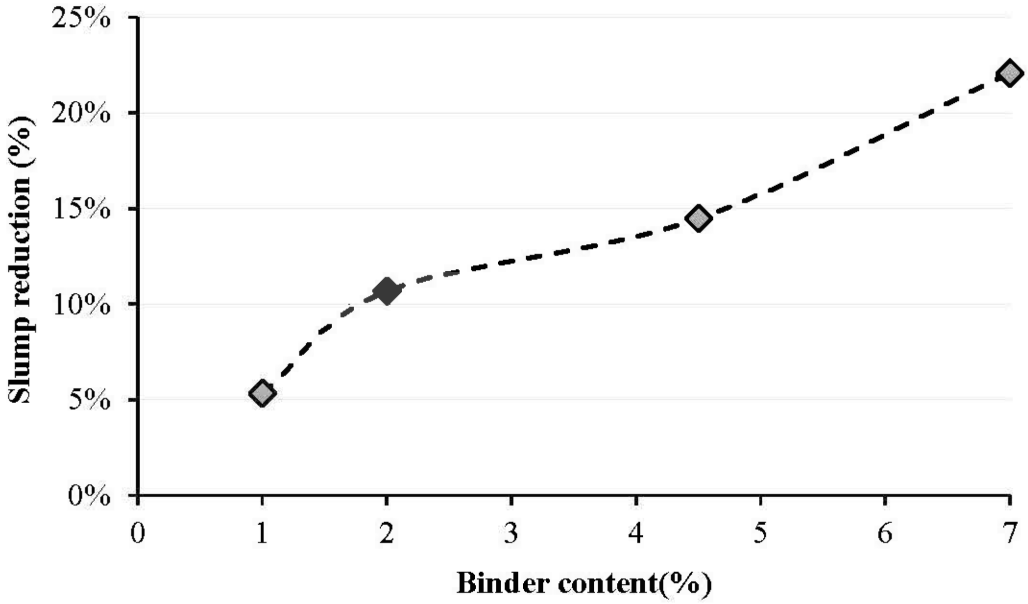


Figure A.6- Effect of maple sawdust on slump height change

A.3.6 Effect of paper sludge on CPB fluidity

Paper sludge also changed the consistency of CPB materials as can be seen from Fig. A.7. In comparison to control sample, slump height of specimens containing 11% sludge (by mass of binder) decreased from 4% to 20% when the binder content increased from 2% to 7%.

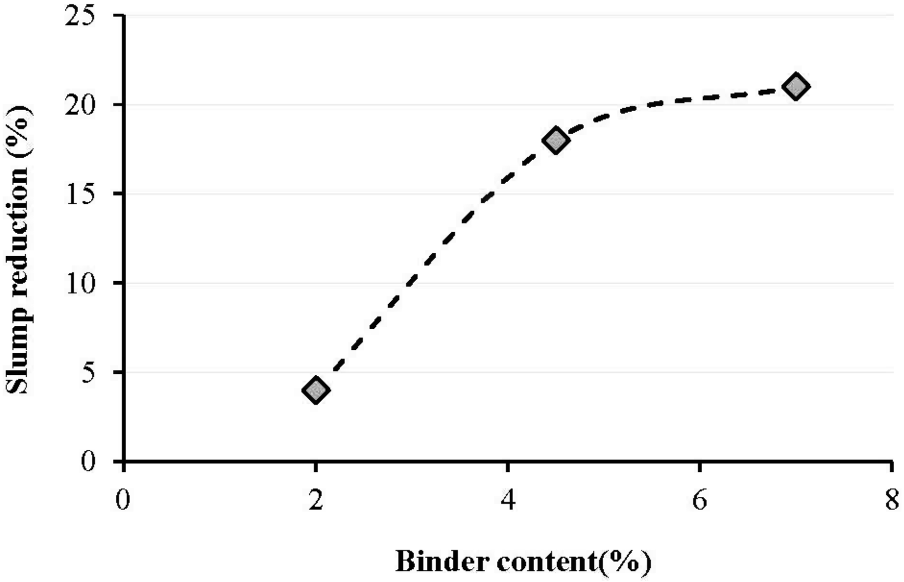


Figure A.7- Effect of paper sludge on slump height change

A.3.7 Effect of powdered bark on CPB fluidity

Since bark mainly is a hydrophobic material (Borgin et al, 1974), its addition to CPB did not noticeably affect the consistency. Fig. A.8 shows the slump height changes of CPBs by addition of 11% powdered bark at different binder contents. Maximum slump drop (6%) occurred at 7% binder content. The difference between maximum slump reduction (7% binder content) and minimum slump reduction (4.5% binder content) is approximately 3 percent and at this condition the measurement of slump height was difficult.

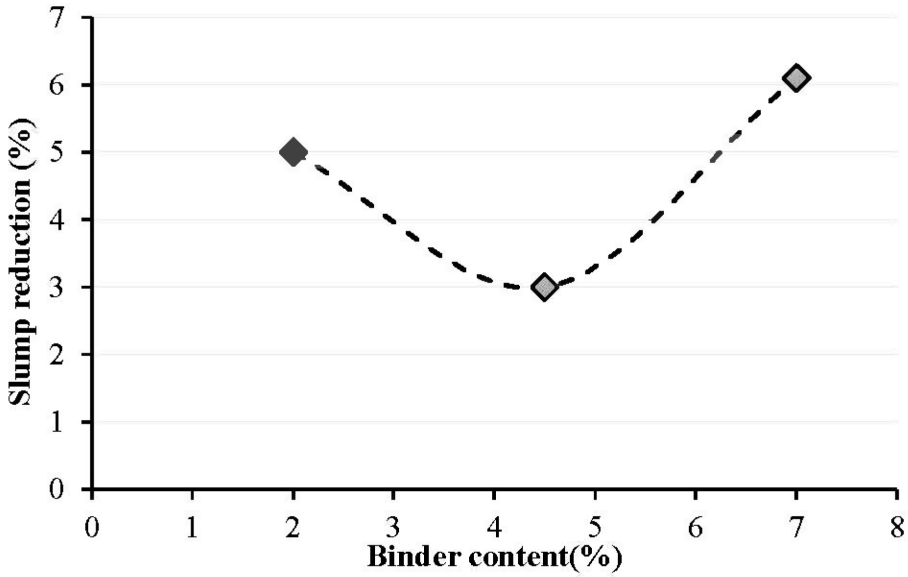


Figure A.8- Effect of powdered bark addition on slump height changes

A.4 Conclusion

This paper investigated the results of different lignocellulose fillers addition on CPB materials. Based on obtained results, used fillers have potential to reinforce CPB. Water retention is not the only factor that affects the mechanical properties of CPBs; chemical interactions play also an important role. Indeed, powdered bark retained the minimum amount of water in CPB while it brought the maximum UCS to the fibrous CPBs.

The use of different tailings for obtaining more comprehensive behavior of fibres in CPB materials is also needed. In addition, it should be investigated if the role of fibres in CPB materials (water retention or adding new chemicals) can be as the binder replacement or not.

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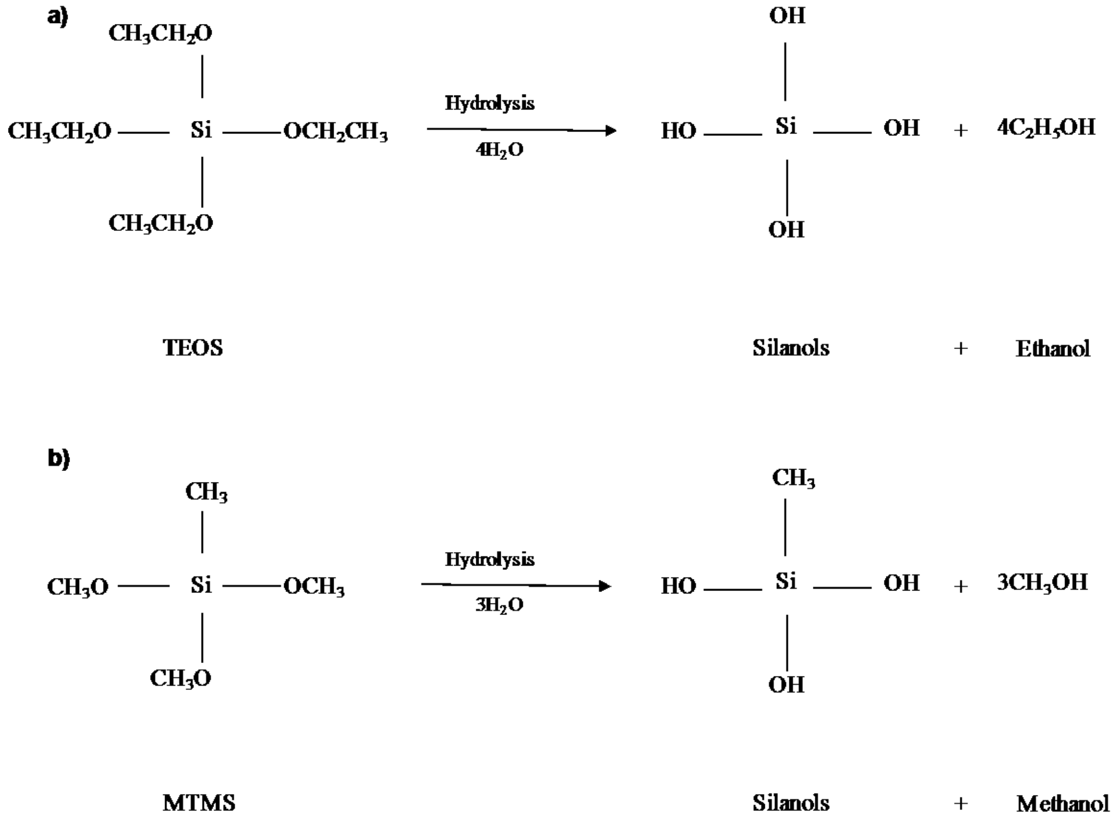
Appendix B

INFLUENCE OF METHYL-SILANE ON DIFFERENT PROPERTIES OF CEMENTED PASTE BACKFILL CONTAINING NANO SILICA

B.1 Introduction

Use of nano-particles in cementitious materials received special attention due to the high stability and sustainability achievements (Sobolev and Gutiérrez, 2005). Nano-silica (NS) is a pozzolanic material that in the case of cementitious materials can accelerate the hydration of cement while filling the nano pores and gaps between the aggregates and cement particles making the total structure more dense and compact (Ji, 2005; Senff et al., 2009; Kong et al., 2012; Hou et al., 2013; Singh et al., 2013). Due to the high pozzolanic reactivity and high specific surface of nano-silica, NS reacts with calcium hydroxide (CH) crystals to form calcium silicate hydrate (C-S-H) gel (Ji 2005, Qing, Zenan et al. 2006, Qing, Zenan et al. 2007, Tobón, Payá et al. 2012) and it reaches the maximum pozzolanic influence so rapidly resulting in strength development at early ages (Flores-Vivian, Pradoto et al. , Abd El Aleem, Heikal et al. 2014). However, nano-particles are extremely susceptible to agglomeration; hence, the addition of any complementary materials (chemicals) that can facilitate the dispersion of which and or use of nano-particles in colloidal form may decrease the agglomeration (Thomas, Jennings et al. 2009, Lin, Akil et al. 2011). In the presence of water, tetraethyl-orthosilicate (TEOS), as the precursor for the produce of nano-silica, hydrolyzes and converts to inorganic solid (silica gel) via inorganic polymerization (condensation); this reaction is called sol-gel process (Sobolev, Flores et al. 2006, Niederberger and Pinna 2009). Chemical reaction of TEOS is plotted in figure 8.1a.

The use of organic admixtures in cementitious materials can influence the hydration of cement and the mechanical performance of final product (Raki, Beaudoin et al. 2010). As a monomeric silicon-based molecule, silane-coupling agents composed of four constituents and organosilanes carrying two different reactive groups including at least one bonded carbon atom. As an organosilane, methyl-trimethoxy silane (MTMS) consists of a non-hydrolysable methyl group covalently bonded to silicon and three hydrolysable methoxy groups; MTMS is broadly used as a co-precursor with TEOS (Matsuda, Matsuno et al. 1998, Venkateswara Rao, Kulkarni et al. 2003, Smitha, Shajesh et al. 2007). In the presence of water, methyl-trimethoxy silane (MTMS) hydrolyzes and forms a highly reactive silanol (SiOH) networks (Fig. B.1b) that can react with hydroxyls (-OH) at the surface of hydrolyzed TEOS (silanols) (Fig. B.1a) and the subsequent condensation reaction results in siloxane (Si-O-Si) covalent bond formation between TEOS and MTMS (Fig. B.1c). Therefore, a highly dispersed and homogeneous system of organic-inorganic phase (three-dimensional silica network) can be formed (Cornelius, Hibshman et al. 2001, Venkateswara Rao, Kulkarni et al. 2003, Švegl, Šuput-Strupi et al. 2008, Hermanson 2010, Klein and Jitianu 2010).



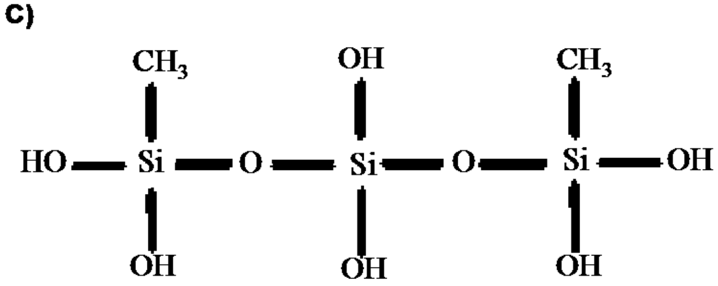


Figure B.1- Hydrolysis of TEOS (a), hydrolysis of MTMS (b), condensation of TEOS-MTMS (c)

Due to the chemical bonding ability between MTMS and NS, grafted organic group of organosilane (methyl in this case) can prevent the agglomeration of nano-particles (because of steric repulsion) (Chen, Zhou et al. 2005). Such linkages also decrease the tendency of the structural phase separation (Wojcik and Klein 1995) while improving the mechanical strength development of cementitious materials (Smitha, Shajesh et al. 2007).

Calcium silicate hydrate (C-S-H) is the major product of cement hydration (50-70% by mass) and is produced from the hydration of dicalcium silicate (C_2S) and tricalcium silicate (C_3S) (Franceschini, Abramson et al. 2007, Beaudoin, Dramé et al. 2009). It consists of a semi-crystalline phase and is responsible for the primary strength developing of cementitious materials (Stepkowska, Blanes et al. 2005, Franceschini, Abramson et al. 2007). It is asserted that C-S-H forms a nano-sized layered crystal with a structure similar to tobermorite. The addition of MTMS and the co-precipitations of its organic part (methyl) into the interlayer of C-S-H, can also covalently bond with the inorganic part of C-S-H via Si-C bond (Minet, Abramson et al. 2006, Raki, Beaudoin et al. 2010). The produced nano structure silica gel from the hydrolysis of TEOS can chemically bond and fill the nano-pores of C-S-H (Geffers, Barralet et al. 2015).

Cemented paste backfill (CPB) is an innovative mine tailings management technology that can return half of the produced tailings stream from mineral processing plant to the underground stopes and voids for secondary ground support and minimizing environmental impact (reducing the amount of waste storage at the surface) (Benzaazoua, Fall et al. 2004, Koohestani, Belem et al. 2013). CPB consists of filtered mill tailings (75 – 85 wt% solids), water (15 – 28%), and a binding agent such as cement (2–10 wt% of the dry mass of tailings) (Benzaazoua, Fall et al. 2004, Coussy, Benzaazoua et al. 2011, Koohestani, Belem et al. 2013). Hardened CPB generally has a low uniaxial compressive strength (UCS ~ 0.2 – 4 MPa), depending on the type of binding agent(s), tailings grain size distribution, and mineralogy of the tailings (Belem and Benzaazoua 2008, Yilmaz, Benzaazoua et al. 2009, Yilmaz, Belem et al. 2011, Yılmaz, Ercikdi et al. 2014). Since being delivered via pumping or gravity, CPB materials should have an acceptable consistency in order not to block or stick in the pipelines. Hence, if being necessary, additional water may be added to the CPB to make it sufficiently flowable. However, the addition of water increases the water to cement ratio that negatively influences the mechanical strength of CPB (typically water/cement ≥ 3) (Belem, Fourie et al. 2010).

To our knowledge, there is no published data regarding the influence of MTMS on the properties of CPB containing NS. Hence, this study attempts to investigate the use of methyl-trimethoxy silane along with tetraethyl orthosilicate. It is assumed that the addition of MTMS can facilitate the dispersion of NS resulting in higher strength development while decreasing the water consumption of CPB. In addition, lesser water consumption in CPB reduces the water run-off from the filled stopes resulting in lesser consolidation and bleeding. Moreover, high strength development of CPB as a result of admixtures (TEOS-MTMS) usage may also decrease the binder consumption. As a result of binder and water usage reduction, the amount of delivered tailings can be increased per unit of delivered CPB. Hence, in the long term, a considerable amount of operations and costs may be saved.

B.2 Materials and methods

B.2.1 Materials

Two different types of tailings (sulfidic from Laronde (G_S=3.7) and non-sulfidic from Goldex (G_S=2.6) Agnico Eagle mines backfill plants, Quebec) were used in this research. The aim was to investigate the influence of used admixtures into the properties of CPB composed of different tailings. Particle size distributions of the used tailings in this study are displayed in Fig. B.2 estimated by using a laser particle size analyzer (Malvern Mastersizer). Table B.1 shows the XRD and ICP-AES analysis of Laronde and Goldex tailings.

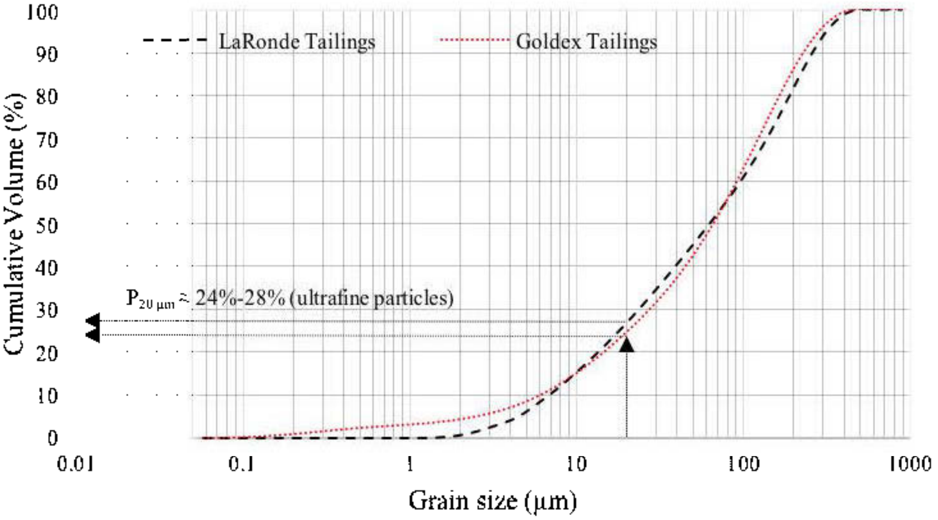


Figure B.2- Cumulative particle size distribution of Laronde and Goldex tailings

In this study, two kinds of admixtures are used including tetraethyl-orthosilicate (TEOS), as the precursor of nano-silica, and methyl-trimethoxy silane (MTMS) as the co-precursor for TEOS. Both of TEOS and MTMS are purchased from Dow Corning Inc. under the brand names XIAMETER® OFS-6697 and XIAMETER® OFS-6070 silane and their specifications are included in Table B.2 and Table B.3.

Table B.1- ICP-AES analysis and XRD quantifications of Laronde and Goldex tailings

ICP-AES analysis (%)			XRD quantification (%)		
Element	Laronde tailings	Goldex tailings	Minerals	Laronde tailings	Goldex tailings
Al	4.5	7.7	Quartz	46	18
Mg	0.36	1.4	Muscovite	9	8
Ca	0.75	3.4	Gypsum	3	-
Fe	17.9	2.2	Pyrite	26	0.7
Ti	0.03	0.04	Chlorite	8	8
Zn	0.22	-	Paragonite	6	-
S	13.8	0.2	Calcite	-	8
K	0.6	0.5	Albite	-	55
Na	0.1	3.6			

Table B.2- Properties of TEOS

Active ingredient %	Chloride content ppm	Specific gravity gr/cm^3	SiO_2 content %	Condition	Viscosity mm^2/S
>99	<10	0.93	28.7	Clear liquid	0.72

Table B.3- Properties of MTMS

Purity Wt %	Refractive index	Specific gravity gr/cm^3	Condition	Viscosity mm^2/S
95	1.37	0.95	Clear liquid	1

Lafarge Inc. provided the ordinary Portland cement general use (GU), as the single source of binder for this study. The mineralogical and physical properties of used Portland cement are included in Table 8.4 and Table 8.5. In addition, potable municipal water (tap water) was used for the preparation of all the mixtures.

Table B.4- Mineralogical compositions of cement

Minerals	Portland cement
SiO_2	20.25
Al_2O_3	5.04
Fe_2O_3	3.16
CaO	63.61
MgO	4.56

Table B.5- Physical characterizations of used binders

Binder	Specific gravity	Specific surface (m^2/g)	Particle size distribution	
			D_{10}	D_{50}
Portland cement	3.14	1.1	0.6	14.11

B.2.2 Mixture preparation and test methods

In this study, 4.5% binder content (based on mass of dry tailings) was used constantly in all the formulations. Based on the weight of used binder, 5% TEOS was constantly used for the preparation of different formulations. The addition of different amounts of MTMS (5% to 20%) was calculated based on the volume TEOS used.

The preparation of CPB mixtures was adjusted at completely saturated condition. The preparation of control mixtures starts with the mixing of tailings (Laronde and Goldex) with the binder for five minutes using kitchen aid mixer while tap water was added to reach 72.9% to 76% solid content (corresponding 74 to 84 mm slump height with Laronde and Goldex tailings respectively). It is reported that the CPB containing 72% to 76% solid concentration can be delivered properly via pumping or gravity (with the related slump height 15-25 cm when standard Abrams slump cone was used) (Clark, Vickery et al. 1995). However, since the mini slump cone (having half of the height of standard Abrams slump cone) was used in this study, it is assumed that the proper slump height of fresh CPB should approximately be half of the height of measured slump with standard slump cone.

Considered curing times specified at 3, 7, 14, and 28 days and for each curing time and formulation a set of triplicate samples were prepared and poured into cylindrical polyvinyl molds (50.8 mm diameter and 101.6 mm height) then sealed and left in a humidity chamber at 23°C and 90% relative humidity. Table B.6 shows all the prepared formulations used in this experiment.

Table B.6- CPBs formulations and specifications - Binder GU

Formulation	Binder content (%)	TEOS content (%)	MTMS content (%)	Curing time (days)	Solid content (%)	Slump height (mm)
*LA-Control	4.5	0	0	3-28	72.9	~74
LA-TEOS	4.5	5	0	3-28	72.9	~74
LA-MTMS1	4.5	5	5	3-28	73.7	~74
LA-MTMS2	4.5	5	10	3-28	73.9	~74
LA-MTMS3	4.5	5	15	3-28	74.1	~74
LA-MTMS4	4.5	5	20	3-28	74.4	~74
*GOL-Control	4.5	0	0	3-28	76	~84
GOL-MTMS	4.5	5	20	3-28	76	~96

*LA: Laronde tailings, **GOL: Goldex tailings

UCS measurements with the standard ASTM D 2166-91 were evaluated for the assessment of mechanical performance. Shape factor (height-to-diameter ratio) of the samples was 2 and a computer-controlled mechanical press (MTS10/GL) with a normal loading capacity of 50kN and a displacement rate of 1 mm/min was used. The mean value of each triplicate samples was selected as the overall outcome. Since different amounts of water added to the formulations containing admixtures prepared with Laronde tailings, the water content of each formulation was measured at each curing time to compare the changes in the amount of water consumed by cement in the presence of TEOS and MTMS admixtures. In addition, since MTMS has a water reducing influence, the amount of water reduction for the specimens containing MTMS was calculated (for the specific slump height similar to control specimen).

Differential thermogravimetric analysis (DTG) was performed to assess the effect of admixtures on mineral evolution of CPB such as minerals formed from hydration of cement such as calcium hydroxide (CH) or portlandite and calcium silicate hydrate (C-S-H) (Vieira, Cestari et al. 2004, Gomes and Ferreira 2005, Gomes, Ferreira et al. 2005, Pane and Hansen 2005, Betioli, Hoppe Filho et al. 2009). Apparatus SDT Q600 from TA instrument was used in an inert nitrogen atmosphere at a rate of 20 C°/ min up to 1000 C°. Prior to the DTG analysis, specimens were over-dried at 60 C° for 3 days.

It is generally accepted that the strength of materials is a function of shape, quantity, and distribution of the voids (O'Farrell, Wild et al. 2001). The configuration of porosity in cementitious materials basically depends on the amount of binder (changing the amount of formed products from hydration) and the time of curing (completeness of hydration) (Aligizaki 2005, Alonso, García Calvo et al. 2012). Mercury intrusion porosimetry (MIP) analysis was performed to understand the influence of admixtures on the microstructural evolution of CPB (pore size and total porosity) at early ages of hydration (3 days) by comparison with the control specimen. For MIP analysis, oven-dried CPB samples were cut into a small pellet shape with approximately 1 cm diameter. An Autopore III 9420 machine (from Micrometrics) with the ability to generate a maximum pressure of 414 MPa (60000 psi) corresponding the theoretical pore diameter of 0.003 μm was used for MIP analysis.

Fourier transform infrared spectroscopy (FTIR) was utilized to understand the effect of admixtures on chemical structure of minerals in CPB. Each spectrum comprises 200 independent scans, measured at a spectral resolution of 2 cm^{-1} within the 4,000–400 cm^{-1} range, with a Bruker Optics Tensor 27 Spectrometer and aperture set of 4 mm.

Scanning electron microscopy (SEM) analysis was also performed to observe the effect of admixtures on the microstructure and morphology of the samples. In fact, SEM observation cannot directly demonstrate the influence of nano particles on the structure of CPB instead it displays the indirect influence as the chemical and physical reactivity of admixtures within the material. A Hitachi 3500-N scanning electron microscope with the accelerating voltage 25 keV and current emission 110 μA was approximately used. The oven-dried specimens were broken and maintained untouched and then coated by carbon prior to SEM observation. The procedure of SEM analysis is explained elsewhere (Belem, Bussière et al. 2001, Deschamps, Benzaazoua et al. 2008).

B.3 Results and discussion

B.3.1 UCS results

To find the most efficient amount of methyl silane that provides the highest UCS value, 5% to 20% of MTMS (based on the weight of TEOS) were added to the CPBs prepared with Laronde tailings. All the obtained UCS results from this phase of experiment are included in Fig. 3. As can be seen from Fig. B.3, none of the specimens containing admixtures (TEOS-MTMS) are cured at 3 days in contrast to the control sample, which indicates the retarding influence of admixtures on the hydration of Portland cement in the CPBs prepared with sulfidic tailings.

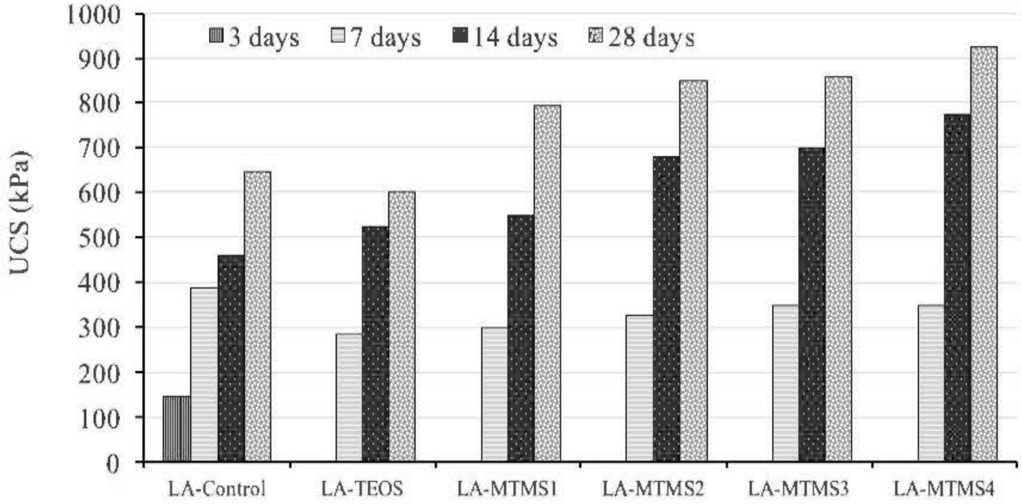


Figure B.3-UCS variations between CPBs composed of Laronde tailings

At seven days, the specimens containing admixtures had less UCS values in comparison to control sample, which again implicates the retarding influence of admixture at this curing time by affecting the strength development of CPBs. As the amount of methyl silane increased from 5% to 20%, the UCS values of specimens increased from ~280 to 350 kPa. The UCS value of LA-MTMS4 at 7 days is 10% lesser than that of control sample. The negative influence of organosilanes on early strength development and hydration of cementitious materials is reported in different studies (Švegl, Šuput-Strupi et al. 2008, Kong, Liu et al. 2015)..

At 14 days of curing, LA-TEOS and LA-MTMS1 specimens display approximately the same UCS values indicating that the addition of 5% methyl silane was insufficient to improve the UCS value at 14 days, but in comparison to control sample some improvement was achieved (~19%). The achieved UCS values of LA-MTMS2 and LA-MTMS3 specimens at 14 days are approximately similar implicating that the addition of 10% and 15% methyl silane influenced the CPB formulations similarly.

The highest UCS value at 14 days was achieved when the amount of MTMS was increased to 20%. It has to be notified that the UCS values of the specimens containing 10% to 20% of methyl silane at 14 days are higher than that of control sample at 28 days. In comparison to control sample, the UCS value of LA-MTMS4 at 14 days is ~68% higher over the control at the same curing time.

At 28 days of curing time, all the formulations containing methyl silane gained higher mechanical strength (UCS values) in comparison to control and TEOS specimens. The inefficiency of the TEOS formulation (especially at 28 days) can be attributed to the agglomeration of nano particles inside the mixture, but it requires more investigation. The UCS values of LA-MTMS2, and LA-MTMS3 at 28 days are approximately similar and LA-MTMS4 specimen obtained the highest UCS improvement among all the formulations (43% improvement in comparison to control sample).

From this part of experiment, it was found that the addition of 20% methyl-silane (based on the volume of TEOS), obtained the best mechanical strength (UCS) to the CPB specimens although the addition of organo silane retarded the early strength development. It can also be notified that the addition of TEOS only was not that efficient and even decreased the UCS value at 28 days.

In the next step of UCS experiment, the most effective amount of MTMS (20%) was used along with 5% TEOS on Goldex tailings (GOL-MTMS) to observe the efficiency of the admixtures on the non-sulfidic tailings in comparison to control sample (GOL-Control). In the preparation of CPBs with Goldex tailings the amount of water was not changed in the mixtures. The addition of 20% MTMS however increased the slump height of GOL-MTMS up to 14% in comparison to GOL-Control. The compositions and specifications of these formulations are mentioned in

Table B.6 and the obtained UCS results from this phase of UCS experiment are presented in Fig. B.4.

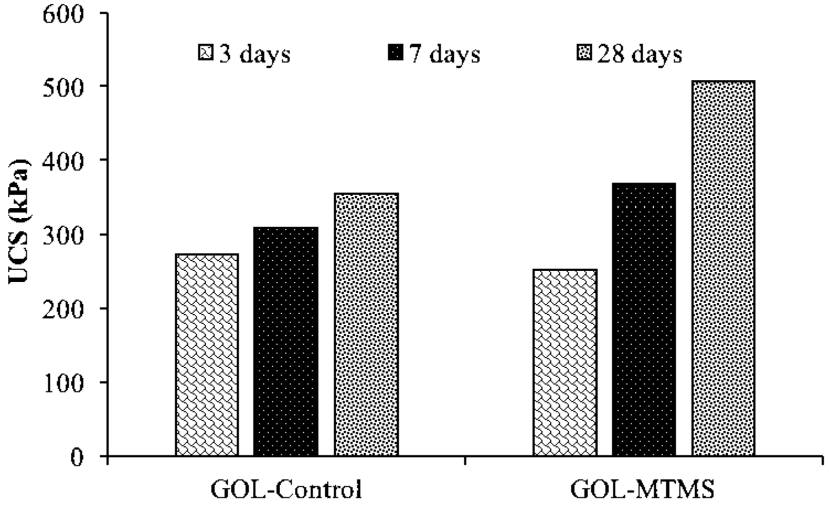


Figure B.4-UCS variations between CPBs prepared with Goldex tailings

As can be seen from Fig. B.4, the addition of admixtures hindered the early strength development of CPB at 3 days by decreasing the UCS value (~10%) of GOL-MTMS specimen in comparison to GOL-Control. At 7 days of curing, the UCS achievement of GOL-MTMS specimen was approximately similar to than that of GOL-Control specimen at 28 days. The retarding influence of used admixtures in CPBs prepared with non-sulfidic tailings was nullified after 3 days whereas in CPBs prepared with sulfidic tailings lasted up to 14 days. The strength development of GOL-MTMS specimen at 28 days was approximately 42% higher over the control, which is in a good agreement with the same improvement on CPBs composed of sulfidic tailings.

The obtained UCS results implicates that the retarding influence of admixtures is more central when used along with sulfidic tailings. This phenomenon is more noticeable specifically since the grain size distributions of both tailings are not very dissimilar (Fig. B.2). More investigations are required in this case to identify the chemical reactivity of different minerals in the CPBs prepared with different tailings in the presence of admixtures.

B.3.2 Water content and water consumption

Changes in the water contents of different CPBs prepared with Laronde tailings at each curing time are included in Table B.7. The maximum water loss occurred from the time of mixture preparation at completely saturated condition to 3 days of curing in control specimen from 37.2% to 31.2% (~6%). None of the specimens containing admixtures cured or hardened at 3 days in order the water content to be measured.

Table B.7- Water content of CPBs prepared with Laronde tailings

Formulation	Water content %			
	3 days	7 days	14 days	28 days
LA-Control	31.23	29.92	29.33	28.45
TEOS	N/A	31.03	29.93	29.21
MTMS1	N/A	30.55	29.94	29.02
MTMS2	N/A	30.33	28.55	27.92
MTMS3	N/A	30.29	29.01	26.53
MTMS4	N/A	30.76	27.19	26.12

As it is shown in Table B.7, the water content of control sample at 7 days is less than that of other specimens, but at 14 and 28 days the water contents of specimens containing admixtures display a minor reduction over the control. It indicates the higher rate of hydration in control sample up to 7 days whereas the hydration of the specimens containing admixtures became more noticeable after 7 days. As can be understood from this part of study the higher rate of water content differentiations occurred from the time of mixture preparation to 3 days (~6%) whereas from 3 to 28 days the water contents between different specimens approximately changed about

3%. The water loss of different CPB mixtures after 3 days was approximately similar although the specimens containing admixtures required lesser amount of water for the specified slump height (Table B.6). This emphasizes the role of self-weight consolidation on water loss from the CPB (mainly occurred up to 3 days) apart from the cement hydration role, thus CPB cannot maintain the saturation condition after ages. In this experiment some amount of water accumulated at the top of CPB specimens on the plastic moulds (bleeding influence).

Fig. B.5 displays the water dependency of the mixtures to MTMS content for the preparation of a target slump height. As can be seen from Fig. B.5, the addition of MTMS decreased the consumption of water in CPB formulations. As the amount of MTMS was increased to 20% (LA-MTMS4), a 22% reduction in the consumption of water was achieved. At this level, the solid concentration of LA-MTMS4 was increased to 74.4% (Table B.6), which displays 1.5% higher solid concentration in comparison to control sample (72.9%). As a result, higher amount of tailings can be delivered to the mine voids on each cycle of backfilling although it is minor. A high correlation coefficient (0.97) was calculated between the MTMS contents and water reduction levels for different CPB formulations prepared with Laronde tailings (Fig. B.5).

By a comparison between Table B.7 and Fig. B.5, it is evident that the specimens containing admixtures have lesser amount of water; for example, LA-MTMS4 specimen contains 22% lesser amount of water over control, but its water content differentiates with a small change (~3%) over control. This minor difference can be justified through the self-consolidation of CPBs that releases or accumulates some amount of water from CPB in the plastic mould or mine stope.

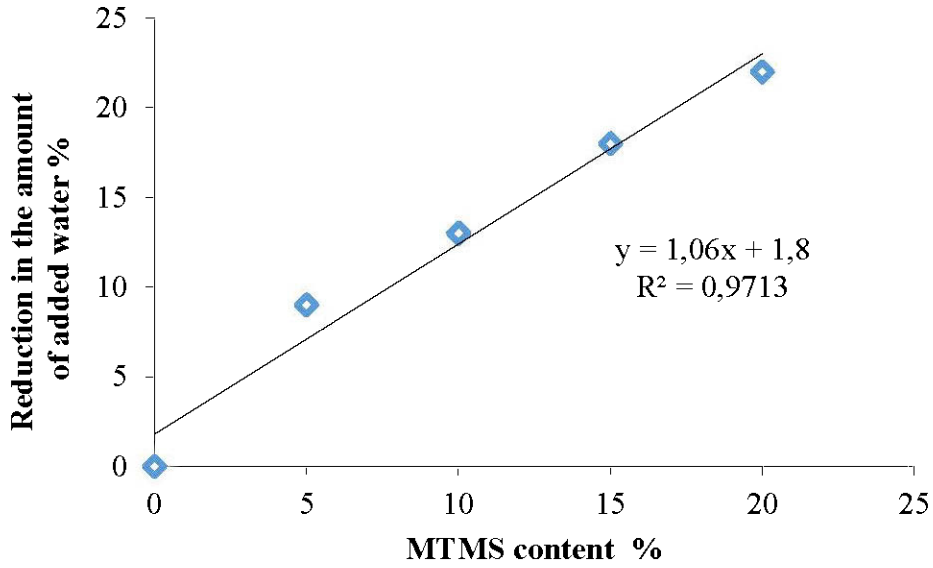


Figure B.5-Correlation between water reduction and MTMS content of sulfidic CPBs

B.3.3 DTG results

Differential thermogravimetric analysis was performed on CPB specimens prepared with Goldex tailings (GOL-Control and GOL-MTMS) at 3 and 28 days of curing time (Fig. B.6). As can be seen from Fig. B.6, there are four major peaks between the temperatures 90-95, 320-445, 609 and 750-775 °C. Generally, existing peak at the range 90 to 95 °C represents the dehydration of C-S-H phase (loss of bonded water) (Alarcon-Ruiz, Platret et al. 2005, Ouellet, Bussière et al. 2006, Cizer 2009, Heikal, Abd El Aleem et al. 2013). The second major peak between the temperatures 320 to 475 °C is generally ascribed to the decomposition of portlandite (Kamel, Sawires et al. 1972, Swamy, Prasad et al. 1979, Swamy and Prasad 1981, Jorgensen and Moyle 1982, Blgham, Schwertmann et al. 1990, Hu, Dam-Johansen et al. 2006, Masset, Poinso et al. 2006). The third major peak and fourth major peaks at 609 °C and 750-775 °C can display the decomposition of albite, chlorite, and carbonate-based minerals (present in the Goldex tailings) (Cheyrezy, Maret et al. 1995, Gualtieri and

Tartaglia 2000, Alarcon-Ruiz, Platret et al. 2005, Makó 2007, Ion, Ion et al. 2010, Feng, Provis et al. 2012). The aim of DTG analysis was to observe the C-S-H and CH variations in this study; hence we did not consider the peaks at 609 and 750-775 °C.

As can be seen from Fig. B.6a, the derivative weight loss between the control sample and specimen containing admixtures regarding the C-S-H at 3 days is minor (changing from 0.021 to 0.022), but the same weight loss in Fig. B.6b at 28 days is really noticeable (changing from 0.037 in GOL-Control to 0.047 in GOL-MTMS specimen). It can be asserted that the formation of C-S-H in control specimen at 3 days was ~5% higher than the other one, but at 28 days the C-S-H content in the sample containing admixtures became ~38% higher than that of the control. The formation of portlandite in both of the specimens at 3 days occurred at 436-442 °C (Fig. B.6a). As can be observed from Fig. B.6a, the amount of weight loss regarding the formation of CH in GOL-Control was approximately two times higher than that of GOL-MTMS changing from 0.0045 to 0.0023 respectively. This phenomenon can justify the retarding influence of admixtures on the hydration of cement at early ages by reducing the formation of CH at early ages (Gomes, Ferreira et al. 2005, Kang, Kim et al. 2015). At 28 days (Fig. B.6b) the formation of CH in GOL-MTMS specimen cannot be observed in comparison to control that may implicate the pozzolanic influence of nano silica on CH resulting in additional formation of C-S-H (Flores-Vivian, Pradoto et al. 2013, Abd El Aleem, Heikal et al. 2014).

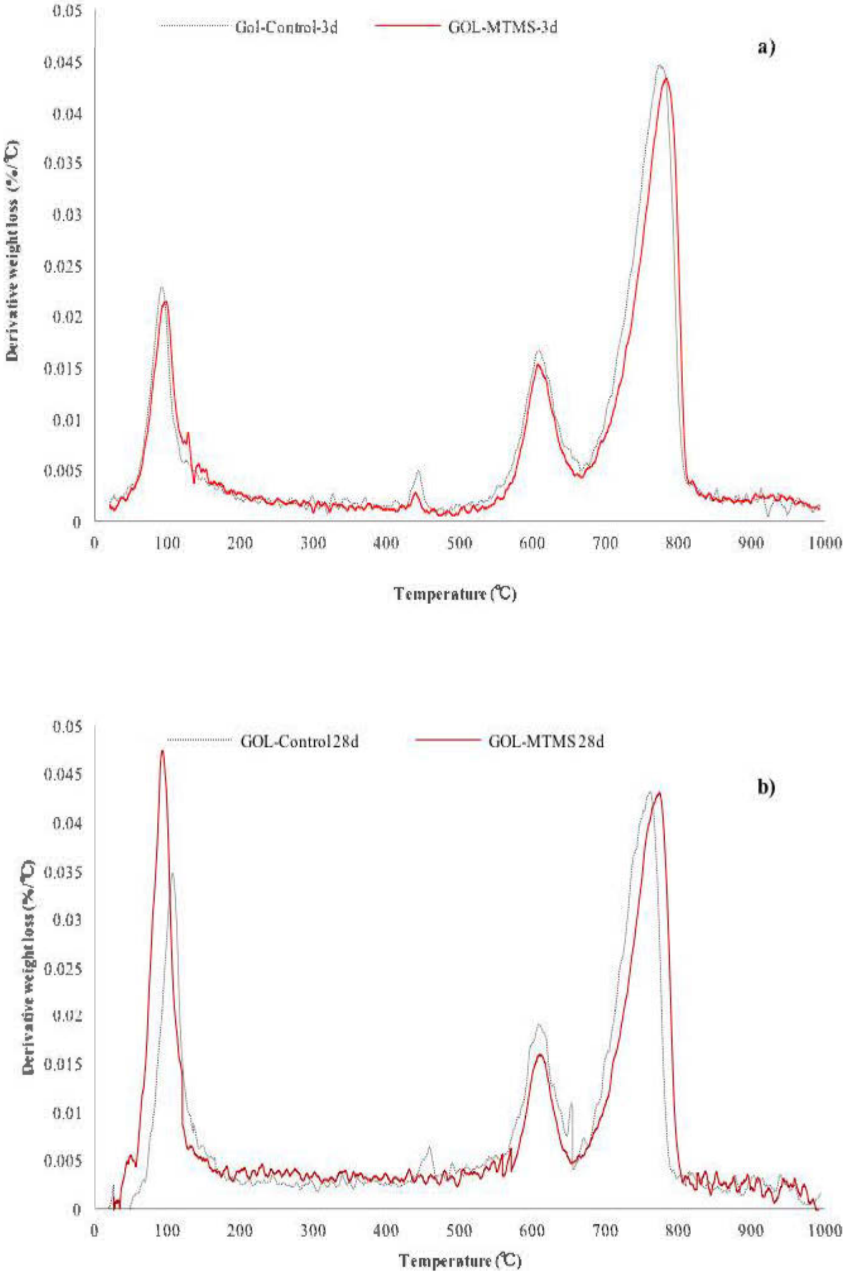


Figure B.6-DTG analysis of control and MTMS4 samples (28 days)

B.3.4 MIP results

MIP analysis was performed on the specimens prepared with Goldex tailings at 3 days of curing. Table B.8 provides the quantitative results of MIP analysis and Fig. B.7 presents the pore size changes as a function of cumulative intrusion porosity for the specimens. Basically, threshold diameter (d_{th}) and critical pore diameter (d_{cr}) represent the influence of curing time, hydration, and binder type and it is stated that any increase in the amount of binder and curing time will decrease both of which. The threshold diameter represents the smallest diameter of pores that geometrically are continuous and the d_{cr} points out the maximum continuous pore diameter corresponding to the steepest slope of the cumulative porosity curve. Both of the d_{th} and d_{cr} are great of importance since being pertinent to the maximum mercury intruded throughout the specimen (Ouellet, Bussière et al. 2007, Yilmaz, Belem et al. 2011).

Table B.8-Quantitative results from MIP experiment - 3 days

CPB mixtures formulation	Binder content (%)	Critical pore diameter (μm)	Threshold diameter (μm)	Total MIP porosity (%)
GOL-Control	4.5	1.79	2.71	42.82
GOL-MTMS	4.5	1.81	3.31	42.99

As can be seen from Table B.8, the total porosity (η_{tot}) of both the specimens are similar. This indicates that the amount of formed minerals (C-S-H) from the hydration of Portland cement affecting the porosity is similar. This is in good agreement with DTG analysis that displayed approximately similar amount of C-S-H in both specimens at 3 days. It also indicates that the amount of formed CH did not influence the total porosity either due to the minor formation (Fig. B.7a displays the amount of CH is approximately 5 times less than C-S-H) or due to the role of CH in the microstructural evolution of CPB. The function of CH on the microstructural evolution of CPB requires more investigation.

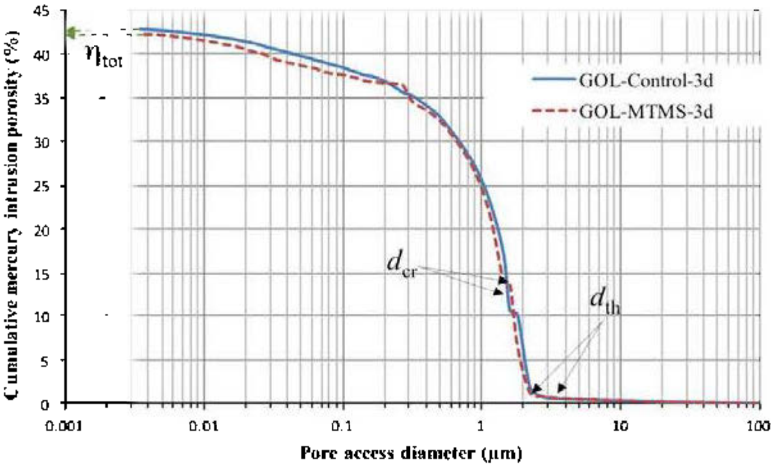


Figure B.7-Pore size distribution curves of CPBs composed of Goldex tailings-3 days

Moreover, the addition of admixtures in this study did not influence both of threshold and critical pore diameter, which implicates the similar hydration procedure and formation of pertinent minerals between the specimens. The obtained MIP results are in a good agreement with DTG achievements at 3 days.

B.3.5 FTIR results

Results of infrared spectroscopy between LA-MTMS4 and LA-Control at 28 days of curing are plotted in Fig. B.8; the spectra were traced in the range 400 to 4000 cm^{-1} (wavenumber) and the band intensities are expressed in transmittance (%T). The spectrum ranges for cementitious materials are discussed in different articles (Björnström, Martinelli et al. 2004, Stepkowska, Blanes et al. 2005, Ylmén, Jäglid et al. 2009, Heikal, Abd El Aleem et al. 2013). The peaks in the range of 3629-3425 and 1653 cm^{-1} correspond to –OH bonds in C-S-H phases and silanols (Launer 1987, Ylmén and Jäglid 2013). The only difference between the control and MTMS4 specimens in Fig. B.8, appeared at 3432 cm^{-1} that may specify the higher availability of C-S-H and silanols groups in MTMS4 specimen as the consequence of higher availability of –OH groups. The higher availability of the C-S-H in DTG and FTIR analyses are in a good agreement, which shows the positive influence of admixtures to bond with C-S-H phase. The other bands in Fig. B.8 represent the C-H bond at 2358 cm^{-1}(Barberena-Fernández, Carmona-Quiroga et al. 2015, Falchi, Zendri et al. 2015), (C-O) bond in CO_3^{-2} regarding the carbonate phase at 1869-1793, 1506, and 800 cm^{-1} (Ylmén, Jäglid et al. 2009, Ylmén and Jäglid 2013), the stretching Si-O mode pertinent to silica gel at 1118 and 1162 cm^{-1} (Barberena-Fernández, Carmona-Quiroga et al. 2015) and regarding the formation of C-S-H at 998, 526, and 428 cm^{-1} (Pajares, Martínez-Ramírez et al. 2003), and Si-O-Si bands at 695 and 471 (García Lodeiro, Macphee et al. 2009).

As can be seen from Fig. B.8, there is not a considerable difference occurred between the control and MTMS4 specimens (apart from –OH band at 3424). In fact, since the amount of added admixtures (TEOS and MTMS) in LA-MTMS4 specimen is very small, it is possible that we could not observe a noticeable distinction between the two specimens by using FTIR analysis.

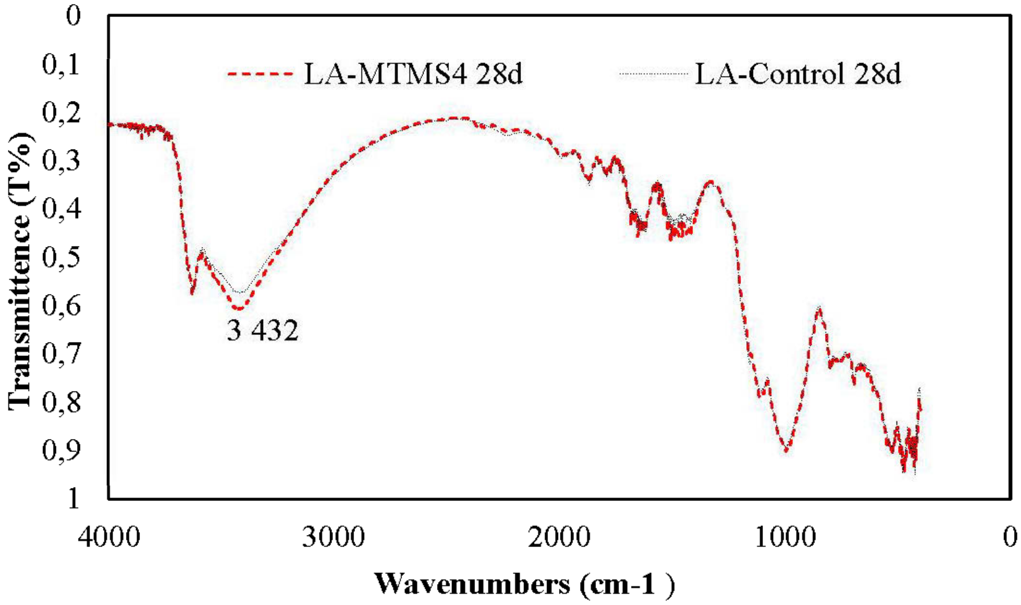


Figure B.8-FTIR spectrum of LA-Control and LA-MTMS4 samples at 28 days

B.3.6 SEM results

SEM observations were performed on LA-Control and LA-MTMS4 specimens at 28 days of curing (Fig. B.9) to observe any difference between the general microstructural views of both specimens. It is supposed that the reactivity of admixtures (TEOS-MTMS) within the CPB mixture will influence the total microstructure of material. As can be observed from Fig. B.9a, control specimen at 28 days of curing displays some discontinuities and fractures inside the CPB matrix whereas the structure of LA-MTMS4 specimen (Fig. B.9b) is more compact and dense. Provided micrographs implicate the higher fulfillment of formed minerals from the hydration of cement (as generally proved via DTG analysis). It can also be asserted that the hydrolysis and condensation of TEOS and MTMS resulted in higher physical bonding influence among particles in LA-MTMS4 specimen.

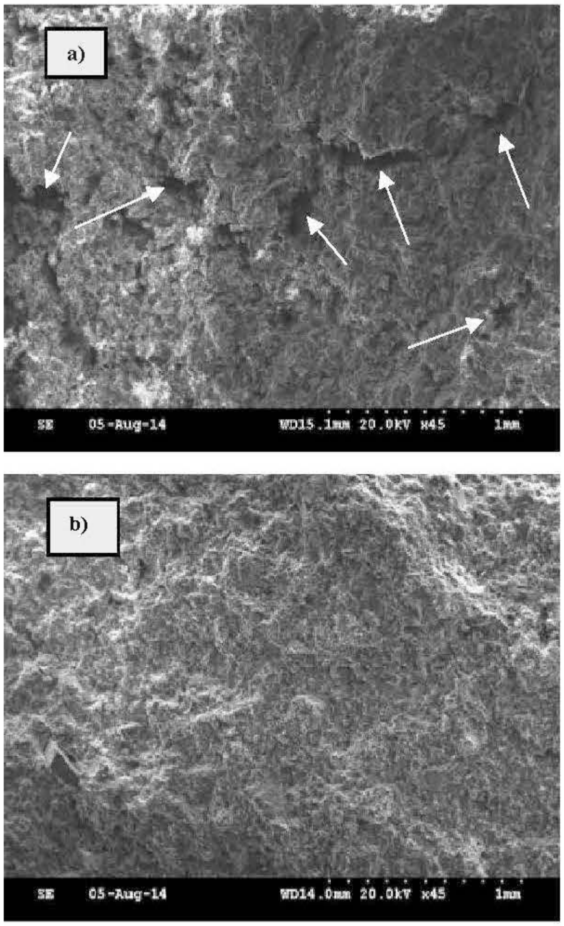


Figure B.9- SEM micrographs of control (a) and MTMS4 (b) specimens

B.4 Conclusion

In this study, the influence of methyl-trimethoxy silane along with tetraethyl-orthosilicate was examined on chemical, microstructural and mechanical properties of CPB. Based on the obtained results, the following conclusion points can be asserted:

- The addition of TEOS only did not generally improve the mechanical strength (UCS) of CPB and it retarded the hydration of cement up to 7 days. The addition of TEOS also did not influence the slump height of CPB (Table B.4) implicating there is no plasticizing effect of TEOS on CPB.

- The addition of MTMS to the specimens containing TEOS improved the UCS values (up to 43% at 28 days), but the hydration process was still postponed up to 14 days depending on the type of tailings. The addition of MTMS also reduced the water requirement of the CPB specimens for a target slump height. In this case, the higher solid concentration of the CPB specimens was achievable.
- The higher amount of C-S-H was achieved by the addition of MTMS and TEOS admixtures to the CPB formulations. This was confirmed mainly via DTG analyses.
- The FTIR analysis declared that the addition of admixtures did not create any new bonding in comparison to control sample. Since the amount of added admixtures was small (less than 1% of total solid concentration of CPB), through FTIR analysis we could not observe any significant change between specimens.
- The SEM images highlighted a higher dense and cross-linked matrix over control as a result of higher formation C-S-H and silica gel, which it was also confirmed with DTG tests.
- The influence of MTMS/TEOS admixtures was not similar on the CPBs prepared with different tailings (sulfidic and non-sulfidic). In both CPBs a reduction in early strength development was observes (as a consequence of retarding influence on hydration), but the retarding influence was more severe on the CPBs prepared with sulfidic tailings.

B.5 References

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