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Temperature dependence of the reactivity of cemented paste backfill

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A R T I C L E I N F O

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A B S T R A C T

The environmental performance of cemented paste backfill (CPB; a mixture of tailings, water and binder), which contains sulphide mineral-bearing tailings, is strongly influenced by its reactivity. However, our understanding of the reactivity of CPB under various thermal loading conditions as well as its evolution with time is limited. Hence, a laboratory investigation is conducted to study the effects of curing and ambient (atmospheric) temperatures on the reactivity of CPB. Oxygen consumption (OC) tests are conducted on CPB specimens cured at different temperatures to study their reactivity. Furthermore, microstructural analyses (e.g., x-ray diffraction (XRD), mercury intrusion porosimetry, and thermogravimetry/derivative thermogravimetry) are performed to assess the microstructural characteristics of the tested CPBs. The results show that the reactivity of CPB is temperature-dependent. As the curing temperature increases, the reactivity generally decreases. The reactivity is also affected by the ambient temperature. The reactivity increases as the atmospheric temperature increases. However, the extent of the effect of the temperature depends on the curing time and is generally more pronounced at the early ages. Furthermore, the presence of sulphate in the pore water of CPB can significantly affect the reactivity of CPB cured at high temperatures (50 °C). The findings of this study will therefore help to better assess and predict the environmental behavior of CPB under various field thermal conditions.

1. Introduction

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

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

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paste backfill (CBP)). Among these alternative techniques, cemented paste backfilling has been the most novel and promising technology for the management of mine tailings, including sulphide bearing tailings. Therefore, this technology has now become a commonly used method and extensively practiced in the mining industry worldwide. The implementation of cemented paste backfilling has several advantages, such as minimizing the amount of storage tailings on the surface of mine site, increasing mining production, controlling the oxidation of sulphides and mobilisation of metals (Alakangas et al., 2013; Yilmaz et al., 2004; Hassani et al., 2001; Hassani and Archibald, 1998).

CPB is an engineered mixture that is mainly prepared from three ingredients: mine tailings (75–85% wt.), hydraulic binder (3–7% wt.), and water (Alakangas et al., 2013; Fall et al., 2008; Yilmaz, 2010). Despite the advantages of using CPB, its environmental performance is still not well understood. In particular, the role of the geochemical reactivity of CPB in terms of its environmental behavior, durability and stability is not well known. Therefore, the reactivity of CPB should be assessed before it is placed into underground mines to avoid potential environmental and economic impacts. Cemented paste backfilling should not be a method that transfers the environmental problems of mine tailings from the surface of the ground to the underground (Ouellet et al., 2006).

Most of the previous studies on CPB have focused on its mechanical properties and economic advantages (less binder consumption and cost optimization) (e.g., Ghirian and Fall 2014; Wu et al., 2012; Fall et al., 2010; Fall and Nasir, 2010; Kesimal et al., 2005; Fall et al., 2004a,b), whereas few studies have evaluated the environmental performance of CPB by investigating its geochemical reactivity (e.g. MEM, 2006; Hamberg et al., 2015). Moreover, some studies have assessed the performance of CPBs that contains sulphide-rich tailings (e.g. Cihangir et al., 2012, 2015; Ercikdi et al., 2013, 2015; Tariq and Nehdi, 2007, Hassani et al., 2001).

The reactivity of sulphidic mine wastes can be measured by using direct and indirect techniques, such as the sulphate release, pH and the oxygen gradient methods (Cihangir et al., 2012, 2015; Ercikdi et al., 2013, 2015; Ouellet et al., 2006), respectively. Among these techniques, the oxygen consumption (OC) test is most preferred because it is simple, inexpensive, fast and accurate. Also, the OC test can be used to obtain both laboratory and field measurements. The OC test was first used in Elberling et al. (1994) and Elberling and Nicholson (1996). The concept is based on measuring the rate that sulphide minerals consume oxygen in a sealed vessel during their oxidation process (Ouellet et al., 2006). This technique was used in both the laboratory and field to quantify the reactivity of various acid generating tailings and mine rocks in several studies (e.g., Martin and Davies, 2000; Mbonimpa et al., 2002; Bussière et al., 2002; Tibble and Nicholson, 1997; Elberling and Nicholson, 1996; Nicholson et al., 1995; Elberling et al., 1994, 1993). However, only a few studies have attempted to measure the reactivity of CPB by using OC testing. Ouellet et al. (2006, 2003) performed OC testing to quantify the reactivity of CPB in both the laboratory and the field. Also, Fall et al. (2004a,b) and Pokharel (2008) used the OC method on CPB samples prepared from natural and artificial tailings with different pyrite contents to investigate their reactivity. The findings of these studies indicate that the pyrite content and degree of saturation significantly influence the reactivity of the tailings and CPB. Furthermore, all of the above studies indicated that the use of cemented paste backfilling to manage sulphide bearing tailings in underground mines could reduce their environmental impacts.

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

2. Materials and experimental program

2.1. Materials used

2.1.1. Binder

Portland cement type I (PCI) was used as the binder in the preparation of the CPB samples because in practice, it is the most commonly used binder in making paste backfill. The effect of different types of binder (e.g., PCV, Slag, Fly Ash) on the reactivity of CPB is outside of the scope of this study. The primary physical and chemical properties of PCI are presented in Table 1.

2.1.2. Tailings

Three types of tailings are used in this study. The first type is called silica tailings (ST), which are a commercially available artificial tailings material that is made of ground silica (manufactured by U.S. Silica Co.). ST are characterized by a particle-size distribution (PSD) that is similar to the average grain size distribution of tailings from nine different mines in eastern Canada. ST also mainly consist of silica (99.8% SiO_2) particles, which are considered to be a chemically inert material (Carraro et al., 2009). The reason for using ST was to minimize and/or control the potential chemical interactions with the other ingredients (e.g. cement) in the CPB mixture, and thus reduce the impact of uncertainty on the results and their interpretation. In addition to ST, two types of natural tailings, including gold tailings (GT) and zinc tailings (ZT) obtained from Canadian hard rock mines, were used. Tables 2 and 3 show the primary physical properties and mineral composition of the tailings used, respectively. The grain size distribution of the tailings (ST, GT and ZT) is presented in Fig. 1.

2.1.3. Mixing water and pyrite

Tap water was used as the mixing water. A commercial pyrite powder (FeS_2; M.W. = 119.98) was used to synthesize the pyrite-bearing tailings (or sulphide bearing tailings). This commercial pyrite has grains with a size similar to that of pyrite minerals commonly found in the natural tailings of hard rock mines. The pyrite-bearing tailings with a pyrite content of 5%, 15% and 45% wt. were prepared by mixing ST and GT with the appropriate amounts of pyrite powder. ZT with a pyrite content of 45% wt. was also prepared by mixing ZT and the applicable amount of pyrite. The physical properties of the pyrite are presented in Table 4.

Table 1
Primary physical and chemical properties of PCI.

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

SSA: Specific Surface Area.

Table 2
Primary physical properties of tailings.

Tailings	Gs	D_{10} (μm)	D_{30} (μm)	D_{50} (μm)	D_{60} (μm)	C_u	C_c
ST	2.7	1.9	9.0	22.5	31.5	16.6	1.3
ZT	3.34	1.6	10.9	29.9	37.8	23.6	2.0
GT	2.78	1.6	10.6	29.5	37.8	23.6	1.9

Table 3
Mineral composition of tailings.

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

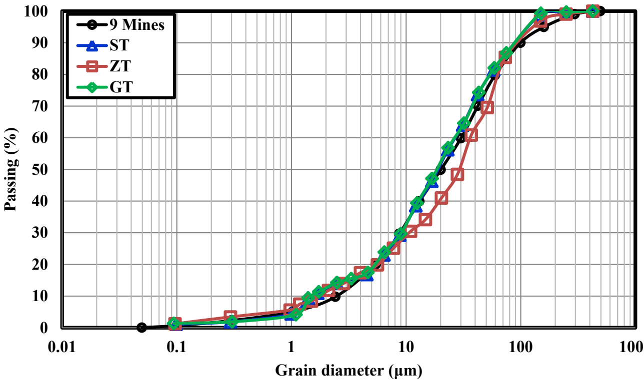


Fig. 1. Grain size distribution of tailings (ST, ZT and GT) used and average grain size distribution of tailings from nine Canadian mines.

Table 4
Physical properties of pyrite (Source: Washington Mills North Grafton, Inc.).

Bulk density (g/cm^3)	Density at 20 °C (g/cm^3)	Specific gravity	pH	Melting point
2.35	4.7	4.6	4.0 −6.0	~1193

2.2. *Specimen preparation and mix proportions*

2.2.1. *Preparation of CPB samples*

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

3. Testing of specimens

Oxygen consumption tests and microstructural analyses were performed on the studied specimens. The UCS development of CPBs cured at different times and temperature were addressed in previous studies (e.g., Fall and Pokharel, 2010).

3.1. *Oxygen consumption tests on CPB samples cured at various temperatures*

The OC tests (Elberling and Nicholson, 1996; Elberling et al., 1994) were performed at room temperature (~20 °C) on the CPB samples cured at various temperatures (2 °C, 20 °C, 35 °C, and 50 °C). The principle of OC testing is based on the measurement of the quantity of consumed oxygen due to the oxidation of the sulphidic material sample in a sealed chamber during a short period of time which ranges from about 3 to 5 h (Schmieder et al., 2012; Ouellet et al., 2003). The main assumption behind this test is that

Table 5
Mix composition of prepared CPB samples.

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

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

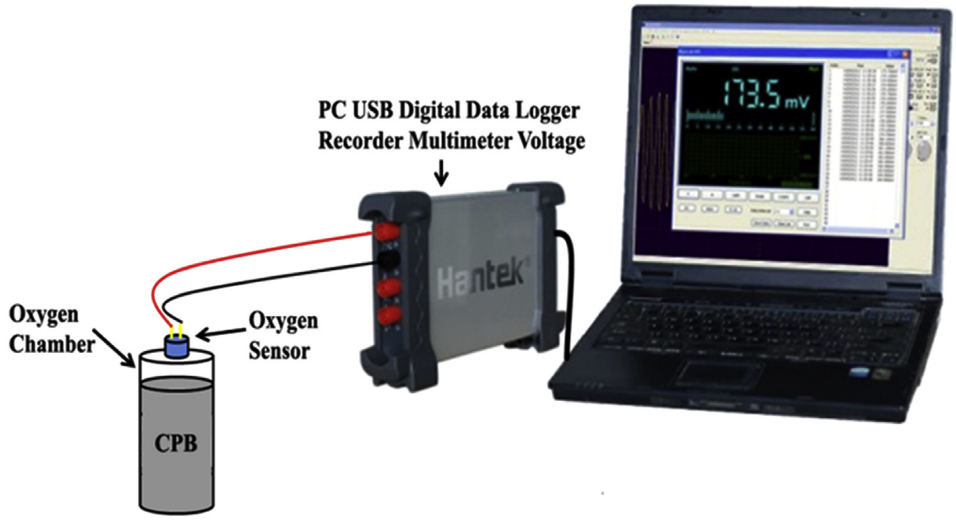
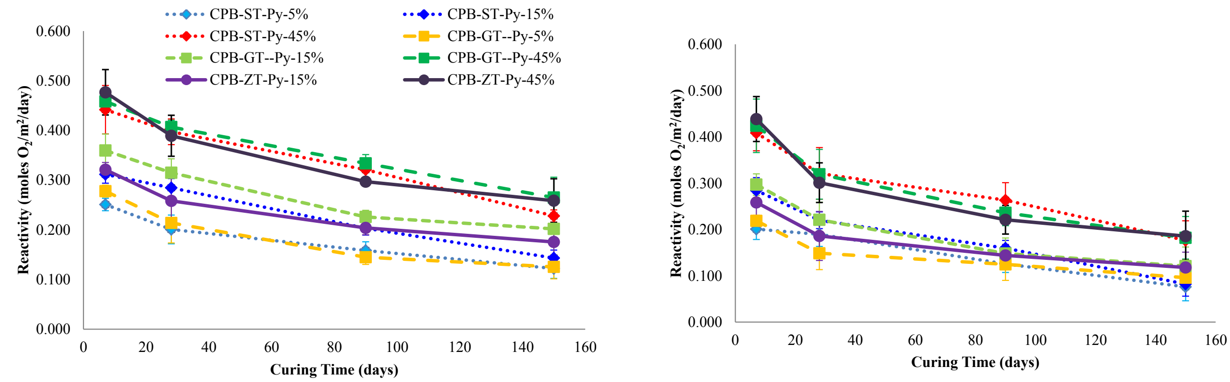


Fig. 2. Schematic of experimental setup of OC testing.

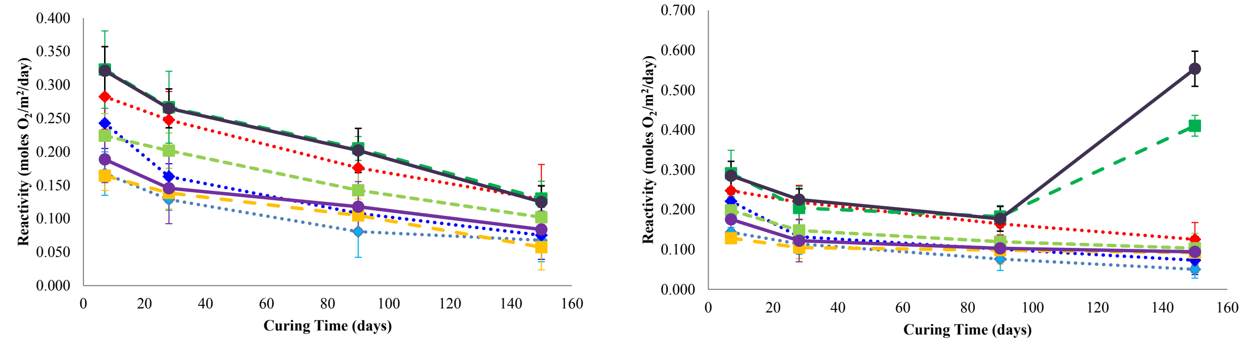
the steady state condition ($\delta c/\delta t = 0$) will be maintained from the beginning to the end of the test. The reactivity of the CPB samples was measured by using a galvanic cell type oxygen sensor (model GC33–200, GC Industries) to estimate the rate of OC. In addition, oxygen sensors (model SO-210, Apogee Instruments, Inc.) were used to measure the reactivity at various ambient (testing) temperatures because this type of sensor has an operating range that is relatively close to the ambient temperatures (−20 to 60 °C). The sensors were connected to a voltmeter (Hantek 365A USB Data Logger Recorder Digital Multimeter Voltage Current PC Base) that measured and recorded the voltage produced by the oxidation reactions in the sealed chamber. The measured voltage of the sensors is directly proportional to the partial pressure of oxygen in the gas phase. The OC tests were performed on the CPB samples by carefully covering the cylinders with an airtight lid that was equipped with an oxygen sensor, as shown in Fig. 2. This figure illustrates the experimental setup of the OC testing. Each OC test was repeated at least four times to ensure the repeatability of the results.

The reactivity of the CPB specimens was evaluated from the flux of oxygen (F_L). Under pseudo steady state conditions, the F_L is determined based on the two following equations (Eqs.((1) and



a)-curing temperature: 2°C

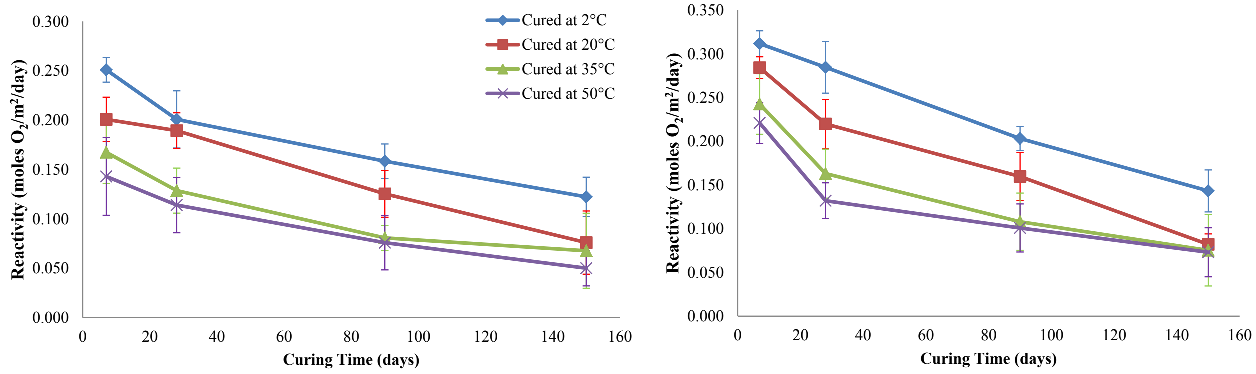
b)-curing temperature: 20°C



c)-curing temperature: 35°C

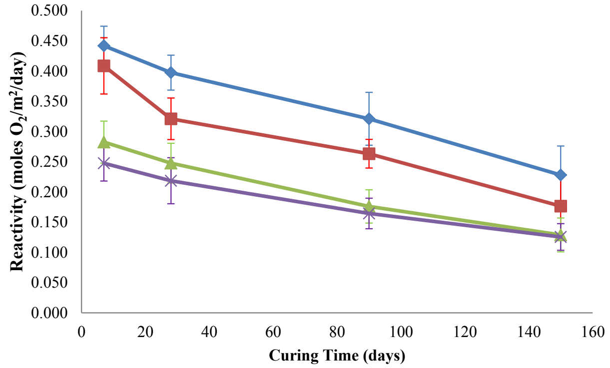
d)-curing temperature: 50°C

Fig. 3. Reactivity of CPB specimens cured at different temperatures for different curing times and tested at 20 °C.



a)-CPB-ST-Py 5%

b)-CPB-ST-Py 15%



c)-CPB-ST-Py 45%

Fig. 4. Effect of curing temperature on the reactivity of CPB for different curing times and tested at 20 °C.

(2)), as proposed by Elberling et al. (1994) and Elberling and Nicholson (1996):

$$F_L = C_o(K_rD_e)^{0.5} \tag{1}$$

where K_r is the first-order reaction rate coefficient for sulphide mineral oxidation (e.g., pyrite), D_e is the effective diffusion coefficient and C_o is the initial concentration of oxygen. The term (K_rD_e) can be obtained from the slope of plotting ln (C/C_o) versus time based on Eq. (2). It can be calculated if the volume of the gas chamber (V) and the surface area of the exposed area of the reactive materials (A) are known (Ouellet et al., 2006).

$$\ln(C/C_o) = -t(K_rD_e)^{0.5}(A/V) \tag{2}$$

3.2. Oxygen consumption testing in various atmospheric temperatures

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

3.3. Microstructural analysis

For a better understanding of the influence of temperature on the reactivity and microstructure of the CPB specimens with time, a combination of various microstructural analysis techniques were adopted. These techniques allow changes that might occur in the porosity, pore structure and binder hydration products of the CPB specimens to be examined, as well as the progress of the binder hydration assessed and phases found in the specimens identified. In this study, x-ray diffraction (XRD), thermal analysis (thermogravimetry–differential thermogravimetry (TG-DTG)), and mercury intrusion porosimetry (MIP) were conducted on selected CPB specimens as well as on hardened cement paste (HCP) specimens with a high w/c ratio (w/c = 1) to simulate the cement matrix of CPB. Prior to undergoing the microstructural analyses, the samples were prepared by using several different processes, such as cutting and drying. The samples were dried at 50 °C in an oven until mass stabilization before being subjected to testing. The XRD patterns of the powdered samples were recorded with a Scintag XDS 2000 X-ray powder diffractometer with monochromatized CuKα radiation ($\lambda = 1.5418$ Å). The data were collected between scattering angles (2θ) of 5° and 70°. The MIP tests were performed on the CPB specimens by using a Micromeritics Auto Pore III 9420 mercury porosimeter in accordance with ASTM D4404-10. The MIP provides information on the pore size distribution in a porous material (i.e., cementitious materials). Finally, the TG-DTG tests were performed on 10 mg (±0.5 mg) of powdered samples (oven dried at 50 °C) by using an Ulvac TGD 9600 thermal analysis system at a heating rate of 10 °C/min from an ambient temperature up to 1000 °C in an atmospheric of N_2 gas (rate of flow: 100 cm^3 min^{-1}).

4. Results and discussions

4.1. Effect of curing temperature on the reactivity of CPB samples

Fig. 3 shows the mean and standard deviation of the reactivity of the CPB specimens (CPB-ST, CPB-ZT and CPB-GT) cured at different temperatures (2 °C, 20 °C, 35 °C and 50 °C) and plotted as a function of curing time. Fig. 4 shows the influence of curing temperature on the reactivity of the CPB-ST specimens (with pyrite content of 5%, 15%, and 45%) cured for various periods of time and tested at 20 °C. The results presented in Figs. 3 and 4 show that in general, the reactivity of the specimens decreases with age regardless of the curing temperature and type of tailings. This reduction of the reactivity with time is due to the decrease of the porosity and refinement of the pore structure of the CPB specimens with time which is a result of the progress of binder hydration and the associated precipitation of higher amount of hydration products, which in turn, reduces the effective diffusion coefficient of oxygen (D_e) (see Eqs. (1) and (2)). This argument with respect to the precipitation of more cement hydration products as the curing time increases is fully supported by the results of the thermal analyses (TG/DTG) performed on the 7 and 28 day CPB specimens as presented in Fig. 5. This figure depicts the TG/DTG diagrams of the 7 and 28 day CPB specimens, respectively. The first peak (DTG) or change in weight (TG) is located between 100 °C and 200 °C, resultant of the dehydration of the hydrates, such as calcium silicate hydrate (C—S—H), the carboaluminates, ettringite, and gypsum, while the apparition of the second peak or change in weight, which is detected at 400°C—500 °C, is mainly caused by the decomposition of the calcium hydroxide (CH; Fall et al., 2010; Pane and Hansen, 2005; Zhou and Glasser, 2001). Finally, the third peak or change in weight is observed between 650 °C and 750 °C, due to the decomposition of the calcite (e.g. Fall et al., 2010; Zhou and Glasser, 2001). A comparison of the TG/DTG diagrams of the 7 and 28 day CPB samples clearly indicates that the first and second peaks or changes in weight are much higher for the 28 day CPB sample, which shows that the amount of hydration products (e.g., CH, C—S—H) formed increases with longer curing time.

Furthermore, it can be noted that a higher curing temperature leads to a reduction of the reactivity of the CPB specimens with the exception of the observations made at 50 °C which will be discussed later in this section. For example, the reactivity of CPB-ST-Py-5% cured at temperatures of 2 °C (Fig. 3a) and 50 °C (Fig. 3d) for 7, 28, 90 and 150 days is reduced by 43%, 43.2%, 40.9% and 59%, respectively. This reduction in reactivity is attributed to the improvement in the microstructure of the CPB (refinement of the pore structure) due to the acceleration in cement hydration caused by increased curing temperatures. The higher curing temperature accelerates the hydration of the cement clinker and promotes the formation of more hydrated cement products, such as C—S—H gel, portlandite (CH), and ettringite (Wang and Liu, 2011; Fall and Samb, 2009; Aligizaki, 2006; Lamond and Pielert, 2006). This higher amount of hydration product, such as C—S—H, and CH associated with higher curing temperatures, is demonstrated by the results of different thermal analyses performed on cement pastes of CPB cured at 20 C and 35 C, respectively, presented in Fall et al. (2010). These hydrated cement products fill the pores (in particular, the capillary pores) in the CPB matrix and around the cement grains (Fall et al., 2010). The capillary pores are a key factor that influences the transport properties (diffusion and permeability) of cement based materials (i.e., CPB). Due to the acceleration in the cement hydration from higher curing temperatures, the volume and size of the capillary pores are reduced. This leads to the improved microstructure of the CPB and a reduced oxygen diffusion coefficient (see Eqs. (1) and (2)). For that reason, the reactivity of the CPB specimens will decrease due to the reduction in the oxygen diffusion which in turn decreases the oxidation rate of pyrite. The results obtained from the MIP tests, as shown in Fig. 6, support this explanation. Fig. 6 illustrates the differential pore size distribution of 90-day CPB-ST-Py-45% Py. specimens cured at 2 °C, 20 °C and 50 °C. It can be observed that as the curing temperature increases, the threshold pore diameter decreases, thus indicating a refinement of the pore structure of the cementitious material. The threshold pore diameter, that is, the pore diameter related to the highest rate of mercury intrusion, has an important influence on the permeability and diffusion of cementitious materials (Fall et al., 2009).

At a curing temperature of 50 °C, it is obvious that the reactivity of the 150 day CPB-GT-Py. 45% and CPB-ZT-Py. 45% specimens do

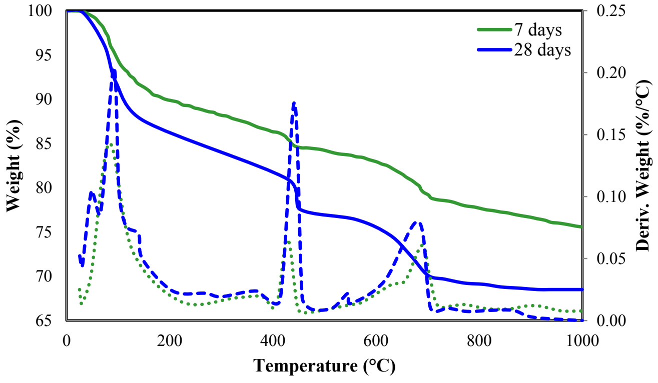


Fig. 5. TG/DTG curves of 7 and 28 day samples.

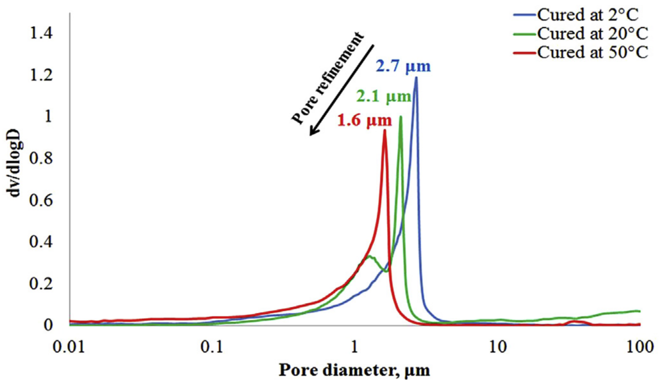


Fig. 6. Differential pore size distribution curves of 90 day CPB specimens (w/c = 7.6) cured at various temperatures (2 °C, 20 °C, and 50 °C).

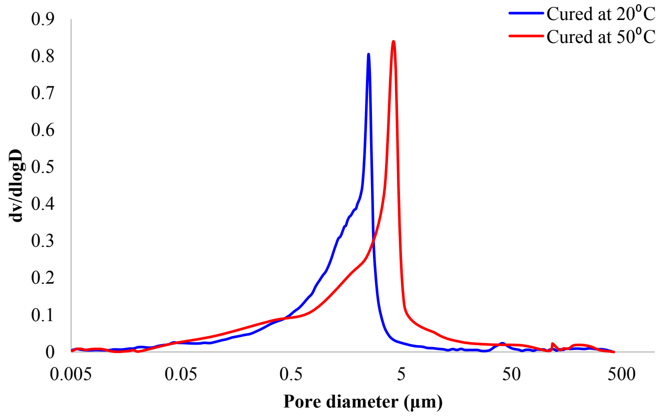


Fig. 7. Differential pore size distribution curves of 150 day ZT-CPB-Py.45% specimens (w/c = 7.6) cured at 20 °C and 50 °C.

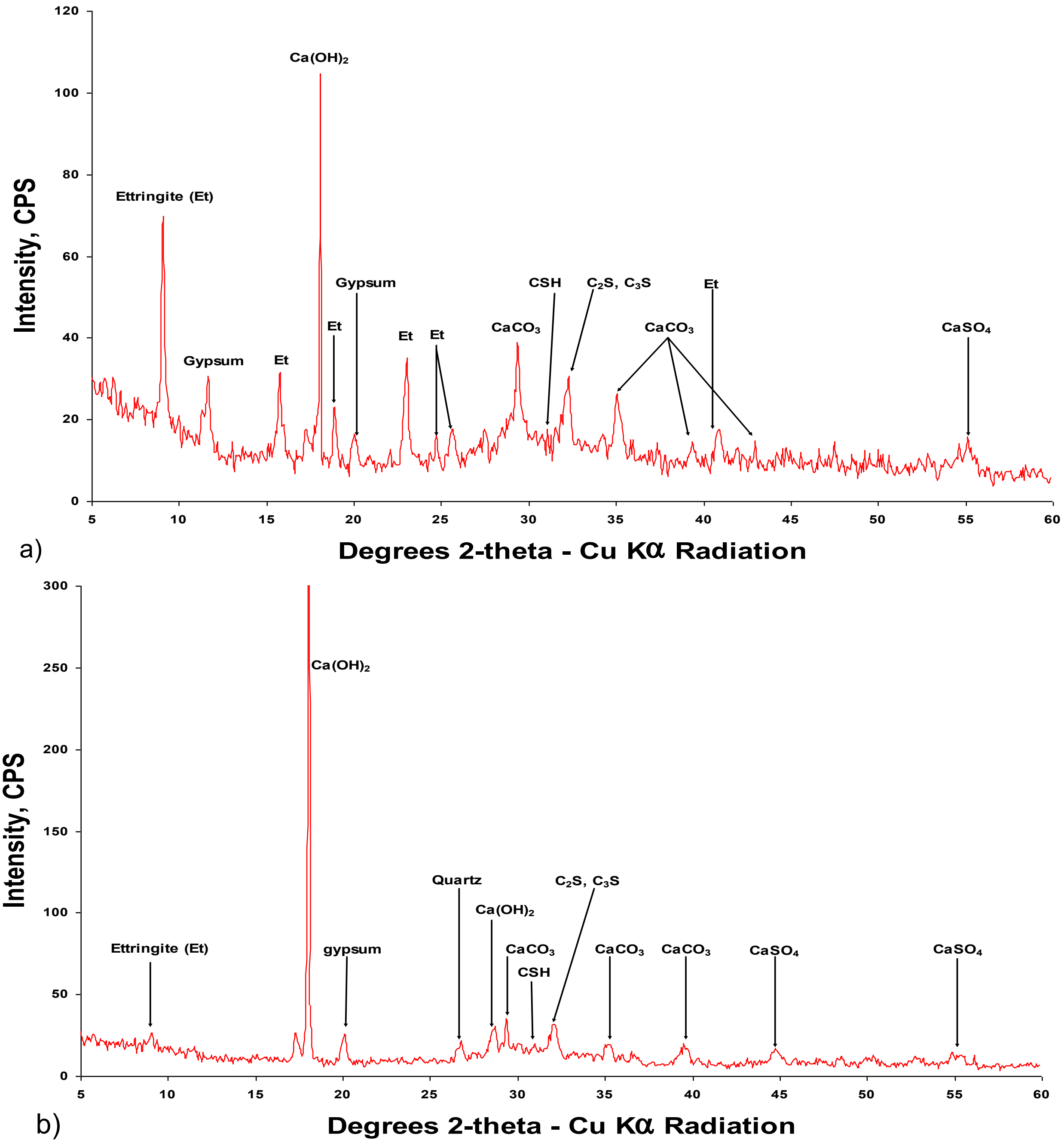
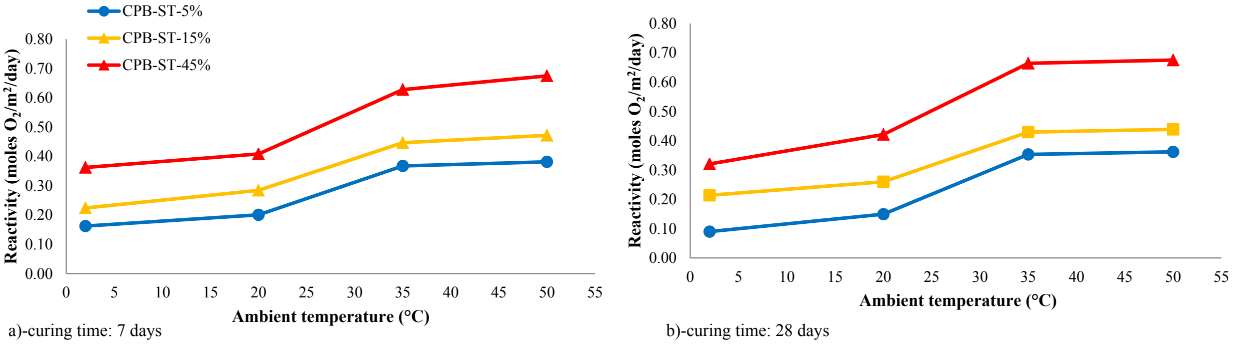


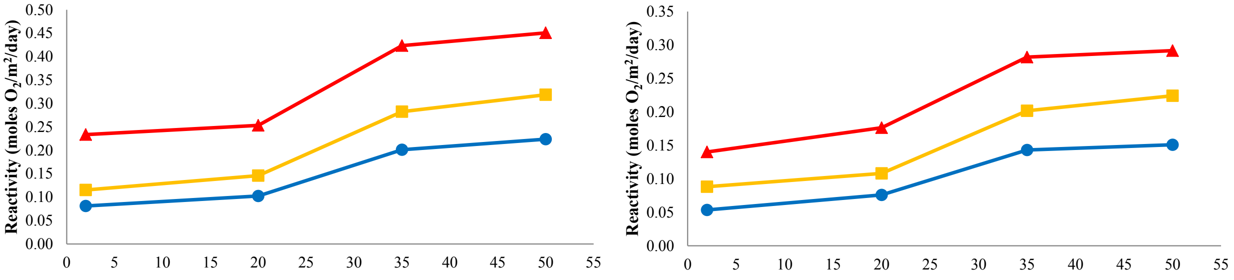
Fig. 8. XRD result of CPB with an initial sulphate content of 25,000 ppm cured at a) 20 °C and b) 50 °C.

not follow the same trend as that of the CPB-ST-Py. 45%, as shown in Fig. 3d. The reactivity of these specimens significantly increases at 50 °C. This increase cannot be explained by the coarsening of the pore structure of the CPB due to the "crossover effect" in cementitious material, a phenomenon in which the curing of CPB at excessively high temperatures results in the loss of strength (Wang and Lee, 2012; Razak and Sajedi, 2011; Sajedi and Razak, 2010; Elsageer et al., 2009; Carino, 1984) because the CPB sample made of ST does not show any increase in reactivity at a curing temperature of 50 °C. Several studies reported that the "crossover effect" is mainly due to the fact that excessively high initial curing temperature leads to coarser pore structure of the cementitious material at advanced ages and decreases the ultimate degree of hydration of the anhydrous cement phases (e.g., Kjellsen et al., 1991; Escalante-Garcia and Sharp, 2001). However, the observed increase of the reactivity of the CPB-GT-Py.45% and CPB-ZT-Py. 45% specimens at 50 °C can be attributed to the fact that these specimens have higher sulphate content (including the initial sulphate content of the pore water of GT and ZT (>10,000 ppm) as well as the sulphate ions generated by the oxidation of the pyrite) than the other CPB samples with a lower pyrite content and the ST-CPB-Py. 45% sample. Previous studies (Pokharel and Fall 2010; Barbarulo et al., 2007; Barbarulo, 2002) have demonstrated that there will be coarsening of the pore structure of CPB that contains sulphate and cured at a temperature of 50 °C due to the combined effects of the following factors: (i) the adsorption of sulphate by C—S—H gel at higher temperatures, and (ii) the destabilization of ettringite at high temperatures (since the solubility of ettringite increases with



a)-curing time: 7 days

b)-curing time: 28 days



c)-curing time: 90 days

d)-curing time: 150 days

Fig. 9. Effect of ambient temperatures on the reactivity of CPB-ST with 5%, 15% and 45% pyrite of different ages and tested at different temperatures.

increasing temperatures (Barbarulo, 2002)). These factors lead to smaller amounts of expansive minerals available to fill the empty pores of the CPB samples with sulphate, thereby coarsening their pore structure, which in turn, increases the effective diffusion coefficient of oxygen (D_e) (see Eqs. (1) and (2)). This coarsening of the pore structure is experimentally demonstrated by the MIP results presented in Fig. 7, which shows the pore size distribution curves of 150 day CPB-ZT-Py.45% specimens (w/c = 7.6) cured at 20 °C and 50 °C. From this figure, it can be observed that the pore size distribution of the sample cured at 50 °C is shifting toward the right, which suggests larger pore sizes, as compared to that cured at 20 °C. Furthermore, the threshold pore diameter of the CPB-ZT-Py.45% sample cured at 50 °C (4.3 μm) is about twice that of the CPB-ZT-Py.45% sample cured at 20 °C (2.6 μm), thus indicating coarsening of the pore structure, which is obviously associated with an increase of the oxygen effective diffusion coefficient. The aforementioned argument with respect to the smaller amount of expansive minerals (e.g. ettringite) is in substantial agreement with the results of the XRD analyses conducted on hardened cemented pastes (HCPs) with sulphate cured at 20 °C (Fig. 8a) and 50 °C (Fig. 8b), respectively. From Fig. 8a, it can be seen that the sample that contains sulphate and cured at 20 °C shows large amounts of expansive minerals due to the availability of sulphate to react with CH and tricalcium aluminate (C_3A). However, in Fig. 8b, the XRD result of the sample that contains sulphate and cured at 50 °C shows very small amounts of expansive minerals. The peak of the CH is also high, especially at 18° 2-theta. The sample that contains sulphate cured at 20 °C in Fig. 8a does not show the presence of any CH at 28.5° 2-theta whereas the sample cured at 50 °C contains CH. Hence, these XRD results clearly suggest that at higher curing temperatures, sulphate is absorbed by the C—S—H gel and ettringite is dissolved, which obviously result in a coarser pore structure.

4.2. *Effect of atmospheric (ambient) temperature on reactivity of CPB*

Fig. 9 shows the influence of ambient temperatures on the reactivity of CPB-ST specimens (with pyrite content of 5%, 15%, and 45%) cured at 20 °C for various curing times (7, 28, 90 and 150 days) and tested at various temperatures (2 °C, 20 °C, 35 °C and 50 °C). These figures show that the reactivity increases with increasing ambient temperatures. This increase is due to the combined effect of the two following factors: (i) the oxygen diffusion coefficient increases with increases in temperature (e.g., Dziejowski et al., 1997; Batterman et al., 1996), thus making more oxygen available on the surface of the pyrite grains for oxidation, and (ii) the oxidation rate of pyrite is temperature-dependent and increases with increasing temperatures as demonstrated by several previous studies (e.g., Meldrum et al., 2001; Evangelou, 1995; Nicholson et al., 1988).

Furthermore, it can also be observed in Fig. 9 that the reactivity rate of the CPB samples is a function of the temperature. For all curing times, the evolution of the reactivity rate of the CPB specimens can be described as three phases in accordance with their testing temperatures: (i) first stage (from 2 °C to 20 °C); (ii) second stage (from 20 °C to 35 °C); and (ii) third stage (from 35 °C to 50 °C). The reactivity gradually increases during the first stage and then rapidly increases in the second stage. In the third stage, the increase in reactivity slightly slows down. These varying rates of reactivity are due to the fact that the oxidation rate of pyrite is strongly temperature dependent. The rate of oxidation increases as the temperature increases (Schoonen et al., 2000; Nicholson et al., 1988). The lower rates of oxygen consumption observed for temperatures ≥35 °C are likely because at higher temperatures, the chemical rate of reaction (pyrite oxidation) substantially increases, thus resulting in the formation of a thick ferric-oxide coating that would inhibit oxygen at the pyrite surface. Ferric hydroxide production was quite obvious during the OC tests. Similar observations have been made by other researchers on pyrite materials (e.g., Schoonen et al., 2000). Further microstructural studies should be conducted to confirm this argument.

5. Conclusions

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

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

This study has shown that temperature is a key factor that affects the reactivity of CPB systems through hydration and oxidation reactions. However, despite the results found in this study, there is still the need to investigate the role of temperature coupled with other parameters (i.e., sulphate content, stress) on the reactivity of CPB systems. This will be the objective of further studies.

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