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Coupled effects of sulphate and temperature on the strength development of cemented tailings backfills: Portland cement-paste backfill

Mamadou Fall *, Mukesh Pokharel

Department of Civil Engineering – University of Ottawa, Ottawa, Ontario, Canada

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A B S T R A C T

Cemented paste backfill (CPB), which is a mix of tailings, water and cement, is subjected to the combined actions of temperature and sulphate during its service life. There is a need to acquire solid knowledge on the coupled effects of temperature and sulphate on the strength of CPBs for a safe, durable and cost-effective design of CPB structures. Hence, the main objective of this paper is to use an experimental approach to study the combined effect of temperature and sulphate on the strength development and microstructure (mineralogical composition of the hardened cement paste) of CPBs. About 200 CPB specimens with various initial sulphate contents (0, 5000, 15,000, and 25,000 ppm) and cured at different temperatures (0 °C, 25 °C, 20 °C, 35 °C, and 50 °C) are tested at different curing times (28, 90, and 150 days). The results show that the coupled effect of temperature and sulphate has a significant impact on the strength and mineralogical composition of the CPB. Depending on the curing time, temperature and initial sulphate content, the sulphate can have a positive or negative impact, i.e., leads to an increase or decrease of CPB strength. The obtained results show a strong indication that the absorption of sulphate by calcium–silicate–hydrate (C–S–H) could lead to the formation of lower quality C–S–H, thereby decreasing the strength of the CPB. This study has demonstrated that the coupled effect of sulphate and temperature on CPBs is an important factor for consideration in the designing of cost-effective, safe and durable CPB structures.

1. Introduction

During the last decade, cemented paste backfill (CPB), a relatively new cemented tailings material, has become increasingly popular in underground mining operations around the world. In addition to its ground support contribution during mining operations, CPB is now an indispensable tailings management method [1–5]. CPB is a mixture of thickened and filtered tailings from the processing operation of mines, water, and a hydraulic binder. It contains between 70% and 85% solids (tailings + binder) by weight. The binder creates cohesion in the CPB through binder hydration. Binders can represent up to 75% of the cost of CPBs. Ordinary Portland cement is traditionally used as a binder in a proportion that is commonly 2% to 7% by total weight. Proportions up to 10% are sometimes used to increase early strength [6]. The components of CPBs are combined and mixed in a plant that is usually located on the mine surface and transported (by gravity and/or pumping) to the underground openings (Fig. 1). To carry fresh and hydrating CPB materials during stope filling and thereby prevent CPB from flowing into the mine working areas, permeable retaining walls; otherwise known as barricades, or retaining walls that are impermeable; known as bulkheads, are built in each of the access ways into the stope prior to stope filling.

One of the most important quality criteria for a CPB structure is mechanical stability at a given time. Once placed in the mine opening (Fig. 1), CPBs have to satisfy certain dynamic and static load resistance requirements to ensure a safe underground working environment for all mining personnel. Mine backfill and/or barricade failures can have considerable financial ramifications and also often result in fatalities or injuries as reported in Canada and around the world [7]. The uniaxial compressive strength (UCS) is undoubtedly the most often used geotechnical property to evaluate mechanical stability of CPBs in underground mine backfill practices because the testing of UCS is relatively inexpensive and can be incorporated into routine quality control programs at the mine [8]. For example, the 28 days compressive strength that is required to maintain backfill stability is generally lower than 1 MPa [7] in cut and fill mining. When the CPB is used for roof support, strength values higher than 4 MPa are required [7]. However, when the CPB is simply used to fill voids or for underground disposal, backfill strength values between 150 kPa and 300 kPa are often used as target values at several mines sites [9] in order to eliminate the risk of liquefaction at an early stage. Furthermore,

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* Corresponding author. Address: Department of Civil Engineering, University of Ottawa, 161 Colonel by, Ottawa (Ontario), Canada K1N 6N5. Tel.: +1 613 562 5800x6558.

E-mail address: mfall@eng.uottawa.ca (M. Fall).

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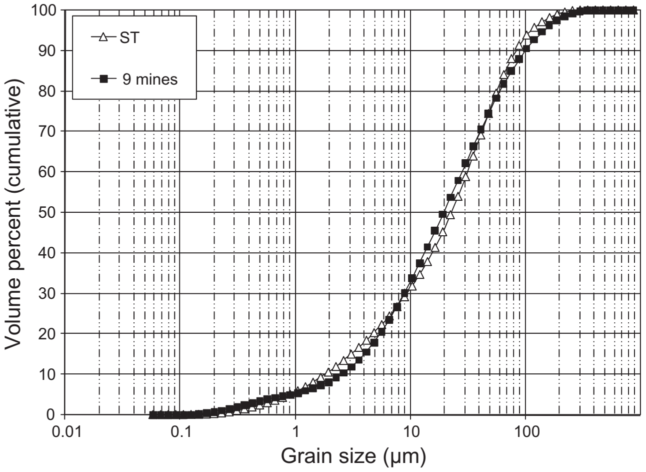

Fig. 1. Grain size distribution curve of the tailings material used.

a high rate of early backfill strength gain is especially important for opening of the barricades and thus, reduces the mining cycle, and increases production, i.e., for increasing the profitability of the mine [10]. Therefore, the designed and built CPB structure should be capable of achieving the desired UCS for ground support as early as possible.

During the past 15 years, several studies have been conducted to understand the factors that affect the UCS of CPBs [e.g., 1,2,4,7,10–15]. These studies have shown that the initial sulphate content can significantly affect the UCS of the CPB [15]. However, technical data about the effect of temperature on the UCS of CPBs is quite limited. Moreover, despite the tremendous progress made in understanding the effect of sulphate or temperature on the UCS development of CPBs, all of the previous studies have only investigated the isolated effects of sulphate [e.g., 10,11] or curing temperature [10] on the strength of CPBs. There are no studies on the coupled effect of sulphate and temperature on the UCS development of CPBs. Yet, there is a need to acquire such solid knowledge, since once built, in the engineering practice, the CPB structure is often simultaneously subjected to coupled thermal (temperatures) and chemical (sulphate) loads from early to advanced ages as explained below.

Various heat sources can significantly affect the temperature of CPB structures as described in [10]. These sources include: (i) the depth of the mine and geological conditions (the temperature of the rockmass which surrounds the CPB increases with depth [16,17]), (ii) the geographical location of the mine (e.g., permafrost region), (iii) the heat produced by the backfill hydration and/or transport (temperature within the CPB can reach 50 °C because of the binder hydration [6,18,19]), (iv) self-heating of the rocks and/or the hardened backfill, and (v) other human-induced temperature [20,21].

CPB materials often contain sulphate. The quantity of sulphate that can be present within the CPB system is usually much higher than that found in conventional concretes or mortars subjected to sulphate attacks. The initial sulphate content of CPBs can be low (<5000 ppm) to very high (25,000 ppm). Four main internal sources of sulphate in the CPB system can be identified. First, the CPB has a high proportion of tailings (75–80 wt.%) that can contain a high proportion of sulphide minerals (up to 60%, [e.g., 22]). The oxidation of the sulphide minerals [23,24] contained in the tailings (before mixing with cement and water) can produce sulphate in the tailings. However, the oxidations of the tailings in the CPB system is considered negligible due to the high water saturation of the CPB, binder hydration products that act as a physical barrier to oxygen and porosity reduction caused by the cement hydration process [21]. Secondly, another source of sulphate in a CPB system is the process of using sulfur dioxide/air for the destruction of cyanides in gold mining [25]. Furthermore, the addition of gypsum ($CaSO_4 \cdot 2H_2O$) or anhydrite ($CaSO_4$) to the clinker to control the setting of the cement can introduce small amounts of sulphate into the CPB mix [15,26]. Finally, the presence of sulphate in the CPB system can result from the use of mine processing waters that are often rich in sulphate in the preparation of CPBs.

In consideration of the facts that are mentioned above, a research program has been conducted at the University of Ottawa by the above authors to thoroughly investigate the effect of sulphate on the development of CPB UCS under various thermal loadings.

The main objectives of this paper are:

- to present the results of the coupled effect of sulphate and curing temperature on the strength of CPBs at early ages;
- to present the results of the coupled effect of sulphate and curing temperature on the strength of CPBs at advanced ages; and
- to develop an understanding of the mechanical performance (UCS) of CPBs when simultaneously exposed to sulphate attacks under various thermal curing conditions.

This study deals with CPB materials whose binder is made of ordinary Portland cement (Type I).

This paper is organized as follows. The experimental program, i.e., the materials used, the preparation of CPB specimens and the tests done are presented in the next section. This is followed by a presentation and discussion of the results obtained. Finally, we present our conclusions.

2. Experimental program

2.1. Materials

Silica tailings, binder and water with different amounts of sulphate were used to prepare the CPB specimens.

2.1.1. Tailings

Silica tailings (ground silica, ST) were used. This allowed the preparation of CPB samples with controlled mineralogical and chemical (e.g., sulphate) composition and physical characteristics (grain size). Natural tailings may contain various (uncontrollable) minerals and chemical elements that can influence the outcome of the study. The ST shows the same particle size distribution from the average of nine Canadian mine tailings (Fig. 1). The ST is made almost exclusively from 99.8 wt.% SiO_2. With 40% fine particles (particles with diameters lower than 20 µm), the ST can be classified as medium tailings. Further physical and chemical properties of the ST are given in Tables 1 and 2. The ST is well-graded with a coefficient of uniformity (C_u) of approximately 16.2 (Table 1) and free of sulphide minerals (Table 2).

2.1.2. Mixing water

Distilled water was used as the basic water. Specific amounts of sulphate salt ($FeSO_4 \cdot 7H_2O$) with a molecular weight of 278.01 were added to a specific volume of distilled water to create mixing water with well known sulphate concentrations (0 ppm, 5000 ppm, 15,000 ppm, and 25,000 ppm). Ferrous sulphate is the most common sulphate type found in cemented backfill mixes.

2.1.3. Binder

Portland cement Type I (PCI) in a weight proportion of 4.5% was used as the binding agent. The relative density of PCI is 3.1. The main chemical characteristics of the binder are shown in Table 3.

Table 1
Physical properties of the tailings used.

Element unit	G_s (–)	D_{10} (μm)	D_{30} (μm)	D_{50} (μm)	D_{60} (μm)	D_{90} (μm)	C_u (–)	C_c (–)
	2.7	1.9	9.0	22.5	31.5	88.9	16.2	1.3

Table 2
Main chemical properties of the tailings used (data source: [27]).

Element unit	SiO_2 (wt.%)	Fe_2O_3 (wt.%)	Al_2O_3 (wt.%)	TiO_2 (wt.%)	CaO (wt.%)	MgO (wt.%)	Na_2O (wt.%)	K_2O (wt.%)
	99.8	0.035	0.05	0.02	0.01	<0.01	<0.01	0.02

Table 3
Main chemical composition of the binder used.

Element unit	MgO (wt.%)	CaO (wt.%)	SiO_2 (wt.%)	Al_2O_3 (wt.%)	Fe_2O_3 (wt.%)	SO_3 (wt.%)
	2.65	62.82	18.03	4.53	2.70	3.82

2.2. Mixing procedures and mix proportions

A total of about 200 CPB specimens with a constant binder content of 4.5 wt.%, water–cement (*w*/*c*) ratio of 7.5, and same tailing type were prepared. The tailings materials, binders and water were mixed and homogenized for about 7 min to produce the desired CPB mixture. The slump (consistency) of all mixes was about 18 cm, which is the most frequent slump used in CPB technology. The produced CPB mixes were poured into curing cylinders that were 5 cm in diameter and 10 cm in height. The prepared moulds were then sealed to avoid the evaporation of water and cured in environmental chambers with controlled temperatures at 2 °C, 20 °C, 35 °C and 50 °C for periods of 28, 90 and 150 days. Table 4 presents the recipes of the prepared CPB specimens.

In addition to the aforementioned CPB specimens, about 50 specimens of cement paste with a high *w*/*c* ratio (*w*/*c* = 2; to simulate the cement matrix of CPBs) and various initial sulphate contents of 0, 5000, 15,000, and 25,000 ppm were prepared. The prepared cement paste mixes were poured into curing cylinders. The sealed cylinders were then cured at various temperatures of 2 °C, 20 °C, 35 °C, and 50 °C for various curing times of 28, 90, and 150 days. Table 5 illustrates the recipes of the prepared cement paste specimens.

2.3. Testing methods

In order to evaluate the UCS of the CPB specimens as well as the mineralogical composition of the cement paste, mechanical tests and mineralogical analysis were performed.

2.3.1. Mechanical tests

In accordance to ASTM C 39, uniaxial compressive tests were performed on the CPB specimens after different curing times for different studied temperatures and initial sulphate contents to determine their UCS values. The press has a normal loading capacity of 50 kN. The load was applied at a slow rate (1 mm/min). Each UCS test was repeated at least twice and the average was considered as the UCS of the tested sample.

Table 4
Composition of the different recipes of CPB prepared in this study.

Mix name	Tailings type	Binder type	% of binder	*w*/*c* ratio	Sulphate (ppm)
CPB-0	ST	PCI	4.5	7.5	0
CPB-5	ST	PCI	4.5	7.5	5000
CPB-15	ST	PCI	4.5	7.5	15,000
CPB-25	ST	PCI	4.5	7.5	25,000

Table 5
Composition of the different recipes of cement paste of CPB prepared in this study.

Mix name	Binder type	*w*/*c* ratio	Sulphate (ppm)
CP-0	PCI	2.0	0
CP-5	PCI	2.0	5000
CP-15	PCI	2.0	15,000
CP-25	PCI	2.0	25,000

2.3.2. Microstructural tests

X-ray analyses were conducted to evaluate the coupled effect of temperature and sulphate on the mineralogical composition of the hydration products of CPB samples. X-ray analyses were performed on the prepared cement pastes (described in Section 2.2) which were cured at different temperatures and times by using a Scintag XDS 2000 XRD.

3. Results and discussion

3.1. Coupled effect of sulphate and temperature on the strength of CPBs at early ages

Fig. 2 shows the evolution for the 28 days UCS of a CPB for different curing temperatures and sulphate content. From this figure,

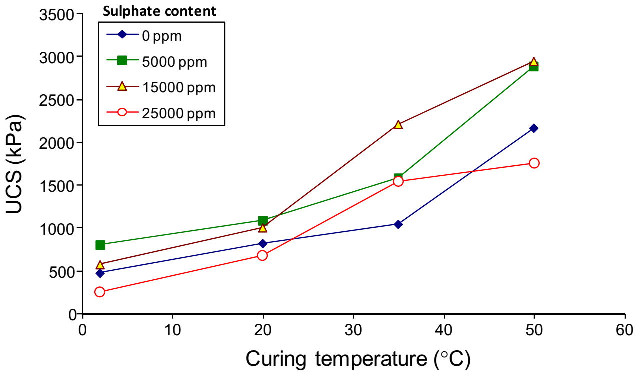

Fig. 2. Coupled effect of temperature and initial sulphate content on the 28 days UCS of CPB.

it is clear that there is a relationship between the sulphate content, temperature and the 28 days strength of the CPB as well as between the sulphate–temperature interactions and the 28 days strength of the CPB.

3.1.1. Effect of the curing temperature on the strength of CPB for a given sulphate concentration

Regardless of the sulphate content, a higher curing temperature results in higher strength of the CPB at an early age. This is because high temperatures accelerate the dissolution of the anhydrous clinker phases and thus, the cement hydration process. Consequently, the amount of hydration products (e.g., calcium–silicate–hydrate or C–S–H, portlandite or $Ca(OH)_2$, calcite) increases with temperature. This is beneficial for CPB strength gain since C–S–H is considered to be the major binding phase in hardened cement [28,29]. This higher amount of hydration product, such as C–S–H and calcium hydroxide (CH) associated with higher curing temperatures, is experimentally demonstrated by the results of different thermal analyses (DTG/DTA) performed on 7 days old cement pastes cured at 20 °C and 35 °C, respectively, and presented in [30]. The authors compared TG/DTA diagrams of the cement pastes cured at different temperatures and noted that the amounts of C–S–H, ettringite, CH, and calcite that are formed increase with the curing temperature. An additional factor is suggested as a contributor to the temperature induced strength increase of CPBs at early ages. This factor is the refinement of the pore structure of CPBs with higher curing temperatures due to the larger precipitation of hydration products. This is graphically demonstrated by the results of mercury intrusion porosimetry (MIP) tests [10] performed on 7 days old CPB samples made of PCI (Fig. 3) and cured at 20 °C and 35 °C. From Fig. 3, it is obvious that the CPB cured at a higher temperature (35 °C) has a denser microstructure with a finer distribution of the pores than the CPB cured at room temperature (20 °C). Fig. 2 also shows that the strength of CPB samples cured at a cold temperature (2 °C) is lower than that of samples cured at higher temperatures. This can be attributed to the inhibition of the cement hydration at low temperatures which is also reported by [31]. At low curing temperatures, the cement hydration rate is slow, thereby leading to lower rates of precipitation of hydration products and thus to the production of lower amounts of C–S–H gel in early ages [32,33]. Also, this in turn results in the formation of a more porous cemented matrix, thereby decreasing the strength of CPBs.

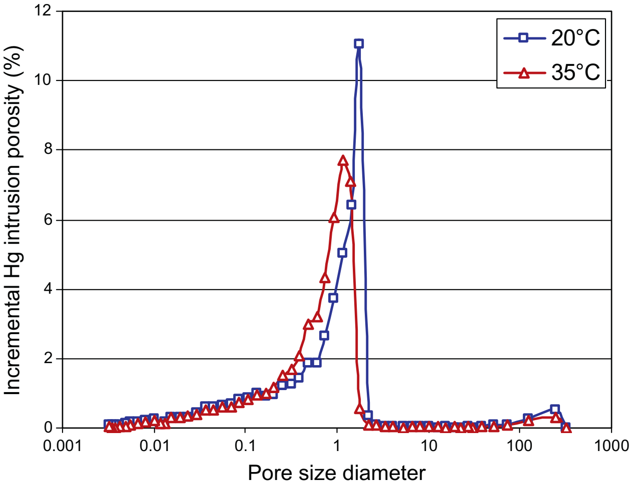

Fig. 3. MIP pore size distribution of CPB with 4.5% Type I Portland cement (PCI) vs. curing temperature after 7 days of curing ($w/c \sim 7.5$; slump ~ 18 cm) [10].

3.1.2. Effect of sulphate content on the strength of CPB for a given curing temperature

It can be also observed from Fig. 2 that regardless of the curing temperature, CPB samples with 5000 ppm and 15,000 ppm of sulphate have higher UCS values than those without sulphate. As mentioned in [19], the higher UCS values can be explained by the fact that sulphate contributes to the decrease of CPB internal porosity, and thus to the increase in CPB strength. This is because of the precipitation of secondary hydrated minerals (such as gypsum and ettringite) within the empty capillary pores of the CPB caused by the reaction of the sulphate ions with CH and tricalcium aluminate (C_3A). This argument is fully supported by the results of scanning electron microscope (SEM) observations performed on sulphate-bearing CPB by [19]. From this study, it can be observed that secondary hydrated minerals precipitate in the pores that were inside the cement matrix of CPB and thus, reduce its porosity. However, CPB samples with higher sulphate content (25,000 ppm) show a lower 28 days UCS value than those with 5000 and 15,000 ppm of sulphate and those without sulphate, regardless of the curing temperature (except at 35 °C). This can be explained by the fact that high sulphate content can inhibit binder hydration, thereby resulting in a lower UCS. This is in agreement with the results of previous studies on cemented paste of CPBs which revealed that a high sulphate content strongly inhibits the early hydration of C_3A [e.g., 19] as well as with studies performed on conventional concrete [e.g., 34]. This argument is also supported by the results of an X-ray analysis performed on cement paste with a 25,000 ppm initial sulphate content, and cured at 50 °C for 28 days (Fig. 4). Fig. 4 shows the mineralogical composition of the cemented paste and illustrates the X-ray pattern of the cemented paste with an initial sulphate content of 25,000 ppm, and cured at 50 °C for 28 days. The XRD result presented in Fig. 4 shows that the 25,000 ppm sample still has unreacted C_2S and C_3S. This means that the sample is not fully hydrated.

3.1.3. Effect of sulphate-curing temperature interactions on the strength of CPBs

From Fig. 2, it is also obvious that the effect of sulphate on CPB strength at 28 days is strongly dependent on the curing temperature. It can be seen that as the curing temperature increases, the positive effect (increase in strength) of the sulphate content of the 5000 and 15,000 ppm samples on the strength of the CPB is generally higher. This can be explained by the fact that a higher temperature is associated with faster binder hydration and thus, the production of a higher amount of CH. Hence, more gypsum will be formed through the reaction of sulphate with CH. This gypsum will contribute to the hardening and the reduction of the porosity of the CPB, thereby increasing its strength. However, for a temperature of 50 °C, CPB samples with an initial sulphate content of 5000 ppm have the same strength as those with an initial sulphate content of 15,000 ppm (Fig. 2). This indicates a decrease of the strength gain rate with higher temperatures for an initial sulphate concentration of 15,000 ppm (compared to a sulphate concentration of 5000 ppm), suggesting that for 15,000 ppm of sulphate, a curing temperature of 50 °C will start to have a negative effect on the early age strength (28 days) of the CPB. The negative effect can be due to the fact that a higher curing temperature leads to a higher absorption of sulphate by C–S–H [35]. This could lead to the formation of a weaker C–S–H gel, i.e., C–S–H of lower quality (e.g., weaker binding ability to other hydration products), thereby resulting in strength decrease since the strength of Portland cemented materials is mainly controlled by C–S–H, especially by the ability of the latter to effectively bond to other products of hydration. Jelenić et al. [36] speculated that sulphate can decrease the strength of C–S–H gel. This argument with regards to the sulphate absorption by C–S–H is fully supported by the results of

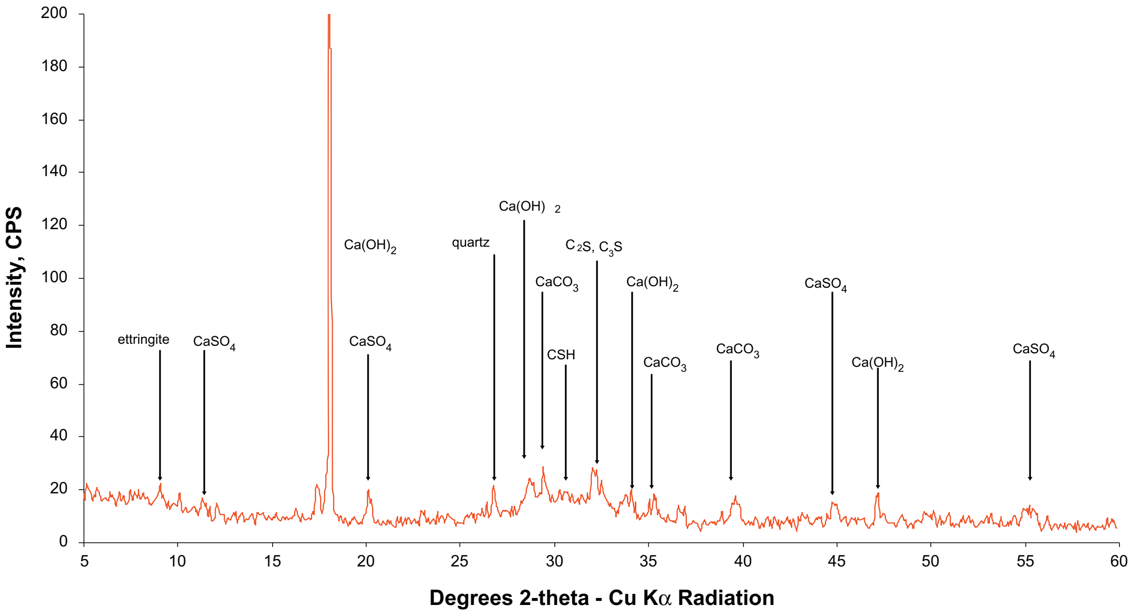

Fig. 4. XRD result of 25,000 ppm of cemented paste made of PCI cured at 50 °C for 28 days.

the experimental studies performed by [37] which reported that sulphate binding to C–S–H increases and is faster as the curing temperature increases. This is also consistent with the XRD results presented in Fig. 4, where despite a high initial sulphate content (25,000 ppm), no gypsum is detected in the 28 days old cemented paste. This figure also shows the presence of an insignificant amount of ettringite and a high amount of CH. The absence of gypsum and a high amount of CH suggests that due to sulphate absorption by C–S–H, there are no enough sulphate ions remaining in the CPB system to react with the CH and thus, form gypsum. Consequently, it is evident that competition for sulphate ions exists between three reactions; (i) the fixing of sulphate ions by C–S–H gel; (ii) the reaction of sulphate ions with CH to form gypsum; and (iii) the reactions of sulphate ions and C_3A to generate ettringite. This competition for sulphate ions is experimentally demonstrated by previous studies performed on C–S–H samples synthesized in laboratories [37]. A higher absorption of sulphate ions by C–S–H will reduce the sulphate concentration in the cement paste solution and thereby limit the amount of sulphate ions that are available to form gypsum as well as generate ettringite (which increases the strength of CPBs at early ages through the mechanism explained above). In addition to the absorption of sulphate ions by C–S–H gel, the high temperature contributes to the destabilization of ettringite in the CPB system since the solubility of ettringite increases with increasing temperatures [38]. As observed in previous studies [e.g., 37], high temperature induced dissolution of ettringite results in an increase of sulphate concentration in pore water solutions of the cemented system, and thus increases the quantity of sulphate bound to the C–S–H. This could lead to the formation of additional lower quality C–S–H, thereby contributing to the reduction of CPB strength. Furthermore, since the ettringite contributes to the filling of empty pores of CPBs at early ages (as explained above), it should be also acknowledged that the dissolution of ettringite will contribute to the coarsening (increase of porosity) of the CPB matrix, and thus to the decrease of its strength. This coarsening of the pore structure agrees well with the findings from the permeability tests presented in Section 3.2.

However, temperature induced-higher absorption of sulphate by C–S–H gel and ettringite destabilization cannot be considered as the only significant parameters that are responsible for a decrease in the strength of CPBs under the coupled influence of temperature and sulphate. Indeed, from Fig. 2, it can be observed that the evolution of the curve of temperature vs. strength of CPB specimens with 25,000 ppm of sulphate is relatively different than that of CPBs with lower initial sulphate content. The UCS of the 25,000 ppm CPB specimens is lower than that of CPBs with lower sulphate content at 50 °C, and higher only than that of the CPB specimen without sulphate at 35 °C. Hence, the high concentration of sulphate should be considered as an additional cause of decrease in CPB strength. This agrees well with the findings of experimental studies conducted by [37], who reported that an increase of sulphate concentration in cement paste solution leads to higher absorption of sulphate by C–S–H gel, thereby resulting in less formation of expansive minerals (e.g., gypsum). This high absorption of sulphate in C–S–H gel could lead to a C–S–H gel of lower quality, thereby negatively affecting the CPB strength. From Fig. 2, it can be also seen that the inhibition of cement hydration by a high sulphate content (25,000 ppm) is more severe in cold temperatures because the binder hydration rate is slow (i.e., lower hydration rate of C_3A) when associated with cold temperatures. This means that in cold temperatures, more C_3A will be available where their reactions will be inhibited by the high sulphate concentration.

3.1.4. Further discussions

The results of the coupled effect of sulphate and temperature on the UCS of CPBs at early ages suggest that for the studied CPBs, a curing temperature of $\leqslant$35 °C and an initial sulphate content that is up to 15,000 ppm appear to have a positive effect on the early age strength of CPB. This finding can have significant and practical applications with regards to the speeding up of the mining process, reduction of liquefaction susceptibility of CPB structures and the cost-effective design of CPB structures. Indeed, a high rate of early backfill strength gain that is achieved in an economical manner is targeted by all in the mining industry. Early strength gain is especially important for opening of barricades and thus, reduces the mining cycle time, increases mining efficiency and speeds up production. This is obviously associated with economical benefits for mines. Furthermore, high early age strength gain may play a significant role in reducing the potential for CPB liquefaction at the early ages of curing and thus, decreases the risk of barricade failure. The decrease in the risk of barricade failure is due to the ability of the binder hydration product to create bonds between individual tailing particles of the CPB and provide strength.

Although early age strength is a key parameter in the cost-effective designing of CPB structures, the strength of CPBs at advanced ages is also highly important for judging long term stability and durability (resistance to sulphate attacks). Consequently, this leads to the importance of answering the following question: How will the coupled effects of sulphate and temperature affect the strength of CPBs at advanced ages?

3.2. Coupled effect of sulphate and temperature on the strength of CPBs at advanced ages

Since the results of the coupled effects of sulphate and temperature on the 90 and 150 days UCS of CPBs are relatively similar, only the results of the 150 days CPB will be presented and discussed in this section so that the paper is a reasonable length. Fig. 5 shows the coupled effect of sulphate and temperature on the 150 days UCS of the CPBs. Again, as at an early age (28 days), it can be seen that a higher curing temperature is associated with a higher 150 days strength of the CPBs (except for the 25,000 ppm CPB, which will be discussed below). The reasons of this strength increase are the same as those previously discussed in an earlier section.

However, from Fig. 5, it is also clear that the effect of temperature on the UCS of CPBs at advanced ages is significantly affected by the initial sulphate content.

3.2.1. At 2 °C curing temperature

It can be observed that at a 2 °C curing temperature, the strength of CPBs with high initial sulphate contents (15,000 and 25,000 ppm) is lower than those of specimens with 5000 ppm of sulphate and without sulphate. As also noted in early age strength, the 5000 ppm CPB specimens show the highest UCS. The lower UCS values of the 15,000 and 25,000 ppm can be explained by the inhibition of cement hydration (especially C_3A) by a high sulphate content (15,000 and 25,000 ppm). The higher UCS value of the 5000 ppm specimens is attributed to the precipitation of expansive minerals, such as ettringite and gypsum, in the empty pores of the CPBs which contribute to their hardening as explained above. Since CPBs have high porosity and large capillary pores [14,30], they can accommodate a large quantity of expansive mineral without any physical damage resulting from the pressure developed by the expansive minerals. Furthermore, CPBs cured at colder temperatures show a coarse pore structure, i.e., more and larger empty pores [10] that can be filled by expansive minerals without any significant physical damage.

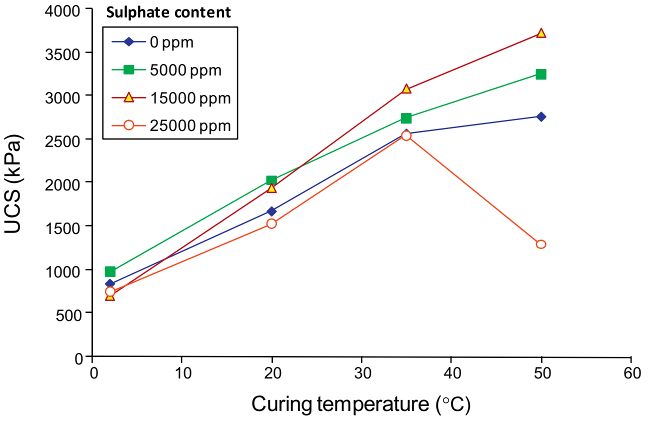

Fig. 5. Coupled effect of temperature and initial sulphate content on the 150 days UCS of CPB.

3.2.2. At 20 °C curing temperature

Fig. 5 shows that at 20 °C curing temperature, the UCS value of the 5000 ppm sample cured at 150 days is 18%, 4% and 25% higher than that of 0 ppm, 15,000 ppm and 25,000 ppm samples for the same curing time and temperature, respectively. This can be explained by the fact that because of the low sulphate concentration of the 5000 ppm sample (in comparison to 15,000 and 25,000 ppm), there is no (or an insignificant) inhibition of the hydration of cement and precipitation of an adequate amount (it is not an excessive amount with respect to the volume of empty pores available) of sulphated expansive minerals. The absence of inhibition will favour a more complete hydration of the cement in the 5000 ppm samples than the highly sulphated CPB samples. This is in accordance with the X-ray analysis results of the 150 days old 5000 ppm cemented paste sample as presented in Fig. 6. An absence of C_2S and C_3S can be noted from this figure, which indicates an almost complete hydration of cement. In addition, the precipitation of an adequate amount (no excessive proportion) of expansive minerals within the empty pores of the 5000 ppm samples play a beneficial role of refining the pore structure (porosity reduction), thereby positively contributing to the strength of the samples. This argument agrees well with the results presented in Fig. 6, where ettringite and gypsum can be observed. However, the amount of ettringite and gypsum detected in the 5000 ppm sample is less than that detected in the highly sulphated samples as shown in Fig. 7, which also illustrates the XRD result of the 25,000 ppm cemented paste cured at 20 °C for 150 days. The lowest 150 days UCS observed for the 25,000 ppm samples at 20 °C can be attributed to the combined effect of two mechanisms. First, an initial sulphate content of 25,000 ppm means a more severe inhibition of cement hydration, which is also demonstrated by the results of the X-ray analysis presented in Fig. 7. The XRD data confirm the presence of the clinker phases C_3S and C_2S in the CPB specimen. These clinker phases were not detected by the X-ray analyses conducted on the 150 days old hardened cement paste with an initial sulphate content of 5000 ppm as shown in Fig. 7. Secondly, a comparative analysis of the XRD results presented in Figs. 6 and 7 indicates that a high proportion of ettringite and gypsum has formed in the 25,000 ppm samples, which suggests the possibility that excessive amounts of ettringite and gypsum may have produced expansive pressure, which contributes to the deterioration of the strength of the 25,000 ppm CPB at 20 °C. Similar observations have been made in other studies on sulphate attacks on cemented tailings backfill cured at room temperatures [e.g., 7,11,15]. This argument is also supported by the main findings on sulphate attacks on conventional concretes cured at room temperatures [e.g., 38–41]. For example, Bing and Cohen [39] mentioned that sulphate attacks on Portland cement concrete, which is cured at room temperature, is often considered to arise from two major sulphate reactions: (1) the sulphate ions react with C_3A and its hydration products to produce ettringite with an increase in volume that results in expansion and subsequent cracking of the concrete, and (2) the sulphate ions react with CH to produce gypsum [39]. This argument is also in perfect agreement with the results of the SEM observations performed by the authors [21] on highly sulphated CPB samples cured at room temperatures. From this study, it can be clearly noted that the pores within the CPB, which are filled with secondary gypsum minerals, have damaged the CPB with their destructive expansive action. However, Metha [40] underlined that in most cases, the loss of adhesion and strength of the cemented material, not expansion and cracking, is the primary consequence of sulphate attacks.

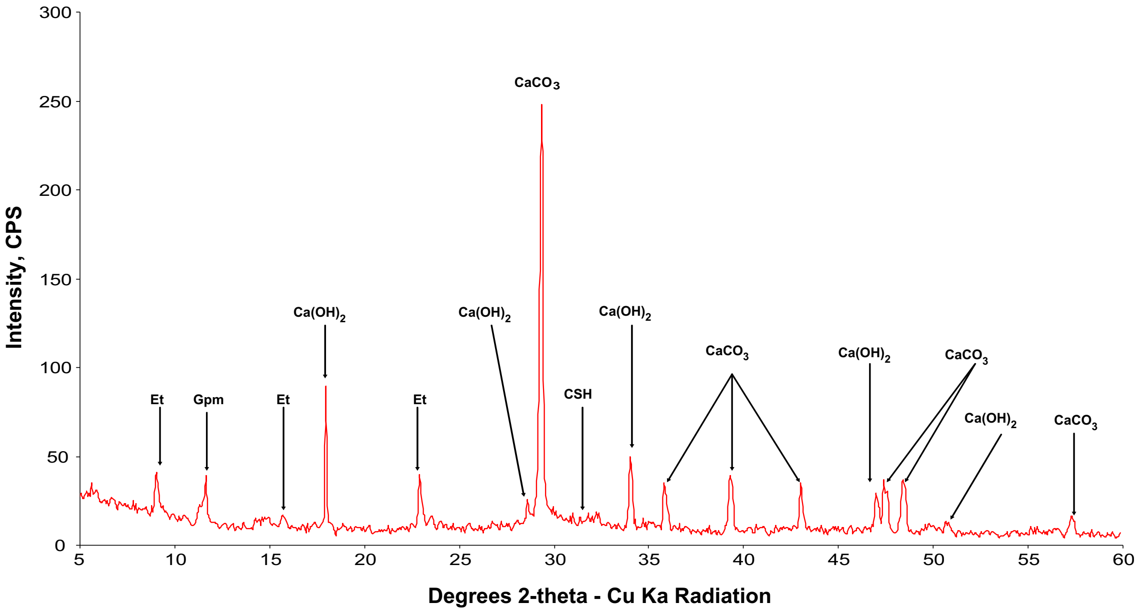

Fig. 6. XRD result of 5000 ppm cemented paste made from PCI cured at 20 °C for 150 days.

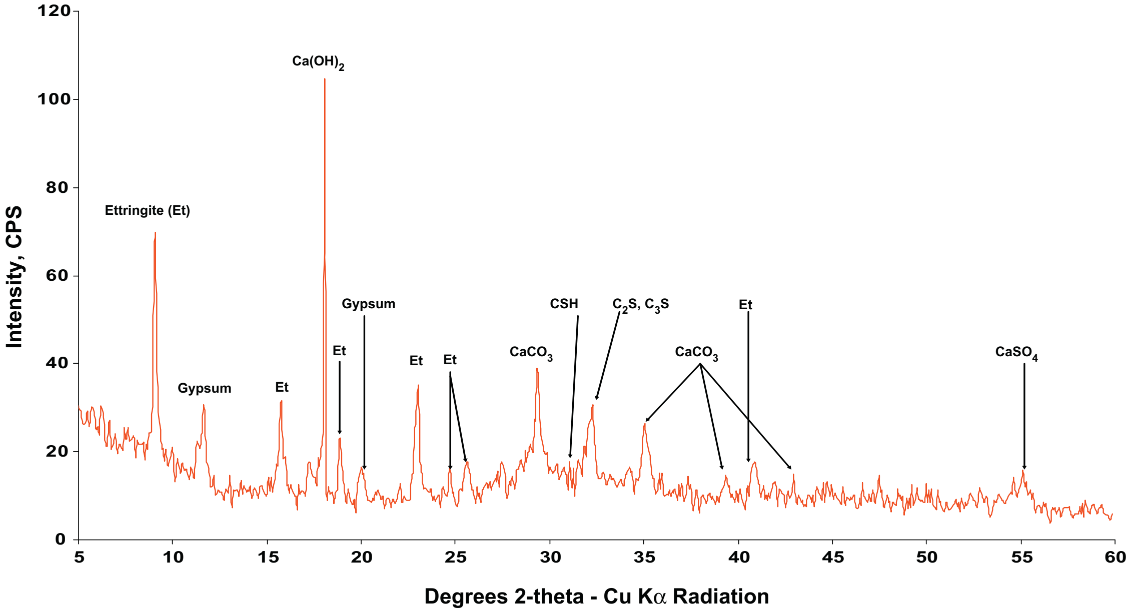

Fig. 7. XRD result of 25,000 ppm cemented paste made from PCI cured at 20 °C for 150 days.

From the results of the effect of sulphate on the strength of mature CPBs cured at 20 °C presented above, it can be concluded that depending on the sulphate content, the sulphate can have two opposite effects on the strength of mature Portland cement CPBs, contributing to an increase or decrease. The increase results from the refinement of the pore structure of the CPB through the precipitation of expansive minerals that are not excessive in the empty pores. The decrease is attributed to the combined effect of the inhibition of the cement hydration by high sulphate content and the physical damage of the CPBs due to the formation of excessive amounts of expansive minerals. Depending on the initial sulphate (see 150 days of 0 ppm and 15,000 ppm samples at 20 °C, Fig. 5), it is evident that competition exists between factors of strength decrease and increase.

3.2.3. At 35 °C curing temperature

Fig. 5 demonstrates that at a curing temperature of 35 °C, the effects of sulphate on the UCS of 150 days old CPB specimens are relatively similar to those observed at 20 °C. The key differences are characterized by the fact that the 15,000 ppm samples show the highest strength and the UCS of the 25,000 ppm samples are closer to that of 0 ppm samples at 35 °C than at 20 °C. Indeed, the 150 days UCS value of the 15,000 ppm specimens is 15%, 10% and 16% higher than that of 0 ppm, 5000 ppm and 25,000 ppm samples at the same temperature, while the UCS value of the 25,000 ppm sample is less than 1% (the difference is negligible when experimental errors related to the UCS test are taken into consideration), which is lower than that of sulphate-free CPBs. The improved UCS performance of highly sulphated samples (15,000 and 25,000 ppm) at this temperature can be mainly attributed to the increased dissolution of ettringite at high temperatures, as previously discussed. This dissolution contributes to the reduction of the quantity of expansive ettringite in the pores of CPBs, thereby reducing the magnitude of damaging expansive pressure applied onto the pores of high sulphate CPBs. Another factor which should be considered as a contributor to the decrease of the aforementioned damaging pressure is the absorption of the sulphate by the C–S–H gel, which means that less sulphate ions will be available in the pore solutions to build expansive minerals.

3.2.4. At 50 °C curing temperature

Finally, from Fig. 5, it is also interesting to notice that at a curing temperature of 50 °C, the CPB sample with a 25,000 ppm of sulphate shows a high drop in strength while the 5000 ppm and 15,000 ppm specimens show no decline in strength. CPB specimens without sulphate are also unaffected by strength loss at 50 °C. This suggests that the observed strength drop is not caused by the well known mechanism (crossover effect) of high curing temperature induced strength loss of cemented materials at advanced ages (this mechanism is well and fully described in the literature [e.g., 42–44]). This argument agrees well with the findings of Fall et al. [10], who noted the absence of a crossover effect on Portland cement CPB samples cured up to 150 days and that the effect of a high initial curing temperature on the strength development of PCI–CPB is not fully similar to that on conventional PC concrete and mortar materials. The origin of this drop of strength can be attributed to the combined effect of several mechanisms. First,

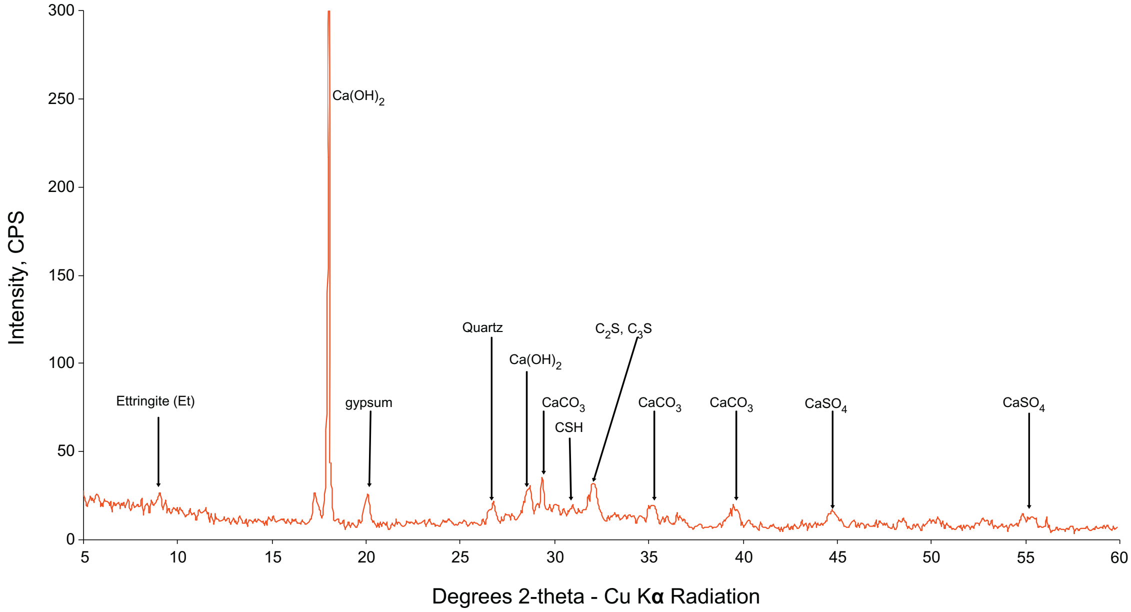

Fig. 8. XRD patterns of 150 days old hardened cement pastes with a high water-to-cement ratio ($w/c = 2$) cured at 50 °C and with initial sulphate content of 25,000 ppm.

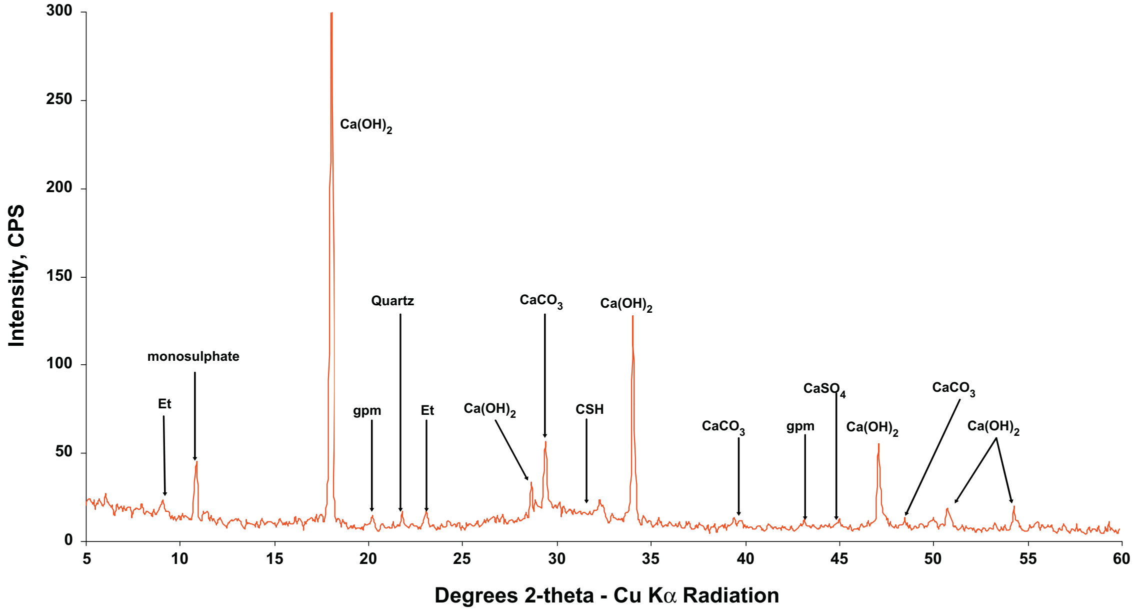

Fig. 9. XRD patterns of 150 days old hardened cement pastes with a high water-to-cement ratio ($w/c = 2$) cured at 50 °C and containing no sulphate.

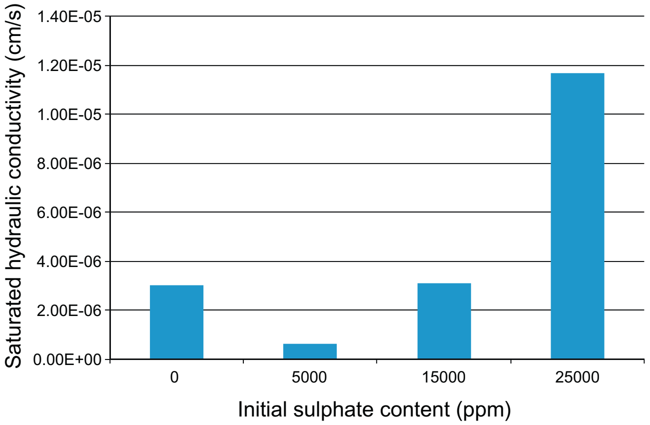

Fig. 10. Effect of initial sulphate content on the saturated hydraulic conductivity of 150 days old CPB containing 25,000 ppm initial sulphate and cured at 50 °C.

the increase of curing temperature increases the amount of sulphate absorbed by the C–S–H gel, while the higher sulphate concentration is also associated with higher sulphate absorption by C–S–H. The binding of sulphate to C–S–H gel may have led to the formation of C–S–H gel of lower quality (e.g., with weaker binding abilities), thereby resulting in decrease of CPB strength. The absorption of sulphate ions may have strongly limited the availability of sulphate to form gypsum or ettringite. This suggests that the observed decrease in strength cannot be attributed to the negative effect of the expansive minerals as commonly observed in sulphate attacks on cemented material in room temperature. The argument is supported by the results of an X-ray analysis performed on hardened cement paste which contains 25,000 ppm of sulphate (Fig. 8) and 0 ppm of sulphate (Fig. 9) and cured at 50 °C. From these figures, it can be observed that the intensity of the gypsum and ettringite peaks is almost the same for both figures. Hence, there is no increase in the quantity of expansive minerals formed with a higher sulphate content (from 0 to 25,000 ppm). Furthermore, since the stability of ettringite decreases with higher temperatures, the destruction of ettringite phases at high temperatures (50 °C) should be considered as an additional cause of low amounts of ettringite observed in samples that contain 25,000 ppm of sulphate and cured at 50 °C. This is fully supported by the detection of calcium monosulphate in the sample presented in Fig. 9. Indeed, increased temperatures promote the formation of calcium monosulphonoaluminate, while the stability of ettringite decreases [38]. This dissolution of ettringite could have also led to the coarsening of the pore structure of the 25,000 ppm CPB, thereby contributing to the decrease of its UCS. This hypothesis is experimentally supported by the results on permeability tests performed by [45] on 150 days old CPB samples with an initial sulphate content of 0, 5000, 15,000 and 25,000 ppm and cured at 50 °C. The results are summarized in Fig. 10. From this figure, it can be observed that the 25,000 ppm sample shows the highest permeability value, which indicates a coarsening of the pore structure. Finally, it can be noticed from Fig. 8 that there remains unreacted clinker phases of C_3S and C_2S in the 150 days old CPB specimen with 25,000 ppm of sulphate cured at 50 °C. This suggests that the inhibition of cement hydration by high sulphate content still plays a non negligible role in lowering the strength of 150 days CPB specimens.

4. Summary and conclusion

This paper presents the results of a study which aims to evaluate the coupled effect of sulphate and temperature on the strength of CPBs. Several CPB mixtures with various sulphate contents (0, 5000, 15,000 and 25,000 ppm) are cured at different temperatures (2 °C, 20 °C, 25 °C, 35 °C, and 50 °C) and curing times (28, 90, and 150 days). Mechanical tests and microstructural (mineralogical composition of the cement paste of CPBs) analyses of these CPB mixtures provide valuable information of the effect of sulphate on the strength and microstructure of CPBs under various curing temperatures.

It is demonstrated that the effect of sulphate on CPB strength is strongly affected by the curing temperature. The sulphate–temperature–cement hydration interactions can have positive or negative effects on the mechanical resistance (strength). The magnitude of the effects depends on the amount of the initial sulphate content and the value of the curing temperature.

It is found that for curing temperatures which are ⩾20 °C, sulphate concentrations up to 15,000 ppm have a beneficial effect on the strength development of the studied CPBs for early (28 days) and advanced (90, 150 days) curing times. However, CPBs with an initial sulphate content of 25,000 ppm generally show lower strength, especially at high curing temperatures (50 °C), regardless of the curing time.

Higher curing temperatures (⩾35 °C) and initial sulphate contents (⩾15,000 ppm) lead to absorption of a larger amount of sulphate ions by the C–S–H. The obtained results show that there are strong indications that the binding of sulphate to C–S–H may lead to the formation of lower quality C–S–H, which in turn, results in the decrease of CPB strength. However, there is still a need to conduct additional investigations, especially on material essentially made of C–S–H, to study the impact of sulphate absorption by C–S–H on its physical, chemical and mechanical properties. This will be the objective of further studies.

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References

[1] Kesimal A, Ercikdi B, Yilmaz E. The effect of desliming by sedimentation on paste backfill performance. J Miner Eng 2003;16:1009–11.
[2] Yilmaz E, Kesimal A, Ercikdi B. Strength development of paste backfill simples at long term using different binders. In: Proceedings of the 8th symposium MineFill04, China; 2004. p. 281–5.
[3] Nasir O, Fall M. Shear behavior of cemented pastefill–rock interfaces. Eng Geol 2008;101(3–4):146–53.
[4] Fall M, Benzaazoua M, Saa E. Mix proportioning of underground cemented paste backfill. Int J Tunn Undergr Construct 2008;23:80–90.
[5] Fall M, Célestin JC, Han FS. Suitability of bentonite-paste tailings mixtures as engineering barrier material for mine waste containment facilities. Miner Eng 2009;22(9–10):840–8.
[6] Williams TJ, Denton DK, Larson MK, Rains RL, Seymour JB, Tesarik DR. Geomechanics of reinforced cemented backfill in an underground stope at the lucky friday mine. Report of Investigations 9655; 2001. 24p.
[7] Hassani F, Archibald J. Mine Backfill, CD-Rom, Canadian Institute of Mine, Metallurgy and Petroleum; 1998. 262 p.
[8] Vergne J. Rules of thumb for the hard rock mining industry. In: Hard rock miner's handbook 2000, 3rd ed. USA: McIntosh Engineering Inc. NIST, 1996. 42p.
[9] Bloss M. Below ground disposal (mine backfill). In: Jewell, Fourie, Lord, editors. Paste and thickened tailings: a guide. University of Western Australia; 2002. p. 103–26.
[10] Fall M, Célestin JC, Pokharel M, Touré M. A contribution to understanding the effect of temperatures on the mechanical properties of mine cemented tailings backfill: experimental results. Eng Geol 2010;114(3–4):397–413.
[11] Ercikdi B, Kesimal A, Cihangir F, Deveci H, Alp I. Cemented paste backfill of sulphide-rich tailings: importance of binder type and dosage. Cem Concr Compos 2009;31(4):268–74.
[12] Grice T. Recent mine developments in Australia. In: Proceeding of the 7th international symposium on mining with backfill (MINEFILL); 2001. p. 351–7.

[13] Yilmaz E, Kesimal A, Ercikdi B. The factors affecting strength and stability of paste backfill. Turk J Earth Sci 2003;28:155–69 [in Turkish].

[14] Fall M, Benzaazoua M, Ouellet S. Experimental characterization of the effect of tailings fineness and density on the quality of cemented paste backfill. J Miner Eng 2005;18:41–4.

[15] Fall M, Benzaazoua M. Modeling the effect of sulphate on strength development of paste backfill and binder mixture optimization. Cem Concr Res 2005;35:301–14.

[16] Rawlings CA, Phillips HR. Reduction of mine heat loads. In: Proceedings of the 7th international mine ventilation congress; 2001. p. 381–9.

[17] Udd JE. A bibliography on deep mining. In: Proceedings of the core project on deep mining, June 2006. 10p.

[18] Fall M, Nasir O. Numerical modeling of the coupled thermo-chemo-mechanical response of cemented paste backfill structures in deep mine temperature conditions. In: 3rd Canada–US rock mechanical symposium and 20th Canadian rock mechanics symposium, 2009 CD-Room.

[19] Nasir O, Fall M. Modeling the heat development in hydrating CPB structures. Comput Geotech 2009;36(7):1207–18.

[20] Fall M, Nasir O, Celestin JC. Paste backfill response in deep mine temperature conditions. Symposium minefill, Montreal, Canada, 2007 CD-Room.

[21] Fall M, Adrien D, Célestin JC, Pokharel M, Touré M. Saturated hydraulic conductivity of cemented paste backfill. Miner Eng 2009;22(15):1307–17.

[22] Kesimal A, Yilmaz E, Ercikdi B, Deveci H, Alp I. Effect of properties of tailings and binder on the short-and long-term strength and stability of cemented paste backfill. Mater Lett 2005;59:3703–9.

[23] Nordstrom DK. Aqueous pyrite oxidation and the consequent formation of secondary iron minerals. In: Kittrick JA, Fanning DS, Hossner LR, editors. Acid sulfate weathering. Madison, WI: Soil Science Society of America; 1982. p. 37–56.

[24] Stumm W, Morgan JJ. Aquatic chemistry: chemical equilibria and rates in natural waters. New York: Wiley-Interscience; 1996.

[25] Akcil A. Destruction of cyanide in gold mill effluents: biological versus chemical treatments. Biotechnol Adv 2003;21:501–11.

[26] Orejerana L. Modeling the effects of sulphate and curing temperature on the strength development of cemented paste backfill using artificial neural network. Master thesis (M.A.Sc.), University of Ottawa; 2010. 174 p.

[27] US Silica Company, Berkeley, Springs, WV.

[28] Taylor HFW. The chemistry of cements, vol. 1. 1st ed. London: Academic Press; 1964.

[29] Gani MSJ. Cement and concrete. 1st ed. London: Chapman and Hall; 1997.

[30] Fall M, Samb SS. Pore structure of cemented tailings materials under natural or accidental thermal loads. Mater Charact 2008;59(5):598–605.

[31] McIntosh JD. The effects of low-temperature curing on the compressive strength of concrete. Gen. report of session BII. In: Proceedings of RILEM symposium winter concreting. Danish Institute for Building Research Copenhagen; 1956.

[32] Barnett SJ, Soutsos MN, Millard SG, Bungey JH. Strength development of mortars containing ground granulated blast-furnace slag: effect of curing temperature and determination of apparent activation energies. Cem Concr Res 2006;36:434–40.

[33] Lothenbach B, Winnefeld F, Alder C, Wieland E, Lunk P. Effect of temperature on the pore solution, microstructure and hydration products of Portland cement pastes. Cem Concr Res 2007;37:483–91.

[34] Tzouvalas G, Dermatas N, Tsimas S. Alternative calcium sulfate-bearing materials as cement retarders: part I. Anhydrite. Cem Concr Res 2004;34(11):2113–8.

[35] Barbarulo R. Comportement des matériaux cimentaires: actions des sulfates et de la temperature. PhD thesis, École Normale Supérieure de Cachan, France – Université Laval, Canada; 2002 [in French].

[36] Jelenić I, Panović A, Halle R, Gaćeša T. Effect of gypsum on the hydration and strength development of commercial Portland cements containing alkali sulphates. Cem Concr Res 1977;7(3):239–45.

[37] Divet L, Randriambolona R. Delayed ettringite formation: the effect of temperature and basicity on the interactions of sulphate and C–S–H phase. J Cem Concr Res 1998;28(3):357–63.

[38] Perkins RB, Palmer CD. Solubility of ettringite at 5–75 °C. J Geochim Cosmochim Acta 1998;63(13/14):1969–80.

[39] Bing B, Cohen MD. Does gypsum formation during sulphate attack on concrete lead to expansion. Cem Concr Res 2000;30(1):117–23.

[40] Metha PK. Sulphate attack on concrete—a critical review. In: Skalny J, editor. Materials science of concrete III. Ohio (USA): American Ceramic Society; 1995. p. 105–30.

[41] Fu Y, Ding J, Beaudoin JJ. Expansion of Portland cement mortar due to internal sulphate attack. Cem Concr Res 1997;27(9):1299–306.

[42] Alexander KM, Taplin JH. Concrete strength, cement hydration and the maturity rule. Aust J Appl Sci 1962;13:277–84.

[43] Kjellsen KO, Detwiler RJ, Gjorv OE. Development of microstructures in plain cement pastes hydrated at different temperatures. Cem Concr Res 1991;21:179–89.

[44] Escalante-Garcia JI, Sharp JH. The microstructure and mechanical properties of blended cements hydrated at various temperatures. Cem Concr Res 2001;31:695–702.

[45] Pokharel M. Geotechnical and environmental response of paste tailings systems to coupled thermo-chemical loadings. Master thesis (M.A.Sc.), University of Ottawa; 2008. 248 p.