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Research article

Evaluation of the neutralization performances of the industrial waste products (IWPs) in sulphide-rich environment of cemented paste backfill

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ABSTRACT

The purpose of this research is to examine the neutralization performances of CaO-rich industrial waste products (IWPs) in the sulphide-rich environment of cemented paste backfill (CPB). A total of 205 CPB samples were prepared by using four different IWPs (type-C fly ash (C-FA), blast furnace slag (BFS), calcitic limestone (CL) and dolomitic limestone (DL)) as 5, 10 and 15 wt% substitute for sulphide-rich tailings. These CPB samples were cured and subjected to the acid (pH) and sulphate (SO_4^{2-}) tests during 7–360 days of curing periods. MIP and XRD tests were also carried out to understand the generation of acid and sulphate and their effect on CPB stability at 28 and 180 days. The findings indicated that the utilisation of IWPs in CPB mixtures mitigated the acid (up to 58.9% higher pH values) and sulphate (up to 72.1% lower SO_4^{2-} ion release) production, and enhanced the microstructure (12.43% lower total porosity) of CPBs owing to the neutralization potential, pore-filling effect, pozzolanic and partially binding characteristics of IWPs. It can be inferred from these findings that the IWPs can be suitably utilised as neutralization materials in CPB of sulphide-rich tailings. This in turn allows the mitigation of potential disposal/pollution problems associated with these IWPs.

1. Introduction

In metal mining industries, the substantial amount of finely ground (<100 μm) sulphide-rich (i.e. pyritic) process tailings are generated during the flotation method for the recovery of precious metals (i.e., Cu, Pb and Zn). If a proper tailings management method is not chosen to dispose of such hazardous material, environmental problems such as acid mine drainage (AMD) will be faced due to the oxidation of sulphide-bearing minerals such as pyrite (FeS_2) when exposed to air (oxygen) and water (moisture) (Quispe et al., 2013; Chen et al., 2014; Plante et al., 2014). Because of AMD, a huge amount of acid and other hazardous constituents such sulphate and heavy metals are produced with severe impact on the ecosystem (Genty et al., 2012).

To prevent or mitigate the formation of AMD from sulphide-rich wastes, alkaline acid neutralizing materials such as natural carbonate minerals (marble waste (MW), limestone, dolomite etc.) (Potgieter-Vermaak et al., 2006; Genty et al., 2012; Tozsin et al., 2014a) and industrial by-products (cement kiln dust, red mud bauxite, fly-ash (FA) and blast furnace slag (BFS) etc.) (Xenidis et al., 2002; Feng et al., 2004; Yeheyis et al., 2009; Abreu et al., 2012; Mackie and Walsh, 2012) have been commonly used by various researchers in recent years. Potgieter-Vermaak et al. (2006) examined the effect of three different fine neutralizing materials (limestone, dolomite and FA) on the change in pH and elimination of contaminants from acid mine water (AMW). They found that the pH of AMW at 6 h of contact time increased from 1.2 to 7.4, 6.9 and 7.9 by the addition of limestone, dolomite and FA, respectively. It was also reported that the removal of sulphate from AMW with limestone, dolomite and FA reached to 64%, 72% and 78%, respectively. Additionally, Genty et al. (2012) focused on the effect of mineralogy and fineness of carbonate rocks on pH and alkalinity production using limestone drains in batch test in anoxic (i.e., no oxygen) and aerobic conditions for the treatment of two different AMD solutions with different levels of acidity. The study showed that pH of the AMD solution with high acidity increased from 3.3 to 5.8 and 5.5 for calcite intermediate (CI) and dolomite intermediate (DI) in anoxic (15 h). After the anoxic period, the pH of all solutions exposed to aerobic conditions tended to decline irrespective of the neutralizing material types. On the other hand, the granulated MW was utilised as neutralizing agent for amendment of acidic soil and the authors reported that the MW was highly beneficial to neutralize the acidic soil (Tozsin et al., 2014a).

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Similar findings were also reported by Feng et al. (2004). They conducted a study on the utilisation of two different BFSs having acid neutralizing capability at different slag dosages (2, 5, 8 and 30 mg/l) for removal of acidity and sulphate (SO_4^{2-}) from AMW. The authors observed that the pH of slurry raised from 2.03 to 6.68 and the removal of SO_4^{2-} in wastewater reached up to 89% depending on the slag dosage irrespective of the slag type. Furthermore, Xenidis et al. (2002) explored the effect of different amounts of Class-C fly ash (C-FA; 10–63% w/w) on the various parameters (i.e. pH evolution, conductivity, sulphate content, oxidation-reduction potential, permeability and metal concentration) of sulphidic tailings (27% S), which was categorized as potentially net acid generating in laboratory column kinetic test carried out for up to 600 days. They monitored that even at low C-FA additions (10% w/w) a highly alkaline leachate with pH 9 (*c.f. 4.1 for control*) was obtained.

European Union (EU) states that Cemented paste backfill (CPB), allowing safely the storage of mineral processing tailings (approximately 50–55%) into underground openings, is one of the most suitable waste management techniques due to its operational, economic, technical and environmental advantages such as i) the reduction of the tailings management costs, ii) increasing the neutralization potential of sulphide tailings, iii) contribution to safe storage of tailings in cemented (alkaline) environment with low permeability (10^{-5}-10^{-8} m/s) (Fall et al., 2009; Cihangir and Akyol, 2018) and iv) considerably prevention or deceleration of the AMD generation (European Commission, 2018; Yilmaz and Fall 2017). The CPB is a hardened composite mixture of dewatered tailings (full or deslimed), binders (up to 9 wt%) and sufficient water to make easier the transport of paste mixture from paste plant to underground stopes (Ouellet et al., 2007; Ercikdi et al., 2017; Chen et al., 2018a). Ordinary Portland Cement (OPC), the most widely utilised cement type to ensure the mechanical performance (strength, durability etc.) of CPB all over the world, has low resistance to the acid and sulphate attack and hence is not particularly suitable for CPB of sulphide tailings (Tariq and Nehdi, 2007; Cihangir et al., 2012; Ercikdi et al., 2015; Chen et al., 2018b; Yin et al., 2018; Wu et al., 2018). In this respect, Tariq and Nehdi (2007) indicated that the pH of CPB samples (CPBs) of sulphide tailings containing 52.3% pyrite decreased from 12.0 to 4.0 at the end of the 180 days. Moreover, they emphasised that the pH of samples declined to 6.0 even if the sulphate resistance cement (SRC) was used. These researchers have concluded that the cement alone is not sufficient for the neutralization of acid generated in CPB of sulphide-rich tailings. Dong et al. (2019) also reported that acid (H+) adversely affect the cement hydration and decompose the hydrated calcium silicate (C–S–H gels) with the eventual loss of CPB strength. Therefore, they suggested to increase cement dosage or use lime and fly ash as alkaline additive to neutralize acid in CPB. Similarly, Yin et al. (2018) ascertained that the expansion rate of CPB raised with the increase in sulphur content of tailings and even when the cement content increased from 8 to 16 wt% to prevent the expansion, the generation of cracks and loss of strength in CPB of sulphide-rich tailings could not be inhibited. However, the excessive increase in cement consumption may negatively influence the operating costs of CPB plant because the binder costs correspond up to 75–80% of CPB operating costs (Dudeney et al., 2013).

In recent years, some studies have reported that the industrial wastes (MW, C-FA, etc.) with high CaO content have influence on the neutralization of sulphide-rich wastes/soils preventing/reducing the release of harmful heavy metals (Ercikdi et al., 2009, 2015). Ercikdi et al. (2009) stated that the utilisation of FA with high CaO content as 10–30% partial replacement to OPC in CPB samples prepared from sulphide tailings did not achieve the required strength but, with no loss of strength in long-term. Furthermore, it was reported that the use of granulated MW (having no pozzolanic characteristic) as 10–30% additive to cement in CPB increased the pH and strength of CPB (Ercikdi et al., 2015). These investigations have confirmed that the utilisation of CaO-rich industrial waste products (IWPs) (MW, BFS, limestone, FA, etc.) can be beneficial for the neutralization of sulphide-rich tailings and prevention of loss of strength, which may occur in CPB in the long-term. However, there is no detailed research on this subject.

The present study aimed to investigate the acid neutralization performances of four different CaO-rich IWPs (type-C fly ash (C-FA), blast furnace slag (BFS), calcitic limestone (CL) and dolomitic limestone (DL)) as 5, 10 and 15 wt% partial substitution for sulphide tailings. The acid (pH) and sulphate (SO_4^{2-}) generation of CPB produced from sulphide-rich tailings were evaluated at OPC dosage of 8.5 wt% over specified curing times (7, 28, 90, 180 and 360 days). MIP and XRD tests were also implemented to show the impact of microstructural and mineralogical characteristics on the generation of acid and sulphate of CPB.

2. Experimental studies

The experimental studies involved size reduction (crushing and grinding) of CaO-rich IWPs, acid base accounting (ABA), preparation of CPBs, acid (pH)/sulphate (SO_4^{2-}) and microstructural (MIP) tests (Fig. 1). All laboratory tests presented in Fig. 1 were performed in paste backfill laboratory at KTU. Further detailed account of tests was given in the following sections.

2.1. Size reduction operations of IWPs

In this study, four different CaO-rich IWPs (C-FA, BFS, CL and DL) were obtained from different industries (thermal power plant, iron and steel plant and limestone quarry-pit). The as received CL and DL blocks were initially reduced in size by hammer and then crushed down to size of −2 mm with jaw crusher. All materials (C-FA, BFS, CL and DL) were then dried in a warm oven (36 h and 50 °C) before fine grinding process. The dried CaO-rich IWPs were separately ground to the required fineness (−100 μm) using a ball mill for CPB and other tests. Approximately 30 kg fine material (by dry weight) for each IWP was prepared.

2.2. Main characteristics of IWPs

The particle size distributions of C-FA, BFS, CL and DL were determined using Malvern Mastersizer Hydro 2000 MU. Fines (−20 μm) contents of IWPs varied in the range of 53.9 and 67.9% (Fig. 2). XRF and ICP-AES analyses of IWPs have shown that all materials contain predominantly CaO (30.62–55.26%), which is characterized as neutralization materials for acid (Table 1). It was also determined that BFS and C-FA are composed of high amounts of SiO_2 and Al_2O_3, whilst, DL contains 20.18% MgO. XRD patterns of IWPs (C-FA, BFS, CL and DL) were obtained from a Philips X'pert PW 3040 Diffractometer. All IWPs except BFS (C-FA, CL and DL) contained calcite while BFS showed the non-crystalline (amorphous) phase (Table 1, Fig. 3). In addition, C-FA, CL and DL contained minerals such as portlandite, anhydrite, quartz and dolomite (Table 1, Fig. 3b–d). The specific gravity and specific surface area of the materials varied in the range of 2.42–2.91 g/cm^3 and 4640–6360 cm^2/g, respectively (Table 1).

2.3. Sulphide tailings and binder

The tailings utilised in the experimental works was procured from Etibakır A.Ş. flotation plant situated in Kastamonu–Kure, Turkey. Fine particle (<20 μm) portion of the tailings measured by using Malvern Mastersizer was found as 48.41% (Fig. 2). The physical, chemical and mineralogical properties of the tailings were presented in detail in Table 1. The tailings has 29.66% pyrite and 15.82% sulphide content. It can be seen from Fig. 3e that the tailings was composed of pyrite as the major mineral phase which was consistent with the chemical characteristics of the tailings.

To prepare the CPB samples, CEM I 42.5R type OPC which is known to be vulnerable within the sulphide-rich environments was chosen as the binder to examine the efficiency of IWPs for preventing or minimizing the generation of acid and sulphate. Table 1 summarizes the chemical and physical properties of OPC in detail.

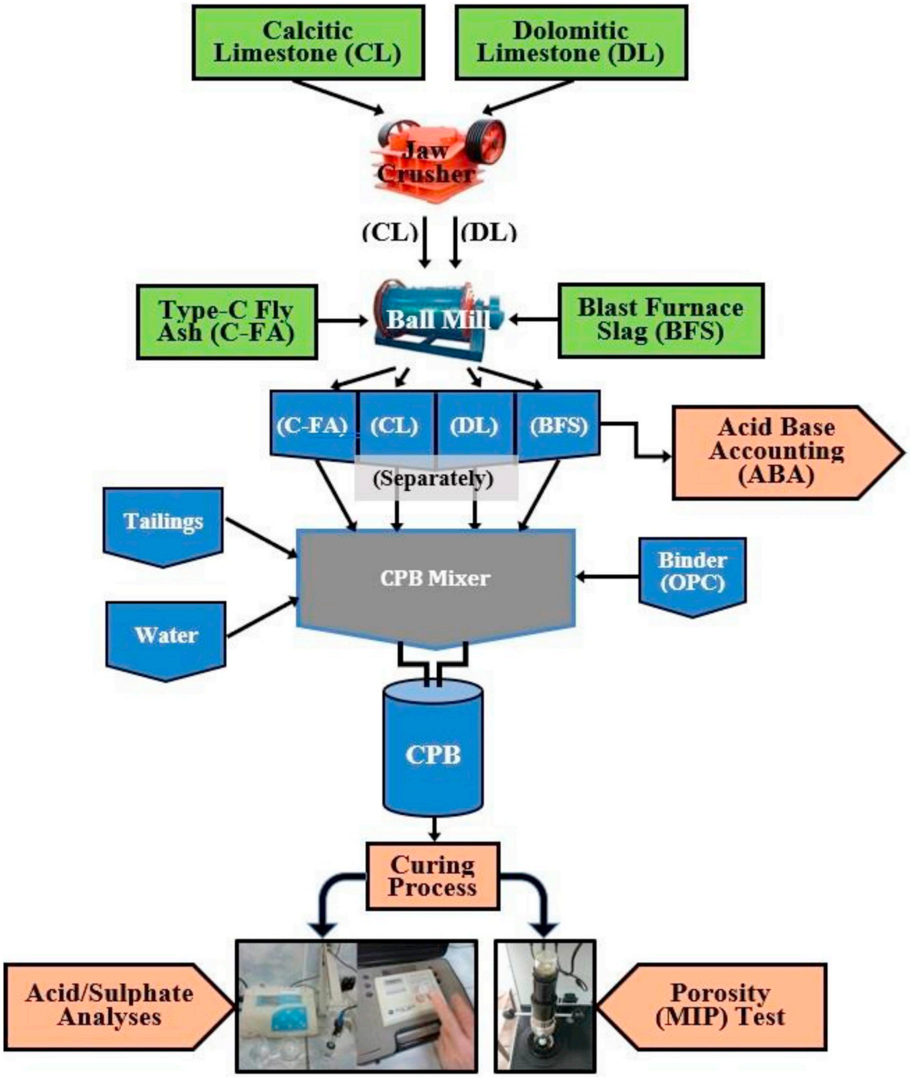

Fig. 1. Main steps of the experimental studies.

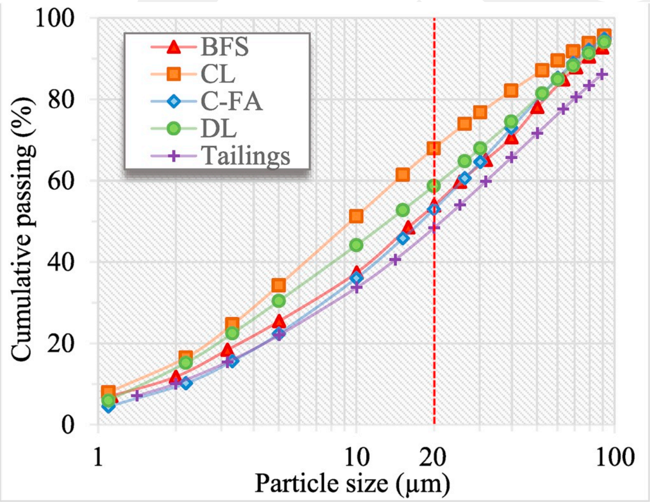

Fig. 2. Particle size distributions of IWPs and tailings.

2.4. *Acid-base accounting (ABA) tests for IWPs*

Acid-base accounting (ABA) tests, investigating the equilibrium between the acid-consuming and acid-generating constituents of mine wastes and/or acid neutralizing materials, are widely utilised to predict the occurrence of AMD calculating the acid generating potential (AP) and neutralization potential (NP) of materials (Paktunc, 1999). In this regard, the AP value was firstly calculated from the amount of total sulphur (%S_{total}) in the tailings using formula (1) given below (Sobek et al., 1978).

$$AP\left(kg\ CaCO_3/_{ton}\right) = 31.25 \text{ x } \%S_{total} \tag{1}$$

To calculate the NP of the tailings and IWPs, a few drops of acid (25% HCl) was primarily added on 0.5 g of sample for the observation of the fizz rating of IWPs according to Sobek test method (Table 2). From the result of the observation of fizz degree, the normality and volume of HCl required in the titration experiment were found out. Thereafter, the titration tests of materials were practiced with reference to standard ABA test method recommended by Sobek et al. (1978). The NP values were calculated with the following formula (2) as given in Table 2. The detailed information related to titration test procedure for the determination of NP values of materials can be seen elsewhere Sobek et al. (1978) and Bouzahzah et al. (2015).

Table 1
Chemical, physical and mineralogical properties of the IWPs, tailings and OPC.

Characteristics	BFS (%)	C-FA (%)	CL (%)	DL (%)	Tailings (%)	OPC (%)
Chemical composition						
SiO_2	39.85	34.96	0.86	0.12	31.89	21.02
Al_2O_3	10.58	13.92	0.23	0.09	8.97	5.27
Fe_2O_3	1.21	6.42	0.06	0.06	33.09	3.06
MgO	6.26	2.32	0.22	20.18	4.08	2.19
CaO	37.02	30.62	55.26	32.28	3.48	62.91
Na_2O	0.30	0.27	0.02	0.01	0.68	0.38
K_2O	0.97	0.91	0.12	0.02	0.36	0.81
TiO_2	0.77	0.71	0.01	<0.01	0.66	0.30
P_2O_5	0.01	0.40	0.02	0.02	0.04	0.11
MnO	2.54	0.04	0.02	<0.01	0.10	0.09
Cr_2O_3	0.019	0.054	<0.002	<0.002	0.032	0.035
Free CaO	–	8.67	0.01	0.03	–	1.19
Loss–on–ignition (LOI)	−0.5	3.4	43.1	46.9	16.1	3.6
Total	99.85	94.16	99.99	99.66	99.48	99.92
Sulphide content (S^{-2}) (%)	–	–	–	–	15.82	–
Pyrite content (FeS_2) (%)	–	–	–	–	29.66	–
Physical properties						
Specific gravity (g/cm^3)	2.91	2.42	2.63	2.79	3.37	3.12
Specific surface area (cm^2/g)	4640	6360	5665	5020	4440	4330

Mineralogical composition

BFS	C-FA	CL	DL	Tailings
Glassy phase	Calcite Portlandite Anhydrite Quartz	Calcite	Calcite Dolomite	Calcite Quartz Albite Pyrite Chlorite

$$NP\left(kg\ CaCO_3/_{ton}\right) = \frac{[(Na \times Va) - (Nb \times Vb)] \times 50}{m} \tag{2}$$

where;

"Na and Nb" are the molarity of acid (HCl) and base (NaOH), respectively,
"Va and Vb are the volume (mL) of acid and base, respectively,
"m" is the sample weight (g).

After the calculation of NP values of the tailings and IWPs, the net neutralization potential (NNP) of all materials were calculated via the formula below and presented in Table 2.

$$NNP = NP - AP \tag{3}$$

2.5. *Preparation of CPB samples*

The materials (tailings, OPC, IWPs and tap water) were mixed and homogenized using a blender (Fig. 4a) to prepare 205 CPB samples at 8.5 wt% of OPC dosage. Generation of acid-sulphate and porosity (MIP) of the samples were studied. The IWPs (C-FA, BFS, CL and DL) were used to partially replace the tailings at 5–15 wt% (Table 3). The CPB mixtures were prepared at 73.25 and 74.55 wt% solids with about 19.05 cm consistency. The process water in the tailings was found to contain 5616 mg/l sulphate ions (SO_4^{2-}) and its initial pH was 6.85. It should be noted that approximately 70–85% of the mixing water for CPBs comes from the tailings collected from the mineral processing plant. Experimental conditions for sample preparation were illustrated in Table 3.

After thoroughly mixed, the CPB mixtures were cast into the plastic cylindrical molds with 5 × 10 cm (diameter x height) having open-top and perforated bottom (Fig. 4b). Then, the CPB specimens/molds were placed on the drainage table for 24 h to drain excess water in CPB (Fig. 4c). Thereafter, the molds were subjected to curing process as open-top in a curing cabinet at 20 °C ± 1 temperature and ~80% ± 1 humidity for 7–360 days of curing ages (Fig. 4d). In this way, they were exposed to the oxidization in the presence of oxygen (air) and water (moisture) on the purpose of speeding up the amount of the sulphide oxidation and the examination of the effect of CaO-rich IWPs on the prevention or mitigation of internal acid and sulphate attack.

2.6. *Measurement of pH and sulphate content of CPB*

After the curing process, the measurement of pH and internal sulphate content in CPB were performed via test method used by Cihangir et al. (2012). Sartorius MA35 type moisture analyzer, Oakton pH/Con 510 pH-meter and Palintest 5000 photometer were used for the determination of the moisture content, pH and sulphate concentration, respectively. The detailed analysis procedure can be found elsewhere (Cihangir et al., 2012).

2.7. *MIP and XRD researches of CPB*

The porosity (total porosity and pore size distribution) development of a total number of 10 CPBs including control (full-tailings) and four different IWPs (BFS, C-FA, CL and DL) produced at the OPC dosage of 8.5 wt% and 15% wt. tailings substitution were analyzed under a mercury intrusion porosimeter (MIP) equipment (Micromeritics Autopore IV 9510) after a curing period of 28 and 180 days. These samples were kept intact for the MIP studies carried out according to the standard of ASTM D 4404-18 (2018). The samples used in MIP studies were dried in an oven (60 h and 50 °C) and preserved in a desiccator before the analysis. The samples were also subjected to the XRD analyses using a Philips X'pert PW 3040 Diffractometer.

3. Results and discussion

3.1. *Effect of IWPs on the neutralization potential of CPB*

Fig. 5 demonstrates the effect of the replacement ratio (5–15 wt%) of IWPs (BFS, C-FA, CL and DL) for the tailings on the acid generation potential of CPBs at the curing age of 7–360 days. All CPBs produced considerably low amount of acid (pH ≥ 11.0) up to 28 days. Hydration products such as $Ca(OH)_2$ formed by cement hydration reaction appeared to contribute to the maintenance of alkaline environment within CPBs in the short-term (≤28 days) (Cihangir et al., 2012; Yılmaz et al., 2018). Except BFS, CPBs having IWPs (C-FA, CL and DL) produced less amount of acid as indicated by the decrease in pH (i.e. pH 12.25–12.78 *c.f.* 12.12) than control sample at 28 days (Fig. 5b–d). It can be attributed to the fact that the C–FAs have binding properties as well as low pozzolanic property (Ercikdi and Yılmaz, 2019). Some authors (Uysal and Sumer, 2011; Zheng et al., 2016) also remarked that a certain amount of finely ground calcite ($CaCO_3$)-based materials such as marble, calcitic limestone and dolomitic limestone contributed to the formation of calcium carboaluminates as a hydration product. Furthermore, compared with the control CPBs, high pH values (pHs) in CPBs of CL and DL at 28 days confirm that these materials have high neutralization potential *(987.63-741.*25 kg *$CaCO_3$/ton)*. In addition, these high pHs at early age can be ascribed to the high specific surface area of these materials (Table 1). In accordance with the findings of this study, Potgieter-Vermaak et al. (2006) reported that the neutralization rate increased with increasing the specific surface area of the neutralizing material.

After an early curing age of 28 days, the trend of rapid decline in the pH of control (full-tailings) CPB was observed over up to 360 days. The pH of CPBs of IWPs decreased more slowly than that of control during the same curing ages (Fig. 5). As can be seen from the XRD profiles in

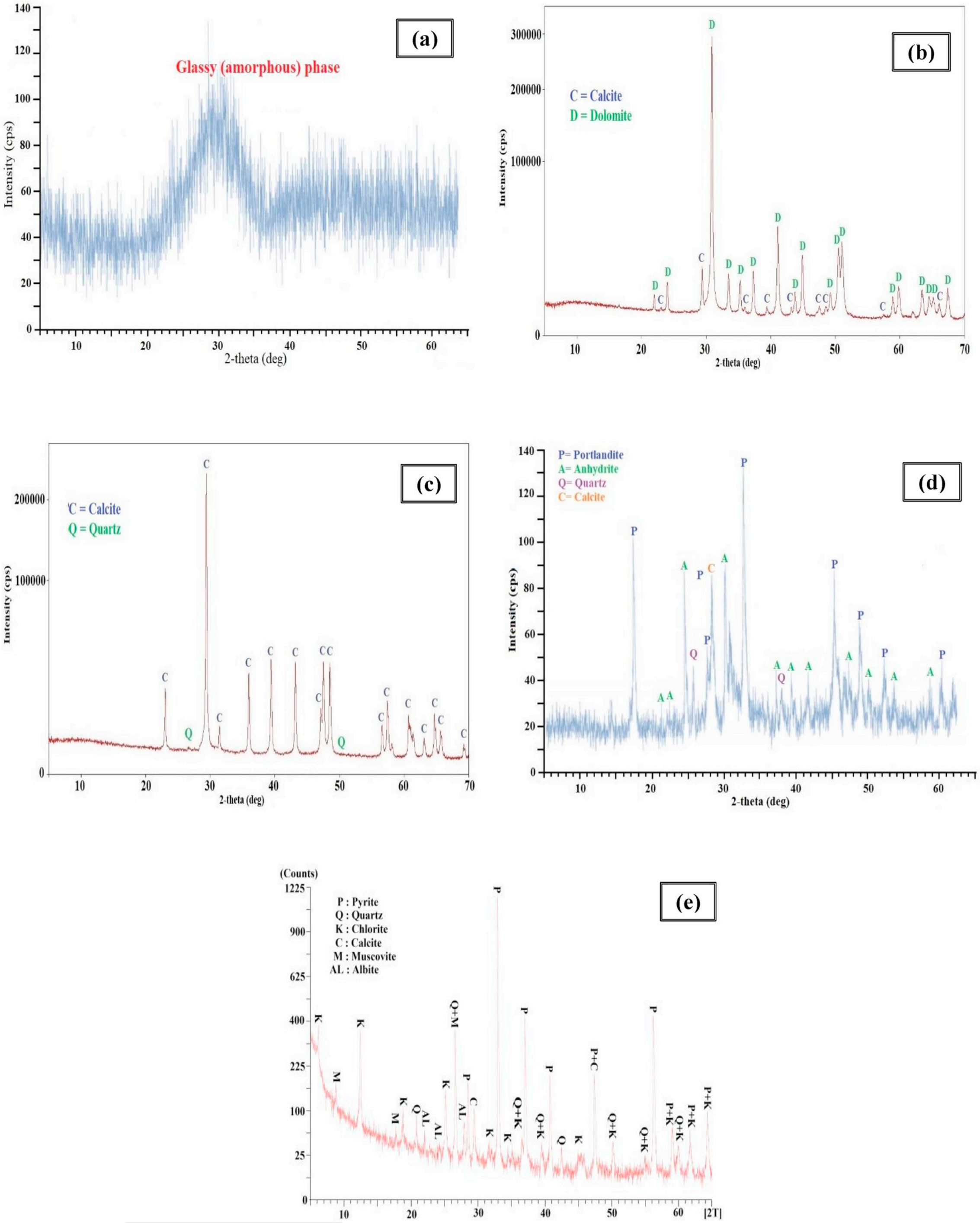

Fig. 3. XRD profiles of BFS (a), CL (b), DL (c), C-FA (d) and, tailings (e).

Fig. 6, the decline in pHs of CPB samples can be linked with the oxidization of sulphide minerals (pyrite etc.). Although the pHs in CPBs produced with all IWPs continued to decrease after 28 days, the resistance against internal acid production in CPBs increased with increasing the amount of IWP added in replacement of the tailings compared with the control CPBs. The pH of control CPBs decreased down to 6.42 at 360 days, while, the pHs of those CPBs prepared at 5 and 15 wt% IWPs were recorded to be 7.50–7.70 and 8.40–9.90, respectively (Fig. 5). Jones and Cetin (2017) investigated the effect of three different FA with CaO contents of 0.7%, 1.07% and 12.5% on the prevention and/or reduction of AMD generation from the mine tailings with pHs of 2.0–4.0. The authors reported that the addition of FA with 12.5 wt% CaO content raised the pH of the mixture to alkaline level (pH > 9.0). On the other hand, Tozsin et al. (2014a) utilised the granulated MW composed mainly of calcite as neutralizing agent for amendment of acidic soil. They observed that the pH of acidic soil increased from 4.71 ± 0.18 to 6.84 with the addition of MW into the soil at the end of 75 days. Similar findings were also achieved by Feng et al. (2004) who conducted an experimental research on the utilisation of BFS for the neutralization of AMW. The authors stated that the pH of slurry raised from 2.03 to 6.68 when the slag dosage was increased. This indicates that the IWP materials used in CPB mixtures have considerable neutralization potential (Table 2) due to their high CaO contents in accordance with the suggestion of Jones and Cetin (2017) who stated that the CaO content of the

Table 2
Acid-base accounting (ABA) test results of the tailings and IWPs.

Properties	Tailings	BFS	C-FA	CL	DL
Sulphide (S^{2-}) content (%)	15.82	–	–	–	–
CaO content (%)	3.48	37.02	30.62	55.26	32.28
Free CaO content (%)	–	–	8.67	0.01	0.03
Fizz rating of materials	None	Moderate	Slight	Strong	Moderate
Acid normality (N) and volume (ml)	0.1/20	0.5/40	0.1/40	0.5/80	0.5/40
Acid potential (AP)[a]	494.38	0	0	0	0
Neutralization potential (NP)[a]	8.58	532.25	318.84	987.63	741.25
Net Neutralization potential (NNP)[a]	−485.80	532.25	318.84	987.63	741.25

[a] : kg $CaCO_3$/ton waste.

IWPs should be higher than 25% for effective neutralization. Furthermore, as explained in the following section (Section 3.3), the IWPs formed less porous and denser matrix in CPB (Fig. 9) by filling the voids between coarse tailings particles (Fig. 2) (Zheng et al., 2016; Yılmaz et al., 2018).

Compared with the control CPBs, CPBs having 15 wt% of IWPs showed noticeably low acid generation by the oxidation of pyrite, which is responsible for the reduction of pH (Fig. 5). It was monitored that the pH of control CPBs dropped from 12.78 to 6.42 at the end of the curing age of 360 days while the CPBs containing 15 wt% of IWPs were able to maintain alkaline levels (pH = 8.35–9.88). Dong et al. (2019) investigated the surface appearances of CPBs having different sulphur contents at the end of 180 days and, reported that the oxidation of pyrite led to the marks darkened from yellow to brown. In agreement, control CPBs in the current study had higher amount of yellow and brown marks (colors) as an indication of oxidation of sulphide minerals at 180 days of curing time (Fig. 7a). However, CPBs containing IWPs at %15 wt% appeared to have relatively low such marks as the evidence of less amount of acid generation than control CPBs (Fig. 7b–d). CPBs containing 15 wt% of BFS and C-FA produced quite low amount of acid (pH ≥ 9.65) over the curing periods tested. On the other hand, lower pHs (pH = 8.35–8.75) was observed for CPBs containing 15 wt% CL and 15 wt% DL (Fig. 5). Although they exhibit less neutralization potential, higher alkalinity (12.91–29.17% and 10.28–34.16% for BFS and C-FA, respectively) of the CPBs of BFS and C-FA particularly in long term could be linked with the fact that the dissolution rate of CaO, which exists in the structure of BFS and C-FA as neutralizing agent, is higher than $CaCO_3$ that available as source of alkalinity in CL and DL (Table 2, Fig. 5). Furthermore, the high pH values in CPBs of BFS and C-FA samples can also be attributed to their low porosity values at 28 and 180 days which mitigated the oxidation rate of pyrite minerals (Fig. 9).

BFS and C-FA could also contribute to the acid resistance and mechanical performance of CPBs by producing additional C–S–H phases due to their pozzolanic activity with $Ca(OH)_2$ (Toledo Filho et al., 2007). Furthermore, it was stated that the neutralization rate increased with the growing of surface area of materials (6360 cm^2/g *c.f. 5665*-5020 cm^2/g *for CL and DL*) (Potgieter-Vermaak et al., 2006). Similarly, CPBs having 15 wt% CL produced slightly higher (1.3–2.7%) pHs than those of DL samples probably owing to finer particle size of calcite compared to dolomite (5665 cm^2/g *c.f.* 5020 cm^2/g *for DL*) (Figs. 2 and 5). Genty et al. (2012) also reported that the calcite had higher neutralization capability than dolomite. Consistent with the findings of previous studies (Tozsin et al., 2014a; Ercikdi et al., 2015), it is clearly seen from XRD profiles presented in Fig. 6d and e that higher amount of calcite in the CPBs of CL and DL dissolved than control samples over the curing period of 28–180 days and thus, a greater amount of the release of OH^- ions occurred in the CL and DL samples.

3.2. Effect of IWPs on the sulphate (SO_4^{2-}) resistance of CPB

The sulphate (SO_4^{2-}) levels of CPBs of control and 5–15 wt% IWPs up to 360 days are illustrated in Fig. 8. The SO_4^{2-} initially present in the sulphide-rich tailings was consumed within the first 7 days due to the reactions with the hydration products such as binding components (C–S–H) and portlandite ($Ca(OH)_2$) irrespective of the mixture types of CPBs. After this initial period, the SO_4^{2-}concentration in all CPBs (control and 5–15 wt% IWPs) increased with increasing of the curing age, which is most evident after 180 days (Fig. 8). This could be attributed gradual decrease in pyrite content in CPBs due to oxidation as the curing proceeded (Fig. 6). However, the generation of sulphate in CPBs of IWPs

Fig. 4. Preparation of CPBs: mixing (a), casting (b), draining (c) and curing (d).

Table 3

A summary of the experimental conditions for the preparation of CPBs.

Mixture name	Materials (wt. %)		Solids content, (SC)[a], wt. %	Cement dosage (CD)[b], wt. %	Water to cement ratio (w/c)[c]	Slump (cm)
	Tailings	IWP				
Control	100	–	73.70	8,5	4.20	19.05
5 wt% BFS	95	5	73.80		4.18	
10 wt% BFS	90	10	74.14		4.10	
15 wt% BFS	85	15	74.55		4.02	
5 wt% C-FA	95	5	73.25		4.30	
10 wt% C-FA	90	10	73.44		4.25	
15 wt% C-FA	85	15	73.90		4.15	
5 wt% CL	95	5	73.38		4.27	
10 wt% CL	90	10	73.69		4.20	
15 wt% CL	85	15	74.02		4.13	
5 wt% DL	95	5	73.65		4.21	
10 wt% DL	90	10	74.03		4.13	
15 wt% DL	85	15	74.31		4.07	

[a] $SC : \dfrac{100 \times (M_{dry-tailings} + M_{dry-cement})}{M_{dry-tailings} + M_{dry-cement} + M_{water}}$

[b] $CD : \dfrac{100 \times (M_{dry-cement})}{(M_{dry-cement} + M_{dry-tailings})}$

[c] $W/C : \dfrac{M_{water}}{M_{dry-cement}}; (M : Weight)$

decreased with increasing the replacement ratio of IWPs for sulphide tailings. In contrast to control CPBs at 360 days (53788 ppm), CPBs containing 15 wt% IWPs produced considerably low amounts of sulphate (18099–32624 ppm) consistent with the alkaline pH conditions (8.4–9.9) of IWPs samples (Figs. 5 and 8). This could well be related to high neutralization performances of IWPs (Table 2), in line with their relatively high CaO contents (Table 1) (Cihangir et al., 2012; Tozsin et al., 2014b). As can be seen from XRD profiles in Fig. 6, lower free sulphate ions in CPBs of IWPs can be linked with the gypsum formation along with the dissolution of CaO in the IWPs, in agreement with the study of Masindi et al. (2017). These findings confirm the results previously obtained by Potgieter-Vermaak et al. (2006) where the sulphate ion concentrations in AMW reduced from 6000 ppm to 2100 ppm, to 1800 ppm and to 1300 ppm with decreasing rates of 64%, 72% and 78% when dolomite, limestone and fly ash utilised for the treatment of AMW, respectively. In another research (Xenidis et al., 2002), the addition of C-FA (10 and 18%) to sulphidic tailings diminished the sulphate content (49% and 72%, respectively) at the end of 600 days. Furthermore, Feng et al. (2004) informed that the decrease of SO_4^{2-} concentration in wastewater reached up to 89% with the utilisation of two different BFSs with acid neutralizing capability irrespective of the BFS type. It can be inferred from these results that the granulated IWPs contribute to the resistance against the sulphate attack in CPB of sulphide-rich tailings.

Relatively slow sulphate formation (6421–15175 ppm) in all CPBs were observed during 180 days. Thereafter, the SO_4^{2-} content in control samples sharply increased (3.5 times) over up to 360 days. However, the SO_4^{2-} formation in all IWPs samples remained at remarkably low levels compared with that in control CPBs. CPB samples with 15 wt% BFS and C-FA produced lower (14.45–44.52% and 29.05–37.29% for BFS and C-FA, respectively) SO_4^{2-} content than CL and DL (Fig. 8). This can be attributed to the fact that BFS and C-FA have partially binding and pozzolanic properties (Ercikdi et al., 2009; Fall et al., 2009, 2010;

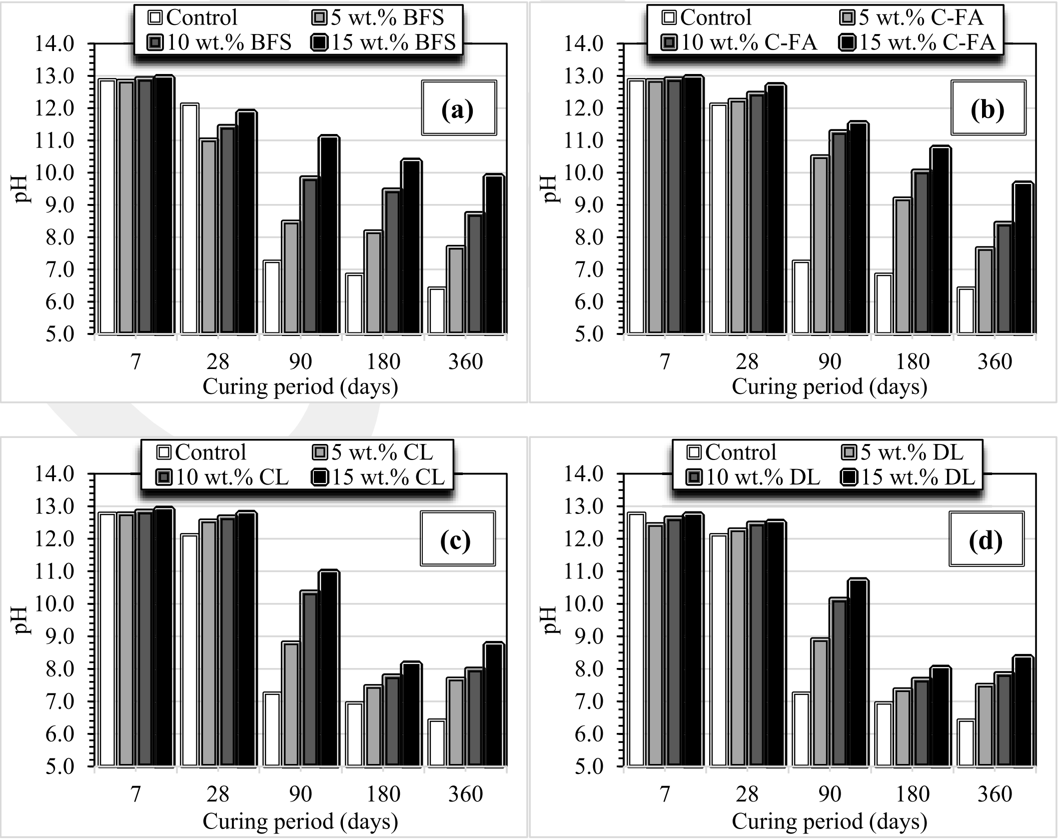

Fig. 5. Effect of BFS (a), C-FA (b), CL (c) and DL (d) on the acid prevention performances of CPBs.

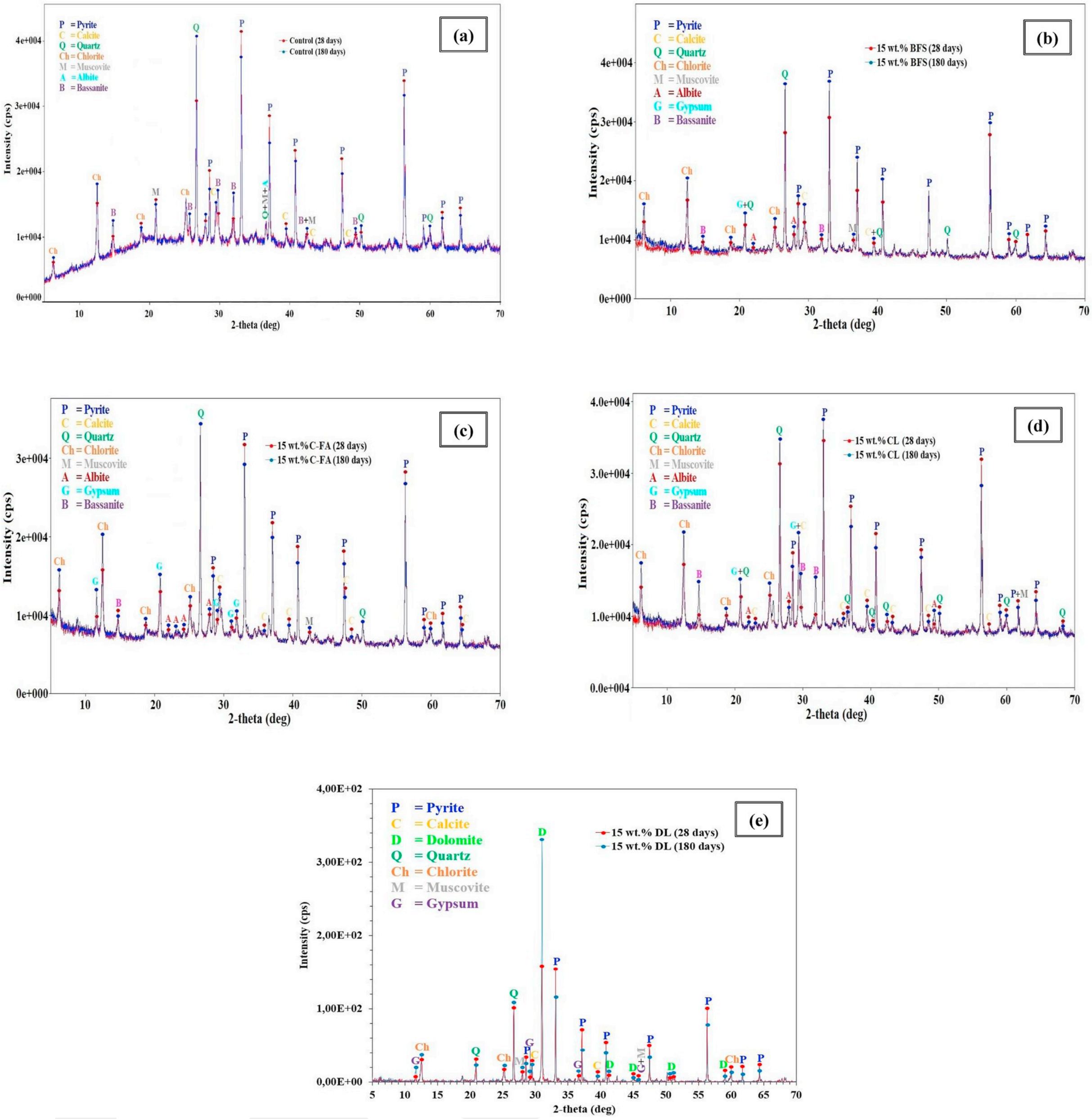

Fig. 6. XRD profiles of control (a) and 15 wt% IWPs (BFS (b), C-FA (c), CL (d) and DL (e)).

Ercikdi and Yılmaz, 2019), and also neutralization capability (Table 2) although CaO + MgO content of these materials are lower (1.8–2.2 and 2.1–2.5 times, respectively) than other IWPs (CL and DL) (Table 1). It can also be seen from Fig. 7 that the CPBs having 15 wt% BFS and C-FA had considerably less yellow and brown marks (colors) than CL samples. Furthermore, as will be explained in detail in Section 3.3, compared with the CL and DL samples, the utilisation of BFS and C-FA at 15 wt% partial substitution contributed to the pore structure (total porosity, meso-porosity, macro-porosity etc.) of CPB by filling the voids between coarse tailings particles (Zheng et al., 2016), by producing extra binding (C–S–H) phases owing to their pozzolanic characteristics (Fall et al., 2009).Thus, the formation of sulphate was reduced by alleviating the oxidation of pyrite.

3.3. *Effect of IWPs on the evolution of pore structure of CPB*

The total porosity (n_{total}) values of CPBs (control and 15 wt% IWPs) obtained from MIP analysis at 28 and 180 days were presented in Fig. 9 to better understand the effect of IWPs on the evolution of the pore structure of CPBs. The technical parameters (total porosity (n_{total}), meso-porosity (n_{meso}), macro-porosity (n_{macro}) and critical pore diameter (d_{cr})) of CPBs were also summarised in Table 4 n_{total} values of all CPBs decreased with increasing the curing period (from 28 to 180 days). It is apparent from Fig. 9 and Table 4 that the utilisation of 15 wt% IWPs as partial substitution for the sulphide tailings significantly ameliorated the microstructure of CPBs compared to the control samples, irrespective of the curing ages. The addition of 15 wt% IWPs decreased the n_{total} values in the range of 4.7–12.3% and 4.5–12.4% at 28- and 180 days of curing age, respectively. Furthermore, the change in the n_{meso} and n_{macro} values of CPBs having IWPs showed that the microstructure of CPBs significantly improved compared with the control CPBs (Table 4). To illustrate, the IWPs reduced the n_{macro} values of about 8.7–25.8% at 28 days and 14.1–38.2% at 180 days with these reductions more extensive for BFS and C-FA. In addition to decreasing the total and macro porosities, IWPs increased the amount of meso porosities in the range of 19.7–70.9% at 28 days and 57.2%–172.3% at 180 days. These

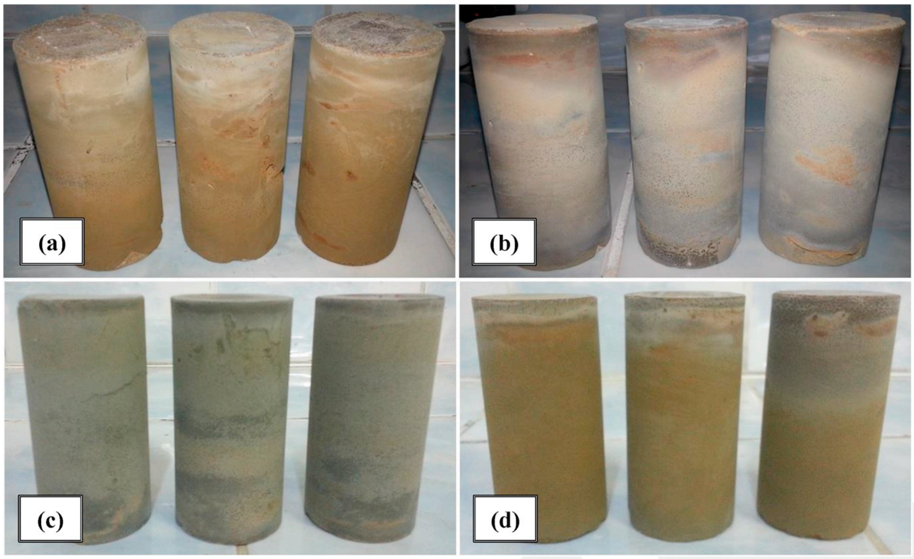

Fig. 7. Surface appearances of control (a) and %15 IWPs (BFS (b), C-FA (c), CL (d)) at 180 days of curing time.

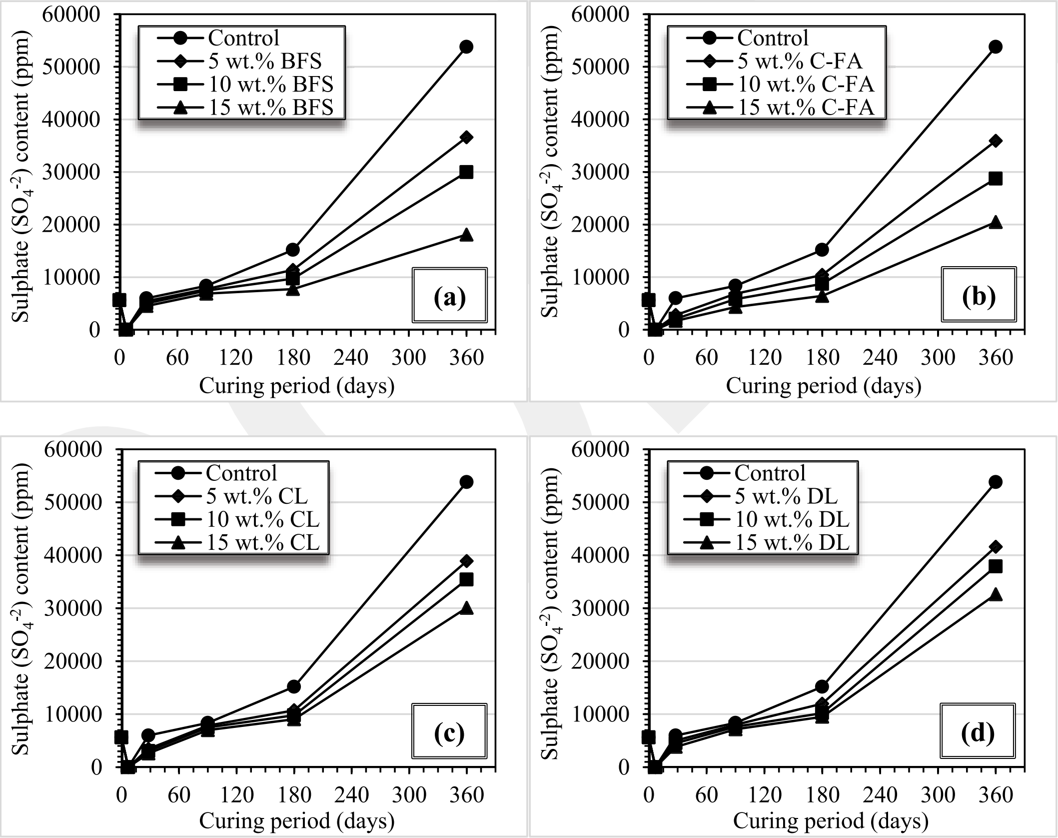

Fig. 8. Effect of BFS (a), C-FA (b), CL (c) and DL (d) on the sulphate (SO_4^{2-}) concentrations of CPBs.

results are in good agreement to those reported by Zheng et al. (2016) and Yılmaz et al. (2018). The authors utilised the finely granulated limestone powder (LP) at 22.5 wt% (Zheng et al., 2016), and construction and demolition waste (CDW) at 15 wt% (Yılmaz et al., 2018) replacement of sulphide tailings in CPB. The findings revealed that the total porosity reduced from 34.8% to 33.43% at 28 days and from 42.72% to 39.16% at 180 days, respectively. Moreover, the n_{macro} values decreased to about 23.5% and the n_{meso} values increased to about 22.8% at the LP replacement level of 22.5% in the study by AZheng et al. (2016). In another study by Yılmaz et al. (2018), 24.8% decline in n_{macro} and 111.5% increase in n_{meso} were obtained at the replacement level of 15 wt% CDW to tailings. The pore technical parameters (Fig. 9 and Table 4) evidently suggest that the IWPs filled the pores between tailings particles, and in this way, provided remarkably a denser microstructure (Huang and Lin, 2010; Yilmaz et al., 2011; Yılmaz and Ercikdi, 2016; Yılmaz et al., 2018). Additionally, as clearly seen from the XRD profiles in Fig. 6b–e, the acceptable amount of secondary neutralization products such as gypsum filled the pores in CPB, consistent with the previous

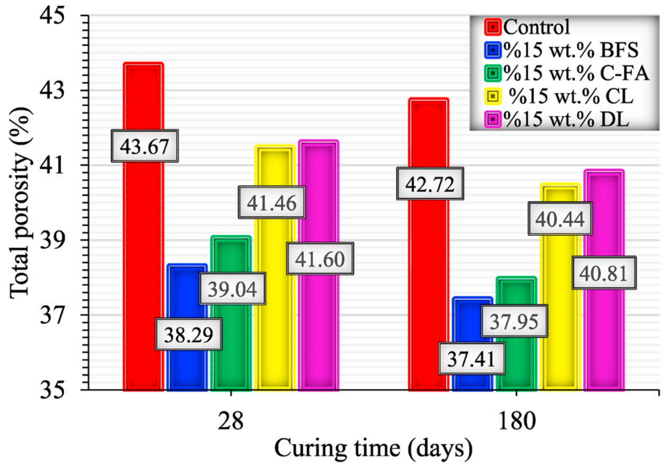

Fig. 9. The total porosity (n_{total}) values of CPBs (control and 15 wt% IWPs) at 28 and 180 days.

Table 4
Technical parameters of the MIP curves at 28- and 180-day CPBs.

Mixture type	Curing period (days)	Total porosity (n_{total}; %)	Cumulative porosity (%)		$^c d_{cr}$ (µm)
			$^a n_{meso}$	$^b n_{macro}$	
Control	28	43.67	6.08	37.59	0.836
15 wt% BFS		38.29	10.39	27.90	0.183
15 wt% C-FA		39.04	8.01	31.03	0.283
15 wt% CL		41.46	8.43	33.03	0.554
15 wt% DL		41.60	7.28	34.32	0.553
Control	180	42.72	5.23	37.49	1.628
15 wt% BFS		37.41	14.24	23.17	0.183
15 wt% C-FA		37.95	10.64	27.31	0.433
15 wt% CL		40.44	8.22	32.22	0.554
15 wt% DL		40.81	10.26	30.55	0.349

[a] n_{meso} (Meso-porosity): Mesopores range between 0.002 and 0.05 µm.
[b] n_{macro} (Macro-porosity): Macropores have pore size larger than 0.05 µm.
[c] d_{cr} (Critical pore diameter): Critical pore size represents the steepest slope of the cumulative porosity curve (Everett, 1972; Yilmaz et al., 2011).

studies (Pokharel and Fall 2013). In this regard, the finer particles are presumed to reduce the pore volume and, increase the packing density. This apparently leads to better sulphate endurance due to the reduced permeability (Kruse et al., 2013). In this regard, compared to control samples, the production of lower amount of acid (Fig. 5) and sulphate (Fig. 8) in CPB containing IWPs could be linked to that the finer IWPs contributed to the improvement of microstructure (total porosity, meso-porosity and macro-porosity etc.) of CPBs.

On the other hand, d_{cr} of control CPBs conspicuously enlarged with increasing the curing time. The utilisation of IWPs was found to reduce the d_{cr} values (33.7–78.1% and 66.0–88.8% at 28 and 180 days, respectively) of CPB compared with control CPBs (Table 4). In this regard, higher resistance of CPBs of IWPs to acid and sulphate attack (Figs. 5 and 8) especially in the long-term could also be ascribed to the lessening of d_{cr} values in addition to the reduction in the porosity and refinement of the pore structure via the beneficial contribution such as pore-filling effect, pozzolanic and additional binding characteristics as well as neutralization capability (Ercikdi et al., 2009; Fall et al., 2010; Zheng et al., 2016; Ercikdi and Yılmaz, 2019). Therefore, as a result of lessening d_{cr} values, oxidation in sulphide-rich environment within CPBs is minimized owing to the decreased permeability restricting the fluid transfer within CPB and the penetration of air into the CPB (Fall et al., 2009; Pokharel and Fall 2013; Mangane et al., 2018; Yılmaz et al., 2018; Cihangir and Akyol, 2018).

4. Conclusion

In this study, the neutralization performance of IWPs in sulphide-rich environment of CPB is highlighted. CPBs containing control (full-tailings) and four different IWPs (BFS, C-FA, CL and DL) at 5, 10 and 15 wt% partial substitution for sulphide-rich tailings were subjected to the acid (pH) and sulphate (SO_4^{2-}) analyses during 7, 28, 90, 180 and 360 days. MIP and XRD tests were also performed at 28 and 180 days to elucidate the effect of microstructures and mineralogical characteristics on the acid and sulphate of CPB. Following conclusions can be drawn from this study;

i. Generation of acid and sulphate in all CPBs increases with increasing the curing time. However, the utilisation of IWPs, having neutralization potential, as partial substitution for sulphide-rich tailings in CPB mixtures may alleviate the generation of acid and sulphate. In this regard, the addition of BFS and C-FA into CPB was particularly effective owing to their pore-filling effect, pozzolanic and partially binding characteristics.
ii. The results of XRD analysis indicated that (a) the oxidization of pyrite increased with curing time, (b) the OH^- ions released from alkaline minerals such as calcite and dolomite in IWPs neutralized the acid products in CPB, (c) free calcium ions from IWPs and sulphate ions from sulphide minerals appear to generate secondary gypsum within CPB mitigating the acid and sulphate attack.
iii. IWPs reduced the total porosity and macro-porosity and increased the meso-porosity improving the pore structure, and thus; resulting in denser CPB. The critical pore diameter (d_{cr}) of control CPB was found to increase with curing time, whilst, the utilisation of the IWPs in CPB mixtures reduced the d_{cr} values. In this way, owing to the decreased permeability, oxidation of pyrite was significantly reduced particularly at 15 wt% IWPs.
iv. Among IWPs used in the current study, BFS and C-FA seem to have better neutralization capacity and performance as replacement material in CPB within sulphide-rich environments owing to their additional pozzolanic and binding characteristics.

It can be inferred from these findings that the ground CaO-rich IWPs (BFS, C-FA, CL and DL) can be appropriately utilised as acid neutralization material to alleviate the unfavourable impact of acid and sulphate generated within CPB. IWPs can also improve the microstructure of CPB and thus produce more durable paste backfill in sulphide-rich environment. In addition, the utilisation of these IWPs can contribute to the management of these waste materials with concomitant environmental benefits.

Author contribution statement

Tekin Yılmaz: Conceptualization, Methodology, Investigation, Writing and Original Draft, Visualization. **Bayram Ercikdi** Validation, Funding acquisition, Writing - Review & Editing, Visualization, Supervision, Project administration. **Ferdi Cihangir** Writing and Original Draft, Writing - Review & Editing, Visualization.

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