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The study of strength behaviour of zeolite in cemented paste backfill

Hasan Eker*[1] and Atac Bascetin[2]

[1]*Eskipazar Vocational School, Property Protection and Safety Division, Occupational Health and Safety, Karabuk University, Karabuk, Turkey*
[2]*Department of Mining Engineering, Mining Faculty, Istanbul Technical University, Maslak, Istanbul, Turkey*

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Abstract. In the present study, reference samples were prepared using ore preparation facility tailings taken from the copper mine (Kure, Kastamonu), Portland cement (PC) in certain proportions (3 wt%, 5 wt%, 7 wt%, 9wt% and 11 wt%), and water. Then natural zeolite taken from the Bigadic Region was mixed in certain proportions (10 wt%, 20 wt%, 30 wt% and 40 wt%) for each cement ratio, instead of the PC, to prepare zeolite-substituted CPB samples. Thus, the effect of using Zeolite instead of PC on CPB's strength was investigated. The obtained CPB samples were kept in the curing cabinet at a temperature of 25°C and at least 80% humidity, and they were subjected to the Uniaxial Compressive Strength (UCS) test at the end of the curing periods of 3, 7, 14, 28, 56, and 90 days. Except for the 3 wt% cement ratio, zeolite substitution was observed to increase the compressive strength in all mixtures. Also, the liquefaction risk limit for paste backfill was achieved for all mixtures, and the desired strength limit value (0.7 MPa) was achieved for all mixtures with 28 days of curing time and 7 wt%, 9 wt%, 11 wt% cement ratios and 5% cement – 10% zeolite substituted mixture. Moreover, the limit value (4 MPa) required for use as roof support was obtained only for mixtures with 11% cement – 10% and 20% zeolite content. Generally, zeolite substitution seems to be more effective in early strength (up to 28th day). It has been determined that the long-term strength losses of zeolite-substituted paste backfill mixtures were caused by the reaction of sulfate and hydration products to form secondary gypsum, ettringite, and iron sulfate.

Keywords: cement; cemented paste backfill (CPB); tailings; uniaxial compressive strength (UCS); zeolite

1. Introduction

Mine tailings generated as a result of exploration, extraction and processing of mines are a threat to the environment and human health when they are not disposed of properly. About 7 billion tons of solid waste are generated annually across the world, and 30 million tons of solid waste is generated in Turkey. Most of these tailings are classified as hazardous tailings because they contain heavy metals (copper, lead, cobalt, zinc, cadmium and chromium). Moreover, a large portion of these tailings is deposited in landfills, waste dams, and submarine disposal locations in contact with air. Therefore, this leads to environmental problems. Particularly, the storage of tailings containing sulfurous minerals (pyrite, etc.) causes the formation of acid mine drainage (AMD) and the release of heavy metals in the tailings, thus, directly polluting the surrounding water resources and soil (Ercikdi *et al.* 2010, Tuylu *et al.* 2019). The cemented paste backfill (CPB) method, which has been widely used in mining operations, provides several advantages to the industry regarding the disposal of mine tailings. CPB is defined as a successful mixture of fine-grained ore processing tailings (75 wt% – 85 wt%), binder (3 wt%- 9 wt%) and water to achieve the desired viscosity and solids ratio (70% - 80%) (Kesimal *et al.* 2005, Ercikdi *et al.* 2013, Yilmaz and Guresci 2017, Yilmaz *et al.* 2017).

Cement is the determining material in the CPB mixture. Therefore; the major financial cost of the paste filling facility is the cost of the cement. The cost of the putty filling mixture containing 1 wt% binder is 1 USD per ton (Naylor *et al.* 1997). According to the study of (Grice 1998) paste backfill operation, costs between 10-20% of the total mining operation costs, while De Souza *et al.* (2003) calculated the cost of the paste backfill mixture with a cement content of 3 wt% as 42% of the total cost of the paste-backfill operation in their study. On the other hand (Fall and Benzaazoua 2003) found that the cost of the paste-filling mixture with a binder content of wt% 5-9 was 50% of the total paste-filler operating cost, and (Ercikdi *et al.* 2017) reported that the binder consumption constituted 75% of the total paste filling cost in their study. Another study reported that 15% of the filling costs consist of binder costs (Belem *et al.* 2000). Therefore, choosing binder type and dosage at the optimum ratio is very significant to ensure the stability according to the desired strength in the plant and to keep the operating costs at the minimum level. For this reason, various studies revealed that the cost of the binder could be reduced and the stability performance of the CPB can be increased by using chemical agents (plasticizers, aqueous sodium silicate, sodium hydroxide) or pozzolanic minerals (marble powder, blast furnace slag, silica fume, fly ash, pumice, etc.) as an additive to Portland cement (PC) (Benzaazoua *et al.* 2002, Benzaazoua *et al.* 2004, Klein and Simon 2006, Tariq and Nehdi 2007, Ercikdi *et al.* 2009, Ercikdi *et al.* 2010, Ercikdi *et al.* 2010, Fall *et al.* 2010, Cihangir 2011, Cihangir, Erçıkdı *et al.* 2011, Cihangir *et al.* 2012, Cihangir *et al.* 2015, Ercikdi *et al.* 2015, Yilmaz *et al.*

*Corresponding author, Ph.D.
E-mail: eker_hasaan78@hotmail.com

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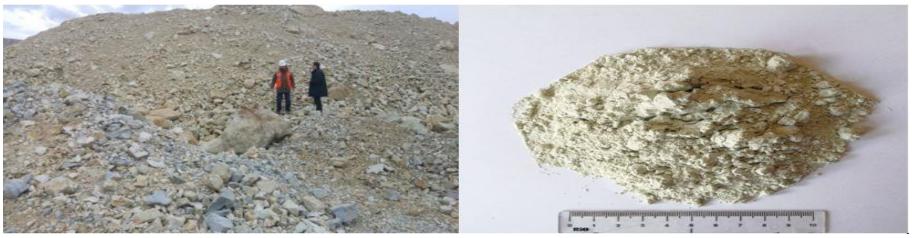

Fig. 1 Zeolite material

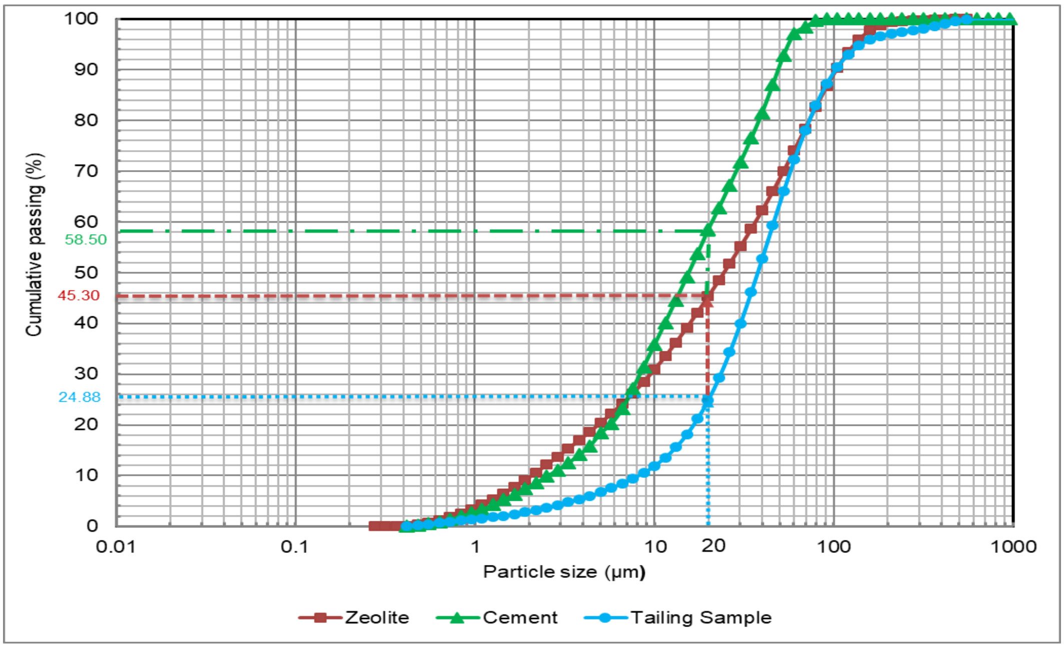

Fig. 2 Particle size distributions of zeolite, cement and tailing sample

2017, Bascetin and Tuylu 2018, Yılmaz *et al.* 2018, Gayana and Ram Chandar 2018, Tuylu *et al.* 2019, Wei *et al.* 2019, Bascetin *et al.* 2020, Wang *et al.* 2020, Eker and Bascetin 2022).

One of the mineral additives used as a substitute for Portland cement is natural zeolite. Natural zeolite shows good pozzolanic reactivity. The zeolite, which is the basis of the study, contains Clinoptilolitee and $Ca(OH)_2$ produced during the hydration of Portland cement, and it reacts to form cement-like hydrated products by showing a good pozzolanic reactivity. Thus, it affects the physical and mechanical properties of the blended cement depending on the amount of zeolite (Perraki *et al.* 2003, Kocak *et al.* 2013). (Sabet *et al.* 2013); reported that natural zeolite had a much more affordable cost with these additives. Several studies; revealed that the alkali -silica reaction (ASR) caused by the addition of zeolite kept the expansion below the value of the critical limit value and prevented the development of ASR (Feng 1998, Ramyar 2003, Turanli *et al.* 2007, Andiç Çakir 2008, Shon and Kim 2013, Valipour *et al.* 2013, Ramezanianpour *et al.* 2015). Moreover, Turan *et al.* (2007) reported that it reduced the chlorine ion permeability in concrete. Zeolite also causes positive improvements in the strength and durability of the concrete (Najimi *et al.* 2012). The zeolite that is used as a cement substitute increases the compressive strength of concrete, decreases water absorption, and increases density and ultrasonic pulse velocity (UPV). Moreover, natural zeolite increases porosity and subsequently improves the freeze-thaw resistance of concrete (Nagrockiene and Girskas 2016). Also, several studies revealed that it behaved similarly to that of sulfate resistant cement (Shon and Kim 2013).

According to the several studies in the literature, samples with natural zeolite substitution were observed to achieve lower or equivalent strength values compared to samples containing only cement (Karakurt and Topçu 2011, Taban *et al.* 2012, Uzal and Turanlı 2012, Toker 2013, Digis 2015, Samimi *et al.* 2017). (Poon *et al.* 1999) emphasized that, according to early strength developments, the mixtures with natural zeolite substitution showed lower strength values compared to reference samples, and the development of hydration reactions slowed down as the natural zeolite substitution ratio increased. The researchers interpreted that this situation was since the samples with natural zeolite (NZ) addition could not get a sufficient amount of CH (calcium hydrate) to react in the environment due to the slow hydration reaction of reactive silica in NZ (Yilmaz *et al.* 2007).

In other studies, the addition of natural zeolite was

Table 1 Chemical and physical properties of zeolite, tailing and cement used (Eker 2019)

Properties	Copper Tailings (%)	CEM I 42.5 R (%)	Zeolite (%)
Chemical Composition			
SiO_2	12.26	19.13	64.36
Al_2O_3	4.08	4.71	10.89
Fe_2O_3	54.28	3.28	1.44
MgO	2.33	1.29	1.34
SO_3	-	3.49	-
CaO	1.76	64.07	3.58
Na_2O	0.03	0.25	0.18
K_2O	0.09	0.86	4.33
Free CaO	-	1.65	
Loss on Ignition	24	2.09	11.0
Physical Composition			
Specific Gravity (g/cm^3)	3.61	3.14	2.33
Specific Surface (cm^2/g)	1801	3640	2687
Mineralogical Composition			

Zeolite		*Tailings*	
Clinoptilolitee	$(Na_{0.5}K_{2.5})(Ca_{1.0}Mg_{0.5})(Al_6Si_{30})O_{72}.24H_2O)$	Calcite	$CaCO_3$
Quartz	SiO_2	Chamosite	$(Fe^{2+},Mg,Fe^{3+})_5Al(Si_3Al)O_{10}(OH,O)_8$
Illite - Mica	$(K_{0.65}Al_{2.0}(Al_{0.65}Si_{3.35}O_{10})(OH)_1)$	Gypsum	$CaSO_4{\cdot}2H_2O$
		Hematite	α-Fe_2O_3
		Mangetite	Fe_3O_4
		Pyrite	FeS_2
		Quartz	SiO_2
		Chalybite	$Fe^{2+}CO_3$

found to increase the strength and resulted in higher strength values compared to reference samples (Janotka *et al.* 2003, Ahmadi and Shekarchi 2010, Karakurt *et al.* 2010, Ranjbar *et al.* 2013, Shon and Kim 2013, Toker 2013, Digis 2015, Vejmelková *et al.* 2015, Vyšvařil and Bayer 2016, Chen *et al.* 2017, MolaAbasi *et al.* 2019, Jafarpour *et al.* 2020, MolaAbasi *et al.* 2020, Ahmadi *et al.* 2021, Tuylu 2021). (Markiv *et al.* 2016) reported that concretes containing natural zeolite were observed to have a lower compressive strength up to 90 days, zeolite-added concretes exceed the strength of concretes without zeolite at the end of 180 days.

In the present study, reference samples were prepared using ore preparation facility tailings taken from the copper mine (Kure, Kastamonu), Portland cement (PC) in certain proportions (3 wt%, 5 wt%, 7 wt%, 9 wt% and 11 wt%) and water. Then natural zeolite taken from the Bigadic Region was mixed in certain proportions (10 wt%, 20 wt % 30 wt% and 40 wt%) for each cement ratio, instead of the PC, to prepare zeolite-substituted CPB samples. The obtained CPB samples were kept in the curing cabinet at a temperature of 25°C and at least 80% humidity and they were subjected to the Uniaxial Compressive Strength (UCS) test at the end of the curing periods of 3, 7, 14, 28, 56, and 90 days. It is also aimed to use Zeolite, which has been used as a pozzolanic material in concrete mixtures until now, in cement paste backfill mixtures with this study. Thus, the effect of using Zeolite instead of PC on the strength of CPB will be investigated. Besides, we will try to determine its effects on sulfate attacks that will occur due to the high content of Pyrite (FeS_2) in the tailings used. Moreover, it is aimed to reduce the cost of cement by using zeolite substitutesinstead of cement.

2. Materials and methods

2.1 Zeolite

In the present study, natural zeolite was used as a cement substitute. Natural zeolite was obtained from the dumpsite of a boron mine located in Bigadic, Balıkesir, Zeolite was subjected to pass through a roll crusher (- 4 mm) in the beginning in the laboratory, then, it was subjected to dry grinding for 45 minutes by a ball mill of 125 microns (Fig. 1). Particle size distribution analysis of the zeolite was determined using the Malvern Mastersizer Hydro 2000 MU device (Fig. 2).

It was found that 45.30% of the zeolite had a particle size below 20 µm (Fig. 1). Its specific surface area was 2687 cm^2/g. Also detailed chemical, physical and mineralogical properties of zeolite are given in Table 1. As the main phase according to the XRD diffraction pattern of the zeolite; Clinoptilolitee, quartz, and mica-illite were found (Fig. 3). The chemical and physical properties of copper plant tailings, cement and zeolite used are given in Table 1.

2.2 Tailings and Binder

Tailings material was obtained from the copper mine located in Kure, Northern part of Turkey. The particle size of 24.88 % of the material was below 20 µm (Fig. 1). Detailed chemical, physical and mineralogical properties of the material are given in Table 1. As seen in the mineralogical analysis; Pyrite 67.82%, Quartz 8.23%, Calcite 3.34%, Gypsum 1.12%, Hematite 3.30 %, Siderite 4.59%, Magnetite 0.96%, Chamosite 10.64%. To reduce the

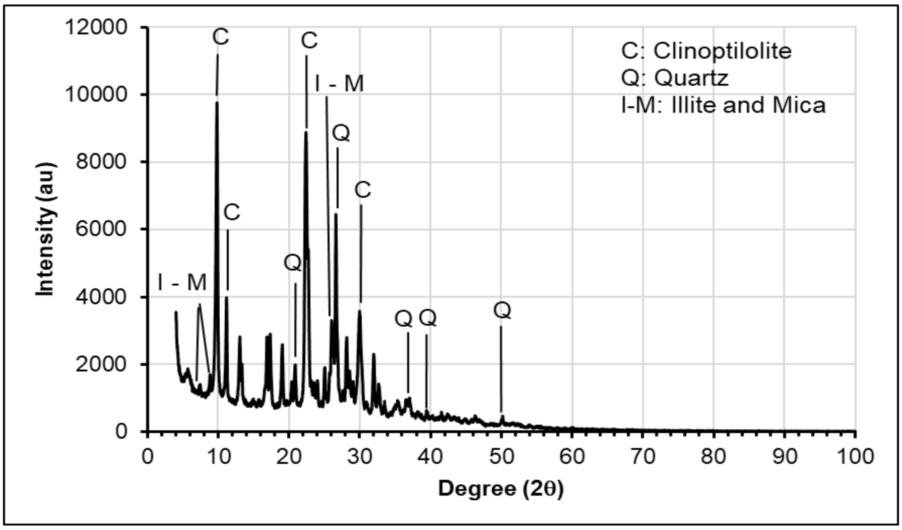

Fig. 3 XRD diffraction pattern of Zeolite

cement costs of paste backfill plants, normal Portland cement was preferred to see the effect of mineral additives used as a cement substitute in paste backfill mixtures. The results of the chemical analysis of the cement used are given in Table 1.

2.3 Preparation of cement paste backfill samples and Uniaxial Compressive Strength (UCS) Tests

Cement paste backfill samples were prepared by homogeneously mixing copper tailings, cement, zeolite and tap water. First, reference samples were created by mixing the tailings with cement and tap water in the ratios of 3 wt%, 5 wt%, 7 wt%, 9 wt%, 11 wt%. Later, cement paste backfill samples containing 10 wt%, 20 wt%, 30 wt% and 40 wt% zeolite substitutes were formed for corresponding cement amounts used (3 wt%, 5 wt%, 7 wt%, 9 wt%, 11 wt%). The paste was mixed for 10 minutes using a mixer to form a homogeneous mixture of the paste backfill. The selected zeolite percentage has been determined based on the values used in previous studies (Janotka *et al*. 2003, Ahmadi and Shekarchi 2010, Karakurt *et al.* 2010, Ghourchian *et al*. 2013, Ranjbar *et al*. 2013, Shon and Kim 2013, Toker 2013, Digis 2015, Vejmelková *et al.* 2015, Vyšvařil and Bayer 2016, Chen *et al*. 2017).

The paste backfill mixtures were prepared according to an 18 cm slump and 81% solid ratio value (Table 2). In CPB applications, the slump value was kept between 15.24 - 25.4 cm, and this value was used because it has been the most preferred slump value. Paste backfill mixtures were poured into cylindrical sample molds with a diameter of 5 cm and a height of 10 cm (with 4 holes at the bottom). Then, they were cured in the curing cabinet at a humidity of at least 80% and a temperature of 25°C for the curing period (3, 7, 14, 28, 56, and 90 days).

The uniaxial compressive strength test was carried out following ASTM C 39 (C39M-18 2018) standard on cylindrical samples of paste backfill prepared in the size of 50×100 mm.

The cement ratios of 3 wt%, 5 wt%, 7 wt%, 9 wt%, 11wt% and the samples obtained using natural zeolite instead of cement with 10 wt%, 20 wt%, 30 wt% and 40 wt were calculated separately for the curing periods of 3, 7, 14, 28, 56 and 90 days by breaking the automatically controlled pressure at 1 mm/min constant loading speed with 50 kN loading capacity. The size/diameter ratio of cylindrical paste backfill samples was at least 2, and the upper and lower surfaces of the samples were corrected before the experiment. In the experiments, 3 samples were tested for each curing period, and the average value of the results was obtained. (Grice 1998) determined the liquefaction risk of 0.15 MPa as the limit value (Been *et al*. 2002, Le Roux *et al.* 2004), sublevel caving values ≥ 0.7 MPa (Brackebusch 1995, Landriault 1995) and roof support values ≥ 4 MPa to determine the quality of paste backfill mixtures.

2.4 Review of SEM analysis results

SEM-EDS analyses were carried out using the JEOL JSM-5600 model Scanning Electron Microscope (SEM-EDS) device in the Faculty of Engineering, Metallurgy and Materials Engineering Department in Istanbul University. Therefore, the mixtures that provide the best strength in curing periods of 28 and 90 days were selected among the paste backfill mixtures, and the broken samples were taken in Uniaxial Compressive Strength (UCS) Tests. Samples are taken from a broken sample in the form of small parts. it is then powdered. Dried and gilded CPB samples must be prepared to obtain a true and clear observation during the SEM-EDS measurements. The basic parameter was listed as follows: resolution is 3 nm; acceleration voltage is 20 kV; magnification is 5–1000,000 and primary energy is 20 keV. The samples were then coated with gold film and placed in the electron microscope and imaged at different magnification values (50–9000).

2.5 Results review of XRD analysis results

Table 2 A summary of the experimental conditions used in the preparation of CPB samples

Mixture Name	Materials (wt. %)		Solids content (wt. %)	Water to cement ratio (w/c)	Slump (cm)	Cement dosage (wt. %)
	Zeolite (Z)	Cement (C)				
Reference	0	100	81	0.59	18	3
10 wt. % Z	10	90	81	0.69		
20 wt. % Z	20	80	81			
30 wt. % Z	30	70	81			
40 wt. % Z	40	60	81			
Reference	0	100	81	0.54	18	5
10 wt. % Z	10	90	81	0.44		
20 wt. % Z	20	80	81			
30 wt. % Z	30	70	81			
40 wt. % Z	40	60	81			
Reference	0	100	81	0.47	18	7
10 wt. % Z	10	90	81	0.40		
20 wt. % Z	20	80	81			
30 wt. % Z	30	70	81			
40 wt. % Z	40	60	81			
Reference	0	100	81	0.43	18	9
10 wt. % Z	10	90	81	0.37		
20 wt. % Z	20	80	81			
30 wt. % Z	30	70	81			
40 wt. % Z	40	60	81			
Reference	0	100	81	0.57	18	11
10 wt. % Z	10	90	81	0.23		
20 wt. % Z	20	80	81			
30 wt. % Z	30	70	81			
40 wt. % Z	40	60	81			

XRD analysis was performed using X-rays of the diffractometer device in the Acme laboratory. At the end of the 90-day curing period, the samples taken from the broken samples were first subjected to certain thinness and then a mineralogic analysis. XRD images were taken between 3º and 80º 2θ. XRD analyses were carried out to reveal the formation of secondary minerals (ettringite and gypsum, etc.), which cause the paste backfill to lose its durability. A detailed evaluation of the effect of the content composition of the samples on the findings of the experiment was given in the Results section.

3. Results and discussion

3.1 Evaluation of Uniaxial Compressive Strength (UCS) tests results

The prepared samples were kept in the curing cabinet at 25°C and humidity of at least 80% to simulate the underground conditions in which the samples were taken. The results of Uniaxial Compressive Strength (UCS) test obtained at the end of the curing period were given in Figs. 4-8.

As can be seen in Fig. 4, adding natural zeolite to a paste backfill mixture containing 3% cement did not increase pressure resistance. Also, samples of no mixture ratios exceeded of ≥ 0.7 MPa during the 28-day curing period. On the other hand, samples of all mixture ratios exceeded the liquefaction, risk limit of ≥ 0.15 MPa

As shown in Fig. 5, the addition of natural zeolite to the mixture of paste backfill containing 5% cement increased the compressive strength. On the other hand, samples containing 10% and 20% natural zeolite, gained about 9% less resistance compared to the reference samples for curing period of 14 days. For the curing period of 28 days, only the mixture with 10% ratio passed the desired strength limit of ≥ 0.7 MPa. Moreover, it has gained 1.5 times greater strength than the reference samples. As of roof support, samples of no mixture ratio exceeded the desired limit of ≥ 4 MPa. Besides, samples of all mixture ratios exceeded the liquefaction risk limit of ≥ 0.15 MPa.

Fig. 6 presents the results of the experiment of samples with a 7% zeolite addition. As can be seen in the figure, the addition of natural zeolite in the mixture of paste backfill containing 7% of cement has increased compressive strength. The samples containing natural zeolite (10%, 20%, 30% and 40%) gained about 1.8, 1.9, 1.4 and 1.1 times more resistance respectively compared to the reference samples for the curing period of 14 days. For the curing

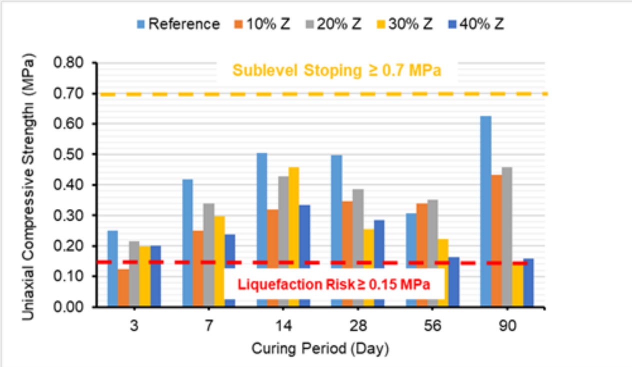

Fig. 4 Effect of zeolite substitutes (10%, 20%, 30% and 40%) for 3% cemented paste backfill samples on uniaxial compressive strength.

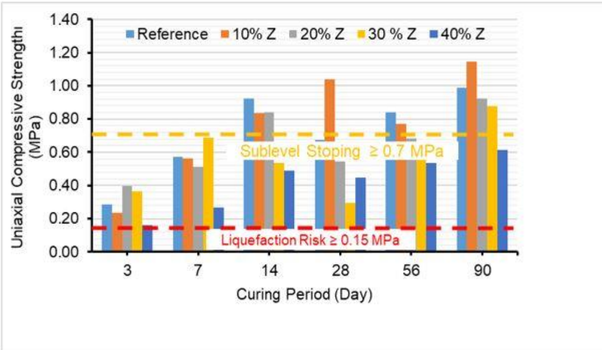

Fig. 5 Effect of zeolite substitutes (10%, 20%, 30% and 40%) for 5% cemented paste backfill samples on uniaxial compressive strength

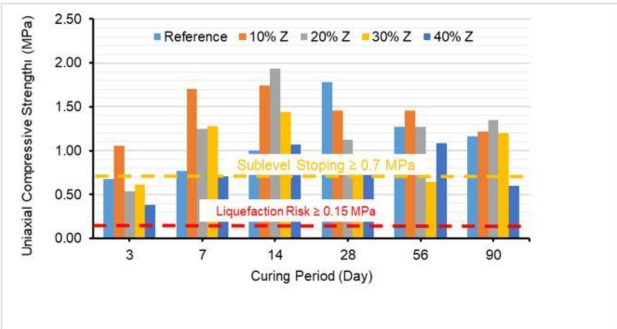

Fig. 6 Effect of zeolite substitutes (10%, 20%, 30% and 40%) for 7% cemented paste backfill samples on uniaxial compressive strength

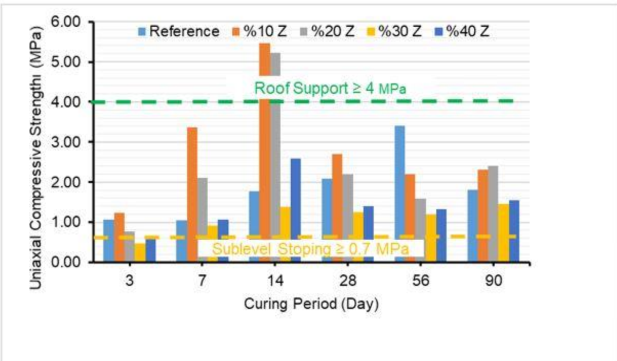

Fig. 7 Effect of zeolite substitutes (10%, 20%, 30% and 40%) for 9% cemented paste backfill samples on uniaxial compressive strength

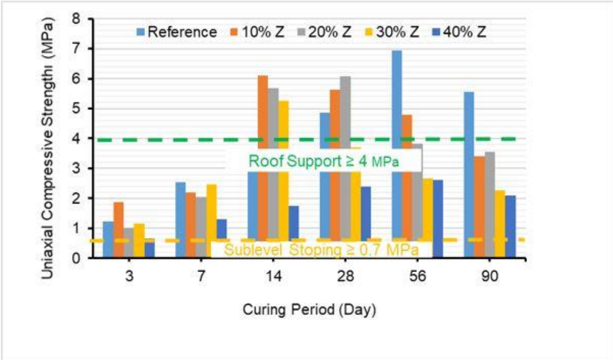

Fig. 8 Effect of zeolite substitutes (10%, 20%, 30% and 40%) for 11% cemented paste backfill samples on uniaxial compressive strength

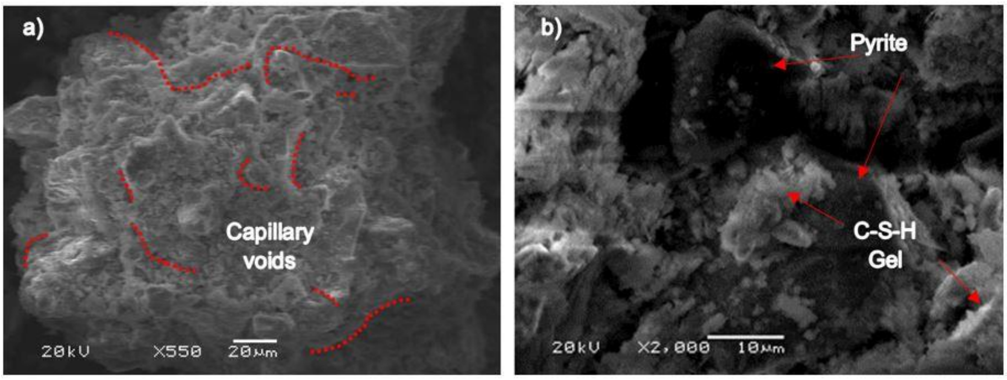

Fig. 9 SEM images of the reference sample for 28 days

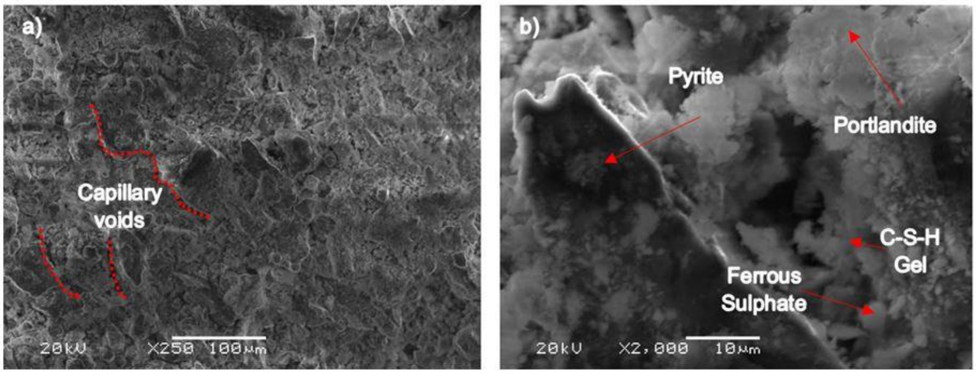

Fig. 10 SEM images of the reference sample for 90 days

period of 28 days, samples of all mixture ratios passed the desired strength limit value of ≥ 0.7 MPa. As of roof support, samples of no mixture ratio exceeded the desired limit of ≥ 4 MPa. Besides, samples of all mixture ratios exceeded the liquefaction risk limit of ≥ 0.15 MPa.

Fig. 7, shows that the addition of natural zeolite in the paste backfill mixture containing 9% of cement has increased compressive strength. The samples containing natural zeolite addition (10%, 20%, and 30%) gained about 3.1, 2.9, and 1.5 times more resistance respectively, compared to the reference samples for the curing period of 14 days. For the curing period of 28 days, samples of all mixture ratios (10, 20, 30 and 40%) passed the desired strength limit of ≥ 0.7 MPa. As of roof support, samples of no mixture ratio exceeded the desired limit of ≥ 4 MPa. Besides, samples of all mixture ratios exceeded the liquefaction risk limit of ≥ 0.15 MPa.

Uniaxial Compressive Strength (UCS) test results of samples containing 11% zeolite were given in the figure. As seen in Fig. 8, the addition of natural zeolite in a mixture of paste backfill containing 11% cement increased compressive strength. The samples of all mixture ratios passed the liquefaction risk limit of ≥ 0.15 MPa. Samples containing natural zeolite addition (10% and 20%) gained about 1.15 and 1.25 times more resistance, respectively, compared to the reference samples. For the curing period of

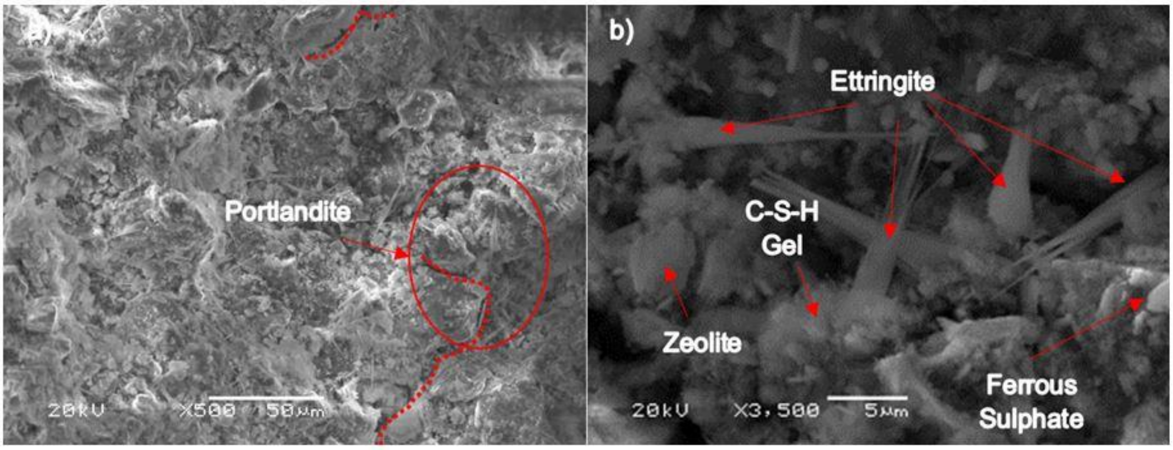

Fig. 11 SEM images of the 28 days Zeolite-substituted sample

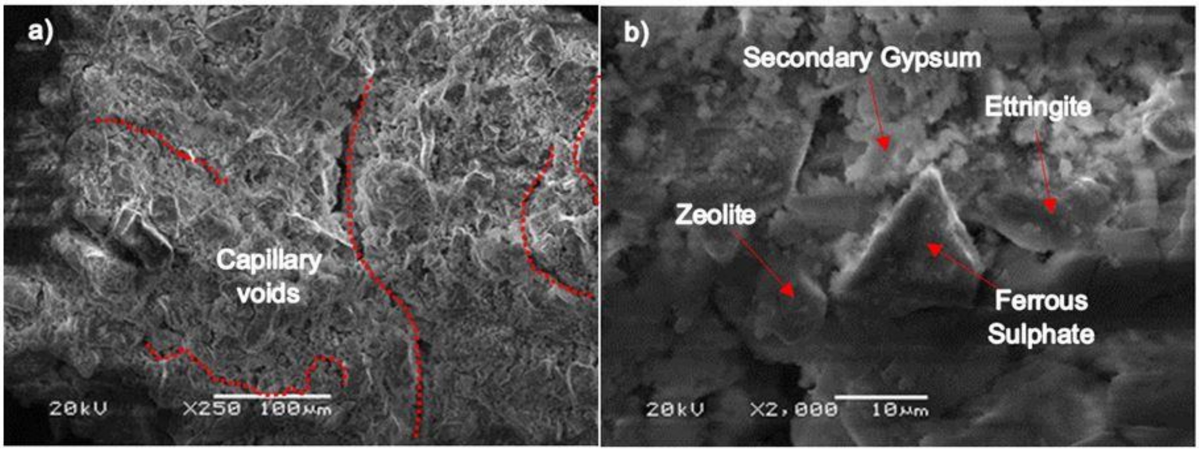

Fig. 12 SEM images of the 90 days Zeolite-substituted sample

28 days, samples of all mixture ratios (10%, 20%, 30%, and 40%) passed the desired strength limit of ≥ 0.7 MPa. Only the samples with the mixture ratios of 10% and %20 passed the desired roof support limit of ≥ 4 MPa. Also, 20% of savings were achieved in the amount of PC used as a result of using natural zeolite, which was listed as tailings in boron plants.

3.2 Examination of SEM analysis results

After the UCS test for the 28 and 90 days the SEM images of the reference (R) and zeolite (Z) samples that provided the best strength were taken using scanning electron microscope (SEM-EDS) device. SEM images are given in Figs. 9-12.

As shown in Fig. 9, there seem many capillary gaps in the reference sample. This causes lower UCS and caving of the paste backfill structure (Benzaazoua *et al*. 2002). The UCS of the reference sample for the curing periods of 28 days is 4.87 MPa. Also, the contents of the paste backfill mixture, in which pyrite minerals are included, are seen in Fig. 9(b). This can result in a decrease in the resistance by causing sulfate attacks during longer curing periods (Hassani *et al.* 2001, Benzaazoua *et al*. 2002, Fall and Benzaazoua 2005, Tariq and Nehdi 2007, Cihangir *et al*. 2012, Ercikdi *et al.* 2013, Ercikdi *et al.* 2017).

As seen in Fig. 10, according to SEM images for the curing period of 90 days, the capillary gaps decreased and the strength increased to 5.56 MPa in 90 days (Fig. 10a). Moreover, the presence of iron sulfate was found to affect the strength of paste backfill in the long term. Since the tailings used in paste backfill mixtures have very fine grains of 20 microns, the material has a high water retention capacity due to its high specific surface areas. The porocyte structure allows oxygen diffusion into the filling. Thus, pyrite minerals are disrupted in the presence of moisture and oxygen; as a result, acid (H^+) and sulfate ($SO4^{-2}$) are formed (Pokharel 2008, Fall *et al*. 2009, Pokharel and Fall 2013, Ghirian and Fall 2014, Adiguzel and Bascetin 2019).

Acid causes hydration products (C–S–H gel) to decompose (pH < 9) and lose their binding properties. Sulfate reacts with portlandite ($Ca(OH)_2$), tricalcium aluminate($3CaO{\cdot}Al_2O_3$), and the minerals of secondary plaster stone ($CaSO_4{\cdot}2H_2O$) and ettringite ($3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$) (Cihangir and Akyol 2018). (Sezer *et al.* 2008) reported secondary minerals formed could be expanded from 2.2 and 2.8 times. These minerals with expansion features cause internal strain cracks in the

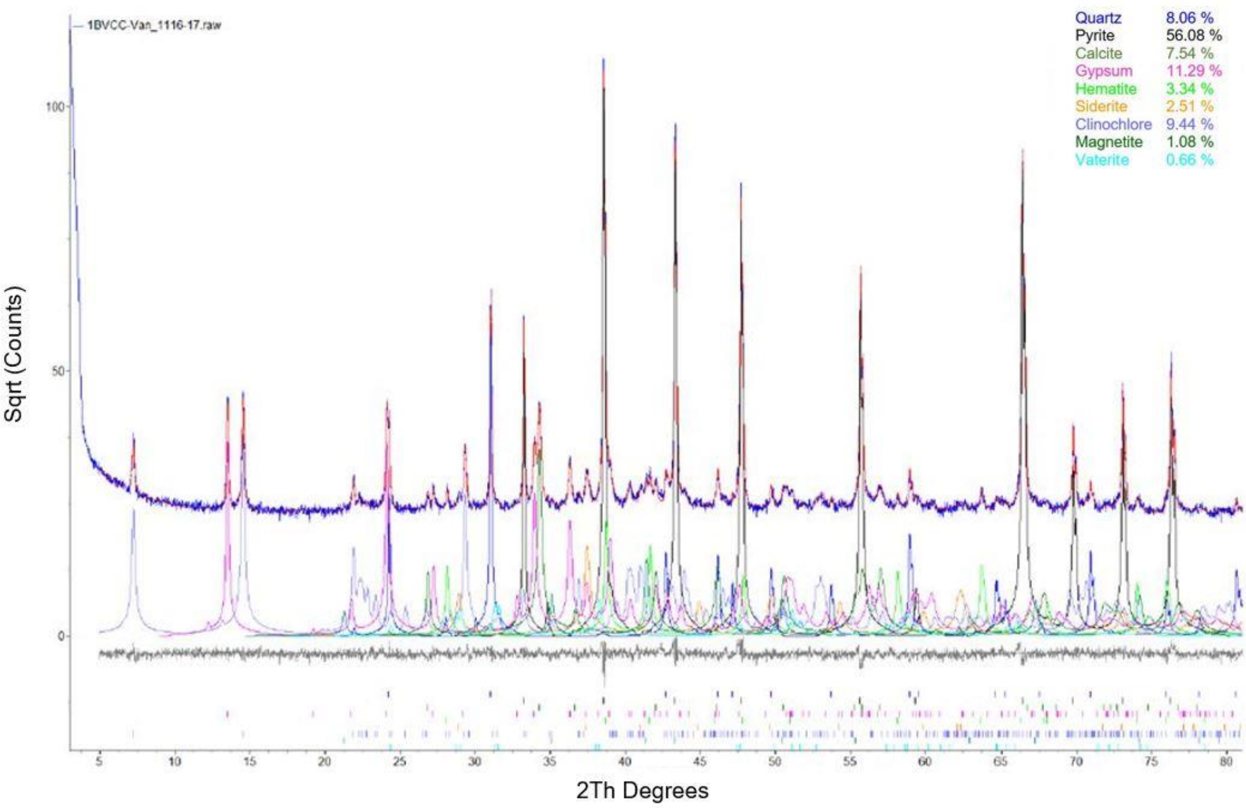

Fig. 13 Mineralogical composition of the reference sample (Eker 2019)

filling. Therefore, long-term strength and durability decreased in paste backfill samples containing high CAO content with acid and sulfate effects (Benzaazoua *et al.* 1999, Benzaazoua *et al*. 2004, Fall and Benzaazoua 2005, Kesimal *et al*. 2005,Tariq and Nehdi 2007, Ercikdi 2009, Ercikdi *et al*. 2009, Ercikdi *et al.* 2010, Cihangir *et al*. 2012, Yilmaz *et al*. 2015, Cihangir and Akyol 2018).

In Fig. 11; capillary cavities are prevented by using gels formed by zeolite -added cement hydration. Besides, long needle-shaped ettringite and iron sulfate formations with a circular cross-section, which adversely affects the resistance in the long term, are observed. Thanks to extra binding gels formed as a result of the puzzolanic reaction, a more dense structure appear (Barnat-Hunek *et al.* 2017). The fact that natural zeolite contains a large amount of Clinoptilolite in the inner surface area provides excellent pozzolanic activity thanks to its porous structure and the basic alkaline structures contained in them. The amount of K^+ and Na^+ in the chemical composition of zeolite constitutes the effect of lime reactivity and consequently puzzolanic activity (Sanytsky and Markiv 2010, Ghourchian *et al.* 2013, Markiv *et al.* 2016). The use of zeolite provides Al_2O_3 and SiO_2 supply, providing the formation of fiber-like hydro silica and long ettringite crystals. This allows pores to shrink and increase the strength of the paste (Kocak *et al.* 2013, Markiv *et al*. 2016).

According to SEM images of the zeolite substituted sample cured for 90 days in Fig. 12; It is seen that the gaps increase compared to the sample with a curing period of 28 days. Also, secondary gypsum, ettringite and ferrous sulfate formations are observed, which negatively affect the compressive strength. This situation explains why the uniaxial compressive strength is 6.07 MPa for the curing period of 28 days and the uniaxial compressive strength decreases up to 3.55 MPa for the curing period of 90 days. The natural zeolite used has a very high pozzolanic activity and most of the pozzolanic reactions occur between 7 and 28 days (Ramezanianpour *et al.* 2015). Therefore, a decrease occurred in 90 days due to sulfate attacks.

3.3 Examination of XRD analysis results

Samples of mixtures that yield the best strength results among the paste backfill samples broken at the end of the 90-day curing period (11% cement, 11% cement and 20% zeolite substituted, samples taken were finely grained; then X-rays of Acme Laboratory were analyzed using the diffractometer device. XRD images were taken between 3º - 80º 2θ. X-ray diffractograms were analyzed by Bruker using PDF-4 and Search-Match software using the International Diffraction Center Database. XRD analysis results of reference and zeolite substituted CPB samples are given in Figs. 13 and 14.

According to Figs. 9-12 is seen that it contains high levels of pyrite and quartz. Long-term strength loss of zeolite-substituted paste backfill mixtures is caused by the reaction of sulfate and hydration products to form secondary gypsum, ettringite, and ferrous sulfate. These

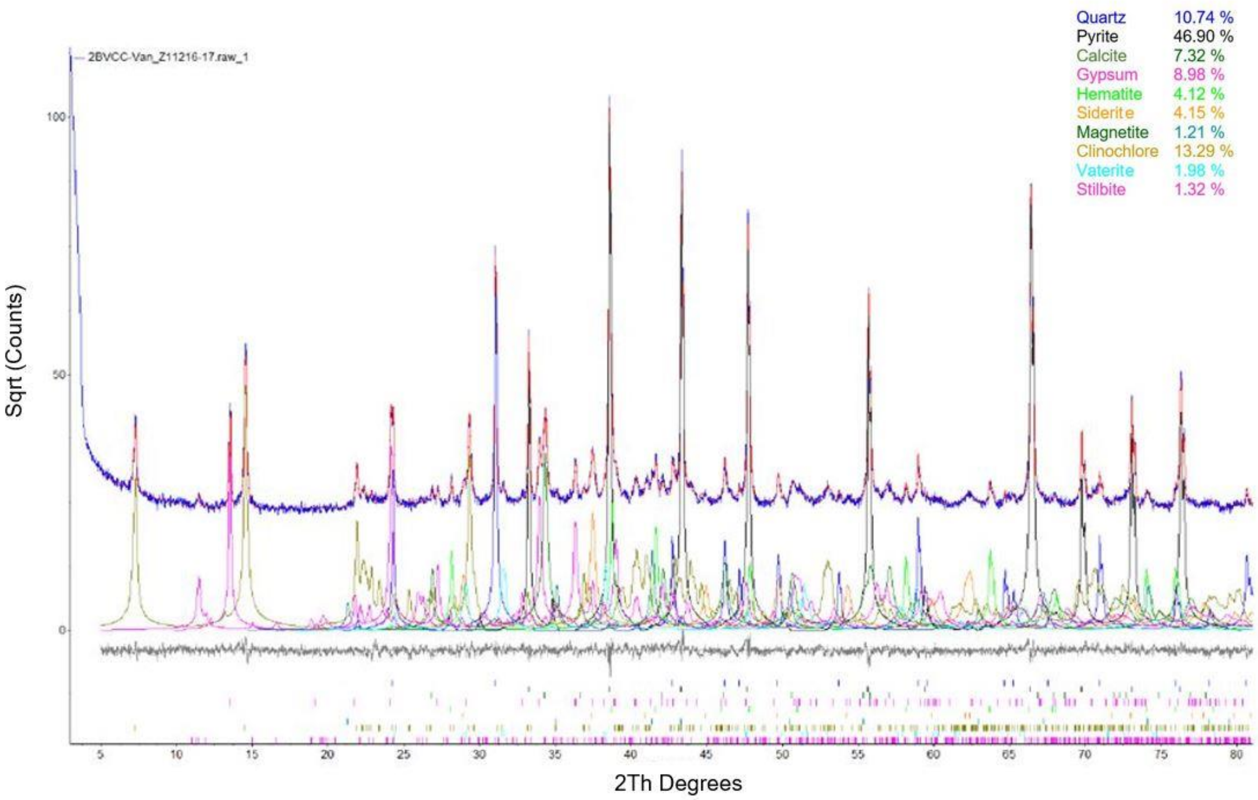

Fig. 14 Mineralogical composition of the zeolite sample

minerals expand in the paste backfill and create internal stresses; also they are known to cause a decrease in the strength of the paste backfill (Benzaazoua *et al.* 1999, Benzaazoua *et al.* 2004, Fall and Benzaazoua 2005, Kesimal *et al.* 2005, Tariq and Nehdi 2007, Ercikdi 2009, Ercikdi *et al.* 2009, Ercikdi *et al*. 2010, Cihangir *et al.* 2012, Cihangir *et al*. 2015, Yilmaz *et al*. 2015). It was has been revealed that zeolite cannot completely prevent sulfate attacks in paste backfill mixtures in the long term.

3.4 Discussion

Sulfur minerals (pyrite, etc.) in the context of the environmental effects of cement paste backfill (CPB). The use of tailings materials found poses a great risk (Hassani and Archibald 1998, Kesimal *et al.* 2005, Orejarena and Fall 2010). The XRD analysis of the tailings material used in the study revealed the presence of Pyrite (67.82%) and magnetite minerals. The SEM analysis results support this. These minerals are expected to increase the risk of AMD by exposure to oxidizing media. This can result in loss of strength in the CBP mixtures. In addition, the majority of minerals containing iron elements in the tailings material ensures high density and strength. In addition, the presence of calcite and siderite minerals in the tailings material is thought to affect the environment pH and help to settle down.

It is a fact known that the amount of binder used in the filling of the paste increases along with the increase in material strength. More hydration products are formed, cohesion is increasing and porosite is reduced, allowing for increased Uniaxial Compressive Strength (UCS) (Kesimal, *et al*. 2005, Fall and Benzaazoua 2005, Fall *et al*. 2008, Klein and Simon 2006, Pokharel and Fall 2011, Cihangir *et al.* 2012, Ercikdi *et al*. 2009, Ercikdi *et al.* 2014, Ghirian and Fall 2016). However, this is a disadvantage in terms of the cost of the paste backfill plant. The UCS must be at least 0.15 MPa in terms of the liquefaction risk limit (Been *et al.* 2002, Roux *et al*. 2004). In addition, it must provide a strength of at least 0,7 MPa at the curing period of 28 days, and roof support limit of ≥ 4 MPa (Brackebusch 1994, Landriault 1995, Grice 1998) to ensure the material's own stability. The limit value of the risk of liquefication (≥ 0.15 MPa) in the CPB mixtures prepared in cement ratios 3, 5, 7, 9, 11% is provided. At curing period of 28 days, they are shown to provide the desired strength of ≥ 0.7 MPa at 7%, 9 and 11% cement ratios. The roof support limit of ≥ 4 MPa is only provided at a cement rate of 11%. When the cement ratio is increased from 7% to 11%, UCS endures increased by 1.9–5.5 times in all curing period of CPB. A noticeable improvement in the long-term performance of the CPB samples has occurred with increased cement ratio. The amount of cement used (3%, 5, 7, 9, 11), zeolite, substituted up to 10%, 20, 30 and 40%, increased compressive strength in mixtures of 5%, 7, 9 and 11 cement. All mixtures provide the limit value of the risk of liquefication (≥ 0.15 MPa) for CPB. The desired strength limit value (≥ 0.7 MPa) for curing period of 28 days provides all mixtures of 7%, 9, 11 cement ratios and a zeolite-10% mixture with 5% cement. The roof support limit of ≥ 4 MPa is obtained only in mixtures with 11% cement - 10% and 20% zeolite substitution.

According to the SEM analysis conducted, the presence of excessive and pyrite minerals in the reference samples in the analysis carried out after 28 days. The addition of the zeolite (Z) material used as a substitution to the filler mixtures of the paste backfill has reduced the gaps in the reference samples. In addition, this curing period has a place in the ettringite, iron sulphate, which has adversely affected the strength in the long term. However, substitution of Z samples have a more concentrated homogeneous structure. This is thought to be the large particle size of the tailings material used and to fill the gaps between cement and with zeolite particles The SEM analysis results in 90 days show that the strength loss of the CPB samples and the result of the secondary gypsum, ettringite and iron sulphate presence caused by the causes of capillary cracks. The loss of strength in the application of the CPB is due to the secondary gypsum mineral (Fall and Benzaazoua 2005, Ercikdi 2009a, Belem and Benzaazoua 2008, Fall and Samb 2008, Ercikdi *et al*. 2009b, Ghirian and Fall 2014, Li and Fall 2016). The pyrite is oxidized in the presence of water and oxygen, forming acid and sulphate. Acid attacks by oxidation of sulfurated tailings occur and break the structure of the formed calcium-silicate-hydrate (C-S-H) bonds. This reduces CPB strength and durability by causing the acid resulting from oxidation to lose the binder properties (pH ≤ 9) of hydration products (C-S-H and $Ca(OH)_2$, portlandit) (Benzaazoua *et al*. 1999, Hassani *et al*. 2001, Tariq and Nehdi 2007, Belem and Benzaazoua 2008, Ercikdi *et al*. 2009 a, b, Cihangir 2011, Cihangir *et al.* 2012). Pores fill and their diameters decrease due to the pozzolanic effect of cement hydration and substituted zeolite material (Fall and Samb 2009). This is due to increased small porous development as a result of binder hydration (Ghirian and Fall 2014). It is also known that the size of tailings used in the CPB mixtures is large and will produce a better mixture of strength and durability with substitution materials with a fine grain content (≤ 20 µ) high (Fall *et al.* 2005, Ercikdi *et al*. 2013, Yilmaz *et al.* 2017). High-strength zeolite samples best fill the intergranular gaps in the CPB mixture due to high particle size below 20 µm (45.30%). The results of the strength also support this situation.

4. Conclusions

In this study reference samples were prepared using facility tailings taken from the copper mine, Portland cement (PC) (3 wt%, 5 wt%, 7 wt%, 9 wt% and 11 wt%), and water. On the other hand, zeolite-substituted cement paste backfill (CPB) samples were prepared by using natural zeolite (10 wt%, 20 wt%, 30 wt%, and wt%) as a substitution for PC by mixing them separately for each cement ratio in certain proportions. Then, they were subjected to the Uniaxial Compressive Strength (UCS) test at the end of the curing periods of 3, 7, 14, 28, 56 and 90 days. Thus, the effect of using zeolite instead of PC on strength of CPB was investigated. According to the results of these tests, the following findings were obtained:

(1) The addition of zeolite in CPB increased the compressive strength of the paste backfill mixture.

(2) The results have revealed that zeolite can be used as a substitute for the cement to reduce the amount and cost of cement to be used in CPB.

(3) Zeolite has provided the opportunity to reduce the amount of CO_2 emission, which creates a greenhouse gas effect during cement production.

(4) Moreover, It also provided economic income from zeolite.

(5) The reuse of zeolite in mining tailings can provide significant benefits for the industry in terms of its operational, environmental and cost advantages.

According to the obtained values of compressive strength, it is seen that zeolite substitution is generally more effective in early strength. It is seen that AMD, which occurs as a result of sulfate attacks in the paste backfill in the long term, is not prevented and it is ineffective against sulfate attacks. However, it is thought that kinetic tests should also be conducted in order to fully understand this situation.

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