

# Evaluation of the sulphate resistance of foamed concrete containing processed spent bleaching earth

R. OTHMAN ET AL.

European Journal of Environmental and Civil Engineering

[AQ0]

Rokiah Othman<sup>1</sup> Khairunisa Muthusamy<sup>1</sup> Youventharan Duraisamy<sup>1</sup> Mohd Arif Sulaiman<sup>1</sup> [AQ6]  Ramadhansyah Putra Jaya<sup>b</sup> Nadiatul Adilah Ahmad Abdul Ghani<sup>b</sup> Sajjad Ali Mangi<sup>c</sup>

<sup>1</sup>. <sup>a</sup>Faculty of Civil Engineering Technology, Universiti Malaysia Pahang, Lebuhraya Tun Razak, Gambang, Kuantan, Pahang, Malaysia;

<sup>b</sup>. Department of Civil Engineering, College of Engineering, Universiti Malaysia Pahang, Lebuhraya Tun Razak, Gambang, Kuantan, Pahang, Malaysia;

<sup>c</sup>. Department of Civil Engineering, Mehran University of Engineering & Technology, SZAB Campus Khairpur Mir's, Sindh, Pakistan

CONTACT Ramadhansyah Putra Jaya Jayaramadhansyah@ump.edu.my Department of Civil Engineering, College of Engineering, Universiti Malaysia Pahang, Lebuhraya Tun Razak, Gambang, Kuantan, Pahang 26300, Malaysia

---

## ABSTRACT

Processed spent bleaching earth (PSBE) is the end product derived from the processing of de-oiled spent bleaching earth (SBE) after the oil is recovered. Bleaching earth is very fine powder clay, and its main component is silicon dioxide used for refining process of palm oil and its by product is known as SBE is commonly disposed to landfill. The bleaching earth that is used for decolouring during the palm oils refining process form a solid sludge called the SBE. The SBE is generated in large quantities and it is becoming increasingly difficult to ignore the disposal of SBE when production of palm oil increases rapidly. Hence, the problem can be overcome by reusing solid waste as construction materials. In this study, the effect of using PSBE as a partial cement replacement in foamed concrete on durability resistance sulphate attack is investigated. Sulphate resistance in terms of expansion, loss in mass and loss in compressive strength after 52 weeks immersed in 5% sodium sulphate was evaluated. On the other hand, the microstructure changes in the specimens were analysed by scanning electron microscopy (SEM), X-ray diffraction (XRD) and thermogravimetry analysis (TGA). Comparisons are made between two mixtures which mainly control foamed concrete (FC) and foamed concrete containing 30% PSBE (PFC). Major findings show that when 30% PSBE added in a concrete mixture, after 52 weeks samples being immersed in 5% sodium sulphate, it will be more durable compared to control specimen (FC). It was recorded that change in mass, in expansion and loss in strength was 1.32%, 0.98% and 7.5% respectively. The microstructure study has confirmed that inclusion of PSBE in foamed concrete is known to improve the internal structure of PFC to be denser than control FC specimen with the visible image of crowded tiny of cotton shaped (CSH) and few hexagonal plates (CH) contributing to enhanced strength and durability. Conclusively, the foamed concrete containing 30% PSBE as partial cement replacement which exhibits enhanced strength and durability than plain foamed concrete has the potential to be used in construction application.

---

**Keywords:** Sulphate ; foamed concrete ; bleaching earth ; concrete ; durability

## FUNDING

Malaysian Ministry of Higher Education and Universiti Malaysia Pahang<sup>39</sup>The support provided by Malaysian Ministry of Higher Education and Universiti Malaysia Pahang in the form of a research grant vote number RDU190339 for this study is highly appreciated.

## 1. Introduction

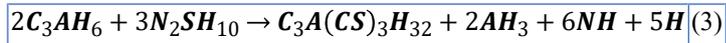
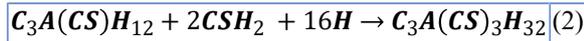
Malaysia is one of the largest producers for palm oil production in the world. Currently, there are 423 palm oil mills in Malaysia and it is estimated that 240,000 tons per annum or more of SBE are utilised in the refining process of crude palm oil (Loh et al., 2017). The SBE generated is large in quantity and it is becoming increasingly difficult to ignore the disposal of SBE when production of palm oil increases. Principally, the main task of bleaching earth is used to remove colouring, soap, gums, metals and oxidising compounds during the oils refining process. The waste is usually dumped in a landfill without any treatment.

SBE is a by-product of the palm oil refining process. Refining of crude palm oil involves several methods such as degumming, bleaching and deodorising. The primary purpose of bleaching is to remove undesirable substances such as soap residues, a trace of heavy metals, a phosphorus compound, as well as coloured matter. It is about 100 000 to 120 000 tons, or more SBE are utilised yearly in the refining process which is commonly disposed at the landfill. In record, some 120 000 tonne (0.8%) SBE was generated from palm oil refining companies based in Malaysia where some 36 000 tonne (30%) of oil is recovered annually from SBE (Loh et al., 2015). With the advancement of technology, the process for regeneration of SBE involves two stages, recovery of oil from SBE for special adsorbents purpose and heat regeneration of de-oiled SBE as a construction material. Overall, the utilisation of SBE in material production can reduce the disposal issue (Eliche-Quesada & Corpas-Iglesias, 2014). It should be noted that SBE can present a potential fire and pollution hazards, because it contains 20 to 40% residual oil by weight, metallic impurities and organic compound upon its disposal. Then, the dumping of SBE in landfill or public disposal sites should be restricted to protect environmentally. In response to these severe issues, SBE disposal has been resolved by removing the oil and colouring materials (Meziti & Boukerroui, 2011). Mostly, the residual oil can be extracted to produce biodiesel (Huang & Chang, 2010) while the deoiled SBE can be reused as an adsorbent in wastewater treatment, as a clay substitute in the bricks, blocks or tile manufacturing process (Beshara & Cheeseman, 2014; Eliche-Quesada & Corpas-Iglesias, 2014) and as filler in asphalts (Sangiorgi et al., 2014).

Recently, in Malaysia SBE is regenerated and reused for biomaterial for water treatment and biofertilizer (Loh et al., 2013, 2017). In Japan and Kenya, SBE has been incinerated for cement manufacturing (Protus, 2014). The increasing production of palm oil may lead to excessive quantities of SBE disposal, which may have a negative impact on the environment if not managed properly. Therefore, this present study investigated the effect of PSBE as partial cement replacement in foamed concrete under sulphate resistance.

Sulphate attack is one of the factors that may affect foamed concrete in its service life when exposed to soil or water containing sulphate and led to softening and cracking of the structures (Drimalas et al., 2011). The most common sulphate that will interact with cement based concrete is calcium, sodium and magnesium sulphate. Sancak and Özkan (2015) reported that the formation of expansive alumina phases such as ettringite occurred in the hydrated before the specimen was immersed in sulphate solutions. If the monosulphate and calcium aluminate hydrate phases are present before immersion, the exposure to sulphate solution results in the formation of ettringite in a hardened state and expansions can result in deterioration through cracking and spalling. It was pointed out that the magnesium sulphate is more destructive than sodium sulphate, and both being more aggressive than calcium sulphate. In addition, the ettringite is stable in sodium sulphate solution due to the formation of the monosulphate phase from calcium aluminate hydrate via ion exchange process. According to Darayathne et al. (2013), the sodium sulphate attacks on the concrete in two different conditions. Firstly, the form of attack between the sodium sulphate and the hydration products, mainly calcium hydroxide (CH) also known as portlandite crystal to form gypsum as shown in Equation (1). Meanwhile, the gypsum will react with monosulfoaluminate to form ettringite as shown in Equation (2). Most of the findings reported ettringite is the weakness product in cement paste which reduced the resistance against the sulphate attack. Nevertheless, the formation of gypsum will discontinue when the calcium hydroxide depletes. As a consequence of this, once the monosulfoaluminate becomes depleted, excess gypsum will form in the system and ettringite formation will cease. On the other form of attack is between the sodium sulphate and tricalcium aluminate (C<sub>3</sub>A) to form ettringite as shown in Equation (3) (Dayarathne et al., 2013).





ASTM C1012/C1012M-18b-18 (2018) is one of the most standard tests used to investigate the sulphate attack. According to Drimalas et al. (2011), the test involves casting the specimen bar, once the compressive strength reaches 28 days, the specimen then immersing in a 5% sodium solution for up to 18 months. In the meantime, of immersion in the sulphate, the expansion measurement was taken every week until 18 months. The test criteria requires a maximum expansion limit of 0.1% at 180 days of sulphate immersion for moderate sulphate resistance and a limit of 0.05% at 180 days for severe sulphate resistance. Furthermore, the expansion relates to the ettringite formation, the ettringite converted to massive type (expansive) that lead to exert pressure in the narrow spaces and cause expansion of specimen. If the form of the available space is spherical (entrapped air voids) the ettringite preserve their initial form and do not cause any expansion (Drimalas et al., 2011).

The concrete deterioration in the sulphate environment was evaluated by visual appearance, measuring mass loss and compressive strength loss. The visual appearance of concrete specimens immersed in sodium sulphate solution was periodically examined to check for spalling, cracking, expansion and mass loss due to sulphate attack. The pore size and porosity affect the resistance towards sulphate attack. This is because the sulphate ion passes through the pores and react with the hydration products, leading to expansion, cracks and loss of mass and strength (Tian & Han, 2017). Another researcher, Siva and Ramamurthy (2012) investigated the foamed concrete deterioration in sodium and magnesium sulphate environments by measuring the linear expansion, mass and strength loss. It has been observed that for a given exposure, the difference in expansion found in foamed concrete with different densities 1000–1500 kg/m<sup>3</sup> was only 5% and increased by 15% in mass. However, the mass change of base mix is 26% higher than foamed concrete under magnesium sulphate which is certified as the very severe exposure conditions. The higher loss in strength was associated with mass loss of 1% observed due to spalling of edges and corners due to deterioration.

However, several approaches were conducted to investigate deterioration under sulphate attack, including using cement with low C<sub>3</sub>A content, reducing calcium hydroxide content in the hydrated cement paste by using supplementary cementitious material and making concrete as denser to prevent the ingress of sulphate solutions. According to Nie et al. (2014), the concrete containing fly ash can improve the sulphate resistance. While, the use of 30% low calcium fly ash in concrete demonstrated greater improvement in sulphate resistance (Kandasamy & Shehata, 2014). Furthermore, by inclusions of natural zeolite in concrete exhibit improved to sulphate attack (Małolepszy & Grabowska, 2015). In most pozzolans, Metakaolin is a pozzolan that shows high performance to produce durable concrete when exposed to sodium sulphate (Duan et al., 2016). Conclusively, low calcium fly ash is more effective than high calcium fly ash to prevent sulphate induced expansion and cracking. While higher calcium fly ash does not perform better in sulphate environments. It is important to note that the C<sub>3</sub>A is the greatest factor influencing the resistance of Portland cement concrete to sulphate attack, while the high contain C<sub>3</sub>A led to increased expansion.

Generally, the sulphate attack on the foamed concrete specimens is considered as the deterioration mechanism caused by the formation of gypsum leading to form ettringite. This led to expansion, loss of mass and changes in physical appearance. It is well known that the pozzolanic reaction consumes calcium hydroxide, making the concrete denser which lead to reduce the product of sulphate attack and ettringite to form. Partial replacement of Portland cement by 30%PSBE has been proven to be effective in increasing compressive strength of foamed concrete (Rokiah et al. (2019). However, the effect of PSBE on durability of foamed concrete is limited in the literature. Required research is needed for further investigation on durability performance under sulphate environment. Therefore, the objective of this study was to investigate the sulphate resistance of foamed concrete containing 30% PSBE. The effect of the PSBE as a cement replacement on the sulphate resistance in terms of expansion, loss in mass, loss in compressive strength and microstructure changes after 52 weeks immersed in 5% sodium sulphate were investigated.

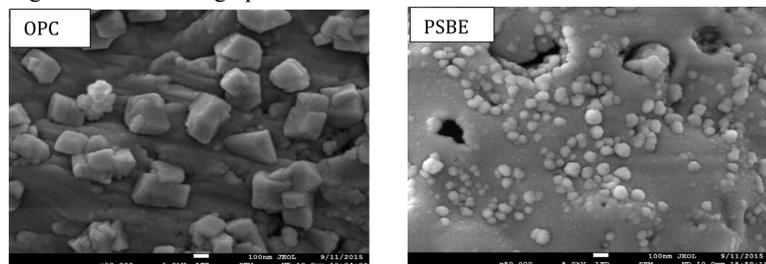
## 2. Method of research

### 2.1. Materials

Among the materials used to prepare specimens in this research are cement, water, silica sand, foaming agent and PSBE. Ordinary Portland cement (OPC) from a single source was used throughout the experimental work. Tap water

was used for mixing and curing purposes. Foaming agent was manufactured by LCM Technology Sdn. Bhd. Kuantan. Silica sand was supplied by Johor Silica Industries Technology Sdn. Bhd and PSBE was provided by Eco Innovation Sdn. Bhd. The PSBE was dried in the oven for 24 hours at a temperature of  $105 \pm 5^\circ\text{C}$  then sieved through a No.300 ASTM. PSBE was classified as Class N Pozzolan in accordance with ASTM C618-12 and conforming to BS Specification for Pulverised-Fuel as for use with Portland cement (BS 3892-1/BS EN 450). Table 1 shows the chemical composition and physical properties of Processed Spent Bleaching Earth. The particle distribution of PSBE is shown in Figure 1.

Figure 1. SEM micrograph of OPC and PSBE.



(a) Ordinary Portland cement (OPC) (b) Processed Spent Bleaching Earth (PSBE)

Table 1. The chemical composition of the OPC and PSBE.

Oxides %	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>	Loss on Ignition	Surface Area (BET) m <sup>2</sup> /g
OPC	16.05	3.67	3.41	62.28	0.56	4.1	1.2	4.459
PSBE	55.82	13.48	8.24	6.6	5.94	1.05	0.18	8.484

## 2.2. Sample preparations and testing

### 2.2.1. Mix design

The mix proportions of FC containing PSBE derived using trial mix method in order to obtain an optimum PSBE content. The water/cement ratio, sand/cement ratio, dilution ratio and percentage of foam dosage in this study were kept constant throughout at 0.5, 1.5, 1:25 and 25% respectively. In this study, a basic control mix of foamed concrete (FC) was designed for density of  $1600 \text{ kg/m}^3$  and 30% of PSBE by weight of cement namely as PFC. The properties of FC containing 30% of PSBE was compared to control mixture FC.

### 2.2.2. Sample preparation

In this study, preformed foam has been prepared by diluting 1 liter of foaming agent with 25 litres of water into the foam machine where the density of foam should be in the range of  $50 \text{ kg/m}^3$ . Then foam is added into the cement paste and mixed continuously until there was no sign of foam during the mixing and the slurry becomes homogeneously mixed as shown in Figure 1. Filled the fresh mix into the cube specimens size  $100 \cdot 100 \cdot 100 \text{ mm}$ . Then the specimens were removed from the mould after 24 hours. All the equipment, materials and procedures in producing foamed concrete have been implemented according to ASTM C796 (Figure 2). [AQ1](ASTM C1012/C1012M-18b 2018)

Figure 2. Production of foamed concrete.

Prepare cement paste by mixing dry material with water	Added pre-foamed foam into cement paste	Continuously mixed
		
		
		

### 2.2.3. Sulphate resistance test

The resistance to sulphate attack test is conducted to investigate the durability performance of foamed concrete containing 30%PSBE when exposed to sulphate environment. The cubes and prism bar were immersed in the 5% Sodium sulphate with pH 5.5 for the duration of 1 year after 28 days of curing. The prism bar specimens were observed weekly where the length change was performed in accordance with the ASTM C1012/ C1012M-18b-18 (2018). The mass loss and compressive strength loss of the cube specimens were calculated by using Equations (4) and (5) (Siva & Ramamurthy, 2012).

$$\text{Mass loss} = \frac{m_{\text{current}} - m_{\text{initial}}}{m_{\text{initial}}} \times 100 \quad (4)$$

where ( $m_{\text{current}}$ ) represent mass of specimen after immersion in sulphate solution (g) and ( $m_{\text{initial}}$ ) mass specimen before immersion in sulphate solution (g).

$$\text{Compressive strength loss} = \frac{f_{\text{current}} - f_{\text{initial}}}{f_{\text{initial}}} \times 100 \quad (5)$$

where ( $f_{\text{current}}$ ) represent compressive strength of specimen after immersion in sulphate solution (MPa) and ( $f_{\text{initial}}$ ) compressive strength of specimen before immersion in sulphate solution (MPa).

### 2.2.4. SEM test

The scanning electron microscopy (SEM) was performed based on ASTM C1723 . The SEM samples were prepared by extraction from the crack surface of specimens of FC and PFC after specimens immersed in 5% sodium sulphate solution for 52 weeks. The SEM samples were labelled in the separated plastic and tested at Central Laboratory of UMP to observe the formation images of specific chemical composition of the specimen such as calcium silicate hydrate, calcium hydroxide and entringite.

### 2.2.5. XRD test

The X-ray diffraction (XRD) test was performed to analyse the effect of PSBE on the formation of hydration products of FC. The XRD analysis is the rapid analytical technique primarily used for phase identification of a crystalline material that is commonly used to determine the composition of materials. The specimen was prepared and labelled in the separated plastic and tested at Central Laboratory of UMP. The FC and PFC of the specimen were tested to identify the peak pattern and intensity of specific chemical composition of the specimen.

### 2.2.6. TGA test

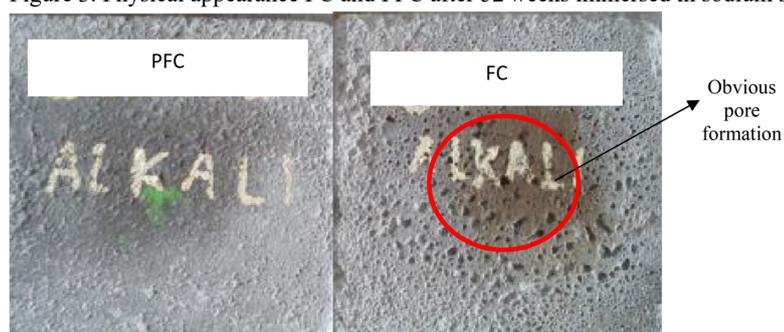
The Thermogravimetric analysis (TGA) test was performed to analyse the effect of PSBE on the formation of hydration products of FC. TGA is the thermal analysis method to analyse the changes in physical and chemical of the specimen by measuring the increasing temperature in time. It is commonly used to determine specific characteristics of a specimen that exhibit either mass loss or gain due to decomposition, oxidation or loss of moisture. The TGA instrument continuously weighs a sample as it heated to temperatures of up 2000 ° C. The specimen was prepared and tested at Central Laboratory of UMP. The FC and PFC of the specimen were tested to identify the peak pattern and intensity of temperature changes point for specific chemical composition in the specimen.

## 3. Result and discussion

### 3.1. Visual assessment

The specimens immersed in 5% Sodium sulphate for a duration of 1 year are presented in [Figure 3](#). Both specimens of FC and PFC show no change in physical appearance after being immersed in sulphate solution up to week 4. However, the PFC exhibited lesser deterioration as compared to control specimen after 52 weeks immersed in sulphate attack for bar specimen. The results revealed that the concrete physical deterioration became worse as the period of immersion increased. The expansion and destruction of the edges were related to the formation of gypsum and ettringite in the foamed concrete. The trend of deterioration is similar with findings reported by Siva and Ramamurthy (2012). Furthermore, Çevik et al., (2018) found that the deterioration increased with an increase in the exposure time and OPC specimens showed severe surface erosion and surface colour changed from grey to white due to higher CaO content. On the contrary, the specimens containing nano silica that have lowest CaO amount and highest SiO<sub>2</sub> content exhibit the lowest surface erosion due to lower CaO amount and porosity resulted from nano silica. Similar results were also reported by Alzeebaree et al. (2018), the specimens remain unaffected after two months of exposure to sulphate environment and the OPC specimens were slightly influenced by the sulphate ions, and the surface colour changed.

Figure 3. Physical appearance FC and PFC after 52 weeks immersed in sodium sulphate solution.



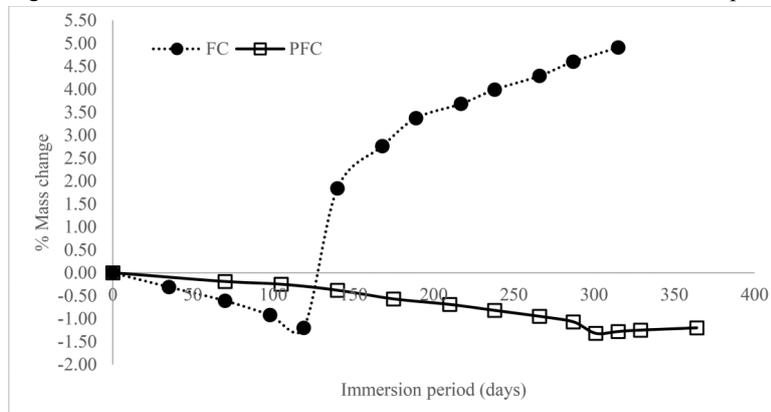
Foamed concrete containing PSBE has better durability towards sulphate attack. The advantage in the specimens containing PSBE was related to the pozzolanic reaction of silica oxide (SiO<sub>2</sub>) with the calcium hydroxide (CH) to produce more calcium silicate hydrate (CSH) leading to denser and less porous structure. As mentioned earlier, the form of attack between the ion sodium sulphate and the hydration products to form calcium hydroxide to form gypsum, and gypsum then will react with monosulfoaluminate to form ettringite. The ettringite is the weakness product in cement paste that reduces the resistance of concrete against the sulphate attack (Tian & Han, 2017). It was interest-

ing to note that the formation of gypsum will discontinue when the calcium hydroxide depletes because it has been consumed in a pozzolanic reaction to form more CSH. As a consequence of this, once the monosulfoaluminate becomes depleted, excess gypsum will develop in the system and ettringite formation will cease. Furthermore, the fineness of the PSBE also acts as a filler by filling up the voids and decreasing the penetration of sulphate ions. Incorporation of pozzolans in concrete decreases the tricalcium aluminate ( $C_3A$ ) content leads to reduce the potential formation of ettringite (Prasad, Jain, & Ahuja, 2006; Olivia, 2011; Siva & Ramamurthy, 2012).

### 3.2. Loss in mass

Figure 4 presents the change in mass of control foamed concrete (FC) and foamed concrete containing 30% PSBE (PFC) as partial cement replacement in sodium sulphate solution. It shows that the mass change gradually decreased as the immersion age increased until week 52. The mass change of foamed concrete starts to decrease after week 5 for FC and week 10 for PFC specimens. Based on the graph, the mass of the FC specimen exhibited the growth after 20 weeks immersed in sodium sulphate solution. Then, the destruction of the FC specimen occurred after 45 weeks immersed in sodium sulphate. It shows that the mass change of PFC is lower than control FC specimen after sulphate attack. It revealed that at the end of the immersion period, the mass change of FC and PFC was 4.9% and 1.32% respectively. The PFC specimen containing PSBE exhibit less mass change due to more dense structure and decreased porosity and permeability. While FC specimen showed higher mass change due to the reaction between CaO in the OPC and absorption ions from sulphate solution. It is discovered that the higher mass change of the control FC specimens is due to the higher destruction of the edges, while the specimens containing the PSBE has minor surface deterioration as shown in Figure 4. It is interesting to note that PFC with 30% PSBE exhibited better durability resistance against sulphate attack based on a lower reduction of mass change obtained in this study. Therefore, it revealed that the lower gypsum and ettringite produced in PFC because it has little deterioration and lower mass change. The greater durability resistance of foamed concrete with mineral admixture as partial cement replacement such as natural pozzolan, fly ash, silica fume, rice husk asks, calcined clay and slag towards sodium sulphate were shown the consistent effect and exhibits excellent performance against sulphate environment were highlighted by previous researchers (Dayarathne et al., 2013; Duan et al., 2016; Lukowski & Salih, 2015; Małolepszy & Grabowska, 2015).

Figure 4. Mass loss of FC and PFC after 52 weeks immersed in sodium sulphate solution.

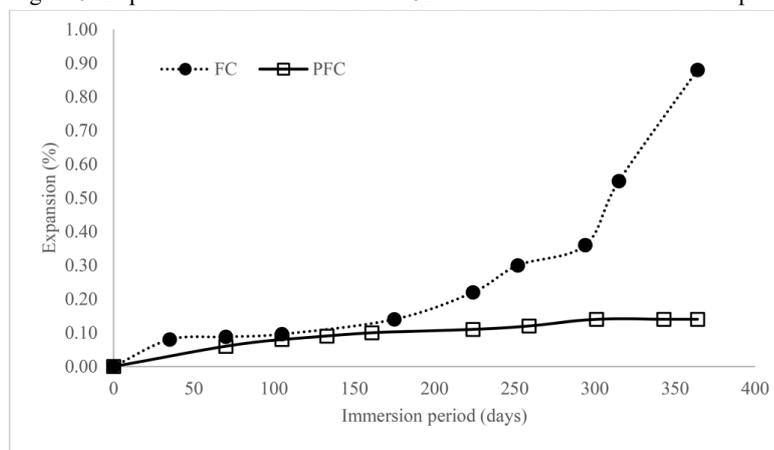


### 3.3. Expansion

The expansion changes of FC and PFC prism bar immersed in 5% sodium sulphate solution after 52 weeks are shown in Figure 5. The expansion of foamed concrete starts to change after week 5 for FC and week 10 for PFC. The trend of expansion demonstrated slowly increased as the immersion age increased until week 52. It has been noted that the expansion FC specimen exhibited the sudden growth after 45 weeks immersed in sodium sulphate solution. However, the expansion for both FC and PFC specimens passed the expansion limit 0.1% after six months. It can be seen that the foamed concrete containing 30% PSBE has the lower value of expansion of bar exposed in sodium sulphate as compared to FC. It is demonstrated that the higher expansion of the control FC specimens is due to the higher ingress of sulphate ion, while the specimens containing the 30% PSBE has lower expansion because the pozzolanic reaction making PFC denser that lead to prevent the ingress of sulphate solutions. PFC specimens exhibited minor

changes due to the lower contain of ettringite upon immersion in sulphate attack. It has been highlighted that the expansion relates to the ettringite formation (Drimalas et al., 2011). From the graph, it was approved that the FC specimen has the maximum expansion and the PFC specimen exhibited a small change in the linear expansion in the sulphate environment. More, it is shown that at the end of the immersion period, percentage expansion of specimens in FC and PFC was 2.71% and 0.98% respectively.

Figure 5. Expansion of FC and PFC after 52 weeks immersed in sodium sulphate solution.

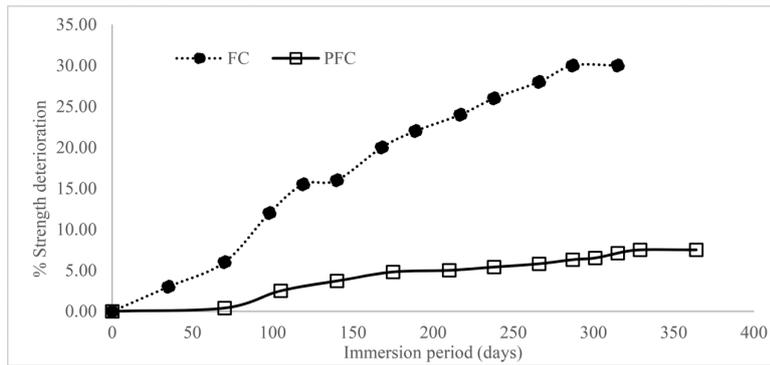


Previous studies of foamed concrete containing fly ash, slag, zeolite, Ahmad and Noor (2010), Prasad et al.(2006) and Małolepszy and Grabowska (2015) concluded that the expansion of mortar bar start to increase after week 8 for control specimen and the other mixture containing pozzolan material increase expansion linearly until week 16 and no longer have expansion from week 16 to 52. It was interesting to note that the higher expansion of the control FC specimens is because of higher ettringite content as compared to PFC specimens. Ranjani and Ramamurthy (2012) found that the expansion of foamed concrete with densities range  $1000 \text{ kg/m}^3$  and  $1500 \text{ kg/m}^3$  was 28% higher when specimen immersed in 5% sodium sulphate than magnesium sulphate due to a higher rate of ettringite formation in sodium sulphate environment. The use of 30% PSBE enhances the foamed concrete resistance to sulphate attack compared to FC.

### 3.4. Loss in compressive strength

Figure 6 shows the compressive strength loss of control foamed concrete (FC) and foamed concrete mixture containing 30% PSBE (PFC) as partial cement replacement after 52 weeks immersed in sodium sulphate solution. The compressive strength gradually decreased as the immersion age increased until week 52. The compressive strength of foamed concrete starts to decrease after week 5 for FC and week 10 for PFC. It is shown that the compressive strength loss of PFC was lower than control FC. The total strength deterioration for cube specimens of FC and PFC was 30% and 7.5% respectively. It indicated that the higher compressive strength loss of the control FC specimens is due to the ettringite formation which leads to expansion loss in mass, surface and edges loss in the sulphate attack. After all, the specimens containing the PSBE which exhibit better resistance towards sulphate attack is related to the pozzolanic reaction of silica oxide from PSBE with the calcium hydroxide (CH) to produce more calcium silicate hydrate (CSH). Consequently, this process decreases the amount of CH. Upon the depletion of CH, the formation of gypsum and ettringite will cease. Similar finding by Saleh (2017) observed that as the period of immersion in sodium sulphate solutions increase, the compressive strength of specimens was found to decrease continuously.

Figure 6. Strength Loss of FC and PFC after 52 weeks immersed in sodium sulphate solution.

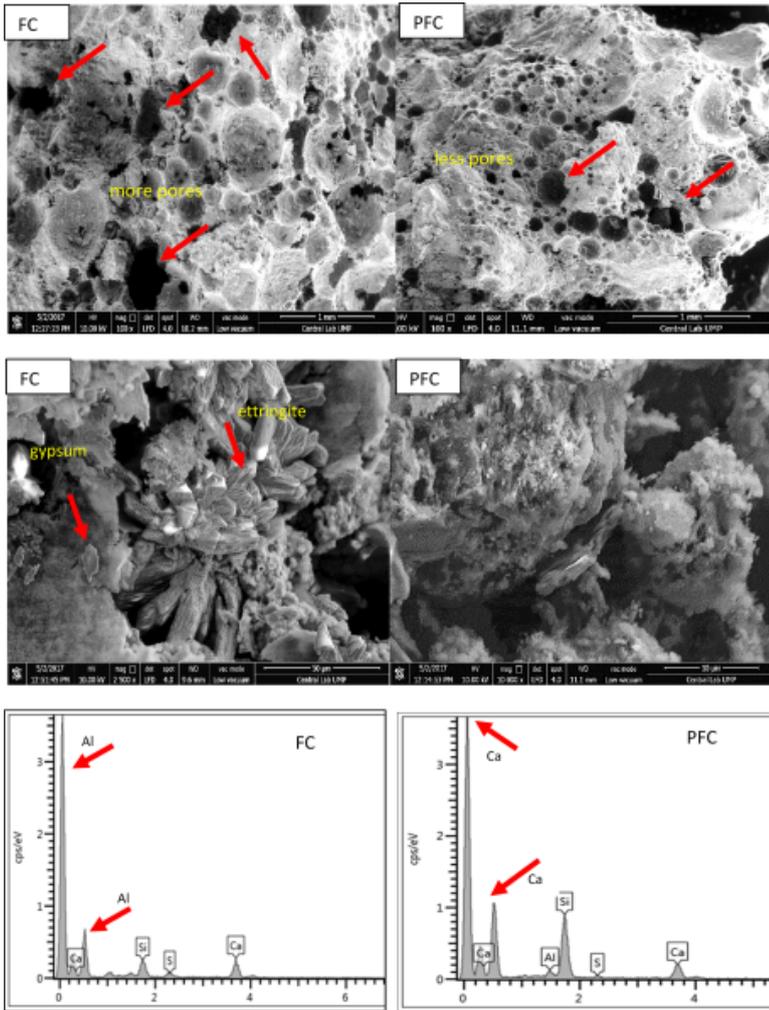


Furthermore, the fineness of PSBE action in filling the voids and contributes to decreasing the porosity that can decrease the penetration of sulphate ions into the internal voids. The specimens containing the PSBE have minor surface and losses because the use of 30% PSBE exhibited better protection in resistance to sulphate attack compared to FC. The results obtained was consistent with the findings by Liu et al. (2015), Rashwan et al. (2015), Saleh (2017), Tian and Han (2017) and Liu et al. (2015) who reported that with the ingress of sulphate ions, the concrete surface layer detached to spalling which resulted in mass loss and compressive strength loss.

### 3.5. Scanning electron microscopy (SEM)analysis

Figure 7 presents the EDX and SEM micrograph of the FC and PFC specimen after immersed in 5% sodium sulphate solution for 52 weeks. It is observed that the ettringite crystals appear more in the SEM morphology of FC specimens in the form of thin needles. In addition, the presence of ettringite (calcium aluminate) products were shown by the strong peaks of calcium (Ca) and aluminium (Al) with weak peaks present for silicon (Si) and ferum (Fe) in the EDX. While, PFC specimens reveal a denser concrete with a higher trace for crowded tiny of cotton (CSH) compared to FC as shown in Figure 6. It discovered that PFC specimens produce higher amounts of calcium silicate hydrate (CSH) gel in a hardened structure due to strong peaks of Ca and Si as shown in Figure 7. It is considered that the CH was reactant with silica from PSBE to form secondary CSH gel in the pozzolanic reaction. Moreover, the denser microstructure shown in the image is related to the filling effect of fineness PSBE. It demonstrated that the PSBE had filled the pores and voids between the unreacted particles in the hydrated cement paste. Ferraris, Stutzman and Snyder (2006) reported that the crowded tiny of cotton shaped and hexagonal plate represents for the formations of calcium silicate hydrate gel and calcium hydroxide, while elongated rod-shaped and long needle-like crystals represent for the formations of sulphate attack products gypsum and ettringite.

Figure 7. SEM and EDX of PFC and FC after 52 weeks of exposure in 5% Sodium Sulphate solution.



On the other hand, for FC specimen presents the porous surface image with a higher trace for hexagonal plate (CH) and a lower amount of crowded tiny of cotton shaped (CSH), while elongated rod-shaped (gypsum) and long needle-like crystals (ettringite) also appeared in the image. It considered that the lower of CSH would increase the amount of CH that leads to creating more ettringite. Therefore, the FC specimen has lower protection against sulphate attack because the ettringite is recognised as the weakening part against sulphate attack and leads to deterioration to the surface and mass loss. Findings reported by Drimalas et al. (2011) observed the gypsum and ettringite image with the EDX spectrum calcium and silica which formed the ettringite to cause the expansion and deterioration.

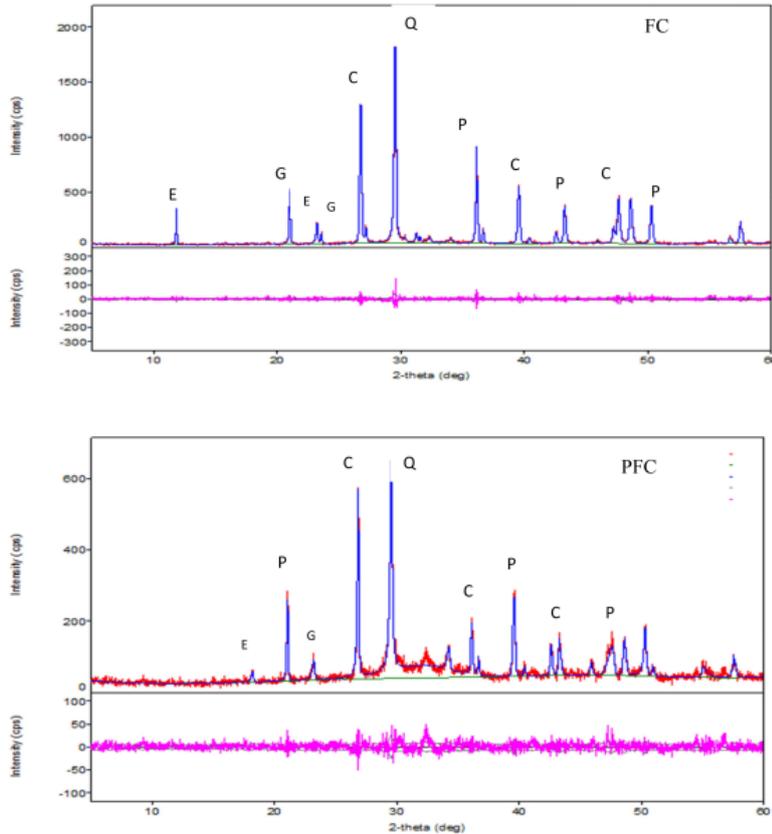
The incorporation of silica fume, slag and fly ash enhances the concrete durability against sulphate attack because the pozzolanic activity increased the additional CSH gel and created the hydrated paste a less permeable to prevent sulphate attack deterioration (Karim et al., 2014; Paiva et al., 2016; Barbhuiya & Kumala, 2017). Therefore, the use of PSBE as cement replacement is vital in decreasing the amount of calcium hydroxide through pozzolanic reaction. Once the calcium hydroxide depletes, then the formation of gypsum and ettringite also decreases.

### 3.6. XRD analysis

Figure 8 shows the XRD patterns of the hydration products for FC and PFC after immersing in 5% sodium sulphate solution for 52 weeks. The intensity of portlandite (CH), ettringite, gypsum, quartz ( $\text{SiO}_2$ ) and calcite ( $\text{CaCO}_3$ ) were marked as P, E, G, Q and C in Figure 8. According to the FC pattern, the amount of gypsum and ettringite was detected two times higher than PFC specimen. It observed that the intensity of ettringite increases as the intensity of

CH increases. For FC specimens, the higher peak of ettringite was detected at  $2\theta = 12$ . It observed that the gypsum has been delivered from the reaction of extensive CH and sodium sulphate ions, while gypsum at that point will respond with the calcium aluminate to produce large intensity of ettringite upon immersion in a sulphate solution. While, for PFC specimen low intensity peaks for CH due to the pozzolanic reaction, which CH has been consumed to create more CSH, and react with the sulphate ions to form gypsum. The intensity of ettringite and gypsum peaks were detected at  $2\theta = 18$  and  $2\theta = 24$  respectively in the PFC specimen. The other effect of PSBE is due to the fineness of PSBE can fill the voids and reduce the porosity leading to decrease ingress sulphate ion and prevent sulphate attack deterioration. Drimalas et al. (2011) reported that the expansion caused by ettringite formation heading to deterioration corner or edges of the specimens after the sulphate attack.

Figure 8. X-ray diffractogram of PFC and FC after 52 weeks of exposure in 5% Sodium Sulphate solution.

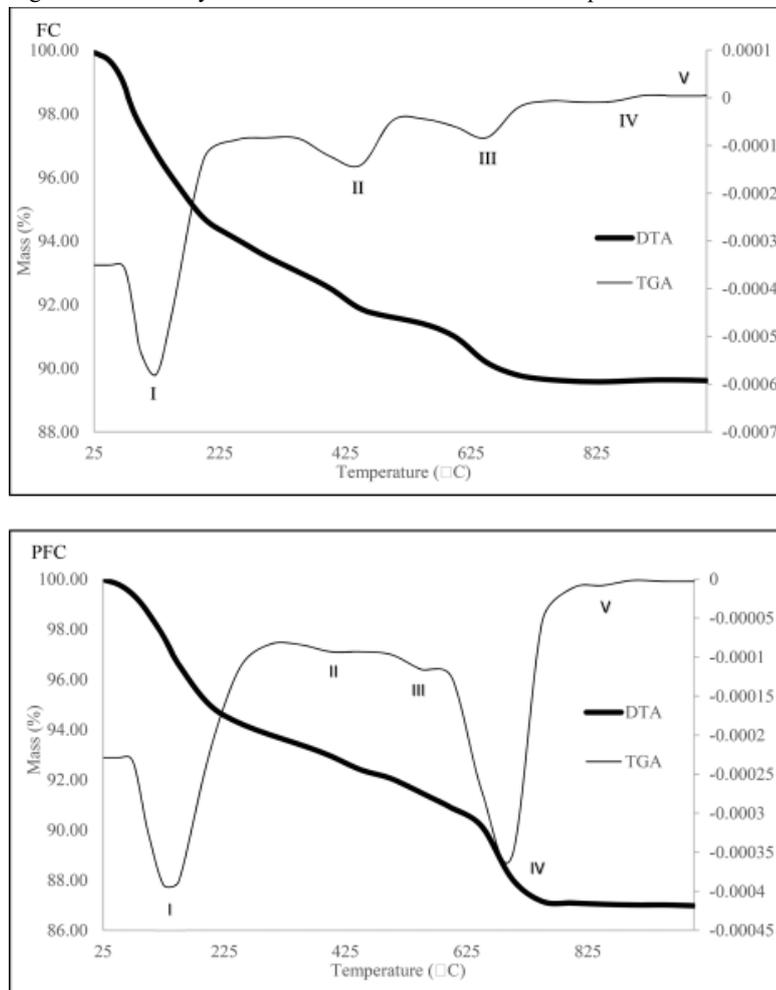


### 3.7. TGA analysis

Figure 9 presents the results of TGA and DTA pattern of weight loss due to the decomposition of hydration products in different ranges of temperature for the specimen FC and PFC in 5% sodium sulphate solution after 52 weeks. It observed that both specimens shared a similar trend of mass loss which is gradually decreasing with different intensity and peaks. According to the pattern, five endothermic peaks were detected within the temperature change. The first endothermic peak of weight loss was observed at lower temperature below  $200\text{ }^{\circ}\text{C}$ , is the result of decomposition of calcium silicate hydrate (CSH) overlapping with dehydration of the ettringite. The TGA results show that the weight loss was 1.9% in FC specimen and 4% in PFC specimen. It can be seen that the effect of PSBE in PFC as compared with FC because the amount of CSH in PFC was higher than FC. This effect has a similar finding by Vedalakshmi, Sundara Raj, and Palaniswamy (2008), that first endothermic peaks at  $0\text{ }^{\circ}\text{C}$  to  $200\text{ }^{\circ}\text{C}$  caused by dehydration of ettringite. The second endothermic peak recognised at temperature above  $200\text{ }^{\circ}\text{C}$  with a 0.13% and 0.63% weight loss in the PFC and FC specimen were referred to the dehydration of gypsum. For a second time, Vedalakshmi et al. (2008), reported the same endothermic peak and temperature of the dehydration of gypsum formation. The third endothermic peak observed at temperature  $450\text{ }^{\circ}\text{C}$  to  $600\text{ }^{\circ}\text{C}$  with a 0.1% and 0.3% weight loss in the PFC and FC specimen contributed to hydration of calcium hydroxide (CH). The fourth endothermic peak observed at temperature

range 600 °C to 760 °C with a 6.85% and 0.11% weight loss in the PFC and FC specimen was referred to the disintegration of calcium silicate hydrate and calcium aluminate. Finally, the endothermic peak has been seen at temperature range 800 °C to 1000 °C with a 0.05% weight loss in PFC specimen was referred to the decarbonation of calcium carbonate in the hydrated paste.

Figure 9. TGA analysis of FC and PFC after 52 weeks of exposure in 5% Sodium Sulphate solution.



## 4. Conclusions

Based on the experimental results, the use of 30%PSBE enable to exhibit higher resistance from deterioration to against sulphate attack compare to control FC specimen. The following findings were summarised below:

1. Visual assessment results indicated that specimen containing 30%PSBE maintained their initial conditions under sulphate environment, while the surface and colour of the FC specimen changed. The effect of PSBE on the durability of foamed concrete was clearly observed even in the short time period of sulphate exposure.
2. After 52 weeks being immersed in 5% sodium sulphate, the mass change of FC and PFC was 4.9% and 1.32% respectively. The specimens containing 30%PSBE exhibit less mass change due to its denser structure, and decreasing in porosity and permeability of foamed concrete, while the FC specimen showed higher mass change due to the reaction between CaO in the OPC and absorption ions from sulphate solution. It was indicated that the higher mass change of the control

FC specimens is due to the higher destruction of the edges, while the specimens containing the PSBE has minor surface deterioration.

3. The foamed concrete containing 30%PSBE has the lower value of expansion of bar exposed in sodium sulphate as compared to FC. It is demonstrated that the higher expansion of the control FC specimens is due to the higher ingress of sulphate ion, while the specimens containing the 30%PSBE has lower expansion because the pozzolanic reaction making PFC denser that lead to prevent the ingress of sulphate solutions. PFC specimens exhibited minor changes due to the lower contain of ettringite upon immersion in sulphate attack.
4. The lowest compressive strength loss under sulphate environment was observed in specimen containing 30%PSBE than control FC. It was indicated that CaO is responsible for the deterioration of foamed concrete under sulphate environment. The total strength deterioration for cube specimens of FC and PFC was 30% and 7.5% respectively. It indicated that the higher compressive strength loss of the control FC specimens is due to the ettringite formation which leads to expansion loss in mass, surface and edges loss in the sulphate attack. After all, the specimens containing the PSBE which exhibit better resistance towards sulphate attack is related to the pozzolanic reaction of silica oxide from PSBE with the calcium hydroxide (CH) to produce more calcium silicate hydrate (CSH). Consequently, this process decreases the amount of CH. Upon the depletion of CH, the formation of gypsum and ettringite will cease
5. The SEM morphology showed that the foamed concrete containing of 30% PSBE was able to minimise the deterioration of foamed concrete exposed to Sodium Sulphate due to the formation of dense microstructure which inhibit the ingress of sulphate ions and reduces the formation of expansive ettringite that leads to reduce the propagation of micro cracks.
6. The XRD pattern showed that the incorporation of high silica in PSBE decreased the amount of portlandite and formed more CSH.
7. The results of TGA and DTA clearly show that the effect of PSBE in the foamed concrete specimen significantly reduced the gypsum content as compared with FC. According to the endothermic peak in FC specimen, the amount gypsum and ettringite was higher than PFC specimen because the gypsum has been delivered from the reaction of extensive CH and sodium sulphate ions, while gypsum at that point will respond with the calcium aluminate to produces large intensity of ettringite upon immersion in a sulphate solution.
8. Conclusively, the foamed concrete containing 30% PSBE as partial cement replacement exhibited better durability than plain foamed concrete has the potential to be used in construction application.

#### Acknowledgement

The authors also would like to acknowledge the help and co-operation received from the lecturers and technical staff of Faculty of Civil Engineering Technology in conducting the experimental work.

#### Disclosure statement

No potential conflict of interest was reported by the author(s). [AQ2]

#### References

- Ahmad, M. H., & Noor, N. M. (2010). Chemical attack of Malaysian Pozzolans concrete. *Journal of Science and Technology*, 1(1), 11–24. [AQ3] [AQ4]
- Alzebaree, R., Gulsan, M. E., Nis, A., Mohammedameen, A., & Cevik, A. (2018). Performance of FRP confined and unconfined geopolymer concrete exposed to sulphate attacks. *Steel and Composite Structures*, 29(2), 201–218.
- ASTM C1012/C1012M-18b (2018). *Standard test method for length change of hydraulic-cement mortars exposed to a sulphate solution*. ASTM International.
- ASTM C618-19 (2019). *Standard specification for coal fly ash and raw or calcined natural pozzolan for use in concrete*. ASTM International.

- Barbhuiya, S., & Kumala, D. (2017). Behaviour of a sustainable concrete in acidic environment. *Sustainability (Switzerland)*, 9(9) **LAQ5**
- Beshara, A., & Cheeseman, C. R. (2014). Reuse of spent bleaching earth by polymerisation of residual organics. *Waste Management ( Management)*, 34(10), 1770–1774. <https://doi.org/10.1016/j.wasman.2014.04.021>
- Çevik, A., Alzebaree, R., Humur, G., Niş, A., & Gülşan, M. E. (2018). Effect of nano-silica on the chemical durability and mechanical performance of fly ash based geopolymer concrete. *Ceramics International*, 44(11), 12253–12264. <https://doi.org/10.1016/j.ceramint.2018.04.009>
- Dayarathne, W. H. R. S., Galappaththi, G. S., Perera, K. E. S., & Nanayakkara, S. M. A. (2013). Evaluation of the Potential for Delayed Ettringite Formation in Concrete [Paper presentation]. Paper presented 19th ERU Symposium, National Engineering Conference 2013, Sri Lanka, University of Moratuwa, 59–66.
- Drimalas, T., Clement, J. C., Folliard, K. J., Dhole, R., & Thomas, M. D. (2011). *Laboratory and field evaluations of external sulphate attack in concrete* (No. FHWA/TX-11/0-4889-1) 7, 190.
- Duan, P., Yan, C., & Zhou, W. (2016). Influence of partial replacement of fly ash by metakaolin on mechanical properties and microstructure of fly ash geopolymer paste exposed to sulphate attack. *Ceramics International*, 42(2), 3504–3517. <https://doi.org/10.1016/j.ceramint.2015.10.154>
- Eliche-Quesada, D., & Corpas-Iglesias, F. A. (2014). Utilisation of spent filtration earth or spent bleaching earth from the oil refinery industry in clay products. *Ceramics International*, 40(10), 16677–16687. <https://doi.org/10.1016/j.ceramint.2014.08.030>
- Kandasamy, S., & Shehata, M. H. (2014). Durability of ternary blends containing high calcium fly ash and slag against sodium sulphate attack. *Construction and Building Materials*, 53, 267–272. <https://doi.org/10.1016/j.conbuildmat.2013.11.080>
- Karim, M. R., Hossain, M. M., Khan, M. N. N., Zain, M. F. M., Jamil, M., & Lai, F. C. (2014). On the utilisation of pozzolanic wastes as an alternative resource of cement. *Materials*, 7(12), 7809–7827. <https://doi.org/10.3390/ma7127809>
- Liu, K., Deng, M., Mo, L., & Tang, J. (2015). Deterioration mechanism of Portland cement paste subjected to sodium sulphate attack. *Advances in Cement Research*, 27(8), 477–486. <https://doi.org/10.1680/jadcr.14.00051>
- Loh, S. K., Cheong, K. Y., Choo, Y. M., & Salimon, J. (2015). Formulation and optimisation of spent bleaching earth-based bio organic fertiliser. *Journal of Oil Palm Research*, 27(1), 57–66.
- Loh, S. K., Cheong, K. Y., & Salimon, J. (2017). Surface-active physicochemical characteristics of spent bleaching earth on soil-plant interaction and water-nutrient uptake: A review. *Applied Clay Science*, 140, 59–65. <https://doi.org/10.1016/j.clay.2017.01.024>
- Loh, S. K., James, S., Ngatiman, M., Cheong, K. Y., Choo, Y. M., & Lim, W. S. (2013). Enhancement of palm oil refinery waste - Spent bleaching earth (SBE) into bio organic fertiliser and their effects on crop biomass growth. *Industrial Crops and Products*, 49, 775–781. <https://doi.org/10.1016/j.indcrop.2013.06.016>
- Łukowski, P., & Salih, A. (2015). Durability of mortars containing ground granulated blast-furnace slag in acid and sulphate environment. *Procedia Engineering*, 108, 47–54. <https://doi.org/10.1016/j.proeng.2015.06.118>
- Małolepszy, J., & Grabowska, E. (2015). Sulphate attack resistance of cement with zeolite additive. *Procedia Engineering*, 108(November), 170–176. <https://doi.org/10.1016/j.proeng.2015.06.133>
- Meziti, C., & Boukerroui, A. (2011). Regeneration of a solid waste from an edible oil refinery. *Ceramics International*, 37(6), 1953–1957. <https://doi.org/10.1016/j.ceramint.2011.02.016>
- Nie, Q., Zhou, C., Shu, X., He, Q., & Huang, B. (2014). Chemical, mechanical, and durability properties of concrete with local mineral admixtures under sulphate environment in Northwest China. *Materials ( Materials)*, 7(5), 3772–3785. <https://doi.org/10.3390/ma7053772>
- Olivia, M. (2011). *Durability related properties of low calcium fly ash based geopolymer concrete* [Doctoral dissertation]. Curtin University.

- Paiva, H., Velosa, A., Cachim, P., & Ferreira, V. M. (2016). Effect of pozzolans with different physical and chemical characteristics on concrete properties. *Materiales de Construcción*, 66(322), e083. <https://doi.org/10.3989/mc.2016.01815>
- Panesar, D. K. (2013). Cellular concrete properties and the effect of synthetic and protein foaming agents. *Construction and Building Materials*, 44, 575–584. <https://doi.org/10.1016/j.conbuildmat.2013.03.024>
- Protus (2014). *Investigation of the pyroprocessing and the optimum mix ratio of rice husks, broken bricks and spent bleaching earth to make pozzolanic cement* [Doctoral Dissertation]. Kenyatta University.
- Rashwan, M. M., Megahed, A. R., & Essa, M. S. (2015). Effect of local metakaolin on properties of concrete and its sulphuric acid resistance. *Journal of Engineering Sciences*, 43(2), 183–199.
- Rokiah, O., Khairunisa, M., Youventharan, D., & Arif, S. M. (2019). Effect of processed spent bleaching earth content on the compressive strength of foamed concrete. *IOP Conference Series: Earth and Environmental Science*, 244(1), 012013. <https://doi.org/10.1088/1755-1315/244/1/012013>
- Saleh, I. S. (2017). Effect of external and internal sulphate on compressive strength of concrete. *International Journal of Applied Engineering Research*, 12(20), 10324–10333.
- Sancak, E., & Özkan, Ş. (2015). Sodium sulphate effect on cement produced with building stone waste. *Journal of Materials*, 2015, 1–12. <https://doi.org/10.1155/2015/813515>
- Sangiorgi, C., Tataranni, P., Simone, A., Vignali, V., Lantieri, C., & Dondi, G. (2014). Waste bleaching clays as fillers in hot bituminous mixtures. *Construction and Building Materials*, 73, 320–325. <https://doi.org/10.1016/j.conbuildmat.2014.09.076>
- Siva, G. I., & Ramamurthy, K. (2012). Cement & concrete composites behaviour of foam concrete under sulphate environments. *Cement and Concrete Composites*, 34(7), 825–834. <https://doi.org/10.1016/j.cemconcomp.2012.03.007>
- Tian, W., & Han, N. (2017). Experiment analysis of concrete's mechanical property deterioration suffered sulphate attack and drying-wetting cycles. *Advances in Materials Science and Engineering*, 2017, 1–13. <https://doi.org/10.1155/2017/5673985>

## AUTHOR QUERIES

**Query:** AQ0: Please review the table of contributors below and confirm that the first and last names are structured correctly and that the authors are listed in the correct order of contribution. This check is to ensure that your names will appear correctly online and when the article is indexed.

Sequence	Prefix	Given name(s)	Surname	Suffix
1		Rokiah	Othman	
2		Khairunisa	Muthusamy	
3		Youventharan	Duraisamy	
4		Mohd Arif	Sulaiman	
5		Ramadhansyah	Putra Jaya	
6		Nadiatul Adilah	Ahmad Abdul Ghani	
7		Sajjad Ali	Mangi	

**Author Response:** 1. Name of authors structured is confirmed. 2. If possible, please add second affiliation for Ramadhansyah Putra Jaya (Earth Resources and Sustainability Center, Universiti Malaysia Pahang, 26300 Kuantan, Pahang, Malaysia)

**Query:** AQ1: Figure 2 was not cited in the text so a citation has been inserted. Please provide a correction if this is inaccurate.

**Author Response:** The inserted figure 2 is confirmed.

**Query:** AQ2: A disclosure statement reporting no conflict of interest has been inserted. Please correct if this is inaccurate.

**Author Response:** Ok

**Query:** AQ3: Please provide complete details for (Huang & Chang, 2010; Darayathne et al. 2013; Ranjani and Ramamurthy 2012; Ferraris, Stutzman & Snyder 2006; Vedalakshmi, Sundara Raj, & Palaniswamy 2008) in the reference list or delete the citation from the text.

**Author Response:** 1. Huang, Yi-Pin., & Chang, J. I. (2010). Biodiesel production from residual oils recovered from spent bleaching earth. *Renewable Energy*, 35, 269–274. <https://doi:10.1016/j.renene.2009.07.014>. 2. PLEASE REPLACE Darayathne et al. 2013 WITH Jaya et al. 2014. Jaya, R. P., Badorul Hisham, A. B., Megat Azmi, M. J., Mohd Haziman, W. I., Mohd Rosli, H., & Dewi Sri, J. (2014). Strength and microstructure analysis of concrete containing rice husk ash under seawater attack by wetting and drying cycles. *Advances in Cement Research*, 26(3), 145–154. <http://dx.doi.org/10.1680/adcr.13.00010>. 3. Ranjani, G. I. S., & Ramamurthy, K. (2012). Behaviour of foam concrete under sulphate environments. *Cement and Concrete Composites*, 34(7), 825-834. <https://doi.org/10.1016/j.cemconcomp.2012.03.007>. 4. PLEASE REPLACE Ferraris, Stutzman & Snyder 2006 WITH Mangi et al. 2019. Mangi, S. A., Mohd Haziman, W. I., Norwati, J., Mohd Fadzil, A., & Ramadhansyah, P. J. (2019). Short-term effects of sulphate and chloride on the concrete containing coal bottom ash as supplementary cementitious material. *Engineering Science and Technology, an International Journal*, 22(2), 515-522. 5. Vedalakshmi, R., Sundara Raj, A., & Palaniswamy, N. (2018). Identification of various chemical phenomena in concrete using thermal analysis. *Indian Journal of Chemical Technology*, 15, 388-396.

**Query:** AQ4: There is no mention of (Panesar 2013; ASTM C618-19 2019) in the text. Please insert a citation in the text or delete the reference as appropriate.

**Author Response:** Please replace ASTM C618-12 (page 4 line 461) with ASTM C618-19.

**Query:** AQ5: Please provide the page range.

**Author Response:** Page range: 1-13

**Query:** AQ6: Please note that the ORCID section has been created from information supplied with your manuscript submission/CATS. Please correct if this is inaccurate.

**Author Response:** Ok