Proceedings of Science and Mathematics
Faculty of Science,
Universiti Teknologi Malaysia
Volume 33, 2026, page 1-9

Effect of Polyvinyl Alcohol (PVA) as an Additive on The Durability of Hardened Ordinary Portland Cement Paste Under Sulfate Exposure

Amirul Eirwan Shah Rosman[a], Fuad Mohamad[a]*
[a]Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor, Malaysia
*Corresponding author: m.fuad@utm.my

Abstract
Sulfate attack occurs when sulfate ions, in seawater or underground soil that rich with sulfate attack the cement paste, leading to expansion, spalling and strength loss of the concrete. This expansion is related to ettringite and gypsum precipitation in the cement matrix. Researchers have proposed a variety of methods to solve this problem by using a polymer with a hydroxyl functional group as an additive in cement-based materials. This research examines the effect of polyvinyl alcohol (PVA) additives on the sulfate resistance of hardened Ordinary Portland Cement (OPC) paste. Specimens with a fixed water-to-cement (w/c) ratio of 0.32 and varying polymer-to-cement (p/c) ratios of 0.016 and 0.032 were prepared and cured for 28 days, followed by immersion in a 10% K_2SO_4 solution. Sulfate content was determined via gravimetric analysis after 30 and 90 days. After 30 days, the recorded sulfate content was 2.18 % for control samples, 2.49 % for 0.016 P/C, and 2.43 % for 0.032 P/C samples. After 90 days, sulfate contents further increased to 2.28 %, 2.58 %, and 2.60 %, respectively. Furthermore, the hydration products of the cement materials were characterized using X-ray diffraction (XRD), thermogravimetric analysis (TGA) coupled with derivative thermogravimetry (DTG) and differential thermal analysis (DTA) and scanning electron microscope (SEM). XRD pattern of the peaks for the hardened cement samples after immersion in 10 % K_2SO_4 solution was the same since every sample was subjected to sulfate attack due to the formation of ettringite and gypsum at approximately $2\theta \approx 23.07$ ° and $2\theta \approx 29.30$ °, respectively. TGA-DTA shows the decomposition of portlandite at 400°C to 450 °C, proving the presence of the hydration product. The morphology of the hydration product was characterized by using SEM. The result of this study showed that the presence of PVA increased sulfate ion penetration, likely due to its effect on porosity, contrary to the general assumption that polymers enhance durability.
Keywords: Sulfate Attack, Polyvinyl Alcohol (PVA), Ordinary Portland Cement (OPC), Ettringite, Gypsum

Introduction

Cement is widely used in the construction of buildings worldwide. It is a chemical substance that acts as a binder, setting, hardening, and adhering other materials to be bonded together. When it is mixed with fine aggregate produces mortar, while cement mixed with sand and coarse aggregate produces concrete, a well-known material commonly used in construction sites. Ordinary Portland Cement (OPC) is the most frequently used cement in construction worldwide. It is a fundamental component of mortar, grout, and concrete and is well-known for its strength, adaptability, and broad range of uses.

The four main components in Ordinary Portland Cement are tricalcium silicate (Ca_3OSiO_5), dicalcium silicate (Ca_2OSiO_4), tricalcium aluminate ($Ca_3Al_2O_6$), and tetracalcium aluminate ($Ca_4Al_2O_3Fe_2O_{10}$). The compounds are abbreviated as C_3S, C_2S, C_3A, and C_4AF, respectively, based on cement chemistry notation. Both C_3S and C_2S, upon reaction with water, will be converted into calcium silicate hydrate (CSH) and portlandite ($Ca(OH_2)$) abbreviated as CH [1] The strengthening of the OPC in the first week is mainly due to the calcium silicate hydrate (CSH), C_3S and C_2S.[2]

Sulfate attack creates a serious risk to cementitious materials' durability. Usually, sulfate attack occurs when external sulfate penetrates into the concrete and reacts with C_3A in the presence of gypsum ($CaSO_4 \cdot 2H_2O$), producing ettringite as a side product. Ettringite is a needle-shaped crystal, and upon excessive formation of ettringite in the cement paste, it can cause expansion and cracking of hardened cement paste, a major problem in cement pastes production.[3]

While various additive has been explored to reduce this ongoing effect, the potential of polyvinyl alcohol (PVA) as an additive to improve the durability of hardened Ordinary Portland Cement (OPC) under sulfate exposure remains under researched. PVA is known for its film-forming ability and chemical resistance, which may contribute to reduced permeability and enhanced microstructural stability. However, its effectiveness in sulfate-rich environments has yet to be comprehensively evaluated. This study aims to investigate the influence of PVA additives on the resistance of hardened OPC paste to sulfate attack, providing insights into its potential as a protective agent in aggressive environments.

Materials and methods

Chemicals and Materials

The chemicals used in this study were hydrochloric acid 37% (Supelco), barium chloride (Qrec), acetone (Sigma Aldrich), polyvinyl alcohol (BDH Limited Poole, England), potassium sulfate (ChemAR) and Ordinary Portland cement (OPC) (CEM I 52.5 N CE CP2).

Production of Hardened Cement Paste

The preparation of hardened cement pastes involved the processes of mixing, casting, moulding, demoulding, and curing. A total of 21 samples with 3 cm in length, 3 cm in width, and 3 cm in height were produced using a constant water-to-cement ratio (w/c) of 0.32 and two different polymer- to-cement ratios (p/c) of 0.016 and 0.032. For the 30-day immersion test in a 10% potassium sulfate (K_2SO_4) solution, 9 samples were prepared: 3 control samples without polymer, 3 samples with a p/c of 0.016, and 3 samples with a p/c of 0.032. The same procedures were repeated for 90 days. In addition, 3 samples, one each for the control, p/c of 0.016, and p/c of 0.032, were not immersed in the sulfate solution. These non-immersed samples were used to analyse the initial condition and sulfate content of the hardened cement paste. Figure 1 illustrates the detailed sample preparation process used in this study.

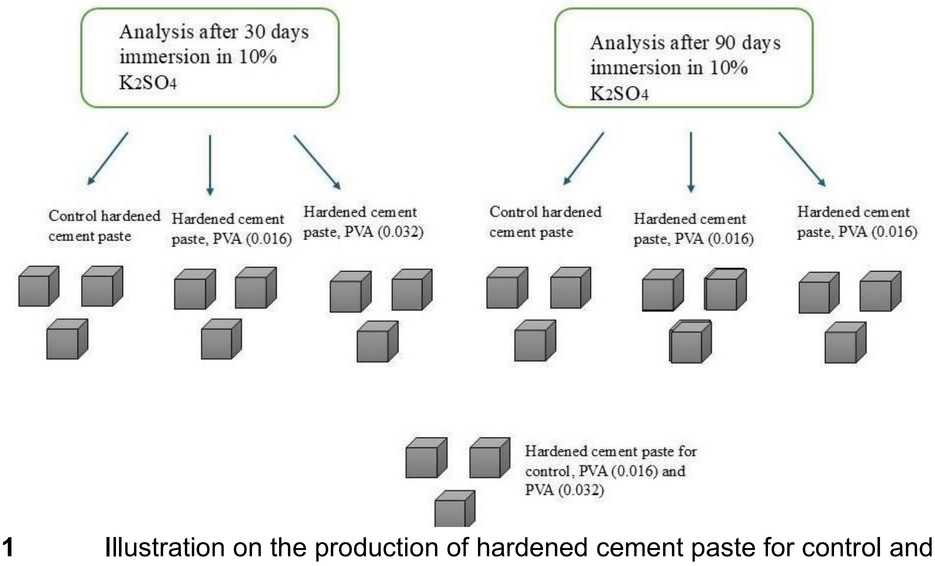


Figure 1 Illustration on the production of hardened cement paste for control and p/c ratio of 0.016 and 0.032.

Gravimetry Analysis

The objective of this test is to determine the concentration of sulfate ions in a cement sample according to BS EN 197-1:2014. Concentrated HCl was used to extract sulphate ion from the cement sample and is precipitated at a pH between 1.0 to 1.5 by a solution of barium chloride, $BaCl_2$. The precipitate was ignited in the furnace and the weight of the precipitate was calculated.

X-ray Diffraction Analysis

The Rigaku Smart Lav X-ray diffractometer with Cu Kα radiation source (λ = 1.5406 Å) operating at 40 kV and 30 mA was used for the XRD analysis. The thin film phase and structure were examined using the glancing incident X-ray diffraction (GI-XRD) measurement mode. The detector scans for 2θ between 20 and 90 degrees with a step width of 0.03 degrees, with a fixed GI angle of 0.50 degrees and a scan time of one second for each step. All the samples were 2.5 cm x 2.5 cm in area, and each sample was directly placed into the chamber for analysis. All the results were compared with the Joint Committee on Powder Diffraction Standards (JCPDS) database for sample identification and structural confirmation.

Scanning Electron Microscopy Analysis (SEM)

The presence of cement hydration products was observed via SEM. The control cement and cement modified with PVA was observed using SEM utilising the JEOL JSM-5510 Low Vacuum Scanning Electron Microscope, which is in V01 the Department of Biomedical Engineering and Health, UTM. Sample preparation was completed before SEM analysis, which includes attaching the sample to a glass slide with carbon tape and coating it with a tiny layer of gold to prevent electron grounding during the examination. Following the sample preparation step, the sample was placed inside the chamber. The image was focused at a resolution of 2.5 to 10 k magnification, depending on which resolution produces the best image look, with the electron voltage set at 10 keV.

Thermogravimetric Analysis

The thermogravimetric analysis was used to evaluate the thermal stability and the presence of hydration products of cement. This technique provides the weight loss when the sample was heated, providing insight into its decomposition behaviour of the samples. Thermal stability of the hydration product was analysed by using thermogravimetric analysis (TGA) (model DTA-TG-60H; Shimadzu). The analysis was conducted under a nitrogen atmosphere with a flow rate of 200 mL/min, heating the sample from 30°C to 800°C at a rate of 10°C per minute.

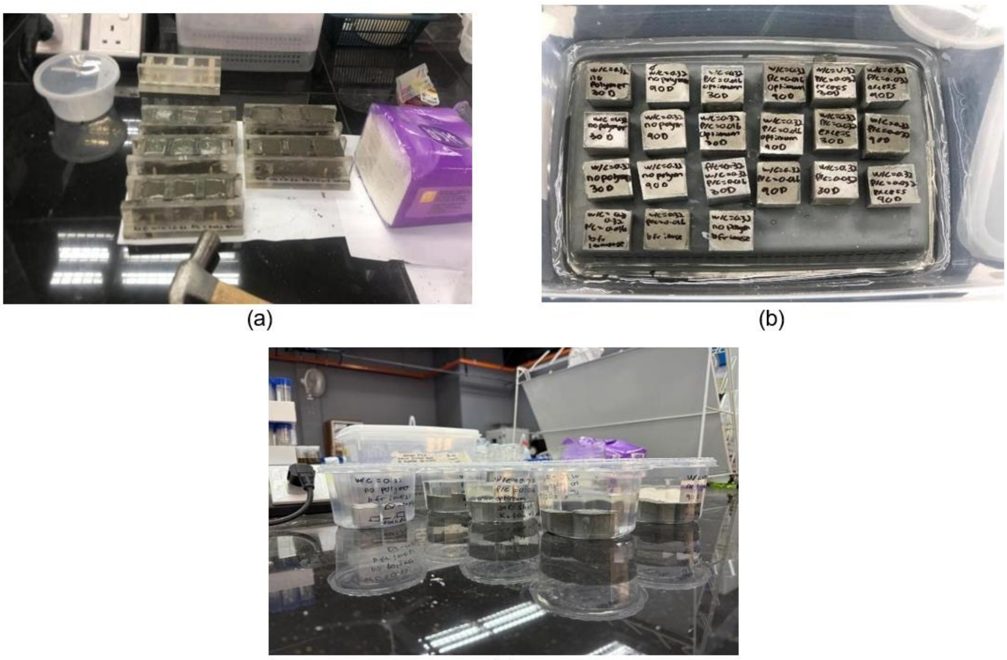
Results and discussion

A conventional gravimetric analysis method was employed to determine the sulfate concentration in the hardened cement paste. It was initially hypothesized that the hardened cement paste containing the polyvinyl alcohol (PVA) polymer additive would exhibit lower sulfate concentrations compared to the control samples without PVA. For Scanning Electron Microscopy (SEM) analysis, it was anticipated that the main hydrated products, namely calcium silicate hydrate (C–S–H), calcium hydroxide (CH), and ettringite, were observed and distinguished. This would help confirm the occurrence of sulfate-related reactions with the hydration products. Furthermore, X-ray diffraction (XRD) was used to exhibit characteristic peaks corresponding to the presence of portlandite and ettringite, thereby supporting the interpretation of sulfate attack and hydration behavior. Thermogravimetric analysis was used to study the mass loss of the hydration product and thermal events occurred during the hydration reaction.

Hardened Cement Paste

All hardened cement pastes were successfully produced for control, and PVA-modified hardened cement paste with p/c ratios of 0.016 and 0.032. Figure 2 (a) shows the process of casting and moulding of the hardened cement paste in 3 cm x 3 cm x 3 cm cubic mould. After all the hardened cement pastes were demoulded, the hardened cement pastes were cured for 28 days as shown in

Figure 2 (b) followed by immersion in 10 % K_2SO_4 solution as shown in Figure 2 (c).



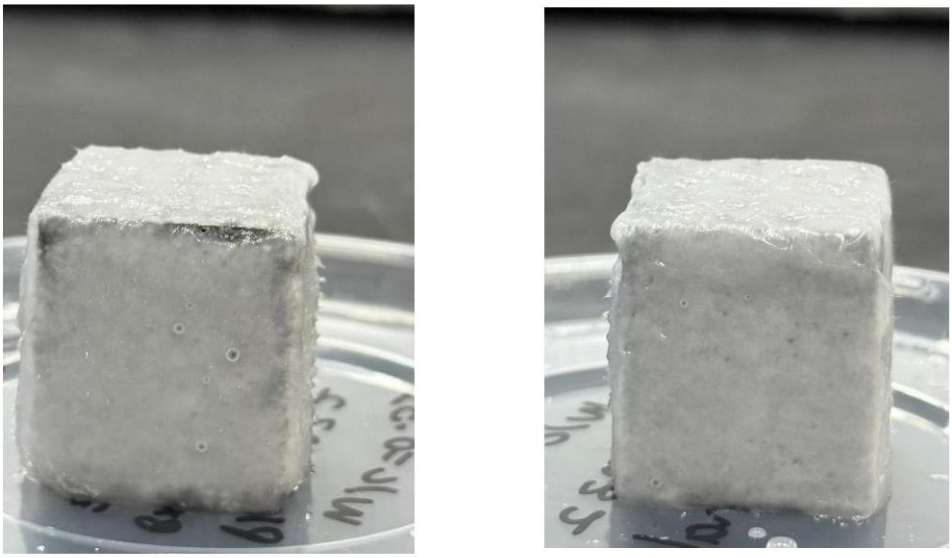
(a) (b)

(c)

Figure 2 (a) Casting of cement paste, (b) curing of hardened cement paste for 28 days and (c) immersion of hardened cement paste in 10 % K_2SO_4 solution for 30 and 90 days.

Determination of Sulfate in Hardened Cement Paste by Gravimetric Analysis Technique

The hardened cement paste was subjected to gravimetric analysis after being immersed in 10% K_2SO_4 solution. Figure 3 illustrates the condition of the hardened cement paste after immersion in 10% K_2SO_4 solution after 30 and 90 days.



(a) (b)

Figure 3 Condition of hardened cement paste after immersion in 10% K_2SO_4 solution for a) 30 days and (b) 90 days.

According to British Standards Institution (2014), the determination of sulfate in cement can be determined by using gravimetric analysis. Gravimetric analysis is an analytical technique that measures the mass of an analyte or its derivative to determine its concentration or quantity in a sample.

Table 1 shows the average sulfate content (%) in hardened cement paste after immersion in 10% K_2SO_4 solution for 30 and 90 days.

Table 1: Average sulfate content (%) of hardened cement paste with and without polyvinyl alcohol additive before and after immersion in 10 % K_2SO_4.

Sample	Before Immersion (%)	After 30 Days (%)	After 90 Days (%)	Percentage Increase (30 Days)	Percentage Increase (30 Days)
Control	1.780 ± 0.011	2.182 ± 0.002	2.282 ± 0.005	22.584	28.202
PVA (0.016)	1.747 ± 0.072	2.486 ± 0.071	2.541 ± 0.010	42.301	45.449
PVA (0.032)	1.752 ± 0.021	2.434 ± 0.078	2.625 ± 0.010	38.927	49.829

Note: PVA (0.016) and PVA (0.032) refer to the polymer-to-cement (p/c) ratio added to the cement paste mixture.

From Table 1, all hardened cement pastes samples exhibited an increase in sulfate content after immersion in the 10% K_2SO_4 solution for both 30 and 90 days, indicating a progressive sulfate ingression over time. From these findings, it can be concluded that the first mechanism of sulfate attack occurs, where extreme external conditions such as seawater or soil containing high sulfate concentration, can be a driving force for sulfate attack to occur.

From the data, the control hardened cement paste sample and the hardened cement paste modified with PVA (0.016) and (0.032) show almost consistent sulfate content before immersion, which were 1.780 ± 0.011, 1.747 ± 0.072, and 1.752 ± 0.021, respectively. After 30 days of immersion, the control sample, PVA modified sample for (0.016) and (0.032) show an increasing trend of sulfate content, from their initial sulfate content, which were 2.182 ± 0.002, 2.486 ± 0.071, and 2.434 ± 0.078, respectively. The sulfate content for control sample and PVA modified sample for (0.016) and (0.032) also shows an increasing trend of sulfate content after they were immersed in 10% K_2SO_4 solution, which were 2.282 ± 0.005, 2.541 ± 0.010, and 2.625 ± 0.010, respectively. The sulfate content for all samples after immersion for 90 days shows higher sulfate content than the samples after immersion for 30 days. This shows that sulfate ingression in the hardened cement paste increases, as the time of immersion increases.

The addition of an additive such as a polymer that contains OH- functional group is to reduce the severity of sulfate attack by adsorbing on the surface of cement particles and cement hydration products through electrostatic attraction or hydrogen bonding. It can also function to fili in the pores or interfacial areas, then transformed into a three-dimensional interpenetrating network structure to densify the matrix materials to prevent some effective diffusion of ion such as sulfate ion ($SO4^{2-}$).

Unexpectedly, the findings revealed that the polymer-modified samples had a higher sulfate content, which is contrary to the initial expectations. The sulfate content data for hardened cement paste immersed in the 10% K_2SO_4 solution for 30 and 90 days demonstrated a consistent trend where the polymer-modified samples consistently exhibited higher sulfate content than the control samples. This consistent pattern supports the reliability of the data obtained. These pores facilitate the ingression of sulfate ions into the matrix, potentially explaining the higher sulfate content observed in the polymer-modified, which is similar reported by Topič et al., (2015) in which there are two (2) mechanisms that responsible for the sulfate attack; the transfer of sulfate ions from the external media into the cement matrix, and the second mechanism is by the dissolution of portlandite and increasing porosity of hardened cement paste.[4]

Thermogravimetric Analysis

TGA-DTA was used to investigate the degree of hydration product and the thermal events that occurred within the hardened cement paste samples. TG curve gives information about the mass loss of hydration products, particularly moisture at 50-100 °C, decomposition of calcium silicate hydrate (CSH) at 130 160°C, decomposition of portlandite at 400 -450 °C and decomposition of calcium carbonate at 600 -750 °C.[5] The endothermic peaks observed in the DTA curve confirm that all thermal events related to the decomposition of hydration products are associated with endothermic reactions. Figure 4 (a) Figure 4 (b) illustrate the TGA-DTA curve for hardened cement paste without PVA and with PVA (0.016) before immersion in 10 % K_2SO_4 solution, respectively. Next, Figure 5 (a) and Figure 5(b) illustrate the TGA-DTA curve for hardened cement pastes without PVA and with PVA (0.016) that were immersed in 10 % K_2SO_4 solution for 30 days, respectively. Lastly, Figure 6 (a) and Figure 6 (b) illustrate the TGA-DTA curve for hardened cement pastes without PVA and with PVA (0.016) 10 % K_2SO_4 solution for 90 days, respectively.

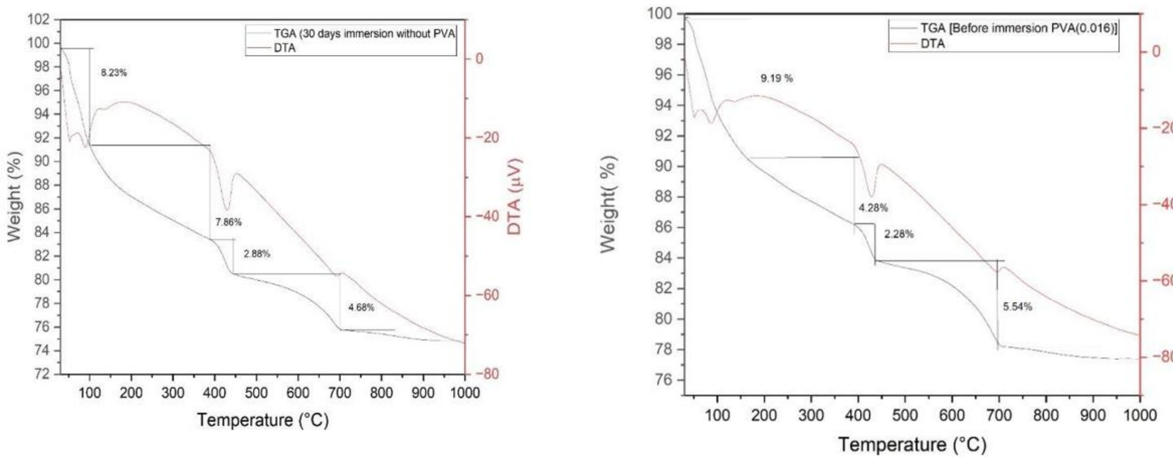


Figure 4 TGA-DTA curve for (a) hardened cement paste without PVA before immersion and (b) hardened cement paste with PVA (0.016) before immersion.

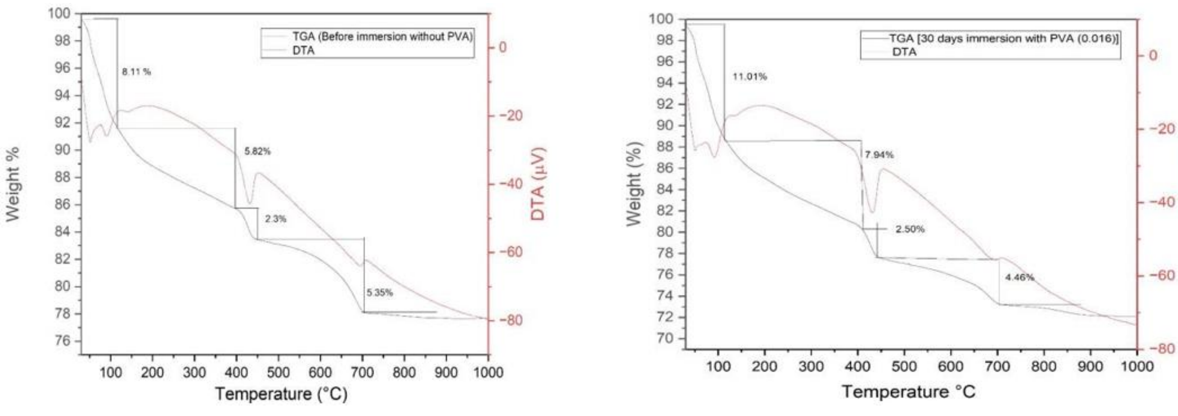


Figure 5 TGA-DTA curve for (a) hardened cement paste without PVA after 30 days of immersion and (b) hardened cement paste with PVA (0.016) after 30 days of immersion.

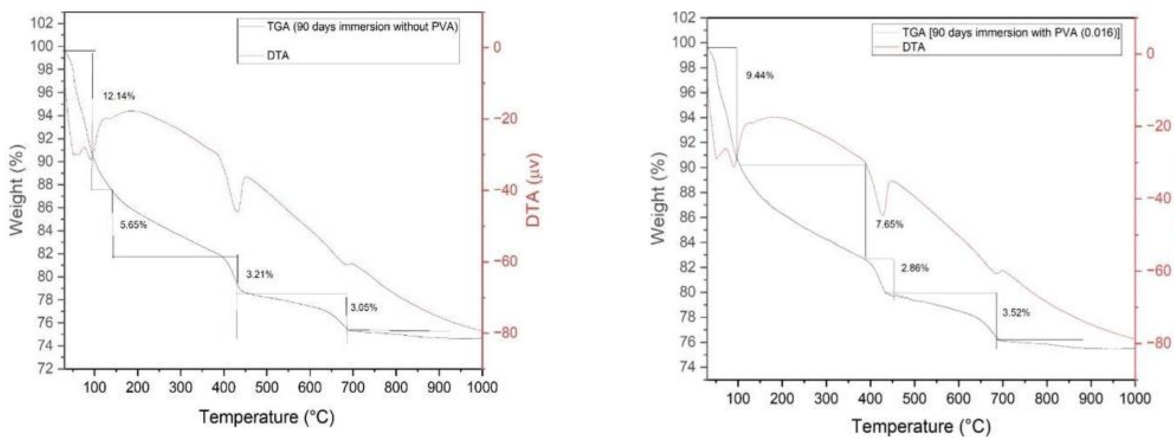


Figure 6 TGA-DTA curve for (a) hardened cement paste without PVA after 90 days of immersion and (b) hardened cement paste with PVA (0.016) after 90 days of immersion.

For every hardened cement sample that contained PVA, it had a lower portlandite mass percentage, where it decomposed at 400 - 450 °C. Table 2 shows the mass loss of portlandite (%) from TGA analysis of cement paste samples before and after immersion in 10 % of K_2SO_4 solution for 30 and 90 days. These findings do support the initial study from Ragoug et al., (2019) which stated that one of the mechanisms of sulfate attack was the dissolution of Ca^{2+} ions from the cement matrix. On the other hand, Topič et al. (2015) also reported that PVA increasing the porosity of the hardened cement paste is by retarding the hydration process [4,5]. Retardation of hydration product resulting in less calcium silicate hydrate (CSH) and portlandite form, which makes the hardened cement paste less dense, and increases porosity. This increases the severity of sulfate attacks.

Table 2: Mass loss of portlandite (%) from TGA analysis of cement paste samples before and after immersion in 10 % of K_2SO_4 solution for 30 and 90 days.

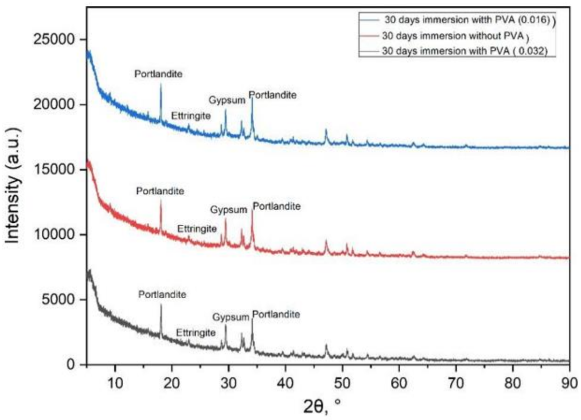
Sample	**Portlandite mass (%)**		
	Before immersion	After 30 days of immersion	After 90 days of immersion
Cement without PVA	2.30	2.88	3.21
Cement with PVA	2.28	2.50	2.86

X-ray Diffraction Analysis

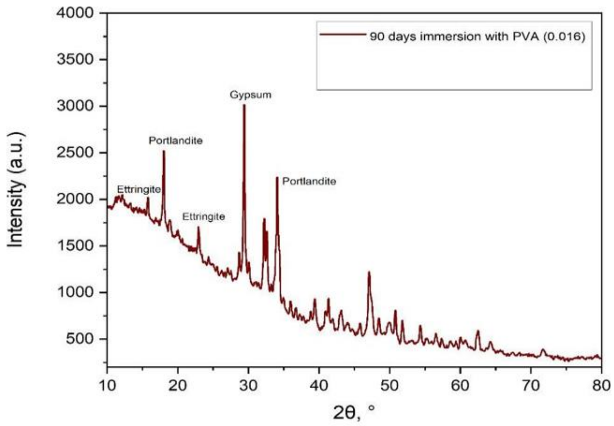
Cement hydration products can be monitored by observing XRD diffractograms. The sharp peak present in the XRD can determine the hydration products such as portlandite, ettringite, and gypsum, due to their crystalline structure. Even though calcium silicate hydrate is one of the most important hydration products, the peak corresponding to (CSH) is hardly visible due to its amorphous and semi crystalline structure. Other than that, the peak for PVA was also hard to observe due to its might overlapping with the CSH peak due to its amorphous structure. Other than that, the small amount of

PVA added into the cement matrix might also be the reason for the peak not appearing.

Figure 7 (a) shows the XRD diffractograms of XRD patterns for hardened cement pastes without PVA and with PVA (0.016) and (0.032) that were immersed in 10% K_2SO_4 solution for 30 days, while Figure 7 (b) shows the XRD pattern for hardened cement paste with PVA (0.016) that were immersed in 10% K_2SO_4 solution for 90 days. From Figure 7 (a), it can be observed that the pattern of the peaks is quite the same since every sample was subjected to sulfate attack due to the formation of ettringite and gypsum at approximately 23.07 ° and 29.30 ° respectively, which aligns to the previous study from Chintalapudi and Panem, (2022).[3] Other than that, from Figure 7 (b) for ettringite and gypsum peaks seems sharper and higher in intensity, due to the sample was subjected to sulfate attack for 90 days, compared to 30 days, resulting more sulfate ingresses in the cement matrix and increasing the production of ettringite and gypsum at the same spot which were 23.07 ° and 29.30° respectively.



(a)



(b)

Figure 7 XRD pattern for (a) hardened cement paste without and with PVA (0.016) and (0.032) after immersion of 30 days (b) hardened cement paste with PVA (0.016) after immersion of 90 days.

Scanning Electron Microscopy (SEM)

SEM was used to observe the morphology of the hydration products, primarily calcium silicate hydrate (CSH), portlandite, ettringite, and gypsum. Figure 8 shows the morphology of the cement hydration products of the hardened cement paste with PVA (0.016) after immersion in 10% K_2SO_4 for 30 and 90 days. The formation of ettringite as needle-like or rod-shaped crystals was well defined after 30 and 90 days of immersion in sulfate solution. Other than that, the structure of portlandite that forms a large, hexagonal plate crystal can also be clearly defined. It is more crystalline and can be easily distinguished compared to (CSH). Lastly, gypsum crystals were hardly visible because they might be overlapped by the structure of CSH and other hydration products.

Conclusion

As a conclusion, hardened cement pastes with 0.016 and 0.032 polymer-to-cement ratios were successfully produced. The determination of sulfate in the hardened cement paste was also successfully carried out. The hydration products of hardened cement paste were also characterized by using X-ray diffraction (XRD), thermogravimetric analysis (TGA) coupled with (DTA), and scanning electron microscopy (SEM). From the analysis, hydration products such as ettringite and gypsum were observed at 23.07 2θ ° and 29.30 2θ °. The percentage of portlandite mass loss was obtained from TGA-DTA data. Morphology of the hydration products, such as CSH, portlandite, and ettringite, was successfully characterized by SEM. It can be concluded that not all polymers with a hydroxyl functional group can be useful as an additive, especially when the cement paste in the concrete is surrounded by extreme sulfate environments. There is no doubt that polymer is generally good as an additive in the cement matrix, but further study and testing are necessary to ensure the suitability of the selected polymer for future applications and specific environmental conditions.

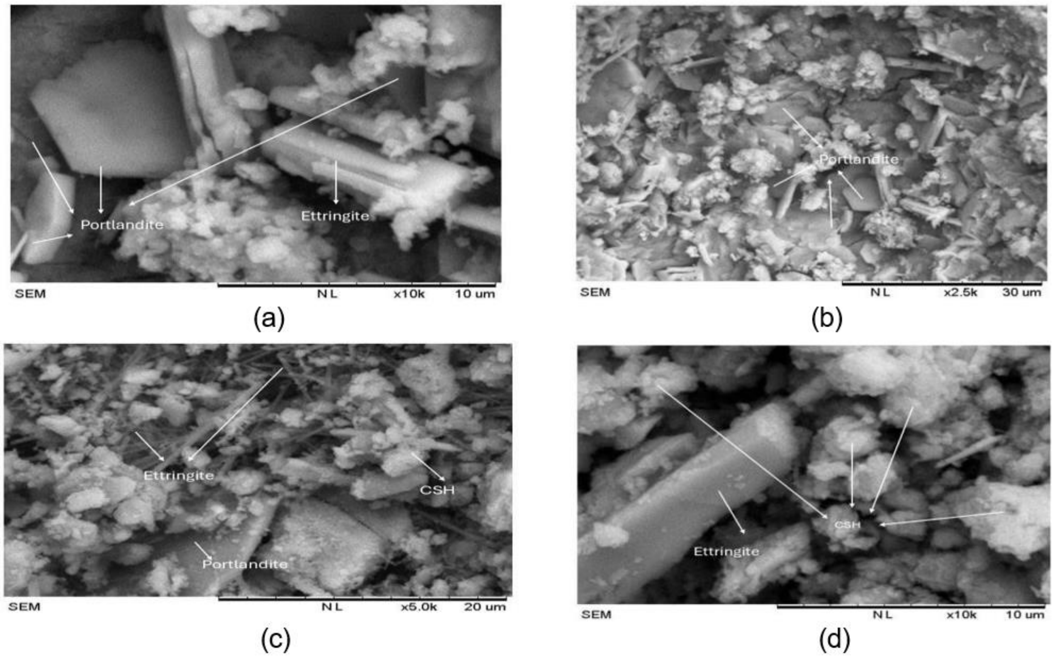


Figure 8 SEM image of the hydration products of the hardened cement paste with PVA (0.016) after immersion in 10% K_2SO_4 for (a) and (b) 30 days and (c) and (d) 90 days.

Acknowledgement
The authors would like to acknowledge all individuals who have supported this research especially the Department of Chemistry and Department of Physics, Faculty of Science, Universiti Teknologi Malaysia for providing laboratory facilities and technical assistance. Only one analysis for this project was supported under research project Matching Grant UTM-UI with cost centre of Q.J130000.3054.04M61 (Reference number: PY/2023/01982).

References

[1] Beaudoin, J., & Odler, I. (2019). Hydration, setting and hardening of Portland cement. In P. C. Hewlett & M. Liska (Eds.), Lea's chemistry of cement and concrete (pp. 157–250). Butterworth-Heinemann.
[2] Mason, T. O., & Lea, F. M. (2024). Cement: Definition, composition, manufacture, history, & facts. Encyclopedia Britannica.
[3] Chintalapudi, K., & Pannem, R. M. R. (2022). Enhanced chemical resistance to sulphuric acid attack by reinforcing graphene oxide in ordinary and Portland pozzolana cement mortars. Case Studies in Construction Materials, 17, Article e01452.
[4] Topič, J., Prošek, Z., Indrová, K., Plachý, T., Nežerka, V., Kopecký, L., & Tesárek, P. (2015). Effect of PVA modification on the properties of cement composites. Acta Polytechnica, 55(1), 64–75.
[5] Ragoug, R., Metalssi, O. O., Barberon, F., Torrenti, J.-M., Roussel, N., Divet, L., & D'Espinose de Lacaillerie, J.-B. (2019). Durability of cement pastes exposed to external sulfate attack and leaching: Physical and chemical aspects. Cement and Concrete Research, 116, 134–145.