

Performance of Sustainable and Low-Carbon Cementitious Composites under Aggressive Environmental Conditions

by Fulin Qu

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DOCTOR OF PHILOSOPHY

under the supervision of
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March 2022

CERTIFICATE OF ORIGINAL AUTHORSHIP

I, *Fulin Qu*, declare that this thesis is submitted in fulfilment of the requirements for the award of Doctor of Philosophy, in the Faculty of Engineering and Information Technology at the University of Technology Sydney.

This thesis is wholly my own work unless otherwise reference or acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

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LIST OF RESEARCH PAPERS

Journal Papers

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- Fulin Qu, Wengui Li*, Wang Kejin, Shishun Zhang, and Sheng Daichao. "Performance deterioration of fly ash/slag-based geopolymer composites subjected to coupled cyclic preloading and sulfuric acid attacks." *Journal of Cleaner Production* (2021): 128942.
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- Fulin Qu, Wengui Li*, Xiaohui Zeng, Zhiyu Luo, Kejin Wang, and Daichao Sheng. "Effect of microlimestone on properties of self-consolidating concrete with manufactured sand and mineral admixture." *Frontiers of Structural and Civil Engineering* (2020): 1-16.
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- Wengui Li, Fulin Qu*, Wenkui Dong, Geetika Mishra, Surendra P. Shah. "A comprehensive review on self-sensing graphene/cementitious composites: A pathway toward future smart concrete", *Construction & Building Materials*, (2022):127284.

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ABSTRACT

Pozzolan materials, like fly ash (FA) and ground granulated blast-furnace slag (GGBFS), are considered promising binder materials as they are industrial by-products, helping to decrease ordinary Portland cement (OPC) demands and further lessen greenhouse emissions. Therefore, the total or partial replacement of pozzolan materials for OPC to fabricate sustainable and low-carbon cementitious composites (LCC) has garnered extensive attention for providing enormous environmental benefits for infrastructure and offshore construction. In addition, the durability of LCC under aggressive environmental deterioration (such as fire, acid, and marine environments) is a progressively significant property for concrete structures due to the increasing demand for extended service life and less maintenance.

For total pozzolan materials replacement for OPC, this work has estimated the performance of fly ash/GGBFS-based geopolymer under combined mechanical loads and aggressive environmental conditions (fire and sulfuric acid attack). For partial pozzolan materials replacement for OPC, this work has also assessed the performance of cementitious composites with GGBFS under the marine environment. The synergistic effects of seawater and undesalted sea sand on the properties of cementitious composites have been firstly analyzed. And then, the fire resistance of GGBFS-based cementitious composites with seawater and undesalted sea sand has been examined. Finally, the chloride-binding capacity of GGBFS-based cementitious composites in seawater and chloride solutions has also been observed.

The results showed that fly ash/GGBFS-based geopolymer with 20 wt.% GGBFS could be regarded as a remarkable alternative for OPC to achieve extraordinary fire resistance by considering the strength and compatibility variations. The fly ash/GGBFS-based geopolymer with cyclic preloading was also confirmed to exhibit less severe performance deterioration even after 18-month exposure to sulfuric acid attacks. In addition, the results illustrated that the chloride, sulphate, and magnesium ions in

seawater and/or undesalted sea sand were assessed to lead to the phase changes of cementitious composites, including the formation of Friedel's/Kuzel's salts, magnesium hydroxide, and magnesium silicate hydrate, etc. The addition of 30 wt.% GGBFS and 1.0 wt.% glass fibers was also supposed to improve cementitious the fire resistance of cementitious composite with seawater and undesalted sea sand. Additionally, the cementitious composite with 30 wt.% GGBFS and 1.0 wt.% NS having the highest value of chloride-binding ratio was expected to enhance the long-term chloride-binding capacity.

Overall, this thesis improves the current understanding of the performance of low-carbon cementitious composites under aggressive environmental environments to produce more reliable data and ensure the reliability and sustainability of LCC-based construction.

CHAPTER 1: INTRODUCTION

1.1 Background

An increase in urbanization demands the growth of infrastructure, which in turn increases the production of the most widely used binder – ordinary Portland cement (OPC). Over 3 billion tonnes of OPC were produced in 2012, and the global demands for OPC are expected to grow due to the rapid infrastructural development of emerging economies (Ashish 2019). The production of OPC contributes to about 8–9% of the global greenhouse emissions and 2–3% energy use (Nedunuri et al. 2020). Improving the sustainable development of the cement industry by decreasing the number of greenhouse emissions and energy used is a significant and enduring challenge. To curtail these emissions, residues (having cementitious potential) generated by various industries are used either as a supplementary or as an alternative cementitious material. Pozzolanic materials, like fly ash (FA) and ground granulated blast-furnace slag (GGBFS), are recognized as promising binder materials due to environmental benefits as they are by-products from other industries and can help reduce the demand for OPC, and in turn, reduce CO₂ emissions. Therefore, the binding materials with partial or total pozzolanic materials replacement for OPC to cast sustainable and low-carbon cementitious composites (LCC) have attracted much more interest from researchers and experts.

For one thing, the cementitious composite made with partial pozzolanic materials replacement for OPC was reported to have prolonged the setting time, improved the concrete rheology refined the porosity, and led to satisfactory compressive strength (Yun et al. 2020). For example, the partial substitution of OPC with GGBFS has been reported to enhance the mechanical properties and improve the durability of cementitious composites (Nedunuri et al. 2020). Regarding its pozzolanic reactivity, the GGBFS shows a satisfactory pozzolanic reaction, absorbing Portlandite (CH) to react with sulphate and reducing the amount of gypsum. The resultant GGBFS concrete is denser and has more excellent sulphate resistance due to calcium silica hydrated (C-S-H) gels formation through a pozzolanic

reaction (Nedunuri et al. 2020). For another, pozzolanic materials, like FA or GGBFS, can be one of the geopolymer materials, which is also considered as an alternative sustainable used to replace OPC in the concrete production fully. Geopolymer materials, entirely made with industrial by-products (FA and/or GGBFS), are activated by calcium aluminosilicate in an alkali source (Zhang et al. 2017). Some previous researches have confirmed that geopolymers perform better than those OPC in certain performances, such as tensile strength, acid resistance, and impact resistance (Aiken et al. 2018; Bakharev 2005; Zhang et al. 2017). The partial or total replacements of pozzolanic materials for OPC in concrete production are expected to provide an excellent performance of low-carbon cementitious composites.

In addition, the durability of LCC is also an increasingly important property for concrete structures due to the growing demand to have a long service life with minimal maintenance (Khan et al. 2019). It is well known that traditional cementitious composites are often subjected to environmental deterioration, such as fire, acid, and marine environments, which leads to severe damage and causes structure degradation or even failure (Khan et al. 2019). The partial substitution of OPC with pozzolanic materials has also been reported to enhance the mechanical properties and improve the durability of cementitious composites by consumption of portlandite through the pozzolanic reaction and pore refinement (Nedunuri et al. 2020). Furthermore, geopolymers, one of LCC, totally prepared with pozzolanic materials and alkaline activators, have also been reported extensively in the past few decades due to the friendly environmental impact and excellent performances, such as high early strength, acid, and alkali resistance (Dai et al. 2020). Although many previous studies contribute to investigating the durability of LCC under different environmental conditions, there are still need more actions to be conducted for considering the specific usage environment.

For a long time, research on the durability of geopolymer was focused on one dominating deteriorating process, such as fire and acid attack (Ismail et al. 2013; Junaid et al. 2017). Service life of cementitious composites is underestimated in many practical applications if only one action is taken into

consideration (Lim et al. 2000a; Pilehvar et al. 2018). In fact, the combined effects of environmental actions and external loads cannot be neglected. The external loading could cause gradual deterioration of concrete usually appears in the form of anomalies, affecting not only the structural performance but also the mechanical behavior, integrity, and permeability characteristics of concrete (Pilehvar et al. 2018). There are a few researchers who carried out relevant experiments to consider coupled environmental deterioration and external loadings for cementitious composites used in concrete infrastructure (Lim et al. 2000a). Besides, cementitious composite-based structures worldwide could be significantly corroded and deteriorate due to the fire and acid attacks, causing considerable economic losses yearly (Bangi & Horiguchi 2012; Dezhampannah et al. 2020; Lu et al. 2020). Therefore, the performance of the sustainable and low-carbon cementitious composites under coupled environmental conditions (fire and acid attack) and external loadings is systematically evaluated in this thesis so as to produce more reliable data.

Meanwhile, with the increase of civil and infrastructure construction in the marine environment, it is necessary to evaluate the durability deterioration of cementitious composites under the marine environment. Various chemical substances in seawater have both beneficial and unfavourable impacts on the performance of cementitious concrete under the marine environment. The primary existence of chloride ions, sulphate ions, and magnesium ions in the seawater can cause complex chemical reactions between cementitious concrete and those solutions. The concentration of specific salt changes with the geographical location, which is incredibly different from the ions in the freshwater taken from rivers. Therefore, the performance of sustainable and low-carbon cementitious composites under the marine environment is evaluated in this thesis so as to ensure reliability and sustainability for marine construction.

1.2 Research objectives and scope

The main objective of this work is to evaluate the performance of LCC under aggressive environmental conditions. The pozzolanic materials, including FA and GGBFS, were used to partially or fully replace the OPC to fabricate the low-carbon cementitious composites. For the cementitious composites with entirely pozzolanic materials replacement, geopolymer, fully made with FA and/or GGBFS and activated with an alkaline solution, were cast. The performance of geopolymer under combined mechanical loads and aggressive environmental conditions has been examined. For the cementitious composites with partial pozzolanic materials replacement, the performance of cementitious composites with partial GGBFS under the marine environment has also been evaluated.

The specific objectives are listed as follows:

- To review the progress in the sustainable and low-carbon cementitious composites under aggressive environmental conditions;
- To examine the elevated temperature resistance of fly ash/GGBFS-based geopolymer after load-induced damage;
- To investigate the sulfuric acid resistance of fly ash/GGBFS-based geopolymer after cyclic preloading;
- To assess the synergistic effects of seawater and undesalted sea sand on the properties of cementitious composites;
- To investigate the thermal performance of GGBFS-based cementitious composites with seawater and undesalted sea sand;
- To evaluate the chloride-binding capacity of GGBFS-based cementitious composites under different salt solutions;

1.3 Research methodology

- ***Progress in low-carbon cementitious composites under aggressive environmental conditions :***

A literature review is conducted to evaluate the necessity of the application of sustainable and low-carbon cementitious composites. Meanwhile, the performance of cementitious composites under different aggressive environmental conditions is also summarized.

- ***High-temperature resistance of fly ash/GGBFS-based geopolymer composites with load-induced damage:*** This work is planned to examine the elevated temperature resistance of fly ash/GGBFS-based geopolymer composites after load-induced damage and to comprehend further the fire attack mechanism coupled with preloading-induced damage. The physical properties of geopolymer mortar, such as volume change, mass change, visual appearance, and residual strength, were tested before and after exposure to different high temperatures. The microstructure alteration before and after load inducing or thermal exposure was evaluated by scanning electron microscope (SEM). The phase change at elevated temperatures was also detected by thermal gravimetric analysis (TGA), X-ray diffraction (XRD), and SEM with energy dispersive X-ray (EDX) analysis.
- ***Performance deterioration of fly ash/GGBFS-based geopolymer composites subjected to combined cyclic preloading and sulfuric acid attack:*** This work is aimed at investigating the sulfuric acid resistance of fly ash/GGBFS-based geopolymer composites after cyclic preloading and exploring the deterioration mechanism of coupled preloading damage and sulfuric acid attack. The testing parameters, including visual appearance, mass change, compressive strength, degradation depth, microstructure, and leaching behavior after exposure to sulfuric acid solutions up to 18 months, were measured. Furthermore, the deterioration mechanism of fly ash/GGBFS-based geopolymer composites with cyclic preloading after exposure to sulfuric acid solutions for up to 18 months is illustrated.

- ***Effects of seawater and undesalted sea sand on the hydration products, mechanical properties, and microstructures of cementitious composites:*** This work is designed to assess the synergistic effects of seawater and undesalted sea sand on the properties of cementitious composites. The influences of seawater and undesalted sea sand on the hydration reaction, mechanical properties, water absorption, and phase change were measured and discussed in detail. This work will provide essential information for investigating the GGBFS-based cementitious composites with seawater and undesalted sea sand subjected to elevated temperatures.
- ***Property degradation of GGBFS-based cementitious composites with seawater and undesalted sea sand subjected to elevated temperatures:*** This work is expected to investigate the effect of GGBFS and glass fiber on the thermal performance of cementitious composites with seawater and sea sand so as to provide a more stable microstructure. The mass loss, visual appearance, compressive and flexural strength were examined in this study. The change of microstructure and hydration products was measured by using various techniques, including XRD, Fourier transforms infrared spectroscopy (FTIR), TGA, and backscatter electrons with energy dispersive X-ray (BSE-EDX).
- ***Chloride-binding capacity of GGBFS-based cementitious composites in seawater and chloride solutions:*** This work is supposed to evaluate the effects of GGBFS and nano-silica (NS) on the chloride-binding capacity of cementitious composites in seawater and chloride solutions. The chloride binding and phase assemblages were analyzed by inductively-coupled plasma mass spectrometry (ICP-MS), TGA, XRD, FTIR, Scanning electron microscopy with energy disperse spectroscopy (SEM-EDX). The phase change of the cementitious composites after exposure to different salt solutions was also predicted based on the GEM-Selektor 3.

1.4 Layout of the thesis

This thesis is presented in eight chapters, and the contents of each chapter are shown as follows:

Chapter 1: This chapter introduces the background, research objectives and scope, and research methodology for this work.

Chapter 2: This chapter contains a literature review on sustainable and low-carbon cementitious composites under aggressive environmental conditions.

Chapter 3: This chapter provides an experimental study on the fire resistances of fly ash/GGBFS-based geopolymer composite after load-induced damage. The physical properties, mechanical strength, and microstructure characterization are analyzed and discussed.

Chapter 4: This chapter presents an experimental study on the sulfuric acid resistance of fly ash/GGBFS-based geopolymer composite under cyclic preloading. The changes in physical properties, mechanical properties, degradation depth, microstructure, and mineralogy were compared and analyzed.

Chapter 5: This chapter conducts an experimental study on the performance of cementitious composites with seawater and undesalted sand. The changes in hydration rate, compressive strength, water sorptivity, leaching behavior, and microstructural characterization were evaluated.

Chapter 6: This chapter carries out an experimental study on the fire resistance of GGBFS-based cementitious composites with seawater and undesalted sea sand. The physical properties, flexural and compressive strength, and microstructure characterization were assessed.

Chapter 7: This chapter illustrates an experimental study on the chloride-binding capacity of GGBFS-based cementitious composites in seawater and chloride solutions. The changes in chemical chloride binding, phase assemblages, and physical chloride binding were tested and discussed.

Chapter 8: This chapter highlights the primary contributions of this work and the recommendations for future research.

CHAPTER 2: LITERATURE REVIEW

The production of ordinary Portland cement is consuming a large number of resources and energy, bringing out considerable greenhouse emissions; thus, the building materials with a low carbon footprint are gaining more and more concerns worldwide. Meanwhile, the durability of cementitious composites is becoming more and more imperative for concrete structures due to the increasing demand for extended service life and less maintenance (Neto et al. 2021). Traditional concrete structures are generally known to be severely damaged when exposed to aggressive environmental deterioration, such as fire, acid, and marine environments (Dezhampanah et al. 2020; Lu et al. 2020). Such conditions shorten its service life and increase its maintenance and renewal expense requirement, which also has an adverse effect on the environment on the basis of greenhouse emissions and conservation of natural resources.

This chapter, therefore, firstly evaluates the development and achievements of the sustainable and low-carbon cementitious composite. Secondly, the effects of fire and acid attacks on the properties of cementitious composite is assessed and research about the performance of cementitious composites under combined environmental conditions and mechanical load is also examined. Finally, the performance of cementitious concrete under marine environment at both the material and structural levels is also reviewed. Overall, this work evaluates the potential of using low-carbon cementitious composites in a specific aggressive environmental condition.

2.1 Sustainable and low-carbon cementitious composites

From infrastructure to national defense construction, ordinary Portland cement is used as the primary cementitious material in concrete, the production of which is also estimated to increase yearly, as shown in Figure 2.1 (Imbabi et al. 2012). However, the OPC industry is generally energy-consuming. Moreover, it has been estimated that OPC production leads to approximately 8–9% of the total global greenhouse emission, engendering ever-increasing concerns about the greenhouse effect. Thus, finding

strategies to decrease the environmental impact associated with OPC production is an urgent task. In the last decades, the search for alternative cementitious materials as OPC replacements has intensified.

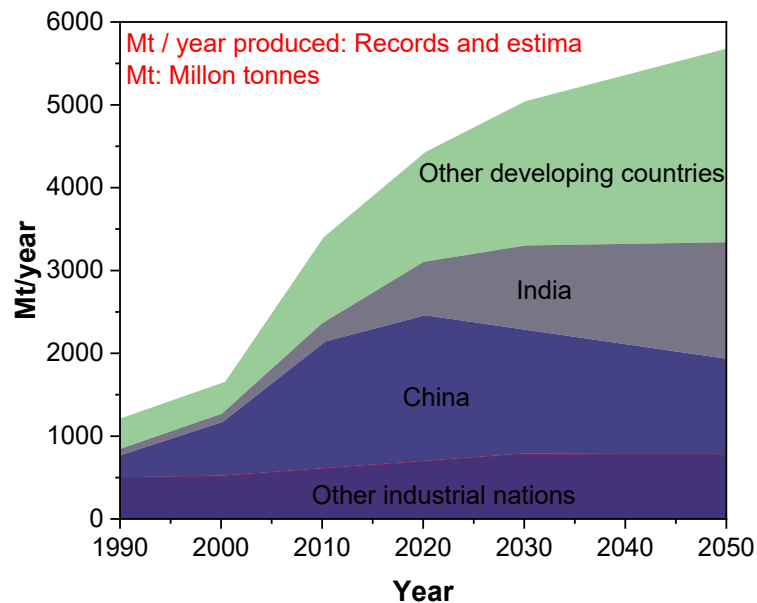


Figure 2.1. Forecasted world Portland cement production 1990–2050 (Imbabi et al. 2012).

One of the most imperative methods is to use pozzolanic materials, such as GGBFS and FA to replace the OPC in concrete production. These industrial by-products are being used as alternatives to OPC because they are served as supplementary cementitious materials (SCMs). Due to the high demands for natural resources to meet growing infrastructure needs, there are enormous opportunities to use industrial by-products to construct low-carbon infrastructure (Rashad & Sadek 2017). The benefits of substituting GGBFS for OPC include improved durability and long-term strength (Özbay et al. 2016). The benefits of using FA for replacing OPC in concrete productions include enhanced compressive strength, bulk density, linear shrinkage, flexural toughness, ductility, and decreased porosity (Hemalatha & Ramaswamy 2017; Xu & Shi 2018). Moreover, the use of GGBFS or FA in concrete was also reported to provide additional environmental benefits, including conservation of natural resources and recycling of industrial by-products (Rahla et al. 2019). As mentioned in some references

(Flower & Sanjayan 2007), the application of GGBFS and FA in concrete can reduce CO₂ emissions by 22% and 14%, respectively.

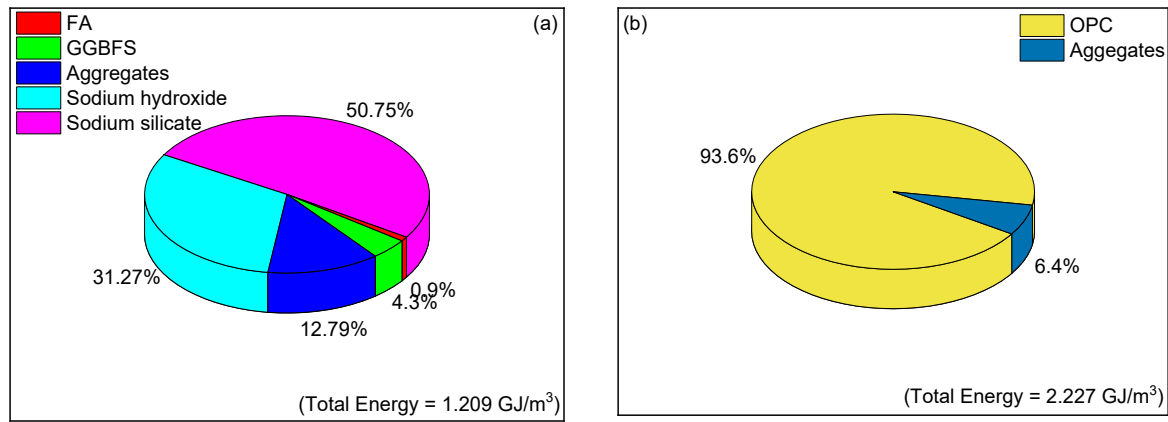


Figure 2.2. Energy of 40 MPa concrete mixtures (a) geopolymer concrete (b) ordinary Portland cement concrete (Alsalman et al. 2021).

Among the candidates, geopolymer or alkali-activated materials have also attracted much attention in the scientific community for the past several decades. This is because most of these materials are industrial byproducts, and they can be effective alternatives to OPC (Pacheco-Torgal et al., 2012a). Geopolymer can be divided into two major categories depending on the calcium (Ca) content of the precursors (Li et al., 2010). Geopolymer with low calcium contents is referred to as geopolymers, which are based on metakaolin (MK) or FA (Gao et al. 2015). Similarly, the representative case for geopolymer with high calcium content is GGBFS. Geopolymer materials, produced by the geopolymerization of alkali activating solutions with aluminosilicate-rich materials, such as FA, GGBFS, and MK, might be used to replace OPC concrete in many different exposure conditions, such as high temperature (Jiang, Xiao, et al. 2020; Jiang, Zhang, et al. 2020) and sulfuric acid environments, and in turn, significantly reduce the emission of CO₂ (Chindaprasirt et al. 2013; Moghaddam et al. 2021; Sturm et al. 2018; Xie, Lin, et al. 2019). As shown in Figures 2.2 and 2.3 (Alsalman et al. 2021), the normal strength geopolymer concrete (40MPa) was reported to show 40% less energy and 73% less greenhouse emission than ordinary Portlandite cement concrete. It is reported by many studies that

geopolymers have excellent properties in fire and acid resistance (Aiken et al. 2018; Ariffin et al. 2013; Mehta & Siddique 2017; Valencia-Saavedra et al. 2020). Ariffin et al. (2013) displayed that after exposure to a 2% sulfuric acid solution up to 18 months, the mass loss of blended ash geopolymer concrete was 8%, compared to 20% of OPC concrete. Similarly, Mehta and Siddique (2017) reported that the mass loss of fly ash-based Geopolymer concrete increased with the increasing OPC substitute for fly ash when exposed to a 2% sulfuric acid solution for one year. Fernández - Jiménez (2008) examined the flexural strength of geopolymers after being exposed to elevated temperatures and discovered that the flexural strength of geopolymers at a temperature of 600 °C displayed 1.2 times than that of geopolymers before being exposed to high temperature.

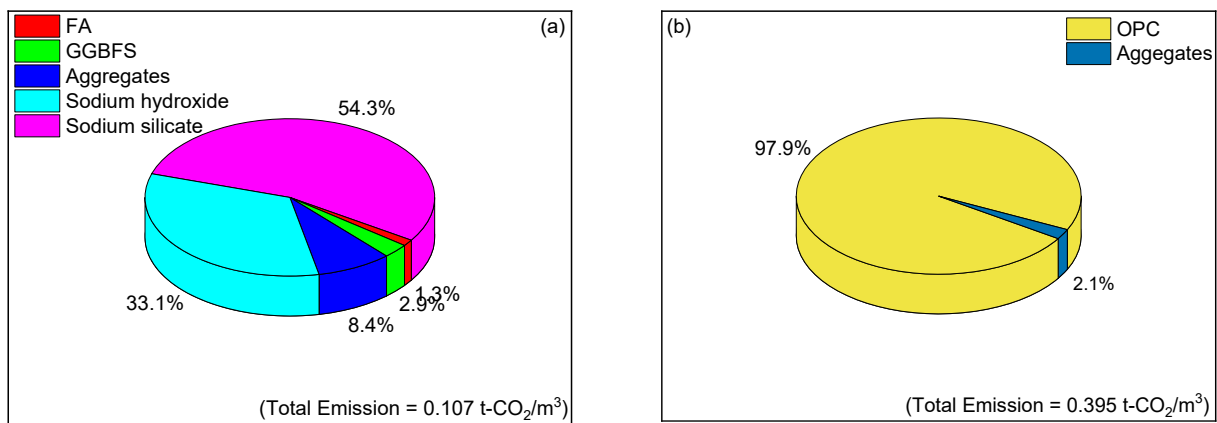


Figure 2.3. Emission of 40 MPa concrete mixtures (a) geopolymer concrete (b) ordinary Portland cement concrete (Alsalman et al. 2021).

2.2 Cementitious composites under fire environment

2.2.1 Properties of cementitious composites at high temperature

Fire or high temperature is an extreme environmental condition to which any building or structure could be exposed during its service life. Fires are known to damage the microstructure and

mesostructure of concrete, which can lead to general mechanical decay of concrete and even adverse effects at the structural level due to concrete spalling and exposure of rebar to flames. Due to the correlation between high temperature and concrete performance in fire environments, the most relevant parameters (including compressive and tensile strength, elastic modulus, stress-strain curve, spalling, etc.) of cementitious composites at high temperature have recently been examined and researched (Carabba et al. 2019; Liu, Xu, et al. 2019; Manjunath et al. 2019; Nguyen et al. 2020).

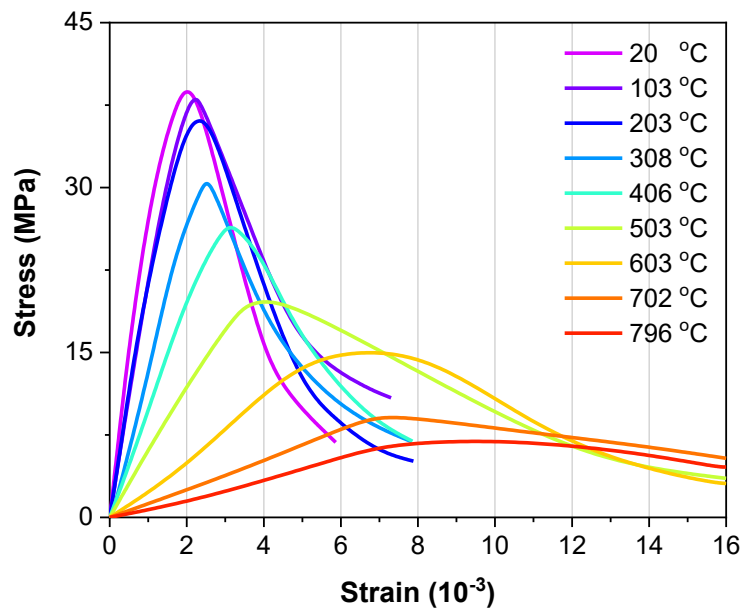


Figure 2.4. Residual stress–strain relationship of concrete exposure to different high temperatures(Chang et al. 2006).

OPC-based concrete could be suffered wide-ranging damage due to physical and chemical changes at high temperatures, leading to severe deterioration of mechanical performances (Carabba et al. 2019; Manjunath et al. 2019; Nguyen et al. 2020). It is inevitable that the mechanical strengths (including compressive strength, flexural strength, splitting tensile strength, and modulus of elasticity) of concrete will decrease with the increasing temperature (Rama Seshu & Pratusha 2013; Yan et al. 2013). As shown in Figure 2.4, It has also been found that with increasing temperature, the stress-strain curve becomes flatter, and the peak stress shifts downward to the right, indicating that the peak stress and elastic modulus of concrete decrease with increasing temperature, but the strain increases at the peak

stress (Chang et al. 2006). Concrete may spall at high temperatures, significantly reducing the mechanical properties of cementitious composite concrete structures and even leading to structural collapse. (Bangi & Horiguchi 2012).

In addition, some researches have also demonstrated that geopolymers have better fire resistance than OPC-based composites as the result of the different thermal evolution of their chemical structure (Sarker & Mcbeath 2015; Zuda et al. 2010). Fernández - Jiménez (2008) examined the flexural strength of geopolymers after being exposed to elevated temperatures and discovered that the flexural strength of geopolymers at a temperature of 600 °C displayed 1.2 times than that of geopolymers before being exposed to high temperature. A comparable result was also reported by Pan et al. (2018), the findings of which illustrate that the compressive strength of fly ash-based geopolymer was increased when the temperature was up to 600 °C. More recently, research on geopolymer-based concrete has further convinced the trend of strength increase after being exposed to high temperatures. Shaikh and Vimonsatit (2015) investigated the compressive strength of fly ash-based geopolymer concrete under the simulated fire environment. They found that at the temperature of 600 °C, fly ash-based geopolymer concrete performed outstanding high-temperature resistance with improved compressive strength of 110% of the compressive strength detected before exposure to a fire environment. The results of XRD and nuclear magnetic resonance showed that the structure of the fly ash-based geopolymer did not change below 600 °C (Dombrowski et al. 2007; Shaikh & Vimonsatit 2015). Vickers et al. (2016) also evaluated the mechanical properties of fly ash-based geopolymers concrete manufactured with alumina aggregate. The fire resistance of fly ash-based geopolymers concrete could be enhanced as the addition of alumina aggregate for its low thermal conductivity.

2.2.2 Physical and chemical changes

With increasing temperature, cementitious composite concrete undergoes some physical and chemical changes, which are believed to be responsible for changes in mechanical properties. The composition of OPC, including aggregate and cement paste, can be affected by the increasing temperature since the

OPC is a heterogeneous building material (Fernandes et al. 2017; Horszczaruk et al. 2017; Zhang et al. 2018). OPC's performance under fire environments lies in its ingredient and the characteristics of its elements. The hydration product of OPC, such as CH, can decompose to form calcium oxide and release water at approximately 400 to 500 °C. Under fire conditions, phase changes, pore pressure changes, and the limited thermal conductivity in OPC could significantly affect the mechanical properties (Khaliq & Mujeeb 2019). When the temperature exceeds 400 °C, the strength is practically lost as the result of the dehydration of CH and rehydration of CaO (Shaikh & Taweel 2015). The strength loss of OPC exceeds 50% when exposure temperatures are up to around 400 to 500 °C due to the dehydroxylation of hydroxide and constant dehydration of calcium silicate hydrate (C-S-H) starting at 105 °C (Zaidi et al. 2012). Some primary changes in microstructure are summarized in the following: Water evaporation (Feldman & Ramachandran 1971): At around 105 °C, the hydration product completely loses its free water and physisorbed water and starts to lose its chemically bound water. At about 300 °C, the hydration degree of unhydrated cement particles can be enhanced due to the evaporation of water and high temperature, creating internal autoclaving conditions. Capillary water is entirely lost when the temperature is up to 400 °C.

Hydration products (Taylor 1997): Around 120 to 150 °C, ettringite/monosulfate (AFt/AFm) can be dehydrated. When the temperature is up to 350 °C, CH is either decomposed into lime and water or further converted into C-S-H due to the accelerated pozzolanic reaction.

Pore structure (Janotka et al. 2000): Elevated temperature increases the porosity and pore size of cement matrices due to water evaporation and chemical changes in hydration products.

Microstructure (Heikal et al. 2013): At temperatures below 200 °C, no obvious microcracks can be examined in the hardened cement matrices or in the interfacial transition zone. When the temperature is raised to 400 °C, microcracks in the cement matrix and interfacial transition zone begin to propagate, the intensity of which is also increased with temperature. As the temperature continues to rise, even reaching above 1000 °C, the porosity and microstructure of the cement matrices are smaller and better

than at lower temperatures because the concrete has already been sintered.

Aggregates (Masse et al. 2002): When the temperature is at approximately 573 °C, the siliceous aggregates can be transformed from phase a to phase b, causing the concrete to expand. When the temperature is over 600 °C, the decomposition of calcareous aggregates, like limestone, can be observed

2.2.3 Test modalities to simulate the fire environment

There are mainly two test modalities to simulate the fire environment, including electrical furnace heating and gas/oil heating (fire). These two different test modalities have been widely employed in the research to examine the fire resistance of cementitious composite concrete. Electrical Furnace heating has been commonly adopted to investigate the thermal properties changes of cementitious concrete, while gas/oil heating has been often used when the experiments are at structural element levels (Ma et al. 2015).

2.3 Cementitious composites under sulfuric acid attack

2.3.1 Manifestations of sulfuric attack

The structures of OPC-based concrete are generally known to be severely damaged when exposed to acidic environments, which shortens its service life and increases its requirement for maintenance and renewal expense (Dezhampanah et al. 2020; Lu et al. 2020). Concrete may contact various types of aggressive chemicals (such as inorganic and organic acids) in multiplied ways (Gutiérrez-Padilla et al. 2010; Yuan et al. 2013). Sulfuric acid is one of the aggressive inorganic acids that could significantly reduce the durability of OPC concrete (Huber et al. 2017; Mahdikhani et al. 2018; Omrane et al. 2017). The formation of the sulfuric acid environment may be related to fertilizer and metal production (Nunes et al. 2014; Tian et al. 2012). Sulfuric acid may also exist in groundwater or be produced by the oxidation of sulfur compounds in the filling, resulting in degradations of the underground OPC concrete structures (Ong et al. 2018). In addition, the sewer networks and wastewater systems across

the world are significantly corroded and deteriorated due to the sulfuric acid attack, causing considerable economic losses every year (Grenng et al. 2018). The generation of sulfuric acid in the sewer network is shown in Figure 2.5 (Wu et al. 2018). Especially, the difficulties in the sewer network present enormous challenges for maintenance and repair (Grenng et al. 2017; Grenng et al. 2018).

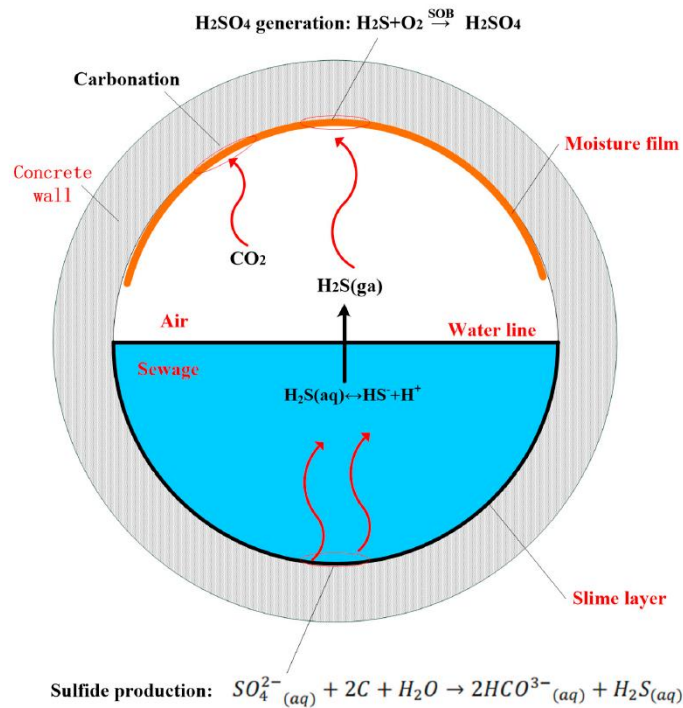


Figure 2.5. The formation of sulfuric acid in the sewer network (Wu et al. 2018).

As is the case with other aggressive chemicals, sulfuric acid can be one of the most harmful to cementitious composites. Some visible examples of damage (including spalling, delamination, macroscopic cracking, and possible loss of cohesion) can be observed caused by the reaction between concrete components and sulfuric acid as the consequences of the physicochemical processes. In sulfuric acid environments, in addition to the dissolution effect caused by hydrogen ion attack, sulfate ion also causes sulfate attack. A typical sulfuric acid attack may be primarily involved in the following physicochemical processes (Biricik et al. 2000; Diamond 1996, 2000; Girardi et al. 2010):

Formation of gypsum (Monteny et al. 2003): The CH and C-S-H gels can be significantly dissolved, leaving a skeleton of silica and gypsum. The formation of gypsum might deplete available calcium

sources, so its formation is related to the secondary consequences by enhancing other sulfate-related phenomena. It is generally accepted that the formations of gypsum have a softening effect, resulting in loss of mass and strength.

Formation of ettringite (Zivica & Bajza 2001, 2002): Sulfate ions that have penetrated into hardened cement matrices can react with calcium aluminate hydrate (C_3A) to form ettringite, which increases the internal pressure, resulting in the formation of cracks. The cracks, in turn, could create a larger surface area for corrosion processes and provide additional sites for acid penetration. Due to its low solubility, AFt can generate at a relatively low sulfate concentration; this is why ettringite-induced swelling is more common than gypsum-generated swelling.

In addition, it should be noted that the existence of AFt can only be detected when the pH exceeds 10.7, while the gypsum can be examined when the pH is below 10.0. It appears that gypsum can be formed exist in surface layers that contribute less to the structure of concrete, while ettringite can form in deeper layers, creating a swelling effect.

2.3.2 Sulfuric attack on the properties of cementitious composites

It is reported by many studies that geopolymers have excellent properties in acid resistance (Aiken et al. 2018; Ariffin et al. 2013; Mehta & Siddique 2017; Valencia-Saavedra et al. 2020). Ariffin et al. (2013) displayed that after exposure to a 2% sulfuric acid solution for up to 18 months, the mass loss of blended ash geopolymer concrete was 8%, compared to 20% of OPC concrete. Similarly, Mehta and Siddique (2017) reported that the mass loss of fly ash-based geopolymer concrete increased with the increasing OPC substitute for fly ash when exposed to a 2% sulfuric acid solution for one year. After exposure to a 5% sulfuric acid solution, the geopolymer mortars had a lower strength loss than OPC mortar, as reported by Aiken et al. (2018). Valencia-Saavedra et al. (2020) also demonstrated that the fly ash-based geopolymer concrete had 20% strength loss after exposure to 1M H_2SO_4 , compared to 55% for OPC concrete.

However, some studies have illustrated that the properties of geopolymer might be affected by a variety of factors such as alkali dosage, proportions of aluminosilicate-rich materials, curing methods, etc. (Djobo et al. 2016; Sata et al. 2012; Thokchom et al. 2009). Thokchom et al. (2009) had illustrated that decreasing the alkali dosage led to a higher strength loss in geopolymer mortars after 24 weeks in sulfuric acid solution. The increasing calcium content could increase the strength loss of bottom ash geopolymer mortar after 120-day immersion in a 3% sulfuric acid solution (Sata et al. 2012). Djobo et al. (2016) had emphasized that after exposure to a 5% H_2SO_4 solution for 180 days, the strength loss of volcanic ash-based geopolymer mortars when cured at 27 °C was 24%, compared to 60% when cured at 80 °C.

2.4 Under combined environmental actions and mechanical load

2.4.1 The method of mechanical loading

Most concrete will be affected by many external factors during service, such as load damage, dry and wet cycles, freeze-thaw cycles, chemical reactions, etc. In particular, load damage significantly influences the essential parameters of the durability of concrete structures, pore structures, and the generation and expansion of micro-cracks. The compressive load is the most frequently preloading on the concrete structures and has a variety of modes of action. For the damage caused by compressive load, the primary research is the influence of a preloading, cyclic compressive load, and continuous compressive load on the durability of concrete (Konin et al. 1998; Lim et al. 2000b; Saito & Ishimori 1995; Samaha & Hover 1992).

One-time preloading: The effect of compressive load on the durability of cementitious concrete is carried out after the preloading and reloading of the concrete specimens. Therefore, the damage of the concrete mainly related to cracks after loading is primarily studied.

Cyclic compressive load: The research on the influence of cyclic compressive load on the durability of concrete is mainly carried out by repeatedly loading-unloading the concrete specimen.

Continuous compressive load: The study of the effect of the above-mentioned compressive load on the durability of concrete, whether it is one-time preloading or cyclic loading, is carried out after the unloading, and then the durability test is carried out after the unloading, and the crack generated or expanded after the unloading is reclosed. This is inconsistent with the fact that the concrete is subjected to continuous compressive loads in actual engineering. Due to the limitations of the tested devices, only a few researchers have studied the durability of concrete under constant compressive loading.

2.4.2 Under combined fire attack and mechanical load

When subjected to fire, structural members might go through several stages: the initial-loading stage, the heating stage as the fire develops, and the cooling stage when the fire is extinguished. After the fire, if the member survives, its residual strength is expected to be evaluated to verify its suitability for continual use. So far, little research has been performed with the aim to solve the complexity involved with combined fire attack and mechanical load. Table 2.1 summarizes the methods of studying different types of concrete and its structures under combined fire attack and mechanical loads.

Galek et al. (2010) have investigated the strain behavior of concrete exposure to combined thermal and mechanical loading, and new experimental results have been presented for monitoring longitudinal and radial strains of uniaxially loaded specimens. Beneberua and Yazdan (2018) have examined a full-scale single-span prestressed concrete bridge under a fire environment and simulated live load. The concrete bridges cannot be well-protected for extreme fire events. Gyu-Yong et al. (2009) subjected the concrete specimens to a 25% of ultimate compressive strength at room temperature and sustained during heating. They found that the concrete specimens were loaded to failure when the target temperature was reached. Wang et al. (2016) focused on the quantitative relationship between the horizontal restraint force and the deformation, cracking mode, and spalling of reinforced concrete in the furnace. Ndoukouo et al. (2011) numerically studied the dynamical behavior of steel beams under combined ISO fire and transversal mechanical loads on the basis of vibration equations that explicitly include temperature dependence.

Table 2.1 The performance of cementitious composites and structures under combined fire attack and mechanical loading

Item	Materials	Fire environment	Types of loading	Primary parameters	Ref.
1	Concrete	400 °C	45% of ultimate compressive strength	The stress-strain results depend on the applying load level.	(Galek et al. 2010)
2	Bridge	Hydrocarbon pool fire	Live load	The nation's concrete bridges with girders are highly vulnerable and unprotected for extreme fire events.	(Beneberu & Yazdani 2018)
3	Concrete	From 20 °C to 700 °C	25% of ultimate compressive strength	The relative compressive strength and elastic modulus values decrease with the increased compressive strength grade.	(Gyu-Yong et al. 2009)
4	Reinforced concrete slabs	from 20 °C to 930 °C	Uni-axial in-plane and out-of-plane loads	The cracking patterns of the three restrained slabs are similar and considerably different from the slab without restraint force.	(Wang et al. 2016)
5	steel beam	ISO fire	Transversal mechanical load	A numerical simulation of the dynamical equation has been carried out to analyze the deflection and bending moment variation.	(Ndoukouo et al. 2011)
6	GFRP concrete slabs	−30 to 60 °C	20% of the ultimate load	The thermo-mechanical behavior of GFRP bars embedded in the concrete slabs is linear elastic.	(Bellakehal et al. 2014)
7	Steel columns	Heating, post-fire	Axial load	The ultimate strength under the interaction of temperature and load is lower than that after fire exposure without the initial load.	(Song et al. 2010)
8	Concrete	Up to 800 °C	0 to 60% load level	When concrete is higher loaded during heating up, the influence of these incompatibilities is not increasing	(Ring et al.)
9	Fiber-reinforced polymeric composites	Single-sided surface heat	Axial displacement control	The thermal moment induced in the column is significantly reduced.	(Liu et al. 2011)

It is noted that only a little of the research reported the performance of concrete under combined fire attack and mechanical loads, as mentioned above. There is also some research related to the modeling of concrete under combined temperature and loading. Bellakehal et al. (2014) presented experimental and analytical investigations on the effective thermo-structural behavior of unidirectional glass fiber reinforced polymer-based (GFRP-based) concrete slabs with various concrete cover thicknesses. Song

et al. (2010) developed a finite element analysis (FEA) model to predict the load-deformation relationships of concrete-filled steel tube (CFST) short columns exposure to a combination of temperature and axial compression. Some researchers developed a two-scale model formulated within the framework of continuum micromechanics, giving access to the elastic properties as a function of temperature and load level, based on experimental results obtained from specimens subjected to combined thermo-mechanical loading. Liu et al. (2011) studied the compressive response of composites under combined fire and compression loading through thermal model.

2.4.3 Under combined sulfuric acid attack and mechanical load

Degradation of cementitious composites exposed to aggressive sulfuric acid environments has been a vital durability issue that affects the life-cycle properties and perverse expenses of essential civil infrastructures (Marchand et al. 2001). In addition to sulfuric acid attack, these cementitious composites-based structures are also simultaneously affected by external loading, likely accelerating the chemical degradation. Under actual in-suit aggressive environmental conditions, damage to cementitious composites-based structures typically occurs due to multiple mechanisms (including chemical, physical, and structural) acting collaboratively probably. Research on the coupling function of mechanical loading and sulfuric acid attack is quietly limited in the literature. As mentioned above, the effect of sulfuric acid attack on the performance is significantly related to the sulfate ions. Therefore, some studies that have previously been done on the combined effects of external sulfate attack coupled with loading action are listed in Table 2.2.

As shown in Table 2.2, Gao, Li, et al. (2012) and Yang and Luo (2012) have investigated the coupling effect of salt solution attack and long-term loading, which is mainly due to the self-weight of marine structures or these structures have to bear loading for a long time, such as the pillars of bridges, baseplates of dams and railway bridges. Their research shows that long-term loading can accelerate the sulfate and chloride attack. Yu et al. (2016) have examined the coupling function of sulfate attack and dynamic flexural loading, and the results indicated that solution concentration and stress

levels are two critical factors that affect the durability of concrete, and dynamic flexural loading make cracking occur early and promote sulfate ion diffusing rate. Schneider and Plasta have investigated the effect of coupling stress and sodium-sulfate solution attack on the deterioration rate of cementitious structures using various experimental methods (Schneider & Piasta 1991). Bassuoni and Nehdi (2009)) have investigated self-consolidating concrete exposed to combined sulfate attack and flexural loading and pointed out that the cyclic environmental conditions could cause cracking in the cement matrices, resulting in direct ingress of the solution into noticeable depths of the self-consolidating concrete. Liu et al. (2012) studied the effect of sulfate attacks on the dynamic performance of concrete columns with the axial strain. Chen et al. (2017) have investigated the damage progress of cementitious structures exposed to coupling effects of salt attacks, drying-wetting cycles, and external flexural loadings. Two different loading regimes (long-term loading and short-term loading), which contain three different stress levels and both tensile and compressive regions, are applied in this test. Gao et al. (2013) have also evaluated the durability of self-compacting concrete with different mixture designs exposed to combined effects of salt attacks (sodium sulfate) and other external cyclic loadings (flexural loading). The results showed that the synergistic effects of combined exposure conditions on the degradation mechanisms of cementitious structures is likely related to the mixture designs.

Table 2.2 The combined effect of sulfate ions and mechanical loading on the performance of cementitious compositions

Item	Materials	Environmental conditions		Types of loading	Primary parameters	Ref.
1	Cement mortar	6.9%	Sodium sulfate	20, 40, and 60% of the ultimate flexural load	The tensile stresses can increase diffusivity by initiating or developing microcracks.	(Gao, Li, et al. 2012)
2	Self-consolidating concrete	5%	sodium sulfate solution	25 and 50% of ultimate flexural strength	The cyclic environmental conditions could cause cracking in the cement matrices.	(Bassuoni & Nehdi 2009)
3	Concrete, fly ash, GGBFS	5%	sodium sulfate	40% ultimate flexural strength	The addition of admixtures could enhance the performance of concrete under external loadings and drying–wetting cycles.	(Gao et al. 2013)
4	Fly ash concrete	Sulfate solution of 10% mass concentration		axial strain rate in the range of 10^{-5} – 10^{-3} s ⁻¹	The peak strain and energy absorption capacity of control and sulfate attacked concrete tend to increase with increasing strain rates.	(Liu et al. 2012)
5	Concrete	3%, 5%	sodium sulfate	According to the relationship between the load applied and the frequency	Sulfate attack initially has a positive effect on concrete performance, but this reverses with time, and significant deterioration can occur in concrete suffered from a long-term sulfate attack.	(Yang & Luo 2012)
6	Concrete, fly ash, GGBFS	A complex solution of 5% by mass of NaCl and 5% by mass of Na ₂ SO ₄		35%, 50% and 70% stress level	Mineral admixtures, such as FA and GGBFS, can improve the resistance of concrete under combined environmental conditions (sulfate-chloride attacks and drying-wetting cycles) and flexural loadings.	(Chen et al. 2017)

2.5. Cementitious composites under marine environment

2.5.1 Description of the marine environment

With its commonality and comparatively low cost, concrete has turned into the most extensively used human-made construction materials worldwide and has become the preferred material for civil and infrastructure construction in the marine environment (Shi et al. 2012). With the increase of offshore structures (including civil and military terminals, offshore airports, offshore wind power stations, sea lighthouses, radar stations, island reefs, and fortifications, etc.), some of which are shown in Figure

2.6 (Manzur et al. 2019; Wan Ibrahim et al. 2020; Wang et al. 2019), it is critical to comprehend the durability deterioration of concrete under marine environment. Concrete exposed to marine environment is vulnerable to a variety of physical and chemical degradation procedures (Glasser et al. 2008). For example, the chemical action of seawater composition on the hydration products of cement and crystallization pressure of salts within concrete if one side of the structure is affected by moisture and dry conditions, corrosion of embedded steel in reinforced or prestressed members, and physical erosion as a result of wave action and floating objects (de Medeiros-Junior et al. 2015). Therefore, it is necessary to study the behaviour of cementitious concrete and reinforced concrete (RC) under different seawater exposure conditions to evaluate seawater degradation of buildings working in the marine environment.

Various chemical substances in seawater have both beneficial and unfavourable impact on the performance of cementitious concrete under marine environment. The primary existence of chloride ions, sulphate ions and magnesium ions in the seawater can cause complex chemical reactions between cementitious concrete and those solutions (el Mahdi Safhi et al. 2019; Islam et al. 2012; Ragab et al. 2016; Wegian 2010). The average content of dissolved salt in seawater is about 35 g/L (ASTM 2008); however, the concentration of specific salt changes with the geographical location, which is especially different from the ions in the freshwater taken from rivers. Therefore, the ions in the seawater have a chemical attack in all the exposed cementitious concrete. Chlorides are able to be incorporated in calcium chloroaluminate hydrates such as Friedel's salts or Kuzel's salts, which can be attached to calcium silicate hydrate (C-S-H) and preserved in the pore solutions. Moreover, cementitious concrete in contact with seawater is corroded by sulphate, which can also cause deterioration to the structures (Eglinton 1998). The higher content of magnesium ions in seawater cannot be saturated in seawater to form brucite ($\text{Mg}(\text{OH})_2$) because the pH of seawater is low. However, when seawater encounters high pH value, such as in one of the porous solutions (pH of 12.5-13.5) of typical concrete, brucite precipitates (Buenfeld & Newman 1986).



Figure 2.6. Types of concrete structures under marine environment (Manzur et al. 2019; Wan Ibrahim et al. 2020; Wang et al. 2019): (a) Docks, Ireland, UK; (b) Longest sea bridge, connecting mainland China to Hong Kong and Macau; (c) Wharf, Victoria, Australia; (d) Gigantic Troll field, Norway

In addition, for the reinforced concrete, when the concentration of chloride in the RC reaches a certain threshold value, the chloride ion is absorbed on the surface layer of the steel bar, which accelerates the corrosion rate. In the case of sufficient oxygen and moisture, steel rebar starts to corrode with the existence of chloride ions (Hussain & Ishida 2010). As the corrosion occurrence, the extension volume of the corrosion product can be as high as two to six times of the original steel volume, which produces an increasing expansive pressure on the interfaces among concrete and reinforcements. Afterward, tensile stress loss leads to surface cracking, delamination, spalling of concrete, a decrease of the transverse-sectional area of reinforcement, and loss of the bond between the concrete and steel reinforcement (Hussain & Ishida 2010). In construction industries, different corrosion protection and maintenance methods of RC are usually adopted when being in the marine environment. One of the most typical methods is the addition of mineral admixtures in cementitious concrete, which can

facilitate the enhanced performance of the concrete and RC, such as strength, durability, and bio-deterioration resistance through a pozzolanic reaction (Dong et al. 2019; Saha 2018; Vanesa et al. 2018; Yan et al. 2018). The cementitious concrete and reinforced concrete structures, used in marine projects, usually need to be added by some supplementary materials to improve its performance.

2.5.2 Deterioration mechanism of concrete and reinforced concrete structure

The service lifespan of concrete in the marine environment depends on the interaction of change of its physical characteristics and chemical reaction mechanisms (el Mahdi Safhi et al. 2019). It is well recognized that deterioration of concrete composites and construction under marine environment is principally controlled by permeability performance of concrete, which might be related to the different exposure marine environments and chemical reactions. Multiple chemicals in seawater possess a beneficial or secondary action on the characteristic of concrete in seawater environments, which has also been studied. Table 2.3 presents the chemical concentrations in seawater as specified by ASTM D1141-98 (Standard Practice for the Preparation of Substitute Ocean Water) (ASTM 2008). It can be seen that the main chemical compositions contain KCl, $MgCl_2$, Na_2SO_4 , $CaCl_2$, and NaCl and so on. In particular, chloride ions in seawater corrode steel bars most seriously. The effect of $NaHCO_3$ and KBr is not discussed in this paper for its low content in seawater. In addition, the deterioration mechanism of different exposure marine environments on cementitious concrete is discussed. The effect of marine environments on the properties of cementitious concrete is mainly caused by the different salts with high concentrations, whose effects will be further discussed in the next subsection.

Effect of chloride salts on cementitious concrete

As can be seen from Table 2.3 (ASTM 2008), the chloride ions from seawater environment are mainly originated from sodium chloride (NaCl), magnesium chloride ($MgCl_2$), calcium chloride ($CaCl_2$) and potassium chloride (KCl). Chloride ions can permeate into cementitious concrete exposed to chloride salt solutions through diffusion, wicking and absorption processes. In the procedure of chloride ions'

migration, a specific proportion of chloride ions is bound by the cement matrix, and some free chloride ions are left in the pore solution (Justnes 1998). Fundamentally, chloride ions can trap in C-S-H. Meanwhile, chloride ions from NaCl, MgCl₂, CaCl₂, KCl can react with calcium aluminate (C₃A) and monosulfoaluminate (AFm) to form Friedel's salt (Ca₄Al₂(OH)₁₂Cl₂·4H₂O) (Birnin-Yauri & Glasser 1998; Rocha et al. 2015) and Kuzel's salt (Ca₄Al₂(OH)₁₂Cl(SO₄)_{0.5}·5H₂O) (Mesbah et al. 2011; Rocha et al. 2015).

Table 2.3 Main chemical composition of seawater (ASTM 2008)*

Chemical	NaCl	MgCl ₂	Na ₂ SO ₄	CaCl ₂	KCl	NaHCO ₃	KBr
Concentration (g/L)	24.53	5.20	4.09	1.16	0.695	0.201	0.101

*Chemicals at concentrations below 0.1 g/L are not included in Table 2.3.

Concrete exposed to NaCl or KCl solutions usually changes its microstructure owing to various chemical reactions, such as the formation of Friedel's salts (Rao D 2012; Tinnea & Young 2000). Suryavanshi et al. (1996) revealed that in the existence of sodium chloride solution, Friedel's salt was formed through two independent mechanisms: adsorption and anion-exchange mechanism. Farnam et al. (2016) confirmed that with the coexistence of NaCl and calcium sulfoaluminate phases in the cement matrix, there is an additional chemical phase transition to Friedel's salt. Jiang et al. (2012) studied the effect of KCl as a chloride source on steel reinforcement corrosion. The decalcification from Portlandite and C-S-H is a reaction in slow processes. The leaching of calcium leads to the increase of porosity and larger pores. In the existence of NaCl or KCl, Friedel's salt is constituted from a calcium aluminate hydrate and a soluble chloride origin after Eq. (2-1) and Eq. (2-3), or Eq. (2-2) and Eq. (2-4), as shown in Table 2.4.

Table 2.4 Formation of Friedel's salt and Kuzel's salt

Num.	Salt	Equations	References
2-1	NaCl	$2NaCl(aq) + 3CaO \cdot Al_2O_3 \cdot 6H_2O(s) + Ca(OH)_2(s) + 4H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 10H_2O(s) + 2NaOH(aq)$	(Suryavanshi et al. 1996)
2-2		$2NaCl(aq) + 3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O(s) \rightarrow 3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 10H_2O(s) + 2Na_2SO_4(aq) + 2H_2O$	
2-3	KCl	$2KCl(aq) + 3CaO \cdot Al_2O_3 \cdot 6H_2O(s) + Ca(OH)_2(s) + 4H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 10H_2O(s) + 2KOH(aq)$	(Jiang et al. 2012)
2-4		$2KCl(aq) + 3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O(s) \rightarrow 3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 10H_2O(s) + 2K_2SO_4(aq) + 2H_2O$	
2-5		$Ca(OH)_2(s) + MgCl_2(aq) \rightarrow Mg(OH)_2(s) + CaCl_2(aq)$	(Bilinski et al. 1984;
2-6	MgCl ₂	$(3or5)Ca(OH)_2(s) + MgCl_2(aq) \cdot H_2O \rightarrow (3or5)Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O(s)$	Dehua & Chuanmei
2-7		$3Ca(OH)_2(s) + CaCl_2(aq) + 12H_2O \rightarrow 3Ca(OH)_2 \cdot CaCl_2 \cdot 12H_2O(s)$	1996)
2-8	CaCl ₂	$3Ca(OH)_2(s) + CaCl_2(aq) + 12H_2O \rightarrow 3Ca(OH)_2 \cdot CaCl_2 \cdot 12H_2O(s)2$	(Shi 2001)
2-9		$CaCl_2(aq) + 3CaO \cdot Al_2O_3 \cdot 6H_2O + 12H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 10H_2O(s)$	
2-10	Na ₂ SO ₄	$2Na_2SO_4(aq) + Ca(OH)_2(s) + H_2O \rightarrow 2NaOH(aq) + CaSO_4 \cdot 2H_2O(s)$	(Bellmann et al.
2-11		$3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O(s) \rightarrow 2CaSO_4(aq) + 20H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O(s)$	2006; Ogawa et al. 2012)

Cementitious concrete exposed to MgCl_2 solution usually changes its microstructure owing to chemical reactions, including the formation of $\text{Mg}(\text{OH})_2$, Friedel's salts, magnesium silicate hydrate (M-S-H), magnesium oxychloride, and/or calcium subordinate oxychloride; these changes may be followed by critical ruptures (Bilinski et al. 1984; Dehua & Chuanmei 1996). Peterson et al. (2013) reported the formation of $\text{Ca}(\text{OH})_2$ and related ripping through cementitious concrete under the solution of MgCl_2 exposure. Farnam et al. (2015) showed that the conformation of calcium oxychloride follows the phase diagram of $\text{Ca}(\text{OH})_2\text{--CaCl}_2\text{--H}_2\text{O}$, which results in the deterioration in cementitious concrete under chloride ion and magnesium ion environments. MgCl_2 can react with Portlandite in cementitious concrete to generate $\text{Mg}(\text{OH})_2$ and CaCl_2 , as displayed in Eq. (2-5). When $\text{Mg}(\text{OH})_2$ and MgCl_2 exist together in the ternary system on account of the $\text{Mg}(\text{OH})_2\text{--MgCl}_2\text{--H}_2\text{O}$, magnesium oxychloride ($3\text{Mg}(\text{OH})_2\cdot\text{MgCl}_2\cdot 8\text{H}_2\text{O}$ and $5\text{Mg}(\text{OH})_2\cdot\text{MgCl}_2\cdot 8\text{H}_2\text{O}$) are formed as shown in Eq. (2-6). As shown in Eq. (2-5), if $\text{Ca}(\text{OH})_2$ is left in the matrix, CaCl_2 created as Eq. (2-5) results in the formation of calcium oxychloride. Sutter et al. (2006) reported that calcium oxychloride was formed in detected specimens under the MgCl_2 solution owing to the reaction between calcium hydroxide and calcium chloride. In some cases, calcium ions can be substituted by the magnesium ions resulting in the transformation from C-S-H to M-S-H (Bernard et al. 2017). M-S-H can only be stabilized at a low pH range (7.5–11.5), while C-S-H can be stabilized in a pH range (10–12.5), which is mainly determined by the molar ratio of Ca/Si for C-S-H (Bernard et al. 2017).

Cementitious concrete under CaCl_2 solutions exposure shows different phases, resulting in deterioration during a reversely short time. Concrete exposed to CaCl_2 solutions showed significant damage due to the formation of calcium oxychloride (Chatterji 1978). The deterioration mechanism of calcium oxychloride on the cementitious concrete has also gained attention (Qiao et al. 2019). The phase diagrams of both $\text{Ca}(\text{OH})_2\text{--CaCl}_2$ solution systems (Qiao et al. 2017; Shi 2001) and cement paste- CaCl_2 solution systems have been established. Concrete exposed to CaCl_2 solutions showed significant damage, which is because the formation of calcium oxychloride is able to react with calcium hydroxide

(Ca(OH)₂) to form CaCl₂, as shown in Eq. (2-8). Additionally, Friedel's salt is formed from calcium aluminate hydrate and the source of CaCl₂ after Eq. (2-9). All the equations of Friedel's salt and Kuzel's salt are shown in Table 2.4.

Effect of sulphate salts on cementitious concrete

From the view of the chemical attack, the deterioration of concrete made with ordinary Portland cement (OPC) is partly or principally because of the existence of Portlandite (CH), which is the hydration product most susceptible to sulphate attack (Ogawa et al. 2012). The sulphate ions from seawater environments are mainly from Na₂SO₄. Bellmann et al. (2006) examined the impact of sulphate on gypsum conformation of mortar immersed in Na₂SO₄ solutions of different concentrations. Ogawa et al. (2011) determined the performance of ordinary and mixed types of cement under the attack of 10% Na₂SO₄ through the loss of compressive strength of cubic specimens. When the external sulphate ions (Na₂SO₄) enters the porous cement and interacts with the hydration products of cement, the attack of external sulphate in the seawater environment will continue. Portlandite (Ca(OH)₂) can absorb sulphate ion and become gypsum (CaSO₄·2H₂O), as shown in Eq. (2-10). The combination of monosulphate (3CaO·Al₂O₃·CaSO₄·12H₂O) and external sulphate forms ettringite (3CaO·Al₂O₃·3CaSO₄·32H₂O), as shown in Eq. (2-11). Both these products i.e. gypsum and ettringite occupy a greater volume after crystallization in the pores of concrete than the compounds they replace.

The growth of pressure with the increasing ettringite crystals results in surface cracking known as the softening type of crack. Gypsum formed as a result of cation exchange reactions can also lead to expansion. It is reported that the process of metamorphism of silicate cement paste hardening due to gypsum formation results in a reduction in stiffness and strength, followed by expansion, cracking, and ultimately the transformation of the material into a paste or non-cohesive material. Thus, the sulfate attack in seawater is associated with a progressive loss of strength and loss of mass of structural concrete. Sulfate constitutes the second not characterized by expansion caused due to a large amount of ettringite formed as a result of sulfate attack. According to Nehdi et al. (2005), concrete attacked by

sulfates has a characteristic whitish appearance. The damage was initially found at the edges and corners of the structure, followed by the gradual cracking and peeling of the concrete.

Effect of seawater on reinforced concrete

When RC is exposed to marine environment, many elements (sulphate, carbon dioxide, chloride, silicate, oxygen, water) participate in chemical reactions in different ways; there are various reactions that contribute to the corrosion process (Castaneda et al. 2018). Corrosion starts by attacking the preventive layer on steel bars; after the destruction of that layer, concrete becomes highly reactive or ionize for the electrochemical corrosion process (Cairns et al. 2008). Corrosion is not constant at all over reinforcement because at different cross-section and environmental condition (ionic behaviour, water, oxygen salts, etc.), ions concentrations are different, which make the different intensity of corrosion at different places (Ahmad 2003). Because of chemical and salts reactions, anions and cations are formed at a different portion of the RC system, which makes a full circuit for electrical current supply from one end to another (cathode and anode end). Due to the difference in ions (anode and cathode), salts react in the presence of oxygen and creates a heterogeneous environment and water solution, which acts as an electrolyte and starts an electrochemical process (Zaki et al. 2015). Figure 2.7 demonstrates the fundamental reaction mechanism of corrosion activities.

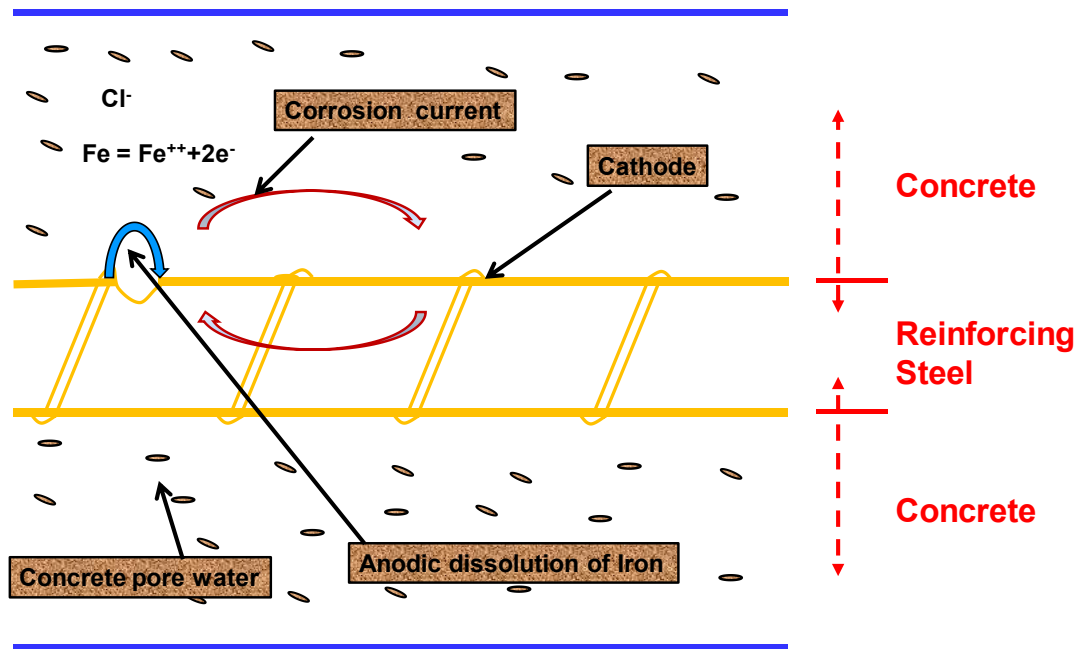


Figure 2.7. Chloride induced corrosion mechanism surrounding zone of reinforcement (Imam et al. 2012)

Dispersion of passive film embedded over the reinforcement and occurrence of corrosion reaction occurs due to two reasons: chloride salt or carbonation (or combination of both processes) (Zaki et al. 2015). Chloride salt also participates in corrosion reactions. Typically, it reacts with cement to form calcium chloro-aluminates and calcium chloro-ferrites. However, chloride-hydroxides ($[\text{Cl}^-]/[\text{OH}^-]$) ratio reduces and causes the devastation of the negative protective film, and initiation of corrosion occurs. After this, either chloride makes threshold concentration or pH solution reduces steel with the carbonation process (Zaki et al. 2015). In the case of carbonation, carbon-dioxide (CO_2) reacts with water present in pores because of the ingress of moisture from the atmosphere or soil. It decreases the pH of concrete from 13.5 to around 9 (Femi 2014).

Effect of marine exposure zones on reinforced concrete structures

The RC structures under marine environment are mainly exposed to three different environments, including atmospheric, tidal, and submerged zone. Different exposure conditions under marine environment are shown in Figure 2.8 (Standard 2000). The primary transport processes under marine

environment are usually included by the following parts: capillary absorption, permeation, ionic diffusion, migration, and convection, etc. (Ross et al. 2016). In the atmospheric zone, structures are exposed to airborne chloride. The steel reinforcement corrosion, mainly caused by chloride, maybe a deterioration mechanism of this condition (Angst et al. 2009). Furthermore, the RC structures can withstand deterioration due to carbonization, which may be related to other factors, including relative humidity or changing of temperature. However, corrosion caused by chloride is the main degradation mechanism compared with deterioration corrosion caused by carbonization (Safehian & Ramezaniapour 2013). As for the transport mechanism, both gas and water vapor diffusion can occur under such exposure conditions. In addition, absorption is one of the most common transport mechanism under atmospheric conditions, as rain occurs, resulting in alternate wetting and drying. Meanwhile, the RC structures may undergo physical degradation due to salt crystallization.

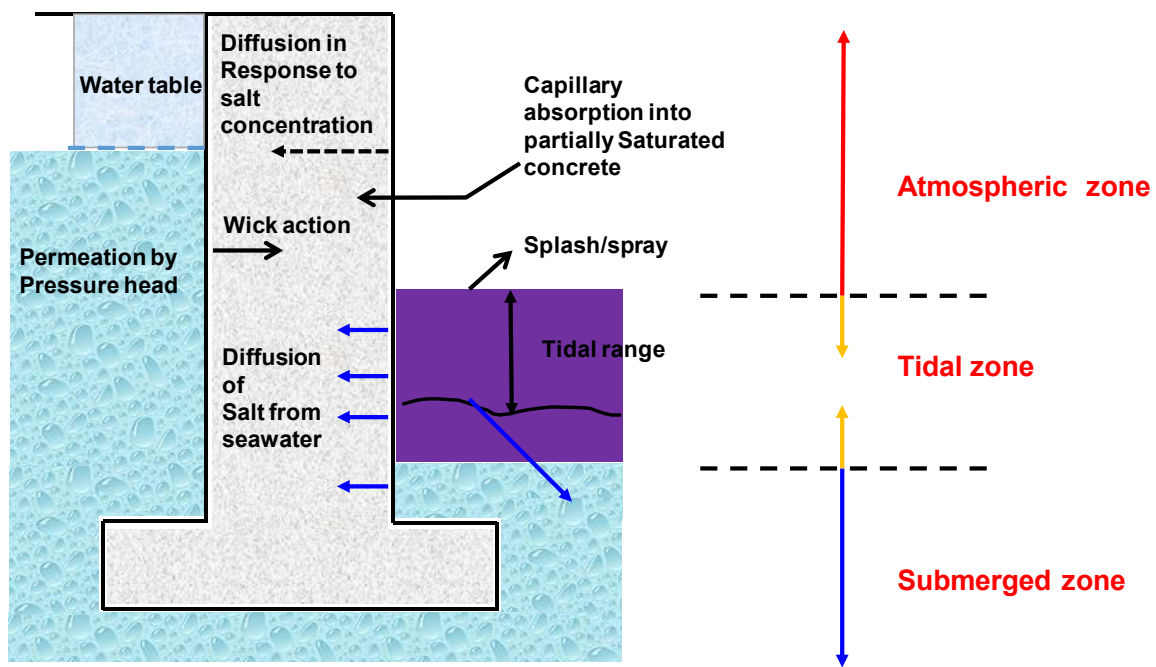


Figure 2.8. Different exposure conditions under marine environment (Standard 2000)

RC structures exposed to the tidal zone are generally considered in the worst state of deterioration (Wu et al. 2017). The aggressiveness of the tidal exposure zone should be characterized, taking into account other factors, including climatic conditions, spatial variability, and frequency of the high and low tides.

All mechanisms, such as diffusion, absorption, core-absorption, and osmosis, play an indispensable part in the transport of invasive kinds in the region. In addition, the mechanical action of waves may lead to visible wear. The deterioration caused by such wear can interact with the wetting-drying cycle resulting in salt crystallization. As for the cementitious concrete and RC structures wholly immersed in the seawater (submerged zone), no absorption occurs compared to the most common transport mechanism in atmospheric and tidal conditions. However, the permeability of the concrete is more important than in other conditions, resulting in the fact that the characteristics of diffusion can be a significant role (Bamforth & Price 1993; Dhir et al. 1996; Mohammed et al. 2002). Therefore, in this exposure condition, it is increasingly significant to evaluate the permeability of cementitious concrete and reinforced concrete structures than that of strength. Cementitious concrete may mainly deteriorate as a result of individual and combined chemical deterioration procedures such as sulphate erosion or leaching and deterioration by chloride, etc., which has already been discussed in detail in the above subsections. In addition, corrosion of steel has been reported to progress at different rates in the tidal and atmospheric marine environments, with very little corrosion activity being reported in the submerged zone.

2.5.3 Marine environment on the macro-scale properties of concrete

The effect of marine/seawater environments on cementitious concrete is mainly manifested in the mechanical properties, durability, and microstructural characteristics. This section presents the compressive strength, durability including chloride permeability and carbonization of concrete under marine environment. The microstructure and pore structure changes of cementitious concrete under marine environment are also discussed. In addition, the performance of concrete exposed to marine environment with mineral admixtures was also compared.

Compressive strength

Compressive strength of cementitious concrete can be significantly influenced by marine environment.

It is well known that concrete performance is associated with the characteristic of raw material, including cement types (Hossain 2008) and aggregate (Yue et al. 2013). In addition, investigations have also been concerned with the beneficial impact of mineral admixtures on the performance of cementitious concrete under marine environments, mainly including fly ash (FA) (Ramachandran et al. 2017; Ramachandran et al. 2016), pulverised fuel ash (PFA) (Bai et al. 2003), bark ash (BA) (Chalee et al. 2013), metakaolin (MK) (Bosc et al. 1993), ground granulated blast furnace slag (GGBFS) (Jau & Tsay 1998), silica fume (SF) (Duan et al. 2015), and also pumice (Hossain 2008), etc. Table 2.6 summarizes the compressive strength of cementitious concrete under marine environment.

As shown in Table 2.6, Hossain (2008) observed the compressive strength of concrete cast with distinct ordinary cement (ASTM Types I, II, and V). Among them, Type I has the highest content of C_3A , while Type V has the lowest content of C_3A . After the cement replaced by the pumice used in casting concrete, it was noticed that the strength of concrete with Type I and Type II cement enhances with the addition of pumice content, with a maximum of about 20%, while the strength of concrete with Type V cement decreases with the increase of pumice under marine environment. Yue et al. (2013) examined the compressive strength of recycled aggregate concrete in seawater corrosion for 16 months, which indicated that with the enhancing of substitution rate and corrosion period, seawater had a considerable impact on the mechanical strength of recycled aggregate concrete.

Table 2.6 Effects of compressive strength of cementitious concrete under marine environment

Item	Replacements	Exposure conditions	Age (years)	Important notes	References
1	MK	Seawater	0.5	1) The compressive strength of concrete decreases in seawater 2) The defect in strength was pretty smaller for the specimens with MK	(Bosc et al. 1993)
2	PFA, MK	Synthetic seawater	1.8	1) MK greatly reduced the strength retardation of the specimens exposed to seawater environment 2) Both PC-PFA) and OPC-ML-PFA blends cause significant improvement in compressive strength	(Bai et al. 2003)
3	GGBFS, Type I, II, V cement	Tidal environment	20	1) The exact mechanism is related to the increase of the compressive strength in the early stage of exposure 2) The decrease of the compressive strength in the middle stage 3) The stability of the compressive strength in the later stage of exposure	(Mohammed et al. 2004)
4	GGBFS	Artificial seawater	1	1) After accelerated test, the compressive strength of OPC concrete without GGBFS began to decline 2) The strength for GGBFS concrete continued to increase	(Jau & Tsay 1998)
5	SF,GGBFS,MK	Synthetic seawater	1	The strength of the concrete with pozzolanic mixtures was higher than that of the specimens with only OPC	(Seleem et al. 2010)
6	Pumice, Type I, II, V cement	Seawater	1	The minimum compressive strength development was found in concrete mixed with sea condition	(Hossain 2008)
7	BA	Tidal environment	5	No compressive strength loss was found in concrete made with BA.	(Chalee et al. 2013)

8	GGBFS, SF, MK	Artificial seawater	0.5	The compressive strength of the concrete can be increased by adding the mineral admixture regardless of curing environment	(Duan et al. 2015)
9	FA, superplasticizer	Seawater	1	1) The compressive of FA concrete decreased in the early stage 2) Increased significantly by the end of one year even when exposed to seawater	(Ramachandran et al. 2017)
10	Recycled aggregate	Seawater	1	When the replacement rate and corrosion time increase, seawater has a significant effect on the compressive of recycled aggregate	(Yue et al. 2013)

When mineral admixtures are applied as partial substitutes for cement, the strength reduction of cementitious concrete under seawater exposure conditions can be reduced. Bose et al. (1993) prepared different mortars immersed in seawater, replacing 0% and 30% of OPC with MK, and found that the specimens exposed to seawater displayed reduced strength, but the delay in compressive strength was smaller for the mortars with MK. Jau et al. (1998) used GGBFS to replace OPC for up to 50% by weight to make GGBFS-OPC concrete, which has experienced wetting-drying cycles accelerated test for over one year under seawater corrosion. The compressive strength of concrete without GGBFS began to drop after half-year exposure, while the compressive strength for GGBFS concrete kept on increasing with time. Duan et al. (2015) examined the effects of pozzolanic materials, including GGBFS, SF, and MK, on the compressive strength in a seawater condition for up to half-year exposure, and concluded that with the supplement of GGBFS, SF and MK, the strength of concrete would progressively increase without considering exposure conditions. Chalee et al. (2013) utilized BA as a mineral admixture to be a substitute for OPC after 5-year marine conditions exposure, and found that there was no strength loss for the BA concrete in the marine environment. Hence, the seawater had a little influence on the strength reduction of the concrete containing BA.

Some studies also examined the concrete properties by replacing OPC with binary or ternary mineral admixtures blends under marine environments. Bai et al. (2003) manufactured the concrete with 10%, 20%, 30%, and 40% replacements of OPC by MK and PFA, and immersed the specimens in synthetic seawater for 18 months. Both binary (OPC-PFA) and ternary (OPC-PFA-MK) blends can obviously improve the strength of concrete immersed in seawater, while further mixing the control and OPC-PFA concrete with MK greatly reduced the strength delay of specimens exposed to seawater environments. Seleem et al. (2010) investigated the deterioration ratios (strength deterioration factor, SDR) of concrete incorporating SF, GGBFS, and MK in binary and ternary combinations and exposed them to synthetic seawater for more than 1 year. Except for mineral mixtures containing GGBFS, the SDR of all specimens increased with age increasing apart from the specimens containing GGBFS, which

appreciates GGBFS as the most effective additive to maintain the strength of concrete in marine environments, compared to OPC–SF specimens exhibiting reversely higher strength values in the whole ages with rarely suitable as GGBFS in retaining strength. Ramachandran et al. (2016) studied the mechanical behaviours of FA concrete with or without superplasticizer (SP) immersed in seawater environments for a year. Although the strength of OPC concrete is higher than concrete with FA and with only SP in the early stage, the strength of OPC concrete reduces slightly after exposure to marine environments.

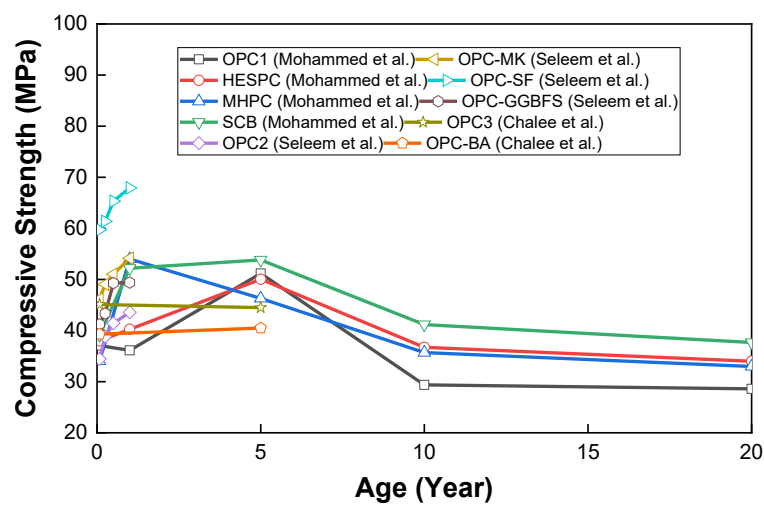


Figure 2.9. Changes of compressive strength of concrete at different ages of seawater corrosion (Chalee et al. 2013; Mohammed et al. 2004; Seleem et al. 2010)

Note: All the test results in the figure are caring for concrete, and the numbers are used to distinguish the test results of different authors on the same cement. The group with mineral admixtures indicated that some cement was replaced. Figures 2.10 and 2.11 are the same

Additionally, Mohammed et al. (2004) investigated the mechanical behaviours of concrete with distinct binders of OPC, high early strength cement (HESPC), moderate-heat cement (MHPC) and B-type slag cement (SCB) under tidal environment for up to 20 years. It was noted that only after 5 years, the compressive strength of concrete has increased. Then it decreases gradually after 10 years, and after 20 years, it is equal to or less than the compressive strength of concrete at 28 days. Figure 2.9 displays the compressive strength at different testing ages. It can be seen that with the increase of immersion

time in a seawater environment, the strength of concrete declines, and the mineral admixture can delay the decrease of compressive strength. In conclusion, when mineral admixtures are adopted to partially replace cement, the strength reduction of cementitious concrete under marine environments can be reduced. High-quality aggregate used in casting concrete under the marine environment is an essential choice.

Chloride diffusion

Intuitively, permeability influences concrete durability, the reason of which is that it evaluates the ability of both harmful ions and salts to penetrate the cementitious concrete. Generally, Fick's diffusion law is applied to simulate the transport of chloride through concrete, one of the identification parameters of which is the chloride diffusion coefficient (D_c). The D_c is determined by adjusting to the error function solution to Fick's diffusion law, which has been pointed out to be a time-varying parameter (Bader 2003; Chalee & Jaturapitakkul 2009; Mangat & Limbachiya 1999). The corrosion degree of concrete due to chloride transport are different for the various marine environments (environmental temperature, humidity, and lots of sulfate ions exist in the seawater), which will lead to the difference of the chloride diffusion coefficient. Currently, many investigators have reported that several concrete mixtures differ in D_c under the seawater environment, as shown in Table 2.7.

Table 2.7 Diffusion coefficients D_c of cementitious concrete exposed to marine environment

Item	Detail of specimen		Times (years)	Environments	Detection method	Diffusion coefficients $D_c (\times 10^{-12} \text{ m}^2/\text{s})$	References
	Binder	W/B					
1	OPC		5	Exposed to the tidal zone of Gulf of Thailand.	Fick's second law	3.10, 4.00, 5.60	(Chalee & Jaturapitakkul 2009)
	15% FA	0.45				1.20, 1.50, 2.10	
	25% FA	0.55				0.98, 1.30, 1.90	
	35% FA	0.65				0.80, 1.10, 1.20	
	50% FA					0.45, 0.55, 0.95	
2	OPC		1	Immersed in artificial seawater according to ASTM D1141	Fick's second law	6.20	(Jau & Tsay 1998)
	10% GGBFS					4.90	
	20% GGBFS	0.60				4.70	
	30% GGBFS					4.80	
	50% GGBFS					6.50	
3		0.40	4.5	Along the Arabian Gulf	Fick's second law	1.18, 5.95, 6.92	(Bader 2003)
	OPC	0.50					
4		0.65	1	Different distance to seashore	Fick's second law	4.41-4.91	(Mustafa & Yusof 1994)
	OPC	0.50					
5	OPC	0.66	3, 8	A tidal environment	Fick's second	6.53, 7.85	(Bamforth & Price 1993;

	30%PFA	0.54			law		0.89, 0.78	Dhir et al. 1996)
	70% GGBFS	0.48					0.76, 0.56	
	8% SF	0.72					3.98, 3.25	
	OPC						2.14	
6	GGBFS	0.45	15	A tidal environment	Fick's law	second	0.48	(Mohammed et al. 2002)
	PFA						0.55	
7	OPC	0.35	1.25	Atmosphere, Splash, Tidal and	Fick's law	second	0.76,1.30,4.50,3.70	(Zuquan et al. 2018)
	50%GGBFS+FA			Submerged zone in Wheat Island			0.73,2.00,3.70,5.60	
				Atmosphere, Splash and Tidal			0.96, 0.88, 0.86	
8	7% SF	0.35	5	zone in Persian Gulf I zone	Fick's law	second		(Safehian &
				Atmosphere, Splash and Tidal			0.31, 0.34, 0.75	Ramezaniapour 2013)
				zone in Persian Gulf II zone				
				Atmosphere, Splash and Tidal				
				zone in the Beibu Gulf I zone			0.70, 0.83,0.75	
9	OPC (C40 concrete)	0.40	3	(Fangcheng)	Fick's law	second		(Wu et al. 2017)
				Atmosphere, Splash and Tidal				
				zone in the Beibu Gulf II zone			0.74,1.01,0.91	
				(Qianzhou)				

				Atmosphere, Splash and Tidal zone in the Beibu Gulf III zone (Tieshan)		0.84, 1.18, 1.07	
10	OPC	0.56	0.5	In artificial seawater	Darcy's law	1.81	(Mangat & Limbachiya 1999)

As can be seen from Table 2.7, the primary factors influencing the D_c of cementitious concrete under marine environment include W/B ratios, type of mineral admixtures, exposure time and locations, etc. Bader (2003) reported the influence of W/B ratio of D_c on OPC concrete exposed to underground conditions in a coastal area. The chloride concentration is generally reduced as a reduction in the ration of water to binder. Some researchers (Chalee & Jaturapitakkul 2009; Mangat & Limbachiya 1999) investigated the effect of water to binder ratios and FA replacements percentage on D_c under marine environment for up to 5 years. It is reported that D_c of all mixes were reduced with the extension of curing time, and the reduction of water to bind ratio led to the reduction of D_c . When the water to bind ratio decreased, the D_c in all mixes just with OPC was lower than that in FA-concrete. Jau and Tsay (1998) used GGBFS to replace OPC for up to 50 wt.% to manufacturing OPC-GGBFS concrete and tested the D_c of the OPC-GGBFS concrete immersed in seawater environment. Under the same exposure condition, the coefficient is smallest when the GGBFS substitution ratio is up to 20%, compared to relatively high permeability when the GGBFS substitution ratio is up to 50%. This is possibly because that the pozzolanic reaction of proper GGBFS can optimize the pore structure of concrete, while the calcium hydroxide provided by cement is not sufficient for full pozzolanic reaction for high GGBFS substitution. In addition, the D_c of OPC-GGBFS concrete decreases with the increase of time due to pozzolanic reaction, compared to an increase in OPC concrete. Bamforth, Dhir, and Mohammed et al. (Bamforth & Price 1993; Dhir et al. 1996; Mohammed et al. 2002) also determined the effects of SF, GGBFS and PFA on the concrete immersed in tide environments. The appropriate SF, GGBFS, and PFA replacement for OPC reduced the D_c in tide environment. Besides, the D_c of the concrete with appropriate content of SF, GGBFS, and PFA could be decreased as the exposure time increased from 3 to 8 years (Bamforth & Price 1993; Dhir et al. 1996).

Additionally, chloride transport levels can differ remarkably being up to the site of the cementitious concrete, the level of exposure to the different concentrations of chloride ions solutions environments, and efflorescence conditions related to temperature and moisture. Consequently, the situation of

climate has an essential effect on the transport speed of chloride. Song et al. (2008) evaluated chloride convey of concrete from three different coastal regions: Japan, Britain and Venezuela, concluding that cementitious concrete under tropical environment were more vulnerable to chloride ions penetration and indicating that tropical climates were poor conditions for chloride ion penetration as a result of high relative moisture, temperature, and chloride ion concentration. Mustafa and Yusof (1994) studied the influence of different distances from the coastline on the D_c of concrete. The longer was the time in exposure, the greater was the surface chloride content, and the smaller was the noticeable diffusion coefficient. Jin et al. (2018) tested the D_c of concrete with different contents of mineral admixture in the marine atmosphere zone, splash zone, tidal zone, and submerged zone for up to 13 months. The effect of FA and GGBFS on the migration and binding capacity of chloride ion was examined, and the optimum substitute ratios of mineral admixture in the marine environment were also put forward. The decreasing trend of chloride ion binding capacity was more evident in the submerged and tidal zones than in other zones. Safedian and Ramezaniapour (2013) assessed the effects of exposure conditions, including atmosphere, splash, and tidal zones on the D_c of concrete containing SF of 7 wt.%. It should be noted that D_c in most normal specimens is approximately the same, and the curing conditions do not show a significant on them for up to 5 years. Wu et al. (2017) studied the influences of exposure conditions, including atmosphere zones, tidal zones, and splash zones on chloride ingress and the D_c of concrete, indicating that the difference in D_c value caused by exposure conditions is not apparent. From the result of the chloride diffusion mentioned above, the primary factors influencing the time-dependent D_c of cementitious concrete under marine environment include W/B ratios, type of mineral admixtures, exposure time, and locations. The D_c of concrete could be decreased by the reduction of water to bind ratio and appropriate content of mineral admixtures. Compared to the marine exposure zones, the concentrations level of chloride ions and efflorescence conditions related to temperature and moisture would have more profound influences on the change of D_c . Therefore, it is very necessary to select the appropriate concrete with appropriate content of mineral admixtures to cast offshore

structures according to the location related to multiple concentrations, temperature, and efflorescence degree.

2.5.4 Reinforced concrete product and infrastructure under marine environment

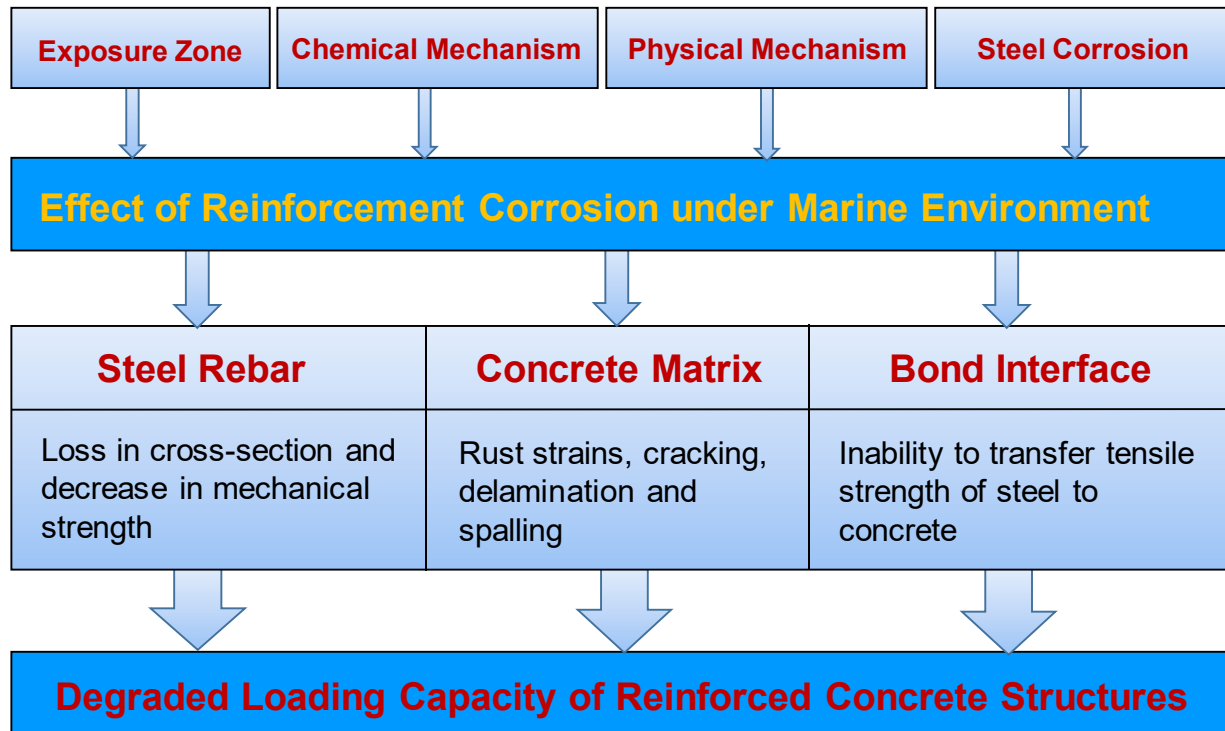


Figure 2.10. Effects of steel reinforcement corrosion on reinforced concrete structures under marine environment (Imam et al. 2012)

In marine environments, high humidity, sulphate attack, and chloride ion concentration and air lead to much more severe corrosion to offshore structures than structures in inland areas. As illustrated in Figure 2.10 (Imam et al. 2012), the corrosion causes tremendous mass loss of reinforcement bars, cracking of concrete protective layer (Brandt 2008), and a decrease in the binding capacity of the interface between concrete and reinforcement (Baruah & Talukdar 2007). For the structural part, as a result of the sustained aging and deterioration of marine environments in the service life, the strength (Moreno et al. 2018; Ramli et al. 2013), stiffness, ductility (Sawpan et al. 2012), and energy consumption capacity (Marar et al. 2001) is decreased. Beams and slabs are two types of primary

constituent parts of concrete structures, such as coastal bridges and harbours. This section generalizes the previous findings of structures and productions based on reinforced concrete structures under seawater environment, including beam and slab, and protection coating or repairing materials.

Concrete beam under marine environment

Up to now, some studies have investigated the capacity decrease of aging RC beams in the marine environment. In the initial stage, the flexural strength of RC beam is not significantly affected by the corrosion of longitudinal reinforcement. In contrast, the stiffness and flexural strength are remarkably reduced owing to the deficit of the longitudinal section (El Maaddawy et al. 2005; Mangat & Elgarf 1999). Some results showed that the RC beams under the marine environment using supplementary cementitious materials showed slight influences on the performance change. De Weerd et al. (2016) submerged concrete beams using different binders, including OPC, SF, FA, or GGBFS in seawater environment for 16 years and examined the chloride ingress. Figure 2.11 displays the chloride profiles after 16 years of exposure evaluated by titration. There were limited significant differences in physical-mechanical properties and chloride ingress between those different types of concrete, which indicate that either the substitution content of OPC is too low or the ingress of chloride is primarily controlled by the corresponding physical properties. Otieno et al. (2016) prepared the concrete beam with different binders containing GGBFS and FA and different W/B ratios of 0.40 and 0.55 and curing those specimens under accelerated laboratory corrosion or went through physic corrosion in a tidal zone. The results displayed that the coverage depth, crack width, and partial substitute of OPC with FA or GGBFS lead to a reduction in the corrosion rate. However, there was no significant discrepancy in the corrosion rate between the two curing conditions owing to the replacement of OPC by FA or GGBFS.

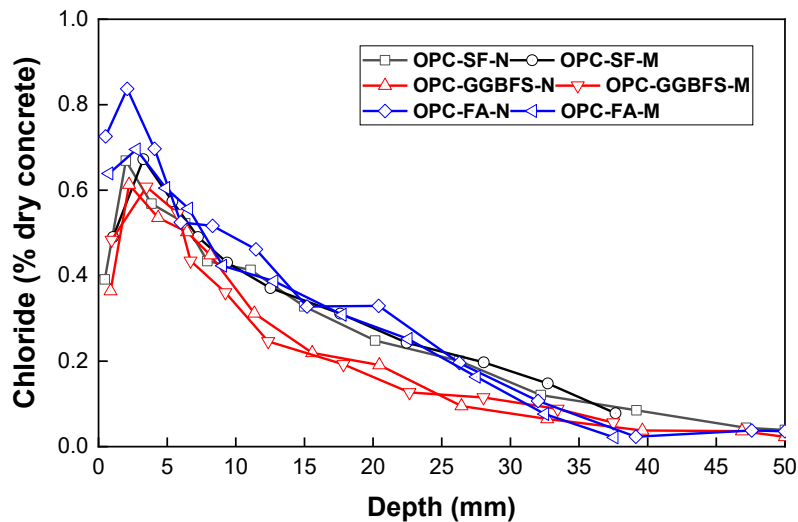


Figure 2.11. Comparison of chloride profiles from reinforced concrete beams (De Weerd et al. 2016) (N: laboratory environment; M: marine environment)

The effect of the exposure conditions on the properties of the geopolymer concrete beam was also considered. Darmawan et al. (2019) studied the behaviour of high geopolymer concrete beam (GCB) in a splashing zone for up to 28 days. Compared to those cured at room temperature, geopolymer concrete in seawater environment showed lower compressive strength, higher porosity and lower concrete resistivity. According to the load test of the geopolymer concrete beam under the action of shear load, the seawater environment has no effect on the crack pattern and crack growth of the GCB. Reddy et al. (2012) reported an experimental evaluation of low-calcium FA-based geopolymer concrete beam under a marine environment. The results pointed out that the geopolymer concrete beam is additionally uniform, well-bonded to the aggregate, and shows more excellent resistance to seawater attack than OPC concrete. Consequently, geopolymer concrete beam can obtain improved crack resistance and enduring durability regardless of marine environment.

The influence of the location is also a vital factor in the durability of the RC beam under the marine environment. Poupard et al. (2006) presented the diagnostic results of chloride-induced corrosion damage of RC beam for 40 years exposed to marine environments and concluded that the chloride was responsible for the corrosion attack by the physicochemical measurements, and the corrosion activity

in the beam varies depending on the position. It was also concluded that the location of both "high corrosion zone" and "low corrosion zone" distinguished by the result data did not change over time. Zhu et al. (2018) studied the corrosion-induced cracking procedure of RC beam with sustained load under marine environments for 26 years. In the compression region caused by the sustained load, the crack for the corrosion appears first, while the length and width of the crack for the corrosion increase significantly, which is related to the top-bar impact and the top-surface-ponding impact.

The influence of moisture is also a vital factor in the durability of the RC beam under marine environment. Medeiros et al. (2013) studied the chloride-ion contents of RC beam under the marine environment for 40 years, where located about 700 m away from a coastline. The result showed that the relationship between the position of the concrete columns and the seawater has limited effect, and the concrete located in the wet and dry cycle area is more susceptible to chloride attack. Yin et al. (2017) examined the durability of the RC beams under the coupling effect of loads and a chloride wetting-drying cycle and freeze-thaw cycle and concluded that the coupling effect of corrosion and loads environment has a munificent impact on the RC beams, resulting in failure mode, and changes in the bearing capacity and deflection of the beams. Generally, the properties of RC beams could be strongly affected by the exposure of marine environment. It is very necessary to choose suitable raw materials and low-corrosive steel for offshore construction taking the location into consideration.

Concrete slab under marine environment

Up to now, the capacity decrease of aging RC slabs has also been examined by some studies. Akiyama et al. (2010) presented the time-dependent dependableness analysis of RC slab in the marine environment. It is concluded that it can assess the impact of marine environment by time-dependent analysis, inspection results and inspection times on the latest estimates of the reliability of one-way plates, resulting in decision applications that consider dependableness based acceptance criteria and / or cost-benefit analysis of risk. Gao et al. (2017) established a practical method to predict the diffusion coefficient, staring time and flexural failure possibility of RC slabs with load-induced cracks under the

marine environment. The results showed that the crack caused by the load significantly affects the prediction accuracy of the change of the ability to withstand the corrosion failure of the reinforcement. Kondratova et al. (2003) investigated the influence of the pre-crack and corrosion inhibitors on the corrosion rate of the RC slabs with a 20 mm cover. In the process of casting, a 0.2 or 0.4 mm wide simulated crack was formed transversely to the steel axis and two commercial corrosion inhibitors (organic corrosion inhibitor (OCI) and anodic calcium nitrite-based corrosion inhibitor (CNI)) were added to the concrete mix to prevent corrosion. After 12, 24, and 36 months of exposure to marine environments in natural marine exposure site, the corrosion damage of concrete slabs were evaluated. As shown in Figure 2.12, in terms of reducing the corrosion rate of concrete with no inhibitors, OCI is more effective than CNI. In contrast, the efficiency of both corrosion inhibitors is relatively low in cracked concrete. Additionally, Heede et al. (2014) conducted a series of tests on the effect of crack width on the chloride penetration of RC slabs using FA and SF. The results show that to reduce the inevitable cracks in these slabs, it is necessary to include additional reinforcement throughout the life cycle to decrease the property crack width to 0.05 mm. As aforementioned, simulating crack development and predictive models are effective ways to ensure the safety of RC slabs under seawater environments.

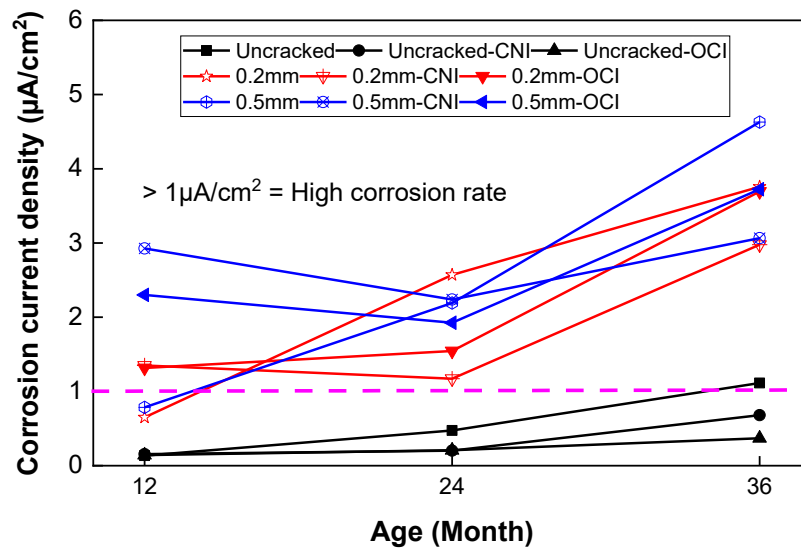


Figure 2.12. Corrosion current densities of reinforced concrete slabs with or without corrosion inhibitors (Kondratova et al. 2003)

Concrete structure with corrosion protection under marine environment

Different corrosion protection and maintenance methods of RC in the marine environment have been studied. (François et al. 2018; Wang et al. 2014). Lists of protection methods for RC under the marine environment are shown in Table 2.8. There are five main ways to deal with the corrosion of RC in the marine environment: repair or partial reconstruction; corrosion inhibitor; protective coating; cathodic protection; replacement of reinforcements.

Swamy and Tanikawa (1993) considered the utilization of preservative operation in structures. In concrete structures contaminated with chloride ions, partial or patching can just solve this trouble and is merely applicable when the damage is relatively slight. Asrar et al. (1999) replaced OPC with microsilica to provide better corrosion protection to the RC under seawater environment. It has been noted that its protective effect on the sulphate resistance cement is better than that with OPC. Besides, Malik et al. (2004) pointed out that migratory corrosion inhibitors as possible chemicals for rehabilitating can indeed protect reinforcement concrete in a seawater environment.

Table 2.8 Protection methods for reinforced concrete under marine environment

Item	Name of method	Conditions of use	Important notes	Country	Ref.
1	Surface coatings	Epoxy polyurethane and aliphatic acrylic	1) Reduce the chloride penetration 2) Enhance the service of life 3) Surface coatings is time-dependent	Iran	(Moradllo et al. 2012)
2	Coated Reinforcing bars	Patch with an epoxy compound	1) Extend the service life 2) Cannot provide total protection	Turkey, Canada	(Erdoğan et al. 2001)
3	Coated Reinforcing bars	Polymer composite coating (CPCC), interpenetrating polymer network coating (IPN) and epoxy coating (EC)	1) Different types of coating have different effects 2) Less visual inspection on coated rebar	India	(Venkatesan et al. 2006)
4	Epoxy-coated bars	An active single component epoxy zinc primer	No significant difference in bond strength for both coated and uncoated bars	Kuwait	(El-Hawary 1999)
5	Coated rebar	Epoxy/zinc duplex	1) Higher anti-corrosion performance 2) More serious corrosion once coating is mechanically damages	China	(Dong et al. 2012)
6	Cathodic Protection	Protection method/system	Expanding pressure and tensile stress	Korea	(Kim et al. 2008)

		Open circuit potential (OCP), linear			
7	Electrochemical Methods	polarization resistance (LPR) and electrochemical impedance spectroscopy (EIS) methods.	Have self-catalysis effect of chloride	China	(Yang et al. 2016)
8	Cathodic Protection	Cathodic protection and sacrificial or galvanic anodes	1) Provide long-term corrosion control 2) Stop further corrosion		(Daily 1999)
9	Partial replacements	Microsilica added concrete	Decrease the corrosion rates	Saudi Arabia	(Asrar et al. 1999)
10	Corrosion inhibitors	Migratory corrosion inhibitors	1) Show in general little corrosion 2) Less corrosion rates	Saudi Arabia	(Malik et al. 2004)
11	Alternative reinforcements	GFRP	1) Enhance the ductility 2) Slight deterioration in load capacity	China, USA	(Zhou et al. 2018)
12	Alternative reinforcements	FRP	1) Exhibit excellent residual strength 2) Slightly compromised by seawater environment	Korea	(Won et al. 2013)
13	Alternative reinforcements	FRP, GFRP, BFRP, CFRP	1) The ultimate strain of CFRP is much less than that of BFRP and GFRP 2) Slightly enhance the concrete and lower axial strain	Australia	(Li et al. 2016)

Electrochemical chloride extraction (ECO) is a proverbially used protective method (Fajardo et al. 2006; Orellan et al. 2004; Yang et al. 2016), to reduce existing chloride levels and prevent further damage. Kim et al. (2008) prepared slab specimens to evaluate the effectiveness of cathodic protection under the seawater environment. The Zn-mesh sacrificial anode has been used as an anti-static protection system. Bertolini et al. (2002) introduced the productiveness of immersion sacrificial anode in preventing pitting corrosion in marine piles. The results show that, at least under the current test conditions, the sacrificial anode is additionally efficacious in avoiding the start of corrosion (i.e., providing cathodic protection) than in controlling the ongoing pitting (i.e. ensuring cathodic protection). Steven et al. (1999) used cathodic protection to control the corrosion of RC structures under the marine environment. Moradillo et al. (2012) used six different concrete surface coatings on concrete surfaces and studied the properties of those coatings during 5 years of exposure in a marine tidal area of the Persian Gulf. In terms of the results obtained, it has been proved that epoxy polyurethane and aliphatic acrylic acid are the most effective coatings, which can reduce chloride penetration and prolong the service life of cement-based structures. However, the properties of the surface coating relies on the time and the concrete have to be coated again with a different surface coating within the appropriate time, which means before the coating deteriorates. Erdoğan et al. (2001) prepared the concrete slabs with no damage, 1% damage and 2% damage epoxy-coated bars. It is shown that reinforcement with a damaged epoxy coating has no proof of adequate rust build-up at the surface of steel concrete to cause concrete cracking. Venkatesan et al. (2006) carried out a one-year study of RC specimens exposure to three different levels. The properties of three different types of corrosion protection against cement, namely cement polymer composite, interpenetrating polymer network coating, and epoxy coating, were assessed stately by measuring open circuit potential measurements. Hawary et al. (1999) evaluated the bond strength properties of epoxy coated bars by a battery of axial tensile tests of epoxy coated bars embedded in concrete cylinders and undergone drawing tests of epoxy coated bars in the marine environment. Dong et al. (2012) assessed the

corrosion behaviour of epoxy/zinc-coated steel bars embedded in concrete compared to black steel, galvanized, and epoxy-coated steel bars in the marine environment.

Zhou et al. (2018) used glass fiber reinforced polymer (GFRP) to replace the rebar to cast concrete owing to its exceptional corrosion resistance to seawater environment. Some researchers (Li et al. 2016) also utilized the fiber-reinforced polymer (FRP), GFRP, basalt fibre-reinforced polymer (BFRP), carbon fibre-reinforced polymer (CFRP) to replace the rebar in the RC under seawater environment, indicating that CFRP has the highest strength and elastic modulus in both longitudinal and transverse directions. The CFRP may be a better alternative to cast concrete in marine environments.

In general, a partial or partial repair can only solve this problem in concrete structures, and only in the case of minor damage. Corrosion inhibitors are modifiers because they are mixtures of compounds or have been applied to the interface of concrete (Malik et al. 2004). The protective coating provides an impermeable layer on the concrete to prohibit the entry of chloride ions (Kim et al. 2008; Moradillo et al. 2012). Electrochemical chloride extraction is a proverbially used measurement methodology to reduce existing chloride levels and prevent further damage (Dong et al. 2012; El-Hawary 1999; Erdoğan et al. 2001; Venkatesan et al. 2006), which is a cost-efficient and enduring method for removing large quantities of contaminated chlorine ions. Using FRP to replace the rebar in casting concrete under the seawater environment is also an effective method (Won et al. 2013).

2.6 Summary

This chapter presents a general review of sustainable and low-carbon cementitious composites. The effects of different aggressive environmental conditions on the performance of cementitious composites were also summarized. It can be concluded that the application of industrial by-products to fabricate low-carbon cementitious composites is a sustainable way to decrease CO₂ emissions and optimize its performance. Although previous researches have confirmed that geopolymers perform better than those OPC in certain performances, such as tensile strength, acid resistance, impact resistance, etc., only a few researchers carried out relevant experiments to take both the external

loading and environmental actions into consideration for geopolymer materials used in concrete infrastructure, which is more related to the practical engineering. In addition, the durability issue of offshore cementitious composite concrete structures under marine environments has also attracted tremendous attention from experts or industries. Although some supplementary materials were added to improve the properties of the cementitious concrete and reinforced concrete structures, there are still need more actions and research to be conducted to provide more reliable data to ensure its safety.

CHAPTER 3: PERFORMANCE OF LOW-CARBON GEOPOLYMER UNDER FIRE ENVIRONMENT AND MECHANICAL LOAD

3.1 Introduction

Recently, lots of studies have focused on searching for alternative low-carbon binders like geopolymers to replace Ordinary Portland cement (OPC). Geopolymers, also regarded as inorganic polymer or zeolitic precursor, are formed when an alkali solution is mixed with aluminosilicate materials made of industrial by-products including metakaolin, fly ash and ground granulated blast furnace slag (GGBFS), which not only decrease the demand for OPC but also reduces carbon emissions in turn. Some previous researches have confirmed that geopolymers perform better than those OPC in certain performances, such as tensile strength (Nath & Sarker 2014; Ryu et al. 2013) acid resistance (Aiken et al. 2018; Babae & Castel 2018) and impact resistance (Khandelwal et al. 2013; Noushini & Castel 2018).

In addition, some researches have also demonstrated that geopolymers have better fire resistance than OPC-based composites as the results of the different thermal evolution of their chemical structure (Sarker & Mcbeath 2015; Zuda et al. 2010). Fernandez-Jimenez and Palomo (2008) examined the flexural strength of geopolymers after being exposed to elevated temperatures and discovered that the flexural strength of geopolymers at a temperature of 600 °C displayed 1.2 times than that of geopolymers before being exposed to high temperature. A comparable result was also reported by Pan et al. (2018), the findings of which illustrates that the compressive strength of fly ash-based geopolymer was increased when the temperature was up to 600 °C. More recently, research on geopolymer-based concrete has further convinced the trend of strength increase after being exposed to high temperatures. Shaikh and Vimonsatit (2015) investigated the compressive strength of fly ash-based geopolymer concrete under the simulated fire environment. They found that at the temperature of 600 °C, fly ash-based geopolymer concrete performed outstanding high temperature resistance with improved compressive strength of 110% of the compressive strength detected before exposure to a fire

environment. However, the compressive strength of OPC-based concrete decreased by about 46.5%, as the result of the dissociation of calcium hydroxide (CH). The results of X-ray diffraction (XRD) and nuclear magnetic resonance showed that the structure of the fly ash-based geopolymer did not change below 600 °C (Dombrowski et al. 2007; Shaikh & Vimonsatit 2015). Vickers et al. (2016) also evaluated the mechanical properties of fly ash-based geopolymers concrete manufactured with alumina aggregate. The fire resistance of fly ash-based geopolymers concrete could be enhanced as the addition of alumina aggregate for its low thermal conductivity.

However, it also should be noted that previous studies (Dombrowski et al. 2007; Fernández - Jiménez et al. 2008; Pan et al. 2018; Shaikh & Vimonsatit 2015; Vickers et al. 2016) only investigated the mechanical performance of geopolymer materials at simulated fire environments with no consideration of the influence of mechanical loading. Actually, environmental exposure (such as high temperature exposure) interacting with loadings can lead to deterioration and damage of concrete materials and structures during their service life. The gradual deterioration of concrete usually appears in the form of a crack or other anomalies, affecting not only the structural performance but also the mechanical behavior, integrity, and permeability characteristics of concrete (Elzafraney & Soroushian 2004; Lim et al. 2000a; Win et al. 2004). Only a few researchers carried out relevant experiments to take both the external loading and fire resistance into consideration for geopolymer materials used in concrete infrastructure. Junaid et al. (2017) studied the stress–strain relationship of fly ash geopolymers under compression loading at elevated temperatures. The geopolymer composites were heated until the target temperature was reached, and then loaded to failure by displacement control while heating. Furthermore, although excellent resistances to certain aggressive environments are often regarded as an advantage of geopolymer composites (Ismail et al. 2013; Li & Liu 2007), there is still limited understanding of the effects of combined fire exposure and external loadings on the performance of geopolymer materials.

Besides, numerous combinations of GGBFS and fly ash were utilized to investigate the behavior of fly

ash/GGBFS based geopolymers for their environmentally-friendly characteristics (Hu et al. 2019; Pilehvar et al. 2018; Tang et al. 2019; Tang et al. 2020). Consequently, the purpose of this study is to examine the elevated temperature resistance of fly ash/GGBFS based geopolymer mortars (GSM) after load-induced damage and to comprehend further the mechanism of fire attack coupled with preloading-induced damage. The physical properties of geopolymer mortar, such as volume change, mass change, visual appearance, and residual strength, were tested before and after exposure to different high temperatures. The microstructure alteration before and after load inducing or thermal exposure was evaluated by SEM. The phase change at elevated temperatures was also detected by TGA, XRD, and SEM-BSE analysis. The related outcomes will contribute to an in-depth understanding of the fire performance of fly ash/GGBFS geopolymer systems after load-induced damage.

3.2 Experiment program

3.2.1 Raw materials

ASTM Type F fly ash and GGBFS were used in this study conforming to the standard of AS/NZS 3582.1:2016 and AS 3582.2:2016, respectively. The fly ash was supplied by Boral Cement, New South Wales, Australia, and the GGBFS was sourced from Building Products Supplies Pty Ltd, Victoria, Australia. Ordinary Portland cement CEM I 42.5N produced by Independent Cement & Lime Pty Ltd, Victoria, Australia, was used according to the standard of AS/NZS 2350.1-2006 (Methods of testing Portland, blended and masonry cements-Sampling). The physical properties and chemical compositions for fly ash, GGBFS, and OPC are exhibited in Table 3.1. The XRD patterns of fly ash, GGBFS, and OPC are displayed in Figure 3.1. The primary crystalline phases detected in fly ash are quartz (PDF #00-046-1045), mullite (PDF #00-015-0776), and hematite (PDF #98-000-0240). GGBFS showed gypsum-related peaks (PDF #00-033-0303), and a small amount of calcite (PDF #00-005-0586) are also identified. OPC has many crystalline phases including alite (PDF #00-042-0551), belite (PDF #00-033-0302), aluminate ((PDF #01-070-0134), brownmillerite (PDF #00-030-0226), and

gypsum (PDF # 04-008-9805).

Table 3.1 Physical properties and chemical compositions of fly ash, GGBFS and OPC

Physical properties	FA	GGBFS	OPC
Blaine ($\text{m}^2 \cdot \text{kg}^{-1}$)	390	418	347
Residue 45 μm (%)	18.4	1.1	4.1
Specific gravity	2.76	2.92	3.15
Chemical compositions	FA (%)	GGBFS (%)	OPC (%)
SiO ₂	65.90	36.00	20.51
Al ₂ O ₃	24.00	13.80	5.37
Fe ₂ O ₃	2.87	0.30	2.10
CaO	1.59	42.60	57.05
MgO	0.42	5.80	3.86
MnO	0.06	0.40	0.02
K ₂ O	1.44	0.27	1.44
Na ₂ O	0.49 (equivalent)	0.21 (equivalent)	0.64 (equivalent)
P ₂ O ₅	0.19	0.10	0.13
TiO ₂	0.92	0.80	0.16
SO ₃	—	0.56	6.37
LOI	1.78	1.64	2.35

The fly ash/GGBFS-based mortar or paste mixes were activated by the combination solutions of sodium silicate (PQ Corporation, PA, USA) and sodium hydroxide (Chem-Supply Pty Ltd, SA, Australia). The sodium silicate solution had a solid content of 44.1% with SiO₂ of 29.4%, Na₂O of 14.7%, and a modulus of 2.0. NaOH solution (10 M) was obtained from dissolving 400 g of sodium hydroxide pellets (98% purity) in 1 L of distilled water and then allowed to cool down for 24 hr before casting (Hanjitsuwan et al. 2017; Rattanasak & Chindaprasirt 2009; Wongsu et al. 2016). The ratio of Na₂SiO₃ to NaOH was fixed at 2.0, and the modulus of SiO₂ to Na₂O was 1.94. The fine aggregate used was Sydney sand; it has a specific gravity of 2.65 and fineness modulus of 1.81, which was tested according to AS 1141.11.1-2009 (Methods for sampling and testing aggregates particle size distribution). The sand was dried in an oven at 105 ± 5 °C for 48 hr to eliminate all water. It is then cooled and kept under stem conditions before being cast.

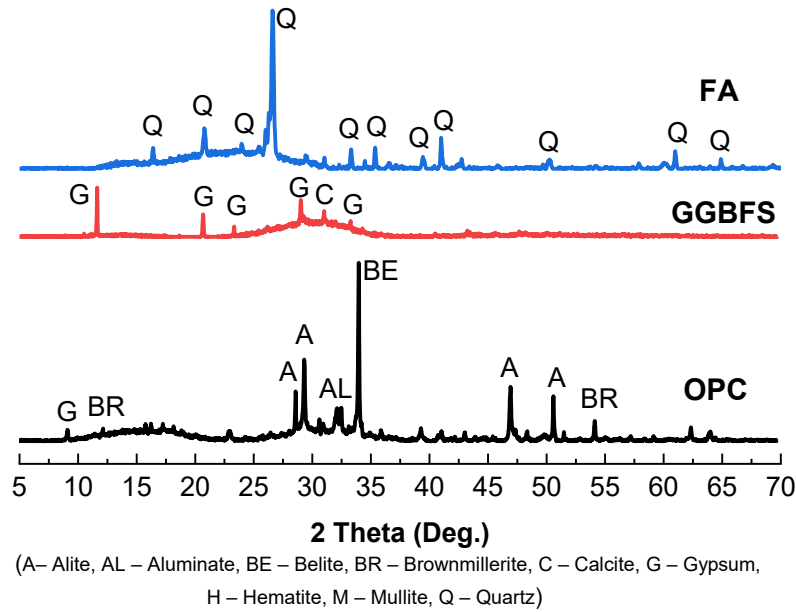


Figure 3.1. XRD patterns of fly ash, GGBFS and OPC

3.2.2 Mix proportion

A sum of 4 mortar mixtures was prepared in this study: one mixture was made of OPC and sand (PCM), and 3 mixtures were made of geopolymer and sand (GSM). In GSM, GGBFS was used at 0, 20, and 40% by weight replacement of fly ash, with the name of GSM1, GSM2, and GSM3. The ratios of liquid-to-binder and sand-to-binder were fixed at 0.55 and 1.25, respectively, in GSM. However, to obtain a similar compressive strength to GSM, the rates of water to OPC and sand to OPC in PCM were designed to be 0.50 and 1.25, respectively. For paste mixtures, the rates of liquid to solid binder and water to OPC were also fixed at 0.55 and 0.50, respectively. Geopolymer pastes (GP) with 0, 20, and 40% GGBFS was named GP1, GP2, and GP3, respectively, and the OPC paste was named PCP. The mortar and past mix proportions used are presented in Table 3.2.

Table 3.2 Mix proportions for geopolymer and OPC mortars and pastes

Mixture	Mix proportions (kg/m ³)						
	FA	Slag	OPC	Na ₂ SiO ₃	NaOH	Water	Sand
GSM1	600	— (0%)	—	220	110	—	750
GSM2	480	120 (20%)	—	220	110	—	750
GSM3	360	240 (40%)	—	220	110	—	750
PCM	—	—	600	—	—	300	750
GP1	600	— (0%)	—	220	110	—	—
GP2	480	120 (20%)	—	220	110	—	—
GP3	360	240 (40%)	—	220	110	—	—
PCP	—	—	600	—	—	300	—

3.2.3 Specimen preparation

Mortar specimens were manufactured by a 10-L plane high-shear mixer. First, the sand in saturated-surface dry condition and the binder (fly ash and GGBFS, or OPC) were dry-mixed thoroughly in the mixer for 2 min. After that, the premixed alkaline activator solution or water was slowly added into the mixer for 1 min. Then, the admixture was blended for 4 min. Paste mixture preparation adopted the same method.

The fresh mortar or paste was cast in 50 × 100 mm cylinder molds in two stories and was consolidated by a vibrostand for tamping. Afterward, the specimens were hidden with plastic sheets to prevent water evaporation. For geopolymer mortar or paste, the specimens were kept at homeothermy for one hr, and then were heat-cured at 70 °C for 24 hr. The demoulded specimens were then covered with a plastic sheet and stored into a curing room at 20 ± 1 °C and 50% relative humidity (RH). For PCM mortar or paste, the specimens were kept in the curing room for 24 hr at a temperature of about 20 ± 1 °C and 100% RH, and they were then demoulded and set into the curing room. It is worth noting that the mechanical properties of heat-cured geopolymer mortar at the age of 7 days is equivalent to that of OPC mortar curing for 28 days (Aiken et al. 2018). In addition, in this test, the 28-day compressive strength of PCM is similar to the 7-day compressive strength of GSM2 and GSM3 mentioned in section

3.2. Therefore, the comparison between GSM and PCM primarily focused on the group with equivalent compressive strength (PCM, GSM2, and GSM3).

3.2.4 Experimental methodology

The following items were investigated in this test including the effect of GGBFS content (0, 20 and 40%) on the fire resistance after load-induced damage of GSM, the effect of preloading level (0, 20, 40, and 60% of ultimate compression strength (UCS)) on the performance of both Portland cement mortar (PCM) and GSM, and the effect of exposure temperature (300, 500 and 700 °C) on the performance of PCM and GSM.

In this study, a total of 240 specimens were cast with 48 mortars and 12 paste specimens for each mix. When up to the test age, the compressive strength mortar specimens, including GSM and PCM, was tested first and seen as the ultimate compressive strength (UCS). After that, mortars specimens were preloaded up to 0, 20, 40 and 60% UCS for 1 min, and then heated to target elevated temperatures of 300, 500 and 700 °C and kept at a stable temperature for 2.5 hr. Mortar specimens were applied to study the physical properties (including volume change, mass change, visual appearance), residual capacity strength, and microstructural characterization with SEM or SEM-EDX. Paste specimens were also exposed to the same high temperature remained but at a stable temperature for 2.0 hr. The analysis of TGA and XRD measured the phase change of paste specimens, and the isothermal calorimetry also assessed the hydration evolution of paste mixtures.

3.2.5 Test methods

During testing, 3 duplicate GSM specimens at 7 days and 3 duplicate PCM specimens at 28 days were tested at first with an unchanging load rate of 1.0 kN/s used to measure the values of UCS. Other mortar specimens for each mix were then loaded up to 20, 40, and 60% UCS at a low rate of 0.20 mm/s and then kept under loading for 1 min (Lim et al. 2000a). After one hour later, three mortar specimens of each mix after different preload levels were measured for the residual strength with a constant load

rate of 1.0 kN/s applied, and other preloading specimens were placed in a furnace oven, where the temperature was raised at a rate of 10 °C/min (*AS/NZS 3582.1:2016 Supplementary cementitious materials part 1: fly ash* 2016a). After the oven temperature reached 300, 500, or 700 °C, the temperature was kept constant for 2.5 hr and then cooled down to room temperature. The residual strength of each specimen after exposure to high temperature was measured. The schematic diagram of this experiment is shown in Figure 3.2. As a result, the specimen ID was designed as XXXX-A-B, where XXXX denotes specimen material (the first column in Table 3.2; A-% is the preloading rate (20, 40, or 60% of UCS); and B represents exposure temperature (300, 500, or 700 °C); the ambient temperature is set at 23 °C. For example, specimen GSM3-60-700 indicates that the mortar specimen had a mix proportion marked as GSM3 in Table 3.2, preloaded to 60% UCS and then exposed to 700 °C.

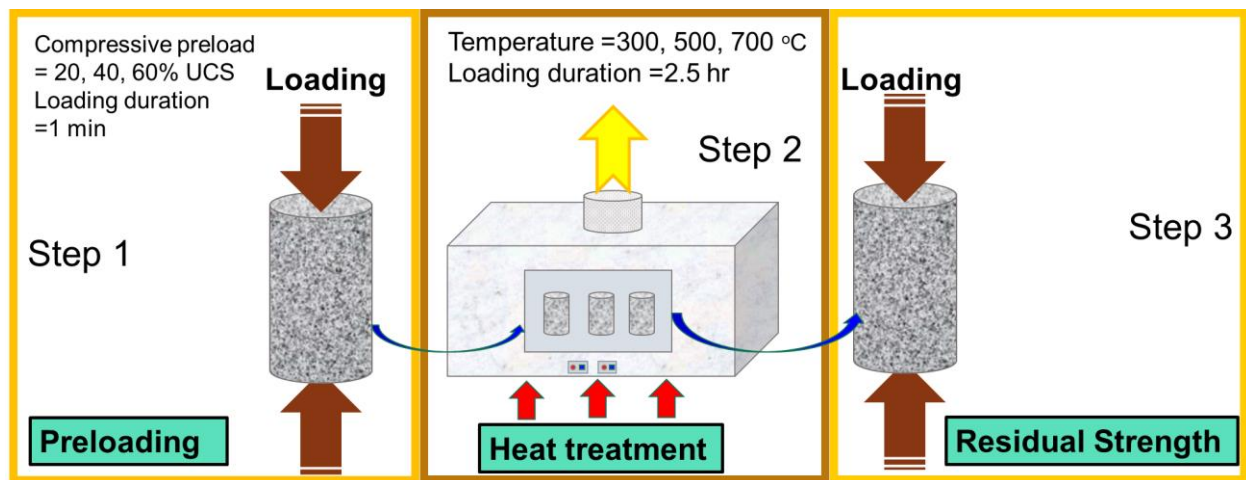


Figure 3.2. Schematic diagram of geopolymer composites subjected to different steps of testing

In addition to strength tests, the mass and volume of all mixtures before and after exposure to high temperatures were measured. Besides, the mass was measured by using a scale with an accuracy of 0.01 g, and the volume was measured by using a digital ruler with an accuracy of 0.01 mm. The

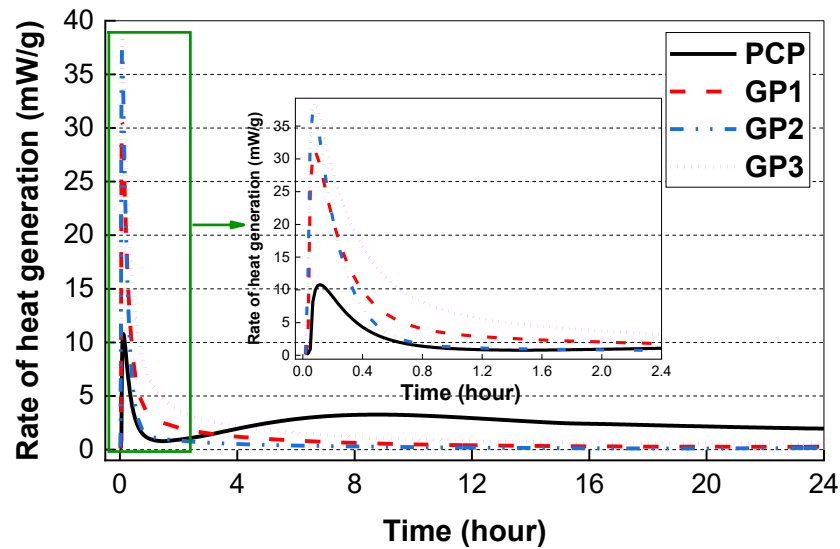
dimensions of the bottom, middle, and top sections, as well as the height of each specimen, were measured. The visual appearance of each specimen was evaluated before and after loading and before and after temperature exposure.

I-calmetrix 4000 was applied to measure the heat evolution by weighing 50 g of paste for each mix at a constant temperature of 20 °C. Besides, powder samples before and after the temperature exposure were acquired by crushing and grinding pastes with a pestle. Some powder samples were tested for TGA immediately, while others were kept in a drying apparatus at 50 °C with ethanol for 24 hr before XRD analysis. Before and after preloading and after exposure to elevated temperatures, Mortar samples with a dimension of 2.5 ~ 5 mm were extracted by sawing, polished, and dried in a desiccator at 50 °C with ethanol for 24 hr prior to SEM and EDX analysis. The following are some details of the analytical techniques used: TGA analysis was conducted by adopting Netzsch's STA449. In the nitrogen environment, the temperature is heated from 20 to 1000°C at 10°C/min to eliminate the potential impact of air on the test results (Li et al. 2017). The weight loss of information achieved from the thermogravimetric analysis (TG) curve and derivative thermogravimetry (DTG) curve was applied to examine the kinds of hydrates and reaction products. XRD analysis was performed using the Bruker D8 Discover diffractometer, utilizing CuK α radiation of wavelength 1.54 Å. Diffraction patterns were measured from 5 to 70° 2 θ with a step size of 0.02° (Elakneswaran et al. 2019; Rahier et al. 2007). The Jade 6.5 software with the powder diffraction file (PDF) database was utilized to analyze the XRD patterns. The equipment used was Zeiss Supra 55VP SEM with Raith Elphy Plus E-beam Lithography System as a chemical composition analyzer. EDX was operated by Aztec version 2.0 software for chemical composition analysis (Elakneswaran et al. 2019; Pan et al. 2018).

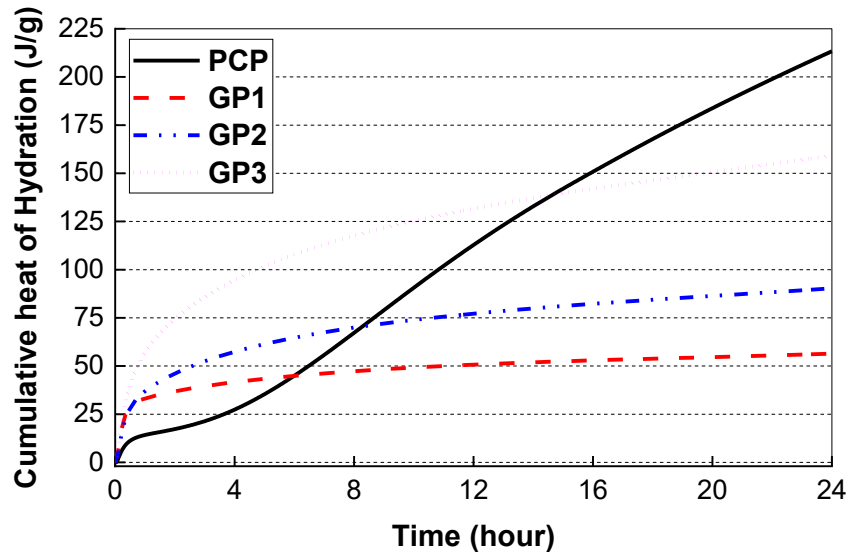
3.3 Hydration heat

Figures. 3.3 (a) and (b) displays the rates of heat generation curves and the cumulative heat of hydration curves of GP and PCP paste, respectively. It can be seen from Figure. 3.3 (a) that GGBFS can accelerate the hydration reaction of GP displaying a higher rate of heat generation and GP3 with 40% GGBFS

has the highest heat generation rate among all mixes indicating that GGBFS reaction with the alkali is faster than that only with fly ash. The rate of heat generation of all GP samples is higher than that of PCP, which may be related to the fact that alkali can accelerate the hydration reaction in an early age. However, the PCP mix presents the most massive cumulative heat of hydration in 24 hr compared with other GP mixes, as shown in Figure 3.3. (b) GP3 with 40% GGBFS has the most significant cumulative heat of hydration among all GP mixes but is still lower than that of PCP. The GP mixes are usually cured at high temperature while the heat evolution is tested at 20 °C. Thus, the cumulative heat of hydration of all GP mixes is lower than the PCP mix, which indicates that the GP samples need to be cured at a high temperature at an early age.



(a) Rate of generation



(b) Cumulative heat of hydration

Figure 3.3. Rate of heat generation and cumulative heat of hydration curve of GP and PCP pastes in 24 hrs

3.4 Residual compressive strength

The compressive strengths of PCM and GSM under all circumstances are shown in Table 3.3. Figure 3.4 (a) displays the percentage change in compressive strength for the PCM and GSM with preloading before and after exposure to high temperature. At 23 °C, the percentage change is the relative ratio of residual compressive strength after preloading to UCS. After being exposed to high temperature, the percentage change is the relative ratio of residual compressive strength after exposure to a high temperature to residual compressive strength after preloading. The positive values indicate a strength increase and the negative values indicate a strength loss. It can be seen from Table 3.3 that GSM3 with 40% GGBFS achieved the maximum compressive strength among all mixes, while GSM1 only with fly ash has the lowest compressive strength. The compressive strength of PCM is only lower than that of GSM3 and slightly higher than that of GSM2. The compressive strength of GSM1 is quiet low and inapplicable for practical application, which is probably related to the chemical composition and

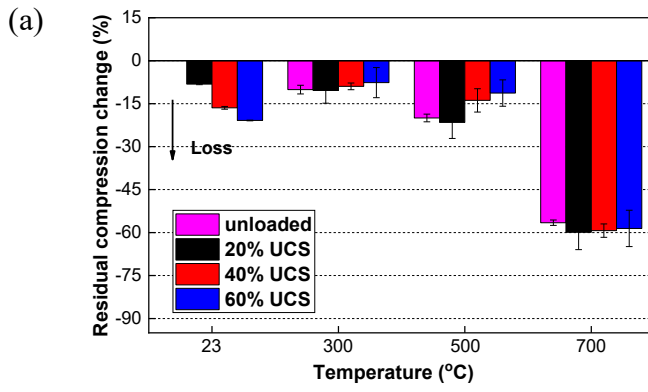
fineness of the fly ash (Pan et al. 2009). This study will mainly focus on the effect of GGBFS on the performance of GSM and the comparison among the mixes with equivalent compressive strength (PCM, GSM2, and GSM3).

Table 3.3 Compressive strength of PCM and GSM under different circumstances (MPa)

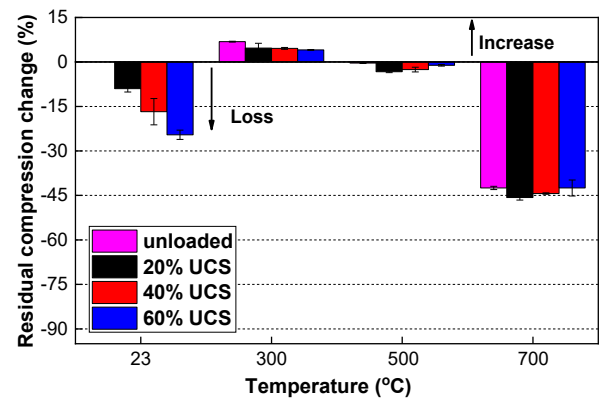
Types	Before preloading	After preloading				After exposure										
						300 °C				500 °C				700 °C		
		20%	40%	60%	unloaded	20%	40%	60%	unloaded	20%	40%	60%	unloaded	20%	40%	60%
PCM	27.40	25.16	22.89	21.68	24.63	22.54	20.84	20.02	21.92	19.74	19.72	19.23	11.90	10.09	9.31	8.99
GSM1	8.10	7.37	6.74	6.11	8.66	7.72	7.05	6.36	8.07	7.13	6.57	6.04	4.66	4.00	3.75	3.51
GSM2	26.5	21.38	16.57	14.01	28.51	22.41	17.31	14.60	23.19	17.36	13.53	11.44	8.85	6.61	5.16	4.58
GSM3	34.11	27.09	20.77	17.38	34.99	27.51	20.96	17.52	19.71	13.36	10.99	9.85	5.31	2.87	2.58	2.40

As can be seen from Figure 3.4 (a), the residual compressive strengths of both GSM and PCM gradually reduce as the preloading level is increased at the temperature of 23 °C. The compressive strength loss of GSM for the same preloading level is more significant than that of PCM and is also increased as the GGBFS content is increased. The strength loss of GSM3 caused by preloading is the highest among all mixes, especially for the sample loaded up to 60% UCS with nearly 50% strength loss. Although the additional GGBFS enhances the strength of GSM, it also causes a higher strength loss at an increased preloading level. This could be related to the fact that the higher curing temperature and GGBFS content in GSM lead to a high rate of hydration reaction but a more weak interface in GSM than that of in PCM (Puligilla & Mondal 2013). After being exposed to high temperature, it can be observed from Figure 3.4 (a) that there is a strength increase only for GSM after being exposed to 300 °C, while the compressive strength of PCM decreases for all circumstances. The unloaded GSM mixtures have a higher strength increase at 300 °C and a lower strength loss at 500 °C and 700 °C compared to that of GSM suffered from preloading. The evaporation of free and combined water in PCM mortar after heated at high temperature may be the main reason for strength loss of PCM, compared with a strength increase of GSM2 and GSM3 at 300 °C due to the on-going reaction in GSM (Lee et al. 2014). The strength loss of unloaded PCM is lower than that of PCM with 20% UCS but higher than that of PCM with 40 and 60% UCS at 300 and 500 °C, respectively. When the temperature reaches 700 °C, the strength loss of PCM unloaded is lower than those of all other PCMs with different preloading levels. At 300 °C, the percentage of compressive strength gain of GSM with preloading gradually reduced as both GGBFS content and preloading level increased. At 500 °C and 700 °C, the compressive strength loss for GSM with preloading increased as both GGBFS content and preloading level increased. The percentage of residual compressive strength loss of GSM3-60-700 is nearly 90%, compared to 70% for GSM2-60-700. The percentage of compressive strength loss for PCM after preloading gradually reduced as the preloading level increased at all exposure temperatures.

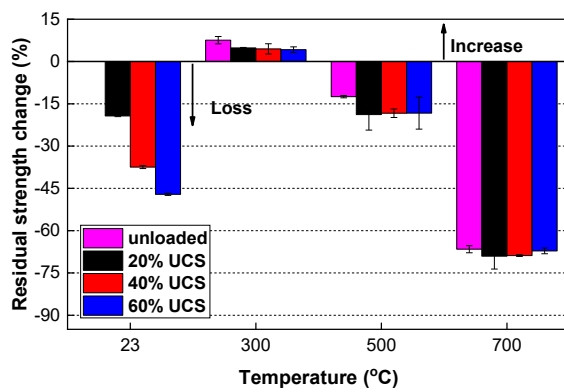
Figure 3.4 (b) illustrates the compressive strength change of PCM and GSM caused by preloading or high temperature. The percentage of compressive strength change is calculated as the relative ratio of residual compressive strength change after preloading or heating to UCS. A negative value represents a strength increase. It can be seen from Figure 3.4 (b) that the residual strength percentages of both PCM and GSM decreased as the preloading level, and high temperature were simultaneously increased. At 300 °C, the percentage of residual strength with preloading PCM below GSM2, but higher than GSM3. At 500 °C and 700 °C, the residual strength percentage of PCM with preloading is higher than those of all GSM specimens. The main reasons for these results are different GGBFS content and curing conditions between PCM and GSM. Although there is higher strength loss for unloaded PCM after exposure to high temperature than that PCM after preloading, after the same high temperature exposure, the residual strength of unloaded PCM is higher than those of PCM after preloading. The residual strength of PCM after the same temperature exposure decreased as the preloading level was increased, and the residual strength of PCM after the same preloading level also decreased as the exposure temperature increased. At the temperature of 700 °C, PCM-60-700 showed the lowest residual strength, with only 32.8% UCS among all other PCM specimens. The strength increase of GSM at 300 °C and residual strength of GSM with the same preloading level at 500 and 700 °C decreased as the GGBFS content increased. The combined high preloading level and high exposure temperature indeed cause more serious damage to the GSM specimens than those of only suffered to preloading or high temperature exposure. At a temperature of 700 °C, GSM3-60-700 showed the lowest residual strength, with only 7.0% UCS among the other GSM specimens.



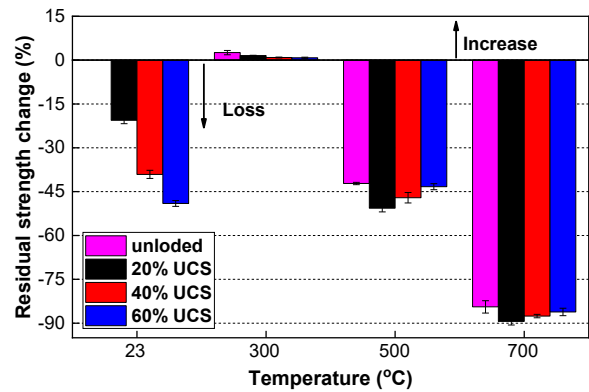
(a1) PCM



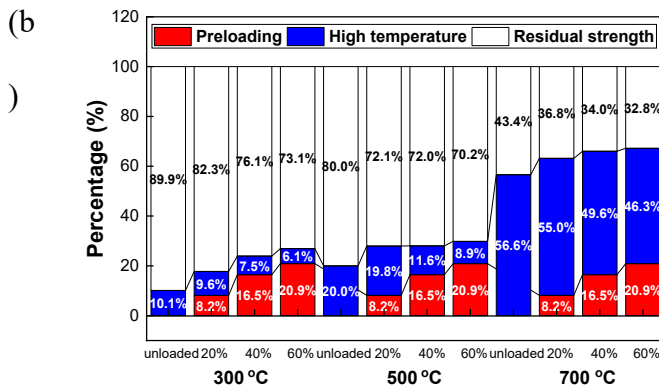
(a2) GSM1



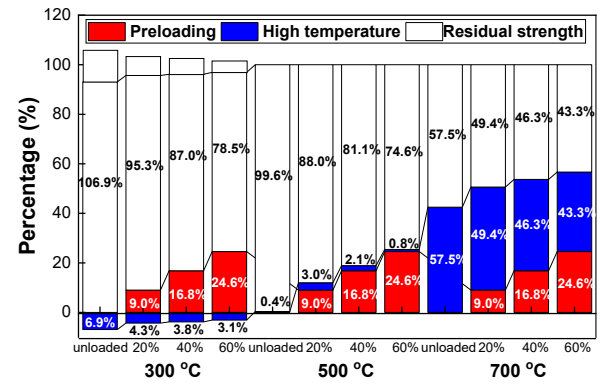
(a3) GSM2



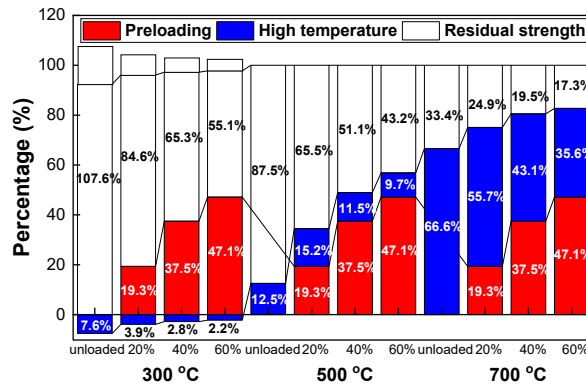
(a4) GSM3



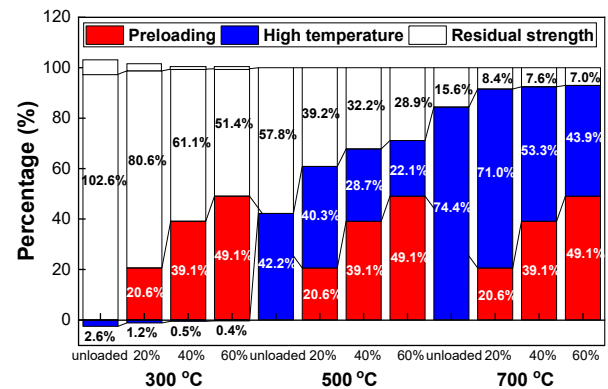
(b1) PCM



(b2) GSM1



(b3) GSM2



(b4) GSM3

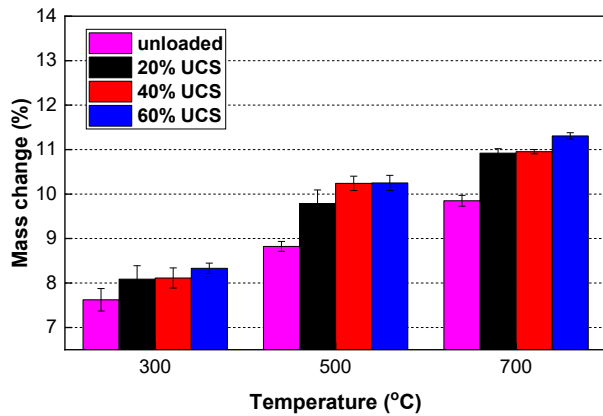
Figure 3.4. Compressive strength change percentage of PCM and GSM mortars. (a) After being exposed to high temperature; (b) Caused by preloading or high temperature.

3.5 Physical properties

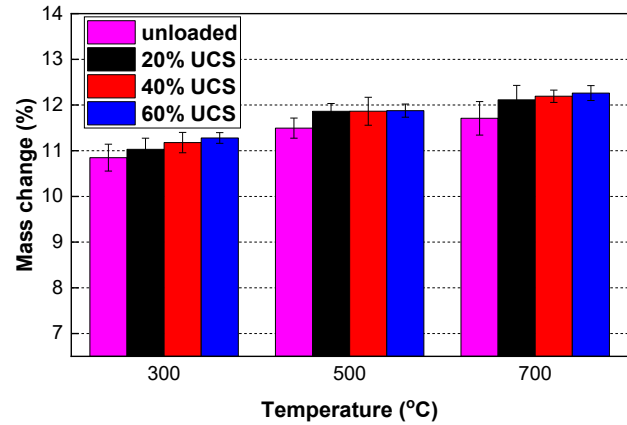
3.5.1 Mass change

Figure 3.5 shows the mass change of all mortar specimens with preloading before and after exposure to temperatures of 300, 500, and 700 °C, in which the positive values indicate a mass loss. Each data displayed in Figure 3.5 was the average of calculations from three specimens. It can be observed that the mass loss of all mixes after the same preloading level is more indubitable as the temperature increases, especially in GSM3 (9.6 to 13.6%). The mass loss of both PCM and GSM exposed to the same temperature also increases with increasing preloading level. In addition, the mass loss of PCM at the same temperature and preloading level is lower than those of GSM mixes. The mass loss of PCM mixture preloaded with 60% UCS at 300, 500, and 700 °C was 8.08, 9.78, and 10.92%, respectively, while the GSM3 mix preloaded with 20% UCS in Figure. 5 (d), having the lowest mass loss among all GSM mixes with preloading, has a mass loss of 10.00, 11.06, and 12.01% after exposure to elevated temperature, respectively. For GSM specimens with GGBFS, GP3-60-700 in Figure. 5 (d) has the most extensive mass loss of 13.57% among all mixes. In general, elevated temperature has less effect on the

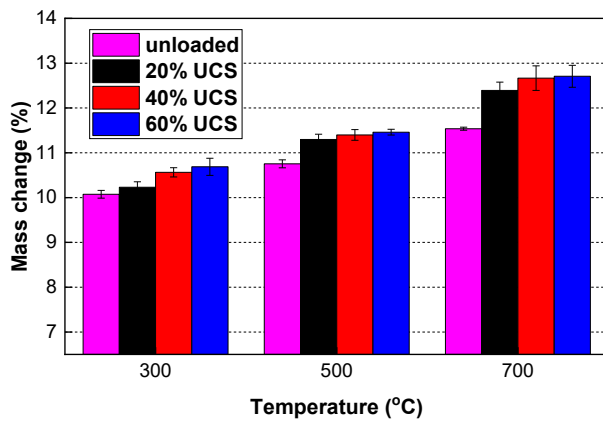
mass loss of PCM mix than GSM with GGBFS, and the mass loss of GSM seems to significantly increase when increasing GGBFS content. The mass loss of all mixes with high preloading levels becomes greater as temperature increases, and internal cracks are widening. Besides, the chemical composition of GGBFS may govern the high mass loss observed in GSM compared to that of PCM.



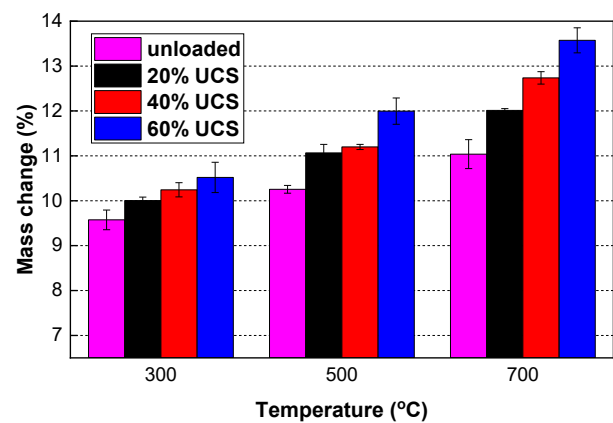
(a) PCM



(b) GSM1



(c) GSM2



(d) GSM3

Figure 3.5. Effects of preloading on mass changes of mortars after temperature exposure

3.5.2 Volume change

Figure 3.6 displays the volume change of the PCM and GSM with preloading after exposure to temperatures of 300, 500, and 700 °C, in which positive values indicate a volume expansion, and

negative values represent shrinkage. Each data point displayed in Figure 3.6 was the average of calculations from 3 specimens. For both PCM and GSM mortars, shrinkage could be observed after being exposed to a lower temperature (300 °C and 500 °C), while an expansion appeared after being exposed to 700 °C. When the temperature is from 300 °C to 500 °C, there is a decreased shrinkage of the PCM, GSM1, and GSM2 mixes compared to an increased shrinkage of GSM3 mix. Overall, there is a small increase in volume change for PCM and GSM mortars exposed to the same temperature after suffered from the increased preloading level. The volume change of the PCM mix is the lowest among all mixes for both shrinkage and expansion. For GSM, its volume change can be significantly influenced by increasing GGBFS content. GSM1 mix with only fly ash showed higher shrinkage at 300 °C while showing lower shrinkage and expansion at 500 °C and 700 °C, respectively, compared to GSM only with GGBFS. There is a lower volume change at 300 °C for GSM with GGBFS than with fly ash but higher volume shrinkage of GSM3 at 500 °C. In addition, the increasing GGBFS content in GSM leads to an expansion increase at 700 °C, in particular, the GSM3-60-700 presented the maximum expansion among all mixtures. All mixes at the temperature of 300 or 500 °C shrink mainly due to the water evaporation. However, expansion is observed at a temperature of 700 °C, together with the appearance of large holes in the matrix. In addition, the increase in the preloading level makes all mixes more sensitive to the high temperature, resulting in a greater shrinkage or expansion.

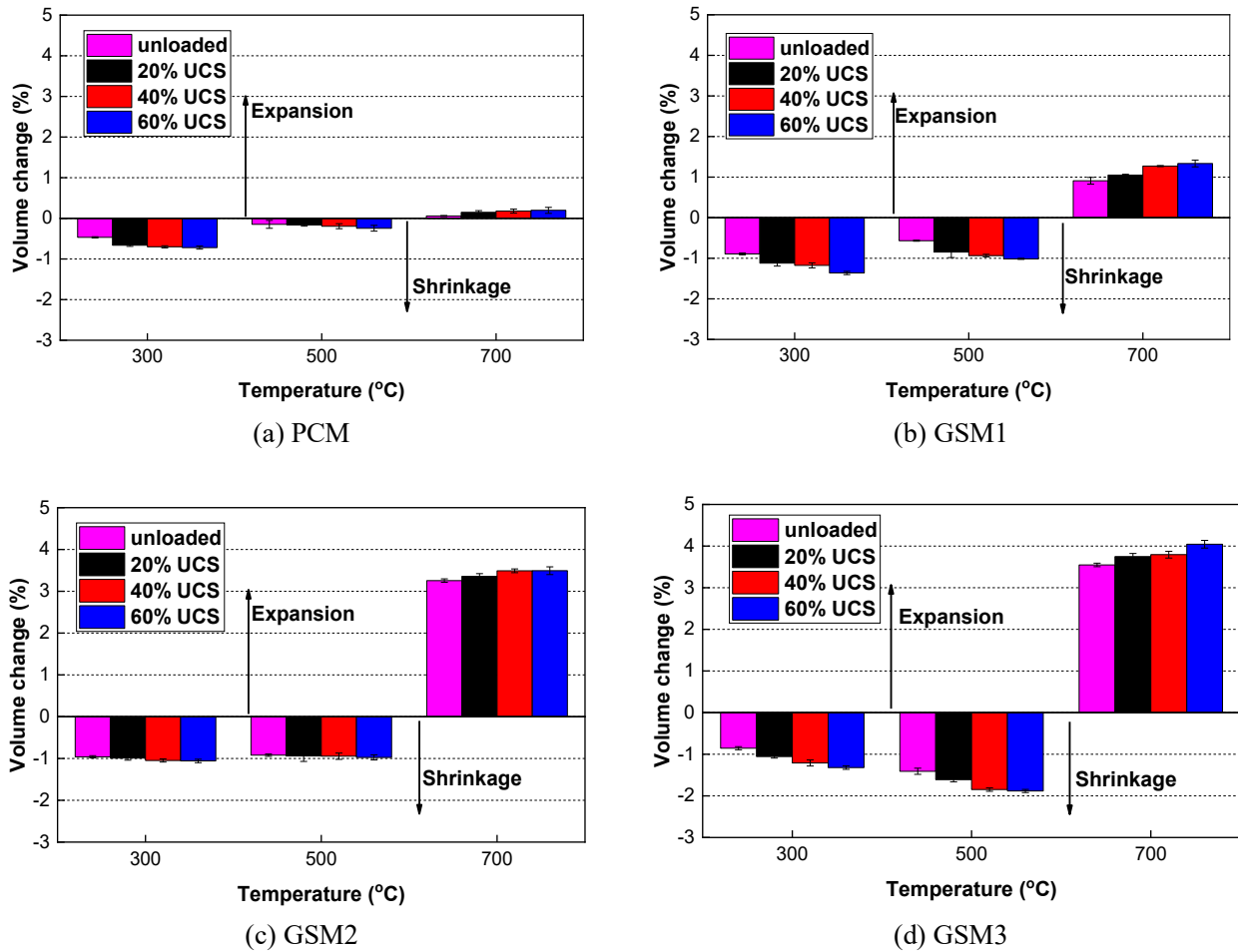


Figure 3.6. Effects of preloading on volume changes of mortars after temperature exposure

3.5.3 Visual appearance

Figure 3.7 shows the visual appearance change of the mortar specimens before and after being heated at high temperatures of 300, 500, and 700 °C. The specimens after preloading at different percentages of UCS did not show apparent changes in visual appearance. It can be seen from Figure 3.7 that there are apparent changes after being exposed to elevated temperature, including color change, cracks, and other surface damage. Before exposure, many small bubbles were observed on the surface of GSM1, and as GGBFS content (e.g., GSM3) increased, the number of bubbles on the surface of GSM decreased, leaving no bubbles on the surface. For PCM, there are some big air bubbles on the surface. When the temperature is 300°C, the surface color of PCM and GSM changes significantly relative to

the ambient temperature. The color of the surface of PCM and GSM changed from dark to light. When the temperature reached 300 to 500 °C, the color of the surface of the PCM and GSM became lighter than the original ones, and finally turned to pale yellow partially. When the temperature reached 700 °C, some cracks became visible. GSM3 containing 40% GGBFS exhibited obvious surface cracking compared to other geopolymer mortars and PCM.

When the heating temperature is 300 °C, there is no crack visible on the exterior of the specimens; when the temperature reaches 500 °C, fine cracks begin to appear on the exterior of the specimens; as the temperature increases, the number of cracks and crack width gradually increase. When the temperature reached up to 700 °C, the surface severely cracked, and the largest crack width reaches about 0.2 mm. Some connected cracks even cause specimen disruption. In general, the development of surface cracks in PCM and GSM specimens after exposure to high temperature is mainly caused by the following reasons: firstly, the evaporation of water inside the GSM causes some micro-cracks on the surface; secondly, the decomposition of internal components; and finally, during the high temperature heating process, the internal sand of the GSM expands, while the gelled material shrinks, leading to incompatible deformation between them.

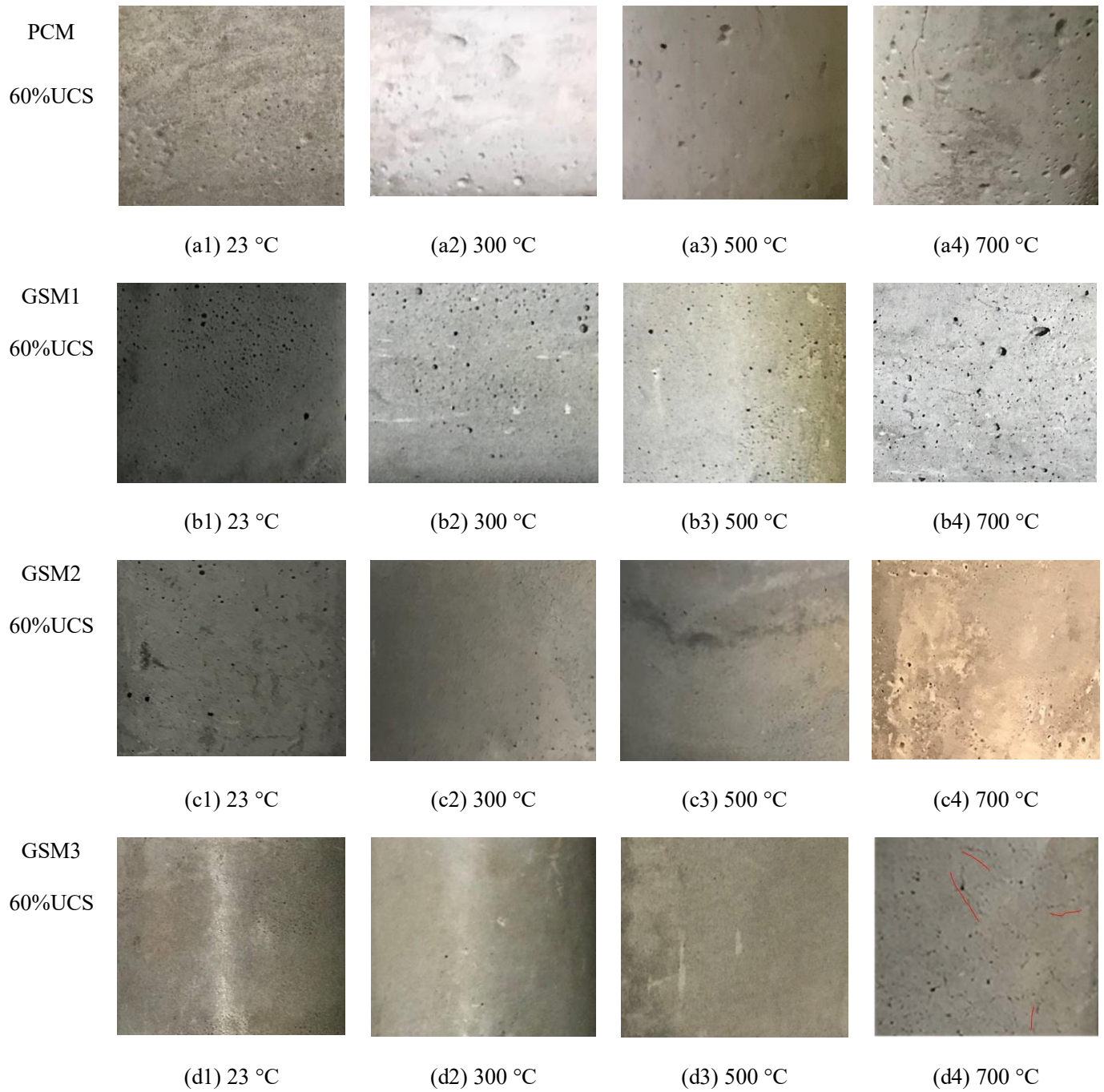


Figure 3.7. Cracking behavior of PCM and GSM at various elevated temperatures

3.6 Microstructural characterization

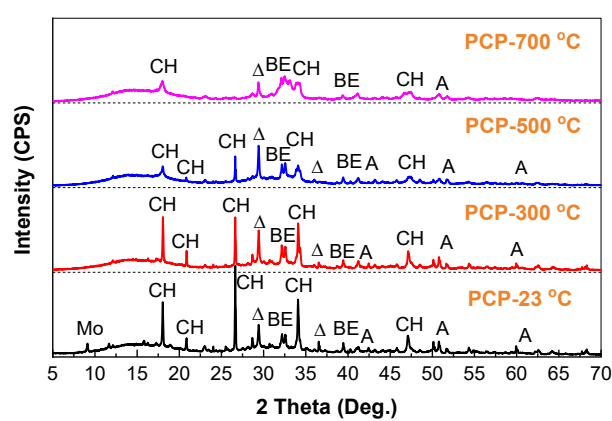
3.6.1 X-ray diffraction

Figure 3.8 (a) shows the XRD results of PCP pastes before and after exposure to high temperatures. In PCP paste samples, a reduction in the intensity of the CH peak (mainly around 18.0° , 26.6° and 34.1° 2θ , PDF00-41-1451) and calcium silicate hydrate (C-S-H) peak (around 29.4° 2θ , PDF00-33-0306) are observed after exposure to high temperature. The intensity of the CH and C-S-H peak also decreased as the temperature increased with no detected CH around the peak 26.6° 2θ at the temperature of 700°C . This is mainly due to the chemical deteriorations occurring at high temperatures where both chemically bound and intercalated water are lost with the decomposition or dehydration of CH and C-S-H, accounting governing the strength loss of PCM with the increasing exposure temperature. For GP1 paste samples with no GGBFS, as shown in Figure 3.8 (b), peaks of quartz (SiO_2 , PDF #00-046-1045) at 20.8° , 26.5° , 42.5° , and 50.2° 2θ , and mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$, PDF #00-15-0776) at 16.4° , 26.6° , 33.2° , 35.2° , 42.6° and 60.7° 2θ have been identified. These phases are expressed as the result of embedded unreacted fly ash particles (Lloyd et al. 2009) and are also detected in raw fly ash (Figure 3.1). Quartz and mullite are presented in GP1 at all temperatures, suggesting that high temperature exposure has little effect on these phases. No hydrotalcite-like crystalline phase formation was examined in the GP1 paste. The intensity of the peak of mullite at 26.6° is the most extensive for the 100% fly ash mixtures (GP1) than GP2 and GP3, which slightly decreases after being exposed to elevated temperature. The mini reduction of mullite is possibly related to the on-going reaction of SiO_2 .

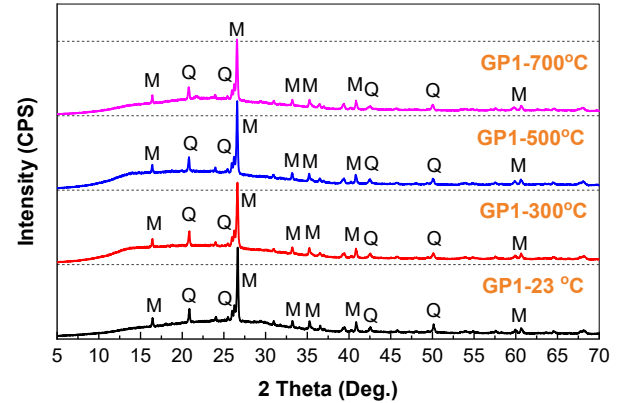
In the GP with GGBFS, various crystalline phases are observed. The fly ash/GGBFS ratio plays an important role in the appearance of these phases. For GP2 paste samples with 20% GGBFS (Figure 3.8 (c)), peaks of quartz (SiO_2) at 20.8° , 26.6° , 42.6° and 50.2° 2θ , and mullite) at 16.4° , 26.5° , 33.2° , 35.2° , 42.5° and 60.7° 2θ have been identified. The main intensity at 26.6° 2θ for GP2 is quartz, compared with the mullite for GP1. The phase changes are due to the embedded unreacted GGBFS particles. Quartz and mullite exist in GP1 and GP2 for all the exposure temperatures, suggesting that

high temperature exposure has a bare impact on these phases. In general, the X-ray diffractograms of GP1 with 100% fly ash and GP2 with 20% GGBFS are relatively similar but distinct with the results of GP3. No C-S-H peak has been found in GP1 and GP2. No new crystalline reaction product formation has been determined. This reveals that the incorporation of fly ash changes the reaction kinetics in the geopolymer matrix with GGBFS. The formation of C-S-H may be delayed when the utilization ratio of Ca^{2+} decreases due to lower GGBFS content. Calcium aluminum silicate hydrate (C-A-S-H) gel will be formed by replacing the silicon with aluminum in the bridge (Puertas et al. 2011). N-(C)-A-S-H is a hybrid of C-A-S-H gel, which is formed in GGBFS systems (Puertas et al. 2011) and N-A-S-H gel, which is formed in fly ash geopolymer systems (Lee et al. 2014).

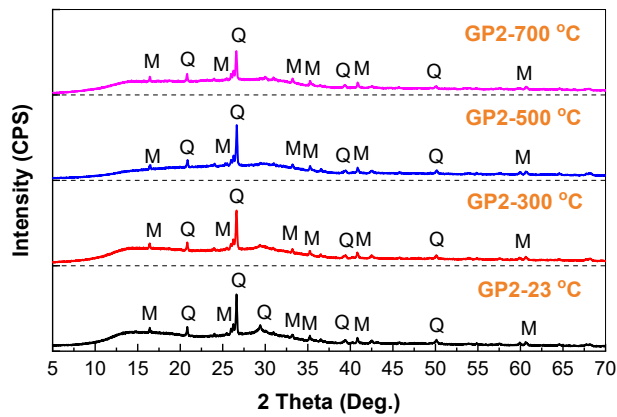
In terms of GP3 with 40% GGBFS, a small intensity peak centered at a 2θ angle approximately 26.3° is determined in Figure 3.8 (d), indicating the poorly crystalline C-S-H gel, together with traces of calcite at a 2θ angle around 33.5° . The elevated temperature exposure has a significant effect on microstructural development. When GP3 samples were heated to 300°C , a considerable increase in the intensity of the peak at $26.3^\circ 2\theta$ is examined. When the exposure temperature rose to 500°C or 700°C , the peak intensity of $26.3^\circ 2\theta$ was significantly reduced. The samples mainly produce some new C-S-H by hydration reactions around 300°C , confirming that GSM strength has increased in intensity at 300°C . No crystalline phase formation of zeolite and hydrotalcite was detected in the GP3. At 500°C and 700°C , the XRD patterns of GP3 are very comparable to those at ambient temperatures, except that the peak strength at 700°C is somewhat reduced ($26.6^\circ 2\theta$). The peak value of quartz drops sharply because of the high temperature sintering reaction consuming a large amount of SiO_2 . This is different from the central peak observed in GP3 samples, where the strength of the principal peak is different. This discrepancy again demonstrates that the properties and structures of the primary binding phases in GP2 with 20% GGBFS and GP3 with 40% GBFS are different.



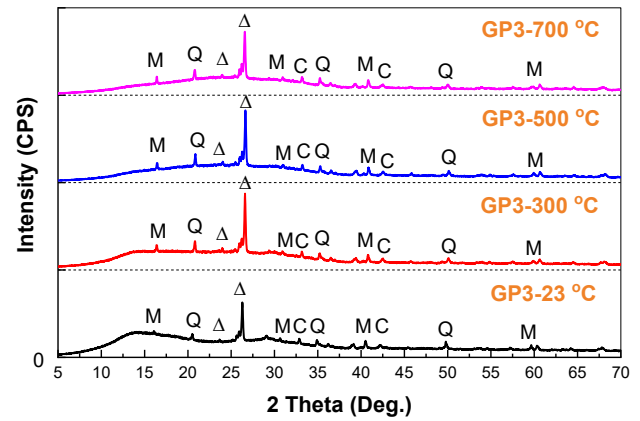
(a) PCP



(b) GP1



(c) GP2



(d) GP3

(A – Alite, BE – Belite, BR – Brownmillerite, C – Calcite, CH – $\text{Ca}(\text{OH})_2$, Δ – C-S-H, M – Mullite, Mo – Monosulfate, Q – Quartz)

Figure 3.8. XRD patterns of fly ash/GGBFS geopolymer and PCP pastes before and after exposure to high temperature

3.6.2 Thermogravimetric analysis

Figure 3.9 displays the TG and DTG curves for the GP and PCP pastes before and after being exposed to high temperatures. The high exposure temperature (at 23, 300, 500 and 700 °C) represents the fire simulated temperature and the heating temperature represents (up to 1000 °C) the thermogravimetric temperature in this part. It can be seen from the DTG curve at 23 °C that an endothermic peak in GP

pastes observed between 50 and 200 °C (Haha et al. 2012), which is attributable to the loss of moisture in the sample and the combined water in the aluminosilicates (N-A-S-H or C-A-S-H gel) confirmed to occur at around 100 °C (Fernández - Jiménez et al. 2008). The DTG curve of PCP at 23 °C shows three main peaks. The first peak is possibly attributed to the loss of free water (heating from 50 to 110 °C), the partial dehydration of C-S-H (heating from 85 to 90 °C), and the decomposition of ettringite (heating from 114 °C to 116 °C), the three of which are usually overlapped. The second peak, located at approximately 400 °C to 450 °C, is related to the decomposition of CH. The third peak (between 650 and 750 °C) mainly corresponds to the hydrated calcium silicate. After the samples were exposed to high temperature, it can be seen from the DTG curve that a small endothermic peak in GP pastes was observed between 50 °C and 70 °C and the peaks related to the decomposition CH and hydrated calcium silicate were also found in the PCP paste, which indicates that the high exposure temperature indeed has an influence on the loss of evaporable water for all mixes.

It can also be seen from the TG curve that all GP pastes before or after being exposed to high temperature have no obvious mass losses after heating around 300 °C, indicating that the decomposition component is mainly composed of amorphous gel and water that is physically and chemically combined (Gao et al. 2015). The massive mass loss for all GP pastes arises at about 100 °C, in part as the result of the evaporation of free water heated to under 100 °C (Shearer et al. 2016), which is believed to have been wholly removed heated at 120 °C (Alarcon-Ruiz et al. 2005). The final mass loss of all GP pastes at 23 °C ranges from 12% and 24% after heating to 1000 °C. Among all GP pastes, the final mass loss of GP1 is the highest at 23 °C but become the lowest after being exposed to high temperature. The final mass loss of both GP samples and PCP in different exposure temperatures reduced as the exposure temperature increased. The increasing exposure temperature has little effect on the final mass loss of GP1, especially at 500 and 700 °C. The mass loss of both GP2 and GP3 increased with increasing exposure temperature, which is consistent with the mass change of GSM2 and GSM3 mortar mixes. The GP specimens with high GGBFS content are more sensitive to high

temperature exposure, displaying a higher mass loss at all exposure temperatures. The mass loss of PCP paste also increased with increasing exposure temperature, and the mass loss of PCP paste after being heated at 700 °C is higher than those of all GP samples, which is consistent with the low mass change of PCM at 700 °C shown in Figure 3.5(a).

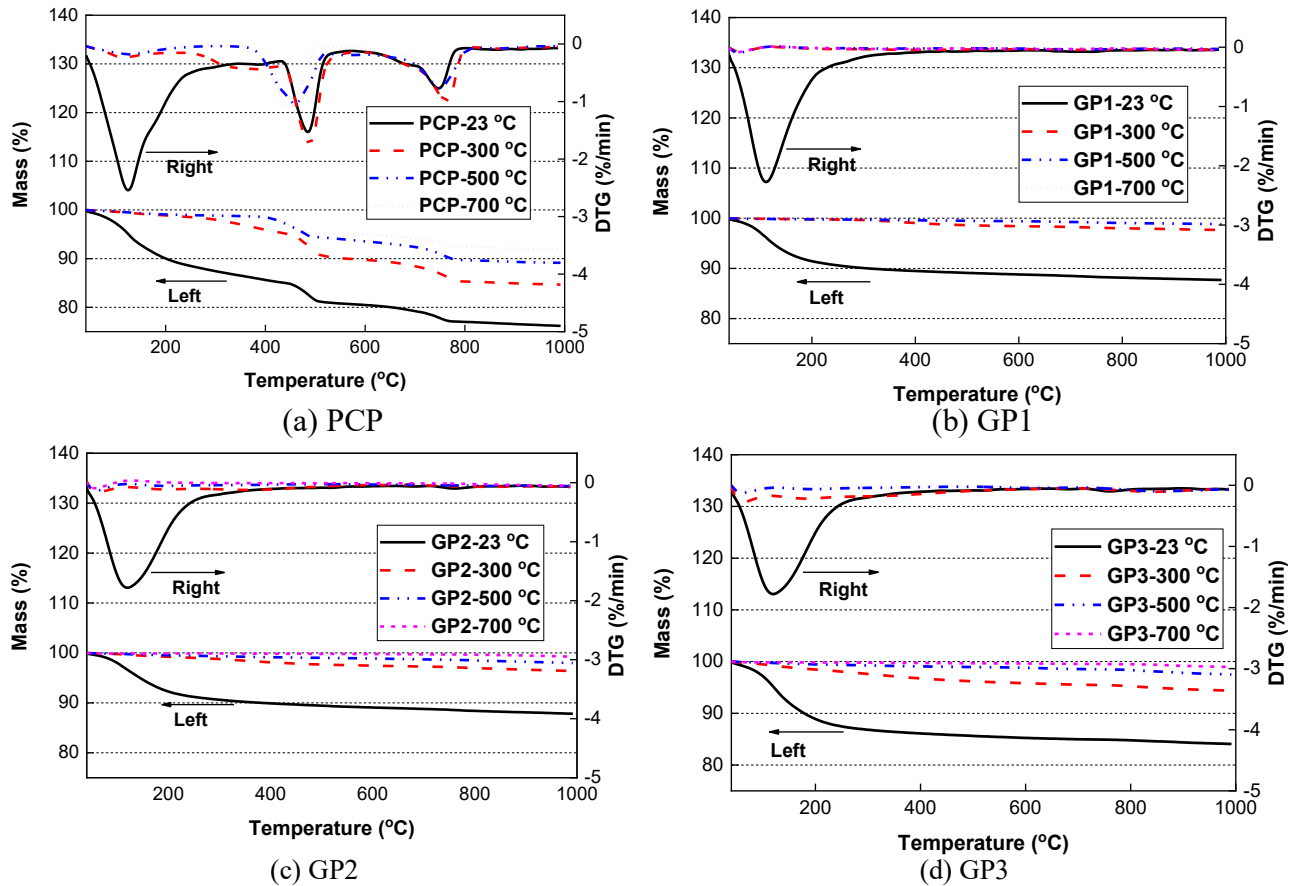


Figure 3.9. Thermogravimetric and derivative thermogravimetry curve of GP and PCP pastes before and after exposure to 300, 500 and 700 °C

3.6.3 SEM with energy dispersive X-ray (EDX) analysis

For the effect of preloading, though there are no obvious changes in the visual appearance of the samples after being preloaded with different percentages of UCS in Figure 3.7, there are indeed some changes in the microstructure of the PCM and GSM. The effects of the preloading level on the microstructure of GSM3 with 40% GGBFS are presented in Figure 3.10. In general, GSM3 samples

before preloading (Figure 3.10 (a)) have relatively small marginal microcracks. As the preloading level increased, obvious microcracks appeared in the samples, especially when the pressure reached 60% of UCS, larger microcracks were found than under lower preloading. Cracks mainly occurred in the transition zone between sand and hydration products. The higher the applied load, the more microcracks are, accounting for the decreasing residual compressive strength after preloading (Figure 3.7).

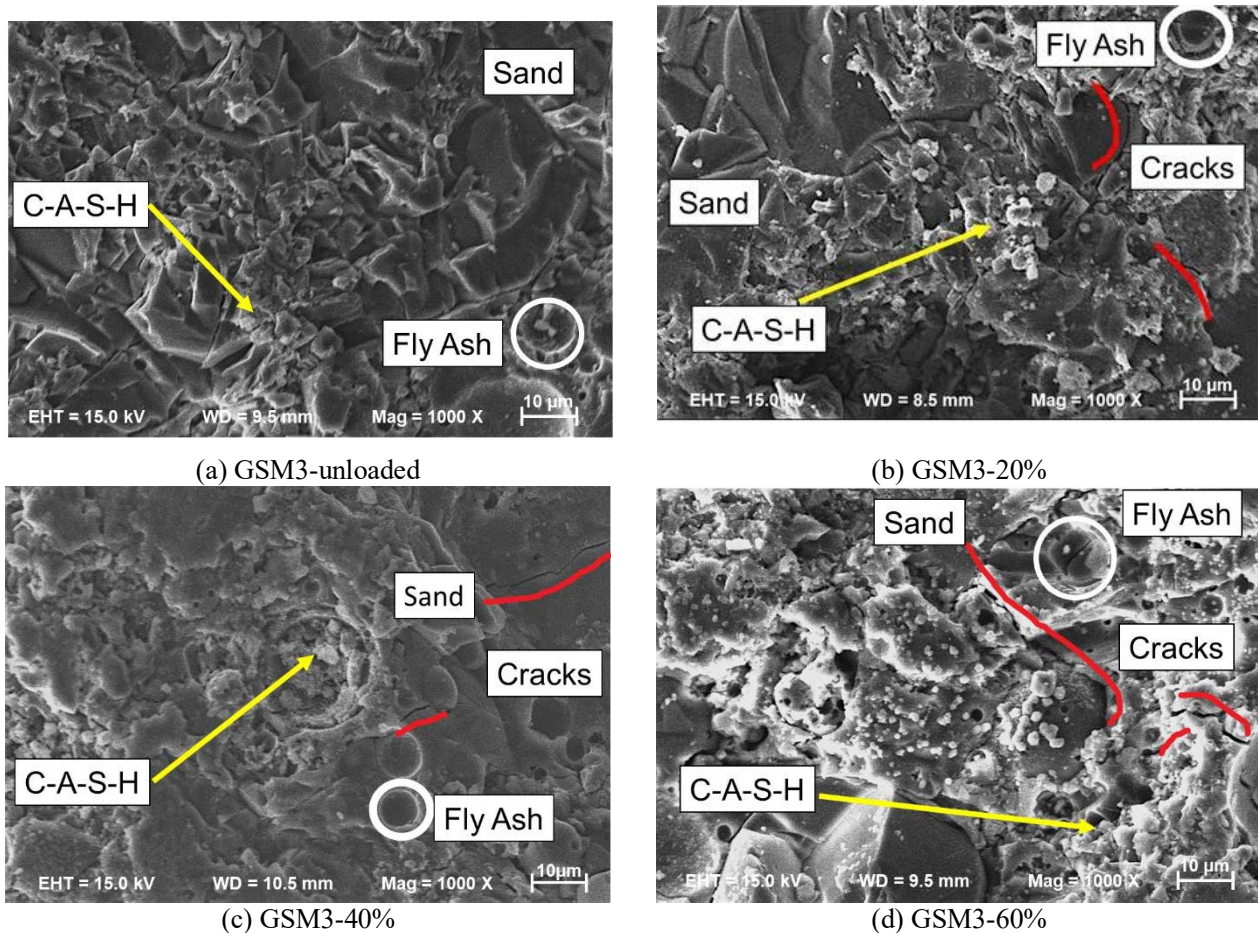


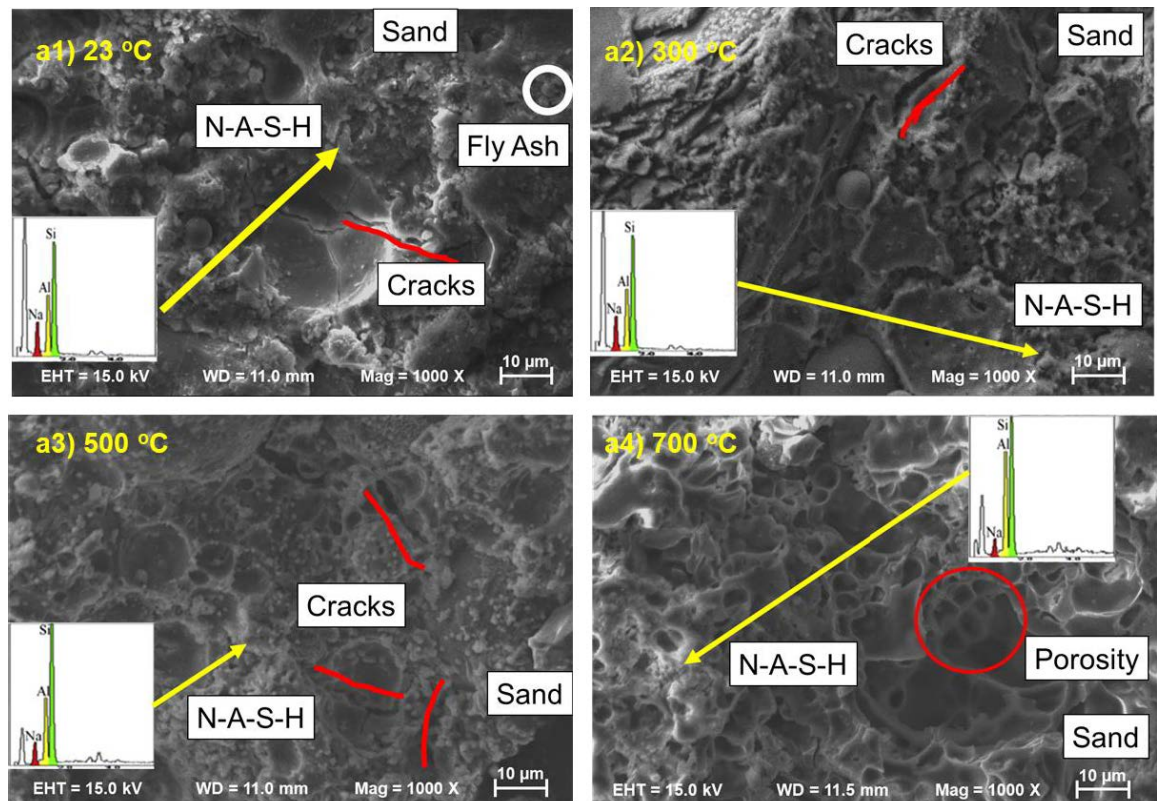
Figure 3.10. SEM images of GSM3 mortars before and after being preloaded

In addition, for the effect of GGBFS content, as it can be seen from the SEM images with EDX results of GSM shown in Figures 3.11 (a1), (b1) and (c1), tomography of GSM3 with 40% GGBFS show crystallized hexagonal plates with high Al content, as identified by the EDX result, while GSM1 and GSM2 pastes exhibit amorphous morphology. The thinly scattered holes are randomly spread in GSM1

and GSM2. Unreacted fly ash and GGBFS particles are embedded in the matrix of GSM2. However, the binder phases in GSM2 mortar appear to adhere to the surface of the unreacted particles loosely. Many voids are observed in the whole paste of GSM1 with only fly ash. Some voids are dispersed in the matrix, while others are examined on the exterior of unreacted fly ash particles. This is a representative microstructural characteristic observed in the GSM1 binder. The minor discrepancy between GSM2 and GSM1 is that sharp-cornered particles (GGBFS) are embedded in GSM2 matrix. In GSM1, just spheric particles (fly ash) are embedded in the matrix, which indicates that geopolymerization has not been completed.

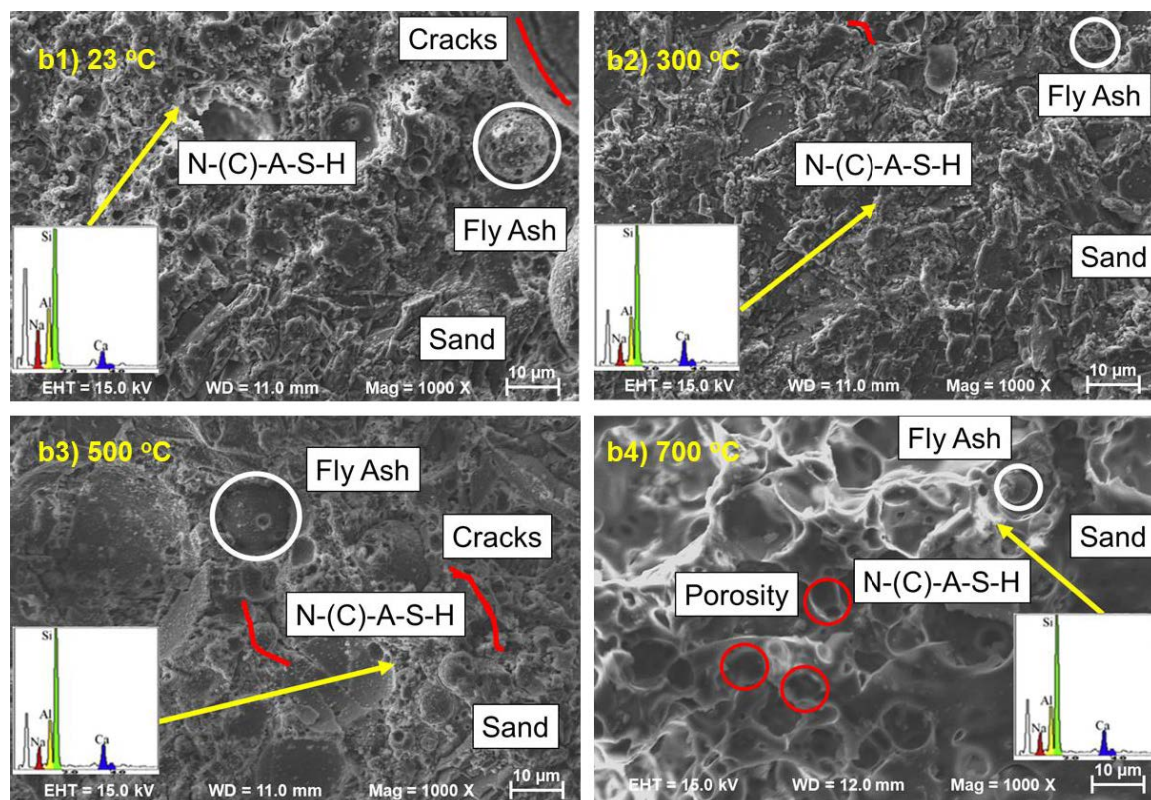
(a)GSM

1-60%



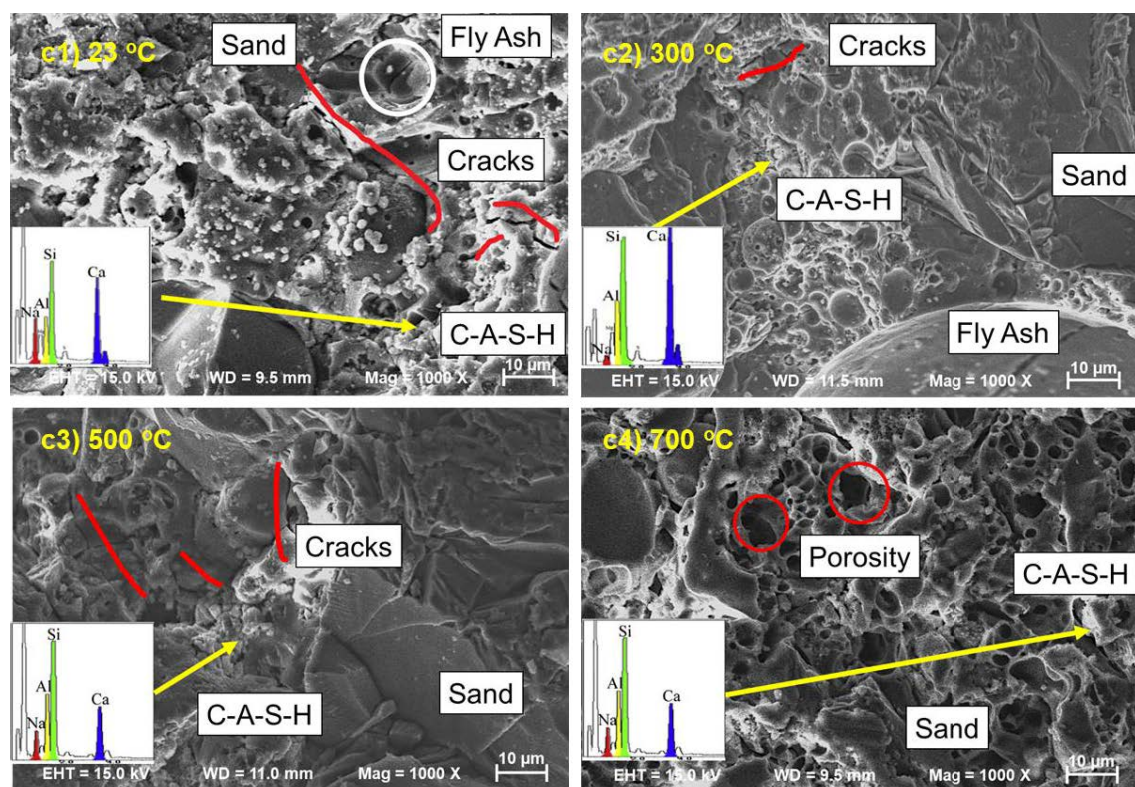
(b)GSM

2-60%



(c)GSM

3-60%



(d)PCM-
60%

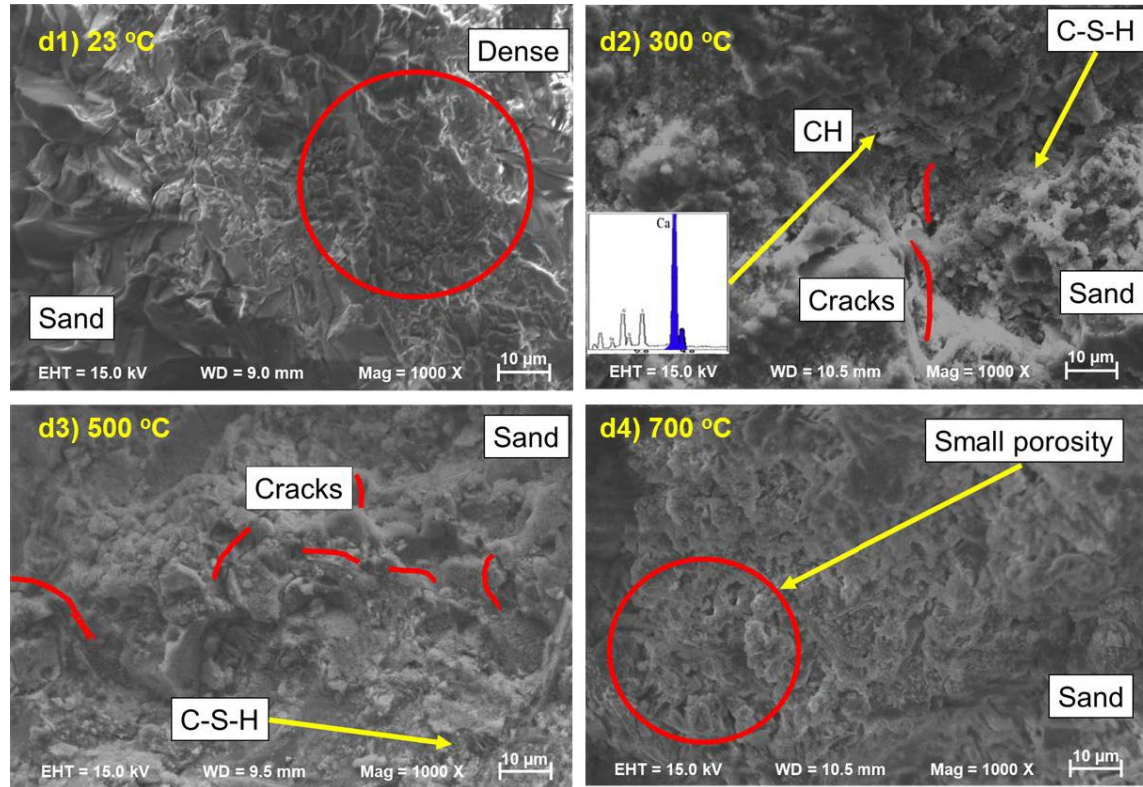


Figure 3.11. SEM images with EDX results of GSMs and PCM mortar with 60%

USC induced damage before and after exposure

For the effect of elevated temperature, the SEM images of all mixes preloaded with 60% USC before and after exposure to different high temperatures are shown in Figures 3.11 (a) to (d). In GSM1 and GSM2 exposed to a temperature ranging from 23 to 300 °C (Figures 3.11 (a2) and (b2)), a decrease in the amount of residual particles is observed, indicating that fly ash is active during heat exposure. As a result, the matrixes of GSM1 and GSM2 at 300 °C are more homogeneous than at ambient temperature or 500 and 700 °C. The microstructure of GSM3 seems to show no change from 23 to 300 °C. At 500 °C, more discontinuous cracks were found in the whole matrix of all THE GSM samples. The gels, including C-A-S-H, N-(C)-A-S-H, or N-A-S-H in the matrix of GSM, can be detected in all exposure temperatures. The formation of a three-dimensional gel, a network $[Q^4(Al)]$ made up of alternating SiO_4 and AlO_4 tetrahedra connected by shared O atoms (Li et al. 2010), accounts for no

change of gels in the matrix. At 700 °C, a few residual GGBFS particles are loosely embedded into the matrix of GSM3 with 40% GGBFS. Pores can be examined in the matrix of all GSM samples and the interface between the matrix and particles. The exposure to 700 °C resulted in significant changes in morphology for both PCM and GSM. In GSM1, GSM2, and GSM3 samples, the high temperature exposure led to an enlargement in porosity. At 700 °C, the aggregation of cracks resulted in major cracks that almost propagate through the whole matrix.

In the PCM samples, the microstructure is relatively more compact than those of GSM after preloaded with 60% UCS as shown in Figure 3.11 (d1). The Ca(OH)_2 is easily detected in the PCM sample under room temperature and can also be detected at 300 °C. However, it is difficult to detect Ca(OH)_2 after exposure to 500 and 700 °C. C-S-H in the PCM matrix is also almost undetectable when exposed to 700 °C, which may be due to decomposition at 700 °C. In addition, there is much less porosity in PCM after exposure to 700 °C than that in GSM3, though the microstructure of PCM at 700 °C is more uncompacted than that of GSM3 observed at 300 and 500 °C.

3.7 General discussions

The mechanism of fire resistivity after load-induced damage is drawn schematically for GSM and PCM mixes in Figure 3.12. In all three mixes (GSM1, GSM2, and GSM3), the mechanism of fire attack seems to be comparable and in contrast to that of PCM. Before exposure to high temperature, GSM2 and GSM3 show a basic network formation due to the formation of an aluminosilicate-like geopolymer at a very early age, showing a higher rate of heat generation and cumulative heat (Figure 3.3) and an increase in compressive strength (Puligilla & Mondal 2013). Besides, the curing temperature of 70 °C can accelerate the hydration reaction, which may cause uneven heating, leading to the formation of heterogeneous products and the generation of the weak interface. In addition, GGBFS reaction with the alkali is faster than that only with fly ash, resulting in a weaker interface in GSM with GGBFS content. Therefore, strength loss is higher for GSM with GGBFS than for PCM

with the same preloading level.

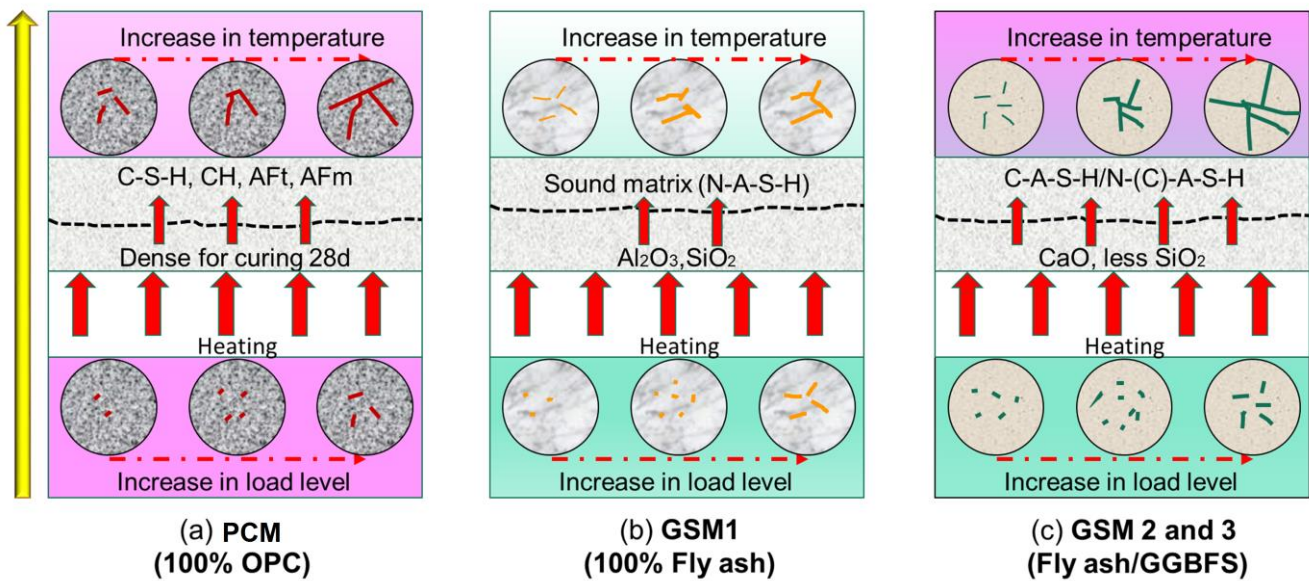


Figure 3.12. Schematic diagram of the mechanism of fire resistance after preloading
in 100% fly ash GSM, fly ash/slag GSM and 100% PCP mixes

At the temperature of 300 °C, the microstructure of the gel in GSM3 is primarily C-A-S-H type gel and/or N-(C)-A-S-H gel (Figure 3.8 (c)) and barely displays noticeable variations except for a slight enhancement in the intensity of the peak at 26.3° 2θ in Figure 3.8 (d), indicating that the amount of C-A-S-H or N-(C)-A-S-H gel may slightly increase. In the GSM2, the primary binding phase is a low calcium N-(C)-A-S-H type gel in Figure 3.11 (b3), which also shows structural stability at 300 °C. Together with elevated exposure temperature, an alteration in the T-O bond concerning a higher rate of recurrences demonstrates the strengthened Si content in N-A-S-H or N-(C)-A-S-H gels (Dombrowski et al. 2007). This indicates the gradual reaction of residual fly ash particles exposed to elevated temperature further promoted the formation of N-A-S-H or N-(C)-A-S-H gels. As the reaction continues, the matrix changes into more homogeneous as the results of further gels formation, resulting in an increase in strength from 25 °C and 300 °C. In GSM2 mixture exposed to a temperature ranging from 25 °C to 300 °C, the amount of residual fly ash particles observed in Figure 3.11 (c2) decreased,

indicating that fly ash was still reacting during thermal exposure. There are much less fly ash particles in GSM3, resulting in a small increase in strength. The compactness of GSM can be enhanced by the addition of GGBFS, which contributes to reducing the quantity of through holes, allowing the water to dissipate and decreasing the mass loss of GSM, which was confirmed by the TG results in Figure 3.9. The volume shrinkage increase of GSM with GGBFS is basically consistent with the on-going reaction of fly ash particles from 25 °C to 300 °C. The increased porosity or microcracks caused by preloading accelerates the transfer of heat, which increases the mass loss of GSM and makes GSM more sensitive to the elevated temperatures leading to an increase in volume shrinkage or volume expansion for all high temperature (300, 500 and 700 °C). However, the evaporation of free and combined water in PCM mortar after being heated at 300 °C may be the main reason for the mass loss, volume shrinkage, and strength loss of PCM.

At 500 °C, it is known that the water evaporation and the substitution of Ca by Na reduce the thermal stability of zeolite materials with increasing temperature (Breck 1984; Rovnaník et al. 2013). This might explain the decrease in strength observed from 300 °C to 500 °C in GSM. The increased strength loss of GSM caused by the adding GGBFS is mainly related to the CaO content in the raw materials, as shown in Table 3.1. GSM with a high CaO content is more susceptible to high temperatures due to a relatively low glass transition point, resulting in a high strength loss. The high content of CaO and low content of SiO₂ in the GSM with high GGBFS content can as well explain the higher volume shrinkage, and mass variation observed on GSM3 compared GSM2. The GSM3 with a low SiO₂ belongs to heat-resistant materials with low thermal conductivity and thermal expansion coefficient. In addition, although GSM3 thermal conductivity is high, GSM3 has high compressive strength and dense microstructure, leading to a lower mass loss compared to GSM2. As the temperature increases, the exfoliation of crystalline water leads to crack propagation and widening. In addition, the bonding performance between cementitious materials and sand in mortar is reduced due to the dissociation of CH showed in Figure 3.11 (d1). However, there might be more water left in the GSM specimens than

in PCM, leading to a higher mass loss and volume change as a result of their different curing conditions. At 700 °C, the XRD results in Figure 3.8 show that the N-(C)-A-S-H or C-A-S-H in GSM3 can be detected at all high temperatures, indicating that the gel's structure of GSM3 is stable. There are many pores in GSM at 700 °C (Figures 3.11 (a4), (b4) and (c4)), which may mainly be caused by the different crystalline phases contained in the raw materials. The presence of quartz and mullite was detected at all exposure temperatures, illustrating that elevated temperature has a marginal impact on these phases. With the increase in GGBFS content, high strength loss of GSM may be mainly caused by calcite and gypsum content. High temperature can seriously affect the compactness of GSM (Figure. 6), allowing for more voids formation and more water content, which could explain the high mass loss and volume expansion observed on of GSM and confirmed by the TG results in Figure. 9. With a further increase in temperature, cracks begin to connect, and mortar becomes loose, which leads to further compressive strength reduction. There is less damage after preloading in PCM than in GSM, and the PCM showed a lower strength loss than GSM2 and GSM3 when heated at 700 °C which is consistent with the observation from SEM observations (Figures 3.11 (a) to (d)), possibly due to the 28-day curing of PCM. In addition, the decomposition of C-S-H at the temperature of 700 °C, leading to a higher strength reduction of PCM.

In terms of fire or high temperature resistance, the increasing GGBFS content can indeed improve the compressive strength of GSM, but also increases the strength loss caused by preloading. However, the compactness of GSM can also be enhanced by increasing the GGBFS content, which can protect the microstructure from being severely deteriorated by high temperature exposure. Considering the combined strength and compactness enhancement, GSM with a small percentage of GGBFS (no more than 20%) may be optimal for PCM to achieve high fire or high temperature resistance.

3.8 Summary

(1) The compression strength of fly ash-based geopolymer can be improved by adding GGBFS.

However, increasing GGBFS content can increase the percentage of strength loss caused by

preloading. 40% GGBFS in GSM3 led to a low strength increase at 300 °C and a high strength loss at 500 and 700 °C. GSM2 with 20% GGBFS content displays excellent properties, and strength increases at 300 °C and higher compressive strength than that of GSM3 after being exposed to 500 and 700 °C

- (2) Increasing the preloading level led to GSM compressive strength to gradually decrease, possibly due to an unstable internal microstructure, increasing porosity, and microcracking. The mass loss and volume shrinkage or expansion of GSM increase with increasing preloading level, making GSM more sensitive to elevated temperature. The increase in the preloading level is affecting the most GSM3, showing the highest strength loss, which could be related to a higher hydration rate and the curing conditions.
- (3) Compared to PCM, GSMs are significantly more affected by the preloading level. GSM with GGBFS after load-induced damage has superior fire resistance at 300 °C but inferior fire resistance at 500 and 700 °C than PCM. Besides, GSM2 has a good fire resistance with high strength increase at 300 °C and low strength loss at 500 and 700 °C, mainly due to the stability of its crystalline hydration products and high SiO₂ content. However, the mass loss and volume change of GSM are overall higher than that of PCM. This might be related to more water left in the GSM than in PCM, and a much weaker interface with aggregates in GSM caused by the different curing conditions.
- (4) The effect of preloading and cracking on high temperature or fire resistance of the geopolymer composites depends on the mix design of its binders. For the exposure temperature of 700 °C, considering only the residual compressive strength, GSM1 made with only fly ash performs the best followed by PCM, GSM2, and GSM3. For the exposure temperature of 500 °C, GSM1 performs the best, followed by PCM, GSM2, and GSM3. For the exposure temperature of 300 °C, GSM2 performs the best, followed by GSM1, GSM3, and PCM.
- (5) In a summary, in accordance with the analysis of the experimental results in this chapter, GSM with a small percentage of GGBFS (no more than 20%) may be the best choice for PCM to

achieve high fire or temperature resistance in practical engineering applications, taking into account the combined strength and densification gains.

CHAPTER 4: PERFORMANCE OF LOW-CARBON GEOPOLYMER UNDER ACID ENVIRONMENT AND CYCLIC LOAD

4.1 Introduction

The durability of concrete is becoming more and more imperative for concrete structures due to the increasing demand for extended service life and less maintenance (Neto et al. 2021). The structures of ordinary Portland cement (OPC) concrete are generally known to be severely damaged when exposed to acidic environments, which shortens its service life and increases its requirement for maintenance and renewal expense (Dezhampanah et al. 2020; Lu et al. 2020). Concrete may contact various types of aggressive chemicals (such as inorganic and organic acids) in multiplied ways (Gutiérrez-Padilla et al. 2010; Yuan et al. 2013). Sulfuric acid is one of the aggressive inorganic acids that could significantly reduce the durability of OPC concrete (Huber et al. 2017; Mahdikhani et al. 2018; Omrane et al. 2017). The formation of the sulfuric acid environment may be related to fertilizer and metal production (Nunes et al. 2014; Tian et al. 2012). Sulfuric acid may also exist in groundwater or be produced by the oxidation of sulfur compounds in the filling, resulting in degradations of the underground OPC concrete structures (Ong et al. 2018). In addition, the sewer networks and wastewater systems across the world are significantly corroded and deteriorated due to the sulfuric acid attack, causing considerable economic losses every year (Grengg et al. 2018). Especially, the difficulties in the sewer network present enormous challenges for maintenance and repair (Grengg et al. 2017; Grengg et al. 2018). Thus, it is essential to provide a better alternative to enhance the resistance of concrete structures to sulfuric acid deterioration.

Geopolymer (GP) materials, produced by the geopolymerization of alkali activating solutions with aluminosilicate-rich materials, such as fly ash (FA), ground granulated blast furnace slag (GGBFS), and metakaolin, might be used to replace OPC concrete in many different exposure conditions, such as high temperature and sulfuric acid environments, and in turn, significantly reduce the emission of

CO₂. It is reported by many studies that geopolymers have excellent properties in acid resistance (Aiken et al. 2018; Ariffin et al. 2013; Mehta & Siddique 2017; Valencia-Saavedra et al. 2020). Ariffin et al. (Ariffin et al. 2013) displayed that after exposure to a 2% sulfuric acid solution up to 18 months, the mass loss of blended ash GP concrete was 8%, compared to 20% of OPC concrete. Similarly, Mehta and Siddique (2017) reported that the mass loss of fly ash-based GP concrete increased with the increasing OPC substitute for fly ash when exposed to a 2% sulfuric acid solution for one year. After exposure to a 5% sulfuric acid solution, the GP mortars had a lower strength loss than OPC mortar, as reported by Aiken et al. (2018). Valencia-Saavedra et al. (2020) also demonstrated that the fly ash-based GP concrete had 20% strength loss after exposure to 1M H₂SO₄, compared to 55% for OPC concrete.

However, some studies had illustrated that the properties of GP might be affected by a variety of factors such as alkali dosage, proportions of aluminosilicate-rich materials, curing methods, etc. (Djobo et al. 2016; Sata et al. 2012; Thokchom et al. 2009). Thokchom et al. (2009) had illustrated that decreasing the alkali dosage led to a higher strength loss in GP mortars after 24 weeks in sulfuric acid solution. The increasing calcium content could increase the strength loss of bottom ash GP mortar after 120-day immersion in a 3% sulfuric acid solution (Sata et al. 2012). Djobo et al. (2016) had emphasized that after exposure to a 5% H₂SO₄ solution for 180 days, the strength loss of volcanic ash-based GP mortars when cured at 27 °C was 24%, compared to 60% when cured at 80 °C. Therefore, in order to ensure that the GP materials have favorable performance after sulfuric acid attack, more relevant research should be carried out.

Additionally, it should also be noticed that many previous investigations (Aiken et al. 2018; Ariffin et al. 2013; Djobo et al. 2016; Mehta & Siddique 2017; Sata et al. 2012; Thokchom et al. 2009; Valencia-Saavedra et al. 2020) merely examined the performance degradation of GP materials after the sulfuric acid attack, and only a few investigations examined the effects of sulfuric acid attack interacted with external loading, which was more relevant to the actual situation. In practice, environmental exposure

(e.g., sulfuric acid attack) combined with external loading could cause deterioration and damage of cementitious materials and structures during their service lives (Bassuoni & Nehdi 2009; Lin et al. 2020). The external loading could cause cracks or abnormalities inside GP concrete, which not only could affect the performance of GP structure in an acidic situation but also affect the mechanical properties, integrity, and permeability. Alzeebaree et al. (2019) have only studied the static and cyclic stress-strain responses of GP concrete after exposure to sulfuric acid attacks, without considering the effect of external loading. Moreover, although it is generally considered that excellent resistances to acidic environments are the superiority of GP materials, there are still insufficient insights into the influences of combined sulfuric acid attack and external loading on the properties of GP materials. Therefore, the aim of this study is to investigate the sulfuric acid resistance of fly ash-based GP mortar (GPM) after cyclic preloading and explore the deterioration mechanism of coupled preloading damage and sulfuric acid attack. There were three specific objectives in this study: firstly, to investigate the effect of cyclic preloading on the sulfuric acid resistance of GPM; secondly, to examine the effect of GGBFS content on the sulfuric acid resistance of GPM; and thirdly, to compare the different sulfuric acid resistance between GPM and OPC mortar (OPM) after cyclic preloading. The relevant results may provide insight into the sulfuric acid resistance of fly ash-based GP materials after cyclic preloading, thus ensuring a better alternative for OPC under aggressive environments.

4.2 Materials and methodology

4.2.1 Raw materials

The fly ash and GGBFS employed to manufacture GPM were supplied from the Boral Cement and Building Products Supplies Pty Ltd (Australia), respectively. The Blaine and specific gravity of fly ash were 390 m²/kg and 2.76, respectively, and these of GGBFS were 418 m²/kg and 2.92, respectively. OPC (CEM I 42.5N) adopted to cast OPM was supplied by Independent Cement & Lime Pty Ltd (Australia). The Blaine and specific gravity of OPC were 347 m²/kg and 3.15, respectively. The oxide

compositions for fly ash, GGBFS, and OPC measured by X-ray fluorescence (XRF) are presented in Table 4.1. Fly ash could be classified as class F due to its low calcium content in accordance with ASTM C618 (Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete), while GGBFS had a high calcium content of 42.60%, lower than OPC. The river sand employed to fabricate mortar was supplied by County Materials Corp (Australia). The fineness modulus of river sand was 2.39. Before fabricating mortar, the river sand was dried for 48 hrs and then stored at room temperature and in dry conditions. In addition, the MasterGlenium 8703 superplasticizer (SP) supplied by BASF was added to the mortar mixtures to improve flowability.

Table 4.1 Chemical compositions and loss on ignition (LOI) of FA, GGBFS and OPC (%)

Compositions	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	MnO	K ₂ O	Na ₂ O	P ₂ O ₅	TiO ₂	SO ₃	LOI
FA	65.90	24.00	2.87	1.59	0.42	0.06	1.44	0.49	0.19	0.92	—	1.78
GGBFS	36.00	13.80	0.30	42.60	5.80	0.40	0.27	0.21	0.10	0.80	0.56	1.64
OPC	20.51	5.37	2.10	57.05	3.86	0.02	1.44	0.64	0.13	0.16	6.37	2.35

To active the GP materials, the commercial sodium silicate (SS) and sodium hydroxide (SH) were adopted to prepare the alkaline solution. The 16 M sodium hydroxide solution was prepared by the SH pellets with 98% purity supplied by Chem-Supply Pty Ltd, and mixed with SS solution (the mass ratio of SS to SH was 3.0) at least 24 hrs before fabricating (Hanjitsuwan et al. 2017; Rattanasak & Chindaprasirt 2009; Wongsu et al. 2016). The SS solution with a modulus (M_s) equal to 2.0 (where $M_s = \text{SiO}_2/\text{Na}_2\text{O}$, $\text{SiO}_2=29.3\%$, $\text{Na}_2\text{O}=14.6\%$, and $\text{H}_2\text{O}=56.1\%$) was supplied by PQ Corporation. Besides, a commercial sulfuric acid (99%) for analysis, supplied by Merck Pty, was utilized to prepare the exposure sulfuric acid solution.

4.2.2 Mix proportion and sample preparations

The OPM and GPM mix proportions are listed in Table 4.2. Three different GPM groups were prepared, in which fly ash was replaced by GGBGS at dosages of 0, 20%, and 40%, respectively. The OPM group mixed with water and sand was prepared as the reference group. The ratios of liquid-to-binder

and sand-to-binder in GPM were set as 0.4 and 2.0, and the ratios of water-to-cement and sand-to-cement in OPM were 0.4 and 2.0. In addition, a 0.6 % superplasticizer was added to the GPM.

Table 4.2 Mix proportions of OPM and GPM mortar specimens

Specimens	Mix proportions (kg/m ³)							
	FA	GGBFS	OPC	SS	SH	Water	Sand	SP
GPM1	450	—	—	135	45	—	900	2.7
GPM2	360	90 (20%)	—	135	45	—	900	2.7
GPM3	270	180 (40%)	—	135	45	—	900	2.7
OPM	—	—	450	—	—	180	900	—

For mixing, to begin with, the binders (FA and GGBFS, or OPC) and sand were jointly dry-mixed in a 10-L plane high shear mixer for approximately 4 min. The water or premixed alkaline solution with SP was gradually poured into the dry-mixed materials, and the wet-mixing was sustained for a further 4 min (Pavithra et al. 2016; Reddy et al. 2018). Cylinder moulds with the size of 50-mm diameter and 100-mm height were used to prepare the test specimens. The cylinder specimens were fabricated in two layers and vibrated for compaction. Heating curing was employed for GPM specimens in this investigation. The GPM specimens with moulds were wrapped by plastic vacuum sheets to prevent redundant moisture loss and stored at room temperature (20 ± 1 °C) for 24 hrs. The wrapped GPM specimens with moulds were then heat-cured at 80 °C for 7 days. At the end of 7 days, the demoulded GPM specimens were wholly wrapped with other plastic vacuum sheets and kept at 20 ± 1 °C and 50% relative humidity (RH) for 49 days. Standard water curing according to ASTM C192 (Standard Practice for Making and Curing Concrete Test Specimens in the Laboratory) for 56 days was adopted for the demoulded OPM specimens.

4.2.3 Exposure conditions

In this study, a total of 400 mortar specimens was fabricated and were equally divided into four mortar

specimens. After 56-day curing, 3 specimens of each specimen were used to test the compressive strength to obtain the average ultimate compressive strength (UCS). There were two protocols designed for the exposure conditions, as shown in Figure. 4.1. For protocol 1, two end faces of each specimen were firstly coated with acid-proof resin; Next, all specimens were soaked in distilled water for 24 hrs to reach saturation; Then, 4 specimens were immersed in four different sulfuric acid solutions and kept in the solution until the test ages.

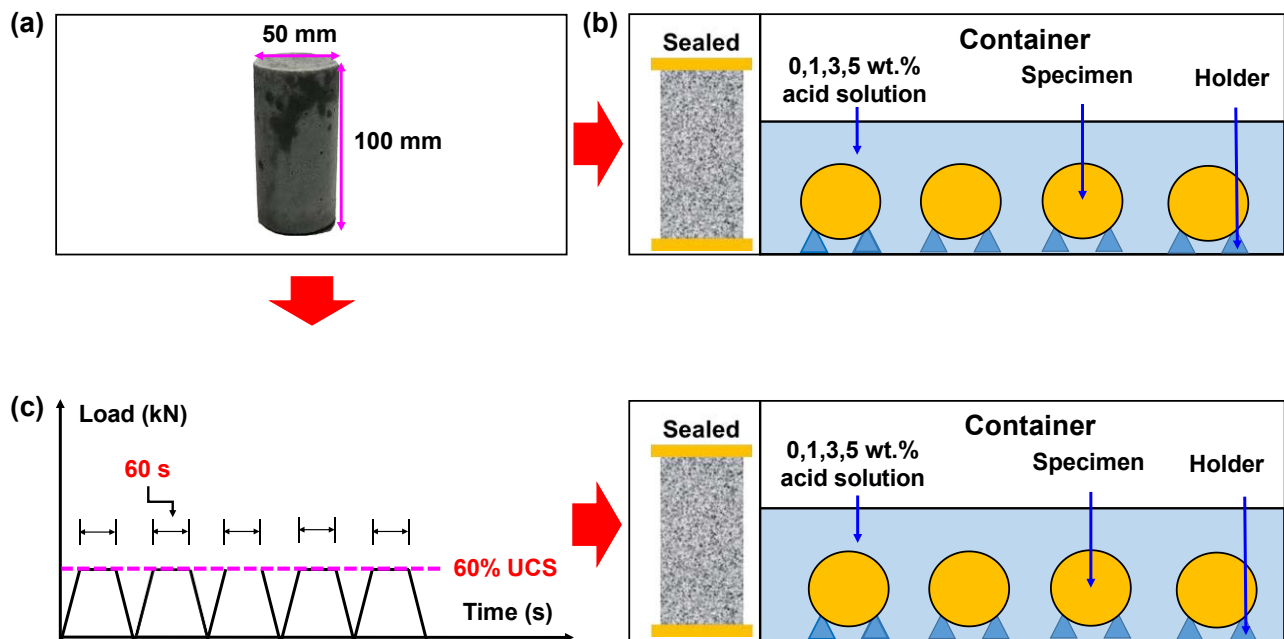


Figure 4.1. Experimental methods of combined preloading and acid solutions: (a) Specimen preparation; (b) Exposure to the acid solution after curing (Protocol 1); (c) Exposure to the acid solution after cyclic preloading (Protocol 2).

For protocol 2, the specimens were firstly preloaded with 60% UCS and kept at the aimed load for 1 min with 5 cycles; next, two end faces of each specimen were coated with acid-proof resin; Then, all specimens were soaked in distilled water for 24 hrs to reach saturation; Finally, the coated specimens were immersed in the various solutions. After processed with the two protocols, the main experimental types for all mortars are classified and named in Table 4.3. Each specimen had 8 different experimental types. The numbers 1 and 2 following the different specimens were used to stand for protocols 1 and 2,

respectively. The numbers 0, 1, 3, and 5 following the protocols were adopted to represent the deionized water, 1, 3, and 5 % sulfuric acid solution.

Table 4.3 Experimental parameters of OPM and GPM exposed to acid solution

Specimen	Preload level (UCS %)	Acid solution (wt.%)	Exposure methods	Specimen	Preload level (UCS %)	Acid solution (wt.%)	Exposure methods
Group 1 (OPM)				Group 3 (GPM with 20% GGBFS)			
OPM-1-0	—	—	Protocol 1	GPM2-1-0	—	—	Protocol 1
OPM-1-1	—	1	Protocol 1	GPM2-1-1	—	1	Protocol 1
OPM-1-3	—	3	Protocol 1	GPM2-1-3	—	3	Protocol 1
OPM-1-5	—	5	Protocol 1	GPM2-1-5	—	5	Protocol 1
OPM-2-0	60	—	Protocol 2	GPM2-2-0	60	—	Protocol 2
OPM-2-1	60	1	Protocol 2	GPM2-2-1	60	1	Protocol 2
OPM-2-3	60	3	Protocol 2	GPM2-2-3	60	3	Protocol 2
OPM-2-5	60	5	Protocol 2	GPM2-2-5	60	5	Protocol 2
Group 2 (GPM with 0% GGBFS)				Group 4 (GPM with 40% GGBFS)			
GPM1-1-0	—	—	Protocol 1	GPM3-1-0	—	—	Protocol 1
GPM1-1-1	—	1	Protocol 1	GPM3-1-1	—	1	Protocol 1
GPM1-1-3	—	3	Protocol 1	GPM3-1-3	—	3	Protocol 1
GPM1-1-5	—	5	Protocol 1	GPM3-1-5	—	5	Protocol 1
GPM1-2-0	60	—	Protocol 2	GPM3-2-0	60	—	Protocol 2
GPM1-2-1	60	1	Protocol 2	GPM3-2-1	60	1	Protocol 2
GPM1-2-3	60	3	Protocol 2	GPM3-2-3	60	3	Protocol 2
GPM1-2-5	60	5	Protocol 2	GPM3-2-5	60	5	Protocol 2

The sulfuric acid resistance test was carried out according to the common principles in ASTM C267

(Standard Test Methods for Chemical Resistance of Mortars, Grouts, and Monolithic Surfacing and Polymer Concretes), which was also employed in some studies (Aiken et al. 2017). After processing with the protocols, 4 mortar specimens of each type in one test age were immersed in deionized water, 1, 3, and 5% sulfuric acid solution with a specimen to solution volume ratio of 1:10 (see Figure. 4.1). The mortar specimens were immersed in the solution for up to 1.5 years. In the first half-year, the deionized water and sulfuric acid solution were refreshed in one, two, and three months, compared with every half year in the following 1 year.

4.3 Testing procedures

4.3.1 Methodology

The changes of visual inspection, compressive strength, and degradation depth of each type were recorded after being immersed in different solutions for 1, 6, and 18 months. The mass of each type was measured before and after being immersed in the different solutions for 0.5, 1, 2, 3, 6, 9, 12, 15, and 18 months. A scale with an accuracy of 0.01 g and a high-resolution camera was used to record the mass and visual inspection, respectively. Before measuring the mass of specimens, the surface was slightly wiped by a clean tissue to remove the moisture and leached crystals. The percentage change in mass was calculated by the mass change between the exposed specimens and corresponding unexposed specimens, compared to the mass of unexposed specimens.

The average compressive strength was examined by a constant load rate of 1 kN/min, while the cyclic preloading process was applied with a load rate of 2 mm/min (Şahmaran et al. 2008; Xue et al. 2020). Before the compressive strength test, the exposed specimens were kept in a dry environment at 40 °C for 1 hr. The compressive strength was all calculated based on the force of tested specimens and the area of corresponding unexposed specimens. The percentage change in compressive strength was also calculated by the strength change between the exposed specimens and corresponding unexposed specimens, compared to the strength of unexposed specimens.

Three of the 4 specimens immersed in the sulfuric acid solution were adopted for the compressive strength and mass test, and the left one was adopted for degradation depth measurements. The flowchart for the preparation of degradation depth, leaching, and microstructure test samples is displayed in Figure. 4.2. The surface of the specimen immersed in acid solutions was wiped cleanly. After that, the wiped specimen was divided into 5 equal parts, the middle three parts were adopted for degradation depth test, and the other two parts were adopted for scanning electron microscopy and energy dispersive X-ray (SEM-EDX) analysis.

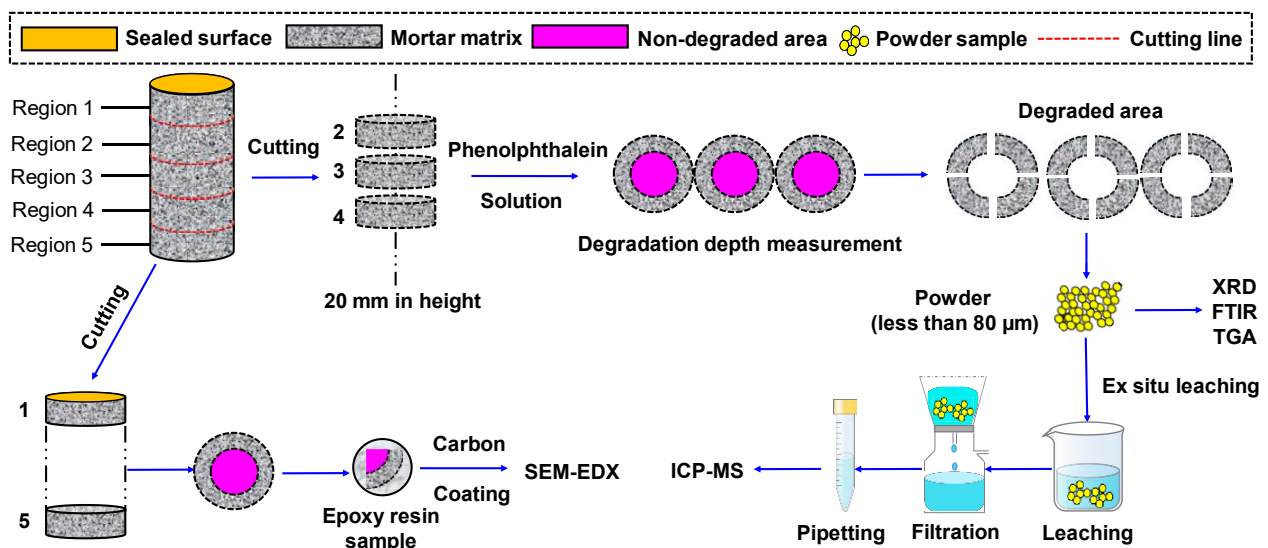


Figure 4.2. Diagram of preparation of degradation depth, leaching, and microstructure tested mortars.

Due to the protection of acid-proof resin, the thickness of each part was approximately 20 mm. After the degradation depth test, the degradation area of all specimens was adopted for preparing the samples of inductively-coupled plasma mass spectrometry (ICP-MS), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and Thermogravimetric analysis (TGA). For the specimen with a smaller degradation area, the test samples were obtained from the area as close to the surface as possible.

4.3.2 Measurement of degradation depth

The cross-section surfaces of the middle three parts mentioned above were first rinsed with deionized running water to clear away loose particles and dried with a clean tissue, ensuring the accuracy of degradation depth measurement (Lloyd et al. 2012). The phenolphthalein solutions, prepared with 1 g phenolphthalein, 70 mL ethanol, and 100 mL deionized water, were sprayed on the cross-section surfaces to exhibit the degraded and undegraded area. It was assumed (Ren et al. 2020) that the pH of the degraded area was higher than 8.3, while the pH of the undegraded area was lower than 8.3. The phenolphthalein solution could change the color of the cross-section surfaces to pink when the pH was higher than 8.3. The degradation depth was measured by the LECT microscope OLS5000, which was displayed in Figures. 4.3(a) and (b).

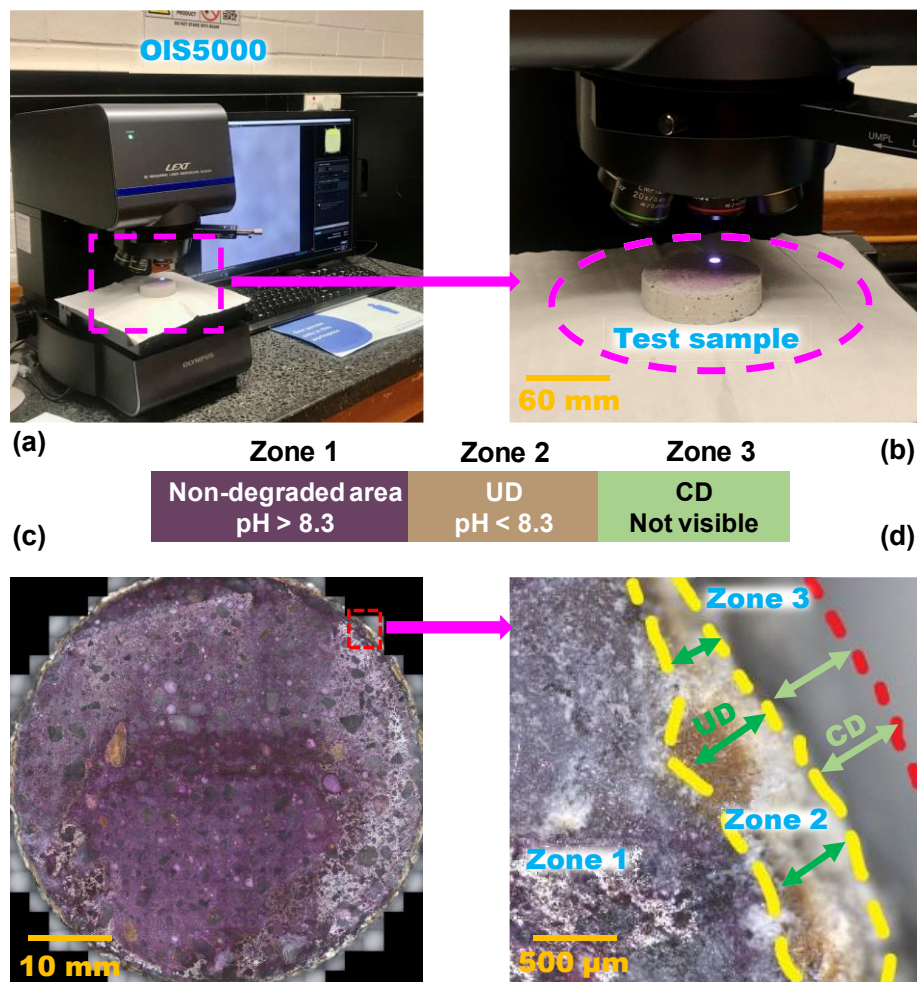


Figure 4.3. Degradation depth measurement in accordance with the pH: (a) OLS5000 equipment;

- (b) Tested sample sprayed with phenolphthalein; (c) A cross-section surface of a test sample and
(d) The identification of UD and CD.

A cross-section surface of a sample is also displayed in Figures. 4.3(b) and (d). Zone 1 was a non-degraded area with a pink color; zone 2 was a degraded area without color change, the range of which was represented by uncolored deterioration depth (UD); zone 3 was a dissolved area, where the deterioration depth (DD) could be calculated by comparing the unexposed and exposed diameters of each sample. Generally, the total degradation depth (TD) could be calculated by a numerical sum of UD and DD.

4.3.3 Microstructure and mineralogical characterization

The sample crushed from the degradation area was grinded into powders that passed through an 80 μm sieve. The powders specimens were immersed in an alcohol solution of 99.9% purity for 48 hrs and dried in the vacuum oven at 40 °C before analysis. The XRD analysis was employed to evaluate the composition changes that occurred in all specimens exposed to the sulfuric acid solution. The Bruker D8 Discover diffractometer applying $\text{CuK}\alpha$ radiation of wavelength 1.54 Å was adopted to measure the diffraction patterns gathered from 5° to 70° 2θ , with a 0.02° step.

The FTIR analysis was applied to examine the change in molecular characteristics after the sulfuric acid attack. Nicolet 6700 FTIR spectrometer was adopted to measure the spectra obtained from 450 to 4000 cm^{-1} wavenumber at 8 cm^{-1} resolution. The TGA analysis using NETZSCH STA 449 F3 Jupiter was employed to detect the hydration reaction product changes of all samples before and after exposure to sulfuric acid. The powder samples were held in an alumina crucible, kept at 40 °C in an N_2 environment for 30 min, and then heated to 1000 °C at a speed of 10 °C/min (Li et al. 2017). The thermogravimetry (TG) and derivative thermogravimetry (DTG) curves were adopted to analyze the TGA results.

From Figure 4.3, the samples included non-degraded and degraded areas, were first taken out from the

cutting cross-section and dipped into an alcohol solution, which was then dried in a vacuum oven at 40 °C and cured with epoxy resin. The cured samples were cleaned with alcohol and ultrasonic cleaner, dried in a vacuum oven at 40 °C, and coated with carbon before SEM-EDX analysis. The SEM-EDX analysis using Zeiss Supra 55VP SEM with Raith Elphy Plus E-beam Lithography System was performed at an accelerating voltage of 5KV and a spot size of 5. EDX results were applied for point and line scanning in atomic and mass percentages, respectively. Each result of point and line scanning was tested three times to reduce experimental error. The elements, including O, Si, Al, Na, Ca, S, Mg, and K, were analyzed by Aztec version 2.0 software according to EDX results (Kashani et al. 2019; Wardhono et al. 2017).

4.3.4 ICP-MS analysis

In order to figure out what elements had been leached from the mortar matrix into the sulfuric acid solution, the ex-situ leaching (ESL) method (Plusquellec et al. 2017; Vollpracht et al. 2016) was adopted for preparing the sample for the leaching behavior test. The samples smashed from the degradation area were grinded into powders passing through an 80 µm sieve. It should be noted that the surface of the mortar specimens was wiped and cleaned with an alcohol solution. 10 g of powder was mixed with 100 ml (1:10) HNO₃ (68%) and heated in a furnace oven at 80 °C for 2 hrs. About 10 ml extracted solution was cooled down, topped up to 500 ml with deionized water, and filtrated with 4 µm cellulose filter before analysis. The resulting solution was analyzed by ICP-MS to determine the element concentrations of Al, Si, Ca, and Na, so as to explore the deterioration mechanism of the geopolymers mortar under coupled cyclic preloading and sulfuric acid attack.

4.4 Change of physical properties

4.4.1 Physical appearance

Figure 4.4 presents the visual appearance of OPM and GPM without preloading exposed to 1, 3, and 5% sulfuric acid solutions for up to 18 months. Since the cyclic preloading did not affect the appearance

of the mortar, the visual appearance of mortars after preloading was not presented in this section. As could be seen from Figure 4.4, the precipitated white or yellow crystals could nearly be found in all exposed specimens, especially in OPM specimens. The white crystals were primarily attributed to the formation of gypsum (G) and ettringite (AFt) (Mantellato et al. 2016), while the yellow crystals were predominantly attributed to the dehydration of AFt, which could transfer it from white to yellow (Sarkar et al. 2019; Speziale et al. 2008).

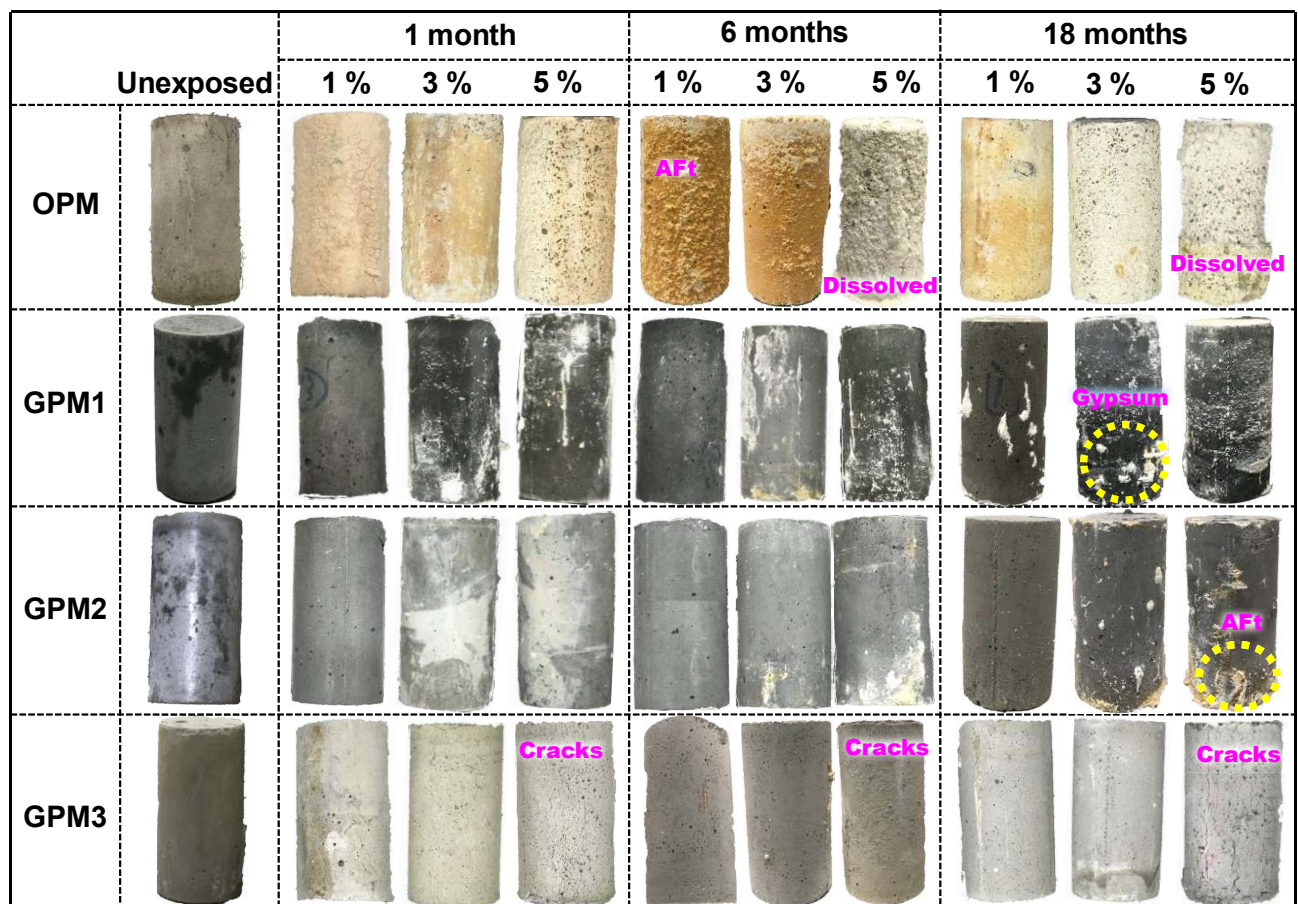


Figure 4.4. Surface appearances of OPM and GPM without preloading after 1, 6 and 18 months exposed to different sulfuric acid solutions.

The GPM1 and GPM2 had no apparent change in visual appearance even exposed to 5 % sulfuric acid for 18 months. After 18-month exposure, only a small part of G crystals was be found on the surface of GPM1 specimens, compared to some G and AFt crystals detected in GPM2 specimens. However, as the sulfuric acid concentration increased, the deterioration on GPM3 also became severe, where

some apparent cracks could be detected in the GPM3 specimens after exposure to 5% sulfuric acid. These indicated that more and more GGBFS replacing FA could increase the deterioration possibility of GPM, which might be related to the higher content of CaO in GGBFS than in FA (Song et al. 2020). Compared to GPM, there was more deterioration on OPM specimens. The deterioration of OPM was seen to increase with time and with increasing sulfuric acid concentration, where the OPM specimens could be partially dissolved after the specimens were exposed to the 5% sulfuric acid solution. Due to the high content of CaO in OPC, a large number of G and Aft crystals were produced, which could be dissolved in sulfuric acid solutions (Selim et al. 2020).

4.4.2 Mass change

Figure 4.5 presents the mass change of all mortar specimens exposed to 0, 1, 3, and 5% sulfuric acid solutions for up to 18 months. The results showed that the mass of most OPM and GPM types was decreased with time. The mass loss of each type increased by the cyclic preloading, and this difference between specimens with preloading and specimens without preloading would become more evident as the sulfuric acid concentration increased. After 18-month exposure, the mass loss of OPM-2-5 was 17.2% higher than that of OPM-1-5, compared to 2.8% higher in OPM-2-3 than in OPM-1-3. The combination of cyclic preloading and high sulfuric acid concentration could cause significant damages to OPM and GPM mortars. The cyclic preloading could lead to small cracks and abnormalities inside the mortars, which might cause more crystals to precipitate and dissolve in the sulfuric acid solution, thereby increasing the mass loss (Wu et al. 2020). After exposure to the same sulfuric acid solution and preloading level, the GPM specimen with high GGBFS content had a higher mass loss than that with low GGBFS content, indicating that the addition of GGBFS could increase the mass loss of GPM. After 18-month exposure, the highest mass loss in GPM1 (GPM1-2-5) was 4.1%, while the highest mass loss in GPM2 and GPM3 were 10.4% and 14.9%, respectively. The GPM with high GGBGS content could have high Portlandite (CH) products, which could be converted to gypsum by the sulfuric ions and finally lead to the formation of Aft (Hossain et al. 2018). The formation of gypsum could

decrease the density of GPM mortars, which might decrease the mass and further increase the mass loss in the GPM2 and GPM3. Compared to GPM in the same exposure condition, the OPM had a higher mass loss, which indicated a higher deterioration, primarily caused by the reaction between OPC with a large amount of CaO and the sulfuric acid solution occurred in OPM than in GPM.

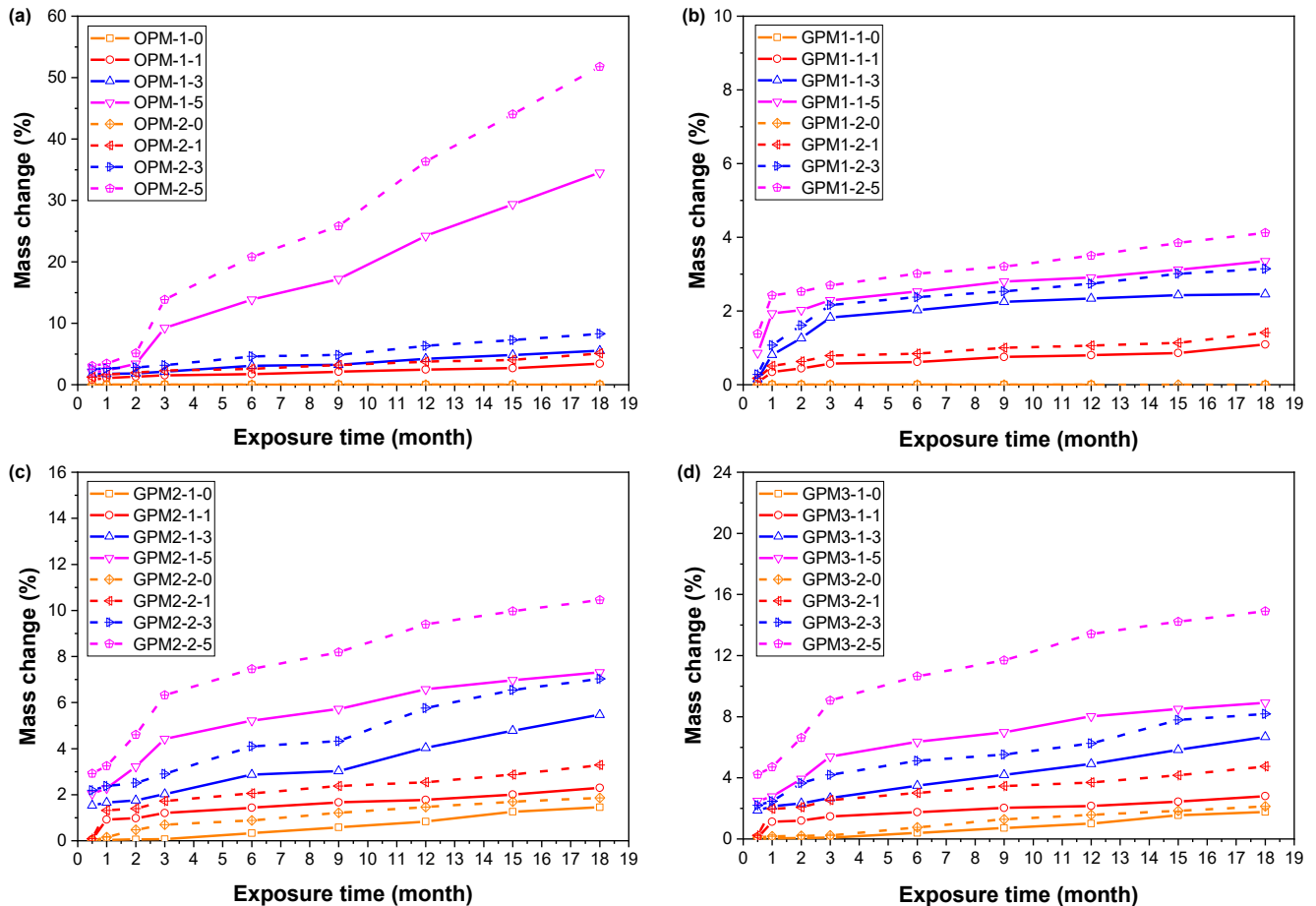


Figure 4.5. Mass changes of OPM and GPM specimens subjected to different sulfuric acid solutions for 18 months: (a) OPM; (b) GPM1; (c) GPM2 and (d) GPM3.

4.5 Changes in mechanical properties and degradation depth

4.5.1 Compressive strength

Figure 4.6 presents the evolution of compressive strength of mortars before and after 18-month exposure to 0, 1, 3, and 5 % sulfuric acid solutions. After 56-day curing, the GPM3 with 30% GGBFS content had the highest compressive strength, followed by GPM2, OPM, and GPM1. The less reactive

Ca decreased the amount of hydration product gels (partially responsible for strength) (Bai et al. 2018), which might account for less compressive strength founded in GPM1 than OPM. The addition of GGBFS could increase the reactive Ca ion and further increase the productions of gels (Bellum et al. 2020), which would contribute to higher compressive strength in GPM2 and GPM3 than in OPM and GPM1. After cyclic preloading, the compressive strength of all types of mortars was decreased. The preloading could cause more significant damage to the GPM specimen with GGBFS content than other specimens, even leading to the compressive strength of GPM2 being lower than that of OPM.

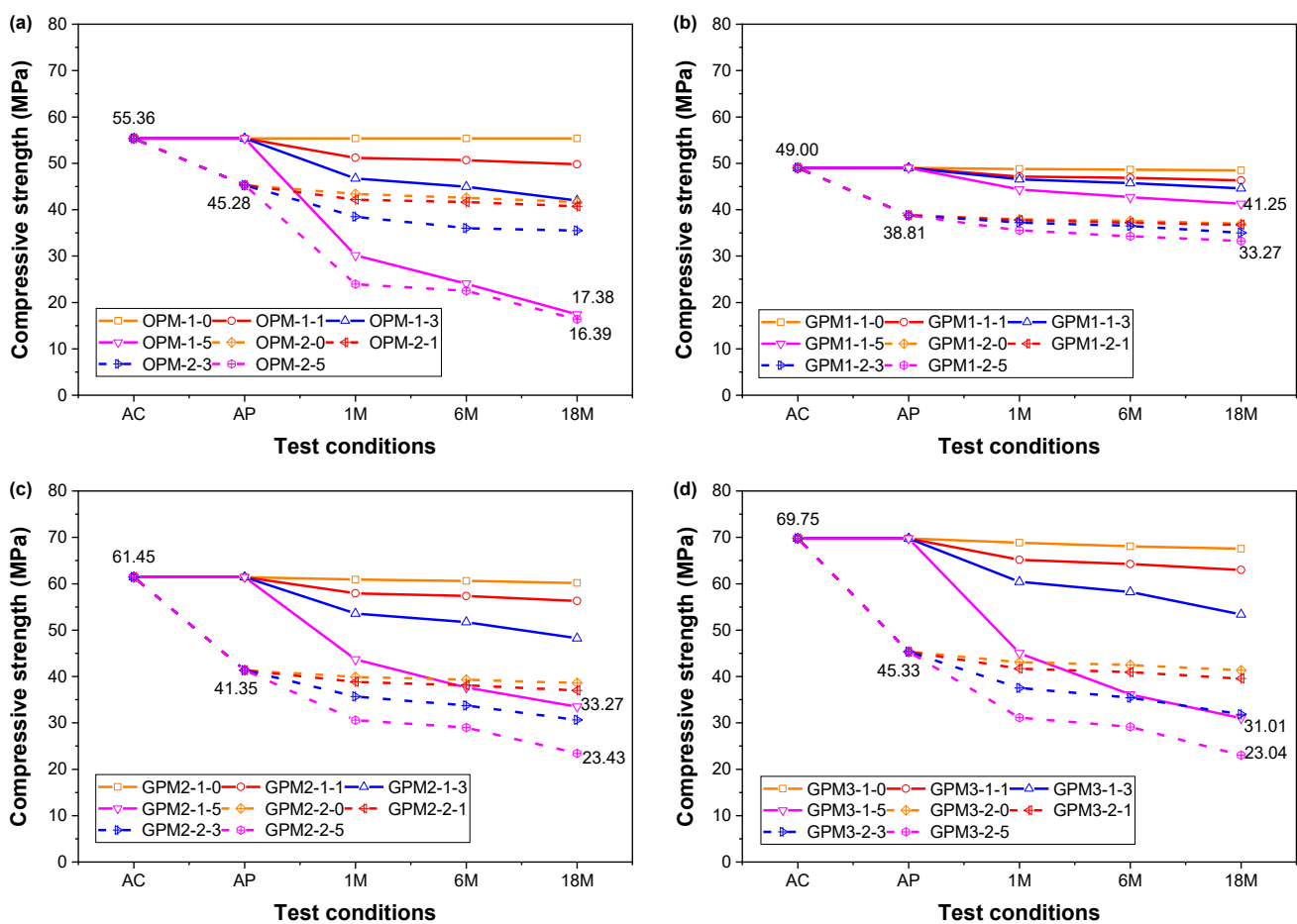


Figure 4.6. Compressive strength of OPM and GPM before and after exposure to different sulfuric acid solutions for 18 months: (a) OPM; (b) GPM1; (c) GPM2 and (d) GPM3.

After the exposure to different sulfuric acid solutions, the compressive strength of most types of mortars was decreased with time, except that the compressive strength of OPM-1-0 was nearly kept consistent. The preloading and increasing sulfuric acid concentrations could cause more damages to

the mortars. The types of mortar with preloading and after exposure to 5% sulfuric acid solution (such as OPM-2-5 and GPM-2-5) had the lowest compressive strength in all mortar specimens. The lowest compressive strength in all types was founded in OPM-2-5, followed by GPM3-2-5, GPM2-2-5, and GPM1-2-5.

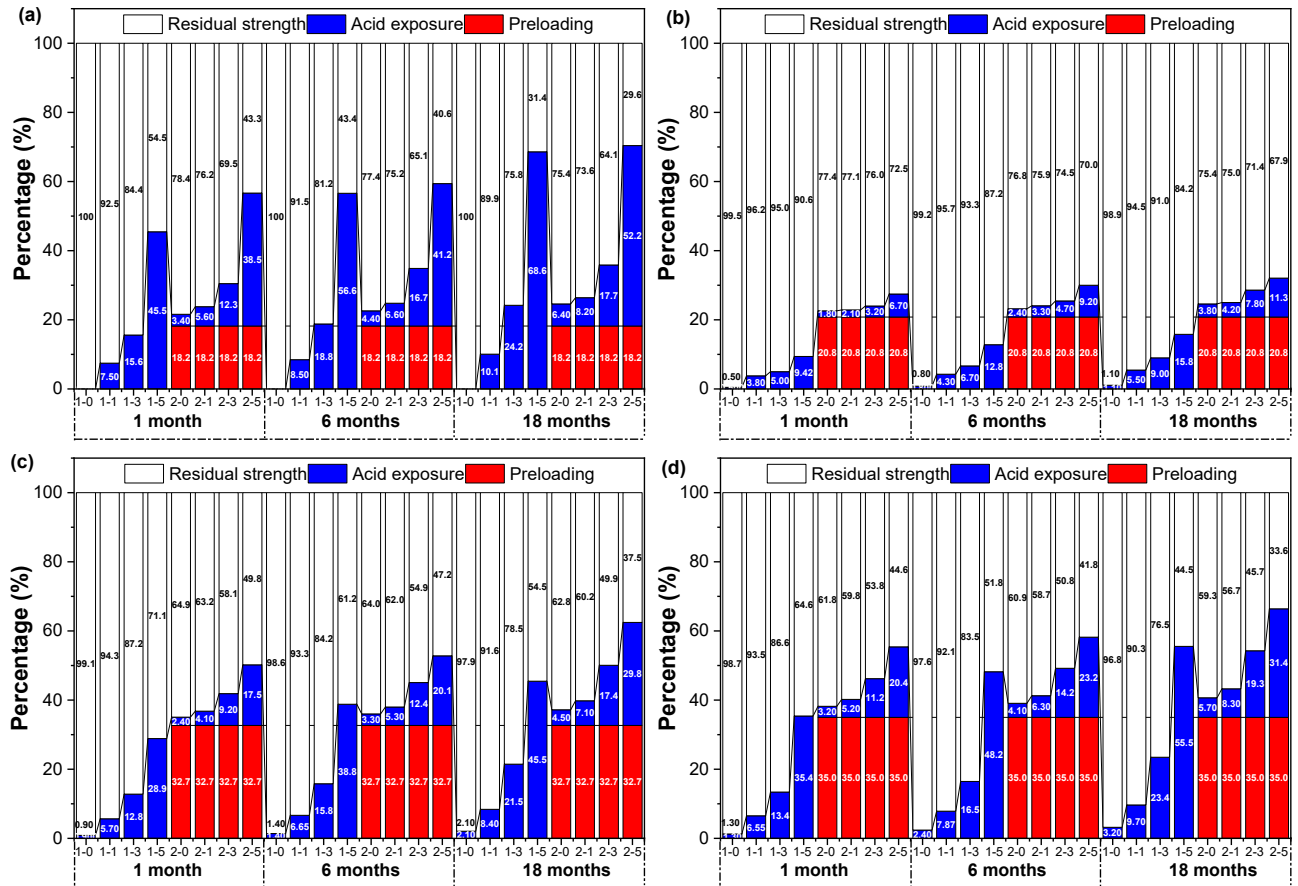


Figure 4.7. Compressive strength change caused by preloading and sulfuric acid solution: (a) OPM; (b) GPM1; (c) GPM2 and (d) GPM3.

Figure 4.7 presents the percentage of compressive strength change of all mortar types after 18-month exposure to sulfuric acid solutions. The results showed that the increasing GGBFS content could increase the strength reduction of GPM caused by preloading, leading to a higher strength reduction in GPM3 (35.0%) and GPM2 (32.7%) than that in GPM1 (20.8%). Compared to the GPM specimens, the OPM specimen had less strength reduction (18.2%) caused by preloading, which might be related to the curing temperature. The high curing temperature of 80 °C for the GPM could accelerate the

hydration reaction, which induced non-uniform heating, resulting in the generation of non-uniform hydrated products and weak interfaces (Qu et al. 2020). Besides, the high calcium content in GGBFS could fasten the hydration reaction (Puligilla & Mondal 2013), which could increase the weak interface in the GPM specimen with high GGBFS content. Thus, there was a higher strength reduction caused by cyclic preloading for the GPM specimen with GGBFS than OPM.

After the exposure to different sulfuric acid solutions, the residual compressive strength of all samples was decreased with time and the increasing sulfuric acid concentrations. For the same specimen, the combination of preloading and sulfuric acid attacks could cause more damage to the compressive strength. When exposed to 5% sulfuric acid solution for 18 months, the percentage of residual compressive strength of GPM1 with preloading (GPM1-2-5) was 67.9%, which was lower than that without preloading (GPM-1-5) of 84.2%. In the GPM specimen, the GPM1 only with FA had the lowest compressive strength loss after exposure to different sulfuric acid solutions, compared to the corresponding GPM2 and GPM3 specimens with high GGBFS content. As seen from Figure 4.7, the highest compressive strength loss of GPM1 caused by sulfuric acid for 18 months was GPM1-1-5 of 15.8%, compared to GPM2-1-5 of 45.5% and GPM3-1-5 of 55.5%.

In addition, compared with the GPM specimens, the OPM specimens had a higher strength loss caused by sulfuric acid attacks. After 18-month exposure to 5 % sulfuric acid, the final residual compressive strength percentage of OPM with preloading (OPM-2-5) was only 29.6%, which was even higher than GPM3-2-5 of 33.6%. Therefore, the residual compressive strength percentage of GPM3-2-5 was the lowest among all specimens of GPM. This indicates that although there was a higher strength reduction caused by preloading in GPM than in OPM specimens, the strength loss causing by sulfuric acid and preloading was lower in GPM than in OPM specimens. The strength loss of the OPM specimen was primarily caused by the high amounts of CaO, which could lead to the generation of Aft and G, resulting in a more significant strength reduction for the expansion, cracking, and spalling in the OPM matrix (Alzebaree et al. 2019).

In addition to the effect of the amounts of CaO in the GPM specimen, the destruction of the hydration products gels was another primary factor leading to strength reduction (Aiken et al. 2018). Due to the lower CaO content in fly ash than in GGBFS, there might be less strength loss in GPM1 than in GPM2 and GPM3. Since the geopolymer gels in GPM specimens after exposure to sulfuric acid solutions were probably more stable than the C-S-H gels in OPM (Sturm et al. 2018; Valencia-Saavedra et al. 2020), there was less strength loss in GPM than in OPM specimens. Overall, the 18-month sulfuric acid resistance of GPM with cyclic preloading was relatively better than that of OPM.

4.5.2 Degradation depth

Figure 4.8 presents the total degradation depth (TD) of all types of mortars after 18-month exposure to different sulfuric acid solutions. The results showed that the degradation depth of all types was increased with time and the increasing sulfuric acid concentrations. For the same specimen, the cyclic preloading could increase the degradation depth after exposure to the same sulfuric acid solution, indicating that the combination of cyclic preloading and sulfuric acid attack could cause more significant damages to all types of mortars. After 18-month exposure to 3% sulfuric acid solution, the degradation depth of OPM with cyclic preloading (OPM-2-3) was 6.33 mm, which was higher than the 4.25 mm of OPM-1-3.

For the GPM specimens in the same exposure conditions, the lowest degradation depth was detected in GPM1, the degradation depth of which could be increased by the addition of GGBFS, resulting in a higher degradation depth in GPM2 and GPM3. The GPM1-2-5 had the highest degradation depth of 0.12 mm in GPM1, which was even lower than that 0.46 mm of GPM2-2-1 and 0.96 mm of GPM3-2-1. After exposure to the same conditions, the OPM specimen had a higher degradation depth than the corresponding GPM specimen in all exposure times. The GPM3-2-5 had the highest degradation depth of 8.15 mm in all GPM specimens, which was lower than 8.25 mm of OPM-1-5. The OPM-2-5 had the highest degradation depth of 10.7 mm in all specimens. In general, the GPM specimen had a lower degradation depth than OPM, while increasing the GGBFS replacement for fly ash could make the

GPM had a higher degradation depth. These might be related to the lower CaO content in FA than in GGBFS and the relatively more stable geopolymer gels structure in GPM than in OPM (Lloyd et al. 2012; Ren et al. 2020).

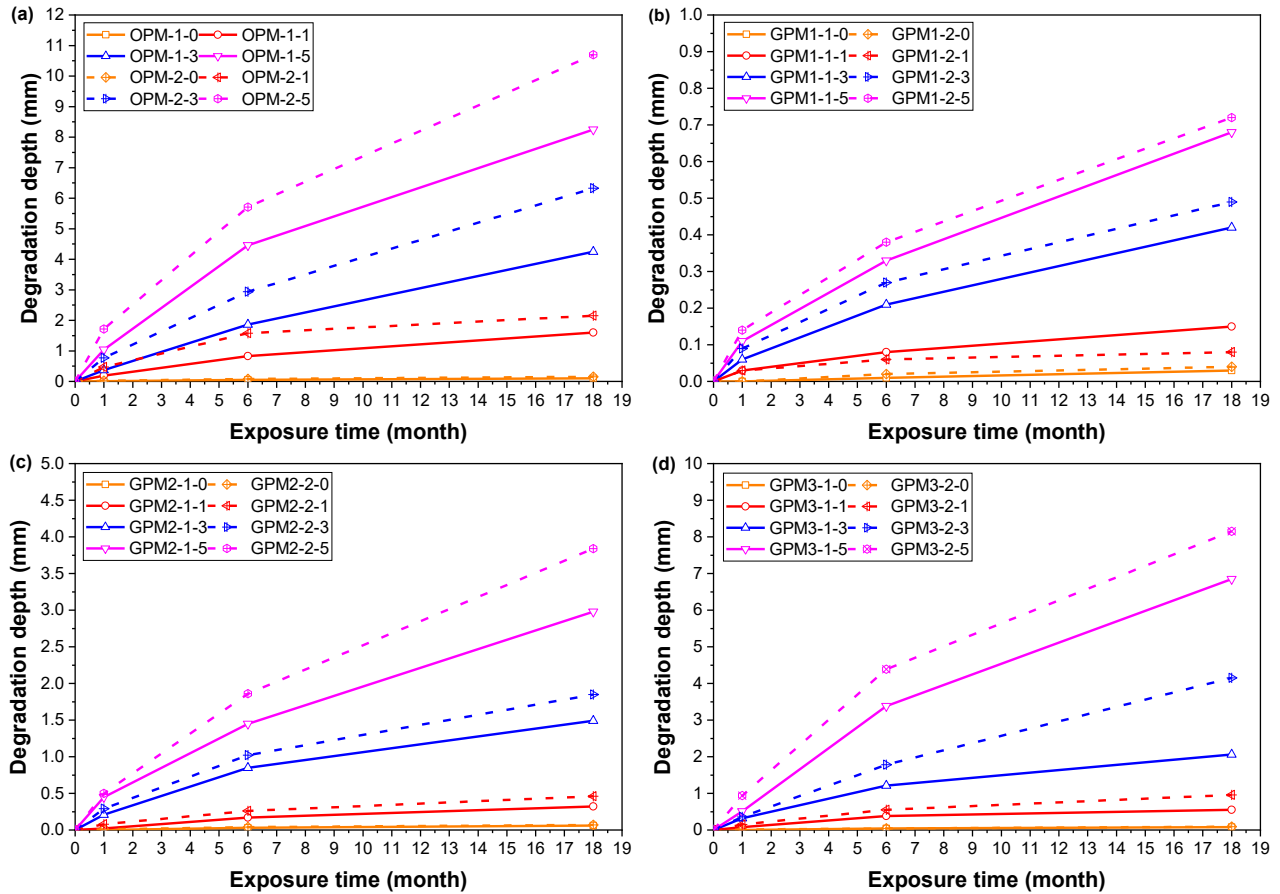


Figure 4.8. Degradation depth of OPM and GPM exposed to different sulfuric acid solutions for up to 18 months: (a) OPM; (b) GPM1; (c) GPM2 and (d) GPM3.

4.6 Changes in microstructure and mineralogy

4.6.1 X-ray diffraction

Figure 4.9 presents the XRD results of all mortar types with cyclic preloading after 18-month exposure to different sulfuric acid solutions. The XRD results of the mortar samples after 56-day curing (unexposed samples) are also presented. Since the XRD results between the mortar types with preloading and without preloading are similar, the XRD results of the mortar types without preloading

are not exhibited in this section. Before exposure to the sulfuric acid solution (unexposed samples), there was only a prominent intensity peak of mullite (around $16.3^\circ 2\theta$, PDF-15-0776) and quartz (around $33.3^\circ 2\theta$, PDF-46-1045) in GPM samples, while the primary intensity peak of gypsum (around $9.0^\circ 2\theta$, PDF-33-0311), ettringite (around $11.5^\circ 2\theta$, PDF-41-1451), and Ca(OH)_2 (around 18.0 and $34.0^\circ 2\theta$, PDF-04-0733) could be detected in the OPM sample. After exposure to various sulfuric acid solutions, there was still a pronounced intensity peak of mullite and quartz in all GPM specimens, which might be primarily attributed to the fine aggregate (sand) and the chemical compositions in GGBFS and FA.

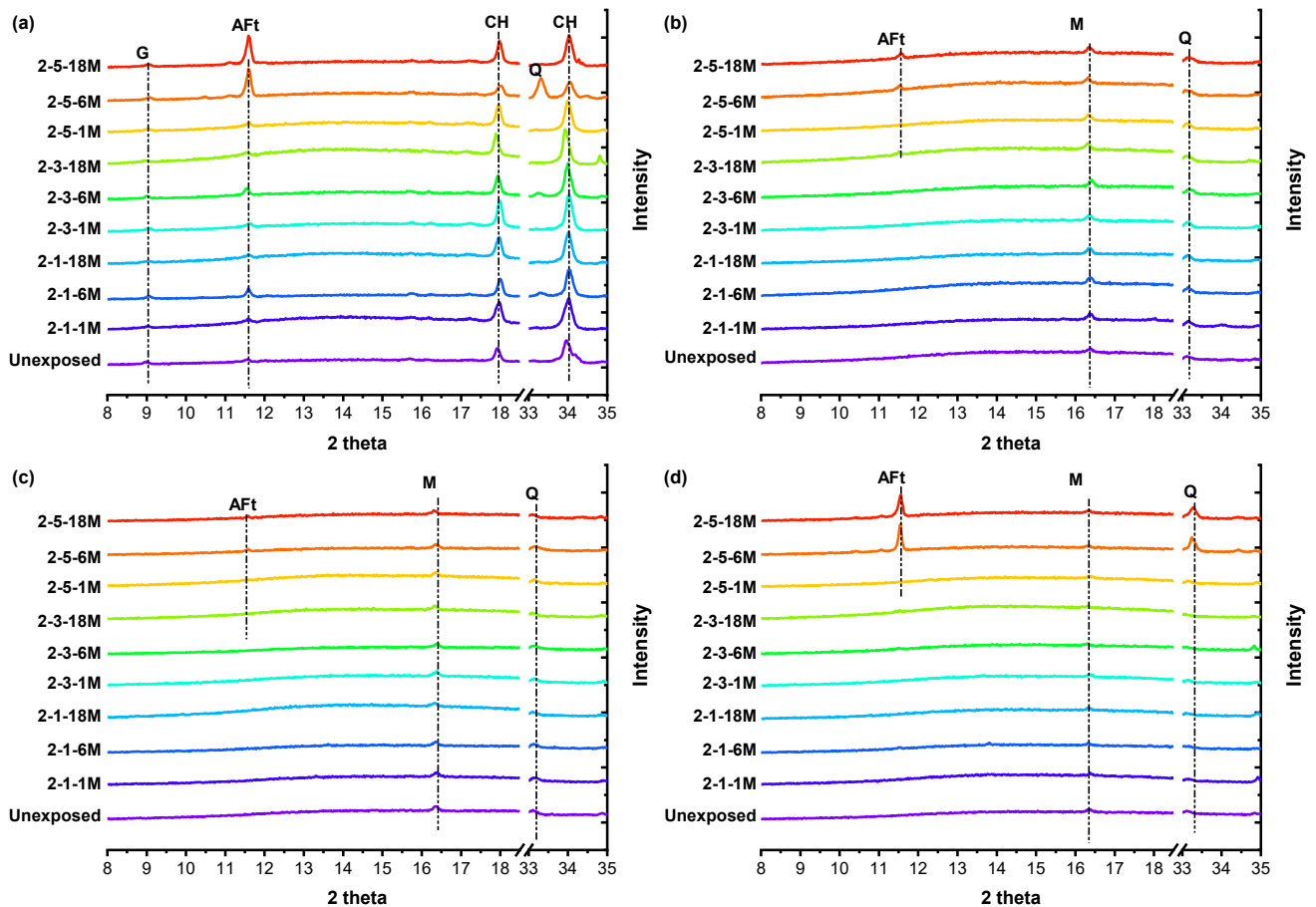


Figure 4.9. XRD patterns of GPM and OPM mortars after exposure to sulfuric acid for 18 months:

(a) OPM; (b) GPM1; (c) GPM2 and (d) GPM3 (AFt-Ettringite, CH- Ca(OH)_2 , G-Gypsum, M-Mullite, Q-Quartz).

After exposure to a low concentration of 1% and 3% sulfuric acid, no apparent intensity peaks of AFt

and gypsum were detected in all GPM specimens, indicating that the two phases were relatively low. After exposure to a 5% sulfuric acid solution, the primary intensity peak of AFt could be detected in all GPM specimens, especially for 6-month and 18-month exposure. Due to lack of CaO, the intensity of AFt peak in GPM1 was not as evident as in GPM2 and GPM3, the latter of which had much more formations of AFt and could be more deteriorated to the sulfuric acid solutions. Compared to GPM specimens, the noticeable intensity peaks of AFt, gypsum, and CH could be detected in the OPM specimen under all the exposure conditions. The intensity of AFt and G peaks in OPM might be generally increased with the exposure time and the increasing sulfuric acid concentrations, indicating that large amounts of AFt could generate due to the reaction between the OPM matrix and the sulfuric acid.

4.6.2 Fourier transform infrared spectroscopy

Figure 4.10 presents the FTIR spectra ($500\text{--}1600\text{ cm}^{-1}$) of OPM and GPM mortars with preloading before and after exposure to different sulfuric acid solutions for 1, 6, and 18 months. Before exposure to sulfuric acid, the asymmetrical extending band of Si-O-Al, usually attributed to geopolymer gels, was detected in all GPM samples. Except for the band of Si-O primarily assigned to C-S-H or sand, the bands of C-O (CO_3) and S-O (mainly for AFt) were also detected in the OPM sample. After exposure to sulfuric acid, the center of the Si-O-Al band in GPM samples was shifted in a vibration range, which was primarily due to the dealumination and depolymerization of GPM specimens attacked by sulfuric acid (Ahmari & Zhang 2013; Bakharev 2005). The GPM3 had the most comprehensive wavenumber range from 975 to 1050 cm^{-1} (75 cm^{-1}), followed by GPM2 and GPM1. The GPM2 had the wavenumber range of 989 to 1055 cm^{-1} (66 cm^{-1}), while the GPM1 had the vibration range from 1008 to 1058 cm^{-1} (50 cm^{-1}). These indicate that the processes of dealumination and depolymerization could occur more easily in the GPM with GGBFS content than in that without GGBFS.

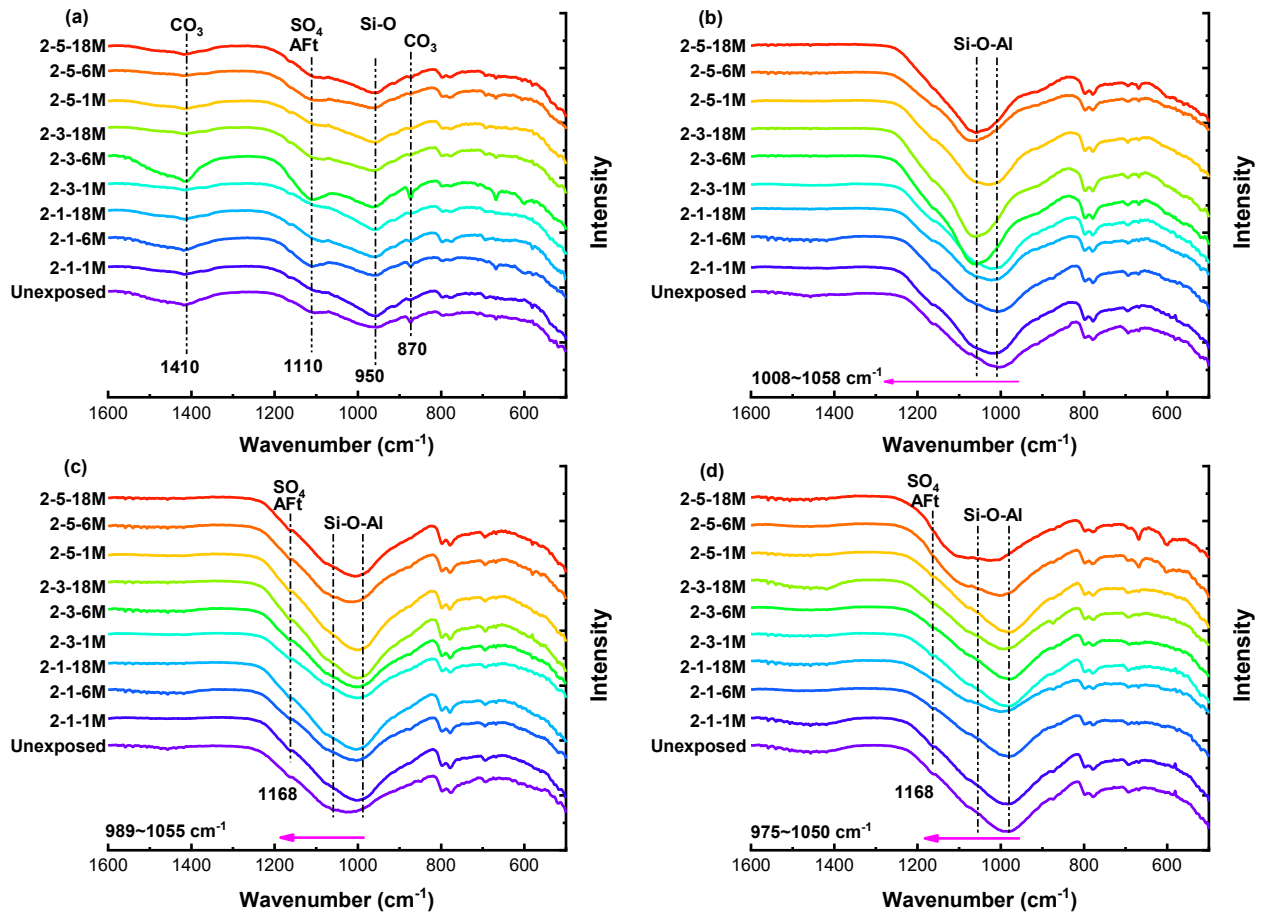


Figure 4.10. FTIR spectra of GPM and OPM mortars after exposure to sulfuric acid for up to 18 months: (a) OPM; (b) GPM1; (c) GPM2 and (d) GPM3.

In addition, the band of Aft around 1168 cm^{-1} was examined in GPM2 and GPM3 after exposure to sulfuric acid, while no similar band was detected in GPM1. Except for the high CaO content, the dealumination and depolymerization might be another reason for large amounts of Aft detected in GPM2 and GPM3. However, the intensity of Aft was more significant in OPM than in GPM samples, indicating that much more Aft was formed in OPM. The center of Si-O band in the OPM sample was basically unchanged, which was probably due to the high sand content in the tested samples. In addition, the generation of Aft due to the reaction between CaO and sulfuric acid was more evident than the decalcification of C-S-H (Bassuoni & Nehdi 2007). Thus, the stretching band of Si-O in the OPM sample was almost kept unchanged.

4.6.3 Thermogravimetric analysis

Figure 4.11 presents the TG and DTG results of OPM and GPM with preloading before and after 18-month exposure to 1, 3, and 5% sulfuric acid solutions. Before exposure to sulfuric acid solutions, various peaks could be detected in the DTG curves. For the OPM, it can be seen from Figure. 11(a) that the peak around temperature of 106 °C could be attributed to the dehydration of C-S-H, while the other two peaks around temperature of 450 and 700 °C could be assigned to the decomposition of Ca(OH)_2 and CaCO_3 , respectively. However, there only one peak then could be detected in GPM (around temperature of 131 °C), GPM2 (around temperature of 134 °C), and GPM3 (around temperature of 135 °C), which could be attributed to the dehydration of geopolymer gels. The higher dehydration temperature of hydrated gels in GPM samples than that of C-S-H in OPM could be due to the stable structure of geopolymer hydrated gels (Aiken et al. 2018).

After exposure to different sulfuric acid solutions, the final weight loss of all samples was increased with the sulfuric acid concentrations. For the GPM samples, the GPM3 exposure to a 5% sulfuric acid solution (GPM3-2-5) had the most prominent weight loss of 15.4%, followed by GPM2-2-5 (12.4%) and GPM1-2-5 (10.5%). The peak temperature of geopolymer hydrated gels in GPM samples was generally increased with the sulfuric acid concentrations, primarily related to AFt and gypsum formation. In particular, the weight loss of GPM3 due to the phases (AFt/gypsum/gels) decomposition around 100–200 °C was noticeably increased. The decomposition temperature of AFt could be around 105 °C, while the gypsum could be decomposed from 110 to 150 °C through an intermediate $\text{CaSO}_4 \cdot 5\text{H}_2\text{O}$ phase to CaSO_4 (Ioannou et al. 2014; Iucolano et al. 2018). The formation of a large amount of AFt and gypsum could fluctuate the peak temperature around 100–200 °C and make the GPM sample with GGBFS content have a high weight loss. Compared to all GPM samples, the OPM exposure to 5% sulfuric acid solution had a higher weight loss of 16.2%. The generation of a large amount of AFt and gypsum could also make the OPM-2-5 have a high peak temperature and have a high weight loss around 100–200 °C due to the decomposition of those phases.

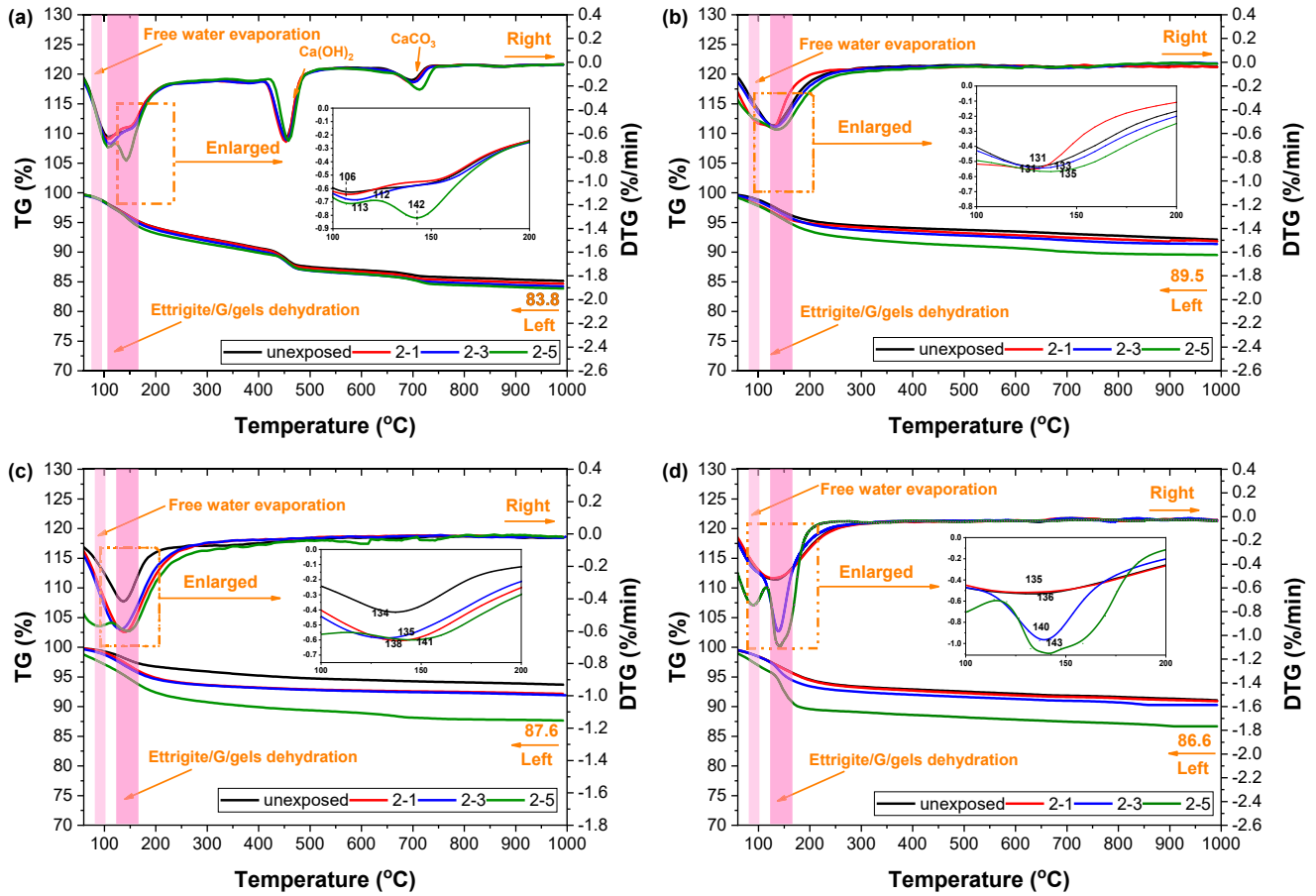
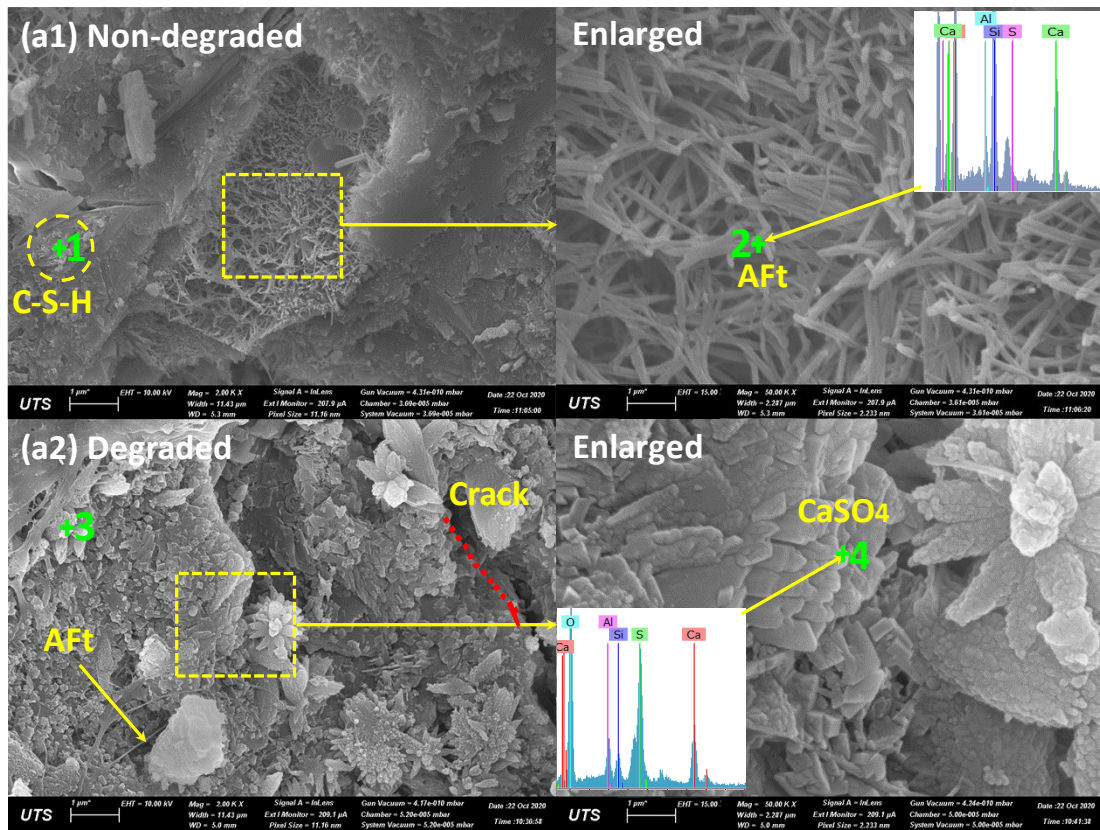


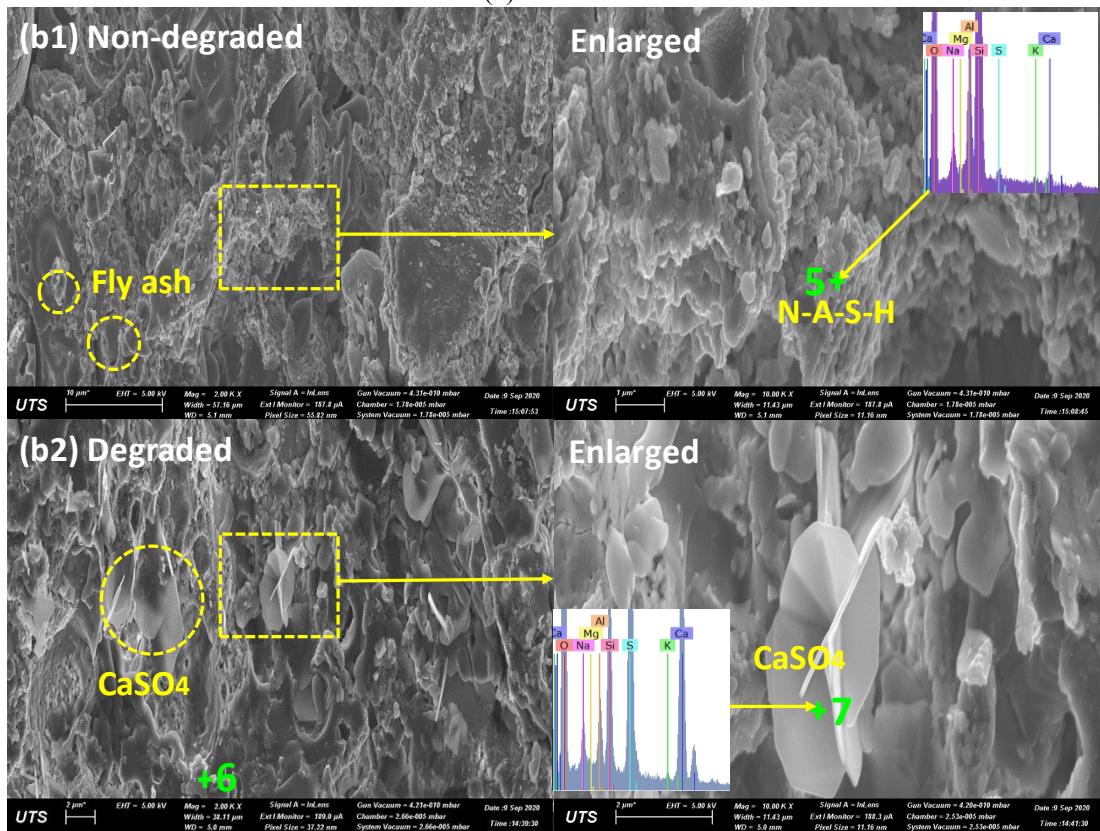
Figure 4.11. TG and DTG results of OPM and GPM after 18-month exposure to different sulfuric acid solutions: (a) OPM; (b) GPM1; (c) GPM2 and (d) GPM3.

4.6.4 SEM with energy dispersive X-ray (EDX) analysis

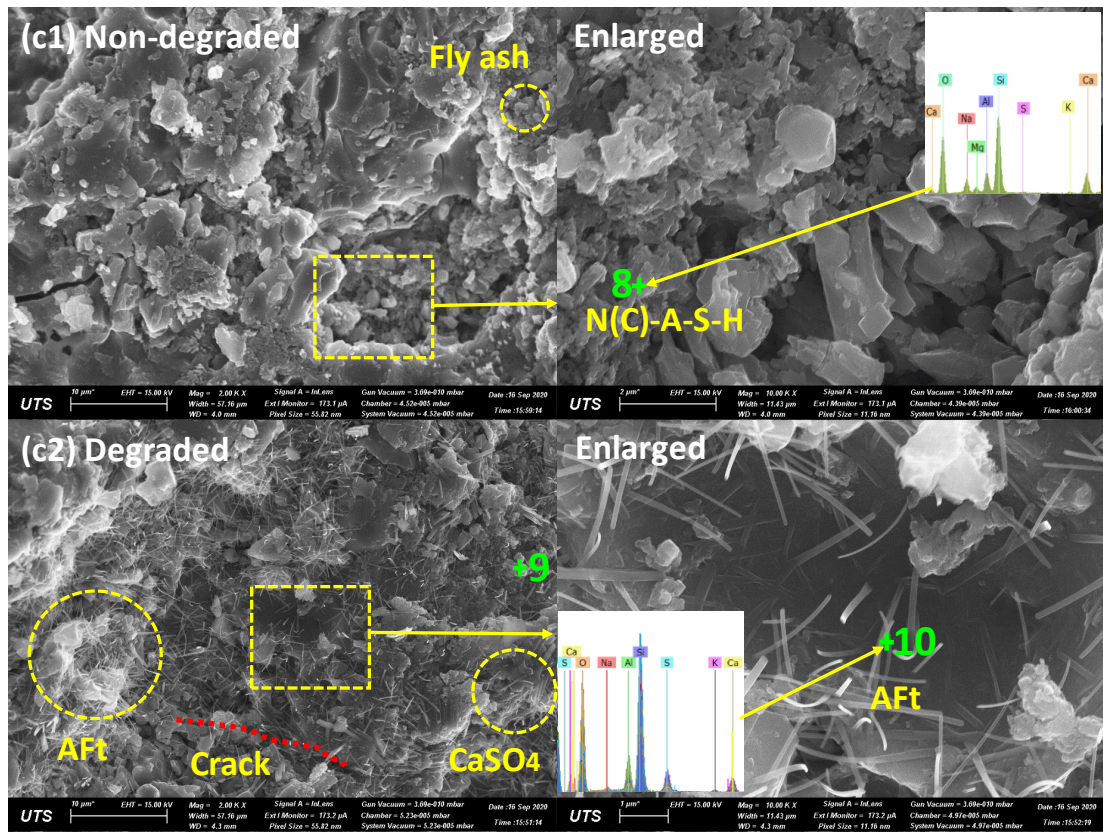
Figure 4.12 presents the SEM micrographs with EDX of OPM and GPM with preloading exposure to sulfuric acid solution for 18 months. Figures 4.12(a1) to (d1) display the non-degraded area of the mortar specimens cured with epoxy resin, while the degraded area of the mortar specimens is exhibited in Figures 4.12 (a2) to (d2). The results of points EDX results marked in different mortar matrices for some hydrated phases are also listed in Table 4.4. For the non-degraded area, there were still some unreacted spherical-like fly ash particles randomly distributed in the GPM mortar matrix.



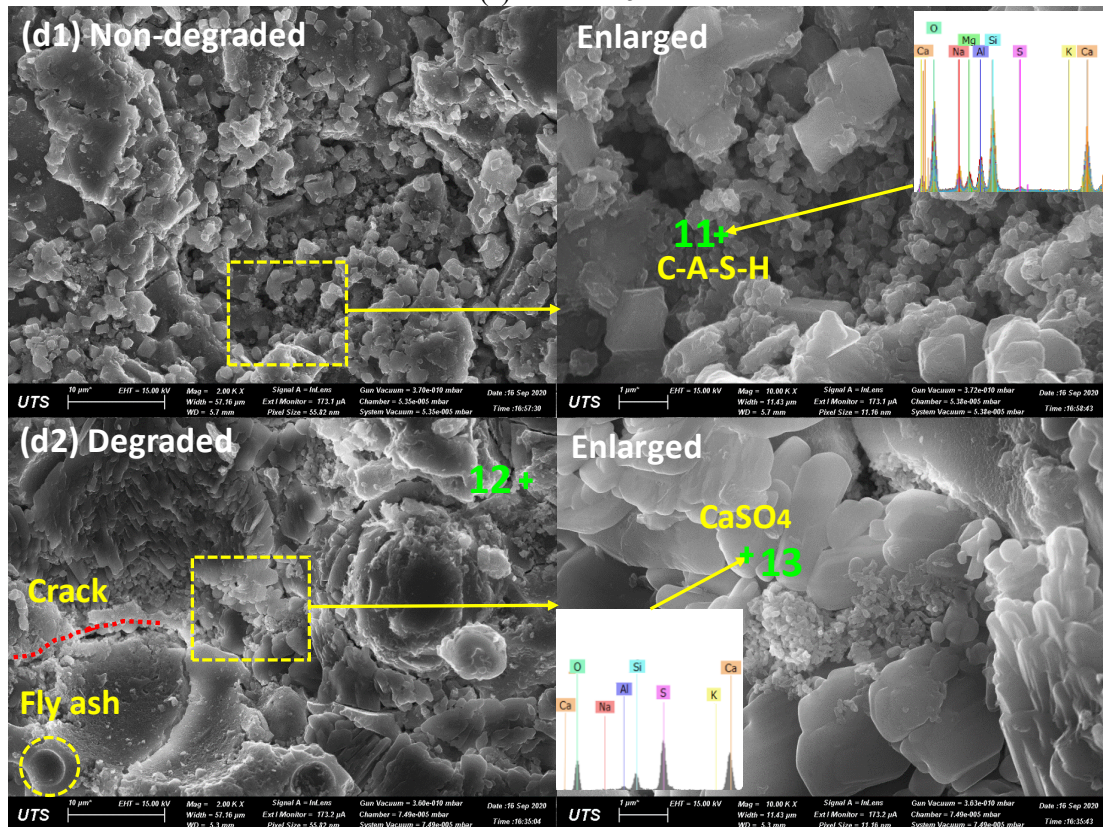
(a) OPM-2-5



(b) GPM1-2-5



(c) GPM2-2-5



(d) GPM3-2-5

Figure 4.12. SEM micrographs with EDX of OPM and GPM after 18-month exposure to 5 % sulfuric acid solution.

The EDX results demonstrated that the geopolymer hydrated gel in GPM1 was seen as N-A-S-H gel with Ca/Si and Al/Si ratios of 0.03 and 1.19, respectively (Provis et al. 2012), which also had a high proportion of sodium element. The N(C)-A-S-H with Ca/Si and Al/Si ratios of 0.29 and 1.10, respectively, and C-A-S-H gels with Ca/Si and Al/Si ratios of 1.31 and 0.35, respectively (Aiken et al. 2018; Ismail et al. 2014), having a high proportion of calcium elements, could also be detected in GPM2 and GPM3, respectively. The addition of GGBFS with high CaO content increased the ratio of Ca/Si but decreased the ratio of Al/Si in the geopolymer gels. Besides, it was difficult to detect the formation of needle-like AFt in the GPM matrix, while the flocculent needle-like AFt and C-S-H gel with Ca/Si and Al/Si ratios of 2.63 and 0.11, respectively, could be examined in the OPM matrix. This indicates that the formation of AFt in GPM samples was primarily attributed to the reaction between the geopolymer hydrated products and sulfuric acid.

For the degraded part, it could be seen from Figures 4.12(a2) to (d2) that the microstructure in all mortar matrices became looser than that in the non-degraded part; in particular, more cracks could be detected in OPM, GPM2, and GPM3 matrix. This indicated that the OPM sample and the GPM group with GGBFS content could be more deteriorated by sulfuric acid than the GPM only with fly ash. The EDX results illustrated that only some sheet-like gypsum was detected in GPM1, while a more considerable amount of hexagonal gypsum could be agglomerated in the OPM and GPM3 matrix, confirming that less gypsum was formed in GPM1 compared to the other specimens. In addition, needle-like hydrated products of AFt could also be detected in the GPM2 matrix, which confirmed a reaction between the GPM2 matrix and sulfuric acid to form AFt.

Table 4.4 Ca/Si or Al/Si atomic ratios of OPM and GPM in non-degraded and degraded area

Location	Elemental atomic percent (%)								Phase	Ca/Si	Al/Si
	O	Si	Al	Na	Ca	S	Mg	K			
#1	81.18	4.97	0.57	0.00	13.04	0.21	0.02	0.01	C-S-H	2.63	0.11
#2	67.99	12.96	4.42	0.04	8.42	5.69	0.23	0.25	AFt	—	—
#3	57.63	24.24	0.11	0.00	17.6	0.29	0.01	0.12	C-S-H	0.73	0.01
#4	67.95	3.51	0.58	0.00	15.93	11.99	0.04	0.00	Gypsum	—	—
#5	71.36	12.1	14.44	1.39	0.41	0.06	0.21	0.03	N-A-S-H	0.03	1.19
#6	63.56	19.25	16.13	0.77	0.18	0.06	0.00	0.05	N-A-S-H	0.01	0.83
#7	67.95	3.51	0.58	0.00	15.93	11.99	0.04	0.00	Gypsum	—	—
#8	71.46	9.7	12.26	2.66	2.97	0.56	0.25	0.14	N(C)-A-S-H	0.29	1.1
#9	71.84	18.61	8.5	0.71	0.17	0.07	0.00	0.1	N(C)-A-S-H	0.01	0.44
#10	45.02	33.08	6.67	0.05	13.21	1.66	0.00	0.31	AFt	—	—
#11	77.02	7.79	2.72	1.78	10.22	0.05	0.28	0.14	C-A-S-H	1.31	0.35
#12	74.87	16.83	4.14	0.69	1.49	1.80	0.16	0.02	C-A-S-H	0.09	0.25
#13	79.16	1.13	0.23	0.25	8.98	10.16	0.08	0.01	Gypsum	—	—

As could be seen from Table 4.4, the Ca/Si ratios of N-A-S-H, N(C)-A-S-H, C-A-S-H, and C-S-H gels in the degraded part were decreased for the sulfuric acid attack, indicating that the decalcification occurred with Ca leached from the mortar matrix to acid solutions. Although the Al/Si of N-A-S-H, N(C)-A-S-H, and C-A-S-H in the degraded part were also decreased for the acid attack, the reduction of the Al/Si ratio was not significant as the Ca/Si ratio, indicating that the cross-linked aluminosilicate polymer gels with a higher Al/Si ratio were more stable in the sulfuric acid solution (Ariffin et al. 2013).

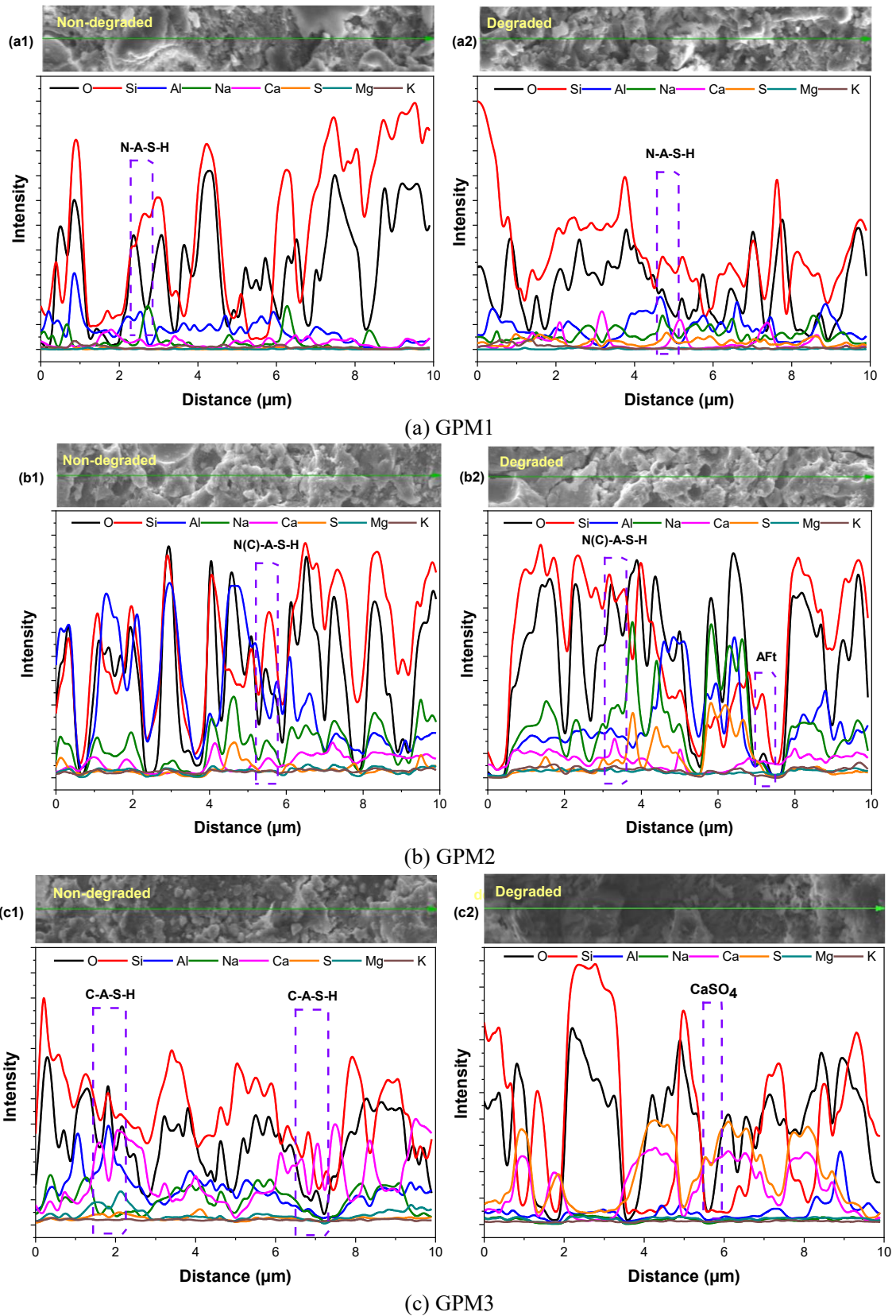


Figure 4.13. SEM-EDX elemental line analysis profiles of GPM mortars after 18-month exposure to 5% sulfuric acid solution

Figure 4.13 presents the EDX elemental line-scan distributions of GPM exposure to 5% sulfuric acid solution for 18 months. Figures. 13(a1) to (c1) display the EDX line-scan results of non-degraded areas, while the results of degraded parts are shown in Figures 4.13(a2) to (c2). The SEM micrographs with a magnification of 500 were captured in both non-degraded and degraded areas and were used to identify O, Si, Al, Na, Ca, S, Mg, and K along the horizontal line of the area of the micrographs. It should be noted that the existence of sand particles in the mortar matrix primarily led to confusion for the elemental distributions. However, the sand particles could be categorized according to elemental distributions, where Si and O had considerably higher intensity with almost no existence of other elements. For the non-degraded area, the intensity of O, Al, Si, and Na in all GPM1 matrices was significantly higher than other elements, and almost no S was detected in the matrix. The N-A-S-H gels could be detected by elemental distributions, where there was a higher intensity among O, Al, Si, and Na with almost no other elements.

Compared to the GPM1, the GPM2 and GPM3 also had a higher intensity of Ca in addition to the high intensity of O, Al, Si, and Na. In particular, the intensity of Ca was even higher than that of Na in some distances of the GPM3 matrix shown in Figure 4.13(c1). The N(C)-A-S-H with relatively similar intensity of Na and Ca and the C-A-S-H with a higher intensity of Ca than Na could also be determined in GPM1 and GPM3, respectively. For the non-degraded area, the intensity of Ca and S in Figures. 4.13(a2) to (c2) was higher than in Figures. 4.13(a1) to (c1), indicating that the intensity Ca and S in the degraded area could be increased due to the sulfuric acid.

Compared with GPM1, the GPM2 and GPM2 exhibited significantly higher intensities of Ca and S, where Ca had much high intensity with high S and O, which could be considered to be gypsum. The AFt with high elemental intensity among the O, Si, Al, and S could also be determined due to the reaction between the mortar matrix and the sulfuric acid solutions. The intensity of Al in the degraded part was lower than in the non-degraded part of GPM specimens, indicating that the dealumination could be caused by the sulfuric acid solution, which was also reported by Bakharev et al. (2005).

4.7 Changes in leaching behavior

Figure 4.14 presents the maximum concentrations of Ca, Al, Si, and Na in the degraded area of OPM and GPM specimens before and after 18-month exposure to sulfuric acid solutions. Before exposure to a sulfuric acid solution, the OPM had a higher concentration of Ca than the GPM specimens, where the addition of GGBFS could increase the concentration of Ca, resulting in the highest concentration of Ca in GPM3, followed by GPM2 and GPM1. This might primarily be related to a higher CaO content in OPC and GGBFS than in FA shown in Table 4.1. A high concentration of Al was founded in the GPM specimens than in the OPM specimen, and the concentration of Al could be increased by the addition of GGBFS, making the GPM3 had the highest concentration of Al. For one reason, more Al-riched gels (see Figure 4.12) like C-A-S-H, N(C)-A-S-H, and N-A-S-H could be detected in the GPM specimen than in the OPM specimen. For another reason, more C-A-S-H/N(C)-A-S-H gels could be produced in the GPM2 and GPM3 than in GPM1.

Similar to Al, the concentration of Si and Na in GPM3 was higher than in other GPM and OPM specimens, which could be related to the fact that the ratio of Ca/Si in GPM specimens was also lower than in the OPM specimen (L'Hôpital et al. 2016; Ye & Huang 2020), except for higher geopolymer gels in GPM3 than in other specimens. After exposure to different sulfuric acid solutions, all element concentrations were decreased as the proportion of sulfuric acid increased, demonstrating that all elements in the degraded parts could be leached to sulfuric acid solutions. The Ca leached from OPM and GPM specimens might be related to the formations of CaSO_4 and Aft in the acid solution (Zhang et al. 2016). The dealumination and depolymerization caused by sulfuric acid primarily accounted for the Al, Si, and Na leached from the GPM specimens. The decalcification of C-S-H in OPM as the result of sulfuric acid attack might also account for the decreasing concentrations of Ca and Si. The Al leached from the OPM specimen was also related to the dissolved Aft in the sulfuric acid solution (Lloyd et al. 2012; Ren et al. 2020).

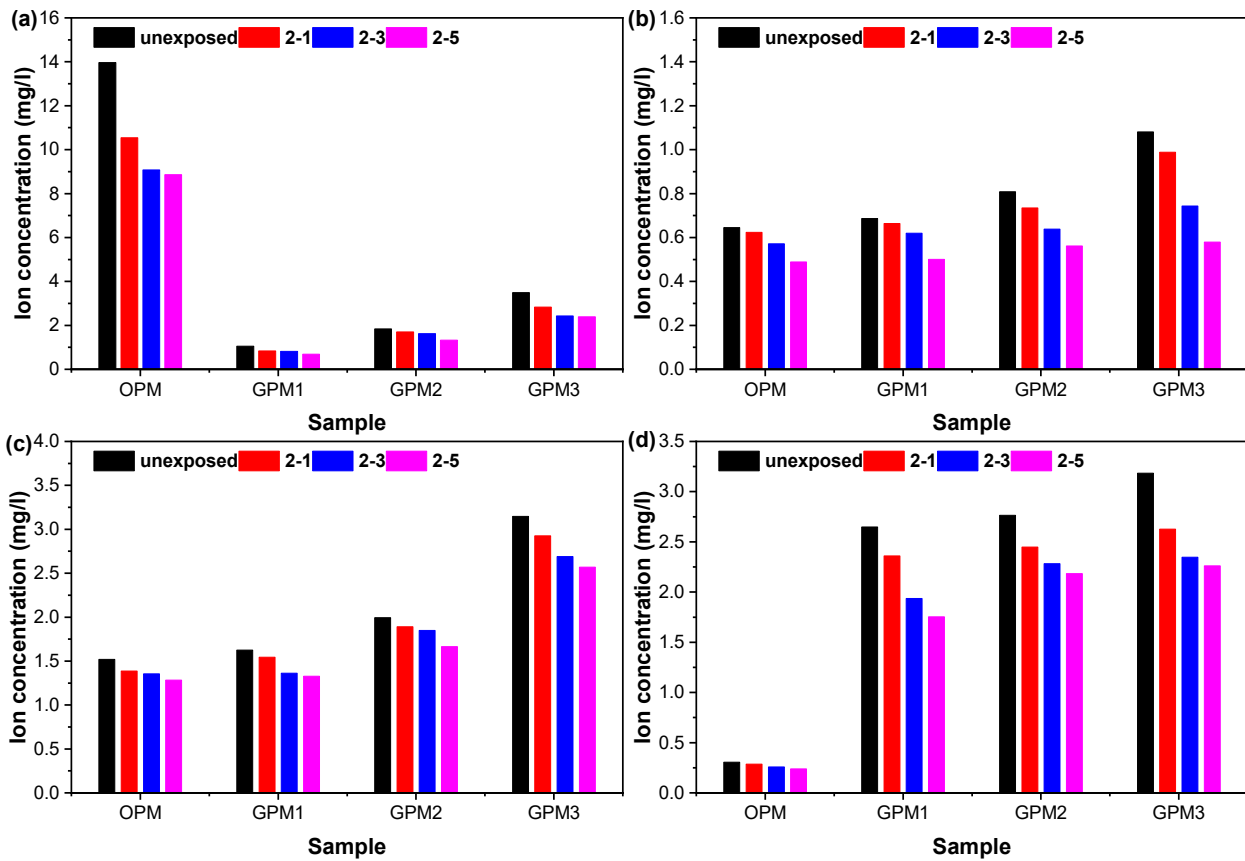


Figure 4.14. Maximum concentrations of different elements in GPM and OPM before and after 18-month exposure to different sulfuric acid solutions: (a) Ca; (b) Al; (c) Si and (d) Na.

4.8 Deterioration mechanism

Table 4.5 concisely summarises the primary findings of OPM and GPM caused by preloading and/or sulfuric acid attacks. It can be seen that under any different environments, the response of GPM specimens increased with the increase of GGBGS content. Compared to the OPM, the response of GPM specimens to the cyclic preloading was more substantial. However, there was a higher response to sulfuric acid attacks and the combined effects in OPM than in GPM. The response caused by sulfuric acid attack was also more significant than that caused by preloading. Compared with other environments, the response of all specimens under the combined effects was more significant. All responses of all specimens could be related to the deterioration mechanism.

Table 4.5 Performance of OPM and GPM mortars exposed to cyclic preloading and sulfuric acid attack

Attacks	Parameters	Response*	OPM	GPM1	GPM2	GPM3
Cyclic preloading	Visual appearance	Barely affected	+	++	+++	++++
	Mass loss	Slightly increased	+	++	+++	++++
	Strength loss	Slightly increased	+	++	+++	++++
	Degradation depth	Slightly increased	+	++	+++	++++
	Microstructural change	Causing cracks or abnormalities	+	++	+++	++++
Sulfuric acid attack	Visual appearance	Relatively generating cracks or partially dissolved	++++++	+++	++++	+++++
	Mass loss	Relatively increased	++++++	+++	++++	+++++
	Strength loss	Relatively increased	++++++	+++	++++	+++++
	Degradation depth	Relatively increased	++++++	+++	++++	+++++
	Microstructural change	Relatively changed in hydration products	++++++	+++	++++	+++++
Combined effects	Visual appearance	Highly generating cracks or partially dissolved	++++++	++++	+++++	+++++
	Mass loss	Highly increased	++++++	++++	+++++	+++++
	Strength loss	Highly increased	++++++	++++	+++++	+++++
	Degradation depth	Highly increased	++++++	++++	+++++	+++++
	Microstructural change	Highly changed in hydration products and cracks	++++++	++++	+++++	+++++

*Note: All response descriptions are for the same group under the same sulfuric acid solution or the same preloading conditions. ‘+’ indicates the response level. The more the number of ‘+’, the greater the response is.

The deterioration mechanism of OPM and GPM with cyclic preloading after exposure to sulfuric acid solutions for up to 18 months is illustrated in Figure 4.15. Before exposure to sulfuric acid solutions,

a higher strength reduction caused by cyclic preloading could be detected in the GPM specimens with GGBFS content, which might be related to the curing conditions with high temperature and the rapid early hydration rate, leading to more generations of microcracks or abnormalities (red dotted triangle area) (Qu et al. 2020). After exposure to sulfuric acid solutions, ions exchanging could occur between the mortar matrix and solutions, where the alumina, sodium, calcium, magnesium, and potassium (yellow arrow) could be transferred into the sulfuric acid solutions, and the H^+ , H_3O^+ , and SO_4^{2-} (red arrow) could be transferred into the mortar matrix (Aiken et al. 2018).

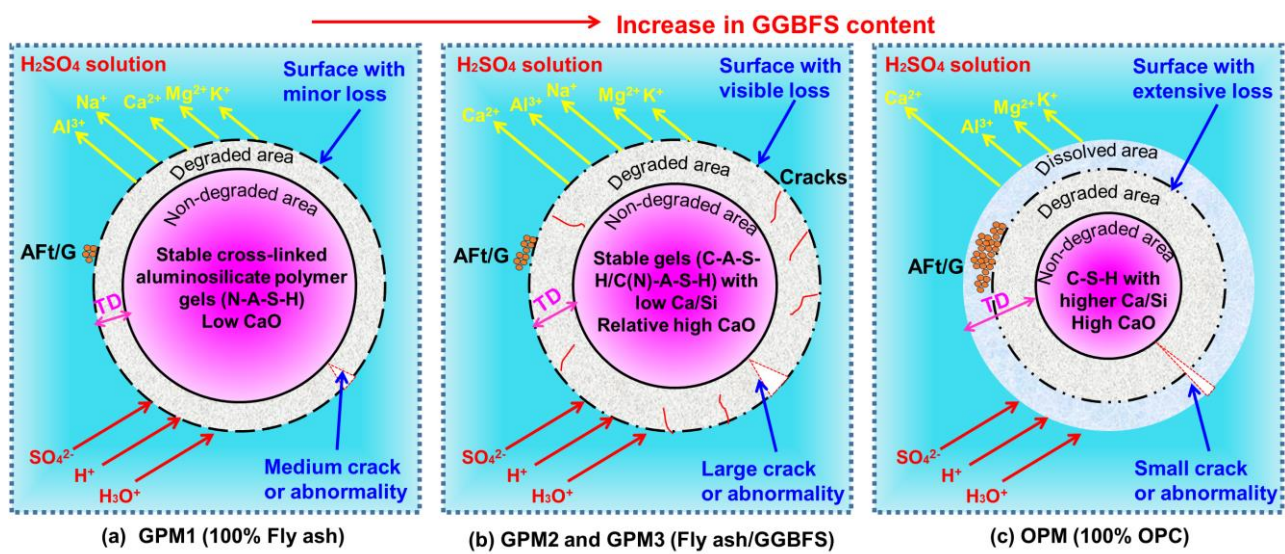


Figure 4.15. Schematic diagram of deterioration mechanism of OPM and GPM groups with preloading after 18-month exposure to different sulfuric acid solutions.

Although the cross-linked aluminosilicate polymer gels like N-A-S-H, C(N)-A-S-H, and C-A-S-H (pink areas in Figures 4.15(a) and (b)) in GPM specimens were reported relatively stabler than the C-S-H gels in OPM (Ariffin et al. 2013), the aluminum and sodium of N-A-S-H and C(N)-A-S-H could partially leach into the acid solution, leaving a highly siliceous framework due to the attack of H^+ and H_3O^+ as shown in Figure 4.15(b) (Allahverdi & Skvara 2001). Besides, the calcium of C-S-H gels in OPM or C-A-S-H gels in GPM2 and GPM3 could also partially leach into acid solutions, but the Ca/Si ratios of C-A-S-H gels was lower than the of C-S-H gels, which could make the cross-linked

aluminosilicate polymer gels more stable in acid solutions (L'Hôpital et al. 2016; Ye & Huang 2020). In addition to sodium, aluminum, and calcium, small amounts of potassium and magnesium were also transferred to sulfuric acid solutions. The sulfate ions dispersed in the solution could react with CaO and make calcium leach in the degraded area to form gypsum and even ettringite. The high CaO content in GGBFS and OPC could lead to much more generations of gypsum and ettringite. In the GPM1 with 100% fly ash, only a small amount of gypsum and AFt could be formed because of the low CaO content. The formations of gypsum and AFt had a negative impact, and it could cause cracks and even massive fractures. Incredibly, some cracks could be detected in GPM3, as shown in Figure 4.15(b), and some areas of OPM could be dissolved into the solution, as shown in Figure 4.15(c). The adverse effect of cyclic preloading on the mortar matrix increased the ions exchanging, which in turn increased the sulfuric acid deterioration.

4.9 Summary

The performance deterioration of fly ash-based geopolymer with different GGBFS contents under cyclic preloading was evaluated after 18-month exposure to sulfuric acid solutions. Based on the results, the conclusions are drawn as follow:

- (1) Before exposure to sulfuric acid solutions, the cyclic preloading caused a significant compressive strength reduction to both the OPM and GPM due to microcracks or damages generated in the mortar matrix. After exposure to sulfuric acid solutions, the cyclic preloading had a negligible effect on the change of visual appearance, while the mass loss of specimens with preloading was higher than the corresponding specimens without preloading, which indicated that the preloading increased the performance deterioration.
- (2) Before exposure to sulfuric acid solutions, the addition of GGBFS increased the compressive strength of fly ash-based geopolymer mortars, and it also increased the strength reduction of GPM caused by preloading. After exposure to sulfuric acid attacks, the addition of GGBFS caused significant damages to the GPM, even leading to some apparent cracks on the surface. The final

residual compressive strength of GPM decreased, and the degradation depth increased with the GGBFS content. It was revealed that the addition of GGBFS had an adverse effect on sulfuric acid resistance of GPM after preloading.

- (3) Before OPM was exposed to sulfuric acid solutions, the compressive strength was higher than GPM1 but lower than GPM2 and GPM3. The preloading caused a lower strength reduction in OPM than in GPM. After exposure to sulfuric acid solutions, the mass loss, strength loss, and degradation depth increased with exposure duration. Although the GPM had a higher strength reduction caused by preloading, the final residual compressive strength of GPM was still higher than OPM. The results showed that GPM under coupled preloading and sulfuric acid attacks exhibited less severe performance deterioration than OPM.
- (4) Increasing concentrations of sulfuric acid solutions increased the deterioration. The severer deteriorations in the GPM with different GGBFS content could be related to the higher CaO content, which more Ca leached from the matrix, leading to the formations of AFt and CaSO_4 . The formations of gypsum and AFt had a negative impact, and it could cause cracks and even massive fractures in GPM. In particular, more obvious cracks could be detected in the GPM with a high proportion content of GGBFS.
- (5) The dealumination and depolymerization of C-A-S-H, N(C)-A-S-H, and N-A-S-H caused by sulfuric acid attacks could cause the GPM deterioration. The high CaO content in OPC and decalcification of C-S-H could account for the severe deterioration in OPM. The microcracks or damages caused by preloading in mortar matrix increased the probability of sulfuric acid deterioration, resulting in a severer deterioration detected with preloading than without preloading.
- (6) The cyclic preloading is confirmed to have an adverse effect of on the mortar matrices increasing the ions exchanging, which increases the sulfuric acid deterioration of cementitious mortars. The relevant results may provide insight into the sulfuric acid resistance of fly ash-based GP materials after cyclic preloading, thus ensuring a better alternative for OPC under aggressive environments.

CHAPTER 5: PERFORMANCE OF CEMENTITIOUS COMPOSITES WITH SEAWATER AND UNDESALTED SEA-SAND

5.1 Introduction

Concrete is one of the most widely used building materials throughout the world, and its output has increased gradually. In consideration of the demand for concrete manufacture and regulatory constraints, the sharp consumption of freshwater and river sand has raised severe environmental concerns (Dhondy et al. 2019; Plattenberger et al. 2020; Wang 2009). Applying seawater (with the 96.5% proportion of the whole water source on earth) instead of freshwater in concrete buildings could offer a sustainable approach to protect freshwater sources from being overused. In addition, utilizing sea sand without desalting has the latest growth to lighten the burden on the exhausting river sand. Although seawater/unwashed sea sand with high salt content is banned in concrete construction owing to its reinforcement corrosion, the fiber-reinforced polymer (FRP) has been reported to be a viable steel reinforcement solution. Therefore, combining seawater and unwashed sea sand in concrete construction with non-corrosiveness steel might produce low-cost and long-durability concrete.

Currently, most existing studies have focused on the effects of using either seawater or unwashed sea sand in concrete, while only a few researchers have studied the influence of utilizing seawater and undesalted sea sand together on the properties of concrete. Compared to freshwater, seawater was generally believed to affect the performance of cement-based composites by the high chemical content. It has been concluded that the multitude of chemicals in seawater will disturb the setting and rheological properties of cement, and may also affect the mechanical properties and durability of concrete (Fu et al. 2020). Some studies reported that the various chemicals in seawater could increase the strength of concrete at an early age, leaving it comparable or relatively higher than concrete manufactured with freshwater (Etxeberria et al. 2016; Li et al. 2015). The content of chloride ions in seawater promoted the cement hydration process, thus reducing cement setting time (Yu et al. 2017)

and fastening its hardening (Sikora et al. 2020). Besides, it was reported that the absorption capacity of concrete with seawater decreased with the porosity reduction in concrete (Etxeberria et al. 2016; Sikora et al. 2019). In contrast to river sand, unwashed sea sand was reported to affect the performance of cement-based composites, mainly reflected in the two following aspects: the salts content and physical properties (Ting et al. 2020; Wang et al. 2017). The unwashed wet sea sand from a shoreline was reported to have a chloride salt content of 6.3%, while no chloride salt content was examined in the river sand from a producer company (Wang et al. 2017). A comparatively smoother surface, poor grade, and relatively finer particle content were founded in sea sand, compared with river sand (Ting et al. 2020). The substitutes of river sand by sea sand could significantly affect the mechanical properties and durability of cementitious concrete (Ozer-Erdogan et al. 2016). However, some studies about the effect of sea sand on the performance of concrete have reached different conclusions (Chu & Yao 2020; Guo et al. 2020; Vafaei et al. 2021). Some studies found that the sea sand could slightly increase the compressive strength of concrete (Vafaei et al. 2021), while others have founded that sea sand had no effect on the compressive strength of concrete (Chu & Yao 2020) or decreased the 28-day compressive strength of concrete (Guo et al. 2020).

In addition, some investigations on the application of undesalted sea sand and seawater in concrete had also subsequently been carried out, with conflicting results published in recent years (Tan et al. 2018; Ting et al. 2020). The primary finding was that concrete mixed with seawater and sea sand (SSC) could obtain higher early compressive strength but was comparable to Portland cement concrete (PC) after 28 days (Tan et al. 2018). In contrast, other studies have figured out that combining using sea sand and seawater for manufacturing concrete can lead to a reduction in the compressive strength, in contrast to PC (Ting et al. 2020). Zhu et al. (2018) found that the application of seawater and sea sand in concrete could reduce the compressive strength of about 50% lower than that of PC, which was conflicted with the experimental results of Yang et al. (2020). Nevertheless, Tan et al. (2018) have mentioned the conclusions by accomplishing a research review about the application of seawater and sea sand in

concrete that the strength development of SSC was not influenced in the early or late ages. Besides, it should also be noted that researches on SSC primarily focused on the investigation of its mechanical properties (Guo et al. 2020; Ozer-Erdogan et al. 2016). However, the effects of seawater and sea sand on concrete are mainly reflected in the changes in hydration phase changes and microstructure, which are primarily related to the content of various chemicals content. Various ions (including sodium, chloride, magnesium, sulphate, calcium, and carbonate ions) in seawater and/or sea sand have been reported to influence the phase change of cement-based concrete in different ways (Jun et al. 2020; Lou & Liang 2020; Qoku et al. 2017; Zeng et al. 2018). The phase and microstructure change caused by the salt content of seawater/sea sand could interfere with the strength and durability of cement-based composites. Some studies only focus on the effect of seawater on the phase change (De Weerd et al. 2015) rather than taking the effect of undesalted sea sand into considerations.

Therefore, the purpose of this study is to assess the synergistic effects of seawater and undesalted sea sand on the properties of cement-based composites towards the reduction of burden on the resource deficiency of river sand and freshwater. To evaluate the influences of seawater and undesalted sea sand on the hydration reaction, mechanical properties, water absorption, and phase change, different types of Portland cement mortar with water to cement ratios (w/c) of 0.3, 0.4 and 0.5 were prepared, respectively. Another cement mortar mix with river sand and demineralized water was manufactured and taken as the reference group. The related results are expected to provide guidance for the academic research and practical application of cementitious composites mixed with seawater and undesalted sea sand.

5.2 Experimental program

5.2.1 Raw materials

All cement mortars were cast according to Australian-made Eureka general-purpose cement CEM I 42.5R, which conforms to the AS 3972 standard (General purpose and blended cement). The oxide

composition detected by X-ray fluorescence, mineral composition measured by the Bogue calculation, and physical properties, including Blaine, density, and water demand of the cement, is shown in Table 5.1. Two types of water were applied in this experiment: seawater and demineralized water. The seawater was obtained from Botany Bay near Sydney. The chemical compositions of the seawater by inductively-coupled plasma mass spectrometry (ICP-MS) and Potentiometric titration are displayed in Table 5.2. The chemical composition of ASTM D1141-98 (Standard practice for the preparation of substitute ocean water) seawater is also shown in Table 5.2. It can be seen that the concentration of NaCl was about 19.0 g/l, slightly lower than that of in ASTM standard seawater. The other chemical composition in seawater was also lower than in ASTM standard seawater.

Table 5.1 Chemical and physical properties of Portland cement

Chemical properties (by weight %)								
Stability	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ Oeq	f-CaO
1.0	21.86	4.56	3.47	65.44	2.6	0.37	0.58	0.93
Minerals and properties								
C ₃ S	C ₂ S	C ₃ A	C ₄ AF	Blaine	Density	Water demand		
54%	16%	7%	11%	552 m ² /kg	3.06 g/cm ³	28.0 %		

Table 5.2 Concentration of salt content in seawater based on Botany Bay (Sydney, Australia) and ASTM standard

Concentration (g/l)	NaCl	MgCl ₂	Na ₂ SO ₄	KCl	CaCl ₂	NaHCO ₃
Botany Bay	19.0	1.35	0.88	0.38	0.40	—
ASTM standard	24.5	5.20	4.09	0.35	1.16	0.20

Two types of sand were also applied in this research: unwashed sea sand and river sand. The unwashed sea sand was also obtained from Botany Bay in Sydney (Australia) without the desalting process. The particle size distribution of unwashed sea sand and river sand determined based on AS 1141.11.1

(Methods for sampling and testing aggregates particle size distribution – sieving method) is displayed in Figure 5.1. The sieves with holes of 0.6 mm and 0.3 mm for river sand could pass 52.1% and 12.9%, respectively, while the corresponding percentage of sea sand was 80.4% and 37.7%, respectively. The fineness modulus of river sand was 2.39, compared to that of unwashed sea sand of 1.86, which indicated the unwashed sea sand was briefly finer than river sand. The chemical composition of sea sand and river sand is displayed in Table 5.3. The main mineralogical component of unwashed sea sand and river sand was quartz. No chloride salt was found in the river sand, while the weight percentage of Cl^- ion and sulphate ions in unwashed sea sand was around 0.83% and 0.09%, respectively. The sea sand mentioned below in this experiment representative the sea sand without desalting.

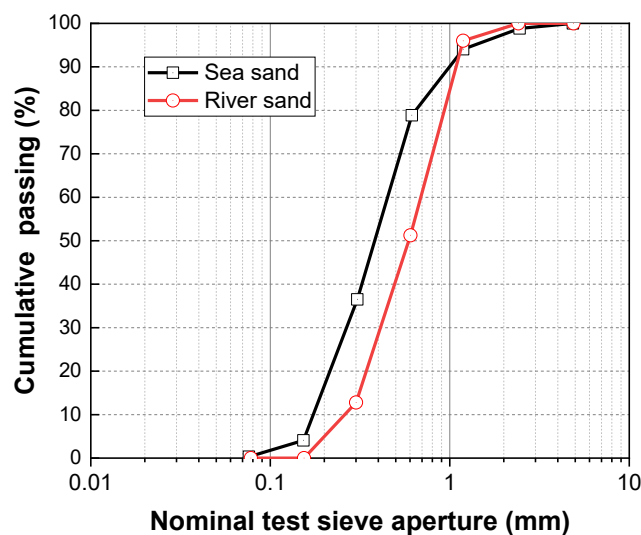


Figure 5.1. Particle size distribution curves of sea sand and river sand

Table 5.3 Chemical composition of unwashed sea sand and river sand (wt%)

Materials	Chemical compositions							
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Cl	SO_4
Sea sand	96.5	0.21	0.43	0.63	0.06	0.07	0.83	0.09
River sand	97.91	1.13	0.50	—	—	0.25	—	—

5.2.2 Mix design and specimen preparation

A total 12 types of cement mortars, including 3 types of DR mortar (using demineralized water and river sand), three kinds of DS mortars (using demineralized water and sea sand), three kinds of SR mortars (using seawater and river sand), three kinds of SS mortars (using seawater and sea sand) were produced. The cement mortars were mixed with a Hobart mixer conforming to ASTM C39 (Standard test method for compressive strength of cylindrical concrete specimens), with three different water to cement (W/C) ratios of 0.3, 0.4, and 0.5, respectively. Table 5.4 presents the compositions of the mortar mixtures.

Table 5.4 Mix proportion of cement mortars (by weight, gram)

Specimens	Cement	Demineralized water	Seawater	River sand	Sea sand	W/C ratio
DR1	300	90	—	600	—	0.3
DR2	300	120	—	600	—	0.4
DR3	300	150	—	600	—	0.5
DS1	300	90	—	—	600	0.3
DS2	300	120	—	—	600	0.4
DS3	300	150	—	—	600	0.5
SR1	300	—	90	600	—	0.3
SR2	300	—	120	600	—	0.4
SR3	300	—	150	600	—	0.5
SS1	300	—	90	—	600	0.3
SS2	300	—	120	—	600	0.4
SS3	300	—	150	—	600	0.5

All the mortars were mixed based on the following procedure: at the beginning, sea sand or river sand with cement was mixed at a slow speed. After 1 min, the demineralized water or seawater was put into the Hobart mixer, followed by another 2 min of slow mixing. After a 1 min rest, high-speed mixing was continued for 2 min before finally poured into oiled moulds with dimensions of 50 mm diameter

and 100 mm height to form specimens. All cement mortars were kept for 1 day in a standard curing room with RH of 95% and at a temperature of 20 ± 1 °C. After the curing of 24 hrs, the mortars were demoulded and kept in the same curing conditions for the various testing ages.

5.3 Experimental methods

5.3.1 Isothermal calorimetry

In order to evaluate the hydration kinetics with calorimetry, the samples were prepared as the following procedure: for the mixture with W/C of 0.3, 6.42 g of cement and 12.84 g of sea sand or river sand was put into a glass container and blended with 2.68 g of seawater or demineralized water; for the mixture with W/C of 0.4, 5.84 g of cement and 11.68 g of sea sand or river sand was put into a glass container and blended with 2.34 g of seawater or demineralized water; for the mixture with W/C of 0.5, 5.36 g of cement and 10.72 g of sea sand or river sand was put into a glass container and blended with 2.68 g of seawater or demineralized water. Afterward, the samples were blended, and the heat evolution of all mixtures was determined by an isothermal heat conduction calorimeter (TAM Air) with a comparable reference containing water of 6.5 g for up to 7 days. The hydration heat and cumulative heat flow were also recorded. Besides, for further analyzing the influences of sea sand and seawater on the hydration dynamics of all mortar mixtures, the accelerating rate of hydration (ΔH) was measured according to Eq. (5-1):

$$\Delta H_i = \frac{H_i - H_{DR3}}{H_{DR3}} \times 100\% \quad (5-1)$$

where H_i (J/g) represents the cumulative heat of the selected mixture; H_{DR3} (J/g) denotes the cumulative heat of the DR3; ΔH_i is the hydration acceleration rate of the selected mixture corresponding with the DR3 of the same age.

5.3.2 Compressive strength

The compressive strength of all mortars was recorded after curing for 1, 3, 7, 14, and 28 days with

three cylinders specimens (Φ 50 mm $\times$ 100 mm) of each mixture, based on the ASTM C109 (Standard test method for compressive strength of hydraulic cement mortars). Besides, further analyzing the influences of sea sand and seawater on the strength development of all the mortar mixtures, the acceleration rate of compressive strength (ΔC) is calculated based on Eq. (5-2):

$$\Delta C_i = \frac{C_i - C_{DR3}}{C_{DR3}} \times 100\% \quad (5-2)$$

where C_i is the compressive strength of the selected mortar mixture; C_{DR3} represents the compressive strength of the *DR3* reference mortar; ΔC_i denotes the compressive strength acceleration rate of the selected mortar corresponding with the *DR3* at the same curing age.

5.3.3 Water sorptivity

The same cylindrical mortar specimens for compressive strength tests after 28-day curing were also adopted for the water absorption test, according to the reference (Li 2020). Before the water absorption test, three specimens per mixtures were immersed in demineralized water for 48 hrs and poured into an oven at 70 °C until no change was found in the specimens' mass, so as to reduce the influence of the unreacted salt in the pore on the sorptivity test results. To ensure the single-track transportation of water, the inclined exterior of the mortar mixtures was attached with tape, and just the bottom surface was immersed in water with a depth of 3 mm. The mass change of all mortars after curing for 28 days was calculated at different times. The cumulative volume of absorbed water per unit area (I) is calculated according to Eq. (5-3).

$$I = \Delta m / (A \times \rho) \quad (5-3)$$

where Δm corresponds to the mass obtain of the mortar (g); A represents the area of the inflow surface (mm^2); and ρ is the density of water (g/mm^3).

5.3.4 ICP-MS analysis

The cement mortars, after curing for 28 days, were smashed into 20 mm thick slices and grinded into

powers passing through a 75 μm sieve. The 10 g of powder was mixed with 100 ml (1:10) HNO_3 and heated in a furnace oven at 80 $^\circ\text{C}$ for 2 hrs. About 10 ml extracted solution was cooled down, topped up to 500 ml with deionized water, and filtrated with 4 μm cellulose filter before analysis. The resulting solution was analyzed by ICP-MS to determine the element concentrations of Al, Mg, and Ca.

5.3.5 Microstructure characterization

To investigate the phase change with the hydration reaction, the smashed samples from the core of mortars were adopted after curing for 1, 3, 7, 14, and 28 days and then were crushed into powder. Isopropanol was applied to prevent the hydration processes of the powder, and then all powdered samples were well dried in the oven at a temperature of 40 $^\circ\text{C}$ for 48 hrs. By the thermogravimetric analysis (TGA), the powder was held at 40 $^\circ\text{C}$ for 30 min at first and heated by temperatures from 40 $^\circ\text{C}$ to 1000 $^\circ\text{C}$ at 10.00 $^\circ\text{C}/\text{min}$ in a N_2 environment. In the process of X-ray diffraction (XRD), a BRUKER AXS D8 ADVANCE machine using 40 kV power and 40 mA with a Cu Ka source was used with 2 theta angles from 5 to 70. The Jade 6.5 software with the powder diffraction file (PDF) database was utilized to analyze the XRD patterns and the different diffraction peaks were also recorded by interplanar spacing (d). In the process of Fourier transform infrared spectroscopy (FTIR), Jasco 4100 series FTIR Spectrometer with attenuated total reflectance attachment was used. The spectra were recorded between the 400 and 4000 cm^{-1} wavenumber at 8 cm^{-1} resolution.

In addition, the polished section from the core samples was measured by scanning electron microscopy with energy dispersive X-ray (SEM-EDX). Zeiss Supra 55VP SEM has Raith Elphy Plus E-beam Lithography System as a chemical composition analyzer at a speed-up voltage of 15 keV. The samples were carbon-coated. The analysis program was established to analyze the elements shown as follow: Na, Mg, Al, Si, Cl, Ca, K, and S. The chemical compositions were analyzed by Aztec version 2.0 software according to EDX results. EDX results were introduced both as profiles in atomic mass, with the attention on chloride, magnesium, and sulphate contours, and in dot plots.

5.4 Results and discussions

5.4.1 Hydration rate

The specific heat flow of all different mortar mixtures is compared in Figure 5.2. As it can be seen from Figure 5.2(a), for the same mortar mixture, the lower the water-cement ratio was, the higher the exothermic peak value had, while the W/C had no apparent influence on the appearing time of the exothermic peak, indicating that the appearing time of the exothermic peak might be primarily caused by the salts content in sea sand and seawater. It can be seen from Figure 5.2(b) that for the mortar mixtures with the same water-cement ratio, the exothermic peak value of DS was slightly higher than that of DR, which indicated that the replacement of river sand by sea sand contributed to a slight enlargement in reaction speed of the early hydration. As the water-cement ratio decreased, the differences of exothermic peak value between DR and DS became more and more obvious. The difference in the exothermic peak value between DR3 and DS3 was not as pronounced as the difference between DR1 and DS1. Compared to the DR in Figure 5.2(c), the exothermic peak of SR came into being earlier, and the peak value of SR was also higher, which confirmed that the application of seawater rather than demineralized water could speed up hydration reaction. There are no apparent differences between the SR and SS in Figure 5.2(d), while the exothermic peak of SR and SS came into being earlier, and the peak value of SR was also higher than that of DS. This indicates that compared with the effect of seawater on hydration, the low salt content of sea sand had a lower promotion for the hydration reaction of cement. In addition, there might be a hysteresis phenomenon in sea sand that the longer time it took for salt in sea sand to dissolve in water.

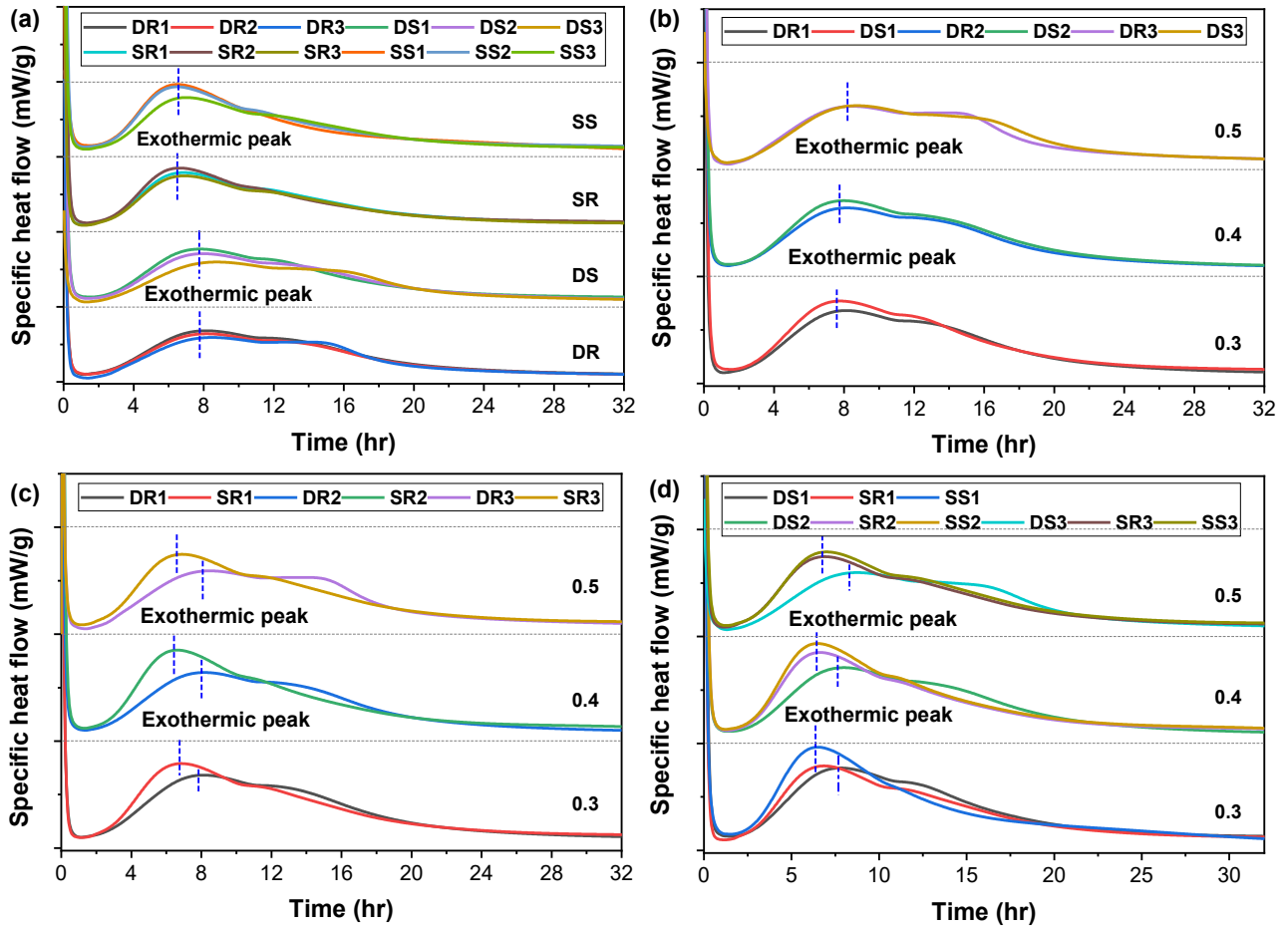


Figure 5.2. Comparison of specific heat flow of different cement mortar mixtures: (a) Effect of W/C ratio; (b) Effect of seawater; (c) Effect of sea sand; and (d) combined effect of seawater and sea sand.

Besides, to gain a thorough comprehending of the isothermal calorimetry investigation, the acceleration rate of hydration measured according to Eq. (5-1) is also listed in Table 5.5. The negative value in Table 5.5 demonstrates that the selected mortar specimens had a lower cumulative heat than that of DR3. Before three days of hydration, for the same mortar mixture, the lower the water-cement ratio was, the higher the hydration acceleration rate had. However, after 3 days of hydration, the amount of acceleration rate in the same mixture with W/C ratio of 0.5 was higher than those with W/C ratio of 0.3 but lower than that of with W/C ratio of 0.4. This may be related to the sealed environment and the fastest water reaction in the mixture with W/C ratio of 0.3 than those with W/C ratio of 0.4 and

0.5. It should be noted that the total cumulative heat of cement mortars after 7 days with W/C ratio of 0.3 would be more than those of 0.4 and 0.5 if there were in the same humidity. With the same water-cement ratio, the sea sand replacing for the river sand could slightly increase the acceleration rate, which made the DS have a higher acceleration rate than that for DR. The seawater could significantly increase the acceleration rate, which made the SR have a higher acceleration rate than that of DR and DS. The combination of sea sand and seawater made the SS have the largest acceleration rate, especially after hydration of 12 hrs. This has verified the previous results from some researchers that the existence of salt ions content in seawater speeds up the hydration reaction of cement at the beginning of hydration (Jiao et al. 2019; Sikora et al. 2020).

Table 5.5 Acceleration rates of cement hydration in comparison to DS3 after 7 days of curing

Samples	Acceleration rate (%)					
	12 hours	1 day	2 days	3 days	5 days	7 days
DR1	50.6	19.0	14.2	4.7	-2.8	-4.1
DR2	17.3	7.0	6.4	5.6	2.3	0.7
DR3	0.0	0.0	0.0	0.0	0.0	0.0
DS1	51.7	22.3	17.0	6.7	-1.1	-2.5
DS2	19.2	9.6	9.9	8.8	5.0	3.4
DS3	11.7	4.5	3.7	3.0	2.1	1.8
SR1	60.1	25.7	22.0	6.4	-1.2	-2.5
SR2	50.2	19.1	15.7	14.4	6.4	4.6
SR3	32.7	13.4	14.5	9.0	2.7	1.7
SS1	67.4	28.1	27.7	8.0	0.2	-1.1
SS2	54.9	22.5	19.5	17.7	11.1	9.2
SS3	31.0	13.8	15.4	10.1	3.8	2.8

Based on the above discussion, it is possibly assumed that seawater had an apparent influence on

accelerating the hydration speed at the beginning and that this influence was further incontestable with the addition of sea sand. The same conclusions were also summarized by Li et al. (2015) and Zhang et al. (2013), indicating that some ions in seawater accelerated the hydration process, accelerated the early Portlandite (CH) formation, and further participated in the reaction. However, it was also essential to take the hysteresis on accelerating hydration reaction caused by sea sand into consideration when preparing SSC.

5.4.2 Compressive strength

Figure 5.3 displayed the compressive strength development of all mortars with curing time. In order to gain a thorough comprehending of the strength development influenced by the seawater and/or sea sand, the acceleration rate of compressive strength, measured from Eq. (5-2), is also displayed in Figure. 5.4. The negative value of the selected mortar specimens in Figure. 4 represents a lower compressive strength than DR3. Generally, for the same mortar mixtures, the lower the water-cement ratio is, the higher the compressive strength.

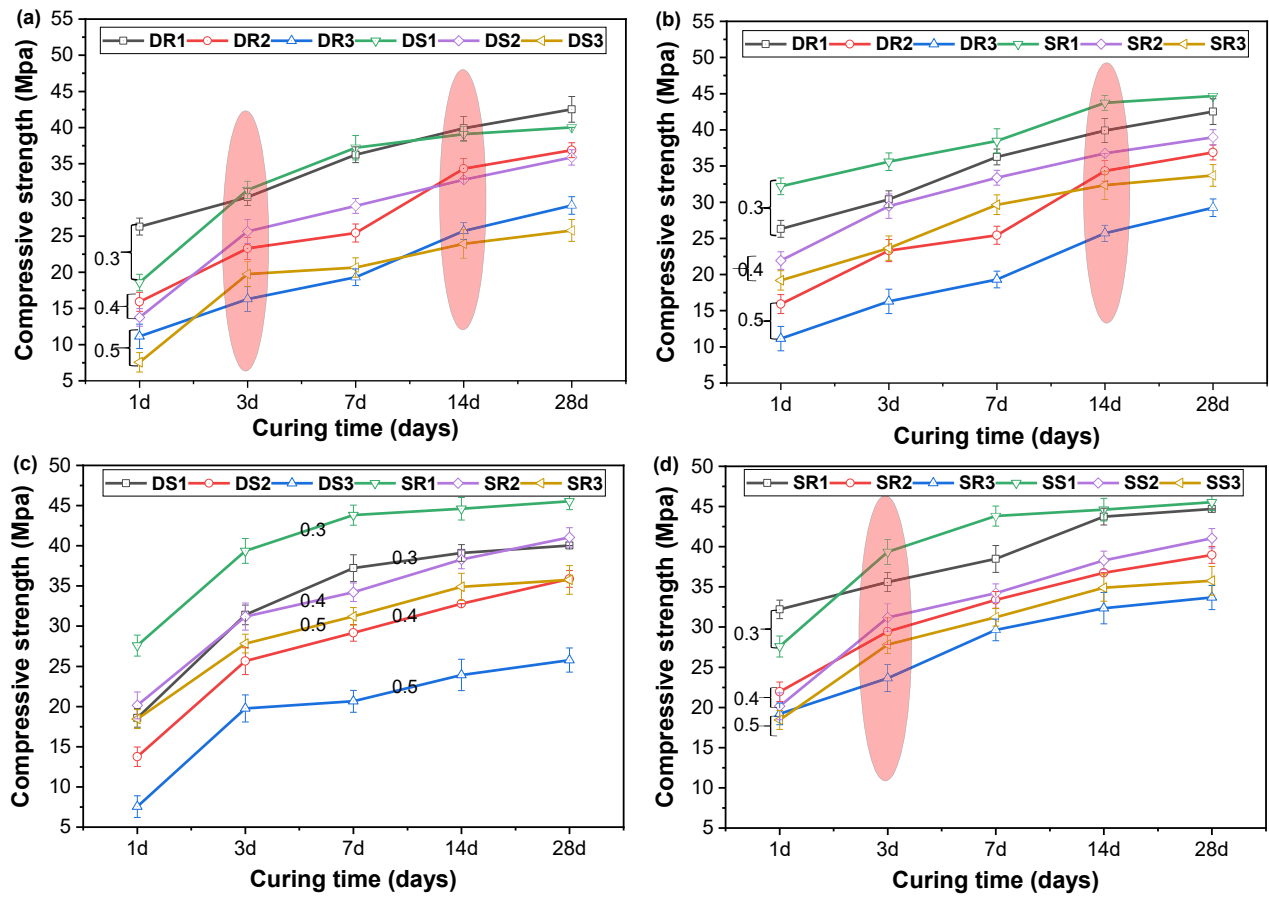


Figure 5.3. Compressive strength of cement mortars at different curing ages: comparison between (a) DR and DS; (b) DR and SR; (c) DS and SR; and (d) SR and SS.

From Figure 5.3(a), obvious alterations in compressive strength development were found between the DR and DS. On the first day of hydration, the DR mixtures presented higher compressive strengths than those corresponding DS mixtures. However, after 3 and 7 days of hydration, there was a higher compressive strength in the DS mortar mixtures than that of corresponding DR mixtures, which might be related to the existence of some ions in sea sand promoting cement hydration during this period. However, as a result of intensive hydration after 14 days, DR mixtures presented higher compressive strengths than the corresponding DS mixtures again. This may be related to the fact that the influence of the physical properties of the sea sand was more dominant than that of the salt contained in sea sand after 7-day curing (Guo et al. 2020).

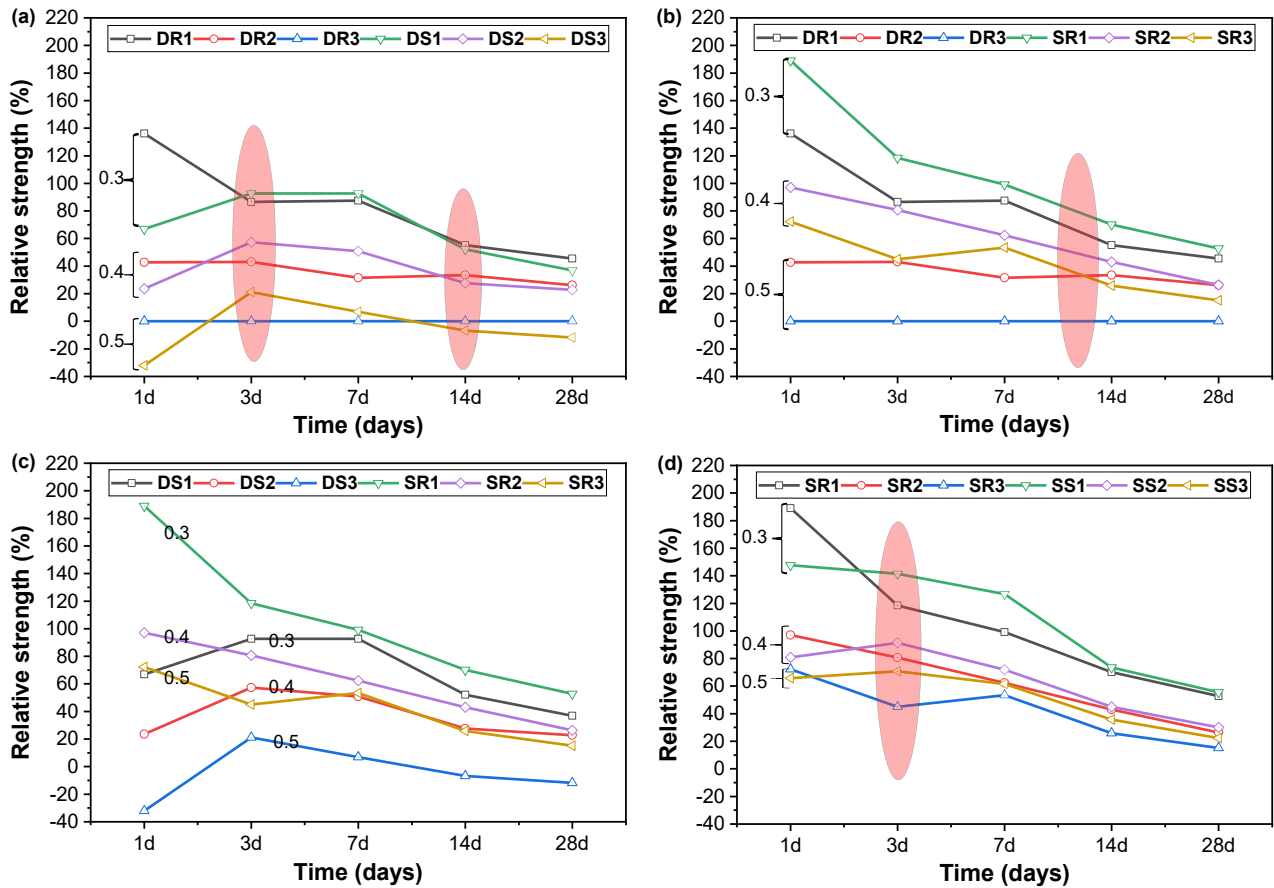


Figure 5.4. Relative strength of cement mortars compared to DS3 at different curing ages: comparison between (a) DR and DS; (b) DR and SR; (c) DS and SR; and (d) SR and SS.

Significant variances in the strength development influenced by seawater were detected between DR and SR mixtures, shown in Figure 5.3(b). After one day, SR displayed higher compressive strengths than that of DR. The 1-day compressive strength of SR1 in Figure 5.4(b) is 53% higher than that of DR1. The corporation of seawater promoted compressive strength development in mortar mixtures in the relatively earlier of the hydration reaction, indicating that the existence of various salt ions in seawater accelerated the hydration reaction of cement in this stage. However, although the strength of mortar mixtures mixed with seawater was higher than the corresponding mixtures with demineralized water, the accelerating effect was relatively limited as time increased. It should be emphasized that the final strength of SR1 at 28 days was just 7.4% higher than that of DR1, and the final strength of

specimens in the SR2 group at 28 days was only 0.3% higher than that of DR2. From Figures 5.3(c) and 5.4(c), the influence of sea sand on the strength development and relative strength was much lower than that of seawater. In the same water-cement ratio, the compressive strength and relative strength of DS were consistently lower than that of SR, the same results of which were also founded in the hydration rate results.

It can be seen from Figures 5.3(d) and 5.4(d) that the effect of both sea sand and seawater on strength development between SR and SS was also evident. Although the compressive strength of SS on the first day was lower than that of SR, the compressive strength of SS gradually increased faster than that of SR after 3-day curing. Nevertheless, owing to intensive hydration after 7 days of curing, the disparity between SR and SS shrank progressively. Nevertheless, after 14 days of curing, mortar mixtures containing seawater and sea sand achieved nearly 100% of 28-day compressive strength. The SS1 in 14 days of curing accounted for a 55.6 % higher compressive strength than DR3, while SR1 exhibited a 52.8% higher compressive strength than DR3. After 28 days of curing, the corresponding mortar mixtures with the same W/C ratio presented just slight differences in the compressive strength among them. It should be noted that after 28 days of curing, SS1 showed the highest compressive strength of 45.5 MPa, while SR1, DR1, and DS1 displayed compressive strengths of 44.7 MPa, 42.5 MPa and 40.0MPa, respectively. Therefore, the side effect of the physical properties of sea sand (low fineness modulus or poor gradation) on the strength development of mortar mixtures could be compensated by the incorporation of seawater.

5.4.3 Water sorptivity

The cumulative absorbed water content in 25 hrs water exposure of various mortar mixtures after 28-day curing is exhibited in Figure 5.5. The cumulative absorbed water content, the millimeter unit, was calculated according to Eq. (5-3). Compared to those mortar mixtures with a higher water-cement ratio, the mortar mixtures with a lower water-cement ratio presented much lower absorbed water content due to more permeable pores occurring with the increasing of water-cement ratio (Vafaei et al. 2021). From

Figure 5.5(a), the replacement of sea sand resulted in a slight increase in cumulative absorbed water content. It could be seen that the cumulative absorbed water content of DS1 was the lowest in the DS, which was also higher than that of DR1. The gradation of sea sand was poorer than that of river sand, and the fineness modulus of sea sand was also lower than that of river sand, which might lead to more permeable pores and increase the cumulative absorbed water content (Wang et al. 2017).

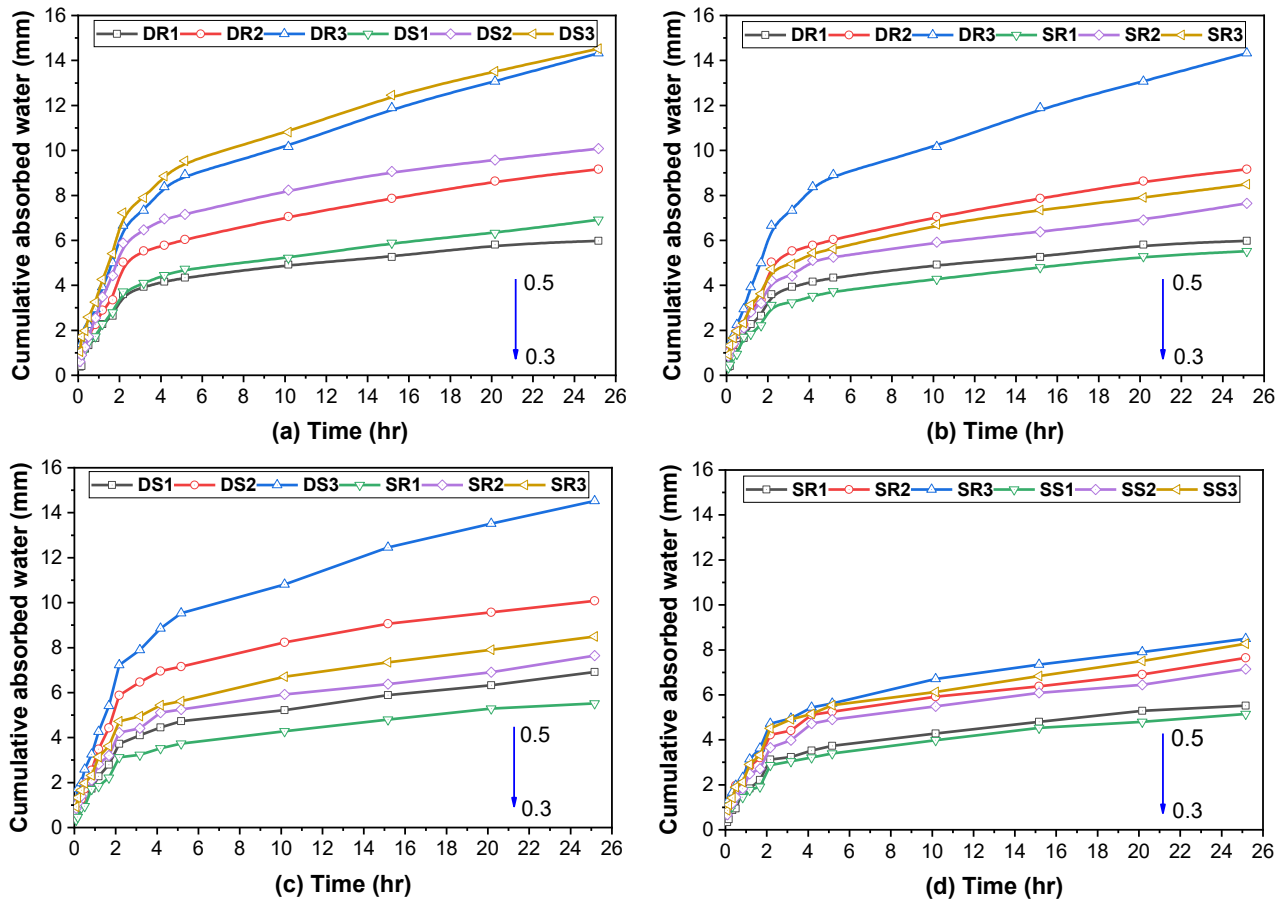


Figure 5.5. Cumulative absorbed water content of cement mortars after 25 hrs exposure: comparison between (a) DR and DS; (b) DR and SR; (c) DS and SR; and (d) SR and SS.

A noticeable change in the cumulative absorbed water content between DR and SR mortars can also be examined in Figure 5.5(b). The SR had lower cumulative absorbed water than those of DR, which might be related to lower porosity and denser microstructure in the SR than DR. Figure 5.5(c) shows that the SR also had lower cumulative absorbed water than those of DS. The combined effects of sea

sand and seawater on the water sorptivity are also noticeably determined from Figure 5.5(d). The cooperation of sea sand with seawater resulted in a slight decrease in cumulative absorbed water content, with the result that the cumulative absorbed water content of SS was less than that of the SR. In particular, the SS1 had the lowest cumulative absorbed water content in all mixtures, which indicated that the replacement of seawater could make up for the negative impact caused by sea sand, leading to lower porosity and denser microstructure in the SS1 mortar. The largest salts content in SS with seawater and sea sand might also accelerate the hydration reaction and densify the microstructure, further decreasing the cumulative absorbed water.

5.4.4 Leaching behaviour

Figure 5.6 displays the maximum concentrations of Al, Mg, and Ca of all specimens after 28-day curing. All the elements were decreased with the increasing water-cement ratio, indicating that for the same quality powder, the content of hydration products in the group with a low water-cement ratio was relatively high, further decreasing the leaching elements. In all mixtures, the concentrations of Ca was the highest, followed by Mg and Al, which might be related to the different proportion of hydration products (De Weerd & Justnes 2015b). For the same water-cement ratio, compared to DR from Figure 5.6(a), the DS has a slightly higher concentration of Al, Mg, and Ca, indicating that there were slightly more generations of hydration products. Compared to DR and DS from Figures 5.6(b) and (c), the SR shows a significantly higher concentration of the three elements. The replacement of seawater could accelerate the hydration reaction and generate more hydration products, and its acceleration effect was also better than that of sea sand. Figure 5.6(d) shows that the combination of seawater and sea sand made the SS exhibit the highest concentrations of Al, Mg, and Ca, which might be related to some ions in seawater and sea sand accelerating the hydration process (Balonis et al. 2010; Sibbick et al. 2003).

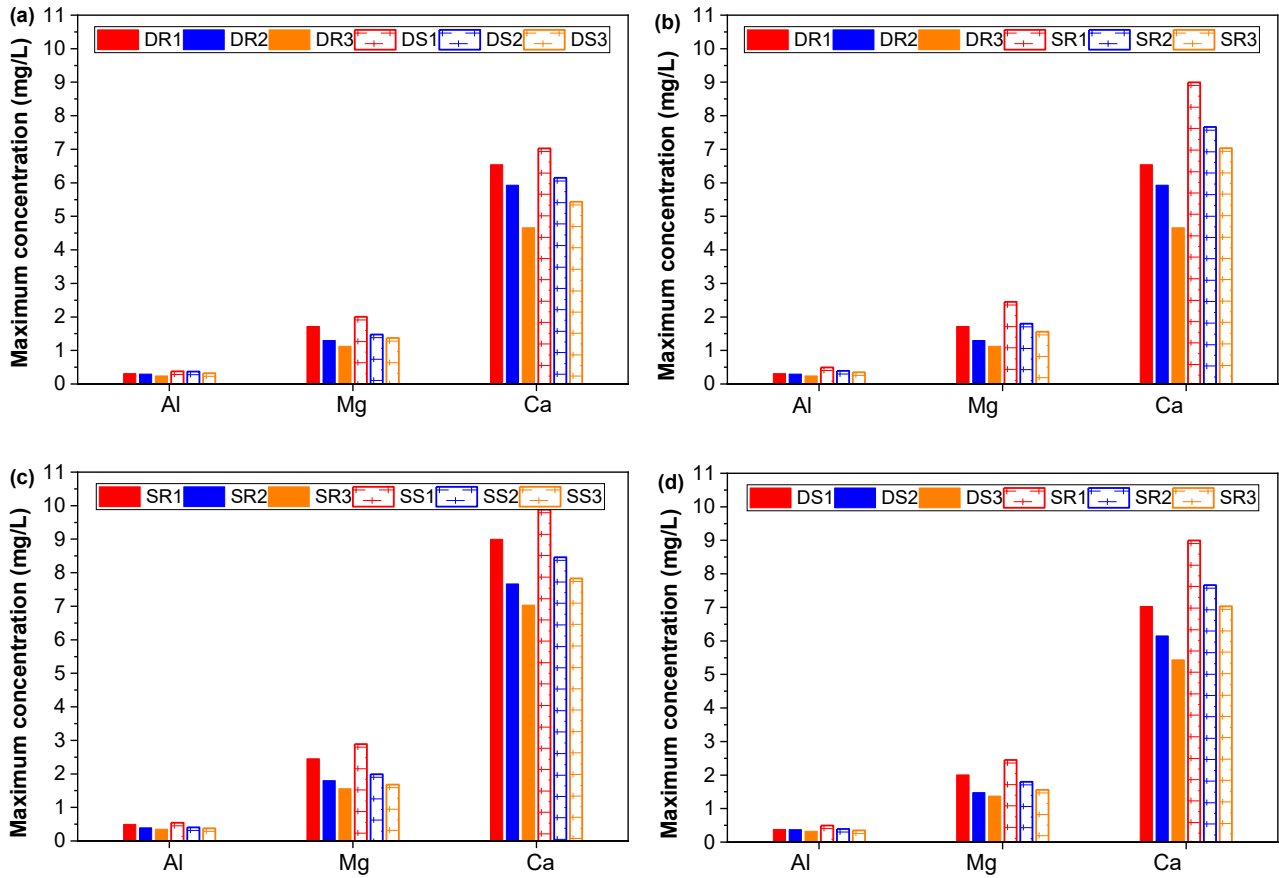


Figure 5.6. Maximum concentrations of the elements leached from cement mortars after 28-day curing: comparison between (a) DR and DS; (b) DR and SR; (c) DS and SR; and (d) SR and SS.

5.4.5 X-ray diffraction

Figure 5.7 shows the X-ray diffraction spectra of the DR1, DS1, SR1, and SS1 specimens after 1, 3, 7, 14, and 28 days of curing. Since the water-cement ratio had little effect on the phase change, the results of other mortars with W/C ratios of 0.4 and/or 0.5 were not shown in this section. It could be observed from Figure 5.7 that the primary phases, including alite ($2\theta = 32.1^\circ$ ($d = 0.278$ nm) and 41.2° ($d = 0.219$ nm), PDF #00-042-0551), belite ($2\theta = 32.5^\circ$ ($d = 0.275$ nm), PDF #00-033-0302), tri-calcium aluminate ($2\theta = 30.0^\circ$ ($d = 0.297$ nm), PDF #01-070-0134), quartz ($2\theta = 20.8^\circ, 23.9^\circ, 25.5^\circ, 26.7^\circ, 29.4^\circ, 36.4^\circ, 39.3^\circ$ and 42.4° with corresponding $d = 0.427, 0.372, 0.349, 0.333, 0.303, 0.246, 0.229$ and 0.213 nm, PDF #00-046-1045), calcium silicate hydrate (C-S-H, $2\theta = 31.0^\circ$ ($d = 0.288$ nm), PDF #00-33-0306), calcite ($2\theta = 23.1^\circ$ ($d = 0.385$ nm), PDF #00-005-0586) and Portlandite (CH, $2\theta = 18.0^\circ$

($d = 0.492$) and 34.0° ($d = 0.263$ nm), PDF #00-41-1451), could be detected in all anhydrous test specimens and at any curing ages. As the curing age increased, there was a slight decrease in the peaks intensity of alite, belite, and tri-calcium aluminate but an enhancement in the peaks intensity of C-S-H and CH in all mixes. This could be related to the results that alite, belite, and tri-calcium aluminate could be consumed continuously as the hydration reaction proceeded, further generating more formations of C-S-H and CH. As the curing age increased, the increase in the peak intensity of calcite might also be related to the increasing formations of CH, which could be reacted with the trapped CO_2 in pores during mixing. In addition, many intensity peaks of quartz could be detected in all mixes and almost kept unchanged in any curing ages, primarily caused by the sand content in the mortars tested specimens. In general, referring to the XRD spectra shown in Figure 5.7, the additions of sea sand and seawater had a barely obvious effect on those phases mentioned above in any curing ages. More detailed discussions about some of those phases were conducted in the following sections.

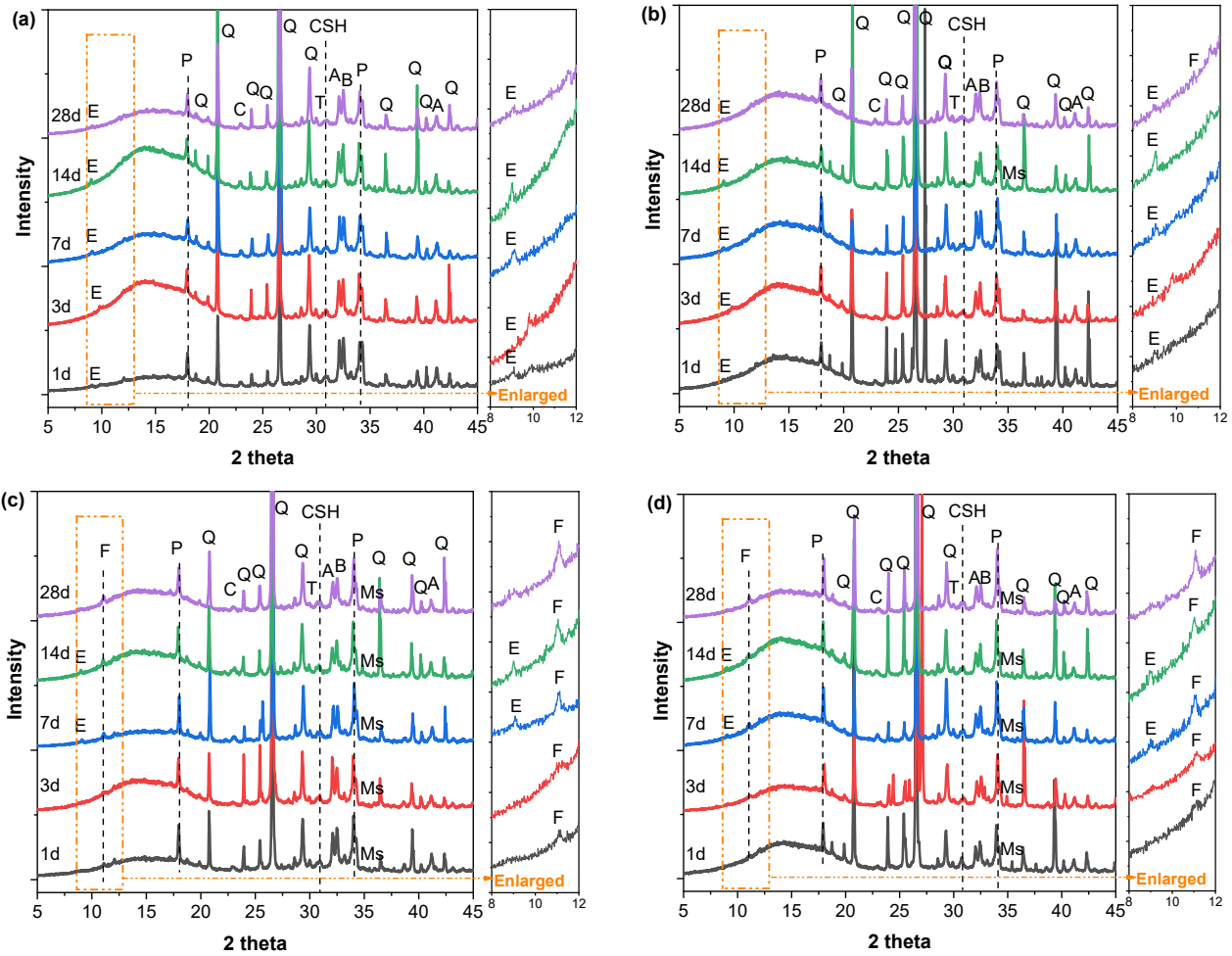


Figure 5.7. Mid-range 2 theta XRD spectra of cement mortars at different curing ages: (a) DR1; (b) DS1; (c) SR1; and (d) SS1.

Peak labels are as follows: A-alite ($3\text{CaO}\cdot\text{SiO}_2$), B-belite ($2\text{CaO}\cdot\text{SiO}_2$), C-calcite (CaCO_3), P-Portlandite ($\text{Ca}(\text{OH})_2$), E-ettringite ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot3\text{CaSO}_4\cdot32\text{H}_2\text{O}$), F- Friedel's salt ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCl}_2\cdot10\text{H}_2\text{O}$), Ms- thaumasite phase ($\text{CaCO}_3\cdot\text{CaSO}_4\cdot\text{CaSiO}_3\cdot15\text{H}_2\text{O}$), Q-Quartz (SiO_2), and T-tri-calcium aluminate ($3\text{CaO}\cdot\text{Al}_2\text{O}_3$)

However, from Figure 5.7, the additions of sea sand and seawater had a relatively apparent effect on some other phases, including ettringite (AFt, $2\theta = 9.1^\circ$ ($d = 0.971$ nm), PDF #00-041-1451), Kuzel's and Friedel's salt ($2\theta = 11.2^\circ$ ($d = 0.789$ nm), PDF #00-031-0245) and thaumasite (Ms, $2\theta = 35.4^\circ$ ($d = 0.253$ nm), PDF #00-046-1360). At the same curing ages, the addition of sea sand had a barely noticeable effect on the phase of AFt, with the result that the intensity of AFt peak was found to be similar in both DR1 and DS1. However, the intensity of AFt peak in mortars mixed with seawater (SR1 and SS1) was relatively lower than that in DR mortars in any curing ages. Especially, after 28-day curing, the intensity of AFt peak in SR1 and SS1 was almost undetectable. This demonstrates that the

effect of seawater on the intensity change of AFt peak was more significant than that of sea sand, which could be related to a high salts content in seawater than that in sea sand. In addition, compared to DR1, the peak of Ms at $35.4^\circ 2\theta$ ($d = 0.253$ nm) was detected in DS1, SR1, and SS1, indicating that the sulphate content in sea sand and seawater could lead to a formation of Ms (Ragab et al. 2016). Compared to the mortar mixed with seawater (SR1 and SS1), the formation of Ms in DS1 was relatively lower, which might also be related to a low sulphate content in sea sand. It could also be seen from Figure.7 that compared to DR1, a slight peak at $11.2^\circ 2\theta$ ($d = 0.789$ nm) for the DS1 and a spacious peak at $11.2^\circ 2\theta$ ($d = 0.789$ nm) for SR1 and SS1 were detected, the peak of which might stand for the generation of Kuzel's and Friedel's salt (Talero & Trusilewicz 2012; Talero et al. 2011). The existence of Kuzel's and Friedel's salt was primarily related to the chloride content in seawater and sea sand, which might directly make the formation of Kuzel's and Friedel's salt by hydration reactions (Ragab et al. 2016). Due to the low salt content in sea sand, the high chloride content in seawater would generate more formations of Friedel's salt in SR1 and SS1. Meanwhile, the generation of Kuzel's and Friedel's salt was also related to the sulphate and chloride contents, which could lead to a conversion from AFt to Kuzel's and Friedel's salt (Ragab et al. 2016). Therefore, the effect of seawater on the intensity change of AFt peak could be more significant than that of sea sand. It should also be noted that the combination of sea sand and seawater had the most significant effect on the phase change, owing to the high concentrations of chloride and sulphate content.

5.4.6 Fourier transform infrared spectroscopy

Figures 5.8(a) to 8(d) show the FTIR data ($600 - 3700$ cm^{-1}) of DR1, DS1, SR1 and SS1 with curing age respectively. For all the samples, the most extensive tremendous feature at 1410 cm^{-1} representative the C-O stretching of the carbonate species in mortar mixtures (Zunino et al. 2020). The mode at 873 cm^{-1} also representative the C-O bending mode of carbonate species (Zunino et al. 2020). The mode at 953 cm^{-1} changed with the increasing curing age because of the Si-O stretching proportion of the primary hydration product, the SiO_2 or C-S-H gel (Landry & Tremblay 2012). The SiO_2 was primarily

derived from sea sand or river sand. In this section, all FTIR results were obtained by running three tests on the same sample so as to ensuring that the sand was essentially constant. Thus, the peak (953 cm^{-1}) variation was assumed to be mainly caused by C-S-H. The absorption feature at 3640 cm^{-1} changed with time on account of the -O-H stretching of CH or water in the mortar. The intense feature at 1110 cm^{-1} changed with time, which could be attributed to the S-O stretching proportion of the AFt/Ms (Ylmén et al. 2009a).

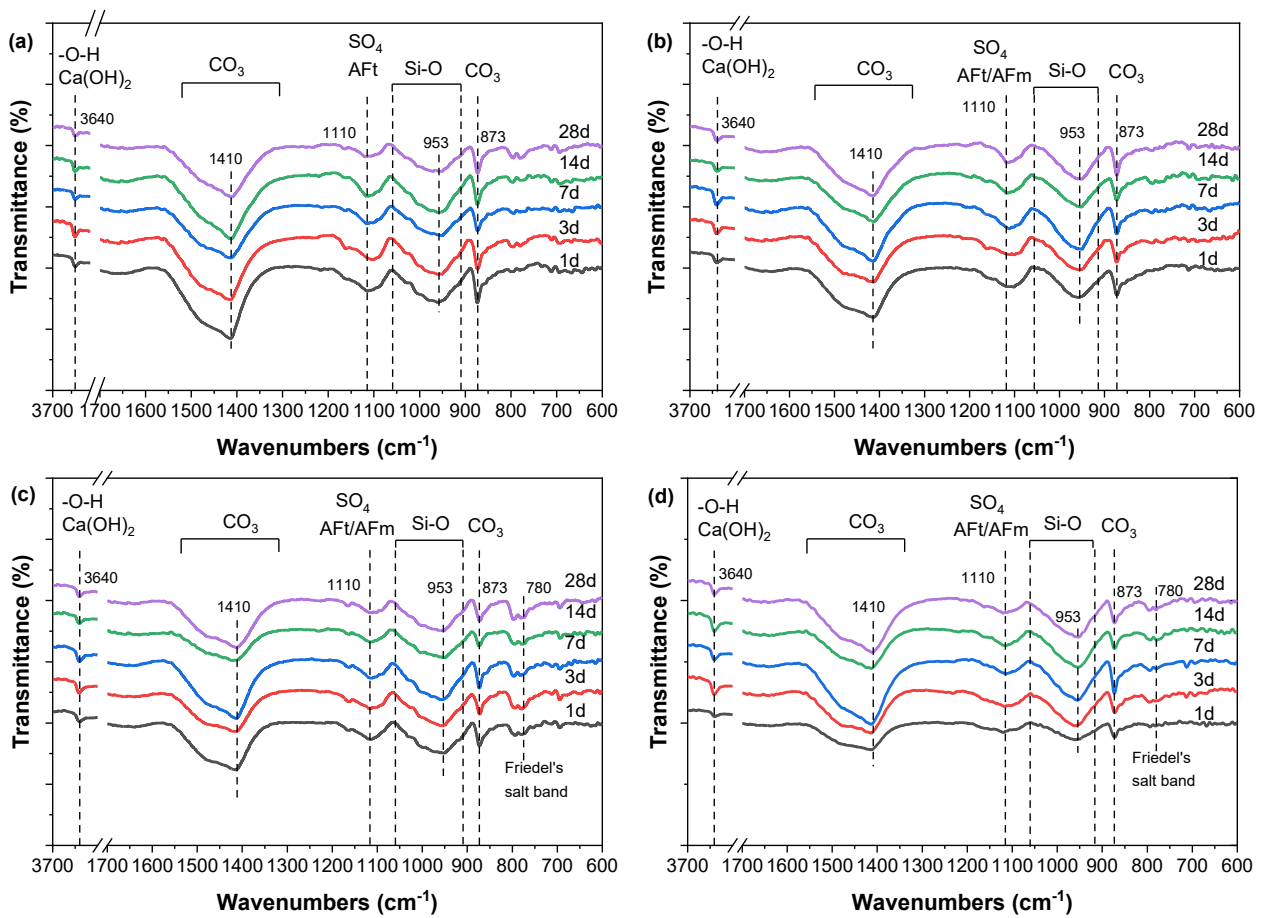


Figure 5.8. FTIR analysis on cement mortars with W/C ratio of 0.3: (a) DR1; (b) DS1; (c) SR1; and (d) SS1.

Generally, these phases described above could be detected at all curing ages. From Figure 5.8, for the intensity of -O-H, S-O, and C-O, there was no significant difference in the intensity of all mortar mixtures with curing time. For the intensity of the C-S-H gel, there were no significant differences in

DR1 and DS1 with time, while there was a relatively obvious change in the intensity of SR1 and SS1. As mentioned above, the peak (953 cm^{-1}) variation was assumed to be mainly caused by C-S-H. The intensity of the major C-S-H gel mode of DR1 at 953 cm^{-1} was slightly increased with the increasing curing time, which illustrated a slight alteration in the calcium/silica (Ca/Si) ratio of the C-S-H gel (Landry & Tremblay 2012). The intensity of the major C-S-H mode of SS1 at 953 cm^{-1} was drastically increased with the increasing curing time, especially a significant increase from 1 to 3 days, which illustrated that a tremendous change in the calcium/silica (Ca/Si) ratio of the C-S-H gel occurred. The addition of seawater might change the Ca/Si ratios of the C-S-H. In addition, compared to DR1 and DS1, the primary absorption bands for Friedel's salt in SR1 and SS1 were marked in the corresponding spectrum, where it was expected to appear a slightly improved absorption at 780 cm^{-1} (Donatello et al. 2013).

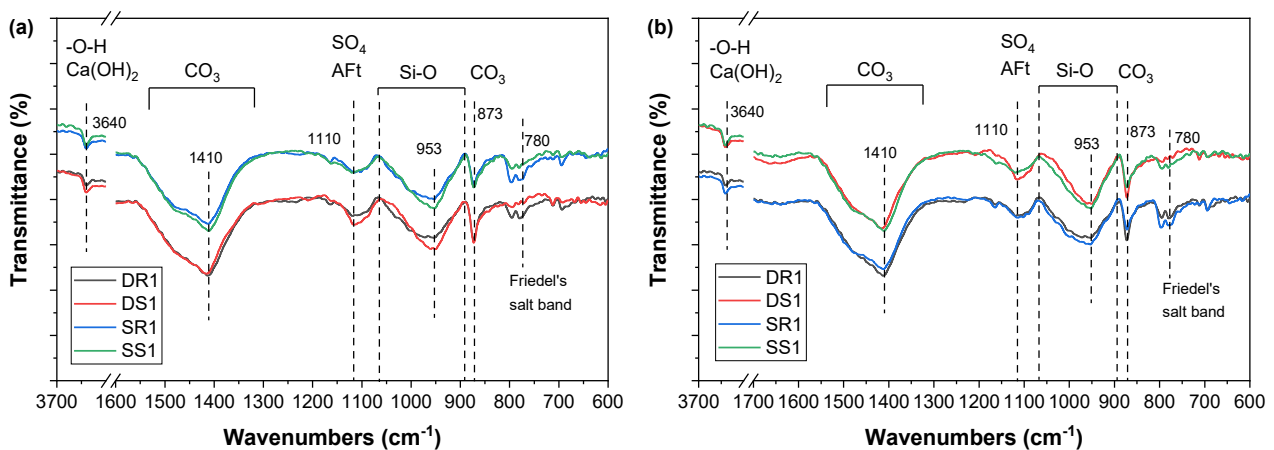


Figure 5.9. FTIR analysis on cement mortars with W/C ratio of 0.3 at 28 days curing: (a) Effect of sea sand and (b) Effect of seawater

To clearly identify the impact of sea sand and seawater on phase change of the all mortar mixture, the FTIR data of mortar, with a W/C ratio of 0.3 after 28 days of curing are displayed in Figure 5.9. For the effect of sea sand on the phase change, there was a higher increasing intensity of the primary C-S-H mode at 953 cm^{-1} in DS1 than in DR1, and in SS1 than in SR1. Both DS1 and SS1 had a higher intensity of the C-S-H mode than DR1 and SR1 after 28-day curing, which demonstrated a slight

alteration in the calcium/silica (Ca/Si) ratio of the C-S-H gel in the group containing sea sand. Besides, there was an increasing intensity of the primary C-S-H mode at 1110 cm^{-1} in the DS1 than DR1, which indicated that the ratio of S/Ca in the phase of AFt/Ms could be changed by sea sand. For the effect of seawater on the phase change, there was a relatively increasing intensity of the primary C-S-H mode at 953 cm^{-1} in the mixture with seawater. Both the SR1 and SS1 had a higher intensity of C-S-H and AFt/Ms mode than DR1 and SS1 after curing for 28 days. After 28 days of curing, the combination of seawater and sea sand could make the SS1 have the most considerable intensity of C-S-H and AFt/Ms mode, which confirmed that more hydration products were generated in SS1.

5.4.7 Thermogravimetric analysis

Figure 5.10 displays thermogravimetric (TG) and differential scanning calorimetry (DSC) curves from $40\text{ }^{\circ}\text{C}$ to $1000\text{ }^{\circ}\text{C}$ of mortars cured after 28 days. As could be seen from DSC and TG curves, in all mortars, the primary decomposition productions around the temperature from $100\text{--}120\text{ }^{\circ}\text{C}$ were the C-S-H and AFt. The decomposition of CH and calcite (CaCO_3) in all mortars were detected at approximately $420\text{ }^{\circ}\text{C}$ and the temperature around $750\text{ }^{\circ}\text{C}$, respectively (Li et al. 2020; Lu et al. 2018). Compared to the DR, a higher temperature of the peak for the Friedel's salt dehydrating in DS, SR, and SS specimens were detected (Birnin & Glasser 1998; Shi, Geiker, Lothenbach, et al. 2017). The decomposition of magnesite was detected in both the SS and SR, but not in DS and DR. This could prove that the chloride ions in seawater and sea sand were related to the production of Friedel's salt, and the magnesium ions in the seawater were related to the production of magnesite. From TG curve, the final weight loss (at $1000\text{ }^{\circ}\text{C}$) of the mortar was increased with the increasing water-cement ratio. The addition of sea sand decreased the final weight loss of DS, which was lower than that of DR. As shown in Figures. 10(b) and 10(c), the addition of seawater made the SR have a lower final weight loss than that of DR and DS. The combination of seawater and sea sand made the SS have the lowest final weight loss among all groups, shown in Figure. 10(d). This might be related to the promotion of hydration by seawater and sea sand, which made the free water content lower, and further decreased

the final weight loss (Pane & Hansen 2005; Vishwakarma et al. 2014).

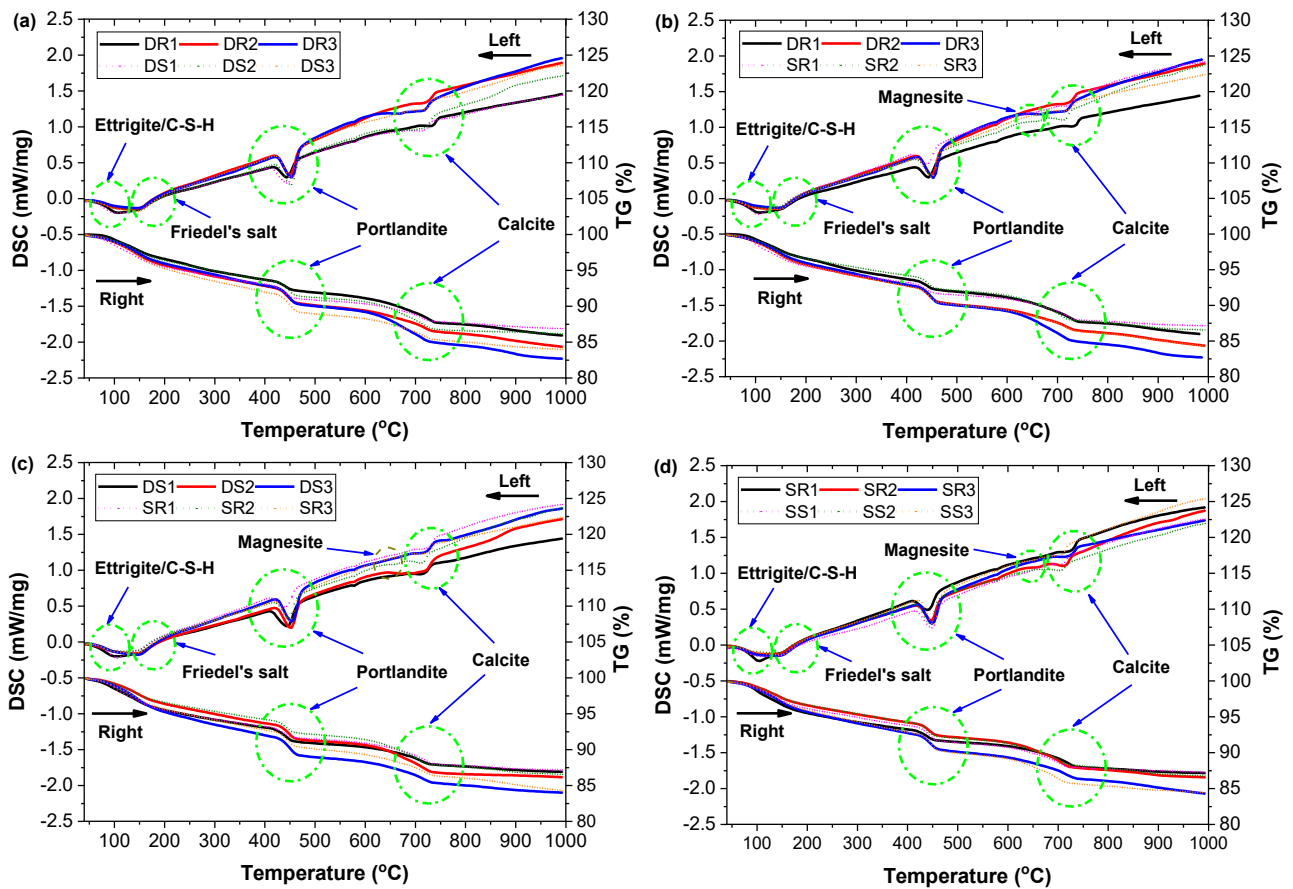


Figure 5.10. TG and DSC curves of cement mortars after 28-day curing: comparison between (a) DR and DS; (b) DR and SR; (c) DS and SR; and (d) SR and SS.

Thermogravimetric analysis of 1, 3, 7, 14, and 28-day curing samples could give particulars on the weight loss owing to decomposition of CH around 400–500 °C (Uthaman et al. 2018). Figure 5.11 shows the TG results with time in weight loss percentage of calcium hydroxide. The weight loss percentage of CH in all mortars was increased with the increasing curing ages. For the same mortars, the higher the water-cement ratio, the higher the weight loss percentage of CH. As shown in Figures. 5.11(a) and 5.11(b), compared to DR, both DS and SR had a higher weight loss percentage of CH, which might demonstrate that the salts content in sea sand and seawater could react with CH, and further decreased the weight loss percentage of CH. The higher salts content in seawater than in sea sand might increase the consumption of CH, with the result that SR had a lower weight loss percentage

of CH than DS. In addition, as shown in Figure 5.11(d), SS had a lower weight loss percentage of CH than SR, which might confirm that the sea sand and seawater could accelerate the early Portlandite formation and further participate in the hydration reaction (Zhang et al. 2020). In general, as the increasing curing ages, the CH could be increased with the hydration reaction and also be consumed by seawater and sea sand.

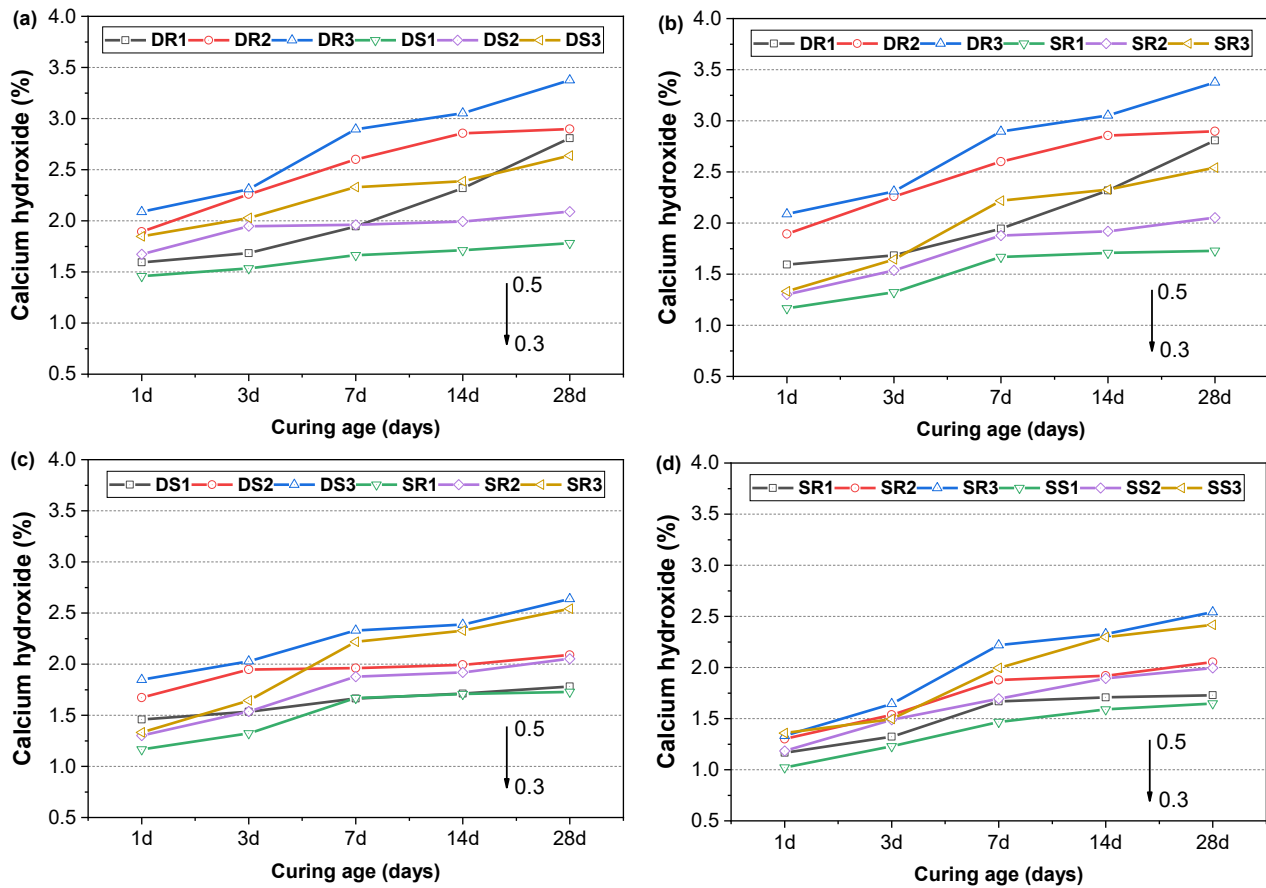


Figure 5.11. Weight loss percentage of calcium hydroxide in mortars by TG analysis: comparison between (a) DR and DS; (b) DR and SR; (c) DS and SR; and (d) SR and SS.

5.4.8 Characterization using SEM and energy dispersive X-ray

The morphology of mortars of DR1, DS1, SR1, and SS1 after 28-day curing is manifested in Figure 5.12. The microstructure of DR1 was more homogeneous than that of DR1, while the microstructure of SS1 was more heterogeneous than that of SR1. The micrograph of DR1 showed more varied shapes and sizes of hydration products surrounding the sand than DS1. This may be related to the different

physical properties and chemical compositions of sea sand and river sand. The gradation of river sand was better than that of sea sand, and the sea sand with low salt content slightly promoted hydration reaction, which could uniformly distribute the hydration products. However, compared to SR1, the micrograph of DR1 showed slightly more various shapes and sizes of hydration products surrounding the sand. This could be related to the fact that the high salts content in SS1 with seawater and sea sand could significantly promote the hydration reaction and compensate for the side effect of the sea sand. In addition, it could be seen that all mixtures had needle-shaped crystals of AFt formation, while the Ms could only be detected in the mixtures with seawater (SR1 and SS1), which might be associated with the suggestion that the high concentration of chloride and sulphate contented in the seawater could suggest a formation of the Ms (Guillon et al. 2006). Friedel's salt could also be detected in SR1 and SS1, which confirmed that chloride and sulphate contented in the seawater and sea sand could react with the cement and produce new hydration production.

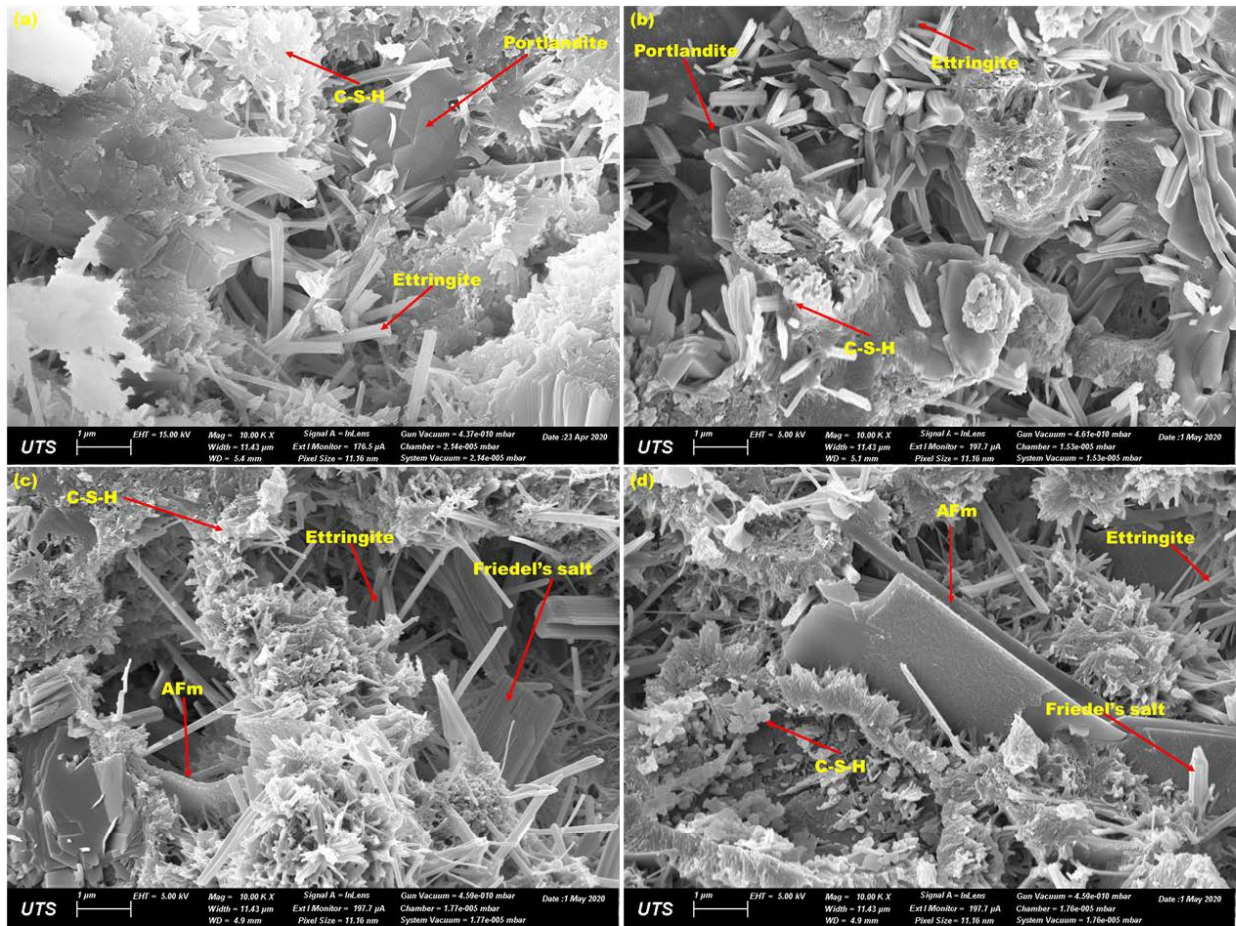


Figure 5.12. Microstructure and morphology of cement mortars at curing age of 28 days: (a) DR1; (b) DS1; (c) SR1; and (d) SS1.

Figure 5.13 displays the SEM-EDX micrographs and elemental maps of the SR1 cured after 28 days. Similar results, which could also be seen in SS1 with seawater and sea sand, were not displayed in this section. As could be seen from the elemental maps, the elements of Ca, Al, S and Cl were almost distributed in the same area of the mortar matrix, while the elements of Na and K were distributed randomly. Most of the Si detected in the red area was the fine aggregate (sand). Partial proportions of Si were also in the same areas as Ca. C-S-H gels, recorded in point 1, could be detected in areas where the content of other elements was relatively low while the elements of Ca and Si were significantly present. In areas rich in Si and Al, if the content of Ca and Cl was also relatively high, the area could examine the presence of Friedel's salt, shown in point 2. In addition, Magnesium silicate hydrate (M-

S-H) gels, detected in point 3, could be examined in areas where the elements of Si and Mg were relatively high. The brucite ($\text{Mg}(\text{OH})_2$) could be detected in the high Mg concentration (such as point 4) of the SR1 matrix. These phases could confirm that the magnesium and chloride content in the seawater could participate in the hydration reaction. No apparent phases with Mg detected in XRD and FTIR results might be related to the low concentration in seawater.

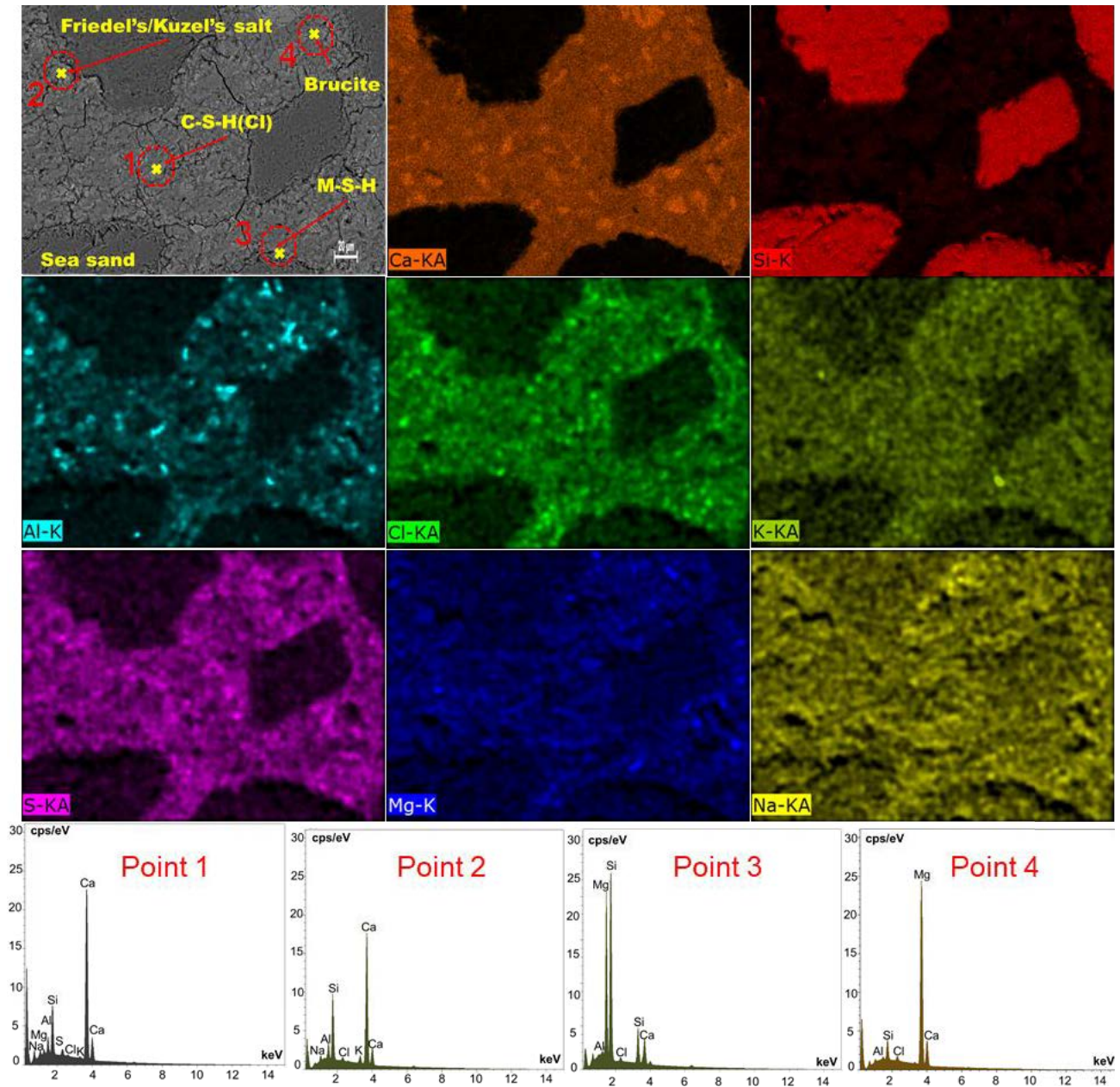


Figure 5.13. SEM-EDS micrographs and elemental maps of SR1 at 28 days of curing (250 x).

To study the influence of the multiplied chemical composition in sea sand and seawater, EDX point

analysis was applied for all mixtures with W/C ratio of 0.3 after 28-day curing. Before EDX point analysis, the element maps in Figure. 13 were carried out in all mixtures. In SEM-EDX elemental maps of all mixtures, the area with high Ca, Al, S, Cl, and Mg concentrations were used as the point analysis area. In the selected area, random 500 square grids were used to detect the atomic mass of Ca, Al, S, Cl, Mg and Si. Representative EDX point analysis results are displayed in Figure. 14. In such dot plots, the EDX results were identified as the ratios of molar and contrasted to the ideal molar ratios of representative phases (e.g. CH and C-S-H) examined in phase systems of cementitious hydration.

The Si/Ca molar ratios as the abscissa and the Al/Ca molar ratio as the ordinate are displayed in Figure 5.14 (a). It can be seen that the sea sand had slight effect on the Si/Ca and Al/Ca ratios in C-S-H. The molar ratios of Si/Ca and Al/Ca in both DR1 and DS1 were in the range 0.2–0.4 and 0.0–0.1, respectively. It also demonstrated that the seawater could decrease the proportion of Ca in C-S-H of SR1 and SS1. The C-S-H detected in mortar samples with seawater (SR1 and DR1) was decalcified (De Weerd et al. 2015) and seen as C-S-H (Cl). The cloud of points related to C-S-H (Cl) had a higher Si/Ca ratio than C-S-H. The Si/Ca ratio of the C-S-H (Cl) could be increased to be about 0.6–1.2, which corresponded with the FTIR results that increasing the intensity of the primary C-S-H mode at 953 cm^{-1} was founded in SS and SR. The Al/Ca ratio of C-S-H (Cl) was similar to that of C-S-H. The combination of seawater and sea sand could increase much more points of SS1 in the range of C-S-H (Cl).

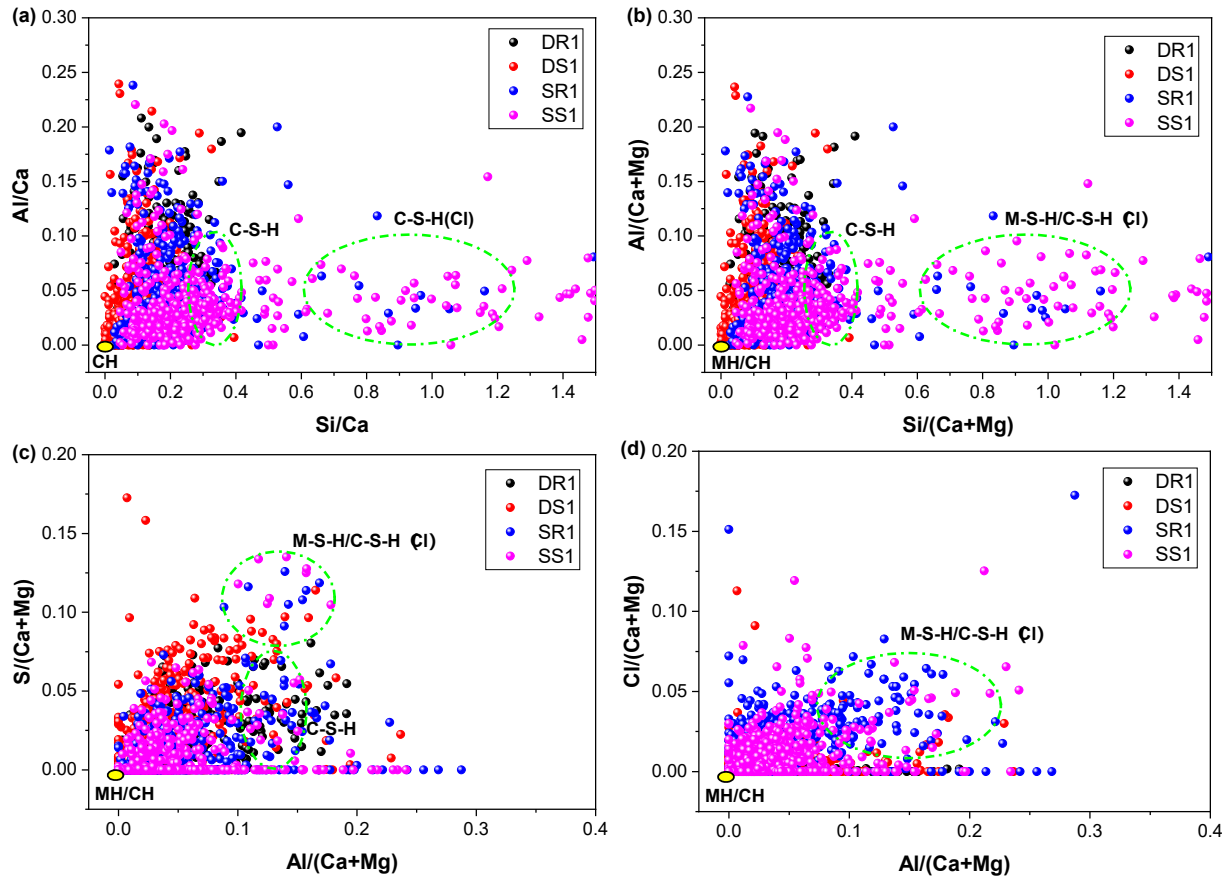


Figure 5.14. EDX phase analysis of different cement mortars at 28 days curing age: (a)

Si/Ca as the abscissa of Al/Ca; (b) Si/(Ca+Mg) as the abscissa of Al/(Ca+Mg); (c) Al/(Ca+Mg) as the abscissa of S/(Ca+Mg); and (d) Al/(Ca+Mg) as the abscissa of Cl/(Ca+Mg).

Note: C-S-H and C-S-H (Cl) are used to distinguish the gels in mortars with freshwater and seawater, respectively.

Figure 5.14(b) displays the Si/(Ca+Mg) ratio as the abscissa of Al/(Ca+Mg) ratio. It could be seen that there were similar Al/(Ca+Mg) and Si/(Ca+Mg) ratios of C-S-H in DR1 and DS1, while the C-S-H (Cl) of the mortar mixtures with seawater (SR1 and SS1) had a higher Al/(Ca+Mg) and Si/(Ca+Mg) ratios. Compared to the C-S-H (Cl) in Figure. 14(a), there were much more points of C-S-H (Cl) appearing in the Si/(Ca+Mg) range of 0.6–1.2, which might be related to the formation of M-S-H (De Weerd & Justnes 2015b). Weerd & Justnes (2015b) had pointed out that when the concentration content of Mg in seawater was up to a certain extent, Ca could be replaced by Mg, possibly leading to form M-S-H. With the progress of hydration, more hydration products with chemical bounded water was produced, which consumed the free water in seawater and at the same time increased the

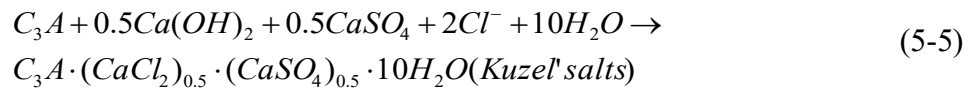
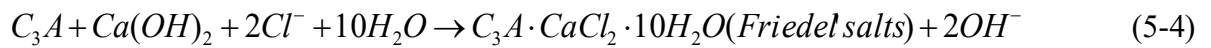
concentration of Mg in seawater, further prompting the substitution of Mg for Ca. Compared to the C-S-H in DR or DS, a higher ratio of Si/(Ca+Mg) was also detected in M-S-H.

In Figures 5.14(c) and 5.14(d), the S/(Ca+Mg) and Cl/(Ca+Mg) ratios are represented as a function of the Al/(Ca+Mg) ratio respectively. Compared to DR, the mixtures with sea sand and/or seawater (DS1, SR1, and SS1) had a higher S/(Ca+Mg) ratio, which possibly confirmed that there were relatively high sulfate ions contained in seawater and sea sand. The increased ratios of S/(Ca+Mg) and Al/(Ca+Mg) in SR1 and SS1 also confirmed the FTIR results that the ratio of S/Ca in the phase of AFt could be changed by seawater to Ms. In Figure 5.14(d), the point analysis demonstrated that there was a higher Cl/(Ca+Mg) ratio in DS1 than that in SR1, while the addition of seawater could make SR1 and SS1 had a higher Cl/(Ca+Mg) ratio than that of DS1. This confirms that there was a higher chloride content in seawater than in sea sand. In addition, compared to DR1 and DS1, there were more significant fractions, within the range 0.0–0.2 of Al/(Ca+Mg) molar ratios and 0.0–0.1 of Cl/(Ca+Mg) molar ratios, in SR and SS. These points might correspond to chloride adsorbent on C-S-H. The ions of chloride and sulphate might have a pivotal effect on the hydration reaction and further increased the hydrated products.

5.5 Mechanism analysis and discussion

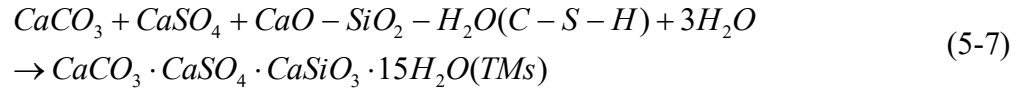
The phase change in the mortar mixtures occurred in the cement phased as the fine aggregates appeared not to be affected by the ions content in the seawater and/or sea sand. In order to explain the effect of seawater and sea sand on the hydration reactions, more detailed descriptions were discussed in this section based on the above test results. From Tables 5.2 and 5.3, the anions in the sea sand were primary chloride and sulphate ions, which was lower than that of in seawater. Except for the chloride and sulphate ions, there were also some cations like Na⁺, Mg²⁺, K⁺ and Ca²⁺ in seawater. The results mentioned above had shown that the influence of sea sand on the phase change was not significant as the seawater, while the influence of seawater on the phase change was not significant as the combination of seawater and sea sand, which might be related to more ions concentration in SS.

Therefore, the SS had the most significant impact on the phase change followed by the SR and DS. The chlorides from NaCl, CaCl₂, MgCl₂, and KCl in seawater and/or sea sand could be reacted with tri-calcium silicate (C₃A) and/or gypsum (CaSO₄), and consume the products of CH by cement hydration, further form the new products, such as Friedel's/Kuzel's salts in Eq. (5-4) and Eq. (5-5) (Balonis et al. 2010; Sibbick et al. 2003). This could explain the reason why the exothermic peak of the mixtures with seawater and/or sea sand appeared earlier than that of DR displayed in Figure 5.2, and a higher compressive strength was found in the mixtures with seawater (SR and SS) than those mixtures with freshwater (DR and DS). As the processing of the hydration reaction, the Friedel's/Kuzel's salts detected in the XRD in Figures 5.7 and 5.13 can be increased, which might also enhance the compressive strength in the DS, SR and SS mixtures in Figures 5.3 and 5.4.

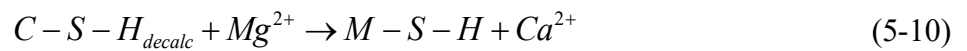
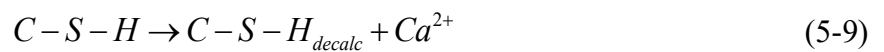


In addition, the sulphate ions in seawater and/or sea sand could form gypsum (CaSO₄) with the products of CH by cement hydration, which would lead to the formation of AFt in the existence of C₃A (Sibbick et al. 2003), as shown in Eq. (5-6). Due to the high sulphate ions in seawater and sea sand, there was also a higher generation of AFt in DR, SR, and SS than in DR, as shown in Figure 5.7. As the hydration progresses, part of the CH could be contacted with the air to form calcite, and more gypsum could be formed for the sulphate ions in seawater and/or sea sand, which would lead to the generations of thaumasite by reacting with the C-S-H (Sibbick et al. 2003), as shown in Eq. (5-7). These could account for a higher ratio of S/Ca in the phase of AFt/Ms detected in the mixtures with seawater and sea sand as shown in Figure 5.8. The formation of Ms also decreased the CH content of the mortar mixture with seawater, which confirmed that there was a lower weight loss percentage of CH in SR than in DR, as shown in Figure 5.11.





The phase change caused by chloride and sulphate could simultaneously occur in the mixtures with sea sand and/ or seawater, while the new products generation ($Mg(OH)_2$ or M-S-H) could be mostly detected in the mixture with seawater (SR and SS), mainly caused by the magnesium. Due to the relatively high content of magnesium in seawater, the $MgCl_2$ in seawater could also react with hydrate products of CH to form brucite due to the high pH of pore solution of the mortar mixtures (De Weerd & Justnes 2015b; Liu, Jiang, et al. 2020), as shown in Eq. (5-8). Some magnesium oxychloride, like magnesite (detected in Figure 5.10) could form when both the $Mg(OH)_2$ and $MgCl_2$ coexist in the mixtures. In addition, when the concentration of Mg^{2+} was sufficient, Mg^{2+} could replace Ca^{2+} in C-S-H to form M-S-H (Bernard et al. 2017). The substitute of Mg^{2+} for Ca^{2+} could be achieved by the following steps: the decalcification of C-S-H could occur at first, and then Mg^{2+} could react with the decalcification of C-S-H (De Weerd & Justnes 2015b; Liu, Jiang, et al. 2020), as shown in Eqs. (5-9) and (5-10). This could also explain there was a higher Si/Ca ratio in the C-S-H (Cl) in SR and SS than that of in DR and DS (see Figure 5.14).



In general, the multiply ions in seawater and sea sand could accelerate the hydration reaction, as shown in Eqs. (5-4) to (5-10). Taking SS as an example, due to much more hydration products generating in the mixture with seawater and sea sand (SS), the maximum concentrations of Al, Mg and Ca leaching from SS was also higher than that of the DR as shown in Figure 5.6. These new hydration products might also optimize the microstructure of SS, further increase the 28-day compressive strength in Figure 5.3 and decrease the cumulative absorbed water content in Figure 5.5. Compared to the SS, similar but inferior results could also be founded in SR and DS for the different ions content. Therefore,

although the salt content of seawater and sea sand in different regions and counties varies, its impacts on cement phase change can be predicted by the reaction formulas in Eqs. (5-4) to (5-10). The related results are expected to provide insight into the academic research and practical application of cementitious composites mixed with seawater and undesalted sea sand.

5.6 Summary

The effects of seawater and undesalted sea sand on cement hydration, mechanical performance, water absorption, leaching and microstructure of Portland cement mortar were fundamentally investigated in this study. The following conclusions could be drawn up as:

- (1) At the same water-cement ratio, the addition of sea sand could slightly increase the hydration rate and decrease the cumulative absorbed water content of DS. The addition of sea sand increased the compressive strength of DS in the early stage of hydration reaction but had an adverse effect on the compressive strength of DS after 14-day curing. The addition of seawater made SR and SS have a higher hydration rate and 28-day compressive strength and lower cumulative absorbed water content than DR and DS.
- (2) The addition of sea sand affected the hydration reaction mainly due to the chloride and sulphate ions content in sea sand, while the physical properties of sea sand, more inferior than the river sand (e.g., fineness modulus and grade), affected the compressive strength of DS after 14-day curing. The addition of seawater with higher salts content than that of sea sand had a more significant effect on the hydration reaction, which compensated for the side effect of sea sand on the compressive strength.
- (3) The different salts ions content in seawater and sea sand primarily account for the phase changes in the mortar mixture. Chloride ions in both seawater and sea sand reacted with the C_3A and cement hydration products of CH to form Friedel's/Kuzel's salts, which could accelerate the hydration reaction and optimize the microstructure of mortars. Sulphate ions in both seawater and sea sand generated much more AFt and probably produced new hydrate products (e.g., thaumasite) due to

the conversion from $\text{Ca}(\text{OH})_2$ to CaCO_3 . Magnesium ions, mainly in seawater, led to the formation of $\text{Mg}(\text{OH})_2$ and M-S-H by replacing Ca^{2+} and the decalcification of C-S-H.

- (4) The compounds and constituent elements of the microstructure could accurately be detected by SEM corresponding EDX point analysis and SEM-EDX mapping. The results of FTIR and EDX dot confirmed that the Si/Ca ratio of C-S-H (Cl) in the mortar mixture with seawater was increased, which was reflected in a higher intensity at 953 cm^{-1} and a higher Si/Ca ratio of 0.6–1.2. The higher ratios of $\text{S}/(\text{Ca}+\text{Mg})$ and $\text{Cl}/(\text{Ca}+\text{Mg})$ were detected in mortars with seawater, which corresponded to the chloride adsorbent in C-S-H.
- (5) Based on the analysis of the experimental results, the utilization of seawater and undesalted sea sand in concrete production provides a sustainable way to solve the shortage of natural freshwater and river sand. In addition, the related results are expected to provide insight into the academic research and practical application of cementitious composites mixed with seawater and undesalted sea sand.

CHAPTER 6: PERFORMANCE OF SEAWATER AND SEA-SAND CEMENTITIOUS COMPOSITES WITH GGBFS AND GLASS FIBER

6.1 Introduction

Currently, cementitious materials, manufactured with freshwater and river sand, are one of the most widely-used buildings and structural materials worldwide for their versatility and economy. It is predicted that there might be a shortage of freshwater and river sand in the 21st century (Wang 2009). The use of seawater, instead of freshwater in concrete, can be a sustainable way to protect freshwater sources from overuse. Similarly, the use of sea sand without desalting is also the latest development trend for releasing the burden of depleted river sand sources. Although high-salt content seawater/unwashed sea sand has been prohibited in reinforced concrete for many years due to steel corrosion, non-corrosive steel such as fiber-reinforced polymers (FRP) could make the application of seawater and sand in low-cost and long-life concrete become a reality. In addition, fire or high temperature is an extreme environmental condition to which any building or structure could be exposed during its service life (Carabba et al. 2019; Manjunath et al. 2019; Nguyen et al. 2020). Concrete buildings and structures adopting the seawater and unwashed sea sand as the raw materials are also supposed to have significant performance under extreme fire conditions.

Up till now, various studies have evaluated the performance of ordinary Portland cement concrete (OPC) after high-temperature exposure (Fernandes et al. 2017; Horszczaruk et al. 2017; Khaliq & Mujeeb 2019; Shaikh & Taweel 2015; Zaidi et al. 2012; Zhang et al. 2018). The composition of OPC, including aggregate and cement paste, can be affected by the increasing temperature since the OPC is a heterogeneous building material (Fernandes et al. 2017; Horszczaruk et al. 2017; Zhang et al. 2018). OPC's performance under fire environments lies in its ingredient and the characteristics of its elements. The hydration product of OPC, such as Portlandite (CH), can decompose to form calcium oxide and release water at approximately 400 to 500 °C. Under fire conditions, phase changes, pore pressure

changes, and the limited thermal conductivity in OPC could significantly affect the mechanical properties (Khaliq & Mujeeb 2019). When the temperature exceeds 400 °C, the strength is practically lost, as the result of the dehydration of CH and rehydration of CaO (Shaikh & Taweel 2015). The strength loss of OPC exceeds 50% when exposure temperatures are up to around 400 to 500 °C due to the dehydroxylation of hydroxide and constant dehydration of calcium silicate hydrate (C-S-H) starting at 105 °C (Zaidi et al. 2012). OPC could be suffered wide-ranging damage due to physical and chemical changes at high temperatures, leading to severe deterioration of mechanical performances (Carabba et al. 2019; Manjunath et al. 2019; Nguyen et al. 2020). Therefore, some researchers have explored the possibility of adjusting the concrete ingredients to provide a more stable microstructure of the cement-base composites.

Incorporating glass fibers as reinforcing agents is one of the most efficient methods to optimize the microstructure of the cement-based composites, especially when the structure is needed to consider to carry tension load, for the fact that the increase of elastic tension will cause great microcracks and integrated rupture of unenhanced matrix (Erdogmus 2015). The quality of glass fibers might be guaranteed by some glass technologies mentioned in previous references (Boukhris et al. 2020). The application of glass fibers in this concrete structure can protect the physical and also chemical characteristics of fibers and their surroundings (Kizilkanat et al. 2015; Mazaheripour et al. 2013). Glass fibers are able to be recognized as the primary load-carrying component (Bertelsen et al. 2020; Kavas et al. 2004). The matrix of cement-based composites encircling fiber is prohibiting them from being affected by the surrounded environment. Besides, glass fibers can also be seen as the load transducers that enable the fibers to move steadily within them (Bertelsen et al. 2020; Kavas et al. 2004). Immensely, adequate fibers in the composite matrix can comfortably improve tensile strength. Besides, it is reasonable to select the glass fibers to optimize the cement-based composites' microstructure for their beneficial physical characteristics and comparatively cheap cost (Güllü et al. 2006). The glass fibers have also been reported to play an essential role in prohibiting the formation of cracks in the

cement-based composites under a fire environment for the high melt point of glass fibers (Fang et al. 2018; Keleştemur et al. 2014). Besides, a large number of investigations have been conducted to confirm the feasibility of using industrial by-products such as ground granulated blast-furnace slag (GGBFS) to provide a more stable microstructure in cement-based composites or GGBFS-based cementitious materials (Bernal et al. 2010; Dulaimi et al. 2020; Mehta & Siddique 2018). Aziz et al. (2020) have pointed out a reduction in the number of pores in alkali-activated slag after exposure to elevated temperatures. Delhomme et al. (2012) have studied the influence of high temperature on cement mortar with substitutes of GGBFS and concluded that an increase of GGBFS content to 20% or above significantly promoted the fire resistance at the water to bind ratio of 0.6. Gao et al. (2012) have studied the splitting strength of OPC and high-strength pozzolanic concretes at high temperatures and illustrated that pozzolanic concrete containing GGBFS had better performance than the OPC.

Most studies on seawater and sea-sand cement-based composites have focused on the influence of hydration reaction and FRP-reinforced concrete structural performance (Ahmed et al. 2020; Etxeberria et al. 2016; Kucche et al. 2015; Ozer-Erdogan et al. 2016). Li et al. (2018) only have investigated the thermal and mechanical properties of geopolymer mortar mixed with seawater and sea sand and concluded that the seawater and sea sand have a slightly detrimental effect on the residual strength of geopolymer mortar. Limited studies have been conducted to investigate cement-based composite fire resistivity utilizing seawater and sea sand (Etxeberria et al. 2016; Kucche et al. 2015; Ozer-Erdogan et al. 2016). Therefore, the aim of this study is to investigate the effect of GGBFS and glass fiber on the thermal performance and flexural behaviors of seawater and sea-sand mortars (FSSM) to provide a more stable microstructure. The mortars mixed with demineralized water and river sand (FRRM) were also manufactured as the reference group. The mass loss, visual appearance, the compressive and flexural strength of all groups were measured. In order to explain the differences (between FRRM and FSSM) caused by sea sand and seawater, and the improvement of the combined GGBFS and glass fiber, the change of microstructure and hydration products was measured by using various techniques,

including XRD, FTIR, TGA, and BSE-EDX. It is expected that the results of this study will contribute to the development of new construction materials that perform well at high temperatures.

6.2 Materials and specimen preparation

6.2.1 Raw materials

The mortar was manufactured based on the Eureka general-purpose cement in accordance with AS/NZS 2350.1-2006 (Methods of testing portland, blended and masonry cements sampling) and GGBFS in accordance with the AS 3582.2:2014 (Supplementary cementitious materials Slag - Ground granulated blast-furnace) as binding materials. Two types of water, demineralized water and seawater, were applied as the mixing water. Two kinds of sand, river sand and sea sand, were employed as the fine aggregate. The seawater and sea sand were obtained from Botany Bay near Sydney, Australia, and the sea sand mentioned in the following section was all the sea sand without desalting.

Table 6.1 Chemical composition of GGBFS and cement, and mineral physical properties of cement

Chemical properties (by weight %)								
Type	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ Oeq	K ₂ O
Cement	21.8	4.5	3.5	65.4	2.6	1.4	0.6	1.3
GGBFS	36.0	11.8	0.3	42.6	5.8	0.5	0.2	0.3
Sea sand	96.5	0.21	0.43	1.3	0.1	0.01	0.07	0.05
Mineral or property of cement								
C ₃ S	C ₂ S	C ₃ A	C ₄ AF	Blaine	Density		Water demand	
54%	14%	7%	11%	357 m ² /kg	3.06 g/cm ³		28.0 %	

The Blaine and specific gravity of GGBFF were 418 m²/kg and 2.92, respectively. The primary chemical composition of cement, GGBFS, and sea sand measured by X-ray fluorescence (XRF) is listed in Table 6.1. The mineral composition and physical properties of cement were also listed in Table 6.1. Sieve analysis was carried out according to AS1141.11.1-2009 (Methods for sampling and testing

aggregates - particle size distribution - sieving method) to determine the particle size distribution (PSD) of cement, GGBFS, river sand, and sea sand. The PSD curves of the materials used are compared in Figure 6.1. The fineness modulus of river sand was 2.39, and that of sea sand was 1.86, indicating the river sand was slightly coarser than the sea sand. The chemical composition of the seawater and sea sand by inductively-coupled plasma mass spectrometry is displayed in Table 6.2. There were high chloride and sulphate ions content in seawater and relatively low weight percentage of chloride and sulphate in sea sand, while no chloride content was founded in river sand and determined water.

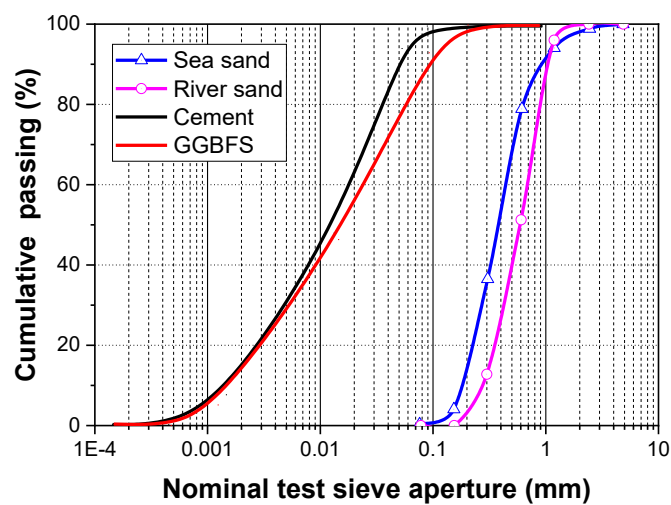


Figure 6.1. Particle size distribution (PSD) curve of the raw materials used

Table 6.2 Chemical compositions in seawater and sea sand from Botany Bay (Sydney, Australia)

Concentration (g/l)	NaCl	MgCl ₂	Na ₂ SO ₄	KCl	CaCl ₂	NaHCO ₃
Seawater	19.0	1.35	0.88	0.38	0.40	—
Salt content (wt%)		Cl			SO ₄	
Sea sand		0.83			0.09	

A kind of commercial compound glass fiber with 12 mm in length and 33 μm in diameter was also used in this experiment. The melting point is around 270 $^{\circ}\text{C}$. Glass fibre-reinforced FSSM mortars were manufactured with 1.0 wt% of the total mass. The furnace test was adopted to identify glass

fibers' physical evolutions after high-temperature exposure (Missemer et al. 2019). The same quantities of glass fibers were held in a quartz crucible and then put into a furnace oven with the heating rate of 10 °C/min, and kept for two hours until the temperature was up to the different target temperatures (200, 400, and 700 °C), and finally, the mass change and physical transformations for the glass fibers was recorded in Figure 6.2. There were indeed some noticeable changes in the physical properties of glass fiber after different high-temperature exposure. There was no mass change of glass fibers after exposure to 200 °C; in contrast, there were 20% and 50% mass loss after being exposed to 400 and 700 °C, respectively, indicating that the glass fiber could be partially melted in 400 and 700 °C.

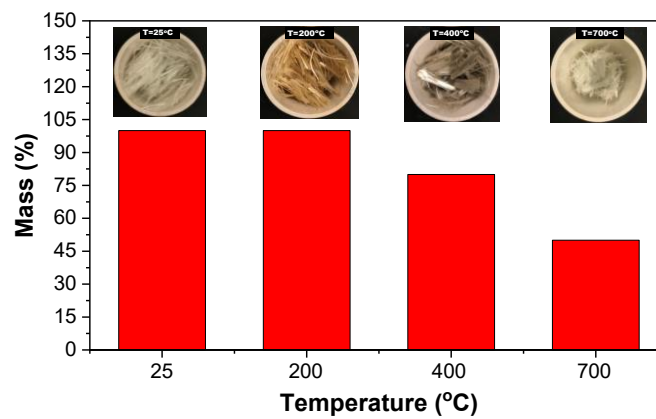


Figure 6.2. Physical transformations and mass change of glass fiber after the furnace test under different heating temperatures

6.2.2 Mix design

Four series of cement mortar mixes with seawater and sea sand were studied: cement mortar mixes only with seawater and sea sand, FSSM mixes with 1 wt.% glass fiber (FSSM-F group, named FSSM-1F), FSSM mixes with 10, 20, and 30 wt.% GGBFS substitutes for cement (FSSM-GGBFS group, named FSSM-10S, FSSM-20S, and FSSM-30S, respectively), and FSSM mixes with GGBFS substitutes and glass fiber (FSSM-GGBFS-F group, named FSSM-10S-1F, FSSM-20S-1F, and FSSM-30S-1F, respectively). The mortar mixed with demineralized and river sand was also cast as the

reference group. All mixes had a 0.30 ratio of water to binder (W/B) and a 2.0 ratio of binder to sand. 0.6 % superplasticizer (SP) was added to the group with the addition of glass fiber. All mortar mixes proportions are illustrated in Table 6.3.

Table 6.3 Mix proportion design of cement mortars (gram)

Sample	Cement	Demineralized water	Seawater	River sand	Sea sand	GGBFS	Glass fiber	SP
FRRM	300	90	—	600	—	—	—	—
FSSM	300	—	90	—	600	—	—	—
FSSM-1F	300	—	90	—	600	—	9.9	1.8
FSSM-10S	270	—	90	—	600	30	—	—
FSSM-20S	240	—	90	—	600	60	—	—
FSSM-30S	210	—	90	—	600	90	—	—
FSSM-10S-1F	270	—	90	—	600	30	9.9	1.8
FSSM-20S-1F	240	—	90	—	600	60	9.9	1.8
FSSM-30S-1F	210	—	90	—	600	90	9.9	1.8

6.2.3 Specimen preparation

Specimens with dimensions of 40 mm × 40 mm × 140 mm were fabricated according to ASTM C348-20 (Standard Test Method for Flexural Strength of Hydraulic-Cement Mortars). All mortars with or without glass fiber were mixed based on the following procedure: First, sand was mixed with binder at a slow speed for 1 min. After the low-speed mix, the water or seawater with SP was put into the Hobart mixer, followed by another 2 min of slow mixing. After a 1 min rest, high-speed mixing was applied for 2 min. After this, for the non-fiber mixtures, they were cast into oiled moulds, while for the fiber-reinforced mixtures, the glass fiber was added into the mixtures along with SP and mixed for another 2-min at a high-speed and they were then cast into oiled moulds to form specimens. All mortars were kept for 1 day in a climate chamber with RH of 95% and a temperature of 20 ± 1 °C. After curing for 24 hrs, the mortars were demoulded and kept in the same curing conditions for the testing date.

6.3 Experimental program

6.3.1 High-temperature exposure

All surface-drying mortar specimens in one layer were exposed to the different target temperatures of 200, 400, and 700 °C with a heating rate of 5 °C/min. After reaching a target temperature, they were maintained at the temperature for 2.5 hrs by employing a furnace oven, as shown in Figure 6.3. Specimens were taken out from the furnace oven, cooled down to room temperature, and finally applied to the following experiments.

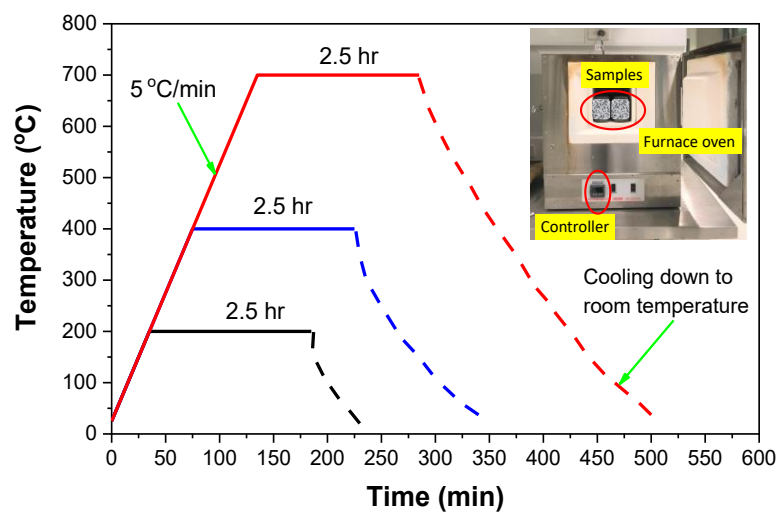


Figure 6.3. The time-temperature curve in the furnace oven

6.3.2 Physical properties

A high-resolution camera recorded the visual appearance before and after high-temperature exposure of all mixes. Before and after high-temperature exposure, the mass of all mixtures was measured by a scale with an accuracy of 0.01 g. The mass loss percentage was calculated by the mass change of the corresponding specimens before and after high-temperature exposure, compared to the mass before high-temperature exposure.

6.3.3 Mechanical strengths

After 28-day curing in the lab chamber and being exposed to high temperatures, three specimens of all mixtures were used for the flexural strength test by a universal testing machine in accordance with ASTM C348-20 (Standard Test Method for Flexural Strength of Hydraulic-Cement Mortars). The fractured portions of the specimens after the flexural strength test were employed for a compressive strength test following ASTM C349-18 (Standard Test Method for Compressive strength of Hydraulic-Cement Mortars). The percentage of compressive and flexural strength loss was calculated based on the original strength and the strength loss caused by high temperature.

6.3.4 Microstructure characterization

The fractured samples with the size of 2-5 mm and powder samples (pass through a 45 μ m sieve), smashed from the core of mortars before and after high-temperature exposure, were used to investigate the change of microstructure and hydration products. To stop cement hydration, the powder and fractured samples were soaked in 100% acetone. All soaked samples were then dried entirely within the drying oven at 40 °C for two days before being measured in the following test. The XRD analysis was employed to examine the composition evaluations occurring in all samples. The XRD analysis for powder samples was carried out by utilizing a BRUKER AXS D8 ADVANCE machine with 40 kV power and 40 mA in a Cu-K α source. The tested angle of the 2θ was in the range from 5° to 70° at a step of 0.02°/min. The changing of molecular characterizations were measured by FTIR analysis. The FTIR analysis for powder samples was performed with an attenuated total reflectance attachment for spectra measurement between 400 and 4000 cm⁻¹ wavenumber at 8 cm⁻¹ resolution.

Thermogravimetric analyses were conducted on powder samples to evaluate the alterations of the hydration reaction products for mortars before and after being subjected to elevated temperatures. The TGA analysis for powder samples was conducted by the application of the NETZSCH STA 449 machine in a nitrogen environment. The powder samples were maintained around 40 °C for 0.5 hr and then heated from 40 to 1000 °C at a rate of 10.0 °C/min in the N₂ environment. The microstructure and

composition change of hydration products in fractured samples were implemented by Zeiss Supra 55VP Backscatter electrons and energy dispersive X-ray with Raith Elphy Plus E-beam Lithography System as chemical composition analyzer at an accelerating voltage of 15 keV. After drying in the oven at 40 °C for two days, the lumpy samples were cured in epoxy resin, then polished with abrasive paper p300, p600, and p1200 by a grinder, and finally polished with 0.3 nm diamond polishing agent for approximately 10 min. The samples were carbon-coated for BSE-EDX analysis. The analytical process was set up to analyze the following elements: Al, Si, Cl, S, Na, and Ca. The chemical components were analyzed by Aztec 2.0 in accordance with the EDX results.

6.4 Results and discussions

6.4.1 Physical properties

The mass loss of all groups after high-temperature exposure is presented in Figure 6.4. The mass of all groups increased with increasing temperature. At all high temperatures, the mass loss of the FRRM group was higher than that of FSSM, which might be related to the influence of seawater and sea sand on the hydration reaction. The addition of 1.0 wt% fiber clearly increased mass loss at all elevated, resulting in a higher percentage of mass loss of FSSM-1F than that of FSSM and FRRM. After exposure to a temperature of 700 °C, the percentage of mass loss for FSSM-1F, FSSM, and FRRM was 12.5%, 11.8%, and 12.0 %, respectively. The mass loss of FSSM mixtures with GGBFS was less than that of the FSSM group and the corresponding FSSM-GGBFS-F group. The mass loss of the groups with GGBFS slightly decreased with the increasing addition of GGBFS. The combination of glass fiber and GGBSF decreased the mass loss as displayed in Figure 6.4 that the mass loss of FSSM-10S-1F was lower than that of FSSM. These were mainly related to a denser microstructure in the groups with GGBFS than in the FSSM group. The addition of glass fiber reduced the relative content of cementitious material in the same volume of samples, and the partial mass loss of glass fiber occurred in 400 and 700 °C, which might account for a higher mass loss in groups with glass fibers.

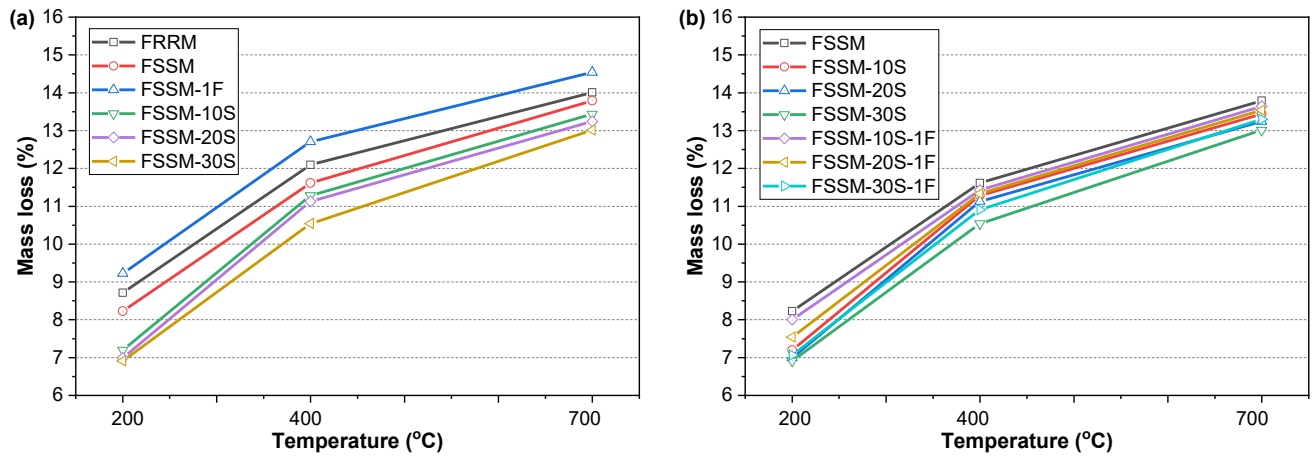


Figure 6.4. Mass loss of mortars after high-temperature exposures: (a) Comparison among FRRM, FSSM, FSSM-F, and FSS-GGBFS group; (b) Comparison between FSS-GGBFS and FSSM-GGBFS-F group

Figure 6.5 displays the visual appearance of all groups after exposure to a temperature of 700 °C. No apparent cracks were detected in the visual appearance of mortars after exposure to 200 and 400 °C. Thus, the visual appearance of all groups at 200 and 400 °C is not displayed in Figure 6.5. As shown in Figure 6.5, more cracks were founded in FRRM than in FSSM after exposure to 700 °C. The alteration of moisture loss, evaporation, and decomposition of the chemical structure for those groups could occur as the increasing temperature could lead to more cracks. The cracks founded in the FSSM-GGBFS group were less than that in FSSM, and the cracks could be relatively decreased with the increasing addition of GGBFS. Both longitudinal and transverse cracks were recorded in the FRRM, FSSM, and FSSM-GGBFS group, compared with only longitudinal cracks detected in FSSM-1F, which indicated that the glass fiber could effectively prevent the formation of cracks caused by the elevated temperature. The combination of GGBFS and fiber could also indeed prevent the formation of cracks at high temperatures, with no apparent cracks founded in the FSSM-GGBFS-F group.



Figure 6.5. Visual appearance of all mortars after exposure to a temperature of
700 °C

6.4.2 Compressive and flexural strengths

The compressive strength for all exposed and unexposed groups and percentage of strength loss for all exposed groups are illustrated in Figure 6.6. For the compressive strength in Figure 6.6(a), the compressive strength of FSSM was higher than that of FRRM, while FSSM-1F, with the addition of fiber, was lower than that of FRRM. The substitutes of GGBFS could increase the compressive strength of FSSM, and the increasing incorporation of GGBFS could also improve the compressive strength of

the FSSM-GGBFS group. However, the compressive strength of the FSSM-F-GGBFS group was lower than that of FSSM, which indicated that the compressive strength reduction caused by the addition of fiber was higher than the compressive strength increase due to the substitute of GGBFS. As the temperature increased, the compressive strength of all groups was decreased, especially at 700 °C, a massive strength reduction of all groups could be founded. Similar differences in the compressive strength of all exposed specimens were examined with those of unexposed specimens. For the compressive strength loss in Figure 6.6(b), the FSSM-GGBFS group had the lowest strength loss followed by FSSM, FRRM, FSSM-GGBFS-F, and FSSM-F group at the temperature of 200 and 400 °C, while a higher compressive strength loss was founded in FRRM than those of FSSM-F and FSSM-GGBFS-F groups at 700 °C.

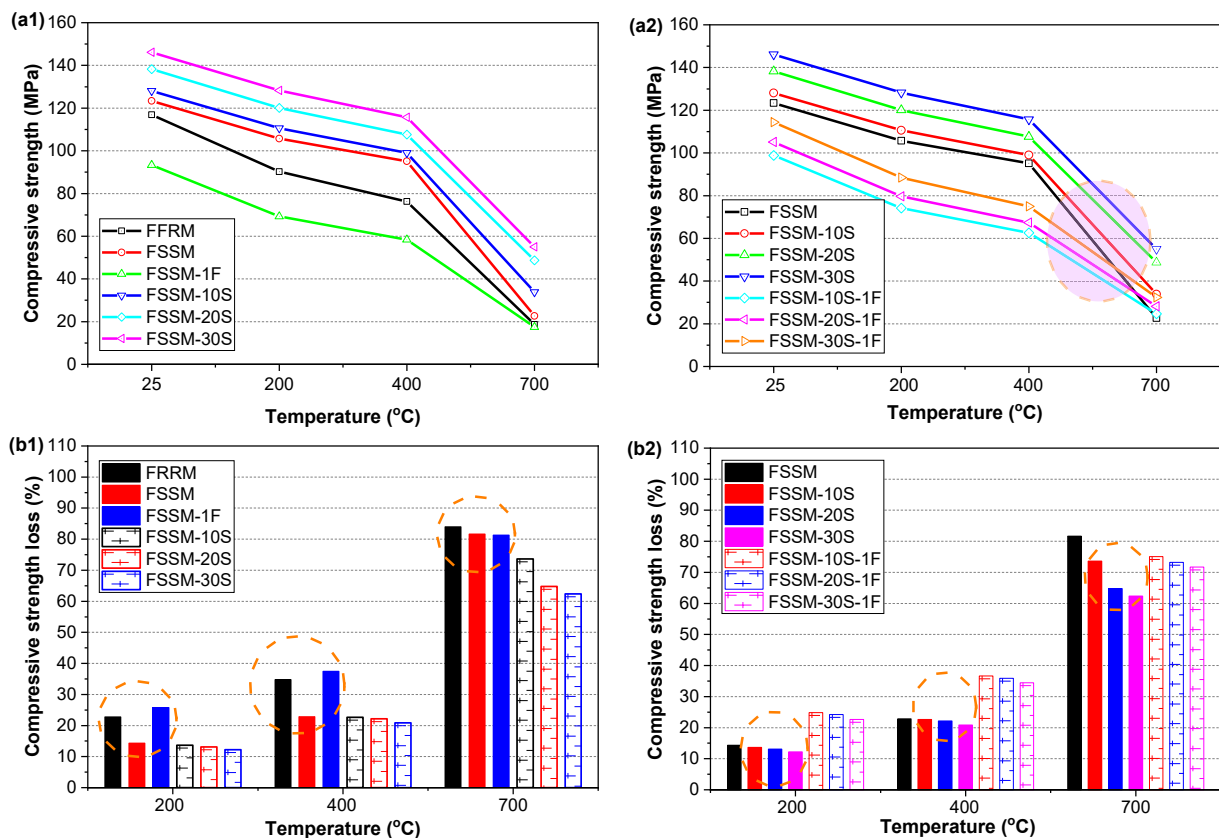


Figure 6.6. Effect of elevated temperature exposure on compressive strength: (a) Compressive strength of all unexposed and exposed groups; (b) Compressive strength loss after high-temperature exposure

The flexural strength for all exposed and unexposed groups and the percentage of flexural strength loss for all exposed groups are illustrated in Figure 6.7. The flexural strength of FSSM was lower than that of FRRM, which was related to the physical properties (low fineness modulus) of sea sand in the FSSM group. The addition of fibers could increase the flexural strength of FSSM, resulting in a higher flexural strength of FSSM-1F than FRRM. The replacement of GGBFS for cement could also increase the flexural strength of FSSM, and the flexural strength of the FSSM-GGBFS group could also be increased with the increasing content of GGBFS. Although the flexural strength of FSSM-10S was lower than FRRM, the flexural strength of FSSM-20S and FSSM-30S was higher than that of FRRM. In addition, while the FSSM-30S had the largest flexural strength among the FSSM-GGBFS group, the flexural strength of FSSM-30S was still lower than that of FSSM-1F, which indicated that the fiber had a higher ability to optimize the flexural strength than that of GGBFS. The combination of fiber and GGBFS made the FSSM-GGBFS-F group have the largest flexural strength. As the temperature increased, the flexural strength of all groups was decreased, especially a large amount of strength reduction of all mixed founded at 700 °C. Only the flexural strength of the FSSM-GGBFS-F group could be recorded. The flexural strength changes of all exposed specimens were founded similarly with those of unexposed specimens, except the FRRM and FSSM after exposure to 400 °C. It should also be noted that the flexural strength in FRRM was higher than in FSSM at 23 and 200 °C, but lower than in FSSM at 400 °C, which indicated that there were some different microstructure changes between FRRM and FSSM groups. For the flexural strength loss in Figure 6.7(b), the FSSM-GGBFS-F group had the lowest strength loss in all exposure temperatures, followed by FSSM-F, FSSM-GGBFS, FSSM, and FRRM groups. In addition, when the temperature was up to 700 °C, the percentage of flexural strength loss in all mixes except the FSSM-GGBFS-F group reached 100% because only the flexural strength of the FSSM-GGBFS-F group could be recorded.

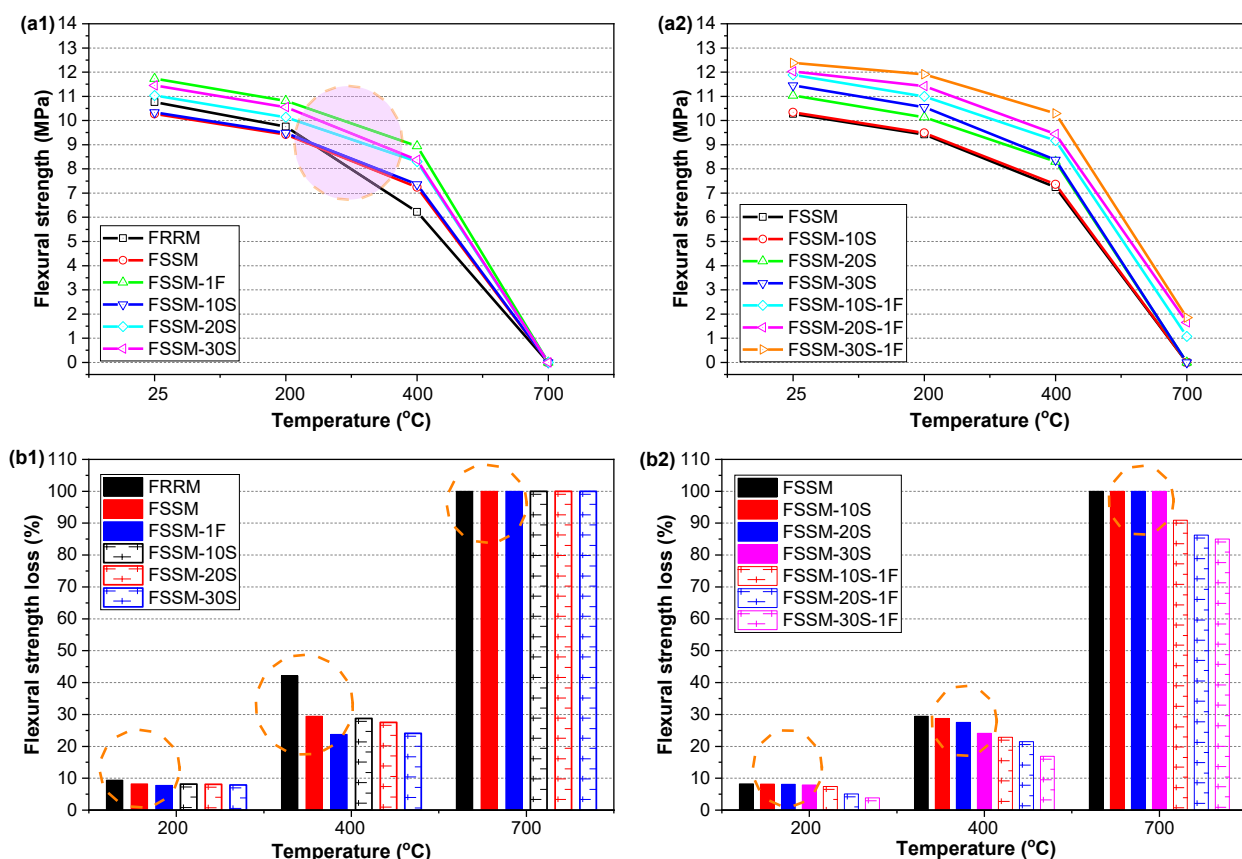


Figure 6.7. Effect of elevated temperature exposure on flexural strength: (a) Flexural strength of all unexposed and exposed groups; (b) Flexural strength loss after high-temperature exposure

In general, the seawater and sea sand could decrease the strength loss of FSSM, resulting in a lower strength loss of FSSM than that of FRRM in all exposure temperatures. The strength loss of FSSM could be decreased by the GGBFS and decreased with the increasing GGBFS. The addition of fiber had an adverse effect on the compressive strength of FSSM but had a positive effect on the flexural strength of FSSM. There are two possibilities for the addition of glass fiber to reduce the compressive strength of FSSM: glass fiber reduces the cement content of a given volume of mortar, and the interface between glass fiber and cement matrix may not be as good as the interface between sand and cement (Fang et al. 2018; Keleştemur et al. 2014). The combination of GGBFS and fiber could optimize the seawater sea-sand mortars' microstructure, resulting in a lower flexural strength loss founded in the FSSM-GGBFS-F group after exposure to 700 °C.

6.4.3 X-ray diffraction analysis (XRD)

The XRD results of all samples at 25 °C and the samples of FRRM, FSSM, and FSSM-30S after high-temperature exposure are displayed in Figure 6.8. It showed the comparative XRD results in all samples before being exposed to elevated temperatures. The data in Figure 6.8 (a) demonstrated that the all anhydrous test specimens before exposure to high temperatures were very similar to each other with the main clinker phase alite ($2\theta = 29.4$ and 47.0°), belite ($2\theta = 34.0^\circ$), tri-calcium aluminate ($2\theta = 29.9^\circ$), quartz ($2\theta = 18.8, 19.8, 20.9, 23.9, 25.2, 26.8, 36.4, 39.3, 42.3, 50.0, 54.8, 59.9$ and 68.2°), C-S-H ($2\theta = 28.7^\circ$) and calcite ($2\theta = 22.3^\circ$), as well as Portlandite ($2\theta = 18.0$ and 50.8°). There were lots of intensity peaks of quartz due to the sand content in the mortar samples. There was still some unreacted cement paste in all samples identified by the appearance of the tri-calcium aluminate or belite. The main difference between the FRRM group and the FSSM group was that there was a high intensity of Kuzel's and Friedel's salt ($2\theta = 11.1^\circ$) in the samples with seawater and sea sand, which might be related to the salt contents in seawater and sea sand. The reason for accelerating cement hydration was primarily due to chloride promoting the precipitation of calcium, aluminate, and ferrite. The peak of ettringite (AFt) at $9.09^\circ 2\theta$ was only founded in FRRM at 28 days. There was no big difference in the XRD results between the FSSM and FSSM-1F mixes, indicating that the glass fiber had no big effect on the hydration reaction. In addition, the intensity of CH was decreased as the increasing GGBFS in the mixes with seawater and sea sand, indicating that there was a reaction between Portlandite and the chemical component in GGBFS (Yun et al. 2020).

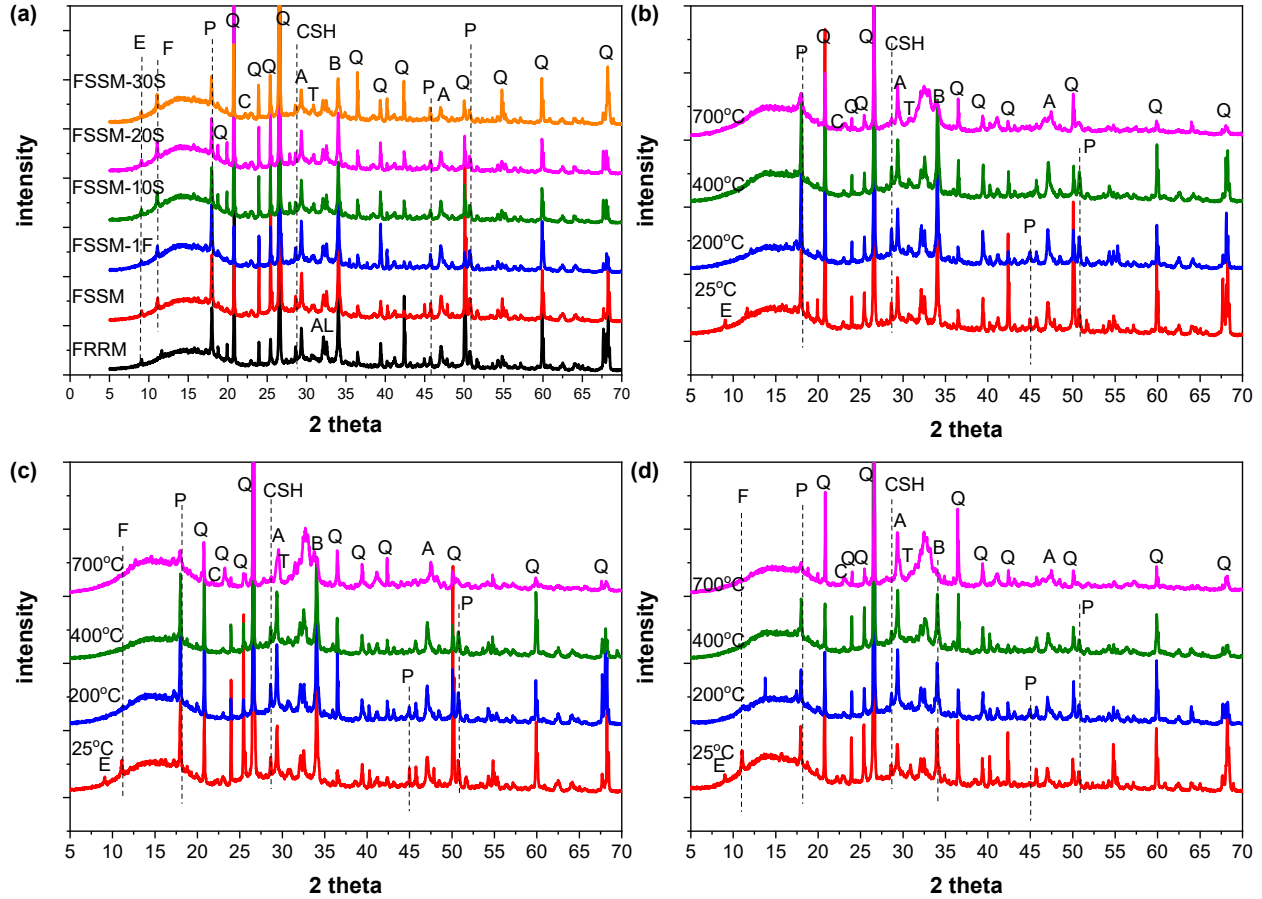


Figure 6.8. XRD diagrams for mortars before and after high-temperature exposures: (a) Comprasion at 25 °C,(b) FRRM, (c) FSSM and (d) FSSM-30S. Peak labels are as follows: A-alite ($3\text{CaO}\cdot\text{SiO}_2$), AL – Aluminate, B-belite ($2\text{CaO}\cdot\text{SiO}_2$), CAF – Brownmillerite ($4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$), C-calcite (CaCO_3), CSH ($3\text{CaO}\cdot 2\text{Al}_2\text{O}_3\cdot 3\text{H}_2\text{O}$), P-Portlandite ($\text{Ca}(\text{OH})_2$), E-ettringite ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaSO}_4\cdot 12\text{H}_2\text{O}$), F-Friedel's salt ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaCl}_2\cdot 10\text{H}_2\text{O}$), Q-Quartz (SiO_2), and T-tri-calcium aluminate ($3\text{CaO}\cdot\text{Al}_2\text{O}_3$)

Figures 6.8(b) to (d) show the comparative XRD results FRRM, FSSM, and FSSM-30S before and after high-temperature exposure. From the results of physical and mechanical properties, FSSM-30S performed best in the FSSM-GGBFS group. Therefore, after exposure to high temperature the discussion about the impact of GGBFS mainly focused on comparing FSSM-30S with other groups (the same below). At a temperature of 200 °C, there was only a noticeable reduction of the intensity for AFt in the FRRM group and a small reduction of the intensity for Friedel's salt in FSSM and FSSM-30S groups, which indicated that the AFt and Friedel's salt could be partly decomposed under this temperature. When the temperature was up to 400 °C, there was a noticeable reduction of the intensity for AFt in the FRRM group and for Friedel's salt in FSSM and FSSM-30S systems, which indicated

that the high temperature could significantly influence the AFt and Friedel's salt. Besides, after exposure to 700 °C, there was a noticeable reduction of the intensity for CH and C-S-H for all mixes. The FRRM had the most significant reduction of CH and C-S-H, followed by FSSM and FSSM-30S, which indicated that the FSSM and FSSM-GGBFS group was relatively lower influenced by the high temperature than that of FRRM. In addition, there was no significant change for other phases, including calcium, and quartz indicating that these phases could be stable after high-temperature exposure, even up to 700 °C.

6.4.4 Fourier transform infrared spectroscopy (FTIR) analysis

Figures 6.9 (a) to (d) show the comparison of FTIR data (600 to 3700 cm^{-1}) among FRRM, FSSM, FSSM-1F, FSSM-30S, and FSSM-10S before and after high-temperature exposure. Before exposure to high temperatures (at 25 °C), absorbance peaks were detected regarding distinct substances as displayed in Figure 6.9: the stretching of the O-H bond in CH was respected to the wavenumber near 3640 cm^{-1} (Zhang et al. 2019), the peak ranging from 1200 to 1400 cm^{-1} was connected to the bending mode of CO_3 (Zunino et al. 2020), the limited peak at approximately 1100 cm^{-1} was allocated to the stretching of SO_4 in monosulphate (AFm) or ettringite (Ylmén et al. 2009b), and the peak ranging from 960 to 1000 cm^{-1} was contributed to the stretching of Si-O bond in C-S-H or SiO_2 (Kapeluszna et al. 2017), and the cramped peak ranging from 820 to 880 cm^{-1} was for another dissymmetry stretching of CO_3 (Zunino et al. 2020). In this section, the peak (960 to 1000 cm^{-1}) variation was assumed to be mainly caused by C-S-H since quartz (SiO_2) could stabilize after exposure to 700 °C (Qu et al. 2020). Before being exposed to high temperatures, the signals from Figure 6.12 (a) for AFt/AFm and C-S-H were slightly substantial in FSSM than in FRRM, which confirmed the superior extent hydration of mortars with seawater and sea sand than those mortars mixed with river sand and distilled water. There were no significant differences in the signals from Figure 6.9 (b) between FSSM and FSSM-1F, demonstrating that the fiber did not affect the hydration reaction. When the addition of GGBFS was increased, the signals from Figures. 6.9(c) and (d) for AFt/AFm and C-S-H could notably be increased,

but for Ca(OH)_2 could be apparently decreased, which confirmed that more gel materials could be formed through the pozzolanic reaction of cement.

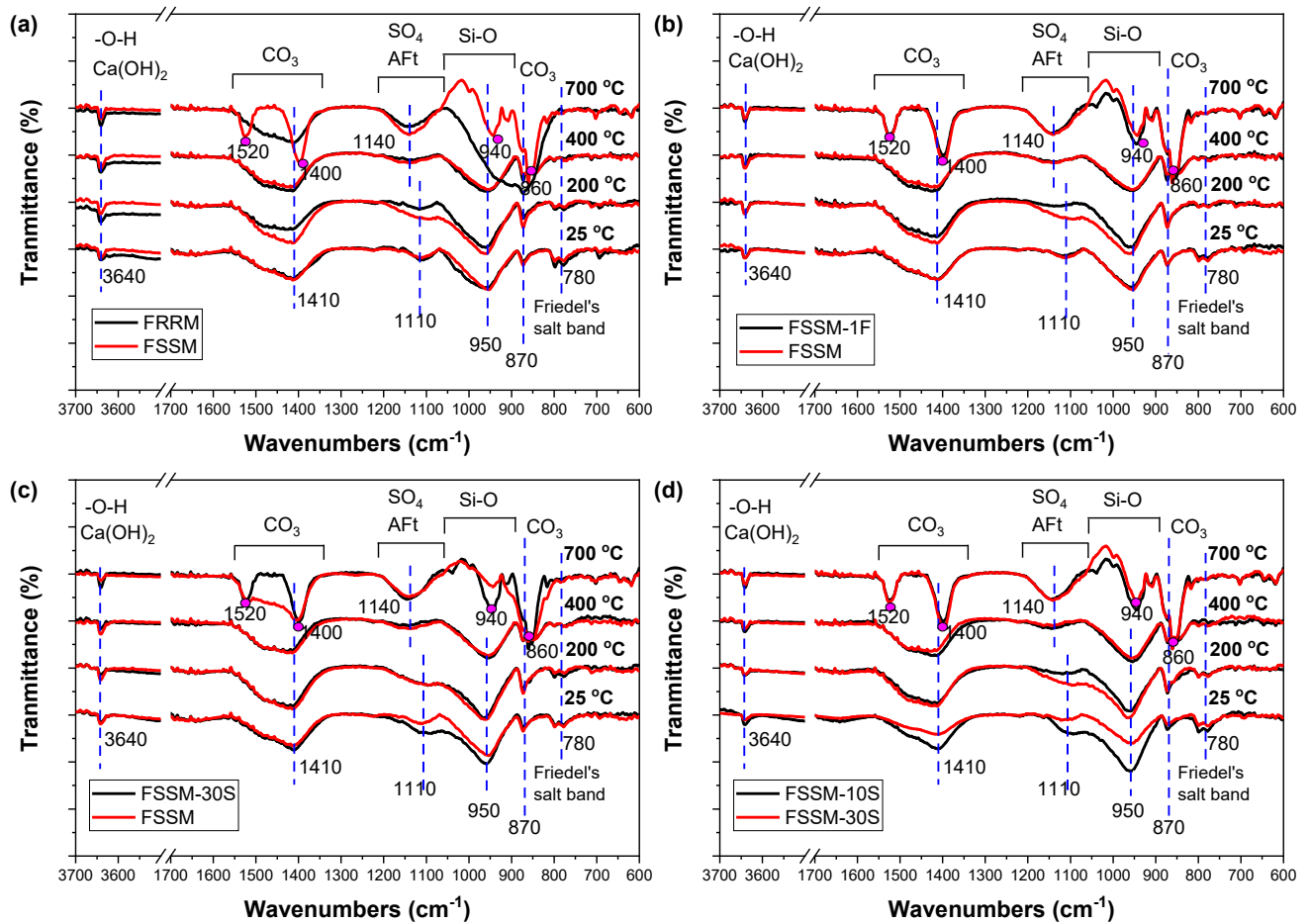


Figure 6.9. FTIR analysis on mortars before and after high-temperature exposures: (a) FRRM and FSSM, (b) FSSM and FSSM-1F, (c) FSSM and FSSM-30S, and (d) FSSM-30S and FSSM-10S

After exposure to 200 °C, there was a reduction in the peak of AFt/AFm and C-S-H among all groups. The chemical bounded water from AFt/AFm, and C-S-H could indeed be decomposed after being exposed to this temperature (Qu et al. 2020). The differences of these peaks were enlarged among FRRM and FSSM groups, which was related to a denser microstructure in the FSSM group. The signals for AFt/AFm and C-S-H in the FSSM-GGBFS group with a high content of GGBFS were also higher than those in the FSSM group. At a temperature of 400 °C, the narrow peak of all group around 1,100 cm^{-1} was gradually disappeared, which indicated that almost all AFt/AFm were mostly decomposed. The peak of C-S-H for all groups was also reduced as the increasing exposure temperature. The

differences in the C-S-H peak were narrowed among all groups. When the temperature reached 700 °C, there has been a sharp reduction in C-S-H peak among all groups. The peak of C-S-H could still be detected in the FSSM, FSSM-F, and FSSM-GGBFS group, compared to no obvious peak of C-S-H detected in the FRRM, which indicated that higher stable microstructure in 700 °C could be founded in FSSM. Besides, the change of the C-S-H peak was also smaller in FSSM-30S than FSSM-10S, demonstrating that the addition of GGBFS could also enhance the stable microstructure of FSSM.

6.4.5 Thermogravimetric analysis

Thermogravimetric analyses were conducted on powder samples to evaluate the alterations of the hydration reaction products for mortars before and after high-temperature exposure. Figure 6.10(a) show the comparative thermogravimetry (TG) and derivative thermogravimetry (DTG) results of mortar specimens before high-temperature exposure. As shown by the XRD and FTIR results above, TGA results for the group with fibers were not shown in this section because no significant differences were founded between the corresponding mixtures with or without glass fibers. According to the DTG results, two narrow peaks in FRRM could be detected approximately ranging from 100 to 200 °C, which was mainly caused by the loss of free water and the dehydration of ettringite, C-S-H, and AFm (Alarcon et al. 2005; AzariJafari et al. 2019; Bahafid et al. 2017; Jia et al. 2019), while two small peaks in the group with seawater and sea sand could be found in the same temperature range owing to the dehydration of ettringite, C-S-H, AFm, and Friedel's salt (Ting et al. 2020). The FSSM-GGBFS group had the most massive intensity of the AFm dehydration peak, followed by the FSSM and FRRM group, which might have something to do with the sulphate content in seawater and sea sand. A noticeable sharp peak between 450 and 500 °C, attributed to the dehydration of $\text{Ca}(\text{OH})_2$, occurred in all mixes (He et al. 2020). Another peak, primarily due to the decomposition of CaCO_3 , was founded around 720 °C. Compared to the FRRM group, the intensity of the CH dehydration peak was much lower in the FSSM group and decreased in the FSSM-GGBFS group with the increasing GGBFS content, which was contributed to the consumption of $\text{Ca}(\text{OH})_2$ by the hydration reaction of ions in seawater/sea sand

(De Weerd & Justnes 2015a) and the pozzolanic reaction of GGBFS (Yun et al. 2020), respectively. In the FSSM-GGBFS group, the intensity of the decomposition peak of CaCO_3 was lower than that in the FSSM group, which indicated that fewer CaCO_3 existed in the FSSM-GGBFS group.

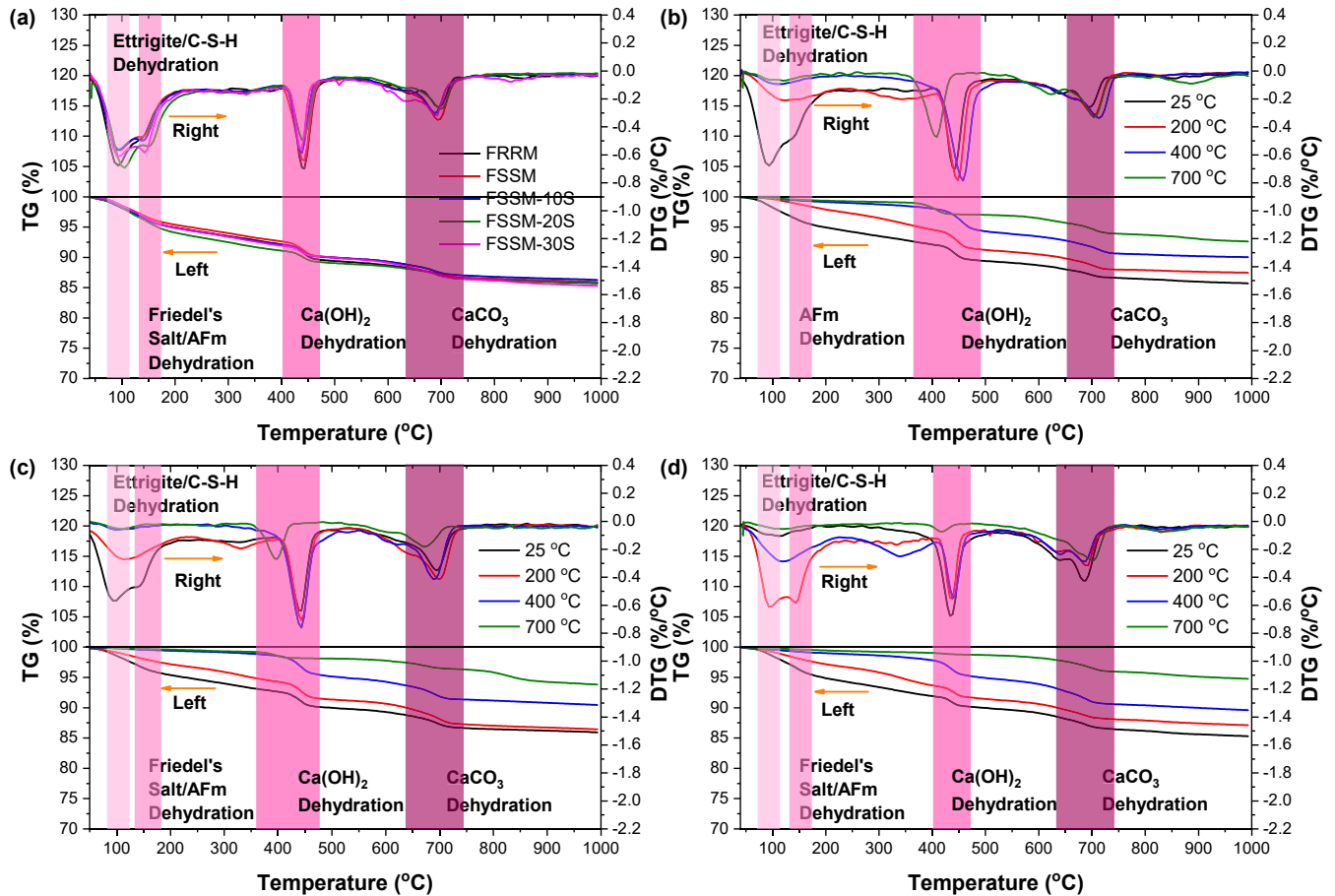


Figure 6.10. TG and DTG analysis of mortars before and after high-temperature exposures: (a) Comparison at 25 °C, (b) FRRM, (c) FSSM and (d) FSSM-30S

Figures 6.10 (b) to (d) show the comparative TG and DTG results of FRRM, FSSM, and FSSM-30S before and after high-temperature exposure. After exposure to 200 and 400 °C, there was an apparent decrease in the intensity of the peak around 200 °C for all mixes in the DTG curves, while there was no noticeable change for the CH and dehydration peaks, which indicated that the decomposition of the AFt, AFm and Friedel's salts primarily accounted for the strength loss after exposure to these temperatures. Besides, the evaporation of some chemically bounded water and the C-S-H gels' shrinkage could also be increased as the increasing high temperature, partially leading to the strength

loss after exposure to these temperatures (Jia et al. 2019). However, after exposure to 700 °C, except for those peaks near 200 °C in the DTG curve, the CH dehydration peak in all mixtures decreased significantly, and the carbonate dehydration also decreased slightly, which might lead to a lower strength reduction in all mixes after exposure to this temperature. In addition, weight changes mainly related to the evaporation of chemically bonded water in the tested samples between 200 °C and 1000 °C were also presented in Table 6.4. It could be known from Table 6.4 that the evaporation of chemically bonded water in the FSSM group was higher than the FRRM group after being exposed to all different elevated temperatures and could be increased by the addition of GGBFS. Besides, the decomposition of C-S-H had been confirmed (Kurihara & Maruyama 2020; Suh et al. 2020) to begin when the exposure temperature is over 500 °C, and it would lead to a noticeable alteration in the pore structure of the mortar matrix. Thus, the gels' distinct decomposition procedure after exposure to 700 °C also led to the incompatible strength loss in all mixtures.

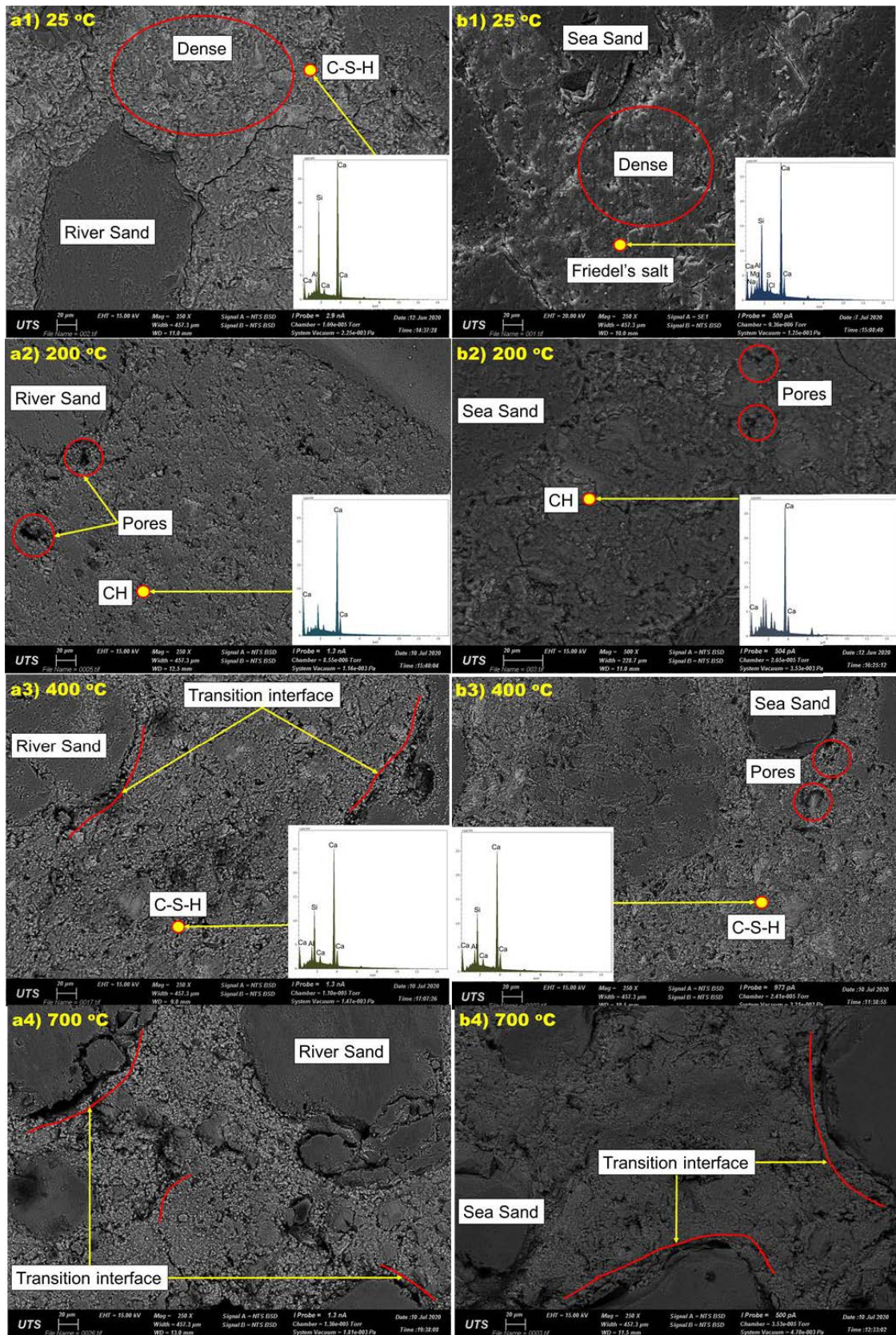
Table 6.4 Weight loss of mortar before and after high-temperature exposures

Specimen	Weight loss (%)			
	25 °C	200 °C	400 °C	700 °C
FRRM	10.1	9.2	8.9	4.7
FSSM	10.4	9.4	9.0	5.8
FSSM-30S	10.8	9.6	9.4	6.7

6.4.6 BSE with energy dispersive X-ray

Figures 6.11(a) to (d) show the BSE morphologies with the EDX results of FRRM, FSSM, FSSM-1F, and FSSM-30S mixes at different temperatures. Before high-temperature exposure in Figures 6.11(a1) to (d1), the BSE morphologies of all mixtures were relatively dense. The detected EDX results of C-S-H in FRRM and Friedel's salts in FSSM and FSSM-30S corresponded to the XRD results mentioned in Figure 6.8. Besides, the existence of glass fibers was confirmed by the EDX results with high intensity of the Si and Na because the primary chemical component of glass fibers was sodium silicate. Figure 6.11 c1) image showed a poor fiber-paste interface along the longitudinal, which might explain

a lower compressive strength in the group with fibers than those without fibers. When the exposure temperature reached 200 °C in Figures 6.11 (a2) to (d2), some small pores were detected in the FRRM and FSSM matrix, compared to a relative dense microstructure detected in FSSM-1F and FSSM-30S, which suggested that the increasing content of glass fiber and GGBFS could improve the fire resistivity of the FSSM group. The EDX results of CH could be detected in all mixes. The microstructure changes in these mixtures were mainly related to the evaporation of the free water, AFm/Aft under this temperature, consistent with the XRD and FTIR results. Besides, most of the glass fibers in FSSM-1F could be detected, which confirmed the unchanged mass of the fiber shown in Figure 6.2.



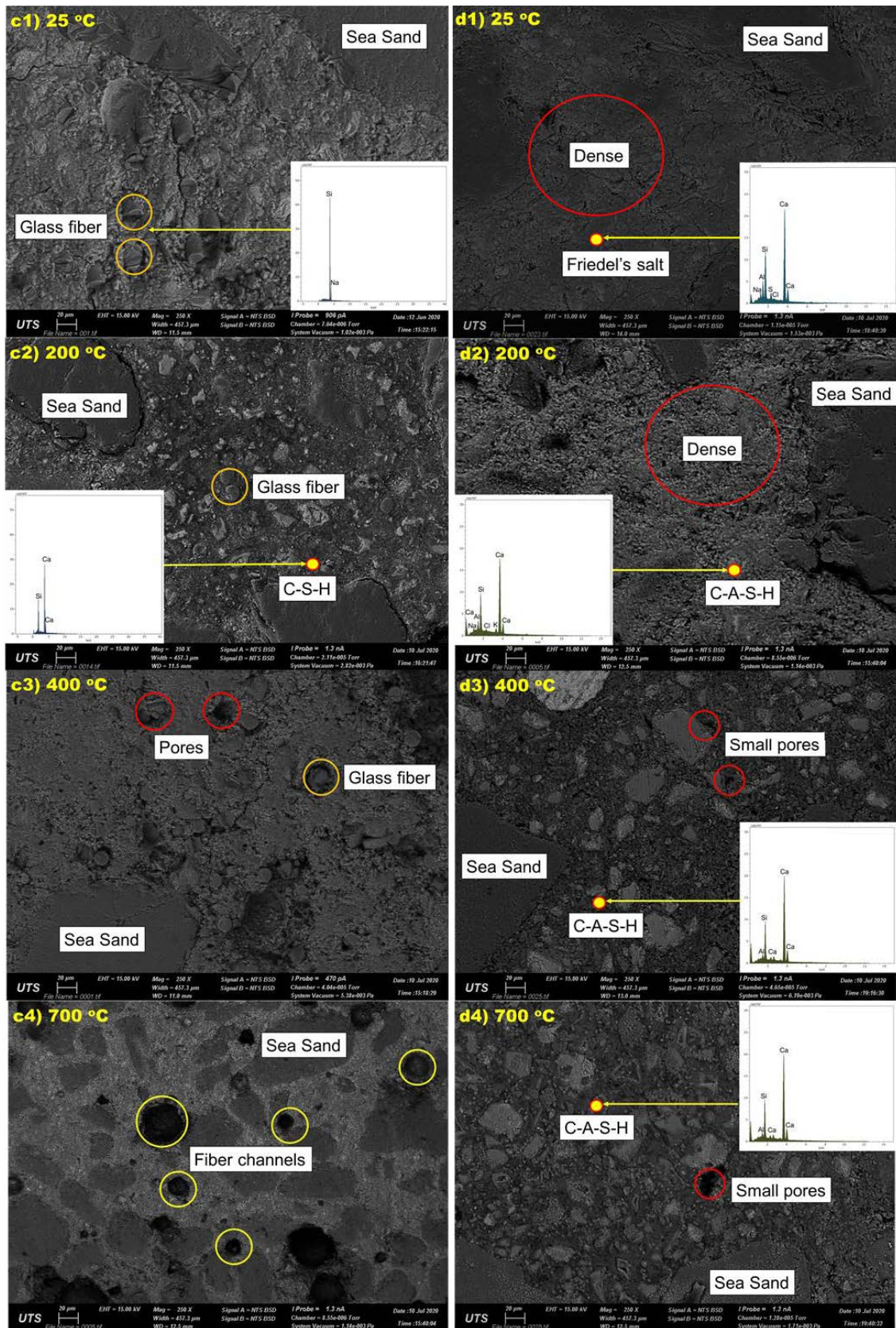


Figure 6.11. Characterization using BSE-EDX (250 magnification) before high-temperature exposure for mixes: (a) FRRM, (b) FSSM, (c) FSSM-1F; and (d) FSSM-30S

After exposure to 400 °C, in addition to the existence of inevitable pores, the cracks along the weak interface between the river sand and paste matrix in FRRM could be observed, while only some small pores could be detected in FSSM, FSSM-1F, and FSSM-30S group. This indicated that the mortars mixed with seawater and sea sand could perform better than that mortars with river sand and demineralized water. C-S-H was examined in all mixes, demonstrating that C-S-H could be stable after exposure to 400 °C. Besides, the relatively complete glass fibers were still able to be recorded in the FSSM-1F, confirming 20% mass loss of fiber in Figure 6.2. Fewer cracks would be generated in FSSM-1F, and spalling could be prevented in FSSM-1F in the contract to these groups without glass fibers. After exposure to a temperature of 700 °C, it seemed that with the increasing exposure temperatures, fibers were nearly melted (nearly 80% mass loss shown in Figure 6.2) and left channels, which could release the internal pressure in the mortar matrix, as shown in Figure 6.11 c4). In addition, more substantial cracks in the FRRM group and apparent cracks in the FSSM group along the weak interface could also be presented in the BSE morphologies. However, some pores were detected in FSSM-30S, which confirmed that adding GGBFS could enhance the microstructure of seawater and sea-sand mortars. The calcium aluminosilicate hydrate (C-A-S-H) could also be detected in the FSSM-30S group even after being exposed to 700 °C. The combination of GGBFS and fiber ought to make a more stable microstructure in the FSSM-GGBFS-F group, even after exposure to 700 °C. Besides, Figure 6.12 displays the BSE maps of FSSM-1F before and after high-temperature exposure. The main chemical composition of glass fibers was Na_2SiO_3 . There were nearly no detected elements of Na after exposure to 700 °C, which also confirmed that most of the glass fibers were melted after exposure to 700 °C.

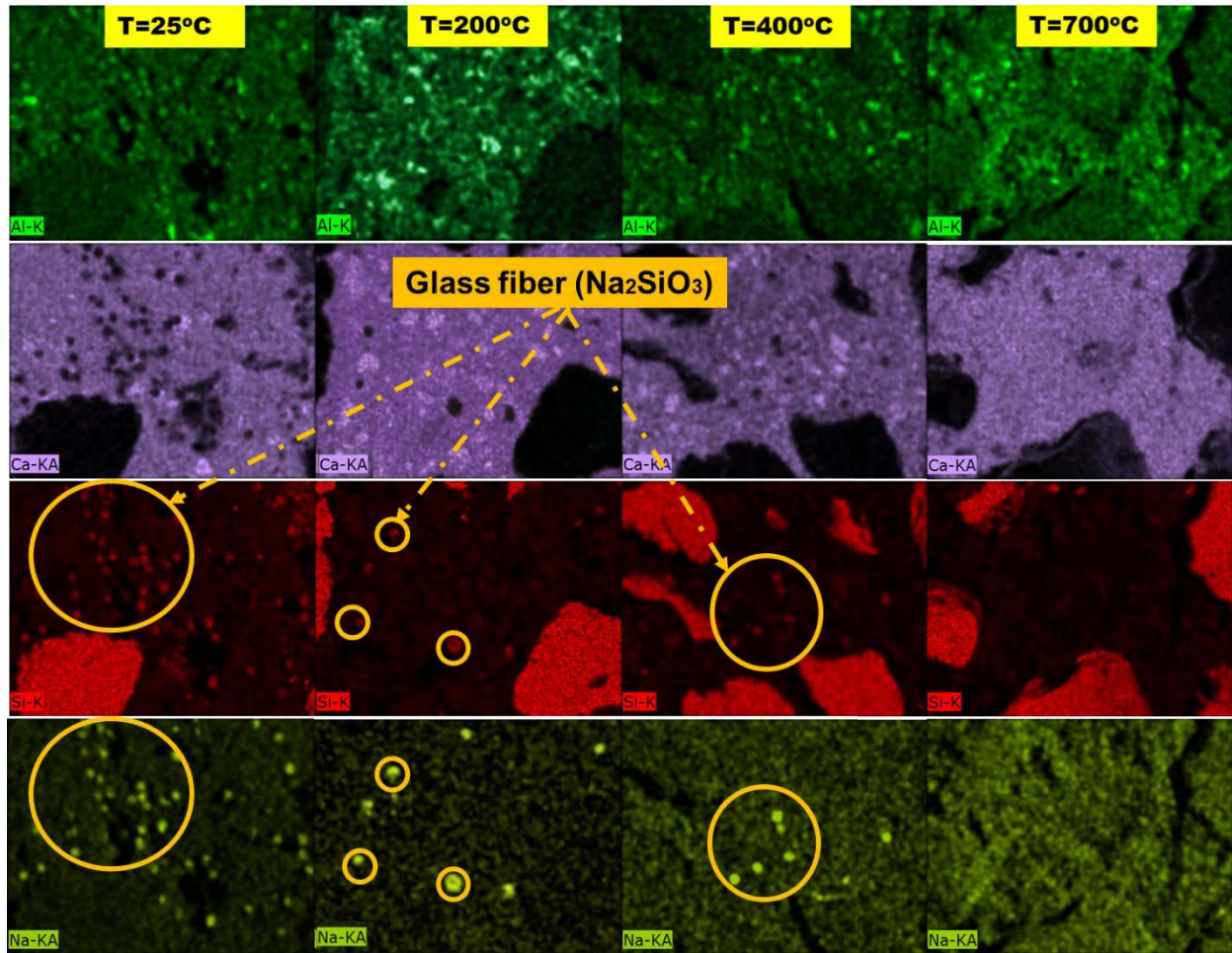


Figure 6.12. Element analysis of FSSM with glass fibre before and after high-temperature exposure

In order to evaluate the phase change, the EDX point analysis for the primary elements (Al, Ca, Cl, and Si) in a volume of approximately $1 \mu\text{m}^3$ was adopted. The results were displayed in ratios lying in between the best possible stoichiometry of these phases (De Weerd et al. 2019). Figures 6.13 (a) and (b) present the Al/Ca ratio as a function of the Si/Ca ratio for FRRM, FSSM, and FSSM-30S before high-temperature exposure and exposure to a temperature of 700°C , respectively. C–S–H/C–A–S–H was expressed by a dotted circle. Before high-temperature exposure, compared to the FRRM group, the Si/Ca and Al/Ca ratios of the C–S–H were higher in the FSSM group, which might be caused by the ions content in seawater or sea sand. The addition of GGBFS could also increase the Si/Ca and Al/Ca ratios of the C–S–H in FSSM. The Si/Ca ratio of C–A–S–H in FSSM-30S was around 0.6 – 0.8,

and the Si/Ca ratio of C-S-H in FSSM was about 0.5 – 0.7, in contrast to the Si/Ca ratio in FSSM-30S around 0.4 – 0.6. After exposure to 700 °C, the Si/Ca ratio of C-S-H in FRRM could be decreased to around 0.4 – 0.5 as the high temperature increased. There were slight changes in the Si/Ca ratios of C-S-H from around 0.5 – 0.7 to 0.5– 0.65. No significant changes of Si/Ca and Al/Ca ratios of C-A-S-H in the FSSM-30S group were founded, which might be to the chain length of C-A-S-H gels (Puertas et al. 2011). The long-chain length would make the C-A-S-H gels more thermally stable after high-temperature exposure (Puertas et al. 2011).

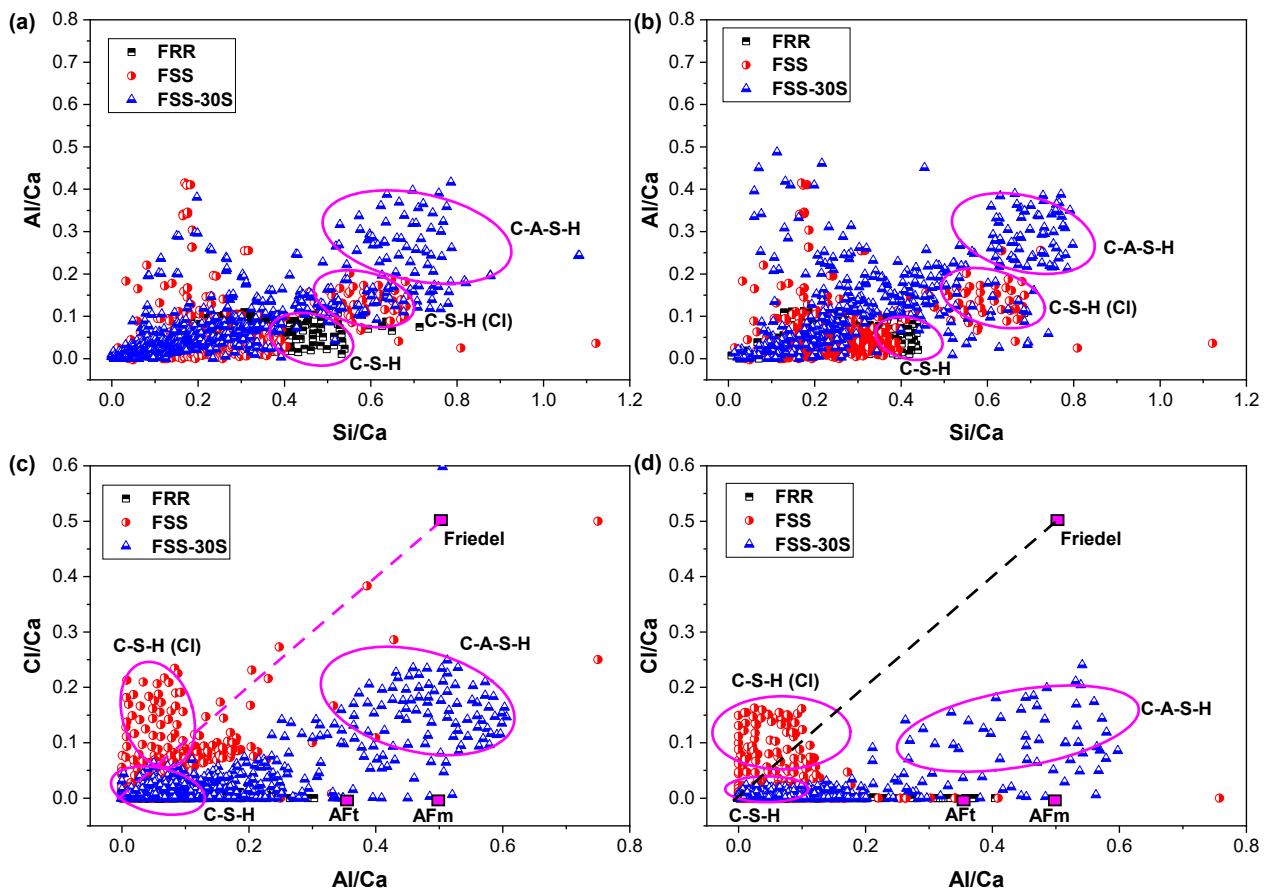


Figure 6.13. BSE-EDX analysis of FRRM, FSSM and FSSM-30S before and after high-temperature exposure: (a) Al/Ca as a function of Si/Ca (at 25 °C), (b) Al/Ca as a function of Si/Ca (at 700 °C), (c) Cl/Ca as a function of Al/Ca (at 25 °C), and (d) Cl/Ca as a function of Al/Ca (at 700 °C).

Note: C-S-H, C-S-H (Cl), and C-A-S-H were used to distinguish the gels in FRRM, FSSM, and FSSM-30S, respectively.

Figures 6.13(c) and (d) presented the Cl/Ca ratio as a function of the Al/Ca ratio for FRRM, FSSM, and FSSM-30S before exposure to high temperature and exposure to a temperature of 700 °C,

respectively, which also showed the ideal stoichiometry of the Friedel's salt, AFm, and AFt phases. Before exposure to high temperature, the AFt could be examined in the FRRM, while no chloride content was detected in the FRRM. Friedel's salts could be examined in the FSSM, while the AFm could not be recorded in the FSSM. The AFm can be detected in the FSSM-30S. These points in Figure 6.13(c), located in the 0.0 – 0.1 Al/Ca and around 0.1 – 0.25 Cl/Ca molar ratio range in FSSM, were supposed to stand for chlorides adsorbed on the C-S-H. Besides, a number of points, located in the 0.4 – 0.6 Al/Ca and around 0.1 – 0.25 Cl/Ca molar ratio range in FSSM-30S, were assumed to represent chlorides adsorbed on the C-A-S-H. This might indicate that the ability to absorb chlorides of C-A-S-H could be higher than that of C-S-H. After exposure to a temperature of 700 °C, Friedel's salt was likely to hardly be detected in the FSSM, which indicated that the decomposition of Friedel's salt could occur at a high temperature. In addition, no significant Cl/Ca ratio changes in FSSM-30S and slight Cl/Ca ratio changes in FSSM were examined, which indicated that the C-A-S-H in FSSM-30S was relatively stable than that of C-S-H gels (Cl) in FSSM.

6.5 Mechanism discussions

As mentioned above, alterations in the microstructure of hydration products could be seen among the different mortar mixtures after high-temperature exposure, which might have contributed to the microstructural change in binder gels, including Friedel's salt and C-S-H. By comparing the results mentioned above, a diagram for the microstructure evolutions of the binder gels before and after high-temperature exposure is schematically drawn in Figure 6.14. The diagrams for FSSM, FRRM, FSSM-1F, and FSSM-30S-1F are drawn in Figure 6.14, primarily caring about the effect of seawater, sea sand, fiber, and GGBFS. In these groups, the mechanism of fire resistivity seems to be different.

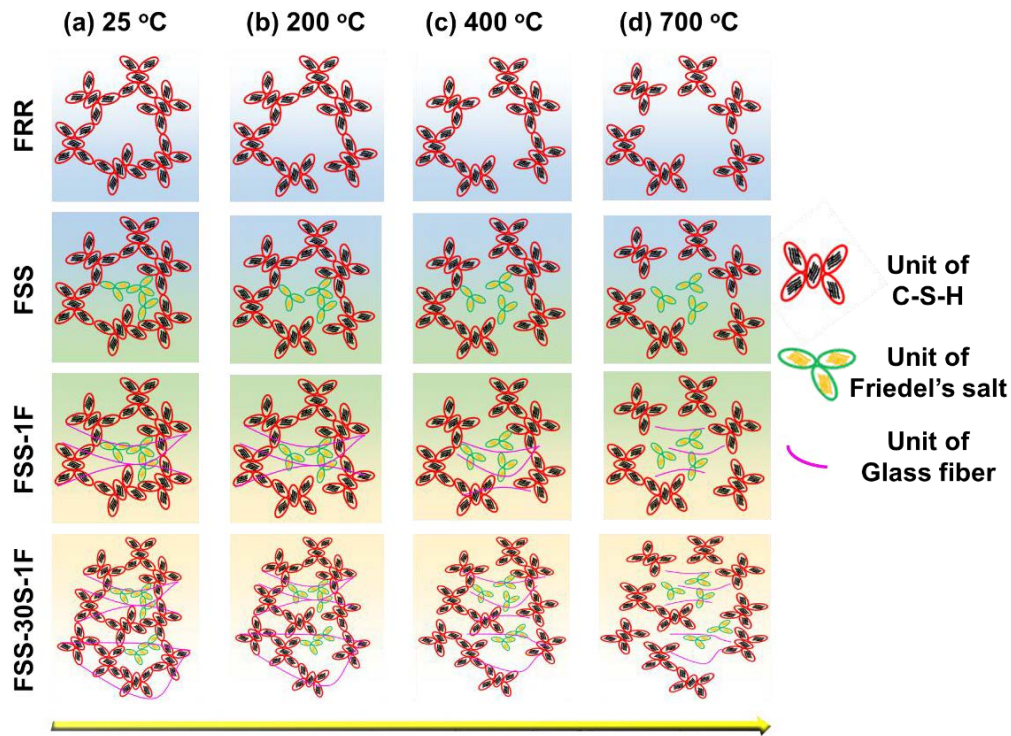


Figure 6.14. Schematically diagrams for the microstructure change of the binder gels before and after high-temperature exposure

Before high-temperature exposure, the salt content (mainly chloride) in seawater and sea sand could accelerate the cement hydration with more hydrates produced, including Friedel's salt (Figure 6.8) in FSSM, resulting in more stable gels structures in the FSSM group than in FRRM group shown in Figure 6.14, which could explain a higher compressive strength was founded in FSSM from Figure 6.6. Though the mean chain length of binder gels in FRRM was normally the same as FSSM, Friedel's salt could make the binder gels more stable. In Figure 6.14, with the addition of the glass fiber, the bridging effect between the mortar matrix and fiber would prevent micro-cracking formation with increased tensile strength. Thus, there was a high flexural strength detected in the FSSM-1F group in Figure 6.6. As the results of the incorporation of GGBFS, the high aluminum content of the FSSM-30S group is higher than that of groups without GGBFS content (Taylor et al. 2010). These changes could be attributed to the pozzolanic reaction between GGBFS and Ca(OH)_2 . The corporation of

GGBFS could optimize the composition and microstructure of C-S-H (Jia et al. 2019); thus, the C-S-H gels in the FSSM group with GGBFS were also called C-A-S-H gels (Wei et al. 2018). The incorporation of glass fiber and GGBFS could provide a more stable microstructure with a longer mean chain length (see Figure 6.14) in the FSSM-30S-1F group, with the highest flexural strength in the FSSM-1F-30S group.

At the temperature of 200 °C, the proportion of C-S-H in Figures. 8 and 9 barely displayed noticeable variations, but a pronounced reduction of the peak around 100 to 200 °C in the TGA curves was detected in Figure 6.12, with a slight decreasing strength founded in Figure. 7. In addition, there was a reduction in the peak of Friedel's salt from Figure 6.10 in all mixes with seawater and sea sand. The significant friction of free water evaporation and small friction of chemical bounded water evaporation would mainly explain the small change of the gel's microstructure for most mixes (Figure 6.14). At this temperature, the glass fiber could perform well, as confirmed in Figures 6.2 and 6.12. Thus, there was only a small flexural strength loss in the group with fiber. Friedel's salt could be partially decomposed, and the glass fiber could be relatively stable, as shown in Figure 6.14. When the temperature was 400 °C, the similar findings about the microstructure of the C-S-H gels and other phases were founded corresponded with those found at 200 °C, except the partially melted glass fiber, detected shown in Figure 6.12. Therefore, a more significant flexural strength loss was founded in all mixes. Due to a denser microstructure in the FSSM group, there was less strength loss in FSSM than in FRRM, which accounted for a higher flexural strength from Figure 6.6 in FSSM than in FRRM. The fitness modulus and physical properties of the sea sand could have an adverse effect on the flexural strength behavior, but the microstructure of all groups would play a critical role in the mortars' fire resistivity. Friedel's salt could be further decomposed, and the glass fiber could be partially melted, as shown in Figure 6.14.

After exposure to 700 °C, C-S-H in FRRM, FSSM, and FSSM-1F mixtures had already started to decompose according to the XRD results, which could cause the collapse of the gel structure. In

addition, the C-S-H gels also endured shrinkage at elevated temperatures with a decrease in the packing density of C-S-H (DeJong & Ulm 2007), which caused great damages to the gel's structure. The glass fiber could also entirely be melted after being exposed to 700 °C. Therefore, the flexural strength loss of FRRM, FSSM, and FSSM-1F group could up to be 100 % showed in Figure 6.7. The gels structure of FRRM, FSSM, and FSSM-1F could be all collapsed, as shown in Figure 6.14. Researches about the high-temperature stability of C-S-H (Rodriguez et al. 2017) presented that C-S-H with higher Si/Ca was more stabilizing at the elevated temperatures, possibly contributing to the silicate microstructure. On the basis of the EDX results, the C-A-S-H in the FSSM-30S had higher ratios of Si/Ca and Al/Si in contrast to the C-S-H in the mixtures without GGBFS or with low GGBFS content (Figure 6.13). It was generally considered that the average chain length of C-S-H is shorter than C-A-S-H (Puertas et al. 2011). Thus, the high Si/Ca and distinct chain microstructure possibly caused the C-A-S-H gels to be more stabilizing than C-S-H gels at elevated temperatures. The C-A-S-H gels in the group with GGBFS could still cover familiarly after high-temperature exposure in the BSE result. The BSE-EDX result in Figure 6.11 illustrated that the C-A-S-H gels in the FSSM-30S group remained high even if the exposure temperature arrives at 700 °C, which possibly indicates that component of C-A-S-H gels could also protect the gel structure from deteriorating even at elevated temperature, further identifying the stability of C-A-S-H. The C-A-S-H gels also endured shrinkage at elevated temperatures, leading to a 100% flexural strength loss in the FSSM-GGBFS group. However, the thermal stable gel's structure would protect the glass fiber from being melted, which would make the most stable gel's structure in the FSSM-GGBFS-F group (Figure 6.14) and lead to a comparatively small flexural strength loss in the FSSM-GGBFS-F group.

In terms of fire or high-temperature resistance, the increasing addition of GGBFS could stabilize the microstructure of FSSM. However, the flexural strength loss of the FSSM-GGBFS group could still be up to 100%. Combining the addition of GGBFS and fiber, the FSSM-GGBFS-F group performed well with high flexural strength and low flexural strength loss after high-temperature exposure. In this

study, FSSM-30S-1F achieved the highest fire or high-temperature resistance.

6.6 Summary

This study investigated the mechanical properties and microstructure of seawater and sea sand mortars after exposure to high temperatures. The effects of GGBFS and glass fiber on the thermal performance of seawater and sea-sand mortars were also evaluated. The conclusions could be drawn up as below:

- (1) Before being exposed to high temperatures, compared with FRRM, the ion content (mainly chloride) in seawater and sea sand reacting with cement increased the compressive strength of FSSM, while sea sand with a lower fineness modulus reduced flexural strength. Although glass fiber could improve the flexural strength of FSSM, the poor microstructures around the fiber-paste interfaces could reduce compressive strength. Although the addition of GGBFS could increase both the flexural and compressive strengths of FSSM for its pozzolanic reaction, the compressive strength of the FSSM with GGBFS and glass fiber was still lower than that of the FSSM with only GGBFS.
- (2) After exposure to high temperatures of 400 and 700 °C, compared with FRRM, the accelerated hydration reaction caused by salt densified the microstructure of FSSM, thereby reducing mass loss, strength loss, and cracking. Glass fibers could be partially and mostly melted after exposure to 400 and 700 °C, respectively, which increased the loss of mass and compressive strength of FSSM. Glass fibers could also effectively prevent the formation of cracks caused by high-temperature exposure and further decrease the flexural strength loss for FSSM.
- (3) The addition of GGBFS could densify the microstructure of FSSM and decrease the strength loss caused by high-temperature exposure. The increased addition of GGBFS could also decrease crack formation, while both longitudinal and transverse cracks were still recorded in the FSSM only with GGBFS. The combination of the GGBFS and glass fibers could improve the fire resistivity of the FSSM. After exposure to 700 °C, FSSM with GGBFS and glass fiber still exhibited certain flexural

strength and less visible cracks on the surface.

- (4) Chloride in seawater and sea sand could accelerate the hydration reaction of cement and produce the Kuzel's and Friedel's salt. The decomposition of the AFt, AFm, and Friedel's salts primarily accounted for the hydration product changes after exposure to 200 and 400 °C. The glass fiber had no effect on cement's hydration reaction, while the bridging effect between the cement matrix and glass fiber could prevent the micro-cracking formation of FSSM.
- (5) The GGBFS could optimize the composition and microstructure of FSSM. The Si/Ca ratio of FSSM without GGBFS decreased after high-temperature exposure, while the Si/Ca ratios of the FSSM with GGBFS almost maintained constant. The C-A-S-H gels in the FSSM with GGBFS were relatively stabler than that of C-S-H. Since the increased addition of GGBFS promoted C-A-S-H gels' formation packed along the glass fibers, the fire resistivity of FSSM with glass fibers and GGBFS was improved. In this study, the optimum high-temperature resistivity was achieved for FSSM with 30% GGBFS and 1% glass fibers by weight.

CHAPTER 7: CHLORIDE-BINDING CAPACITY OF GGBFS-NS-CEMENT SYSTEM IN SEAWATER AND CHLORIDE SOLUTIONS

7.1 Introduction

Cementitious composites have become the preferred materials for marine structures (e.g. military terminals, offshore airports, and wind power stations) due to their versatility and relatively low cost (Dong et al. 2016; Pasupathy et al. 2021). However, the direct utilization of reinforced concrete (RC) will increase the deteriorated and even destroyed possibility of the marine constructions as a result of the potential risk of reinforcement corrosion induced by the diffused and migrated salts (mainly chloride ions) in the marine environment (Feng et al. 2021; Tennakoon et al. 2017). This issue has attracted significant attention of practitioners in civil and infrastructure engineering construction. Accordingly, under the circumstance of the RC in the marine environment, effective measures should be taken before design and construction to avoid the potential risk of reinforcement corrosion. The corrosion inhibitors (Balonis et al. 2019; Harilal et al. 2021; Venkatesh et al. 2019) and protection-layer coatings (Afshar et al. 2020; Goyal et al. 2019; Harilal et al. 2022; Rooby et al. 2021) have been commonly added to the surface of steel bar to reduce the reinforcement corrosion. Increasing chloride-binding capacity (CBC) of cementitious composites was also considered to be another promising method (Guo et al. 2022). It was reported (Machner et al. 2018; Spiesz & Brouwers 2013; Tran et al. 2018) that the potential risk of reinforcement corrosion could be decreased or eliminated if chloride ions could ultimately be bounded and the migration of chloride ions could be effectively prevented. Increasing chloride-binding capacity is considered as a controlling property of the reinforced concrete in the marine environment.

The CBC of cementitious composites is significantly related to hydration products (Yuan et al. 2009). In particular, the physically binding chloride on calcium silicate hydrate (C-S-H) gels and chemically binding chloride in Friedel's salt (FSS) or Kuzel's salt (KSS) are the two primary manifestations of

chloride-binding capacity (Elfmarkova et al. 2015). To enhance the chloride-binding capacity, some supplementary cementitious materials (SCMs), such as metakaolin (MK) and fly ash (FA), were added to cementitious composites (Thomas et al. 2012). The enhanced CBC of SCMs-based cementitious composites is possibly attributed to their alumina content (Plusquellec & Nonat 2016; Yuan et al. 2009). Machner et al. (2018) investigated the CBC of cement pastes containing MK and pointed out that a higher CBC was found in the cement paste with 40.0 wt.% MK than that without MK. Shi et al. (2017) examined the CBC of cement paste with 31.9 wt.% MK and illustrated that the MK increased the CBC mainly due to the increasing formations of Friedel's salts. Similarly, some researchers (Ipavec et al. 2013; Ma et al. 2018) also stated that the addition of FA increased the CBC of cementitious composites due to the pozzolanic reaction of FA, which generated much more C-S-H gels and liberated aluminum into the liquid phase. Besides, ground granulated blast furnace slag (GGBFS), one of the most commonly used SCMs, was also adopted to partially replace ordinary Portland cement (OPC) to improve the CBC of cementitious composites (Florea & Brouwers 2014; Luo et al. 2003). Florea and Brouwers (2014) estimated and quantified the hydration products of cementitious composites with GGBFS by a novel hydration model. They illustrated that the increasing hydrated gels generated by GGBFS increased the CBC of cementitious composites. However, Okiemute and Leon (2017) described that the different chemical compositions (e.g. oxide/basicity ratios) of GGBFS might have different effects on the CBC of cementitious composites. Although the aluminium content in GGBFS can increase the CBC of cementitious composites, more investigations related to the CBC of GGBFS-based cementitious composites are expected to be conducted.

Nanoparticles, such as nano-TiO₂ (NT), nano-CaCO₃ (NC), and nano-Al₂O₃ (NA), etc., were also adopted to promote the CBC of cementitious composites (Harilal et al. 2019; Li 2021; Uthaman et al. 2019; Uthaman et al. 2018). Uthaman et al. (2018) demonstrated that the addition of NT and NC possibly increased the CBC of cementitious composites due to fastening the hydration reaction. Harilal et al. (2019) also stated that the addition of 2.0 wt.% NT and NC improved the CBC of cementitious

composites. Liu et al. (2019) investigated the effect of 0.25, 0.5, 1.0, 2.0, and 4.0 wt.% NA on the CBC of cementitious composites and illustrated that the addition of NA could significantly promote the chloride-binding capacity of cementitious composites in terms of the increasing amounts of C-S-H gels and the Ca/Si ratio. The authors pointed out that more chloride could be bounded due to the increasing amounts of C-S-H gels. Nano-SiO₂ (NS), one of the nanomaterials with high pozzolanic reactivity, was also expected to improve the chloride-binding capacity of FA-based cementitious composites (Hou et al. 2013; Mei et al. 2018). Liu et al. (2020) examined the effect of 0.5 wt.% colloidal NS on the chloride-binding capacity of FA-based cementitious composites and stated that the addition NS improved the chloride-binding capacity due to the increasing generation of hydrated gels. However, research articles about the effect of NS on the chloride-binding capacity of GGBFS-based cementitious composites were rarely reported.

It should be noted that except for the chloride ions, the CBC of cementitious composites can also be affected by other ions (e.g. magnesium) when the reinforced concrete structures are exposed to the marine environment, particularly to the seawater environment (De Weerd et al. 2015; dos Santos et al. 2021). The magnesium ions in the marine environment could react with hydration products, further affecting the CBC of cementitious composites (De Weerd et al. 2015; dos Santos et al. 2021). Therefore, there were three specific objectives in this study: firstly, to evaluate the effect of GGBFS on the chloride-binding capacity of cementitious composites; secondly, to examine the effect of NS content on the chloride-binding capacity of GGBFS-based cementitious composites; and thirdly, to investigate the effect of different concentrations of chloride solutions (e.g. NaCl, MgCl₂, and NaCl + MgCl₂ solutions) on the chloride-binding capacity of cementitious composites. In addition, the chloride binding and phase transformations were systematically analyzed by various analysis methods, including potentiometric titration (PT), ICP-MS, TGA, XRD, FTIR, SEM-EDX. Thermodynamic modelling was also employed to evaluate the phase assemblages for the Portland cement-GGBFS-NS composites exposed to chloride-rich environments. It is expected that these results can provide an

insight into the theoretical investigation into the chloride-binding capacity of cementitious composites and the durability improvement of marine structures.

7.2 Experimental program

7.2.1 Materials

The materials used in this study are CEM I 42.5N ordinary Portland cement (OPC) provided by Independent Cement-Lime Pty Ltd AU, GGBFS provided by Building Products Supplies Pty Ltd AU, and laboratory-grade powder-formed NS provided by General Engineering-Research Pty Ltd AU. The Blaine of OPC and GGBFS is 347 m²/kg and 418 m²/kg, respectively. The specific gravity of OPC and GGBFS is 3.15 and 2.92, respectively. The mean particle size of NS is 20 nm, and it contains 99% SiO₂. Table 7.1 displays the loss on ignition (LOI) and chemical compositions, examined by X-ray fluorescence (XRF), of OPC and GGBFS. The XRD patterns of OPC, GGBFS, and NS are presented in Fig.1, where the broad peaks suggest the amorphous structure. It can be seen that the diffraction peaks of $2\theta = 23.01^\circ$ can be examined, which indicates the crystal form of SiO₂. The chloride solutions were prepared with laboratory-grade salts of NaCl and MgCl₂·6H₂O, provided by Chem-Supply Pty Ltd AU. The chloride concentrations of the preparing chloride solutions were determined before being used as an exposure solution. The seawater (SW), acquired from Botany Bay near Sydney NSW AU, was also used as the exposure solution. The chemical compositions of the seawater were measured by ICP-MS and Potentiometric titration (PT). The concentrations of NaCl, MgCl₂, Na₂SO₄, KCl and CaCl₂ was 19.0, 1.35, 0.88, 0.38 and 0.40 g/L, respectively. The laboratory-grade deionized water (DW) was adopted to prepare the cementitious paste and exposure solution.

Table 7.1 LOI and chemical compositions (%) of OPC and GGBFS

Material	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	MnO	K ₂ O	Na ₂ O	P ₂ O ₅	TiO ₂	SO ₃	LOI
GGBFS	36.00	13.80	0.30	42.60	5.80	0.40	0.27	0.21	0.10	0.80	0.56	1.64
OPC	20.51	5.37	2.10	57.05	3.86	0.02	1.44	0.64	0.13	0.16	6.37	2.35

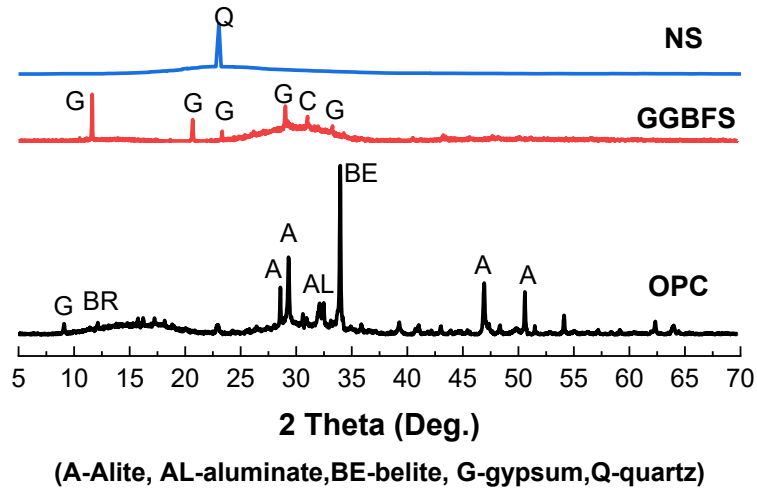


Figure 7.1. XRD results of OPC, GGBFS, and NS

7.2.2 Mix proportion and sample preparation

Table 7.2 displays the proportions of the paste mixes studied. The 100% Portland cement mixed with deionized water (PC) was fabricated as the reference group. Other three different groups of paste were also fabricated in this study: one PC-GGBFS group (30 wt.% GGBFS replacing cement); two PC-GGBFS-NS groups (PC-GGBFS-NS1 (30 wt.% GGBFS and 1.0 wt.% NS), and PC-GGBFS-NS2 (30 wt.% GGBFS and 2.0 wt.% NS)). It should be noted that the different additions of NS were recognized as cement replacements. The cementitious pastes were prepared with a water/binder (W/B) ratio of 0.5.

Table 7.2 Mix proportion for the composite mixtures (g)

Group	OPC	GGBFS	NS	Deionized water	W/B
PC	1000	—	—	500	0.5
PC-GGBFS	700	300 (30%)	—	500	0.5
PC-GGBFS-NS1	693	297	10 (1%)	500	0.5
PC-GGBFS-NS2	686	294	20 (2%)	500	0.5

All binder compositions were mixed in a high-shear N50-619 Hobart mixer. The deionized water or

the deionized water dispersed with NS (ultrasound probe sonication for two hours) was added to the binder, and the blend was firstly mixed at 500 rpm for three min, then no mixing for two min, followed by 2000 rpm for another two min, and finally cast and sealed in a 125ml polyethylene screw-lid bottle and stored in a 38 °C climate chamber. After 24 hrs, a little deionized water was added at the top of the bottle to neutralize self-desiccation, which is shown in the flowchart in Fig 7.2.

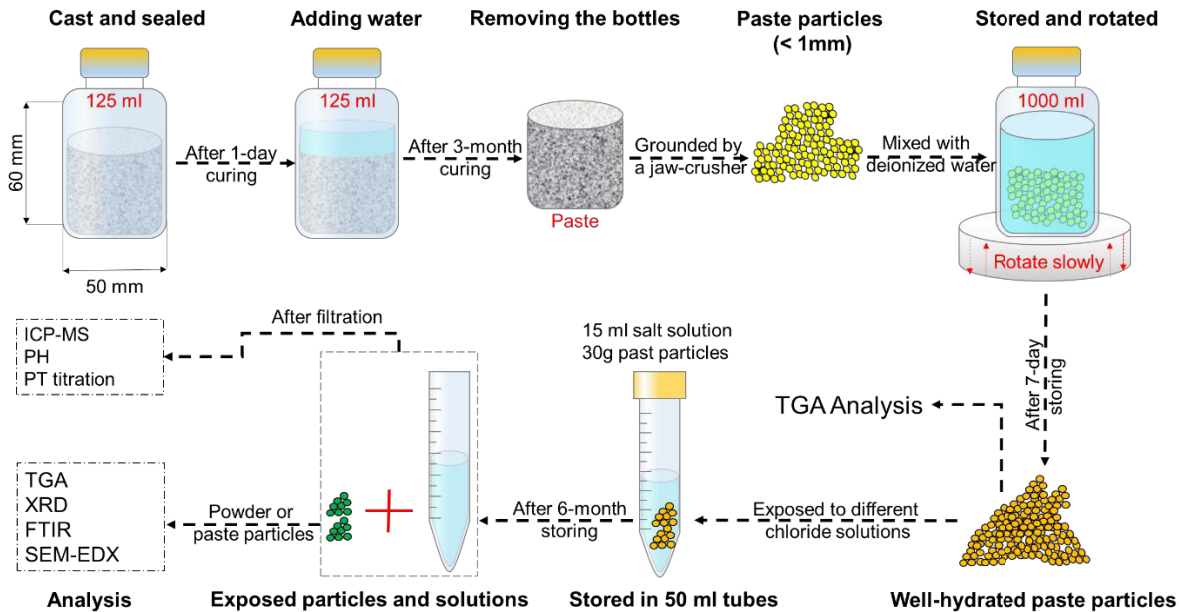


Figure 7.2. The flowchart for the preparation of samples studied.

7.2.3 Exposure conditions

After three months of curing, the hydrated cementitious pastes (HCP) were taken out from the bottles, broken in a jaw crusher, and then grinded into cementitious paste powder (CPP) with a particle size of no more than 1 mm (Figure 7.2). In order to obtain the well-hydrated cement pastes and eliminate the possible carbonation, CPP was stored in a 1L polypropylene bottle and then added with deionized water (30 wt.% DW of the CPP). The new well-hydrated cementitious paste powder (WCPP) with a resulting W/B ratio of 0.95 was shaken gently along the longitudinal axis for another seven days. This step for preparing the cementitious pastes is aimed at maximizing the degree of hydration of the cementitious pastes and minimizing unnecessary carbonation before exposure to different salt solutions. The steps to immerse the WCPP in different solutions are displayed as follows: 30.0 g of the

WCPP (W/B = 0.95) was firstly weighed and poured into a 50 mL plastic centrifuge tube, added with 15.0 ml of the different solutions. Then, the samples were sealed, kept in the tubes at 38 °C for 6 months, and constantly rotated. The 6-month exposed paste powder (EPP) and supernatants were separated and adopted to further analysis. As the concentration of salts may vary from location to location, different concentrations of NaCl and MgCl₂ were prepared. Every type of the samples was measured with three numbers of replicates: three reference samples for the type exposure to deionized water and seawater, respectively; three control samples for the type exposure to the 0.5, 1.0, and 2.0 mol/L NaCl (N1, N2, and N3) solutions; three control samples for the type exposure to the 0.25, 0.50 and 1.0 mol/L MgCl₂ (M1, M2, and M3) solutions; three control samples for the type exposure to 0.5 mol/L NaCl + 0.25 mol/L MgCl₂, 1.0 mol/L NaCl + 0.5 mol/L MgCl₂ and 2.0 mol/L NaCl + 1.0 mol/L MgCl₂ (NM1, NM2, and NM3) solutions. The types of test samples exposed to different solutions are listed in Table 7.3.

Table 7.3 Exposure conditions with deionized water, seawater, and different chloride solutions

Types	DW	SW	Salt concentrations (mol/L)								
			NaCl (N)			MgCl ₂ (M)			NaCl+MgCl ₂ (NM)		
			N1	N2	N3	M1	M2	M3	NM1	NM2	NM3
			0.5	1	2	0.25	0.5	1	0.5+0.25	1+0.5	2+1
X-DW	O	—	—	—	—	—	—	—	—	—	—
X-SW	—	O	—	—	—	—	—	—	—	—	—
X-N1	—	—	O	—	—	—	—	—	—	—	—
X-N2	—	—	—	O	—	—	—	—	—	—	—
X-N3	—	—	—	—	O	—	—	—	—	—	—
X-M1	—	—	—	—	—	O	—	—	—	—	—
X-M2	—	—	—	—	—	—	O	—	—	—	—
X-M3	—	—	—	—	—	—	—	O	—	—	—
X-NM1	—	—	—	—	—	—	—	—	O	—	—
X-NM2	—	—	—	—	—	—	—	—	—	O	—
X-NM3	—	—	—	—	—	—	—	—	—	—	O

Note: X= PC, PC-GGBFS, PC-GGBFS-NS1, and PC-GGBFS-NS2, stand for the different paste mixtures.

7.3 Test procedures

After 6-month exposure to different solutions, the EPP samples were firstly centrifuged (4000 rpm) to extract the supernatants much more easily. Then, 3 ml of supernatants were filtered with a 4 µm cellulose filter and pipetted into a 5 mL plastic tube for ICP-MS and PT measurements, respectively. The remaining supernatants were also filtered with a 4 µm cellulose filter and pipetted into a 15 mL plastic tube for pH measurements. The left EPP was submerged in an acetone solution for 48 hrs and dried in the vacuum oven at 40 °C for another 48 hrs prior to analysis.

7.3.1 pH measurements

All pH measurements were measured based on the Orion Star A3250 supplied by Thermo at 20 °C. The electrode was calibrated daily with buffer solutions of pH 7, 10, and 13. The pH value of the remaining supernatants in a 15 ml tube to cover the electrode thoroughly was measured by the Orion Star A3250. After each test, the electrode was cleaned with deionized water and dried with dust-free paper. Every sample was measured three times.

7.3.2 Chloride-binding ratio (CBR)

As mentioned above, the samples exposed to different solutions were finally centrifuged to separate the EPP and supernatants. Although the chloride cannot be entirely removed from the samples by the centrifuge, the concentration of chlorides in the supernatants is recongized as the concentration in the pore solution. Before the chloride concentration test, 1ml of supernatants in the 5 ml tube was firstly pipetted into a 10 ml tube with 9 ml deionized water and diluted to an approximate concentration for further analysis. The chloride concentration of the diluted solution was determined based on the Mohr method by using an auto titrator supplied by Metrohm, with a 20 ml burette and 0.01 mol/L $\text{AgNO}_3(\text{aq})$. 0.5 mL K_2CrO_4 solution (5.0 wt.%) was adopted as an indicator. When the brick red precipitation Ag_2CrO_4 emerged, the endpoint reached. The amounts of the beaker were titrated to determine the total molar contents of chloride, which was adopted to measure the chloride concentration of the exposure solution.

Before exposure to different salts solution, the free water of the WCPP samples was measured by thermogravimetric analysis. About 1.0 g of the WCPP samples were not tested at 40 °C in the TGA machine treated with a nitrogen environment for 24 hrs until the weight of the sample was kept unchanged. The determined weight loss (free water content) of different groups at 40 °C was 33.4 wt.% (PC), 28.5 wt.% (PC-GGBFS), and 24.4 wt.% (PC-GGBFS-NS1) and 23.5 wt.% (PC-GGBFS-NS2) of the original weight of the corresponding WCPP samples.

The chloride-binding capacity ratio was determined by the following calculations, mentioned in some

references (De Weerd et al. 2014; Machner et al. 2018). The original chloride concentration ($C_{Cl,og}$) is determined by the chloride concentration of the exposure solution ($C_{Cl,ex}$), shown as follows:

$$C_{Cl,og} = \frac{C_{Cl,og} \times V_{Cl,ex}}{V_{H_2O} + V_{Cl,ex}} \quad (7-1)$$

where $V_{Cl,ex}$ is 15.0 mL and V_{H_2O} is the volume of free water determined in 30.0 g of WCPP samples, which is about 10.01 mL for the PC ($30.0 \text{ g} \times 33.4 \text{ wt.\%} = 10.01 \text{ g}$), 8.55 mL for the PC-GGBFS, 7.32 mL for PC-GGBFS-NS1 and 7.05 mL for PC-GGBFS-NS2. The total chloride-binding content ($C_{Cl, tb}$) is determined by the tested equilibrium chloride concentration in the supernatants ($C_{Cl,ms}$), shown as follows:

$$C_{Cl,tb} = \frac{M_{Cl} \times (C_{Cl,og} - C_{Cl,ms}) \times (V_{H_2O} + V_{Cl,ex}) / 1000}{m_s / (1 + 0.95)} \quad (7-2)$$

The difference between $C_{Cl,og}$ and $C_{Cl,tb}$ was the content of the binding chloride, and the chloride-binding ratio (CBR) was determined by the following equation:

$$CBR = \frac{C_{Cl,og} - C_{Cl,tb}}{C_{Cl,og}} \times 100\% \quad (7-3)$$

7.3.3 Chemical leaching behaviour measurements

In order to explain what elements had been bound onto the cementitious composites from the exposure solution or what elements had been leached from the cementitious composites into the exposure solution, the chemical leaching behaviour was determined by ICP-MS (Plusquellec et al. 2017). Before the leaching behaviour test, 1mL of supernatants in the 5 mL tube was acidified by 1:4 HNO_3 (65.0 wt.%). After being diluted with deionized water (X400 or X8000), the diluted solution was analyzed by ICP-MS to determine the element concentration of Na, Mg, and Ca to explore the chloride-binding mechanism of the Portland cement-GGBFS-NS composites after exposure to different salt solutions.

7.3.4 Phase assemblage analysis

To explore the phase change of the Portland cement-GGBGS-NS composites caused by salt solutions,

the left EPP was firstly dried and then divided into two parts: one part was adopted for TGA and SEM-EDX test; another part was blended with 10% titanium oxide (TO) for FTIR test and XRD semiquantitative test. The powder samples were blended with 10% TO as the unique ingredients of the standard internal method for XRD analysis. The intensity of different hydrate products was also compared with TO in FTIR analysis. For the TGA test, a NETZSCH STA F3 Jupiter was adopted. About 30 mg of the sample was firstly held in an alumina crucible and tested at 40 °C in the TGA machine purged with N₂ for 30 min, then heated up to 1000 °C at a speed of 10 °C/min. The quantitative analysis of the Portlandite (CH) was conducted based on the TGA test results. For the XRD test, the Bruker D8 Discover diffractometer applying CuK α radiation of wavelength 1.54 Å was employed to examine the diffraction patterns in the range of 5° to 70° 2 θ with a 0.02° step. After obtaining the XRD pattern, the reference intensity ratio (RIR) analysis was adopted to carry out semiquantitative analysis on the contents of Friedel's salts (FSS) in the well-hydrated cementitious pastes. X'Pert HighScore Plus software was used to refine the XRD pattern by the Rietveld method so as to obtain the refined peak position, width, and intensity. Semiquantitative analysis of these phases was determined by the intensity of corresponding phases' peak heights and peak areas. The relative mass relations between CH and TO (or FSS and TO) can be determined by RIR (Geng et al. 2015; Paul et al. 2015). Since the quantity of CH was directly measured by TGA, the quantity of FSS was also recorded according to the relative mass relations among CH, FSS, and TO. It should be noted that the amount of FSS in the EPP samples was hugely higher than that of KSS. Thus, the content of FSS was recognized as the primary factor determining the chemically chloride-binding capacity, and the content of KSS was not recorded in this article. For the FTIR test, a Nicolet 6700 FTIR spectrometer was employed to examine the spectra ranging from 450 to 4000 cm⁻¹ wavenumber at a resolution of 8 cm⁻¹.

7.3.5 Microstructure characterization

Before the SEM test, the dried EPP was firstly dipped with a cotton swab and shaken evenly on the base with carbon conductive adhesive. Next, the loose powder on the surface of the carbon conductive

adhesive was sprayed away by a nitrogen gun. After being coated with platinum using Leica EM ACE600 Sputtering, the samples were examined by scanning electron microscopy with energy dispersive X-ray (SEM-EDX). Zeiss Supra 55VP SEM has Raith Elphy Plus E-beam Lithography System as a chemical composition analyzer at a speed-up voltage of 15 keV and a working distance of 10 mm for operating the EDX. The analysis procedure was set up to analyze the different elements, shown as follows: Na, Mg, Al, Si, Cl, Ca, O, and S. The chemical compositions were analyzed by Aztec version 2.0 software based on EDX results. For one thing, the different hydrated products were supposed to be distinguished by the morphology and confirmed by the spot EDX scan. For another, after finding the hydrated gel's structure through the morphology and spot EDX scan, approximately 20 spots EDX scans of the gels were conducted to distinguish the Ca/Si ratio change. The test point for the spot EDX scan was enclosed in the range of hydrated gels, and the mean value of Ca/Si ratio could also be obtained from the numerous spots.

7.3.6 Thermodynamics modeling

Thermodynamic modeling was conducted by GEM-Selektor 3 (GEM3) by Gibbs energy minimization, which can obtain the equilibrium phase assemblages in chemical systems from a given total bulk elemental composition (Kulik et al. 2022; Miron et al. 2022; You et al. 2022). The default databases were supplied by PSI-GEMS and extended with the CEMDATA14 database (Lothenbach & Zajac 2019; Miron et al. 2022; Nedyalkova et al. 2022; Yan et al. 2022). The phase change of the cementitious composites after exposure to different salt solutions was predicted based on the GEM-Selektor 3 (Lothenbach & Zajac 2019). The effects of the concentrations of NaCl and MgCl₂ solutions on phase change of the Portland cement-GGBFS-NS composites were modeled based on the constant amount of water as in this investigation (192.5 g water per 100 cementitious composites). The degrees of hydration of the raw materials were not considered in this study, while the phase change caused by the concentrations of different salt solutions was discussed in the following sections.

7.4 Results and discussions

7.4.1 pH values change

Figure 7.3 displays the pH of the supernatants. The pH of all groups in NaCl and seawater solutions was higher than that in deionized water, while the pH of all groups in MgCl_2 and NaCl+ MgCl_2 solutions was lower than that in deionized water. The pH was gradually increased with a higher concentration of NaCl solution but significantly decreased with a higher concentration of MgCl_2 and NaCl+ MgCl_2 solutions. The chloride in the NaCl exposure solutions might be reacted with CH with the generation of CaCl_2 and NaOH, where the NaOH would be dissolved and result in a higher pH of the exposure solution (De Weerd et al. 2019). More NaOH could be generated with the increasing concentrations of NaCl, leading to a higher pH. The magnesium in the MgCl_2 or NaCl+ MgCl_2 exposure solutions could react with hydroxyl ions existing in the solutions with the generation of $\text{Mg}(\text{OH})_2$ (Xie, Dang, et al. 2019), which could precipitate in the solution leading to a decreasing pH. More hydroxyl ions could be consumed with the increasing concentrations of $\text{Mg}(\text{OH})_2$, leading to a lower pH (Yang, Hou, et al. 2020). In addition to a more significant proportion of NaCl, there are also other salts, such as MgCl_2 , in seawater, which could make the pH in seawater be higher than in deionized water but lower in the NaCl exposure solutions. Besides, the PC-GGBFS mixture with GGBFS has a lower pH than PC but a higher pH than the Portland cement-GGBFS-NS group (PC-GGBFS-NS1 and PC-GGBFS-NS2) in all exposure solutions. As the content of NS increased, the pH of the PC-GGBFS-NS group also decreased. These could be related to the fact that the addition of GGBNS and NS could consume more CH due to the pozzolanic reaction (Lavergne et al. 2019; Rahla et al. 2019), which could reduce the CH content possibly reacted with the salt solutions, further decreasing the dissolved alkaline ions.

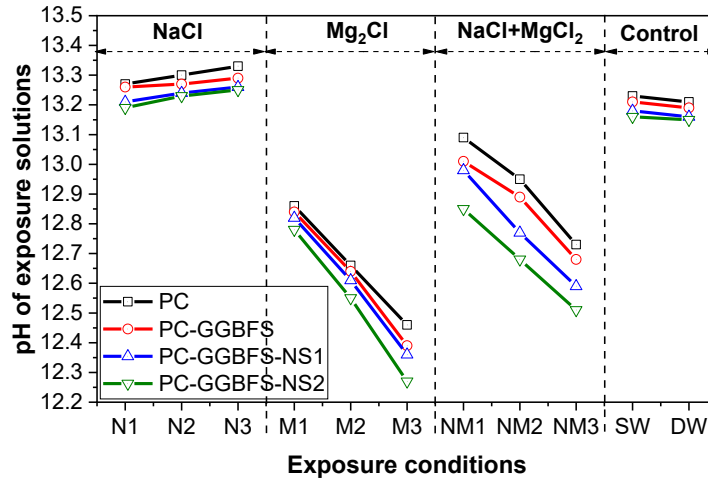


Figure 7.3. pH values of the supernatants after 6-month exposure to different solutions.

7.4.2 Chloride-binding capacity

Figure 7.4 displays the chloride-binding ratio of the well-hydrated cementitious pastes after 6-month exposure. It could be observed that the CBR of all groups in NaCl exposure solutions was lower than that in seawater, while the CBR of all groups in MgCl₂ and NaCl+MgCl₂ solutions was higher than in seawater. This could be related to the fact that the various types of ions in the salt solutions have different effects on the phase change of hydration products. As the concentration of salt solution increased, the CBR of all groups was slightly increased, indicating that the high chloride concentration might increase the chloride bounding by enhancing the reaction probability between hydration products and chloride (De Weerd et al. 2015). The magnesium concentrations had a higher impact on the CBR than the sodium concentrations, which indicated that the magnesium could make more changes for the hydration products. In addition, in any exposure solution, PC-GGBFS have a relatively lower CBR than PC-GGBFS-NS1, but a higher CBR than PC and PC-GGBFS-NS2, which illustrates that the addition of GGBFS can improve the CBR, while the effect of NS on the CBR depends on the amounts of dosage added. The addition of 1 wt.% NS could enhance the CBR of Portland cement-GGBFS-NS composites, while the addition of 2 wt.% NS had an adverse effect on the CBR of Portland cement-GGBFS-NS composites. In general, the influence of different concentrations of various salt solutions on the chloride-binding capacity of the Portland cement-GGBFS-NS mixtures may be related

to the following two aspects: chemically binding of chloride attributed to the generations of chloroaluminate might be different (Chen et al. 2021; Liu, Ma, et al. 2020); physically binding of chloride caused by the amount of hydration products gels could be varied (Florea & Brouwers 2012; Sui et al. 2019). Different content of NS would have different effects on the chemically and physically binding chlorides for Portland cement-GGBFS-NS composites.

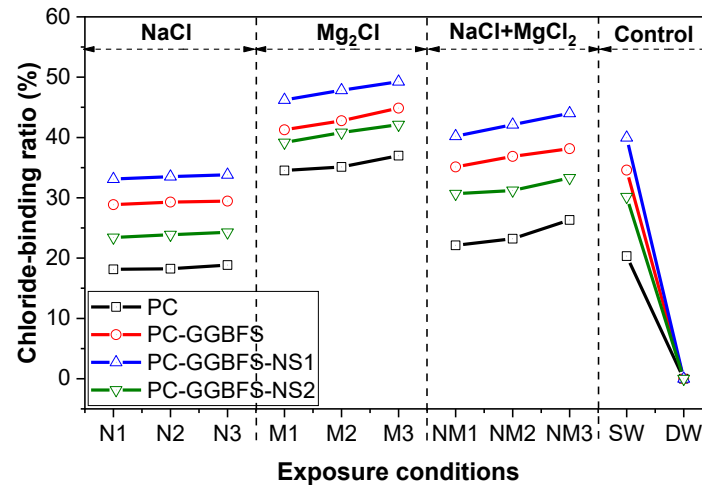


Figure 7.4. Chloride-binding ratio of well-hydrated cementitious pastes after 6-month exposure to different solutions

7.4.3 Chemical leaching behaviour

Figure 7.5 presents the maximum element concentrations (Na, Ca, and Mg) of the supernatants for the cementitious pastes after 6-month exposure. To determine the different maximum concentrations of the three elements, the exposure solutions were diluted with deionized water multiple times. After being diluted by 400 times, the maximum concentration of Ca in NaCl exposure solution is too low to be tested. Therefore, the maximum concentration of Ca of all mixtures in the NaCl exposure solutions is not displayed in this section. This indicated that the Ca leached from the cementitious paste in the NaCl exposure solutions is significantly lower than in the exposure solutions with MgCl₂. For the elements of Na, Ca, and Mg, the maximum concentrations of all groups in seawater were lower than

in NaCl, MgCl₂, and NaCl+MgCl₂ solutions. The maximum Na concentrations of all mixtures in NaCl solutions were higher than that in NaCl+MgCl₂ corresponding solutions, which could be increased with the amounts of salts content. This is primarily related to the following two reasons: under the same circumstances, the concentration of Na ions in the NaCl solution was greater than in MgCl₂ and NaCl+MgCl₂ solutions, and the concentration of Na ions was the smallest in seawater; NaCl could have reacted with the hydration products with generations of NaOH dissolved in the exposure solutions, and it has also been reported that the C-S-H gels had limited physically binding capacity of Na ions (Chang et al. 2019; Ma et al. 2018). In other words, the maximum Na concentrations are primarily related to the amounts of NaCl content. Besides, the maximum Ca and Mg concentrations of all groups in MgCl₂ solutions were higher than that in NaCl+MgCl₂ solutions and could be enhanced with the amounts of salt content. The change of maximum Mg concentrations was primarily attributed to the amounts of MgCl₂ content in the exposure solutions. However, the change of maximum Ca concentrations might be related to the reaction between hydration products and salts content (NaCl and MgCl₂) (Yang, Hou, et al. 2020). The higher the MgCl₂ content in salt solutions, the more Ca ions could be leached from the well-hydrated paste matrix.

In addition, it should also be noted that for the elements of Na and Ca, the addition of GGBFS and NS could decrease the maximum concentrations of these elements in the same salt exposure solutions. The maximum concentrations of Na and Ca in PC were lower than PC-GGBFS, PC-GGBFS-NS1, and PC-GGBFS-NS2. The maximum concentrations of these elements could also be decreased by the increasing amounts of NS content, demonstrating that the maximum element concentrations of Na and Ca in PC-GGBFS-NS2 were lower than PC-GGBFS-NS1. However, for the element of Mg, the addition of GGBFS and NS could enhance the maximum concentration in the same solutions, which could also be increased by the increasing amounts of NS content. The maximum element concentrations of Mg in PC-GGBFS-NS2 were higher than that of PC-GGBFS-NS1. The maximum concentration change of the three elements could be related to the enhancement of hydration reaction

caused by the addition of GGBFS and NS. The addition of GGBFS and increasing content NS added could increase the generations of hydrated gels and decrease the CH content in the cement matrix. The Na ions in the solution were supposed to be partially adsorbed on the hydrated gels (De Weerd et al. 2015). More generations of hydrate gels in the group with the addition of GGBFS and NS could enhance the adsorption of the free sodium ions, further reducing the content of Na in the exposure solutions. For the elements of Ca and Mg, on the one hand, there was less CH content in the groups with GGBFS and NS, the CH of which could be reacted with NaCl and $MgCl_2$, generating dissolvable calcium ions in the exposure solutions. This means that the less CH content, the less dissolved calcium ions. On the other hand, the Ca element in the hydrate gels could be replaced by the magnesium in the exposure solutions with the new generations of hydration products. The more generations of hydrated gels in the groups with GGBFS and NS, the less probability of Ca being replaced by the magnesium.

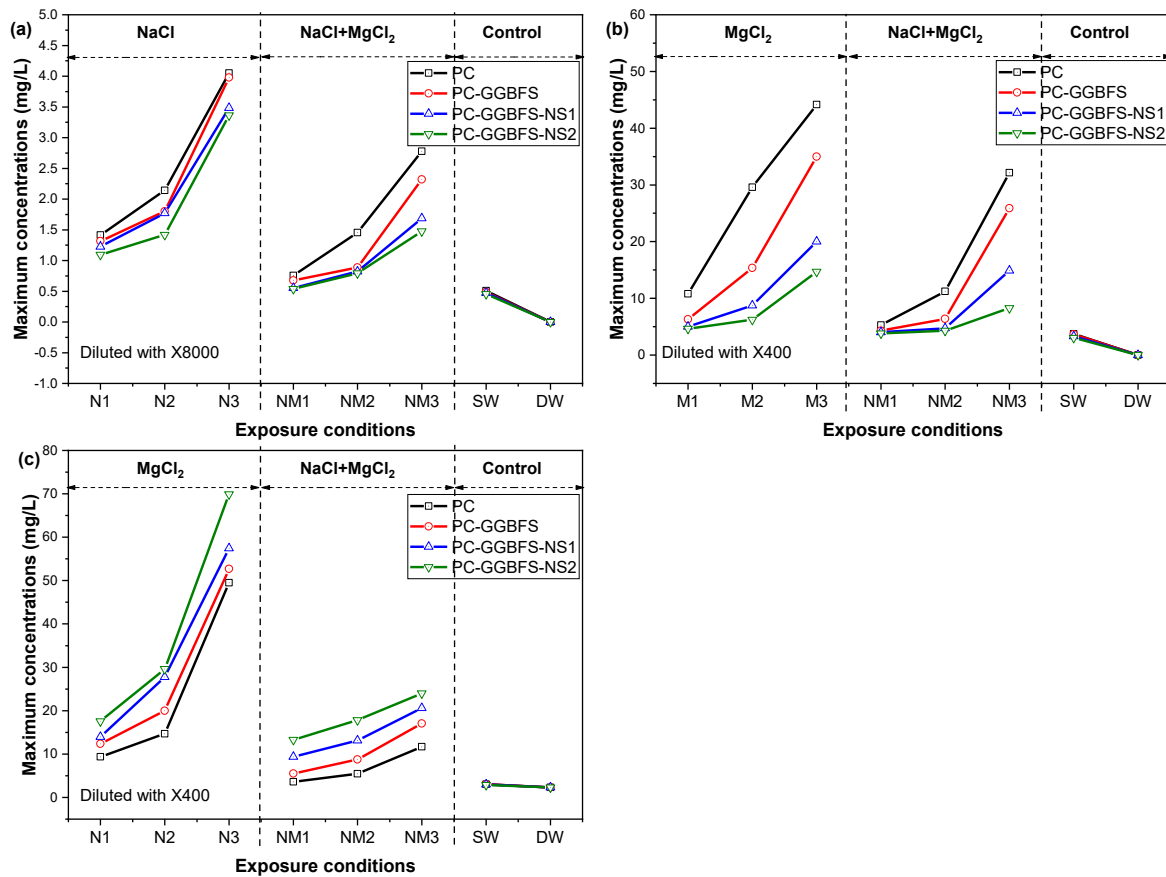


Figure 7.5. Maximum element concentrations of the supernatants for the well-hydrated cementitious pastes after 6-month exposure to the different solutions: (a) Na, (b) Ca, and (c) Mg.

7.4.4. Thermogravimetric analysis (TGA)

After 6-month exposure in different salt solutions, the phase of all groups was analyzed by TGA, and the differential thermogravimetric (DTG) curves are displayed in Figure 7.6. As could be seen from DTG curves, for all groups exposure to deionized water, the dehydration of C-S-H (around 100-120 °C), ettringite (AFt, around 100-120 °C), monosulfate (AFm, around 160-200 °C), CH (around 450-550 °C), and calcite (around 600-800 °C) could be detected in the DTG curves (Qu et al. 2021). After being exposed to seawater and the solutions with NaCl, Friedel's salts were observed around 150-200 and 280-400 °C. Meanwhile, after exposure to the solutions with MgCl₂, except for the existence of FSS detected around 150-200 °C and 280-400 °C (De Weerd et al. 2019), the dehydrations of brucite and magnesite could also be detected around 350-450 °C (Qiao et al. 2018) and 540 °C (Unluer & Al-Tabbaa 2015), respectively. It could also be noted from Figure 7.5 that the changes in the AFt and AFm phases of all groups caused were relatively similar for the different amounts of salt content, while there was a higher amount of dehydrations of FSS with the increasing amount of NaCl and MgCl₂ content. It was reported that both NaCl and MgCl₂ could react with the hydration products to form the FSS (De Weerd et al. 2014; Zhu et al. 2012), which could also be enhanced by the increasing amounts of salts content. In addition, except for the generations of FSS, different products could be generated. For example, brucite might be produced due to the fact that the magnesium cations in the MgCl₂ or NaCl+MgCl₂ exposure solutions could be reacted with hydroxyl ions existing in the exposure solutions (Yang, Hou, et al. 2020). However, the chloride anion in all salt exposure solutions was primarily attributed to the change of AFt and AFm phases, which could also bring about a transformation from AFt/AFm to FSS (Bertola et al. 2020). In addition, the addition of GGBFS and NS has a relatively apparent impact on the quantities of hydration products. For all groups exposed to deionized water, the hydration products (e.g., hydrated gels, AFt/AFm, calcite, and CH) might differ from each group due to the different content of GGBFS and NS.

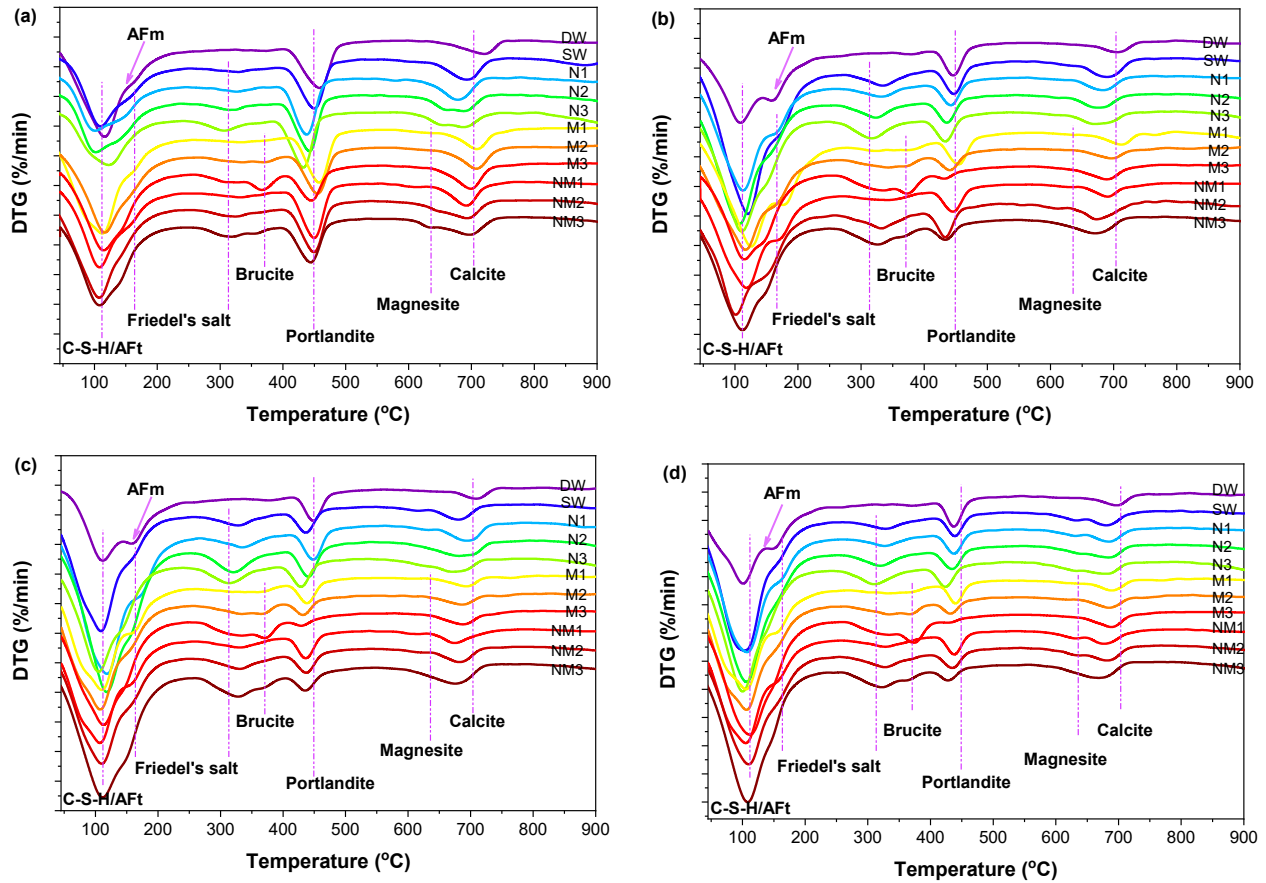


Figure 7.6. DTG curves of the well-hydrated cementitious pastes after 6-month exposure to the different solutions. (a)PC;(b)PC-GGBFS; (3)PC-GGBFS-NS1 and (4)PC-GGBFS-NS2.

In order to clearly determine the effect of GGBFS and NS on the phase assemble after exposure to different salt solutions, the quantitative analysis results of CH were evaluated and shown in Figure 7.7. Compared to the cementitious composites exposed to deionized water, a lower CH content was detected in the cementitious composites exposed to the salts solutions. The CH content could also be decreased with the increasing concentrations of the salts solutions. The CH content of all groups exposed to seawater was lower than that of exposure to the N1 salts solution (0.5 mol/L NaCl) but higher than those exposed to other salts solutions. This confirmed that the salts content in seawater or other exposure solutions could dissolve the CH in the matrix to generate the new hydration products. The CH content of all groups after exposure to different solutions was also primarily related to the concentration of the salts. The higher concentration of the salts, the lower content of the CH. Besides,

compared to PC, the addition of GGBFS could enable the PC-GGBFS to have a lower content of CH both in deionized water and other salt solutions. The addition of NS could also make the PC-GGBFS-NS2 have a lower content of CH content than PC-GGBFS-NS1 and PC-GGBFS. This could be related to the pozzolanic effect of GGBFS and the high activity of NS increasing the consumption of CH to form much more hydrate gels, which reduced the amounts of CH that could be reacted with the salts in the exposure solutions. The addition of GGBFS and NS could affect the chloride-binding capacity by changing the quantities of hydration products.

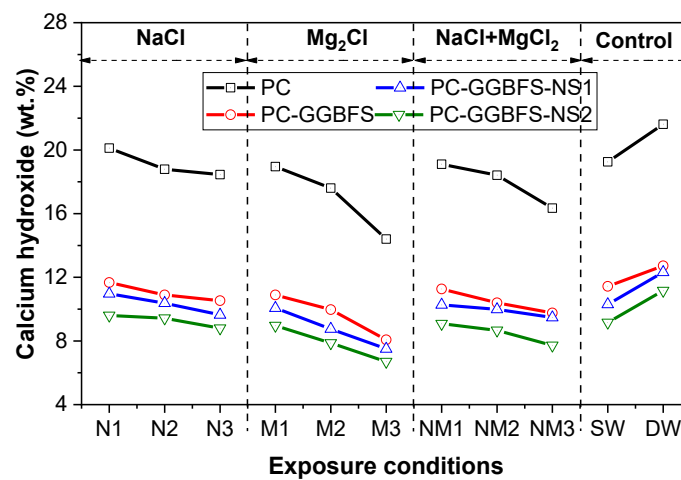


Figure 7.7. Calcium hydroxide contents (wt.%) of the well-hydrated cementitious pastes after 6-month exposure to the different solutions.

7.4.5. X-ray diffraction analysis (XRD)

Figure 7.8 displays the XRD results of all mixtures after 6-month exposure to the different solutions. According to the weight loss of CH obtained from TGA, the FSS content was calculated by the RIR method and illustrated in Figure 7.9. The primary phases, including AFt ($2\theta = 9.1^\circ, 15.8^\circ$ and 18.9° , PDF #00-041-1451), CH ($2\theta = 18.0^\circ, 28.6^\circ$ and 34.0° , PDF #00-41-1451), AFm ($2\theta = 11.6^\circ$, PDF #00-41-0063), TO ($2\theta = 25.2^\circ$, for quantitative analysis), quartz ($2\theta = 29.4^\circ$, PDF #00-046-1045), C-S-H (around $2\theta = 31.0^\circ$, PDF #00-33-0306), and calcite ($2\theta = 23.1^\circ$, PDF #00-005-0586), could be examined in all groups after exposure to deionized water. After exposure to seawater and other

chloride solutions, there was an insignificant change in some phases, including quartz and calcite, indicating that the content of salt has little effect on these phases. The peak of C-S-H of all groups at $11.6^{\circ} 2\theta$ was kept consistently after exposure to salt solutions only with NaCl, while it could be slightly decreased with the concentrations of salt solutions with MgCl_2 . This could be primarily attributed to the magnesium ions in the solutions possibly leaching the Ca from the C-S-H, further decreasing the peak of C-S-H (Lothenbach et al. 2015; Song et al. 2021). In addition, it should be noted that the phase of AFm at $11.6^{\circ} 2\theta$ could not be detected in all groups after exposure to salt solutions, which could be related to the fact that AFm could be transferred to FSS with the existence of chloride ions (Florea & Brouwers 2012). The phase of AFt was also slightly decreased with the increasing concentrations of the same salt solutions, which indicates that there is a high probability that the AFt could also be slightly transferred into FSS due to the chloride ions (Jones et al. 2003). Meanwhile, compared to the groups exposed to deionized water, the phase of FFS ($2\theta = 11.2^{\circ}$, PDF #00–031–0245) could be examined in the mixtures exposure to seawater and chloride solutions, and the phase of brucite ($2\theta = 38.0^{\circ}$, PDF #00–031–0245) could be detected in the groups exposed the solutions with MgCl_2 . The generations of FSS could be primarily attributed to the chloride that existed in the salt solutions, and the formation of brucite could be related to the magnesium ions. The increasing concentrations of chloride solution lead to a higher FSS content in all mixes, especially, there was a higher FSS content in the groups exposed to the solutions with MgCl_2 than those exposed to the solution of NaCl or NaCl+ MgCl_2 . The magnesium ions might play an essential role in changing the chloride-binding capacity of Portland cement-GGBFS-NS composites.

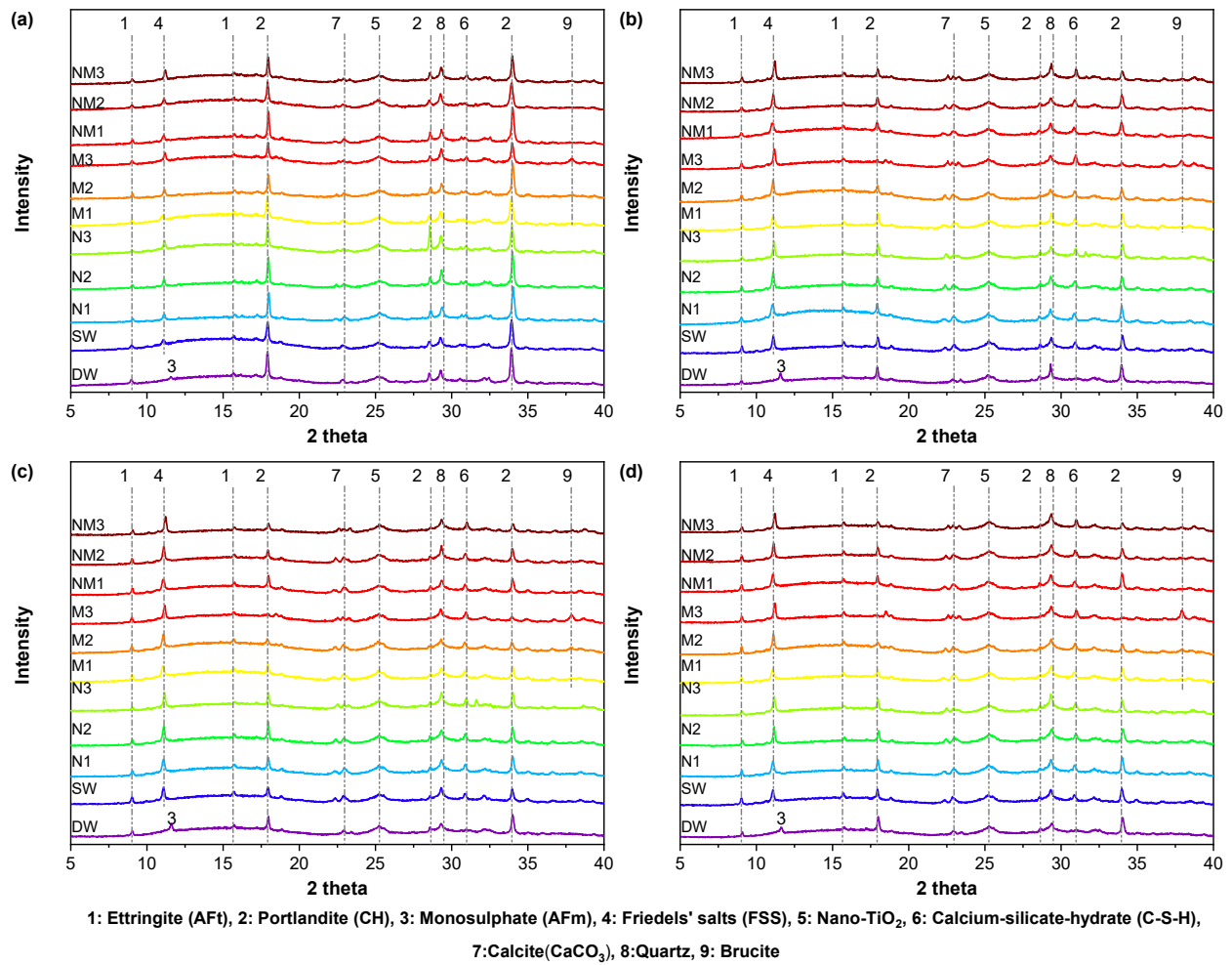


Figure 7.8. XRD patterns of the well-hydrated cementitious pastes after exposure to the different chloride solutions for 6 months. (a) PC;(b) PC-GGBFS; (3) PC-GGBFS-NS1 and (4) PC-GGBFS-NS2.

Additionally, it could be seen from Figure 7.8 that compared to PC exposed to deionized water, the PC-GGBFS, PC-GGBFS-NS1, and PC-GGBFS-NS2 had a higher intensity of C-S-H and AFm peaks but a lower intensity of CH peaks. After exposure to the same salts solutions, the PC was found to have a lower intensity of FSS and C-S-H peaks but a higher intensity of CH peaks than other groups. This could be related to the higher content of highly-active alumina in GGBFS and highly-active silica in both GGBFS and NS. With highly-active silica content, the mixtures with GGBFS and NS (especially PC-GGBFS-NS2) produced more C-S-H gels while consuming more CH. On the other hand, the highly-active alumina in the mixtures with GGBFS (PC-GGBFS, PC-GGBFS-NS1 and PC-GGBFS-

NS2) enables to form much more chloride-alumina hydrates, including AFm and FSS phases. It could be seen from Figure 7.9 that in the same exposure salt solutions, the highest FSS content was found in PC-GGBFS, followed by PC-GGBFS-NS1, PC-GGBFS-NS2, and PC, which indicated that the addition of GGBFS played an essential role in generating much more FSS hydrates. The addition of NS would decrease the FSS content in all groups. However, it should be noted that as mentioned in section 3.1.2, the PC-GGBFS-NS1 with 30 wt.% GGBFS and 1.0 wt.% NS had the highest chloride-binding ratio among all groups. Although the PC-GGBFS-NS1 had a lower FSS content than PC-GGBFS, the total chloride bindings in PC-GGBFS-NS1 were higher than PC-GGBFS.

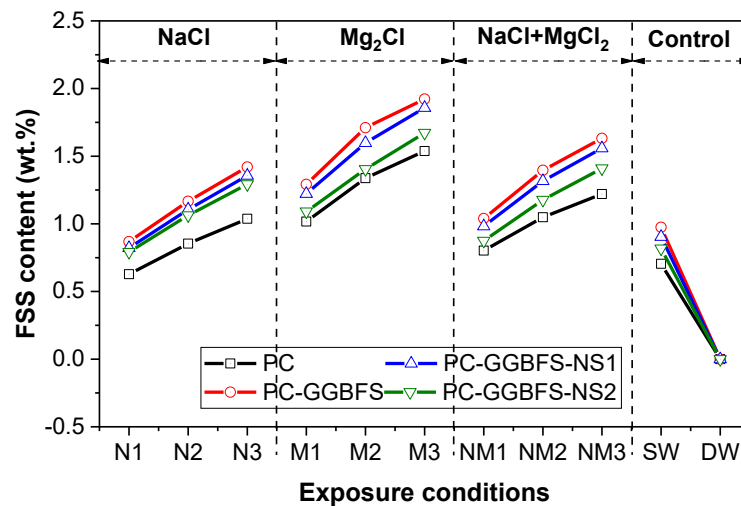


Figure 7.9. FSS contents in the well-hydrated cementitious pastes after 6-month exposure to the different solutions.

7.4.6 Fourier transform infrared spectroscopy (FTIR)

Figure 7.10 displays the FTIR patterns ($500\text{--}4000\text{ cm}^{-1}$) of all groups after 6-month exposure to the different solutions. For all groups exposure to deionized water, some modes primarily attributed to the stretching alteration of some specific molecular structures could be examined from the FTIR patterns and shown as follows: The mode at approximately 3640 cm^{-1} possibly came from asymmetric stretching alteration of O-H in CH (Mendoza et al. 2013); The existence of Ti-O mode could be detected at about 1645 cm^{-1} , which was attributed to titanium oxide (Yang et al. 2015); The mode at

around 1415 cm^{-1} was mainly assigned to the stretching alteration of C-O in calcite (dos Santos et al. 2021), which indicated that the all groups had absorbed CO_2 from the air before exposure to different solutions; The mode at approximately 1110 cm^{-1} was primarily related to the stretching alteration of S-O in SO_4^{2-} , which could be identified as the peak of AFm/AFt (Tang et al. 2015); The mode at approximately 970 cm^{-1} was primarily contributed to the stretching alteration of Si-O in C-S-H gels (Kapeluszna et al. 2017). In addition, the changes in the bands from around 3200 to 3600 cm^{-1} were probably attributed to the stretching vibration of O-H in structural water of hydration products and the bending vibration of O-H in the interlayer water of hydration products (Kupwade-Patil et al. 2018). After exposure different to salt solutions, except for these modes mentioned above, the mode at around 730 cm^{-1} could be detected in all groups and likely related to the stretching alteration of Al-O in $[\text{Al}(\text{OH})_6]^{3-}$, which could be reconginzed as the peak of FSS (Geng et al. 2015). The intensity of FSS mode was not significant as other hydration products and was sightly affected by the increasing concentrations of salt solutions, which could be related to the following reasons: other hydration products like C-S-H had a relatively higher content than FSS; the chloride ions were not absorbed in the range of $500\sim 4000\text{ cm}^{-1}$, further decreasing the relative intensity of FSS and making it difficult to distinguish the differences.

As shown in Fig. 9, the change in those modes mentioned above caused by the NaCl solutions was similar to the seawater but not much significant as the MgCl_2 and NaCl+ MgCl_2 solutions, which was primarily attributed to the magnesium ions. In addition, there was no noticeable change in the C-S-H and calcite modes with the increasing concentrations of seawater, NaCl, MgCl_2 , and NaCl+ MgCl_2 solutions, which suggested that calcite and the structure of Si-O in C-S-H were relatively stable in the salt solutions. The intensity of CH mode of all groups approximately became very weak after exposure to a higher concentration of the salt solution, especially in the M3 and NM3 exposure conditions. This could be related to the consumption of CH by hydration reactions with the different salts, which could be significantly affected by the MgCl_2 solutions (Yang, Hou, et al. 2020). With regard to AFt/AFm,

the intensity of modes at around 1110 cm^{-1} could be decreased with the concentrations of NaCl, MgCl_2 , and NaCl+ MgCl_2 solutions, which could be related to the generation of FSS from AFm (Florea & Brouwers 2012). The changes in the bands from around 3200 to 3600 cm^{-1} were also associated with the changes of CH, AFt/AFm, and FSS. In particular, the intensity of O-H at around 3380 cm^{-1} could be significantly decreased in MgCl_2 and NaCl+ MgCl_2 solutions, which indicated that the MgCl_2 could cause a higher effect on the phase changes than NaCl. When comparing the mixtures with different additions of GGBFS and NS, after exposure to deionized water, the intensity of C-S-H gels was found to be relatively higher in the mixtures with GGBFS/NS than the correspondings without GGBFS, while the intensity of CH was found to be adverse. This could be attributed to the pozzolanic reaction of GGBFS and highly-active NS content consuming much more CH hydrates and producing much more hydrated gels. After exposure to different salts solutions, there was a relatively noticeable change in the bands from around 3200 to 3600 cm^{-1} . Significantly, after exposure to M3 solution (1 mol/L MgCl_2), the intensity of this band was decreased considerably, which could be related to the decreasing CH and the reduction of AFt/AFm in the groups with GGBFS and NS.

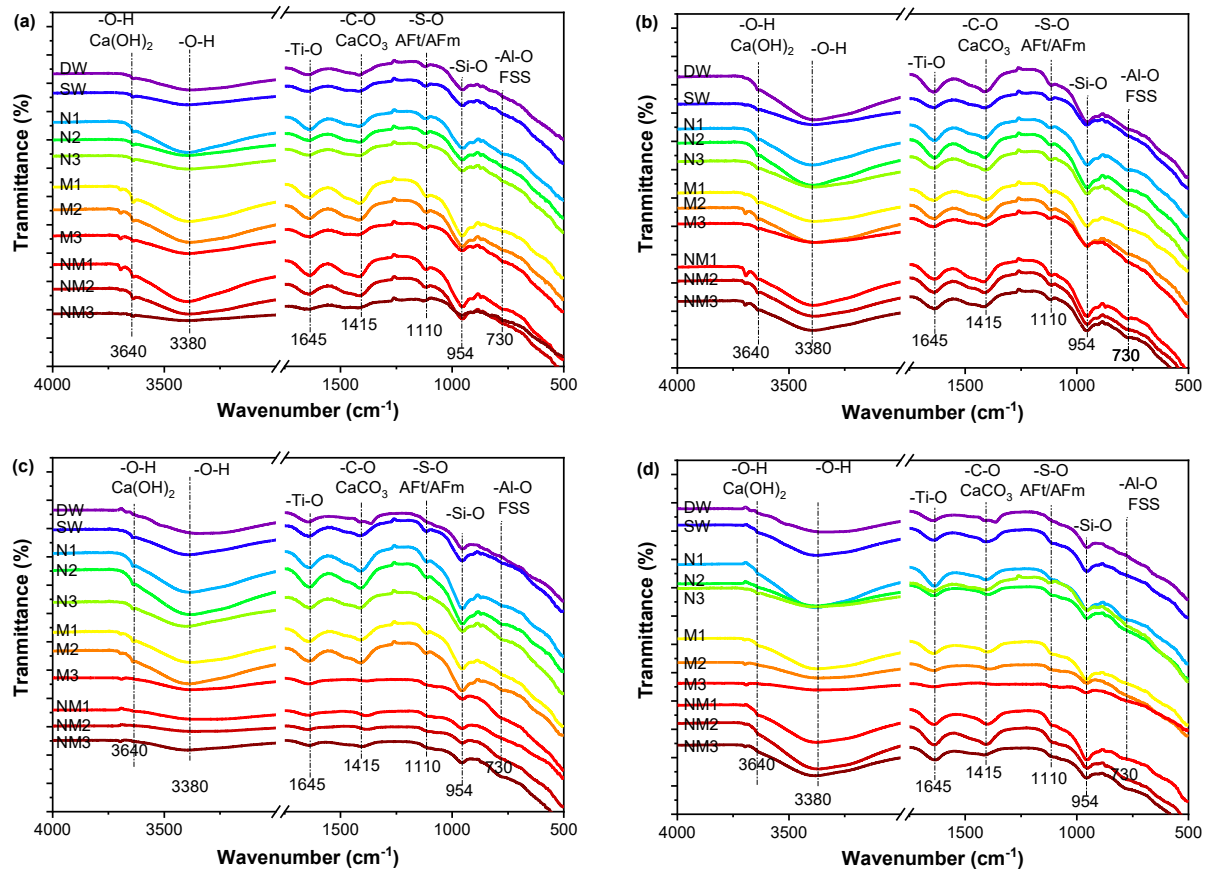


Figure 7.10. FTIR patterns of well-hydrated cementitious pastes after 6-month exposure to the different solutions. (a)PC;(b)PC-GGBFS; (3)PC-GGBFS-NS1 and (4)PC-GGBFS-NS2.

7.4.7 SEM-EDS test results

In order to further compare the phase changes caused by the different salt solutions, the morphologies of PC-GGBFS-NS1 exposure to M3 solutions are displayed in Figure 7.11. The morphologies of different hydration products were further confirmed by the EDX results. It could be seen from Figures. 7.11(a) and (b) that the hexagonal plate-shaped and cubic substances with high ratios of Ca and O recongnized as CH and calcite could be detected (Georget et al. 2021; Harilal et al. 2019). In Figures. 11(c) and (d), the needle-shaped ettringite (AFt) with relatively high proportions of Al and S and the honeycomb-like calcium aluminum silicate hydrate (C-A-S-H) with high ratios of Al could also be detected (Unluer & Al-Tabbaa 2015; Uthaman et al. 2018). In contrast to C-S-H gels, the C-A-S-H gels obtain a higher proportion of Al. The C-S-H and C-A-S-H gels could both be detected in PC-

GGBFS-NS1. Due to the high chloride concentrations in M3 solutions, the platyform plate-like Friedel's salts with a high ratio of Al and Cl could be found. Due to the high concentrations of Mg, the stacked hexagonal particles with high proportions of Mg and O could be examined and recognized as $\text{Mg}(\text{OH})_2$. In addition, the brucite-like layers hydrotalcite (Machner et al. 2018) and tubular-like magnetite with high proportions of Al and Mg could also be detected in PC-GGBFS-NS1 after being exposed to M3 solutions for up to 6 months. In particular, there was a higher proportion of Cl in hydrotalcite, indicating that the chloride-binding capacity could be related to the generations of hydrotalcite, which was also confirmed by some researchers (Machner et al. 2018). In addition, it should be noted that it was difficult to detect the hydrotalcite in the TGA and XRD results. This could be related to its poor ability to be crystallized or amorphous (Machner et al. 2018). The magnesium concentrations were also associated with the generation of hydrotalcite, further affecting the chloride-binding capacity of Portland cement-GGBFS-NS composites.

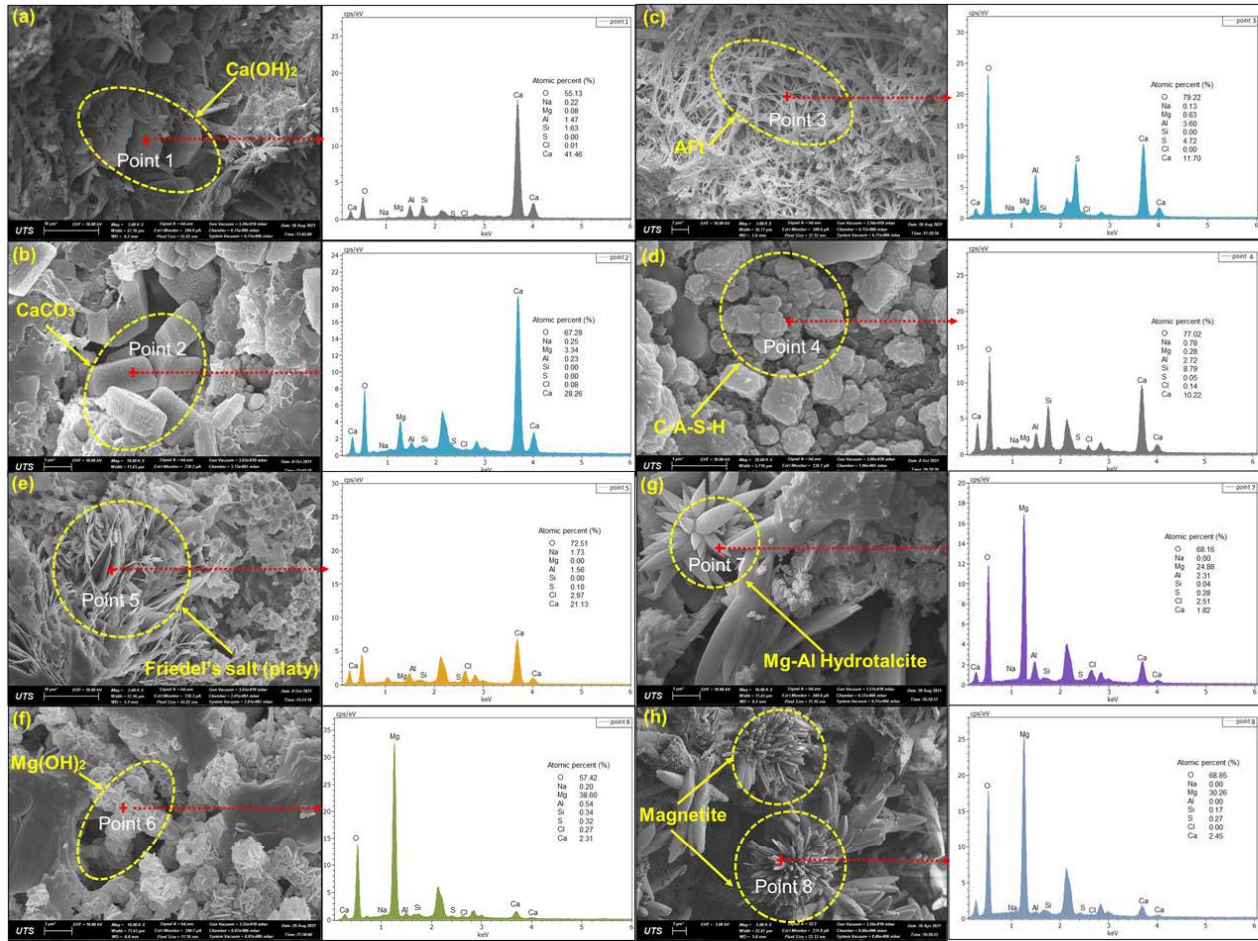


Figure 7.11. SEM morphologies with EDX of PC-GGBFS-NS1 after 6-month exposure to 1.0 mol/L $MgCl_2$ solution

7.4.8 Ca/Si ratio of hydrated gels

As discussed in section 3.3.1, the C-S-H/C-A-S-H gels could be classified by the morphologies and EDX results. After finding the structure of the C-S-H/C-A-S-H gels, about 20 spot EDX scans of the gels were conducted to distinguish the Ca/Si ratios change. Figure 7.12 displays the Ca/Si atomic ratios of hydrated gels (C-S-H/C-A-S-H) in all groups after being exposed to different salt solutions, and the mean value is also labeled. It could be observed from Figure 7.12 that for all mixtures exposed to DW solution, the mean Ca/Si ratio could be decreased by the addition of GGBFS and NS, which might be related to the high activity of SiO_2 . The different salt solutions could also significantly affect the

Ca/Si ratio of all groups. The mean Ca/Si ratio of all groups exposed to DW solution was found to be higher than that exposed to other solutions. The effect of NaCl solution on the change of Ca/Si ratio was not significant as the MgCl₂ solution. In particular, a higher content of magnesium ions in salt solutions, a lower Ca/Si ratio of all groups could be recorded. The mean Ca/Si ratio of all groups exposed to the DS solution was the highest, followed by N3, SW, NM3, and M3 solutions. De Weerd, et al.,(2014) have also reported that the Ca in gels could be slightly leached into the salt solutions due to the existence of magnesium, which accounts for a lower mean Ca/Si ratio found in the groups exposed to the DW solution than that exposed to other salt solutions. The Ca could also be leached out from the gels by the magnesium ions, even leading to M-S-H generations, which further decreases the mean Ca/Si ratio of C-S-H/C-A-S-H gels. The magnesium ions in the layers of C-S-H/C-A-S-H gels were also related to the enhancement of chloride-binding capacity (Yang, Hou, et al. 2020).

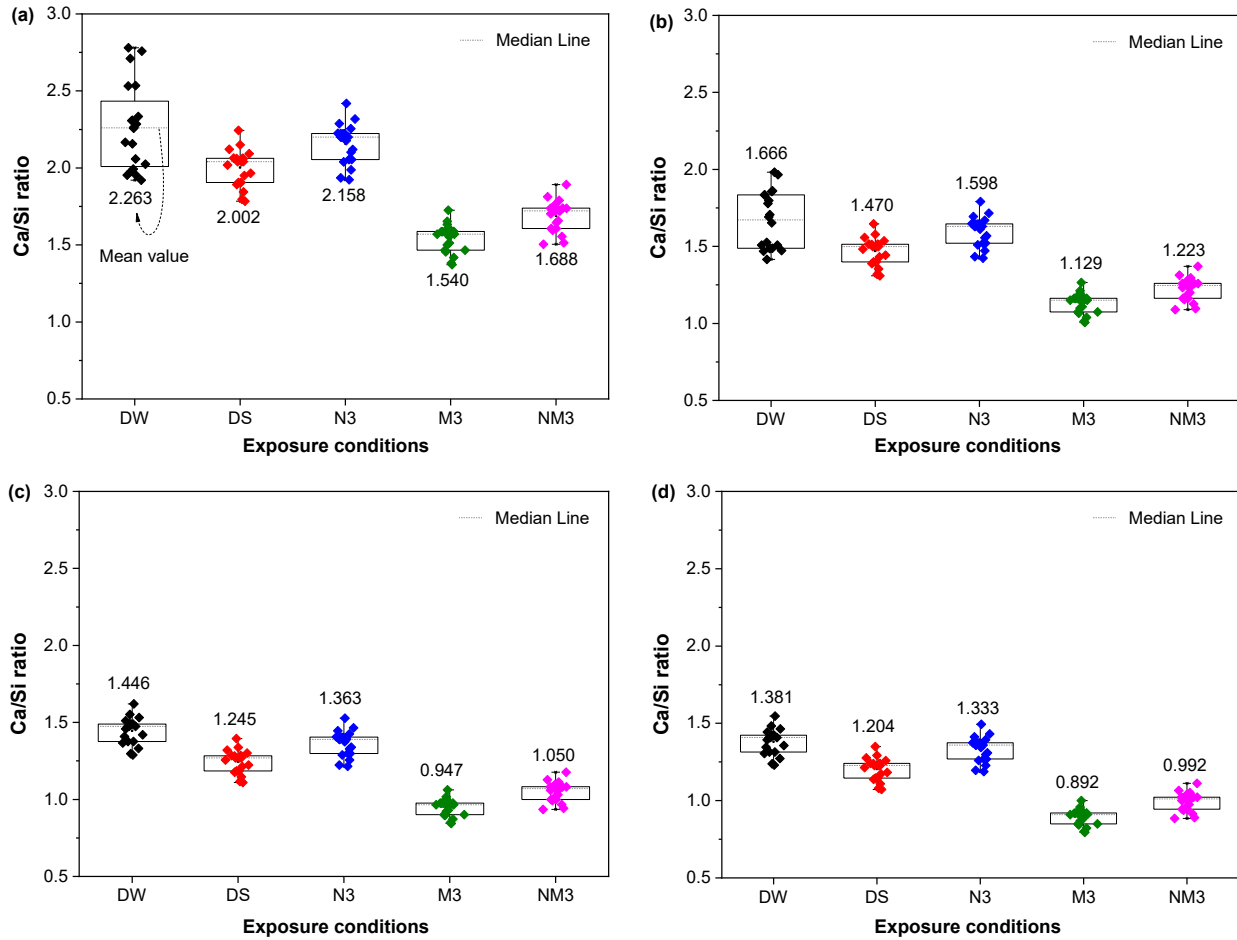


Figure 7.12. The Ca/Si atomic ratios of C–S–H/C–A–S–H gels. (a) PC; (b) PC-GGBFS; (3) PC-GGBFS-NS1 and (4) PC-GGBFS-NS2.

7.4.9 Amount of hydrated gels

Generally, a lower Ca/Si ratio of C–S–H was reported to lead to a weaker physically chloride-binding capacity resulting from chloride adsorption, and the physical chloride-binding capacity was also related to the amounts of gels (Thomas et al. 2012). The amount of C–S–H gels are discussed based on the TGA results, as shown in Figures 7.6 and 7.7. As investigated in the literature, the DTG peak around 100 °C is primarily related to the dehydration of C–S–H gels and Aft, and the overlapping peak is difficult to be distinguished. For all groups exposed to deionized water, the change of CH is primarily due to the addition of GGBFS and NS. Thus, the change of CH of all groups exposed to deionized water is adopted to analyze the amount change of hydrated gels (Liu, Ma, et al. 2020). As shown in

Figure 7.7, the addition of GGBFS could consume the CH and lead to a higher generation of C-S-H gels due to the pozzolanic reaction. The highly-active aluminum in GGBFS might also increase the formation of C-A-S-H gels. The increasing generations of hydrated gels could enhance the physical chloride-binding capacity. Meanwhile, the growing addition of NS could also consume CH and generate much more C-S-H gels, further improving the physical chloride-binding capacity of the Portland cement-GGBFS-NS composites. In addition, although the lower Ca/Si ratio of C-S-H is supposed to weaken the physically chloride-binding capacity (Dousti et al. 2011; Zibara et al. 2008), the higher amounts of C-S-H/C-A-S-H gels due to the addition of GGBFS and NS are expected to compensate for the weakness.

7.5 Thermodynamic modeling and mechanism discussions

The thermodynamic modeling is employed to predict the final phase assemblage for Portland cement-GGBFS-NS-cement system exposure to different salt solutions for up to 6 months. Thermodynamic modeling results of all groups are displayed in Figure 7.13. Before exposure to salt solutions, the group with GGBFS and/or NS was predicted to have a higher content of C-S-H gels but a lower content of CH than that without GGBFS, which is primarily related to the pozzolanic reaction. Meanwhile, compared to the GNP1, a higher proportion of hydrotalcite and AFm could also be found in other Portland cement-GGBFS-NS composites due to a higher content of Al in GGBFS. After exposure to NaCl solution, Friedel's salts in all groups were predicted to be obviously increased with the increasing concentrations of NaCl, while CH and AFt/AFm could be decreased with the increasing concentrations of NaCl. Other phases, including hydrotalcite and calcite, were kept unchanged, which indicated that the NaCl salt environment had little effect on those phases. In addition, compared to the group without GGBFS, there are much more Friedel's salts examined in the group with GGBFS, which is mainly attributed to the content of Al.

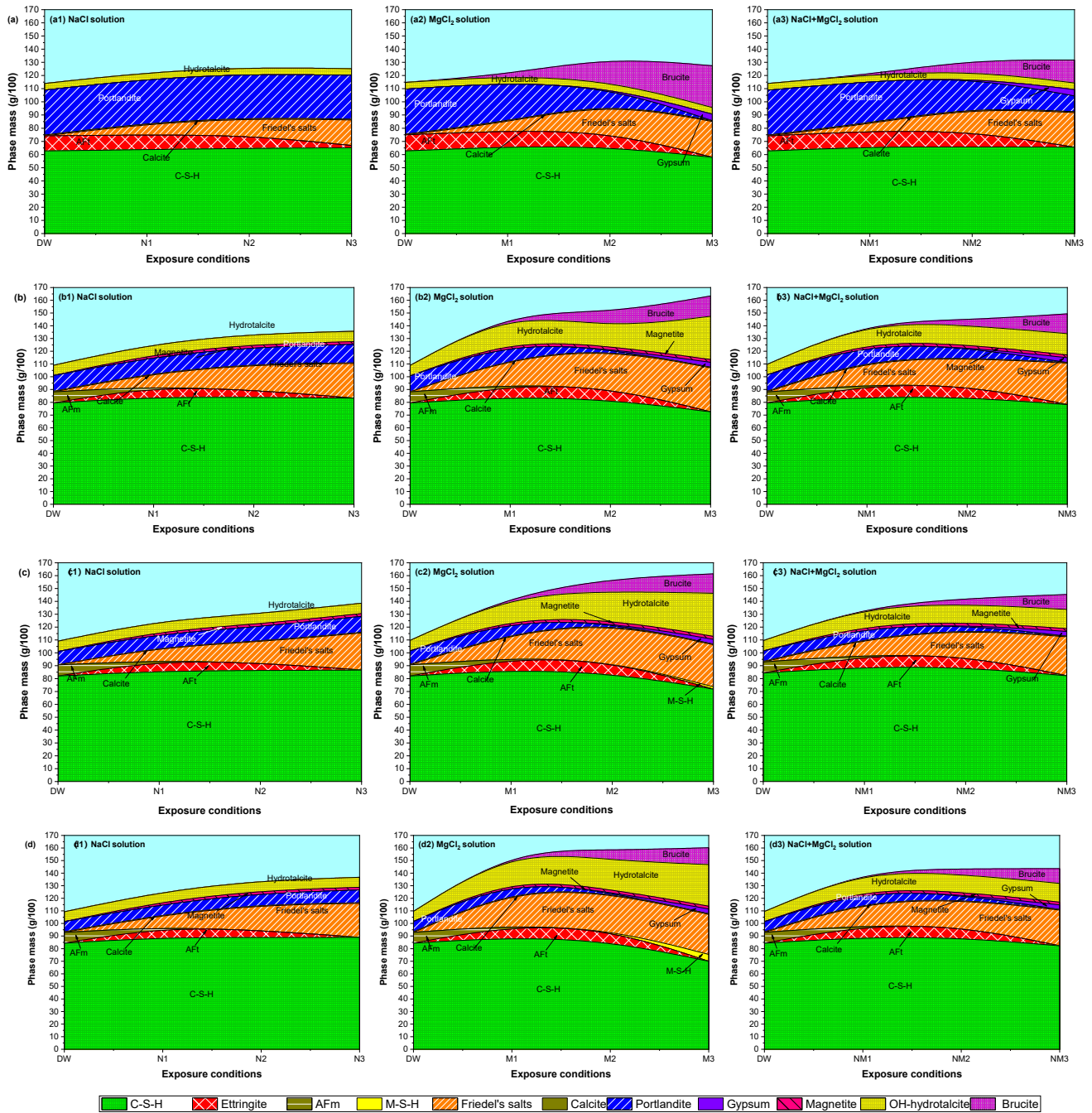
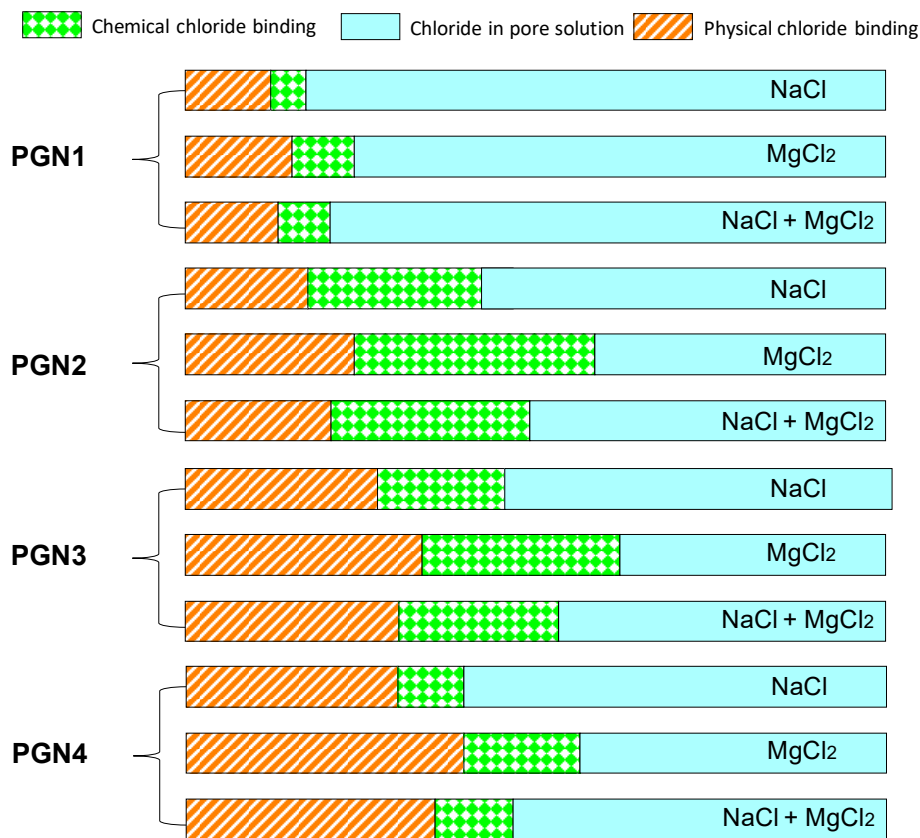


Figure 7.13. Phase assemblages for well-hydrated Portland cement-GGBFS-NS composites exposed to different chloride solutions. (a) PC; (b) PC-GGBFS; (3) PC-GGBFS-NS1, and (4) PC-GGBFS-NS2

After exposure to the salts solutions with MgCl₂, Friedel's salts in all groups were also predicted to be increased with the increasing concentrations of MgCl₂, while CH and AFt/AFm could be decreased with the increasing concentrations of MgCl₂. Additionally, the magnetite, brucite, and gypsum in all

groups were also predicted to be increased with the rising concentrations of MgCl_2 solution. In particular, the increasing concentrations of MgCl_2 solution could also increase the generations of hydrotalcite in the group with GGBFS, while there are no apparent changes of hydrotalcite in PC. It should also be noted that the Al in GGBFS increases the potential possibility to form much more hydrotalcite, further decreasing the generation of brucite. Thus, there is a higher content of brucite in PC than in other mixtures. M-S-H gels are also predicted in the PC-GGBFS-NS1 and PC-GGBFS-NS2 when exposed to the M3 solution. However, there were no detected M-S-H gels in XRD, TGA, and SEM-EDX results, which indicates that the hydration of all groups after 6-month exposure could not reach the final equilibrium. Generally, the thermodynamic model could display relatively accurately in predicting most of the phase assemblage.



Distribution of chloride in the composite mixtures (%)

Figure 7.14. Schematic diagram of the chloride-binding in Portland cement-GGBFS-NS composites after exposure to various salts solutions.

Based on the experimental results and thermodynamic modeling, the mechanism for the chloride-binding capacity of Portland cement-GGBFS-NS composites, considering the effect of GGBFS, NS, and types of salt, could be revealed according to the chemical and physical chloride binding. The schematic diagram of chloride binding in Portland cement-GGBFS-NS composites after exposure to different salts solutions is displayed in Figure 7.14. The chemical chloride binding is primarily due to the formation of FSS, the relative content of which is calculated based on the XRD semiquantitative analysis. The relative content of chloride in bulk solution is calculated based on the PT results, where the relative content of physical chloride binding is calculated based on the chemical chloride binding and the chloride in bulk solution. As shown in Figure 7.14, PC-GGBFS has the highest chemical bound chloride in all salt solutions, followed by PC-GGBFS-NS1, PC-GGBFS-NS2, and PC. PC-GGBFS-NS2 has the most elevated physical bound chloride in any salt solution, followed by PC-GGBFS-NS1, PC-GGBFS, and PC. This indicates that even though the addition of NS could accelerate the hydration of GGBFS to release the aluminum phase into the liquid phase, C-S-H gel formed can noticeably consume the aluminum due to the generation of C-A-S-H gel, further enhancing the physically chloride-binding capacity of the group with GGBFS and NS. Due to much more formations of C-A-S-H gel, there is little aluminum phase available for the formation of FSS when exposed to the salt solutions, which weakens the chemically chloride-binding capacity of the group with GGBFS and NS. This could account for the group with 30 % GGBFS and 1.0% NS (PC-GGBFS-NS1) having the highest value of CBR, as shown in Figure 7.4. The different cations (Na and Mg) have a significant effect on the chemical and physical chloride binding of all groups. The chemical and physical chloride bindings of all groups exposed to the salt solutions with MgCl_2 are higher than those exposed to NaCl solution. The magnesium could increase the potential generations of FSS and increase the chloride binding in the interlayers of the C-S-H/C-A-S-H gels. In particular, the formations of hydrotalcite could also be increased due to the magnesium ions (Huang et al. 2019). Due to magnesium ions in seawater, the CBR of all groups could be higher in seawater than in the NaCl solutions.

7.6 Summary

The chloride-binding capacity of Portland cement-GGBFS-NS composites exposed to seawater and different concentrations of NaCl and MgCl₂ solutions has been investigated. According to the experimental results of PT, ICP-MS, TGA, XRD, FTIR, SEM-EDX analysis, and thermodynamic modeling, the main conclusions could be drawn as follow:

- (1) The GGBFS replacement for cement significantly improved the chemical and physical chloride-binding capacity of cementitious composites and decreased the pH of exposure solutions. Due to the pozzolanic reaction consuming CH, large amounts of C-S-H/C-A-S-H gels are generated, further increasing the physical chloride binding. The higher aluminum content in GGBFS increased the formation of chloroaluminate (Friedel's salts), which enhanced the chemical chloride binding.
- (2) The addition of NS decreased the pH of exposure solutions, and the addition of 1.0 wt% NS further enhanced the total chloride-binding capacity of GGBFS-based cementitious composites. However, when the content of NS is higher than 1.0 wt.%, the total chloride-binding capacity (especially, the chemical chloride-binding capacity) of GGBFS-based cementitious composites was decreased. The addition of NS increased physical chloride-binding capacity due to the formation of more C-S-H/C-A-S-H gels, thus leaving less aluminum phase available for the formation of Friedel's salts.
- (3) Compared to exposure to salts solutions with sodium ions, more chlorides of all cementitious composites were found to be bound when exposed to salts solutions with magnesium ions. The magnesium ions increased the amount of physically bounded chloride in the gels' diffuse layer due to the decreasing pH of the MgCl₂ solutions. Except for Friedel's salts' formation, the hydrotalcite with high element proportions of Cl confirmed by EDX results is expected to be generated, further increasing the chloride-binding capacity.
- (4) The cementitious composite with 30 % GGBFS and 1.0% NS having the highest value of CBR

provide a prospective way to enhance the long-term chloride-binding capacity. Therefore, the utilization of GGBFS and NS in chloride binding is supposed to guide the improvement of marine constructions.

- (5) Generally, based on the analysis of the experimental results in this chapter, the cementitious composite with 30 % GGBFS and 1.0% NS could be considered to be a promising method of increasing the chloride-binding capacity of cementitious composites, further avoiding the potential risk of reinforcement corrosion for reinforced concrete in the marine environment.

CHAPTER 8: CONCLUSIONS AND RECOMMENDATIONS

8.1 Brief Summary

This thesis brings improvement to the existing understanding of the performance of low-carbon cementitious composites under aggressive environmental environments. The performance of geopolymer, fully made by industrial by-products, under mechanical loads and environmental conditions (fire attack and sulfuric acid attack) was evaluated. Meanwhile, the performance of cementitious composites, partially made by industrial by-products, under fire and/or salt attack was tested. The findings can be utilized in the case of the structural design of concrete using low-carbon cementitious composites as the binder under aggressive environmental conditions.

8.2 Conclusion remarks

In chapter 3, these results suggested that the addition of 20 wt.% GGBFS was recongized as an optimal amount for the fly ash-based geopolymer to obtain exceptional high-temperature resistance after load-induced damage. Before being exposed to elevated temperature, the addition of GGBFS increased the compressive strength of fly ash-based geopolymer but made it more sensitive to the load-induced damage, resulting in an increased strength loss. After exposure to combined load-induced damage and elevated-temperature exposure, the fly ash-based geopolymer presented lower residual strength than that only suffered from load-induced damage or elevated-temperature exposure.

In chapter 4, the results showed that cyclic preloading probably caused microcracks or damages in mortar matrices, thus increasing the probability of sulfuric acid deterioration. Although fly ash/GGBFS-based geopolymer mortar exhibited a higher strength reduction by preloading than ordinary Portland cement mortar, after 18-month exposure to sulfuric acid attacks, fly ash/GGBFS-based geopolymer mortar with preloading still performed better than the corresponding ordinary Portland cement mortar. Overall, the fly ash/GGBFS-based geopolymer mortar exhibited less severe performance deterioration even after 18-month exposure to sulfuric acid attacks.

In chapter 5, the results demonstrated that the chloride, sulphate and magnesium ions in seawater and/or sea sand might lead to the phase changes of cement mortars. The chloride and sulphate ions in seawater and sea sand reacted with tricalcium aluminate and the hydrated product of Portlandite to form much more Friedel's/Kuzel's salts and ettringite. Moreover, the magnesium ions primarily in seawater generated magnesium hydroxide and magnesium silicate hydrate formation by replacing the Ca^{2+} and decalcification of calcium silicate hydrate. The substitute of seawater also can make the Si/Ca ratios of the C-S-H (Cl) be increased from the range of 0.2–0.4 to 0.6–1.2, respectively.

In chapter 6, the test results illustrated The highest flexural strength of cementitious composites mortar with seawater and undesalted sea sand was achieved with 1 wt.% glass fiber and 30% GGBFS. The addition of GGBFS could densify the microstructure for cementitious composites mortar with seawater and undesalted sea sand, and decrease the loss of flexural and compressive strength. The calcium aluminosilicate hydrate gels with a higher ratio of Si/Ca and Al/Ca in cementitious composites with GGBFS were considerably more stable at a temperature of 700 °C, compared to the calcium silicate hydrate gels with a lower ratio of Si/Ca and Al/Ca in cementitious composites without GGBFS. Therefore, it indicates that the fire resistivity of cementitious composites mortar with seawater and undesalted sea sand could significantly be improved by adding glass fibers and GGBFS.

In chapter 7, the test results displayed that for all cementitious composites, more chlorides were found to be bounded in samples exposed to salt solutions with sodium ions than those with magnesium ions. Proper addition of GGBFS and nano-silica could enhance the chloride-binding capacity of cementitious composites. The growing amount of hydrated gels in the cementitious composites with GGBFS also improved the physical chloride-binding capacity. The addition of NS increased physical chloride-binding capacity due to the formation of more C-S-H/C-A-S-H gels, while excessive addition of NS left less aluminum phase available for the formation of chloroaluminate, further decreasing the chemical chloride-binding capacity. Magnesium ions in solutions increased the amount of chloride in the diffuse layer of C-S-H and hydrotalcite.

8.3 Recommendations for future works

Although this thesis is expected to promote the current understanding of the performance of low-carbon cementitious composites under aggressive environmental environments to produce more reliable data and ensure the reliability and sustainability of LCC-based construction. However, there are still need more actions to be conducted. In light of the experience gained in this test program, the following recommendations can be made for future works:

- Geopolymer, entirely made by industrial by-products (GGBFS and FA), is usually cured at a high temperature, which can cause massive energy consumption. Therefore, it is essential to carry out more experimental programs to investigate the properties of geopolymer under normal temperature curing.
- The properties of geopolymers will vary due to the applications of different raw materials and activators. Consequently, in order to ensure the large-scale production and application of geopolymer, the related standards about the mix designs of geopolymer should be published based on a more significant number of reliable data.
- The performance of geopolymer under mechanical load and environmental conditions (including fire and sulfuric attack) appears relatively good in this work, but a more detailed investigation of test method validation and standardization is required.
- More detailed investigations about the life cycle and cost evaluations are still expected to be the objective of future research to have a deep understanding of the economic effects of SCMs in substituting OPC. For a fixed quantity of cement manufactured, comparative studies regarding the amount of carbon dioxide reduced and life cycle assessment after the inclusion of a different kind of SCMs are another area's scope.
- The durability of cementitious composite concrete has gained increasing attention as the result of the need for long service life and minimal maintenance costs of the structure. Growing demand for green and sustainable building materials has made low-carbon cementitious

composites alternative to the cement and concrete industries. More research should be conducted to enhance the durability of cementitious composites and their structures under aggressive environmental conditions, which are supposed to significantly improve the service life and decrease the maintenance costs related to concrete structures.

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