

**DEVELOPMENT OF ALKALI-ACTIVATED LOW-
CARBON/NON-CARBONATE BINDERS
UTILIZING INDIGENOUS
MATERIALS**

BY

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A Dissertation Presented to the
DEANSHIP OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

DOCTOR OF PHILOSOPHY

In

CIVIL AND ENVIRONMENTAL ENGINEERING

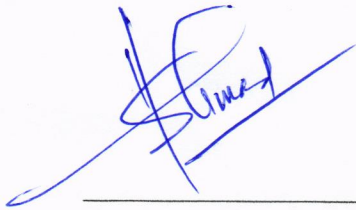
May 2023

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

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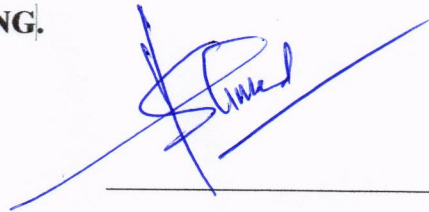
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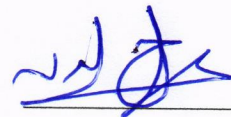
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2022

[This thesis is dedicated to my parents. You have a super hat-trick of doctors in the family now. I could not have been the other kind of “doctor” since a lot of people would be dead if I were.

To my future spouse, this thesis is the reason I lost two of the three brains cells I was born with so whenever we fight in the future, you know why I will be acting as if I have only one brain cell. |

ACKNOWLEDGMENTS

First of all, I would like to thank Allah (i.e., God) for giving the resilience and patience necessary to complete this thesis. For without Him and His blessings, nothing is possible in Life.

Second, I would like to give my sincerest gratitude to my advisors; Professor Shamsad Ahmed and Doctor Mohammed Al-Osta, and my thesis committee members; professors Mohammed Maslehuddin and Tawfik Saleh, and Doctor Salah Al-Dulaijan, for their guidance throughout the PhD program and their valuable input during meetings.

Third, I would like to thank my friends; Hussien Al-Sakka, Mohammed Makkawi, Mohammed Al-Shayea, and Khalid Al-Shigarea, for their counsel and financial support during my PhD journey. I would also like to thank my friends Marwan Abdul Qader and Omar Kamal who have spent countless hours with me in the laboratory during casting and testing.

Fourth, I would like to thank the Kingdom of Saudi Arabia for opening its gates to me as a resident represented by His Majesty King Salman and His Royal Highness Crown Prince Mohammed Bin Salman. I would like also to thank the King Fahd University of Petroleum and Minerals family represented by His Excellency the Director Mohammed Al-Saggaf for allowing me, and others like me, the opportunity of completing my higher studies and providing me with the support, materials, and equipment necessary for the completion of my PhD research.

Finally, I would like to thank my Parents Nabil and Fadheela Al-Duais and brothers Khalid, Mahir, Majed, Abdul Ghani, Mohammed, and Ali for being my port inside the storm of life and for their endless love and support.

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ABSTRACT

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Thesis Title : DEVELOPMENT OF NON-CARBONATE BINDERS UTILIZING
INDIGENOUS MATERIALS

Major Field : Civil and Environmental Engineering

Date of Degree : December 2022

The production of cement is responsible for the consumption of a third of the world's energy output as well as being one of the major sources of carbon dioxide emissions globally. In addition, traditional binders have been reported to be susceptible to degradation upon exposure to harsh environments. The degradation usually manifests in the form of corrosion of the reinforcement due to the binders being more pervious to the diffusion of chloride and carbon dioxide or in the form of the deterioration of the binder matrix itself due to acid attack, sulphate attacks and leeching of the alkaline substances. The need for alternative binders that do not depend on the calcination of calcium carbonate (i.e. low-carbon/non-carbonate binders) and can achieve better durability characteristics has never been more crucial in a world that is heading towards irreversible environmental damage. The development of low-carbon/non-carbonate binders is also necessitated by the need for meeting the forthcoming environmental requirements. This study aimed to develop low-carbon/non-carbonate binders. Special emphasis was placed on developing non-carbonate binders utilizing local materials, particularly natural minerals and industrial waste materials. The raw materials were first procured and characterized in term of their physical, chemical, and microstructural properties. Based on the results gathered during the first step, it was decided to develop non-carbonate binders in the form of alkali-activated binders

(AABs) utilizing limestone powder (LSP), natural pozzolana (NP), red mud (RM), and silicomanganese fume (SMF), in addition to small quantities of ordinary Portland cement (OPC) as precursor materials. The mélange of the raw precursor was activated by a mixture of sodium hydroxide (NH) and sodium silicate (NS) solutions. Initial trials were carried out to optimize the proportioning of the precursor materials, the activation parameters, and curing regimes. Then, six binders that were deemed to possess optimum properties were developed further into concretes and their physical, mechanical, drying shrinkage, acid and sulphate attack resistance, chloride transport, and chloride-induced reinforcement corrosion characteristics were evaluated and compared to properties of traditional OPC concrete. The performance exhibited by the alkali-activated concretes (AACs) was superior to that of the traditional OPC concrete while decreasing the OPC content up to 80%.

ملخص الرسالة

الاسم الكامل: إبراهيم نبيل علي الدعيس

عنوان الرسالة: تطوير المواد الخرسانية غير الكربونية باستعمال المواد المتوفرة محليا

التخصص: الهندسة المدنية والبيئية

تاريخ الدرجة العلمية: ديسمبر 2022

يعتبر إنتاج الأسمنت مسؤولاً عن استهلاك ثلث إنتاج الطاقة في العالم فضلاً عن كونه أحد المصادر الرئيسية لانبعاثات ثاني أكسيد الكربون على مستوى العالم. بالإضافة إلى ذلك ، تم الإبلاغ في الأوساط العلمية عن المواد الخرسانية التقليدية كونها عرضة للتدهور عند التعرض لبيئات قاسية. يتجلى هذا التدهور عادة على شكل صدأ في التعزيزات الحديدية بسبب كون المواد الخرسانية أكثر إنفاذاً لانتشار الكلوريد وثاني أكسيد الكربون أو قد يتجلى التدهور على شكل تداعي مصفوفة الخرسانة نفسها بسبب الهجوم الحمضي أو هجوم أملاح الكبريتات أو استخلاص المواد القلوية من مصفوفة الخرسانة. إن الحاجة إلى مواد خرسانية بديلة لا تعتمد على تكليس كربونات الكالسيوم (أي مواد خرسانية غير كربونية) والتي بإمكانها أن تحقق خصائص متانة وديمومة أفضل من المواد الخرسانية التقليدية أصبحت أكثر أهمية في عالم يتجه نحو ضرر بيئي لا رجعة فيه. إن تطوير مواد خرسانية غير كربونية أمر ضروري أيضاً بسبب الحاجة إلى تلبية المتطلبات البيئية القادمة.

هدفت هذه الدراسة إلى تطوير مواد خرسانية غير كربونية. تم التركيز بشكل خاص على استخدام المواد المحلية ، وخاصة المعادن الطبيعية ومواد النفايات الصناعية. تم استجلاب المواد الخام أولاً وتصنيفها من حيث خصائصها الفيزيائية والكيميائية والبنوية الدقيقة. بناءً على نتائج اختبارات التصنيف التي تم جمعها خلال الخطوة الأولى ، تقرر تطوير مواد خرسانية غير كربونية على شكل مواد خرسانية منشطة قلوية (AABs) باستخدام مسحوق الحجر الجيري (LSP) والبوزولانا الطبيعية (NP) والطين الأحمر (RM) و أبخرة منغنيز السليكون (SMF) ، بالإضافة إلى كميات صغيرة من الأسمنت البورتلاندي العادي (OPC) كمادة أولية. تم تنشيط مزيج المادة الأولية الخام بمزيج من محلول هيدروكسيد الصوديوم (NH) وسليكات الصوديوم (NS). تم إجراء تجارب أولية لتحسين تناسب المواد الأولية، وخصائص التنشيط ، وأنظمة المعالجة. بعد ذلك ، تم اختيار ستة خلطات كانت تمتلك الخواص المثلى وتطويرها إلى خرسانة ، وتم تقييم خصائصها الفيزيائية والميكانيكية وانكماش التجفيف ومقاومتها للهجوم الحمضي وهجوم أملاح الكبريتات ونقل الكلوريد وخصائص تآكل التعزيزات الحديدية ومقارنتها بخصائص الخرسانة التقليدية المكونة من الأسمنت البورتلاندي العادي (OPC). كان الأداء الذي أظهرته الخرسانة المنشطة القلوية (AACs) متفوقاً على أداء خرسانة (OPC) التقليدية مع تقليل محتوى الأسمنت حتى 80٪.

CHAPTER 1. INTRODUCTION

Cement is one of the most used, if not the most used, construction materials in the world. In 2017, cement production was estimated to be 4.1 billion tons worldwide, with more than half of it coming from industrial countries in Asia like China and India [1]. With the forecast increase in the world's population and its expected need for housing, the production of cement is anticipated to rise significantly. What makes cement popular as a construction material is several reasons that include but are not limited to: a) the abundance of the raw materials, mainly limestone and clay, required for cement production, which have been stated to be available in very large quantities by the United States Geological Survey [2], [3], b) the wide applications of cement and concrete which do not require highly trained workmanship compared to other construction materials, such as structural steel or wood, and c) the relatively robust performance of concrete.

However, cement has numerous drawbacks that require action by the scientific and engineering community. First, concrete is relatively weak when present in extreme environments. Researchers have reported failures in concrete structures as early as 12 years after service [4]. Chemical leaching of concrete in high chloride environments and corrosion of reinforcing steel has been well documented and studied in the literature [5]–[12]. Furthermore, concrete's low durability in acidic environments and weak against sulphate attack represent more drawbacks that push towards the search for durable construction material.

Another disadvantage of cement is its environmental impact which has been the focus of numerous studies around the globe. Cement is produced through the calcination and sintering of limestone and clay, in addition to other minor oxides, such as iron and aluminum, in rotary kilns. This production is responsible for a considerable amount of greenhouse gas emissions, especially carbon dioxide, that is released mainly formed due to the heating of limestone. It is reported that about 1 ton of CO₂ is produced during the production of a similar quantity of cement. The cement industry emits 5 to 7% of the total man-caused CO₂, representing more than 1.5 billion metric tons per year [13]. In addition, the production process is responsible for emitting large amounts of dust that is highly alkaline and represents a hazard to human, animal, and plant health. Furthermore, the mining and manufacturing of cement deplete more than a third of the global power each year [14], [15]. Another aspect of cement and concrete environmental damage is creating the “heat island” phenomenon, which is defined as the localized warming of urban areas due to concrete radiation of absorbed heat [16]. This phenomenon makes urban areas much warmer. The difference can be as high as 12 °C at night compared to their surroundings leading to more energy consumption in cooling and making the environment more hostile towards plant and animal habitation. In an already warming world heading towards irreversible environmental catastrophe, the search for a cleaner, more durable, and more environment-friendly substitute has never been more crucial. Consequently, cement and concrete technologists have been experimenting with several materials with the aim of developing non-carbonate binders that are more environment-friendly and durable. Further, it is advisable to experiment with industrial byproducts. The development of binders utilizing waste materials will also solve the associated environmental and disposal issues.

CHAPTER 2. OBJECTIVES

The general objective of the proposed study was to develop non-carbonate binders utilizing indigenous industrial waste materials. The specific objectives were the following:

- 1- Conduct an exhaustive literature review on low-carbon/non-carbonate binders, the implementation of natural minerals and industrial waste materials, and the availability of such materials in the Kingdom.
- 2- Procure and characterize the available indigenous natural minerals and industrial waste materials.
- 3- Develop non-carbonate binders utilizing indigenous mineral and industrial byproducts and optimize their compositions.
- 4- Study the mechanisms of hydration and morphology of the developed non-carbonate binders.
- 5- Evaluate the physical, mechanical, drying shrinkage, durability, and reinforcement corrosion characteristics of the developed non-carbonate binders.
- 6- Assess the technical benefits of the developed binder in comparison with the conventional OPC binders.
- 7- Recommend avenues of application of the developed binders.

CHAPTER 3. LITERATURE REVIEW

3.1. Categorization of Non-Carbonate Binders

3.1.1. Alkali Activated Binders and Geopolymers

Alkali activated binders (AABs) are defined as natural or manufactured mineral oxides that contain alumina and silica, which are activated in alkaline environments to produce strong phases that are stable. On the other hand, geopolymers are binders that hydrate from alumina and silicate monomers to form long- and zeolite-like polymeric chains. Although the terms are used interchangeably in some of the earlier literature, there are differences between them. The first is that geopolymers can be activated by alkaline solutions to form zeolite-like structures or acidic ones [17]. The main-activated geopolymer discussed in the literature is silico-aluminate phosphate activated by phosphoric acid [18]. The second difference is that AABs are named after the process they go through to form their hydrates, while geopolymers are named based on the final hydrates and whether they are zeolitic or not.

The first work with alkali-activated binders goes back to Purdon [19], who, in 1940, first activated Ground Granulated Blast Furnace Slag (GGBFS) with sodium hydroxide. He claimed that the hydration occurred in two steps; the first is the dissolution of calcium, silica and alumina in the alkaline solution and the second is the formation of alumina and silica hydration products while maintaining high alkalinity throughout the reaction. Thus, sodium hydroxide functioned as a reaction catalyst and did not react. Subsequently, Glukovsky [20], [21] who, under the hypothesis that ancient

Egyptian and Roman structures were composed of aluminosilicate hydrates containing calcium which had a chemical structure similar to OPC hydrates and analcite (also known as analcime which is a zeolitic mineral having the chemical formula $\text{NaAl}_2\text{SiO}_6 \cdot \text{H}_2\text{O}$), developed what he named as “soil cement” which was an alkaline binder that contained alumina and silica hydration products. His binder was prepared from the hydration of aluminosilicates mixed with alkaline industrial waste materials. Furthermore, Glukovsky was the first to coin the term “alkali-activated slag” and classify the alkaline activators into five main groups which were:

- 1- Bases like KOH, NaOH, and $\text{Ca}(\text{OH})_2$.
- 2- Alkali silicate, such as like Sodium silicate (Na_2SiO_3), potassium silicate.
- 3- Alkali aluminates, such as Sodium aluminate (NaAlO_2).
- 4- Alkali aluminosilicates, such as Albite ($\text{NaAlSi}_3\text{O}_8$).
- 5- Alkali salts can be divided into two subgroups depending on their acidic counterpart, such as carbonates and sulphates.

Davidovits first coined the term geopolymer after comparing the chemical structure of his patented “geopolymer” binder with the chemical structure of ancient Egyptian and Roman buildings [22]. The “geo-” part distinguishes his binder from organic polymers since it is inorganic, while the “polymer” part describes that the binder solidifies by forming chains under relatively low temperatures. He even suggested that those structures were manufactured from the reaction of alumino-silicate minerals with alkaline solutions since they had a random chemical structure similar to those of manufactured zeolites and dissimilar to natural zeolites, which have a more ordered structure [23]. Furthermore, Davidovits suggested using the term “polysialates” to chemically describe his geopolymer based on

the silicate (SiO_4^{4-} and AlO_4^{5-}) chain that forms geopolymers after the dissolution of alumina and silica during hydration. He even suggested the empirical chemical formula for the polymer chain $\text{A}_x\{(\text{SiO}_2)_y-(\text{AlO}_2)\}_x.n\text{H}_2\text{O}$. where A represents alkali, such as sodium or potassium, x is the polymerization degree, and y is 1,2 or 3. Table 3-1 summarizes some of the major events in the development of alkali activated binders [24][25].

Table 3-1 some significant events in the development of AABs [24][25].

Year	Author	Event
1940	Purdon	First work towards alkali activation of GGBFS
1959	Glukhovsky	Used different types of activators
1965	Glukhovsky	Coined the term “Alkaline cement”
1979	Davidovits	Patented the composition and method of developing Geopolymer
1987	Davidovits	Comparison of ancient and modern concretes
1992	Roy and Silsbee	First review on AAB

In recent years, significant research has been conducted in the development, characterization of alkali-activated binders. Some of these will be discussed in the following sub-sections, but the main emphasis of this paper is on the use of industrial waste materials for the development of alkali-activated binders.

3.1.1.1. Hydration and hydration products

The specific steps in the hydration of AABs are still debated. However, the consensus is that hydration goes through three steps: dissolution, reordering, and condensation (polymerization). These processes

depend on the type of precursor material and the type and concentration of the activator. Glukhovsky [20], [21] in his work with GGBFS as the precursor material and NaOH as the activator, reported the hydration progresses through two steps of dissolution and condensation that are simultaneous and overlap with each other. Dissolution is the process of the breakdown of the alumina and silicate precursor materials into simpler and lighter monomers by the alkaline solution. The dissolution starts by breaking Al-O-Al and Si-O-Al. He reported that there was a buildup in the monomers followed by the condensation and formation of CSH gel.

Davidovits[26] reported a different mechanism and different hydration products while working with metakaolin, sodium hydroxide, and potassium hydroxide. He first reported a dissolution of the polymeric layer of silica and alumina in metakaolin followed by the reordering of the broken down monomers and polymerization into sodium (or potassium)-containing aluminosilicate hydrate polymers, such as albite. Palomo et al. [27] studied the hydration of fly ash while using NaOH, KOH, and Na_2SiO_3 . He noted that the hydration of fly ash, in general, was an exothermal reaction. In the case of NaOH and KOH, the hydration followed three steps; dissolution, reorganization, as proven by the Fourier-transform infrared spectroscopy (FTIR), and polymerization. In the case of activation with the silicate, he reported that the three stages occurred simultaneously, and the reaction was much faster leading to the formation of a random gel that connected the spheres of fly ash, unlike the first case where the spheres were not connected by the hydration gel [25]. In the case of one-part geopolymer (OPG), several researchers reported an extra step in the beginning in which alkaline ions detached themselves from the OPG, thus raising the pH and starting the other three steps [28], [29][30].

The nature of the precursor controls the hydration products in AABs, the pH of the activator and the type of activator in addition to the nature of the AAB (i.e., if it is a one-part or a two-part). A summary

of the precursors and alkaline activators commonly used and possible hydration products is provided in Table 3-2. In systems with low calcium and high pH, zeolites (NASH) are expected to be the hydration products, as reported by Palomo [27], Ke et al. [29] and Davidovits [22]. On the other hand, calcium aluminate silicate hydrate (CASH), calcium silicate hydrate (CSH), and hydrotalcite-like compounds are formed in systems where the calcium content is increased and the pH is moderate, as was reported by Bandar et al. [31] and Bai et al. [32]. Other researchers reported the formation of both CASH, NASH, and an intermediate phase that contained both calcium and sodium attached to the aluminate silicate hydrate (CNASH)[33]–[35]. Furthermore, Jeong et al. [36] showed the formation monocarboaluminate ($C_4AC^*H_{11}$)¹, ettringite ($C_6AS^*_3H_{32}$)², hemi-carboaluminate ($Ca_4Al_2(OH)_{13}(CO_3)_{0.5}.4H_2O$) as well as CSH due to the activation of calcium carbonate and GGBS with CaO and CaSO₄.

Table 3-2 Summary of the hydration mechanisms and products in AAB binders

	High calcium (AAB)	Low calcium (Geopolymer)
Precursors	GGBFS, Class C fly ash	Metakaolin, Class F fly ash, silica fume
Activators	NaOH, Na ₂ SiO ₃ , KOH, CaSO ₄ , CaO, LSP	
Hydration mechanism	Hydration, polymerization	Polymerization
Hydration products	CASH, CSH, NASH, CNASH, hydrotalcite, $C_4AC^*H_{11}$, $C_6AS^*_3H_{32}$, $Ca_4Al_2(OH)_{13}(CO_3)_{0.5}.4H_2O$	NASH, Zeolites (Zeolite P, Faujicite, Chabazite)

¹ C* = CO₂

² S* = SO₄

3.1.1.2. Use of mineral additives and industrial byproducts

The use of mineral additives and industrial byproducts in the manufacturing of AABs has been well documented in recent literature. They can be used as precursors, activators and/or fillers. The rule seems to be that as long as the mineral additive or byproduct contains medium to high proportions of alumina or calcium and/or possesses alkaline nature, it can be used to develop AABs. For example, red mud (a waste material from bauxite mining) was used after calcination by Ke et al. [27] to develop a one-part geopolymer and showed the formation of NASH as well as C_3A and C_2S [29].

Abdel-Gawwad and Khalil [28] used CKD and feldspar to develop a one-part geopolymer by activating them at 1200 °C with sodium hydroxide pellets and soda ash. They showed the development of an amorphous material after the activation. When hydrated, the OPG showed the development of CSH and CASH and showed moderate strength at 28 days (Figure 3-1). Furthermore, Yaseri et al. [34] used CKD and silica fume at different ratios as precursors while using sodium hydroxide and rice-husk ash as activators. They reported an optimum CKD/SF ratio of 45/55 that had the best workability and strength. In another research by Abdel-Gawwad et al. [30], an OPG was developed from milled recycled concrete calcined at 1200°C with NaOH. The OPG developed CSH as the main strength-carrying hydration product.

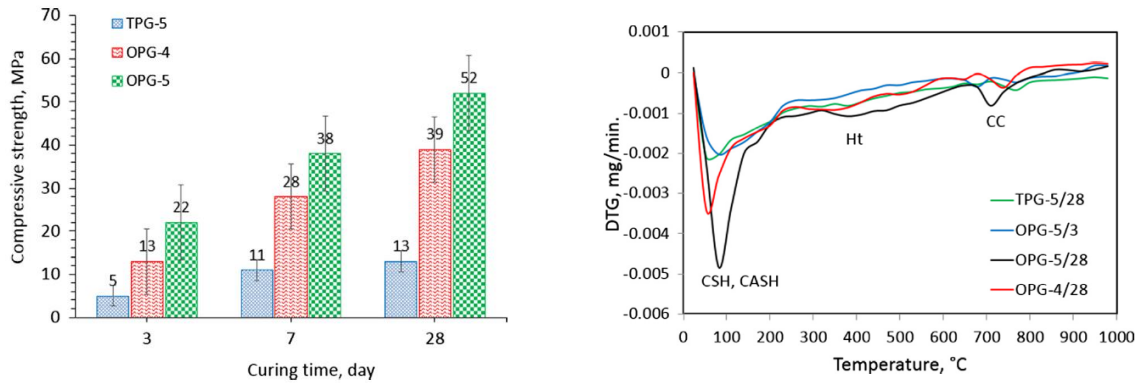


Figure 3-1 Compressive strength of one-part geopolymers (left) and DTG showing CSH, CASH peaks (Right)[28]

Valentini et al. [35] studied the role of sodium hydroxide, sodium citrate, and sodium silicate as activators on the strength development of calcined smectite clay AAB. They showed the development of both CASH and NASH after 18 hours of dry curing. Sodium citrate improved the microstructure and doubled the compressive strength. Furnace calcined and flash-calcined argillite clay was used to develop an alkali-activated binder by Gharzoumi et al. [37] while Park et al. [38] used stone powder sludge and GGBS that were activated by calcium sulphate and sodium sulphate to produce cementless bricks that were economical and satisfactory in terms of brick standards.

Maryam et al. [39] studied the shrinkage behavior of a binary FA and GGBFS binder at different FA/GGBFS ratios. They found that the higher GGBFS content led to higher strength development and higher shrinkage, while higher FA content led to less strength and Lower shrinkage.

Wen et al. [40] used waste-water sludge and rice-husk ash to develop a binder that can be used as permanent storage for sludge. The binder showed good leaching resistance and showed the development of aluminosilicates.

Bayiha et al. [41] studied the hydration, microstructure and hardened properties of thermally-activated halloysite clay (a local clay mainly consisting of silica and alumina compounds) and

limestone powder different dosages that were activated by sodium hydroxide and sodium silicate. They reported that the limestone powder reacted to form additional CASH, CH, and CSH and the NASH formed by the hydration of the thermally-activated clay, which led to better pore refinement and higher compressive strength. Table 3-3 summarizes the latest literature output on the utilization of industrial byproduct and minerals in the development of alkali-activated binders.

Table 3-3: Recent literature summary on AABs.

Reference	Materials used	Type of binder	Tests	Findings
Kaze et al. [42]	Iron-rich laterite soil, NaOH and Na ₂ SiO ₃	Paste with different silica modulus (SiO ₂ /Na ₂ O) of (1.3, 1.5, 1.7, 2)	Setting time, Rheological measurements, compressive and flexural strength, water absorption, porosity, bulk density XRD, FTIR, SEM,	- The optimum silica modulus of the activator is 1.3. - Increasing the activator's silica modulus from 1.3 to 2.0 resulted in a longer setting time, a lower compressive strength and a higher absorption and porosity.
Mustakim et al. [43]	Fly ash, GGBFS, Nano-silica (nSiO ₂), Silica fume (SF), Na ₂ SiO ₃ , NaOH (12M)	Concrete 1:1:3 (Source materials: fine aggregates: coarse aggregates), extra water 0.8%-4% wt. with nSiO ₂ and SF content ranged (0%-2.5%)	Slump, setting time, compressive strength, XRD, XRF, FESEM, FTIR	- Both nSiO₂ and SF facilitated a higher degree of geopolymerization and polycondensation, which led to the improvement of the properties of Fly ash-GGBFS based GPC. - The nSiO₂ incorporated GPC performs better than of the SF modified GPC.

Nana et al. [44]	Metakaolin, natural solid solutions (trachyte, pegmatite and granite), NaOH, Na ₂ SiO ₃ ,	Paste: (Alkaline solution at a liquid/solid mass ratio of 0.37 and natural solid solution 70-85 wt% with metakaolin) with different activator's molarity (8, 10, 12, 14 and 16 M)	Water absorption, compressive strength, FTIR, XRD, ESEM,	- The NaOH concentration of 12 M was optimum for solid solution of trachyte with 98–106 MPa. - The optimum NaOH concentration for solid solutions of pegmatite (94–105 MPa) or granite (101–108 MPa) was 10 M.
Tome et al. [45]	volcanic ash (VA) and municipal solid waste incinerator fly ash (MSWI-FA)	Mortar exposed to sulphuric acid solution and artificial seawater at 56 days	compressive strength, XRD, FTIR, SEM,	- The loss of strength in an acidic medium is due to the decalcification and depolymerization reactions whereas in seawater medium, it is attributed to the movement of content ions and probable formation of Friedel's salt. - The VA + MSWI-FA based alkali activated materials resist better in seawater than in sulphuric acid solution.
Ho et al. [46]	fly ash (FA), ground granulated blast furnace slag (GGBS), lead smelter slag (LSS), natural sand (NS), graphene oxide (GO), Na ₂ SiO ₃ /NaOH wt ratio of 2.5	Mortar with NS or LSS: FA (100, 80, 50) %, GGBS (0, 20, 50) %. An effective alkaline liquid-to-binder (l_{eff}/b) ratio of (0.45, 0.55, 0.75), and the GO dosages (0.05, 0.1)%.	Flowability, compressive and tensile strengths, drying shrinkage at 7, 14, 21, and 28 days, XRD, SEM,	- Mortars with 0.05% and 0.1% GO have better properties than control mixes. - Oxygen functional groups of GO sheets have been reduced in alkaline solution. - Interactions between GO and hydration products decrease crack propagations in mixes.
Nguyen et al. [47]	Ground granulated blast furnace slag (GGBFS),	Paste with water/binder ratio 0.4, four different RHA/(RHA +	Packing density, porosity, water absorption, Chloride penetration	- Increasing RHA content in the binder specimens reduced the packing density of the

	rice husk ash (RHA), circulating fluidized bed combustion fly ash (CFA)	GGBFS) weight ratios (0%, 15%, 30%, and 45%) and three different CFA/(RHA + GGBFS) weight ratios (10%, 20%, and 30%).		granular mixtures significantly. - Total porosity, water absorption capacity, and the charge passed in the chloride penetration test in all the binder specimens decreased over time. - The correlations between water absorption, porosity, and chloride penetration were established.
Joudah et al. [48]	waste ceramic tile powder (WCP), ground blast furnace slag (GBFS), fly ash (FA), NaOH, Na ₂ SiO ₃ .	Mortar: Binder/sand =1 Na ₂ SiO ₃ /NaOH=0.75 alkaline/binder=0.4 WCP=50% wt. binder GBFS replaced by (10%, 20%, 30%, 40%) of FA	Compressive strength, sulfuric acid resistance, drying shrinkage	- The compressive strength decreased with a higher content of FA in the alkali-activated matrix. - The proposed mortar with a higher content of FA showed a lower drying shrinkage and better performance under sulfuric acid environments.
Ibrahim et al. [49]	Natural pozzolans (NPs), nano-silica (nSiO ₂), NaOH, Na ₂ SiO ₃	Concrete: NPs blended with (nSiO ₂) from 0 to 7.5%	5% sulfuric acid (H ₂ SO ₄ aq) exposure: weight loss, and reduction in strength, XRD, SEM, FTIR	- nSiO₂ improved the performance of AAC. nSiO₂ of (5% & 7.5%) modified binder performed better performance. - Developed an artificial neural network (ANN) and response surface methodology (RSM) models to predict and optimize nSiO₂.
Mabroum et al. [50]	calcined marls, Na ₂ SiO ₃ , NaOH	Paste: Na ₂ SiO ₃ /NaOH = 0.5 liquid/solid =1.3	compressive strength, XRD, FTIR, thermogravimetric analysis (TGA)	- Co-formation of C-A-S-H and N-A-S-H type gels - Calcite phase appears in the hardened

				materials after 120 days of curing. - Good compressive strength of 38 MPa after 120 days of curing.
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3.1.2. Celitement (α -C₂S) Binders

Celitement is a relatively new binder that was developed by Stemmermann et al. [51] in 2011 at the Karlsruhe Institute of Technology (KIT). They produced it by hydrothermally treating α -C₂S, synthesized from calcium hydroxide at 200°C and saturated steam environment, then milling it with quartz and GGBFS as silica sources. The literature on this binder is still scarce, and most of the literature available discusses its manufacture and hydration [52]–[56]. Celitement is defined as a binder that is composed of silicone disilicate treated with other sources of silica which hydrates to form CSH. The main differences between it and OPC are the reduction in energy requirement, the reduction in emission of CO₂, and the elimination of other hydration products like Afm (monoaluminoferrite) and Aft (ettringite). Regarding the energy required to produce it, low-lime Celitement is estimated to consume 2170 kJ/kg while OPC requires 4360 kJ/kg, according to Garbev et al. [51]. This decrease comes from the lower temperature required in the manufacturing of Celitement (200°C compared to 1400°C for OPC production). On the other hand, the production of Celitement shows a 50% reduction in CO₂ emission with a total release of 483 kilograms of CO₂ per ton of Celitement compared to the 1 ton of CO₂ released per ton of OPC produced. However, the production of such binders faces some challenges in terms of application in the industry. The machinery required to mass-produce Celitement seems to be the main challenge. Synthesizing the α -C₂S and hydrothermally activating it requires a major change in the cement production industry. However, the authors claim the feasibility of the change [52].

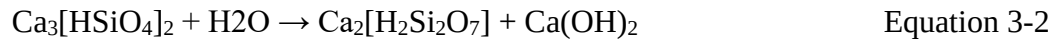
3.1.2.1. Hydration and hydration products

Garbev et al. [57] studied the hydration of Celitement and found that there are three steps in the hydration:

- 1- Hydrolysis: which starts by the reaction of Celitement to form an intermediate phase of calcium silica hydrate following the reaction:



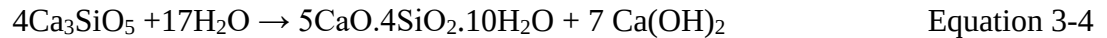
Condensation: in this step, part of the intermediate phase of calcium silicate hydrate forms another intermediate CSH phase following the reaction:



- 2- Hydration: in this step, the second intermediate phase reacts with the first intermediate phase to produce the final CSH gel following the reaction:



By summing the reactions of the three steps, the total reaction becomes:



However, they reported the formation of monocarboaluminate ($\text{C}_8\text{A}_2\text{C}^*\text{H}_{24}$) as well as CSH after 20 hours of hydration, as shown by the FTIR results (Figure 3-2). The authors also mentioned the possibility of changing the additional silicate source to other industrial byproducts like silica fume or natural minerals like feldspar.

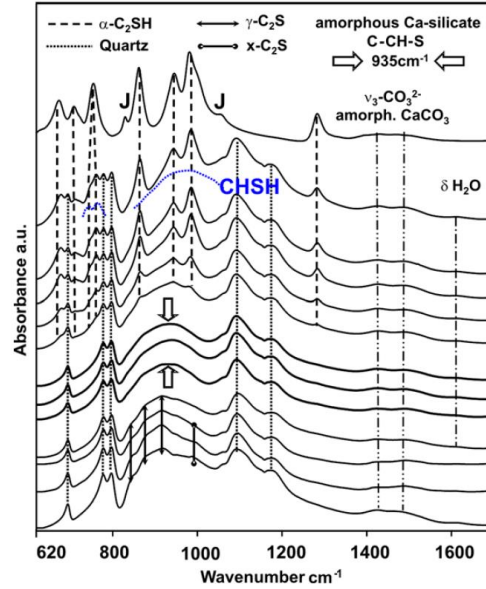


Figure 3-2 : FTIR of different Celitement series showing the formation of the hydration products[52]

Siauciunas et al. [53], [56] produced what they labeled as a “hydraulic cement binder” by synthesizing α -C₂S from the decomposition of local marl and chalk marl and hydrothermally treating it with silica sand to produce an α -C₂S binder similar to Celitement. They confirmed the formation of CSH, calcite, and the consumption of portlandite and α -C₂S by XRD analysis. After hydration for 28 days, the samples produced compressive strengths of around 17 MPa. However, the subject of Celitement is still in its early developmental stages as stated previously. Table 3-4 illustrates the latest literature on Celitement binders.

Table 3-4: Recent Advancements in Celitement binders

Reference	Materials used	Type of binder	Tests	Findings
Stemmermann et al. [58]	industrial-grade slaked lime and quartz sand with a CaO/SiO ₂ (C/S) ratio of 1.28	Pastes: one with (0.35 w/c, 2% superplasticizer) and the other with 0.425% w/c	7 days curing: compressive strength, Nano and micro indentation, Raman micro-spectroscopy, XRD, SEM, elemental mapping,	- Celitement consists of calcium hydrosilicate reaction forms C-S-H phases similar to those of the hydration of the clinker minerals C₃S and C₂S. - Raman micro-spectroscopy is a valuable tool for representing the lateral phase distribution in hardened cementitious materials. - The simple reaction chemistry of Celitement enables for microstructure tailoring by altering content and adding buffering systems to adjust reaction kinetics.

				-
Siauciunas et al. [59]	Lime, CEN Standard sand EN 196-1, Opoka, quartz sand	Paste: α -C ₂ SH with (w/c = 0.125) Mortar: α -C ₂ SH with sand (1:3 by mass, w/c = 0.25), carbonation curing	Compressive strength, XRD, XRF, Simultaneous thermal analysis (STA), SEM with EDX	- Produced, mechanochemically, five different compounds of thermally activated α-C₂SH. - CO₂ hardened concrete can be produced from calcium silicate hydrates. - α-C₂SH binder is suitable for producing a medium strength carbonated concrete.
Siauciunas et al. [60]	Limestone, quartz sand	unstirred suspensions of α -C ₂ SH (CaO/SiO ₂ = 2.0) with NaOH solution and water/solid ratio of the suspension is 10. Then dried for sample characterization tests.	XRD, STA, SEM with EDX, BET surface area	- The presence of Na⁺ ions positively affect the solubility of quartz in CaO-SiO₂-H₂O system. - Na⁺ ions are not incorporated into the crystal structure of the main synthesis product – α-C₂SH. - Alkaline additive decreased the specific surface area of α-C₂SH and the values of total pore volume.

3.1.3. Belite-Ye'elimite binders (CSA)

Belite (C₂S)-ye'elimite(C₄A₃S*) binders, also known as ye'elimite-rich binders or calcium sulfoaluminate binders (CSA), is a family of hydraulic binders that contain large amounts of alumina and sulphate compared to OPC. They were first introduced as a shrinkage control measure in the 1950s by Alexander Klein [61] and then adopted in the Chinese cement manufacturing industry under “the third series binders” in the 1970s. The CSA market is still quite inconsiderable in size. It represents a small proportion of the total cement production industry, with an estimated yearly production of around one million tons (less than 1% of the total cement produced yearly, estimated to be around 4.1 billion tons). Typical OPC is composed of four main phases which are 30% to 60% alite (C₃S), 20% to 50% belite (C₂S), 5% to 10% alumina in the form tri-calcium aluminate (C₃A) and 7% to 12% ferrite in the form of tetra-calcium aluminoferrite (C₄AF) while CSA cement is composed of 50% to 60% ye'elimite, 0% to 20% belite, 5% to 15% ferrite and 15% to 25% gypsum (CS*) [62].

Ye'elimite rich binders are traditionally manufactured in typical rotary kilns by the addition of bauxite, lower amounts of lime, and gypsum. The environmental advantage of CSA over OPC is threefold [63]:

- 1- CSA requires 200°C less kiln temperature than OPC, which decreases the energy consumption of fuel up to 60%.
- 2- Much less lime is used in the production of CSA, which decreases the amount of released CO₂ by up to 50%.
- 3- Due to the higher friability of CSA, less energy is required in the grinding process.

CSA binders have reported better acid resistance since little to no calcium hydroxide (CH) is formed, which reacts with acids and leads to degradation in OPC binders. However, the pH of CSA binders is high enough to ensure the passive layer formation in reinforced CSA concretes. Furthermore, CSA binders have been reported to have excellent resistance against sulphate attacks and chloride ingress [62], [64], [65] (Figure 3-3). Due to those properties, CSA has been suggested in the use of encapsulating radioactive waste[66].

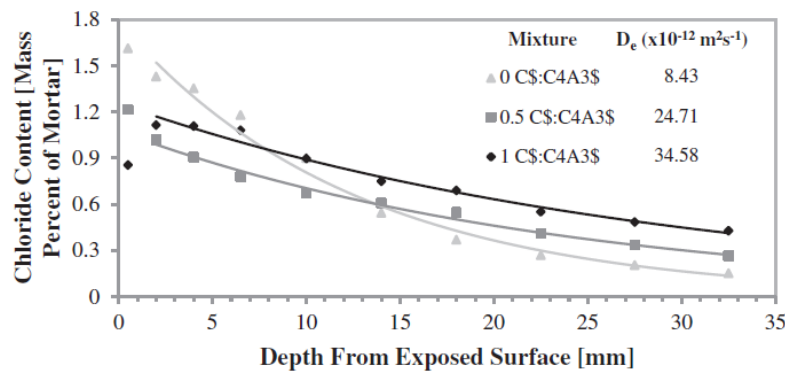


Figure 3-3 Chloride ingress of CSA binders with different Sulfate to ye'elimite ratios[64]

3.1.3.1. Hydration and hydration products

Unlike OPC, where the main hydration reaction is that of C_3S to form CSH and CH, CSA reacts mainly to form ettringite (C_6AS*3H_{32}), amorphous aluminate (AH_3), and calcium monosulphate (C_6AS*H_{18}). CSA is reported to gain 50% of its strength within the first few hours and 90% within the first three days. The reaction periods, as reported by Ben Haha et al. [67] go through five steps which are:

- 1- Initial hydration period where the cement is wetted, and amorphous aluminate is formed with some traces of ettringite formation.
- 2- The slow down or induction period which is characterized by the formation of ettringite and no dissolution of ye'elimite occurring, leading to a continuous decrease in the concentration of the sulphate ions.
- 3- The acceleration period is characterized by the formation of monosulphate and aluminum hydroxide with a slowdown in the formation of ettringite. During this period, sulphate is totally depleted.
- 4- Main hydration period during which ye'elimite reacts and the pH is increased to form amorphous hydration phases.
- 5- Slowing down of the hydration phase and it occurs when ye'elimite dissolution rate becomes low and thermodynamic equilibrium is established. During this period, amorphous phases start to recrystallize and grow.

3.1.3.2. Utilization of industrial byproducts in CSA

Recently, more research has been directed towards the use of less expensive raw materials in the production of CSA, which include the use of alumina and iron wastes (GGBFS, red mud, waste from

aluminum anodizing, calcined clays, electric arc furnace dust) [68]–[70] as well as the use of waste lime and sulphate sources like calcium carbonate from CO₂ sequestration and gypsum produced from flue gas desulphurization [71]. For example, El-Alfi and Gado [72] used gypsum, kaolin, and marble sludge as the raw materials for the making of CSA and used different furnace temperatures to study the hydration and mechanical properties of the resulting binders. They reported the formation of ettringite (Figure 3-4) in their mixes with marble sludge use up to 25% and reported a compressive strength of 36MPa at the age of 28 days. Wan and Fang [73] developed belite binders with high carbon fly ash and studied the microstructure of the formed hydration products.

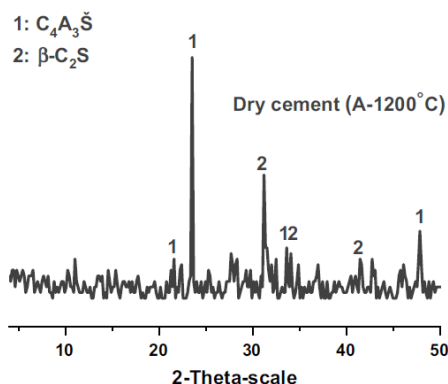


Figure 3-4: XRD pattern for hardened CSA binder showing ettringite formation[72]

Another direction of development in ye’elite rich binders is the incorporation of more ferrite components such as EAFD to form belite-ye’elite-ferrite (BYF) [67] and the addition of alite to CSA systems to develop belite-alite-ye’elite (BAY) in order to improve the overall performance while maintaining a net positive environmental impact [74]. Table 3-5 illustrates the latest literature on the use of waste materials and mineral additives in the development of CSA binders as well as BYF and BAY binders.

Table 3-5: Literature summary of utilization of mineral and industrial waste materials in the development of CSA, BYF and BAY.

Reference	Materials used	Type of binder	Tests	Findings
Žibret et al. [75]	Limestone, flysch, coal combustion bottom ash, white titanogypsum, bauxite, mill scale	Two different BCSA cement clinkers contain 9 wt% bottom ash. Their composition: 1. (65 wt% belite, 20 wt% calcium sulfoaluminate, 10 wt% ferrite) 2. (50 wt% belite, 35 wt% calcium sulfoaluminate and 10 wt% ferrite)	XRD, SEM/EDS, Isothermal calorimetry	- Bottom ash is a suitable raw material for the synthesis of BCSA clinkers. - Clinkers showed a fine-grained texture with a decrease in porosity occurring with an increase in sintering temperature. - The variation in sintering temperature influenced the clinker phase composition and contributed to clinker reactivity.
Li et al. [76]	Alumina-rich sludge (AS), phosphogypsum (PG), silicon oxide (SiO ₂), calcium carbonate (CaCO ₃), alumina oxide (Al ₂ O ₃), gypsum	Paste: CSAB cement, 0.5 w/c ratio Mortar: water/Cement/sand ratio of 1/2/6	compressive strength, setting time, XRD, particle size distribution, specific surface area, Isothermal calorimetry, Thermal gravimetric analysis,	- Using AS and PG in producing CSAB could lower burning temperature and increase hydration reactivity. - From quantitative XRD analysis, adding PG increased the content of ettringite. - The compressive strength of CSAB cement increased when blended with 10 wt% PG.
Negrão et al. [77]	limestone (CaCO ₃), gypsum (CaSO ₄ •2H ₂ O), Belterra Clay.	Paste: CSA cement, w/c ratio of (0.5 & 1). Mortar: w/c ratio of (0.3).	XRPD, EDX, Specific surface area, isothermal calorimetry, compressive strength	- Belterra Clay was successfully used to produce different CSA-based clinkers; CSA-belite cements and CSA-ternesite clinkers. - The produced clinkers reduced CO₂ by 30% compared to OPCs. - The compressive strength of the produced mortar at 28 days is comparable to OPCs tested under the same conditions.
Afroughsab et al. [78]	Type 1 OPC, commercial CSA cement, ground granulated blast-furnace slag (GGBS)	Concrete: four mixes at w/b ratio of 0.35 Mix 1 (100% OPC), Mix 2 (100% CSA cement), Mix 3 (50% OPC, 50% CSA)	compressive strength, splitting tensile strength, water absorption, shrinkage (56 days), electrical resistivity, Potentiostatic test,	- Replacing OPC with CSA cement results in a significant increase in the electrical resistivity and corrosion potential of concrete and reduce the shrinkage. - The main hydration products of pure CSA

		cement), Mix 4 (50% CSA cement, 25% OPC, 25% GGBS)	carbonation depths, SEM	cement are prismatic ettringite crystals that cause an increase in the strengths of concrete. - pH of CSA concrete was of ~9–10.
Zhang et al. [79]	Commercial CSA, fly ash (FA), ground granulated blast-furnace slag (GGBS), OPC, NaCl	Frozen cemented paste backfills (FCPB) with different binder proportions: (90% OPC, 10% CSA). (80% OPC, 10% CSA, 10% FA). (80% OPC, 10% CSA, 10% GGBS).	compressive strength, isothermal calorimetry, XRD, XRF, thermogravimetry analysis (TGA), Mercury intrusion porosimetry (MIP)	- Increasing the NaCl concentration from 0 to 90 g/L significantly lowers the freezing point and frozen water content regardless of the type of binder. - The 2 days-strength of FCPB is controlled by hydration reaction, while 28 days-strength is dominated by the content of frozen. - The binder (80% OPC, 10% CSA, 10% GGBS) with 90 g/L NaCl solution exhibits the lowest CO ₂ emission and cost.
Seo et al. [80]	CSA cement, blast furnace slag	Paste: w/b ratio of 0.5 with slag of (0, 30, 50, 70) % replacement of CSA cement under carbonation with 3% CO ₂ concentration.	compressive strength, carbonation degree, XRD, TGA, NMR, MIP, MAS	- The reaction degree of the slag was increased by carbonation, and it decreased with an increase in the slag content. - Monosulfate and ettringite were the first phases to be carbonated. - C-A-SH gel formation due to the carbonation of belite enhance the microstructural densification results in compressive strength increase.
Alwaeli et al [81]	OPC, CSA cement, metallurgical sludge waste natural quartz sand	Mortar: Sand replaced by sludge waste (10%, 20%, 30%). OPC replaced by CSA cement (10%, 20%, 30%, 50%)	Initial setting time, water demand, compressive strength, shrinkage, hydration heat, MIP, SEM	- CSA cement, as a partial replacement for OPC, has: - solved the problem of delayed setting time of mortars with metallurgical sludge waste. - inhibited the hydration heat evolution. - increased the early compressive strength but decreased it after 28 days due to ettringite formation during CSA cement hydration.
Isteri et al. [82]	Argon Oxygen Decarburisation (AOD) slag, fayalitic slag. Fe slag.	Cement paste and mortar: Four CSAB cement clinkers were prepared; one from	compressive strength, XRD, XRF, FESEM-EDS, TGA,	- Ye'elimite-belite-ferrite clinkers produced by using Fe slag from zinc production and fayalitic slag together.

		reagent grade chemicals and the others from industrial wastes (AOD slag, fayalitic slag, Fe slag)		- Ye'elimite-belite-fluorellestadite-ferrite is produced by using AOD slag which affects negatively the mechanical properties of the clinkers.
Koga et al. [83]	BYF cement, fly ash	Paste & mortar: w/b ratio = 0.5, 25 wt% of BYF cement is replaced by fly ash.	compressive strength, isothermal calorimetry, XRD, TGA,	- The presence of fly ash enhances the long-term appearance of stratlingite and ettringite with a refinement of the microstructure compared to the plain BYF cement pastes. - Replacement of BYF cement by 25 wt% fly ash did not cause long-term strength loss compared to plain BYF cement paste with the same water/binder ratio.
Yeung et al. [84]	CSA cement, OPC, fly ash, GGBS	Paste: 20 different mixes, w/b ratio of 0.45, Delvocrete Stabilizer, superplasticizer.	Shrinkage at (2-365) days	- Developed different k factors for other used binder combinations (CSA, FA or GGBS blended with OPC) to be utilized in the GL2000 Model to predict ultimate shrinkage.
Yoon et al. [85]	CSA clinker, blast-furnace slag (GGBFS), Gypsum anhydrite powder (CaSO ₄)	Paste: w/b ratio of 0.5 GGBFS (0, 30, 50, 70) wt% of binder.	Curing period (360 days) compressive strength, XRD, XRF, TGA, MIP, MAS-NMR	- The addition of GGBFS reduces the formation of ettringite and monosulfate but increases the formation of stratlingite. - The 30% GGBFS replacement sample has a compressive strength comparable to the pure CSA cement. - The GGBFS dissolution was most noticeable at 30% GGBFS replacement and, continuously, occurred up to 360 days with reaction degree of 70%.
Kaufmann [86]	commercial CSA-clinker, gypsum, desert sand	Mortar: (fine quartz sand) Concrete 8 mm: (fine quartz sand, standard sand, gravel up to 8 mm)	compressive and bending strength, drying shrinkage XRD, MIP, TGA,	- In the mortars a much denser microstructure with a lower porosity is found for the CSA/gypsum binder and a high ettringite contents compared with OPC.

		Concrete 32 mm: (fine quartz sand, standard sand, gravel up to 32 mm) w/b of (0.50%, 0.55%, 0.60%)		- In concretes the CSA content can be reduced and the mechanical properties of the CSA/gypsum binder in combination with the desert sand are improved. - Drying shrinkage in CSA/gypsum binder concretes is low.
Liao et al. [87]	CSA cement, steel slag	Pastes: Containing steel slag of (0, 10, 20, 40) wt%. w/b ratio is 0.5	Setting time, compressive strength, chemical shrinkage, electrical resistivity, XRD, bound water content, pH value, MIP,	- At early age, up to 28 days, steel slag worked like a filler and had a dilution effect on CSA cement hydration. - At the late ages (>90 days), the properties of CSA cement paste enhanced by steel slag replacements due to the hydration of steel slag. - Ettringite stabilization and stratlingite formation in (20%, 40%) slag pastes appeared to be the primary mechanisms for strength compensation of CSA cement/steel slag pastes at late ages.

3.1.4. Mg-based binders (MGBB)

When OPC mixtures are exposed to magnesium-rich environments, CSH becomes unstable, and the calcium is leached out of the gel, leaving amorphous silica, which then reacts with brucite ($\text{Mg}(\text{OH})_2$), which then forms magnesium silicate hydrate (MSH). The formation of MSH was first observed by Cole in the late 1950s when he studied the deterioration of OPC concrete exposed to sea water [88]. Mg-based binders today utilize that reaction to produce binders that are more environmentally friendly. At the beginning of the development of Mg-based binders, the focus was on developing them by the calcination of magnesium carbonate, which produces more CO_2 than OPC (1.1 ton per ton of clinker), which is clearly not an environmentally sound option [63]. A possible approach suggested by the United Nation's report included the utilization of mafic rocks which contain magnesium oxide and silica without carbonate, which in theory would be a truly CO_2 negative

approach. However, a new applicable approach has been suggested in the literature in which reactive magnesia collected from the treatment of brine, seawater, and hard groundwater is used instead of magnesium carbonate [89]–[91].

Another challenge that faces the development of magnesium-based binders is the workability and water demand of such binders. It has been reported that mg-based binders require higher amounts of water to produce workable binders than those made with OPC. Tran and Scott [90] studied the role of silica fume, silica fillers, and high range water reducers on the strength development and workability of magnesium silicate binders developed from reactive magnesia. They found that adding silica filler helped increase the workability and the addition of Sodium Hexametaphosphate (SHMP) and reduced the water demand, leading to a greatly improved microstructure (Figure 3-5). However, the addition of silica fume beyond 40% by weight of the binder led to reduced strength. Zhang et al. [92] studied the hydration and workability of magnesium silicate binders treated with 1% SHMP and found that using it as a superplasticizer improved the workability significantly and reduced the water demand to as low as 0.4 while achieving higher strengths comparable to that of commercial OPC binders.

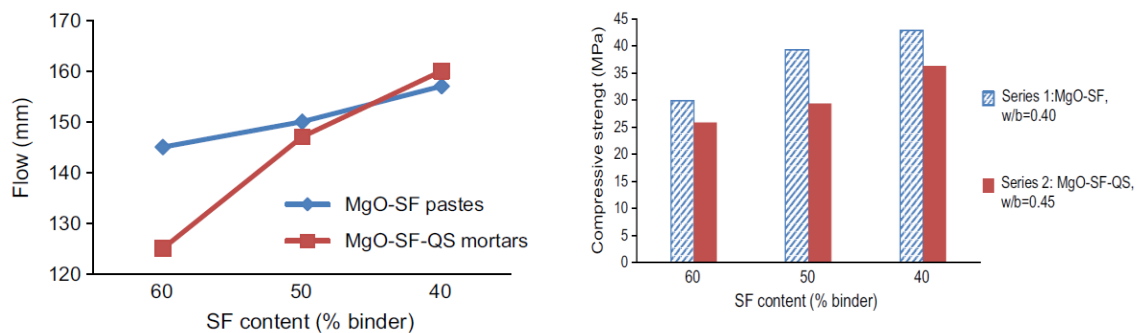


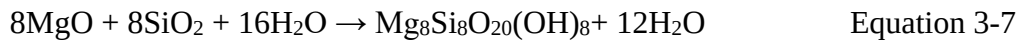
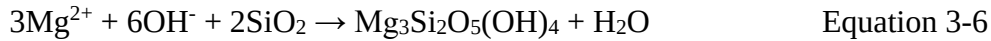
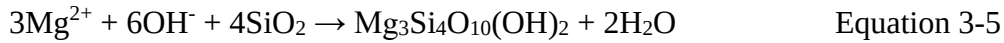
Figure 3-5: Improved workability with the addition of SF (Left). Compressive strength of MGBB vs. SF content (Right)[90]

3.1.4.1. Hydration and hydration products

The hydration of Mg-silicate binders follows three periods, as reported by Martini et al. [93]:

- 1- An induction period where water is slightly consumed. This period has been reported to be shorter in magnesium-based binders compared to OPC binders.
- 2- A nucleation and growth period during which MSH starts to form and grow in size filling the interstitial spaces and water consumption increases significantly. The period goes through an acceleration phase and a deceleration phase.
- 3- A diffusion period where water consumption is decreasing and MSH gel formation continues.

Regarding the hydration products, Mainly MSH and brucite are formed as the reaction products following the suggested reactions [94], [95]:



When SiO_2 is exhausted:



3.1.4.2. Utilization of industrial byproducts

Mg-based binders provide an opportunity for the utilization of industrial byproducts. As stated earlier, mg-based binders are now being prepared with reactive MgO, which in itself is an industrial byproduct. Furthermore, the source for silica to develop MSH can be any other industrial waste that contains a high amount of silica like silica fume and fly ash. For example, Wu et al. [96] developed Mg-Si binders utilizing light burned magnesia and low calcium fly ash at different fly ash dosages

and different water-to-binder ratios. Table 3-6 illustrates the latest literature on the use of mineral additives and industrial waste in the development of magnesium-base binders.

Table 3-6: Latest literature on development of Mg-Based binders utilizing waste materials and mineral additives

Reference	Materials used	Type of binder	Tests	Findings
Tan et al. [97]	Light-burned MgO, MgSO ₄ ·7H ₂ O, citrate acid (C ₆ H ₈ O ₇), Silica fume (SF)	Paste: basic magnesium sulfate cement (BMSC); molar ratio of 8:1:20 for MgO: MgSO ₄ ·7H ₂ O: H ₂ O SF of (0 wt%, 10 wt%, 30 wt%) by MgO's weight, and 0.5% citric acid	Setting time, compressive strength, isothermal calorimetry, XRF, SEM, NMR, MIP	- A secondary hydration products (M-S-H gel) has been generated due to the activation of SF particles by Mg(OH)₂. - Incorporating SF in the BMSC decreased the hydration heat and increased the setting time and compressive strength.
Dong et al. [98]	MgO, ammonium dihydrogen phosphate (ADP), lithium slag (LS), Borax, Sodium triphosphate	Mortar: Lithium slag-based magnesium phosphate cement (LS-MAPC): Sand: MAPC = 1:1 LS range (0%-50%) replacement of MAPC.	Flowability, setting time, compressive and bending strength, porosity, water absorption, SEM, XRD, FTIR.	- The optimum dosage of LS as a replacement of MAPC was found to be a 10%.
Yu et al. [99]	MgO, ammonium dihydrogen phosphate (ADP), pentahydrate borax, (0%-100%) calcined boron muds as replacement of MgO	Paste: Magnesium phosphate cement (MPC) with w/b = 0.18	Flowability, setting time, compressive strength, XRD, SEM, TG/DSC	- The performance of MPC paste is better when replacing the dead burned MgO by a 40% calcined boron muds at 850 °C during production of MPC.
Luo et al. [100]	electric furnace ferronickel slag (EFS), ADP, MgO	Paste: EFS-based magnesium phosphate cement (EMPC)	setting time, compressive strength, XRD, XRF, SEM, FTIR, TG/DSC,	- The compressive strength of EMPC paste at 28d reached 29 MPa at the EFS/ADP of 4.0 which improved by adding little content of MgO to reach (62 MPa at 28d).

			leaching toxicity	- The hydration of EMPC paste is a multi-stage process, including the dissolution of $\text{NH}_4\text{H}_2\text{PO}_4$, MgO and Mg_2SiO_4, the precipitation of the intermediate hydrate phase and the formation of binder phase of struvite. - The leaching toxicity of EMPC paste is lower than that of EFS.
Ma et al. [101]	MgO, ammonium dihydrogen phosphate (ADP), fly ash (FA), silica fume (SF), borax, Sodium triphosphate, glacial Acetic acid	Paste: Magnesium phosphate cement (MPC), Several replacements of MPC by FA (0%, 5%, 10%, 15%, 20%) or SF (0%, 2%, 4%, 6%, 8%)	Compressive strength, Rheological and zeta potential measurements, water film thickness, XRD, NMR	- The rheological behavior of FA-MPC and SF-MPC pastes can be described by Bingham model. - Hydration is the dominant factor for rheological properties of MPC, followed by surface charge and separation distance of particles. - Addition of FA and SF develop the fresh and hardened properties of MPC paste.
Ba et al. [102]	Magnesium sulphate heptahydrate crystals ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), (MgO), sodium silicate (SS), citrate acid	Pastes: MOS cement with different amount of SS additive	setting time, flowability, compressive and flexural strengths, dispersion, SEM, XRD, isothermal calorimetry	- An increase of SS as additive enhances the MOS paste microstructure, increases its strength and water resistance. - The SS forms much denser paste by improving the microstructure and refining the coarse pores of hardened MOS paste. - SS does not change the category of hydration phase composition in hardened MOS cement but it accelerates the endothermic reaction in MOS cement paste by promoting the development of much more $[\text{Mg}(\text{H}_2\text{O})_5(\text{OH})]^+$.
Ruan et al. [103]	MgO, Potassium dihydrogen phosphate (KH_2PO_4), borax, water purifying material waste (WP), red mud (RM)	Paste: w/c = 0.18 Magnesium phosphate cement (MPC) with different dosages of WP and RM were 2.0, 4.0, 6.0, and 8.0 wt% of the total mass of MPC.	Compressive strength, water resistance, XRD, SEM	- The incorporation of WP and RM provided crystallization sites for the MPC hydration products, which improved the strength and water resistance.
Huang et al. [104]	Commercially available MgO, Bischofite ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), fly ash, nano-	Paste: magnesium oxychloride (MOC) cement	Setting time, compressive strength, water resistance, XRD, FTIR,	- Nano-silica addition in MOCs containing fly ash + phosphoric acid further enhances the formation of amorphous aluminosilicate gel phases as a

	silica, phosphoric acid	Fixed molar ratio of active MgO: $\text{MgCl}_2:\text{H}_2\text{O} = 7:1:15$ 1% nano-silica, 30% fly ash, and 1% H_3PO_4 as admixtures	TGA-DSC, SEM	result of activated SiO_2 and Al_2O_3 . - Adding fly ash, phosphoric acid, and nano-silica together into the MOC pastes showed an improvement in the setting times, thermal stability, water resistance and compressive strength retention.
Gu et al. [105]	MgO, MgSO_4 , untreated flue gas desulfurization gypsum (FGDG), ADP, citric acid (CA), ammonium citrate tribasic (ACT)	Paste: Magnesium oxysulfate cement (MOSC), w/b = 0.3 molar ratio of MgO/MgSO_4 >5.1 FGDG replacement dosages of (0%, 25%, 50%, 75%, 100%) by wt. of MgSO_4 Mortar: sand/binder = 1.5	Flowability, setting time, compressive strength, water resistance, shrinkage, XRD, TG/DSC, SEM	- The additives (ADP, CA, ACT) promoted the formation of 5 $\text{Mg}(\text{OH})_2 \cdot \text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (5·1·7) phase. - FGDG reacted with MOSC to form amorphous phase (magnesium-sulfide-calcium- hydrate gel) - A higher compressive strength, water resistance and volume stability were achieved by the samples with 25% FGDG replacement.
Li et al. [106]	magnesia powder (86.44% MgO), magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), ammonia-soda residues (ASR)	Paste: magnesium oxychloride cement. Molar ratio $\text{MgO}:\text{MgCl}_2:\text{H}_2\text{O}$ = 8:1:12 ASR replacements (10%, 20%, 30%, 40%) wt. of magnesia.	Flowability, setting time, compressive and flexural strengths, shrinkage, water absorption, XRD, SEM	- The main components of ASR tested are CaCO_3 (56.1%), gypsum (25.5%), $\text{Mg}(\text{OH})_2$ (9.6%) and $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (3.7%). - ASR-MOC shows slight strength reduction as the dosage of ASR increases. - With the increase of ASR dosage, the formation of magnesium hydroxide chloride hydrate fades away gradually

3.1.5. Lime-clay ternary binders (LC^3)

The literature has well established the use of ternary blends to improve the durability performance of OPC and binary binder systems. Lime-clay (LC^3) binders utilize the benefits of calcined metakaolin-containing clays and the versatility they provide. Metakaolin reacts with Clinker to form CSH and CASH or can be activated on its own to produce NASH, which provides a space for improvement of

the pore structure of the hydrated clinker [107]. Another advantage of LC³ is the reduction in the use of clinker up to 50%, which is why it is considered a non-carbonate binder. Furthermore, LC³ systems utilize lime (calcium carbonate), from artificial or natural resources, which metakaolin reacts with to form aluminocarbonate hydration products which help in working as permanent storage for CO₂. Typical LC³ mixtures use the ratio of clinker:MK:lime of 50:30:20 or 55:30:15 in addition to gypsum at 5% to 10% [108]–[111]. Table 3-7 illustrates the latest developments in LC³ binders utilizing different industrial byproducts, mineral and chemical additives.

Table 3-7: Summary of latest developments in the field of LC3 binders

Reference	Materials used	Type of binder	Tests	Findings
Briki et al. [112]	Calcined clay, limestone, quartz, silica fume, OPC clinker, soluble anhydrite (SO ₃), calcium hydroxide	Paste: LC ³ cement Different w/b = (0.3, 0.4, 0.6)	XRD, XRF, TGA/SDTA, NMR, MIP	- The degree of reaction after 7 days did not increase by adding 5% of calcium hydroxide to LC³ system. - Similar slowing down of the reaction was observed where replacing metakaolin with silica fume. - The presence of portlandite or aluminium in the pore solution is not the only mechanisms that responsible for slowing down metakaolin reaction.
Huang et al. [113]	OPC clinker, calcined clay, limestone, gypsum, alkanolamines (triethanolamine (TEA) , triisopropanolamine (TIPA))	Paste: w/b = 0.4,	Compressive strength, isothermal calorimeter, XRD, SEM, MIP,	- TIPA enhanced the overall hydration degree of LC³ while TEA reduce the porosity of hardened LC³ pastes and enhance the strength at early ages. - Alkanolamines changed the morphology and chemical composition of the aluminate hydrates and C-A-S-H and reduced the porosity of hardened pastes. - The increased sulfate slowed the aluminate reaction by producing more ettringite.
Wang et al. [114]	Calcined clay, OPC cement, limestone, gypsum, silica fume, fine quartz Sand, polyethylene fibers.	Paste: High-strength strain hardening cement-based composites. w/b = 0.192, SP	Flowability, setting time, flexural and compressive strength, Fiber-matrix bond, XRD, XRF, TGA, MIP, MAS-NMR, SEM-EDX	The LC³ substitution resulted in: - slight reduction in the compressive strength, but the formation of highly polymerized C-A-S-H gel and ettringite enhanced the flexural strength of the plain matrices. - higher energy consumption during mixing and in shorter setting times of the fresh, plain matrices - increase the fiber-matrix bond strength and pullout energy.
Liu et al. [115]	OPC cement, limestone, calcined clay, gypsum, polypropylene (PP) fiber	Paste: w/b = 0.4	Compressive strength, XRD, SEM-EDS, MIP	- Obtained a compressive constitutive model of the composites. - The addition of PP fibers enhances the toughness, ductility, and energy absorption. However, it causes internal defects and flaws in the microstructures.
Zolfagharnasab et al. [116]	Kaolinitic calcined clay, OPC type II, limestone,	Paste and Mortar: w/b = 0.4, modified polycarboxylate	compressive strength, water absorption and sorptivity, XRD, XRF, TGA, FTIR, chloride diffusion	- The pozzolanic reactivity of calcined clays is affected by the metakaolin content and thermal activation process in addition to their crystallinity. - LC³ mortar had lower compressive strength, however it showed enhancement in the permeability and resistance against chloride ions ingress.
Li et al. [117]	Calcined clay, OPC cement, polycarboxylate (PCE) superplasticizers	Paste: w/b = 0.5 for OPC up to 1.2 for the neat calcined clay	Workability, XRD, zeta potential, total organic carbon (TOC) analysis	- The calcined clay surface adsorbs huge amounts of Ca²⁺ ions from the pore solution, which enabling adsorption of anionic PCE superplasticizers. - The commercially available PCE products can effectively fluidize OPC/CC blended cements.
Yu et al. [118]	OPC cement, siliceous fly ash,	Mortar: w/b = 0.5, sand/b = 3	Compressive strength, flowability, XRD,	- Replacement of OPC cement by 50-60% LC² obtained sufficient compressive strength, lower hydration heat, lower

	limestone-calcined clay (LC ²)	Five LC ² replacement levels (25%, 50%, 60%, 70%, 80%) by wt. of cement	SEM, isothermal calorimeter	environmental impact and material cost per unit strength, but reduced workability.
Musbau et al [119]	OPC cement, limestone, ground calcined laterite (CL), ground calcined clay (CC), 4 mm fine sand, 19 mm granite coarse aggregates	Concrete: w/c ratios (0.4, 0.5, 0.6), SP Control: (100% OPC) LC3: (55% OPC, 30% CC, 15% limestone), CLC: (70% OPC, 30% CL), LCLC: (55% OPC, 30% CL, 15% limestone).	Workability, compressive strength, water absorption, XRD, SEM	- No significant difference between the performance of the laterite-based and clay-based blended cement concrete. - Laterite can be used instead of clay in limestone calcined clay cements (LC³)
Avet et al. [120]	OPC cement, LC3–50 systems (50% clinker, 30% calcined Clay, 15% limestone, 5% gypsum), quartz	Paste: w/b = 0.5, PCE-SP	XRD, SEM-EDS pH and binding test: NaCl solutions, KOH	- The increase of pH leads to a decrease of the amount of bound chloride. - The decrease of the chloride content in the solid solution and the lower adsorption on C-A-S-H are responsible for the lower total chloride binding
Zhang et al. [121]	OPC cement, fly ash, metakaolin, limestone, silica sand, polyvinyl alcohol (PVA) fibers, polycarboxylate	Paste and mortar (ECC-LC ³)	Compressive and tensile strengths, Single-crack, XRD, DSC/TGA, MIP	- The ECC-LC3 required a higher water/solid ratio for adequate workability and fiber dispersion result in lower 28-day strength. - For the equivalent water content, using LC³ prompts the refining of ECC pore structure and densifying composite microstructure. - ECC- LC³ produces 28% less CO₂ emissions compared to the manufacture of OPC concrete, but only a slightly reduction in energy consumption and production cost.

3.1.5.1. Hydration and hydration products

The hydration of LC3 binders, according to Krishnan et al. [122], show two distinctive phases (Figure 3-6):

- 1- Phase I represents the hydration of the silicate.
- 2- Phase II represents the hydration of the aluminate.

The hydration products reported in the literature include [122]–[127]:

- 1- CSH as a result of the hydration of OPC
- 2- Etringite is a result of the reaction of gypsum with limestone and OPC.
- 3- CASH as a result of the hydration of the clay and OPC.
- 4- Hemihydrate and Monohydrate from the reaction of the lime with the clay and OPC.

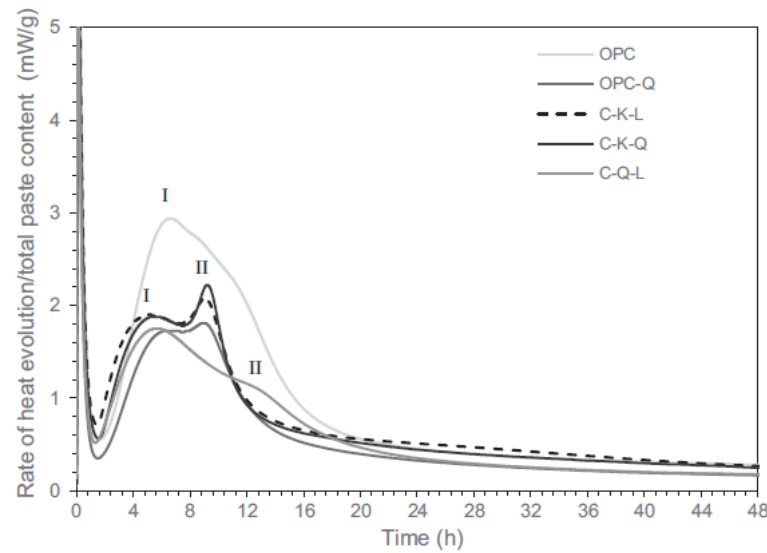


Figure 3-6: Heat of hydration of LC3. C-K-L represent OPC+metakaolin+lime[122].

3.1.6. Supersulfated binders (SSC)

Supersulfated binders are a special case of alkali-activated binders in which GGBFS and calcium sulphates are activated in an alkaline environment. The first recorded patent using this method is by Kuhl in 1909 [128], in which he patented the activation of GGBFS with sulfate. After World War II, some European countries adopted the use of SSC binders and standardized them due to the shortage in OPC [129]. Nowadays, SSC is experiencing a reemergence in the literature due to their very low energy demand and CO₂, their utilization of industrial byproducts, and their low heat of hydration.

Another aspect that favors the use of Supersulfated binders is their high chemical resistance in aggressive environments as well the possibility of using them as repair materials [130], [131]. Table 3-8 illustrates the latest developments in the field of Supersulfated binders.

Table 3-8: Latest developments in SSC binders

Reference	Materials used	Type of binder	Tests	Findings
Zhou et al. [132]	OPC, gypsum, GBFS, NaOH, N-lactate, K-lactate, silver nitrate, phenolphthalein, polycarboxylic SP, silica sand, basalt gravel,	Concrete: w/b = 0.35 SSC: (75% GBFS, 20% gypsum, 5% OPC) Activators:(2% N-lactate solution, 2.4% K-lactate solution, 1.2% NaOH)	Compressive and flexural strengths, chloride penetration, rapid carbonization, water absorption, XRD, SEM, FTIR, MIP	- High strength SSC concrete can be produced by adding lactates, while the addition of NaOH results in little enhancement. - The addition of lactates affects the hydration of GBFS, which produces more ettringite and enhances the microstructure of SSC concrete while NaOH fails. - The addition of lactates can effectively reduce the initial water absorption rate of SSC concrete. However, carbonation resistance is still significantly weak.
Cabrera-Luna et al. [133]	Pumice (PM), quicklime (CaO), Anhydrite-(An; CaSO ₄), Hemihydrate (HH; CaSO ₄ ·1/2H ₂ O)	Paste: SSC-PM, water/solid = 0.45.	Compressive strength, XRD, SEM, TGA/DTA	- The main hydration products were C–S–H and ettringite; minor phases included monosulfate, gypsum, portlandite and calcite. - The higher contents CaO (20%) and An or HH (15%) slowed the hydration reactions. - The SSC-PM showed emissions at least 67% lower than OPC.
Pinto et al. [134]	OPC, GBFS, phosphogypsum, gneiss stone as fine and coarse aggregates.	Concrete: (w/c = 0.40, 0.46, 0.52) Cement/ fine Agg. /coarse Agg. = 1:1.4:2.1	Slump, carbonation depth, chloride migration, XRD, XRF, SEM-EDS	- The exclusive formation of the hydration products (C-S-H and ettringite) in the SSC concretes results in poor resistant to carbonation. - SSC concrete performed very good in terms of resistance to chloride penetration.
Sonebi et al. [135]	OPC, GGBS, Anhydrite (ANH)	Grout: w/b of (0.34–0.44) GGBS (60%–80%) ANH (0%–20%)	Slump, plate cohesion, Marsh cone, yield stress, plastic viscosity, induced bleeding, permeability, compressibility, compressive strength, SEM, isothermal	- C-S-H is the main reaction product with presence of embedded unreacted slag grains in the structure. - Addition of ANH to SSC grouts caused some micro voids which led to lower compressive strength. - Developed statistical models and iso response curves to capture the trends of the tested parameters

			calorimeter, pH-value	
Liu et al. [136]	OPC, GBFS, phosphogypsum (PG)	Paste: w/b = 0.4 SSC cement (80% GBFS, 15% PG, 5% OPC clinker)	Consistency, setting time, compressive strength, XRD, XRF, SEM, pH-value	- Best strength performance at early and late stage were achieved through calcination at 600 °C for 2 h, while the faster setting time and better workability was obtained by calcination at 350 °C for 2 h. - Calcination of phosphogypsum (PG) minimized the adverse effects of the impurities which enhances the performance of SSC in all aspects.
Gracioli et al. [137]	GBFS, phosphogypsum (PG), KOH	Paste and mortar: w/c 0.4	compressive strength, isothermal calorimeter, XRD-DSC, SEM-EDS, pH-value	- The calcination temperature of 350 °C was shown to be only adequate for cements with lower calcium sulfate content. - Lower compressive strength was related to the higher formation of secondary gypsum. - The formation of C-S-H was more in samples with calcined PG at 650 °C and occurred between the ettringite needles leading to a less open microstructure and higher compressive strength. - PG and GBFS having lower alumina content could be considered as raw materials adequate for producing SSC by adjusting the calcination temperature and content of PG
Pinto et al. [138]	OPC, GBFS, phosphogypsum, gneiss stone as fine aggregates.	Mortar: SSC cement cement: sand: water = 1:3.2:0.60	Sodium and Magnesium sulfates attack: Compressive and tensile strengths, shrinkage, mass loss, UPV, XRD, SEM-EDS, TG/DTG	- SSC mortar showed good durability against sodium sulfate attack but presented an expansive behavior when exposed to magnesium sulfate. - The expansion of SSC mortars exposed to magnesium sulfate solution was related to the low portlandite formulation, which anticipated the attack of C-S-H. Also, the non-formation of the brucite layer accelerated the entry of this type of sulfate.
Liu et al. [139]	Lime, OPC, PG, GGBS	Pate: w/b = 0.4 SSC cement (85% GGBS, 15% lime-PG mixture, 5% OPC)	Consistency, setting time, compressive strength, P ₂ O ₅ content and pH-value, XRD, XRF,	- The addition up to 2% Lime can effectively remove the P₂O₅ to form Ca₃(PO₄)₂. - The pH value of PG increased with the increase of Lime content. - Lime neutralization significantly accelerated the hydration and shortened the setting time of SSC. - The main hydration products of Lime-PG mixture incorporated SSC were

				identified as ettringite and C-S-H, which contributes to the compressive strength.
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3.1.6.1. Hydration and hydration products

The hydration of SCC depends on the chemical composition of GGBFS as well as its fineness. Finer GGBFS has been reported to react faster as well as GGBFS containing high alumina compounds. The exact stages of hydration are not fully examined in the literature compared to the stages of OPC hydration [129]. However, it is understood that hydration starts with the dissolution of GGBFS and the formation of ettringite. Ettringite is responsible for the early strength up to 7 days, while the formation of CSH from GGBFS dissolution and hydration is responsible for later age strength gain [140], [141]. Other hydration products have been observed, like hydrotalcite and monoaluminoferrite (AFM) phases as well.

3.2. Local Minerals and Byproducts

Saudi Arabia is located on the Arabian plate and sandwiched between the Persian plate to the east, the African plate to the west, the Indian plate to the south, and the Eurasian plate to the north. It has an area of 2.15 million km², making it the largest country in the Middle East and the 12th worldwide. The country's geography ranges from arid deserts in the east, to plateau in the center, to mountainous regions in the west. Due to its large area and varying geography, it has a lot of natural resources that can be used in the production of non-carbonate concrete. In addition, the country is experiencing an industrial boom with a reported mining sales of \$3.8 billion in 2018, according to Ma'aden (The Saudi Arabian Mining Company) in addition to an oil net income of \$46.9 billion in the first half of 2019 [142], [143]. As a result of industrialization, numerous byproducts are produced and require efforts in managing and reutilization. This section discusses the physical and chemical properties of possible local minerals and industrial byproducts that can be used to develop non-carbonate concrete.

3.2.1. Limestone and limestone powder (LSP)

Limestone is a white calcareous sedimentary rock that contains carbonates as the major portion of its constituents. It is used in the production of cement, as a filler for asphalt concrete, and as an aggregate in cement concrete in addition to many other uses in other industries. The Saudi Geological Survey (SGS) lists more than a hundred limestone quarry sites around the Kingdom, as shown in Figure 3-7. The majority of limestone sites are located in the central region of the Kingdom as well as the eastern region, with some sites in the west and northern regions. Limestone in the Kingdom comprises calcite (CaCO_3) with traces of silica and dolomite (CaMgCO_3) in the eastern region and feldspars and hematite in the other regions. It is characterized by its high alkalinity, moderately porous structure, and moderate compressive strength. An example of the chemical composition and physical characteristics is shown in tables 3-9 and 3-10 based on SGS reports, the work of Maslehuddin et al. [144] and Abd El-Aal and Masoud [145].

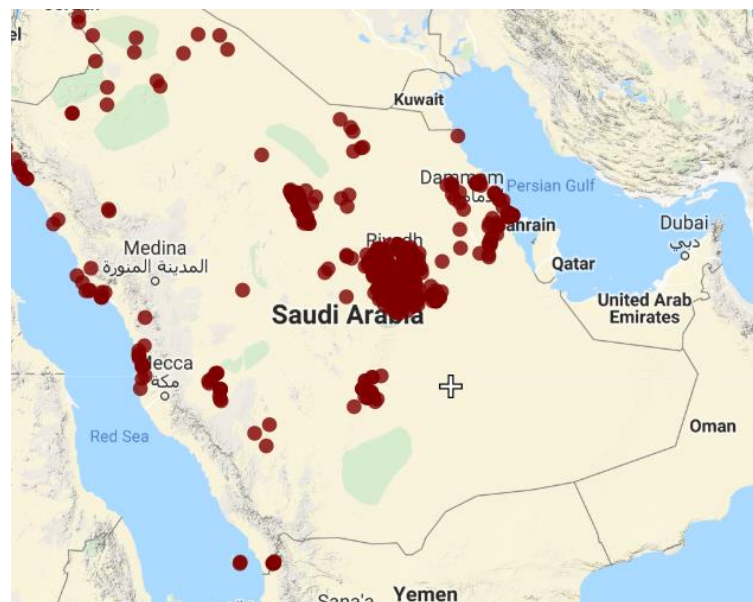


Figure 3-7 limestone sites in the Kingdom [146]

Table 3-9: Example composition of local limestone[144], [145]

	Central region	Eastern region
Calcite	91.5%	95%
Feldspar	3.8%	-
Others	1.2% (As hematite and dolomite)	5% (Mainly as dolomite)

Table 3-10: Physical properties of local limestone[144]

Property	Central Region	Eastern region
Specific gravity	2.5	2.3
Absorption (%)	4.6 to 4.9	4.1 to 4.2
Compressive strength (MPa)	32 to 42	38 to 49
Chloride content	0.011 to 0.066	0.017 to 0.022

Limestone powder is a byproduct of the quarrying of limestone in the industry. It is characterized by being composed mainly of calcium carbonate and having no pozzolanic reactivity. The typical chemical composition of LSP is shown in Table 3-11. Despite that, LSP has a wide array of applications in the construction industry. It is used as a filler in pavements as well as concrete. The possible applications in non-carbonate concretes are:

- 1- As an activator in alkali-activated binders.
- 2- As a major replacement for cement in eco-friendly ultra-high performance concrete up to 70% [125].
- 3- As a major component in lime-clay based ternary binders.
- 4- As a source of silica and calcium in CSA binders.
- 5- In the manufacturing of cement-free bricks [147].

Table 3-11:Chemical composition of LSP[148]

Oxide	Proportion (%)
SiO ₂	11.79
CaO	45.7
Al ₂ O ₃	2.17
Fe ₂ O ₃	0.68
MgO	1.8
K ₂ O	0.84
Na ₂ O	1.72
Loss on Ignition	35.1
Moisture	0.2

3.2.2. Gypsum

Gypsum is a mineral that is composed of calcium sulphate hydrate and is derived from the Greek word “gypsos” after a town in Cyprus. It is the main component in the plaster manufacturing of Plaster of Paris and has numerous uses in various industries. Such uses include but are not limited to:

- 1- As a fertilizer in agriculture.
- 2- An ornamental finishing construction material.
- 3- An additive to the clinker to prevent flash setting [149].
- 4- A sculpting material in art installations.
- 5- As a binding agent in water clarification to capture some metals like Arsenic [150].
- 6- As a major component in the manufacture of cement-free bricks [147].

Gypsum is mined in the Kingdom in over 30 sites, as illustrated in Figure 3-8, with the majority of those sites being located in the eastern and western regions. The chemical composition is shown in Table 3-12, as well as its XRD graph (Figure 3-9).

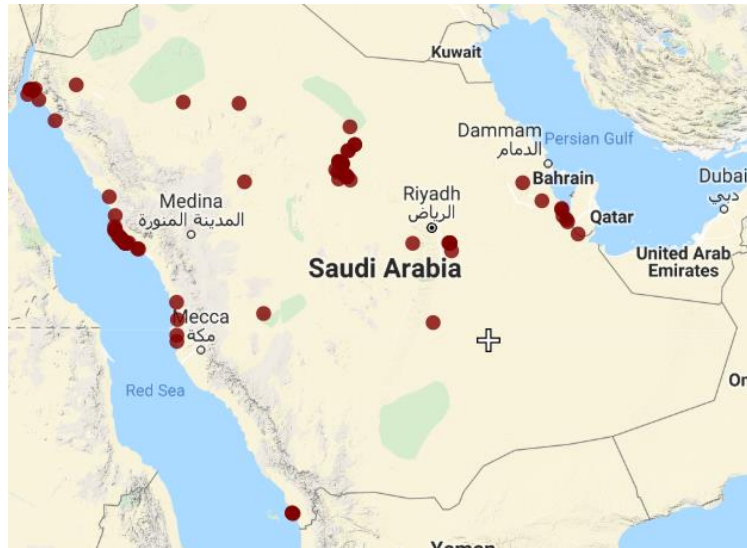


Figure 3-8 Gypsum sites in the Kingdom[146]

Table 3-12: Chemical composition of gypsum[151]

Oxide	Proportion
CaO	32.57
SO ₃	45.5
H ₂ O	20.93



Figure 3-9 XRD analysis of gypsum (G: Gypsum)[151]

Possible uses of gypsum in the development of non-carbonate binder include:

- 1- As an activator in AAB as well as an additive to control shrinkage.

- 2- In the development of sulfoaluminate and supersulfated binders.
- 3- As an additive in lime-clay ternary concretes to control shrinkage and setting time.

3.2.3. Clay

Clay is a natural finely-grained soil that contains clay minerals as well as traces of silica and other metal oxides. It has been used since the dawn of humanity for construction, pottery, and agriculture.

Its uses include but are not limited to:

- 1- The making of pottery upon firing.
- 2- As an ingredient in the making of ceramics and porcelains.
- 3- As an insulation material in traditional houses when mixed with straw.
- 4- Mixed with silts and sand to make loam which is farming soil.
- 5- In the construction of earth dams, due to their low permeability.
- 6- As a source for alumina and iron oxide in the manufacturing of cement.
- 7- As an ingredient in the manufacturing of traditional bricks.

Clay is mined in the Kingdom in more than 70 locations, as illustrated in Figure 3-10. The chemical composition varies from a region to another. Clays in the eastern region have more expansive minerals like montmorillonite and bentonite, as shown by Azam [151], who studied the role of expansive soils in the eastern region in the consolidation of soils. He reported the clays from the Qatif region to contain 13% alumina, 50% silica, and 21% water in addition to other oxides like K_2O and MgO , and CO_2 , as shown in Table 3-13. On the other hand, Mohsen and Al-Maghraby [152] studied the composition of three types of clay in the western region and compared their chemical composition to imported metakaolin. They reported the western region clays having less expansive elements with more alumina, iron oxide, silica, and lower calcium oxide, as shown in Table 3-14.



Figure 3-10 Clay/Kaolinite sites in the Kingdom [91]

Table 3-13: Clay composition in the eastern region[151]

Oxide	Proportion
K ₂ O	1.452
MgO	3.396
FeO	0.37
Na ₂ O	0.565
CaO	3.87
Al ₂ O ₃	12.9
SiO ₂	50.02
SO ₃	0.465
CO ₂	4.773
H ₂ O	21.44

Table 3-14: Chemical composition of clays from the western region[152]

Oxide	Jeddah 1	Jeddah 2	Medinah
SiO ₂	49.28	69.23	53.77
TiO ₂	0.06	0.61	0.93
Al ₂ O ₃	35.69	11.79	15.84
Fe ₂ O ₃	0.97	6.49	9.01
MnO	-	0.17	0.15
MgO	0.07	0.44	2.47
CaO	0.05	1.13	1.08
Na ₂ O	0.28	0.16	0.68
K ₂ O	0.42	0.27	1.82
P ₂ O ₅	0.12	0.21	0.4
SO ₃	0.11	0.11	0.08
Cl	-	0.14	0.14
LOI	12.55	9.15	12.5

The possible uses of local clays in the preparation of non-carbonate binders are:

- 1- As a precursor in alkali-activated binders after calcination.
- 2- As a major component in LC³ binders after calcination.
- 3- As a source of silica in magnesium silicate binders.
- 4- As a source for silica in the production of α -C₂S binders.
- 5- As a partial replacement and a raw material in the manufacturing of calcium sulfoaluminate binders.

3.2.4. Natural pozzolans (NP)

Natural pozzolans are alumina and silica-containing powder minerals that are the results of volcanic activity. They do not exhibit hydraulic activity on their own but react in the presence of alkaline materials to form hydration products similar to OPC like CSH and alumina hydration products. They

are added in raw form or after calcination to OPC and have been reported to increase the mechanical properties of binary and ternary concretes as well as improve and refine their microstructures [153]–[158]. Pozzolans in the Kingdom are mined in the northwestern, western, and southwestern regions along the Sarawat and Shammar mountains, as shown in Figure 3-11. Pozzolans are composed mainly of silica, alumina, and iron oxides, as shown in Table 3-15.



Figure 3-11 Pozzolan sites in the Kingdom [91]

Table 3-15 Chemical composition of different pozzolans in the western region[159]

Oxide	City			
	Yanbu	Rabigh	Tabuk	Jeddah
SiO ₂	42.09	42.69	41.14	42.75
Al ₂ O ₃	16.43	17.2	16.44	16.04
Fe ₂ O ₃	14.97	14.88	17.25	14.4
CaO	9.51	10.55	11.15	8.95
MgO	3.47	2.92	1.22	3.71
SO ₃	0.19	0.39	0.15	0.15
K ₂ O	0.81	0.29	0.95	0.85
Na ₂ O	0.15	0.11	0.11	0.22
LOI	2.7	2.6	3.2	2.9

Natural pozzolans possess great potential in the development of non-carbonate binders, and their possible uses include:

- 1- As a precursor in the development of alkali-activated binders.
- 2- An ingredient in the manufacturing and as supplementary cementitious material in belite-ye'elimte.
- 3- As a source of silica in magnesium-based binders.
- 4- As a source of iron and alumina in belite-ye'elimite-ferrite binders.
- 5- As a source for silica in the development of hydrothermal α -C₂S cement.

3.2.5. Marble dust (MD)

Marble is a metamorphic rock that results from the pressurizing and heating of calcareous sedimentary rocks. It is used in the tiling industry and as an ornamental finishing element. It is quarried in the western and central regions of the Kingdom, as shown in Figure 3-12. Marble dust is a byproduct of the quarrying of marble (collected as dust) and the cutting of marble slabs (collected as sludge). Marble dust is mainly composed of calcium carbonate and silica, similar to limestone powder. An example of its chemical composition is shown in Table 3-16 based on the work of Qadhi [160], who analyzed the chemical composition of marble depositions in the Jeddah area.



Figure 3-12 marble sites in the Kingdom [91]

Table 3-16: Marble composition from the western region[160]

Oxide	Proportion
Fe ₂ O ₃	0.02
TiO ₂	0.01
CaO	48.7
K ₂ O	0.01
SiO ₂	11.7
Al ₂ O ₃	0.09
MgO	4.4
LOI	34.2

The possible uses of marble dust are similar the uses of limestone powder due to their similar chemical composition, which are:

- 1- As an activator for alkali-activated binders as well as a source for additional silica.
- 2- As a major constituent of lime-clay ternary binders.
- 3- As a partial replacement for cement in more environmentally friendly UHPC.

3.2.6. Granite dust (GD)

Granite is an igneous rock that forms from the slow cooling of magma and contains crystalline forms of silica, alumina and/or iron oxides. It is used as foundations in traditional structures as well as tiling and flooring elements in modern structures due to its aesthetic and colorful appearance. Granite is quarried along the northwestern, western, and southern regions in the Kingdom, as shown in Figure 3-13. According to Bakhsh and Alderton [161] and Radain et al. [162], granites in the northwestern and western regions are mainly composed of silica at 70% on average, alumina at 12%, sodium oxide at 4%, and iron oxide at 2.5% with other traces of calcium and metallic oxides.



Figure 3-13 Granite sites in the Kingdom [91]

Granite dust is the byproduct of the quarrying of granite and has a chemical composition similar to granite. With the high silica and alumina contents, the possible uses for granite dust in the development of non-carbonate binders are:

- 1- As a precursor in the development of alkali-activated binders.
- 2- As a major constituent in lime-clay ternary as a replacement for the clay after calcination.
- 3- As a source of silica in the development of Celitement.

4- In the development of CSA binders as well as BYF and BAY.

3.2.7. Cement kiln dust (CKD)

CKD is a byproduct of the manufacturing of cement during the sintering process. When the raw materials are introduced to the kiln, lighter raw particles containing alkalis, chlorides, and sulphates escape the kiln with the exhaust gasses. The fume is collected and precipitated by special filtration mechanisms resulting in the collection of CKD. Each ton of cement produces 70 kilograms of CKD, and it represents a danger to the health of animals and plants in the surrounding areas due to its high alkalinity and fine structure [163]. The chemical composition of CKD is similar to that of cement and contains higher amounts of sulfate, chloride, and zinc, as shown in Table 3-17.

Table 3-17 Chemical composition of CKD[163]

Oxide	proportion
CaO	49
SiO ₂	17
Al ₂ O ₃	4.24
Fe ₂ O ₃	2.89
K ₂ O	2.18
MgO	1.14
Na ₂ O	3.84
P ₂ O ₅	0.12
SO ₃	3.56
Chloride	6.9
LOI	15.8
ZnO (ppm)	65.8

Numerous studies have been conducted on the use of CKD as a partial substitution to OPC in binary and ternary concrete systems. The results show improvement in the mechanical and durability aspects of such systems up to a certain replacement threshold. The possible uses of CKD in the development of non-carbonate binders are:

- 1- As a precursor in the development of alkali-activated binders.
- 2- As a replacement for the lime in lime-clay ternary binders.
- 3- As a partial replacement to GGBS in supersulfated binders.

3.2.8. Red mud (RM)

Red mud is a byproduct of alumina and aluminum mining and production. It consists mainly of alumina oxide, calcium oxide, and iron oxide and is highly alkaline as shown in Table 3-18.

Table 3-18: Red mud chemical composition[29]

Oxide	Proportion (%)
SiO ₂	20.4
Al ₂ O ₃	24.5
CaO	12.9
Na ₂ O	11.5
K ₂ O	0.9
Fe ₂ O ₃	9.5
SO ₃	0.7
LOI	1.4

According to the international institute of aluminum, each ton of alumina produces 1 to 1.5 tons of red mud [164]. In 2018, the Saudi Arabian Mining Company (Ma'aden) reported a net production of 1.8 thousand tons of alumina which means 1.8 to 2.7 thousand tons of red mud was produced [165].

Efforts to utilize red mud in the engineering community include the use of red mud as supplementary cementitious material, as an ingredient in the manufacture of lower quality cement and brick, and in soil stabilization. Due to the high alumina and silica content, red mud has the possible applications in the development of non-carbonate binders:

- 1- As a precursor in alkali-activated binders after calcination.
- 2- As a replacement for the clay in lime-clay binders.

3.2.9. Electric Arc Furnace Dust (EAFD)

Electric arc furnace dust (EAFD) is a byproduct of the steel manufacturing industry. When pig iron is heated in arc furnaces, some particles of iron, zinc, and other metals evaporate and are collected in special filtration systems. The collected powder is very fine and highly dense and is composed mainly of iron oxide and zinc oxide, as shown in Table 3-19.

Table 3-19 Elemental chemical composition of EAFD[163]

Element	Percentage
Fe	33.6
Zn	10
Ca	9.4
Na	2.6
Si	2.4
Mg	2.3
Mn	1.3

Each ton of iron produced is estimated to generate 20 kilograms of EAFD. The Kingdom is estimated to have produced 5.2 million tons of steel in 2018, equivalent to 104 thousand tons of EAFD [166]. The use of EAFD in the development of non-carbonate binders include:

- 1- Development of belite-ye'elimite-ferrite binders.
- 2- As a raw ferrite source in the development of CSA.

3.2.10. Steel Slag (SS)

Steel slag is the byproduct of the steel manufacturing industry. It is reported that it constitutes 20% of the steel output in the industry. It is mainly composed of calcium, silicon, and iron oxides resulting from melting pig iron to produce steel. The typical chemical composition is shown in Table 3-20.

Table 3-20 Typical chemical composition of steel slag [167]

Oxide	Proportion
CaO	41.4
SiO ₂	14.96
Al ₂ O ₃	0.84
Fe ₂ O ₃	7.9
MgO	5.49
K ₂ O	0.12
FeO	13.53
Others	15.76

The use of steel in the production of non-carbonate binders include:

- 1- Development of BYF and BAY binders.
- 2- As a partial replacement for limestone and LSP in the production of AAB, CSA, and LC³.

3.2.11. Oil ash (OA)

Oil ash is the byproduct of burning heavy oil in oil-based power plants. During power generation, oil is burned, which leads to the suspension of unburned materials like sulfur and carbon with the exhaust gasses. The exhaust gasses are collected through specialized filtration baghouses which precipitate oil ash. It consists mainly of carbon and sulfur in addition to traces of alumina, calcium, and iron. In

addition, oil ash contains high traces of heavy metals, making it a hazard to the environment in landfills. Each burned barrel of heavy oil is estimated to produce 0.5kg of oil ash [168]. According to the Saudi Arabian Monitory Authority (SAMA), the domestic consumption of crude oil in 2018 was 150 million barrels, equivalent to 75 million kilograms of oil ash [169]. The typical chemical composition is shown in Table 3-21.

Table 3-21 Chemical composition of oil ash[168]

Oxide	Proportion	Element	Proportion	Metal	concentration (ppm)
CaO	4.72	C	69.16	Ba	101.3
SiO ₂	2.09	H	1.15	Sr	1132
Al ₂ O ₃	3.34	N	1.19	Cr	320
Fe ₂ O ₃	1.49	S	7.32	Zn	532.8
MgO	0.82			Ni	190
K ₂ O	0.4			Ti	862
P ₂ O ₅	3.12			Zr	54.6

Oil ash possesses no hydraulic activity and is used only as mineral filler to improve workability due to its very fine structure or as a black pigmentation for aesthetic purposes.

3.2.12.Waste calcium carbonate and sulphate

Carbon sequestration is a process in which CO₂ is reacted with active calcium oxide (known as quicklime or burnt lime) to form calcium carbonate as a form of carbon dioxide storage in industries where CO₂ is generated. The chemical composition is totally made up of CaCO₃. The use of calcium carbonate from sequestration in the production of non-carbonate binders is similar to the use of LSP, which include:

- 1- As an activator in alkali activated binders.

- 2- As a major replacement for cement in eco-friendly ultra-high performance concrete up to 70%.
- 3- As a major component in lime-clay based ternary binders.
- 4- As a source of silica and calcium in CSA binders.
- 5- In the manufacturing of cement-free bricks.

Calcium sulphate is a byproduct of the desulphurization of fluegas in the oil and gas industry. The precipitated material from desulphurization has the same chemical composition as gypsum. Therefore, its use in producing non-carbonate binder are the same as those of gypsum, which include:

- 1- As an activator in AAB as well as an additive to control shrinkage.
- 2- In the development of sulfoaluminate and supersulfated binders.
- 3- As an additive in lime-clay ternary concretes to control shrinkage and setting time.

3.2.13.Silicomanganese dust (SMF)

Silicomanganese dust or manganese furnace dust (SMF) is a dark brown powder that forms as a result of the production of ferromanganese alloys. The exhaust rises to the top during the melting process and is precipitated by venturi collectors or baghouses, then collected and moved for landfilling. According to Arnoldussen et al. [170], over 60% of the produced MFD is spherical and has a size less than 100nm, and mainly consists of silica and manganese with traces of other metals (Figure 3-14) which represents a major risk for the respiratory track in the case of inhalation. Each MFD does not possess hydraulic or pozzolanic activity on its own, but some work has been conducted on using it as a silica source for the development of AAB, which showed promise [171] as well using it to improve workability in traditional binders. The chemical composition of MFD is shown in Table 3-22.

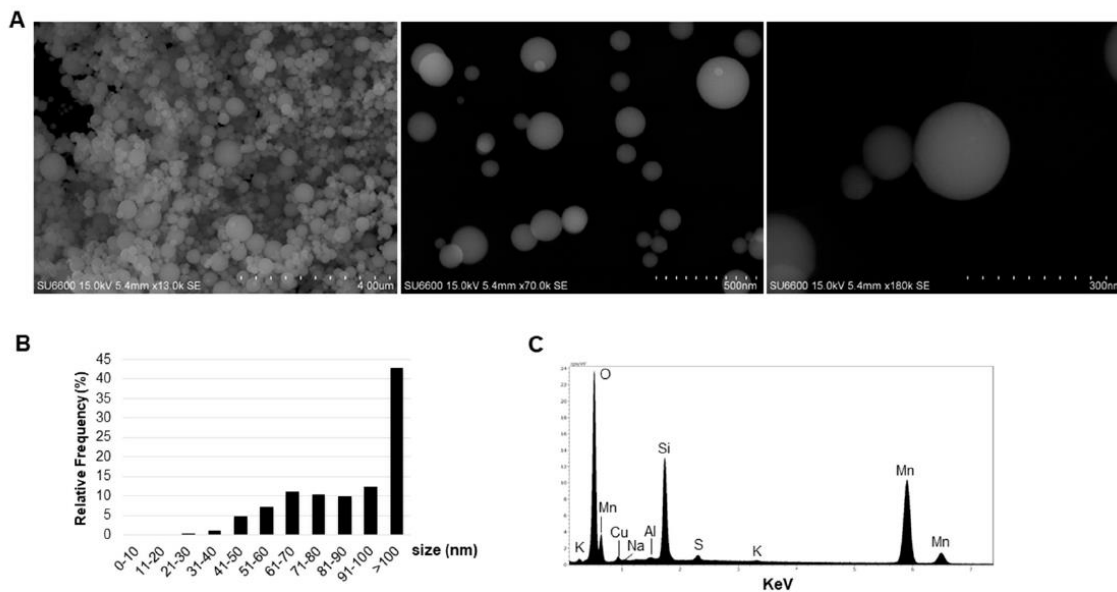


Figure 3-14 a)SEM of SMF. b)Size distribution of SMF. c) Elemental composition of SMF [170]

Table 3-22: Chemical composition of SMF [171].

Oxide	Proportion(%)
SiO ₂	14.57
Al ₂ O ₃	1.24
Fe ₂ O ₃	2.37
CaO	4.61
MgO	4.78
K ₂ O	27.25
SO ₃	6.16
MnO	33.13
Na ₂ O	1.64
Cl	3.28
ZnO	0.73
LOI	5.7

Possible uses of MFD in non-carbonate binders include:

- 1- As a source of silica in the development of AAB.
- 2- As a workability enhancer in Mg-based binders, CSA binders, LC3 binders, and SSC binders.

3.2.14. Phosphogypsum (PG)

PG is a by-product of the synthesis of phosphoric acid by reacting phosphate minerals with sulfuric acid. It mainly consists of calcium sulphate hydrate with traces of phosphoric acid, phosphates, and in some cases, some traces of radioactive elements like uranium, thorium, radium, and polonium. A typical composition of PG is provided in Table 3-23. PG has been gaining popularity as a substitute for gypsum in developing non-carbonate binders like supersulfated binders and can be used before or after neutralization[172], [173].

Table 3-23: Chemical composition of PG [172]

Oxide	Proportion (%)
Na ₂ O	0.04
MgO	0.07
Al ₂ O ₃	2.1
SiO ₂	6.69
P ₂ O ₅	1.37
SO ₃	49.79
K ₂ O	0.25
CaO	38.13
Fe ₂ O ₃	0.91
LOI	0.65

PG has the same possible applications in the development of non-carbonate binders as gypsum which include:

- 1- As an activator in AAB as well as an additive to control shrinkage.

- 2- In the development of sulfoaluminate and supersulfated binders.
- 3- As an additive in lime-clay ternary concretes to control shrinkage and setting time.

3.3. Summary

The development of non-carbonate binders that are more environmentally friendly is an essential task for the scientific and engineering community. The demand for more concrete structures is rising and is expected to rise with the increase in the world population. This chapter discussed the non-carbonate binders available in the current literature, which included: Alkali activated binders, α -C₂S binders, CSA binders, magnesium-based binders, LC³ binders, and supersulfated binders, including their hydration and constituents. In addition, the chapter discussed the chemical composition of local minerals and industrial by-products as well their possible utilization in the preparation of environmentally friendly non-carbonate binders. A summary of the local minerals and byproducts and their possible uses is provided in Table 3-24.

Possible areas of research for the future utilizing the information provided in this report are:

- 1- Development of alkali activated binders utilizing local clays that are activated by LSP and Calcium carbonate from the CO₂ sequestration.
- 2- Studying the hydration and corrosion performance of LC³ binders developed from local materials and exposed to the local environment.
- 3- Studying the feasibility of producing CSA binders utilizing local materials and existing manufacturing facilities.
- 4- Studying the hydration and development of hydrothermal α -C₂S binders made with local silica sand.

Table 3-24: Summary of the Minerals/Byproducts and their possible uses

Mineral/ Byproduct	Non-Carbonate Binder (NCB)					
	AAB	α -C ₂ S	CSA	MGBB	LC ³	SSC
	Justification for possible addition					
LSP	Activator/Filler	Filler	Filler	Filler	Main constituent	Activator/Filler
Gypsum	Activator/Shrinkage compensator	Setting control/Shrinkage compensator	Main constituent	Shrinkage control	Setting control/Shrinkage control	Activator/Shrinkage control
Clay	Precursor	Main constituent	Main constituent/filler	Main constituent	Main constituent	Filler
NP	Precursor	Main constituent	Main constituent/secondary hydration	Main constituent/secondary hydration	Secondary hydration/filler	Secondary hydration/filler
MD	Activator	Filler	Filler	Filler	Lime replacement	Activator/Filler
GD	Precursor	Main constituent	Main constituent/filler	Main constituent	Clay replacement/secondary hydration/filler	Secondary hydration/Filler
CKD	Activator	Filler	Filler	Filler	Cement replacement/Filler	Activator/Filler
RM	Precursor	Filler	Main constituent	Filler	Clay replacement/Secondary hydration/Filler	Secondary hydration/Filler
EAFD	Workability enhancer/Filler	Filler	BYF constituent/Filler	Workability enhancer/Filler	Workability enhancer/Filler	Workability enhancer/Filler
SS	Precursor/Filler	Filler	BYF constituent/Filler	Main constituent/Filler	Filler	Filler
OA	Workability enhancer/Filler	Workability enhancer/Filler	Workability enhancer/Filler	Workability enhancer/Filler	Workability enhancer/Filler	Workability enhancer/Filler
Waste carbonate	Activator/Filler	Filler	Filler	Filler	Main constituent	Activator/Filler
Waste sulphate	Activator/Shrinkage compensator	Setting control/Shrinkage compensator	Main constituent	Shrinkage control	Setting control/Shrinkage control	Activator/Shrinkage control
SMF	Precursor/Filler	Main constituent/Workability enhancer/ Filler	Main constituent/Workability enhancer/Filler	Main constituent/Workability enhancer/Filler	Workability enhancer/Filler	Workability enhancer/Filler
PG	Activator/Shrinkage compensator	Setting control/Shrinkage compensator	Main constituent	Shrinkage control	Setting control/Shrinkage control	Activator/Shrinkage control

CHAPTER 4. CHARACTERIZATION OF LOCAL MATERIALS, INITIAL TRIALS, AND OPTIMIZATION

4.1. Overview

This chapter presents the results of developing alkali-activated binders (AABs) utilizing locally-available natural minerals and industrial byproducts as precursor materials in addition to sodium hydroxide and sodium silicate as activators. Four selected precursor materials (natural pozzolana, limestone powder, red mud, and silicomanganese fume) were characterized in terms of their physical and chemical properties. The proportioning of the four precursor materials was optimized based on the results of flow, setting time, and compressive strength tests conducted on trial mortars. After reaching to an optimal proportioning of the four precursor materials, the natural pozzolan was partially replaced by ordinary Portland cement (maximum by 30%) to significantly enhance the properties of the AABs. The activator to precursor ratio (A/P), sodium silicate to sodium hydroxide ratio (NS/NH), sodium hydroxide (NH) molarity, and water to precursor ratio (W/P), were varied from 0.3 to 0.6, 1 to 2.5, 8 to 14 M, and 0.35 to 0.55, respectively. The influence of those activation parameters (at optimally selected proportioning of precursor materials) on the physical and mechanical properties of AABs besides their mineral composition and morphology was investigated and optimized. Additionally, the effect of curing regimes (oven, steam and ambient-air curing) on the performance of AABs was also examined. The results of this chapter enabled to identify the optimum proportioning of the selected precursor materials, optimum combination of A/P ratio, NS/NH ratio, NH molarity, and W/P ratio for producing the AABs with enhanced performance.

4.2. Materials

4.2.1. Precursor materials

OPC was obtained from the Eastern Province Cement Company (Kharasaniyah, Eastern Province, Saudi Arabia), while LSP was obtained from Shibh Al Jazeera Contracting Company (Khurais, Riyadh Province, Saudi Arabia). NP, SMF, and RM were obtained from Kifah Readymixture and Blocks (Second Industrial City, Eastern Province, Saudi Arabia), Gulf Ferro Alloys Company (Jubail, Eastern Province, Saudi Arabia), and Ma'aden (Al-Baaethah, Al-Qassim Province, Saudi Arabia), respectively. The PMs were used in the condition they were received except the RM which was pulverized by a commercial spice grinder with stainless steel grinding bowl and blades to pass an ASTM E11 standard no.100 sieve. The characterization of the raw precursor materials (PMs) is discussed further in sections 4.7.1 and 4.8.1.

4.2.2. Alkali activators

Commercial-grade sodium hydroxide (NaOH) flakes with 95% purity were dissolved in distilled water procured from a local distillation company at different concentrations to achieve the required molarity. The mixture was stirred for a couple of hours until the sodium hydroxide was totally dissolved. Then it was stored in sealed polyethylene bottles until it cooled down to room temperature. Sodium silicate (Na_2SiO_3) solution with a specific gravity of 1.385 was obtained locally. The solution contained 62.5% water, 28.5% SiO_2 and 8.5% Na_2O with a silica modulus (i.e., $\text{SiO}_2/\text{Na}_2\text{O}$) of 3.3. The sodium silicate solution was mixed at different NS/NH ratios for an hour with the previously mentioned sodium hydroxide solution 24 hours ahead of use in the AAB preparation to ensure homogeneousness and negate any effects of temperature variance on the binders'

characteristics. Additional potable water was added whenever necessary to achieve the required W/P ratio.

4.2.3. Fine aggregate

Dune sand from the region of the ad-Dahna desert in the Eastern Province of Saudi Arabia was used as a fine aggregate in the preparation of the binders. The sand had a fineness modulus, water absorption, moisture content, and bulk specific gravity of 2.9, 0.58%, 0.12%, and 2.64, respectively. The sand was stored at room temperature in plastic drums sealed with tight lids to maintain the same moisture content in all prepared binders.

4.3. Precursor materials optimization

A precursor for producing AAB consisted of a blend of the previously mentioned PMs and used as a source of aluminosilicates. The precursor optimization (i.e., optimum proportioning of the PMs) was carried out by first considering NP as a sole PM and then partially replacing it with the other PMs (RM, SMF, LSP, and OPC) until a blend of PMs used for preparing mortar with adequate flow, setting time, and strength was reached. While optimizing the proportioning of PMs, the levels of activation parameters (i.e., A/P ratio = 0.5, NS/NH ratio = 2, NH molarity = 14 M, and W/P ratio = 0.35) were kept invariant based on the information available in the literature. A fine aggregate to precursor (S/P) ratio of 2.0 was used to prepare the mortar. The results of flow, setting time (initial and final), and compressive strength (3, 14, and 28-day after steam curing for 24 hours) tests are presented in Table 4-1, for each of ten trials of the proportioning of precursors. The standards of these tests are described in section 4.7. The standard deviations for measured flow, initial setting time, final setting time, and 28-day compressive strength ranged between 2 to 4 mm, 1 to 31 min, 1 to 43 min, and 0.1 to 1.7 MPa, respectively.

Based on the test results shown in Table 4-1, the precursor P9, containing 20% OPC, 10% LSP, 40% NP, 10% SMF and 20% RM was considered to be most optimum with acceptable flow, setting time and strength.

Table 4-1 Optimization of proportioning of precursors

Precursor Trial	Proportion of PMs (% by wt.)					Flow (mm)	Initial setting (min)	Final setting (min)	3-Day f_c (MPa)	14-Day f_c (MPa)	28-Day f_c (MPa)
	OPC	LSP	NP	SMF	RM						
P1	0	0	100	0	0	213	181	297	3.76	6.5	7.52
P2	0	0	90	0	10	204	194	341	3.23	5.9	6.46
P3	0	0	80	0	20	192	247	424	2.3	4.1	4.61
P4	0	0	70	10	20	200	301	574	5.46	10.0	10.93
P5	0	0	60	20	20	214	361	704	7.55	14.2	15.1
P6	0	5	65	10	20	194	311	587	8.83	15.5	17.66
P7	0	10	60	10	20	191	325	435	5.02	13.6	18.44
P8	10	10	50	10	20	186	41	53	12.38	24.5	25.99
P9	20	10	40	10	20	171	29	44	18.56	38.8	41.06
P10	30	10	30	10	20	153	12	19	26.68	50.6	56.14

4.4. Alkali activation and curing optimization

Four alkali activation parameters (A/P, NS/NH, NH molarity, and W/P) were considered as variables and their optimal values were identified through an optimization scheme while keeping the proportioning of the PMs invariant at optimal level determined earlier (Section 4.3). The optimization of alkali activation parameters was carried out in four steps, by varying one parameter and fixing the others in each step. The results of preceding optimization step were used in the succeeding optimization step, where the optimum value of the previous activation parameters was incorporated in the next step. A/P ratio, NS/NH ratio, NH molarity, and W/P ratio were varied from 0.3 to 0.6, 1 to 2.5, 8 M to 14 M, and

0.35 to 0.55 at 0.1, 0.5, 2 M, and 0.05 intervals, respectively. Additionally, three curing methods (steam curing, oven curing at 60°C, and ambient air curing) were considered as a fifth optimization step for selecting an optimal curing regime. The alkali activation and curing optimization procedure is illustrated in Figure 4-1.

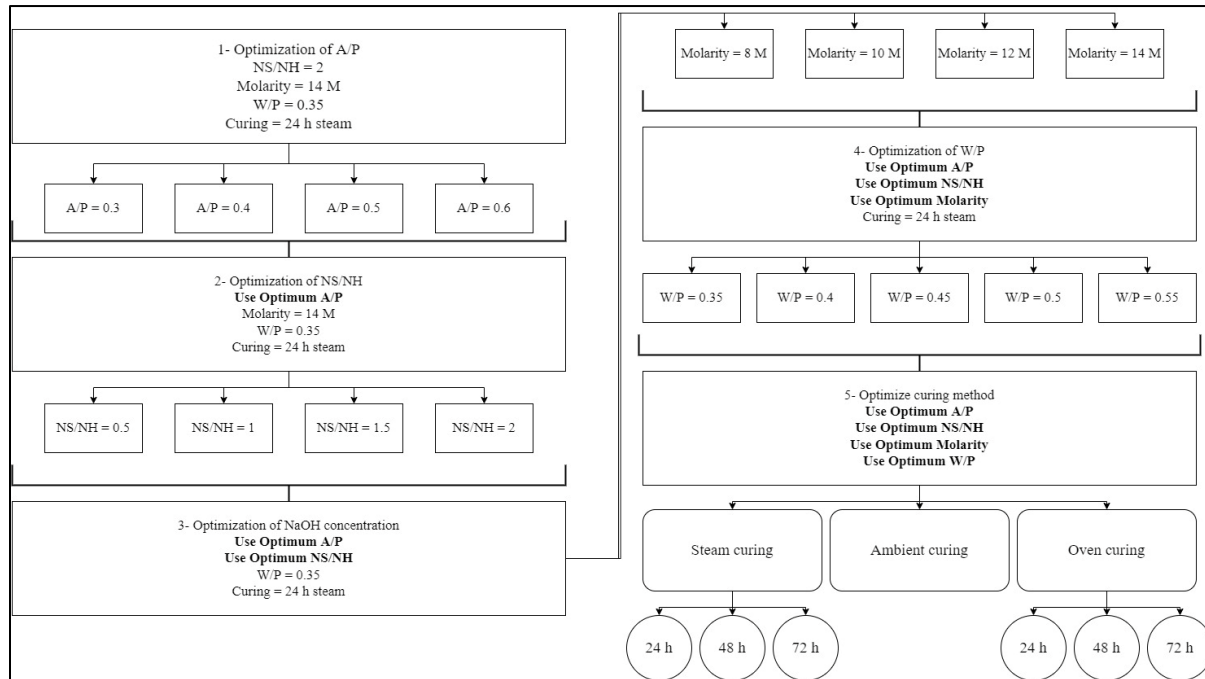


Figure 4-1 Alkali activation and curing optimization scheme

4.4.1. Specimen terminology

The specimens prepared for conducting various tests followed the terminology *a-b*, where ‘*a*’ indicates the optimization level which has values A for the A/P, N for NS/NH, M for NH molarity, W for W/P, and C for curing optimization level, respectively while ‘*b*’ indicates the value of the parameter under investigation. For example, a specimen labeled M-8 belongs to the NH molarity optimization step and has a molarity of 8 molars. For the specimens in the curing optimization step, ‘*b*’ includes the type of curing (A for ambient curing, O for oven curing, and S for steam curing) in addition to the duration in hours (24,

48, and 72). For example, C-O48 is the specimen in the curing optimization level that was oven cured for 48 hours.

4.5. Proportioning and preparation of trial mixtures

In total, 24 trial mortar mixtures were prepared for optimization of activation parameters and curing regime, as shown in Table 4-2. A two-speed, five-quart, bench-mounted Hobart mixer was used in the preparation of the AAB-based mortar trial mixtures. For the mortar specimens, the dry constituents and fine aggregate were first added to the bowl of the mixer and mixed using the low-speed option to minimize dusting for three minutes until a homogenous precursor was achieved. Then the alkaline activators as well as any extra water were added at thirds. When the final third of the activator solution and water were added, mixing on the low-speed option continued for 2 minutes and then on the high-speed option for another 2 minutes. The same procedure was followed for preparation of the paste specimens, used for microstructural tests (XRF, XRD, SEM-EDS, and FTIR) with the exception of fine aggregate inclusion.

Table 4-2 Details of trial mortar mixture (using optimal precursor P9 and S/P = 2 by wt.)

Mortar mixture ID	A/P (By wt.)	NS/NH (By wt.)	Molarity (M)	W/P (By wt.)	Curing regime
A-0.3	0.4	2.0	14	0.35	Steam for 24 h
A-0.4	0.4				
A-0.5	0.5				
A-0.6	0.6				
N-1	Optimum A/P	1.0			
N-1.5		1.5			
N-2		2.0			
N-2.5		2.5			

M-8			8		
M-10			10		
M-12			12		
M-14			14		
W-0.35				0.35	
W-0.40				0.40	
W-0.45				0.45	
W-0.50				0.50	
W-0.55				0.55	
C-A			Optimum Molarity	Optimum W/P	Ambient
C-O24					Oven@60 °C for 24h
C-O48					Oven@60 °C for 48h
C-O72					Oven@60 °C for 72h
C-S24					Steam for 24 h
C-S48					Steam for 48 h
C-S72					Steam for 72 h

The freshly prepared mixtures were cast into oiled, stainless steel, 50-mm cube molds for the mortar specimens and 25-mm cube molds for the paste specimens in two pours. The molds were vibrated on a vibratory table for 15 seconds after each pour to remove any entrapped air bubbles. The specimens were then troweled, leveled, and left to set while covered with polyethylene sheets until demolding which took place after 24 ± 4 hours of casting.

4.6. Curing and specimen storage

Following the casting of the specimens used for compressive strength the specimens were cleaned with a soft brush after demolding and then placed in a curing chamber supplemented with a thermostat-controlled heating element. The chamber was then filled

with water up to a certain level, and the specimens were suspended unsubmerged via a screen. The heating element was set to boil the water, and the chamber was covered with a lid to allow condensation and re-evaporation. After curing, the specimens were allowed to cool down in the chamber and then were dried with a towel before storing in sealed polyethylene bags at room temperature until testing. The specimens subjected to oven curing regime were placed inside plastic bags after demolding, to prevent moisture loss, and then placed inside a Memmert BE 800 stainless steel oven that was set to a temperature of 60°C at varying durations. Then the specimens were allowed to cooldown to room temperature after completion of the curing duration. For the ambient air curing regime, the specimens were stored inside plastic bags at $23 \pm 5^\circ\text{C}$ and relative humidity of $60 \pm 10\%$ after demolding and kept under these conditions until testing.

4.7. Testing and Evaluation

4.7.1. Raw precursor materials (PMs) characterization

The specific gravity of the PMs was determined using the Le Chatelier flask method described in ASTM C188. The moisture content and loss on ignition (LOI) were determined following the ASTM D7348, where samples were heated to a temperature of 100 °C and subsequently to an elevated temperature of 950 °C. Mineral composition and morphology testing of the selected PMs are discussed later in section 4.8.1.

4.7.2. Flow

For measuring the flow of a mortar mixture, a portion of the mortar was picked up after completion of mixing and the flow measurement was carried out using a manual flow table. The flow test was conducted following the ASTM C1437 standard.

4.7.3. Setting time

The initial and final setting times for the mortar were determined for each trial mixture of mortar using a manual Vicat setup with a 1-mm needle following the ASTM C191 standard.

4.7.4. Compressive strength

The mortar specimens were tested for compressive strength after the durations of 3, 14, and 28 days following the ASTM C109 standard using a Matest series C055N compression machine. Four replicate specimens were used for each mixture and the average and standard deviation of compressive strength results were recorded.

4.7.5. Elemental analysis, Mineral composition, and morphology

The elemental composition and chemical bonds of the raw PMs were analyzed by X-ray fluorescence (XRF) spectrometry and FTIR spectroscopy using a Malvern™ PANalytical EPSILON 3 XL spectrometer and a Thermo Fisher Scientific Nicolet 6700 IR spectroscope, respectively. Furthermore, the texture of the precursor constituents was analyzed by SEM using a JEOL JM-6610-LV microscope with EDS capability. The samples were coated with a 15 nm thick layer of gold using a sputter gun.

Based on the flow, setting times, and compressive strength results, two paste specimens were considered to examine the effect of each activation parameter on the microstructure and morphology of the matrix of the AABs. Each set of paste specimens represented the most and least optimum response of the activation parameter. Fragments of paste specimens were extracted from the central portion of the 25-mm cube after curing and aging for 28 days. A portion of the fragments was pulverized to pass a number 200 sieve

and used in analyzing the mineral composition by FTIR and XRD. The analysis was carried using a Nicolet 6700 IR spectroscope and a Rikagu Miniflex II diffractometer under the following conditions: 2 deg/minute scan rate, CuK- α_1 radiation, and 15mA at 20kV tube working conditions. The remaining fragments were polished and scanned by the previously mentioned JEOL microscope.

4.8. Results and discussion

4.8.1. Characterization of precursor materials (PMs)

The physical properties of the PMs are summarized in Table 4-3 and the SEM-EDS images are shown in Figure 4-3. OPC was grey in color and had an irregular texture, as indicated by SEM images. LSP and NP showed the same irregularity in terms of texture while exhibiting a white and a light grey color, respectively. SMF and RM were round in terms of particle morphology; both were brown in color, with SMF having a darker hue (Figure 4-2). The texture of OPC, LSP and NP can lead to better interlocking between the grains on the microscopic level due to their irregularity while the roundness of SMF and RM can enhance the flow, cohesion and spread of the AABs incorporating them due to the ball-bearing effect. The average particle size (D_{50}) for OPC, LSP, NP, RM and SMF was 13.83, 16.21, 15.74, 30.45, and 33.25 μm , respectively.

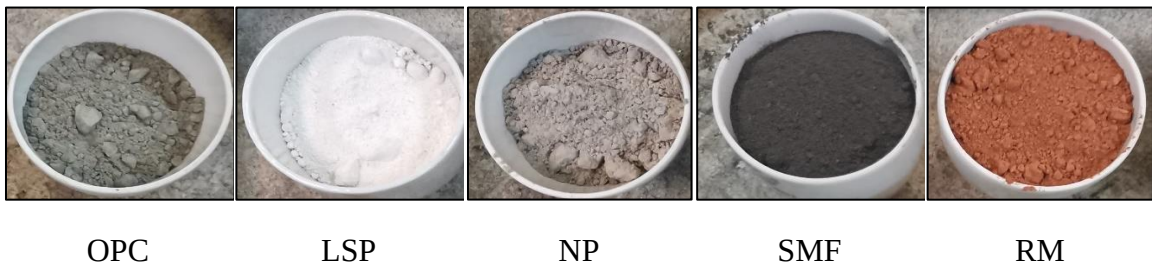
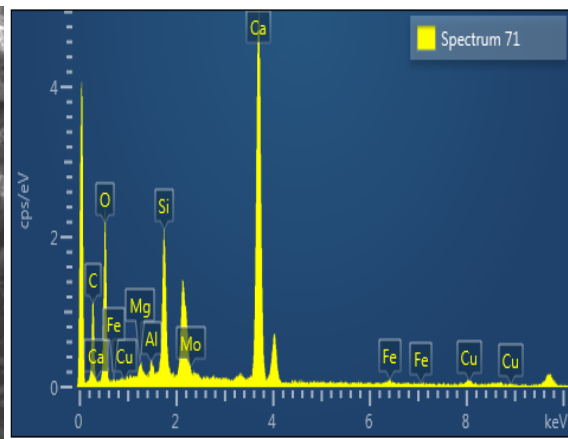
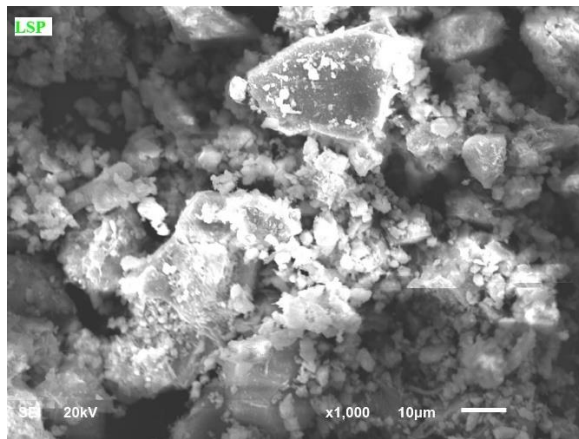
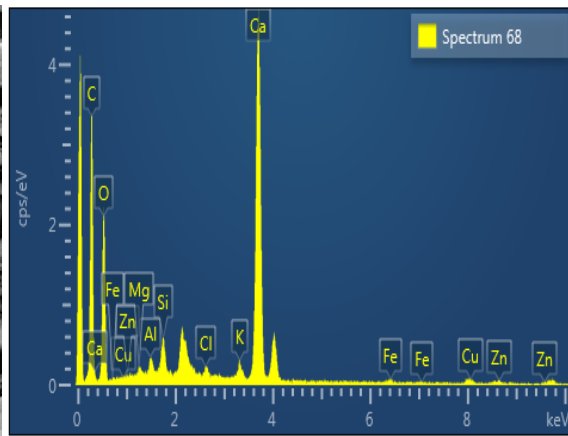
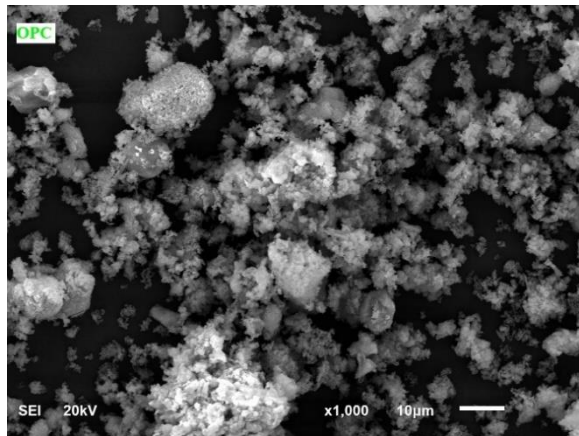


Figure 4-2 Physical appearance of the raw PMs as received

Table 4-3 Physical properties of PMs

PM	Property						
	Color	Texture	Specific Gravity	D ₅₀ (μm)	Moisture	Alkalinity	LOI
OPC	Grey	Irregular/Flaky	3.11	13.83	-	Basic	3.88
LSP	White	Irregular/Angular	2.62	16.21	1	Basic	7.96
NP	Light grey	Irregular/Angular	3.05	15.74	1.23	Acidic	1.23
SMF	Dark brown	Smooth/Round	2.88	30.45	0.96	Acidic	8.61
RM	Reddish brown	Irregular/Round	2.96	33.25	2.08	Basic	7.5
P9	Reddish brown	Mainly irregular	2.98	-	1.622	Basic	3.907



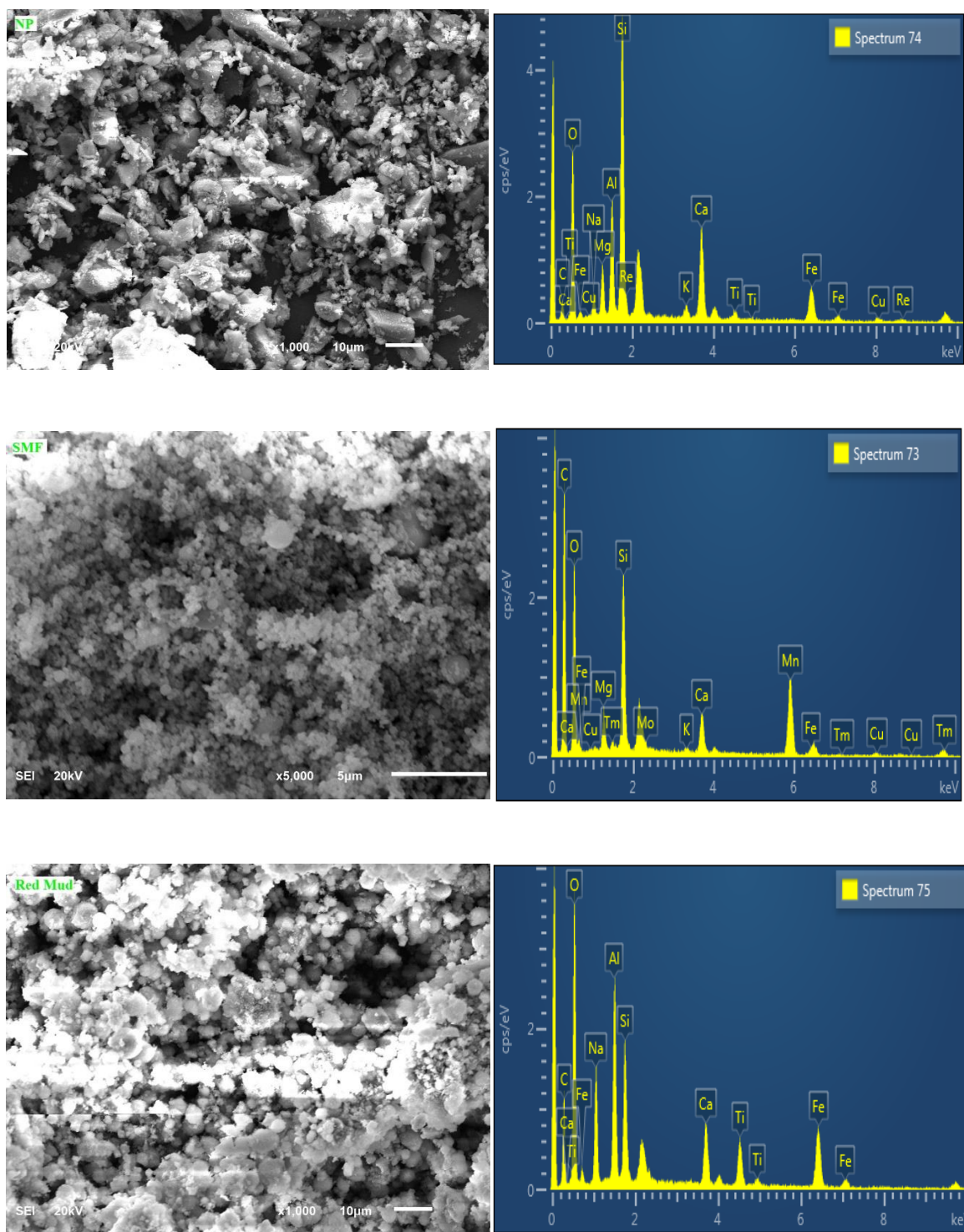


Figure 4-3 SEM and EDS spectra of the PMs

The elemental analysis results of the XRF and EDS (presented in Table 4-4) show overall agreement in the detected elements and their proportions between the two methods.

However, EDS detected minor traces of elemental copper (Cu) in OPC, LSP, and SMF. This can be attributed to two reasons: the nonhomogeneous nature of the raw materials where some traces could be detected in some samples and undetected in others, and possible contamination of the samples from the copper tape used to hold the samples in the EDS setup.

Table 4-4 Elemental composition of raw PMs by XRF and EDS (excluding O and C)

Element (% wt.)	OPC		LSP		NP		RM		SMF	
	XRF	SEM	XRF	SEM	XRF	SEM	XRF	SEM	XRF	SEM
Ca	84.8	78.9	81.6	74.8	15.9	16.2	4.7	9.8	3.4	10.0
Si	6.0	3.9	12.7	15.6	30.8	33.5	6.9	13.5	15.5	24.7
Al	3	2.1	2.9	1.9	8.8	12.4	10.9	20.8	-	-
Mn	-	-	-	-	-	-	-	-	71.6	50.2
Fe	4.5	1.8	1.8	1.7	34.1	16.7	60.7	27.0	4.1	3.0
K	0.5	2.7	-	-	1.2	1.9	-	-	0.7	0.9
Na	-	-	-	-	2.7	3.8	12.4	18.3	-	-
Mg	0.9	1.1	1.0	1.8	4.6	6.0	-	-	4.2	7.0
Ti	-	-	-	-	1.8	2.0	3.5	10.6	-	-
Cl	0.1	1.4	-	-	-	-	-	-	-	-
Cu	-	5.3	-	4.1	-	3.2	-	-	-	3.6

Table 4-5 Oxide composition of the PMs

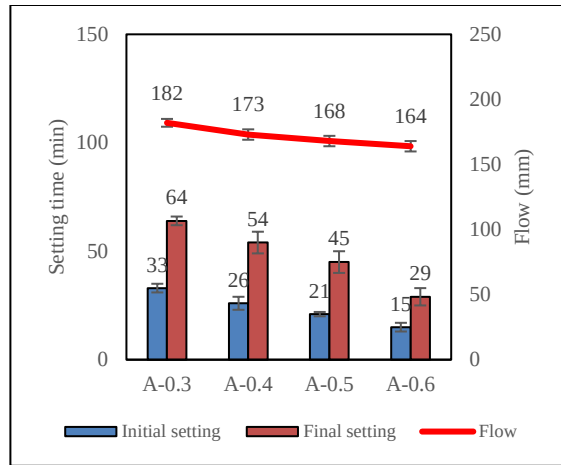
Oxide	OPC	LSP	NP	RM	SMF
CaO	84.36	83.1	13.46	4.56	2.83
SiO ₂	6.32	11.4	37.07	10.24	13.84
Al ₂ O ₃	1.31	2.5	10.03	14.15	-
MnO	-	-	-	-	75.37
Fe ₂ O ₃	5.67	1.66	28.76	53.94	4.31

K ₂ O	0.23	-	0.87	-	0.14
Na ₂ O	-	-	-	11.5	-
MgO	0.54	-	4.62	5.61	2.53
TiO ₂	-	-	1.84	4.04	-
SiO ₂ +Al ₂ O ₃ +Fe ₂ O ₃	13.3	4.16	75.86	78.33	18.49

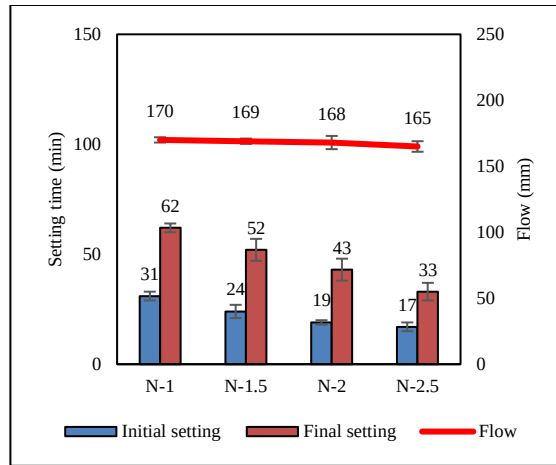
The mineral compositions of the PMs, as presented in Table 4-5, indicates that SMF was rich in MnO and SiO₂ (> 88% by wt.) while RM had significant amounts of Fe₂O₃ and Al₂O₃ (> 60% by wt.). LSP showed an elevated concentration of CaO (83.1% by wt.), which can be beneficial in the alkali activation of the precursor. It also contained moderate SiO₂ (11.4% by wt.), which would enrich the AAB gels. According to the ASTM C618 standard, RM and NP qualify as a pozzolan (Class N, F, or C) since they satisfy the chemical composition (SiO₂+Al₂O₃+Fe₂O₃ >50% by wt.), moisture content (<3% by wt.) and loss on ignition (<10% by wt.) criteria. On the other hand, SMF did not qualify as a pozzolan. However, it is recommended to be incorporated as a supplementary cementitious material due to its high MnO content [174]. The basicity coefficient of the PMs i.e., (CaO + MgO + Al₂O₃ + Fe₂O₃ + 0.5 FeO)/(SiO₂ + 0.5 FeO) ratio was less than 1.0 for NP and SMF and more than 1.0 for OPC, RM, and LSP which indicates that the latter group can be classified as ‘basic’ while the prior can be classified as ‘acidic’ [175].

4.8.2. Flow and setting time

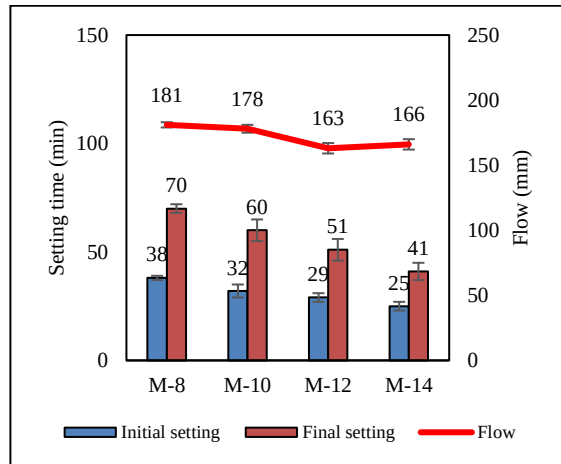
The results of flow and setting times of the mortar mixtures are shown in Figure 4-4.



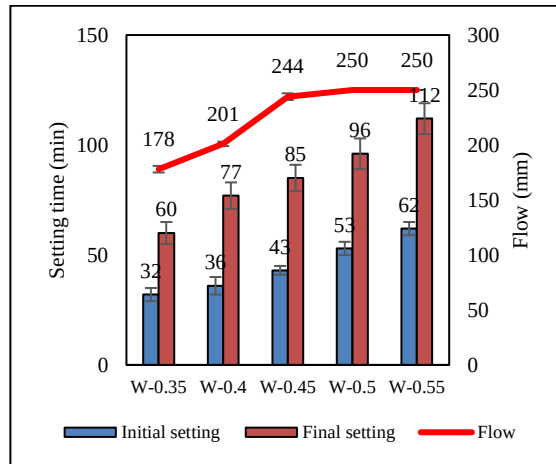
(A: Optimization of A/P ratio)



(N: Optimization of NS/NH ratio)



(M: Optimization of NH molarity)



(W: Optimization of W/P ratio)

Figure 4-4 Flow and setting time results for trial mortar mixtures

At least eight readings were taken to get an average flow representing a qualitative assessment of the workability of the prepared AABs. The flow value of a mortar mixture was considered as the diameter of the specimen after subjecting to 20 blows of the flow table. None of the activation parameters significantly impacted the flowability except for the W/P ratio. The increase in the A/P and NS/NH ratios and the molarity of NH had marginal adverse effects on the flow of the AAB-based mortars. On the other hand, as

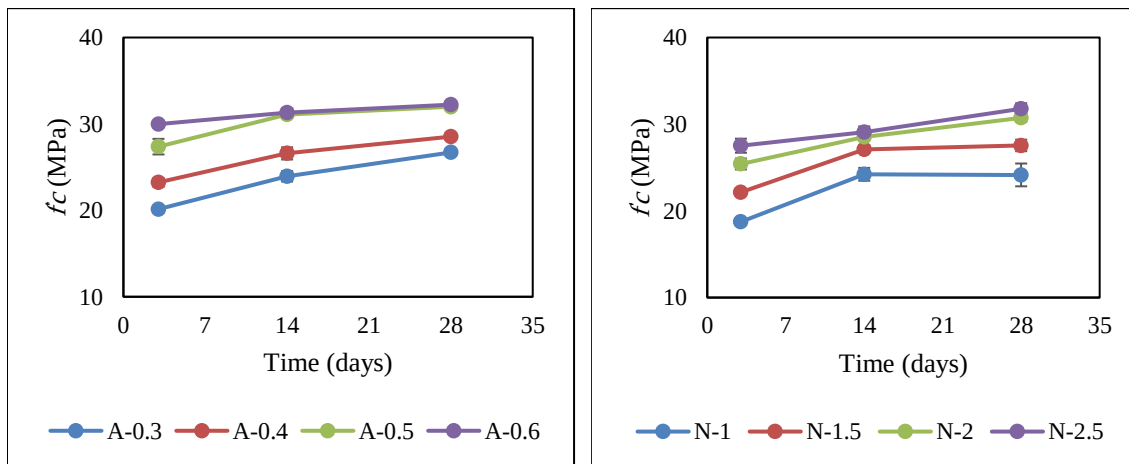
expected, the increase in the W/P ratio increased the flow significantly, which can be owed to the presence of extra free water that lowers the friction between the particles of the precursor, thus increasing the flow. Additionally, as the W/P ratio increased beyond 0.45, the mortar flowed beyond the edge of the flow table, which was 250 mm in diameter. It was also noted that segregation and bleeding increased during casting of mortar with W/P ratio greater than 0.5, as also reported in the literature [135].

As shown in Figure 4-4, the setting times decreased significantly as the A/P ratio increased. Mixture A-0.3 had initial and final setting times of 33 and 64 minutes, respectively, while a decrease of 50% was noted with mixture A-0.6. This is expected since a higher A/P ratio results in the presence of more activator molecules, which promotes faster dissolution of alumina, calcium, and manganese ions that increases the rate of the polymerization and condensation phases of the reaction, thus leading to a faster formation of polymerization products and shorter initial and final setting times. A similar phenomenon is observed with the increase in the molarity of the NH activator, where the initial and final setting times decreased from 38 and 70 minutes (for M-8) to 25 and 41 minutes (for M-14), respectively. The explanation behind the observed phenomenon is that the higher molarity leads to an increase in the pH of the activator solution, which in turn leads to a faster dissolution of the previously mentioned ions and faster formation of condensation products. Furthermore, the setting time decreased with the increase in the NS/NH ratio, where the mixture with the NS/NH ratio of 1.0 (N-1) had initial and final setting times of 31 and 62 minutes, respectively while the mixture with the NS/NH ratio of 2.5 (N-2.5) had setting times half of the former. This reduction in the setting times can be owed to the existence of more soluble silica due to increase in the sodium silicate proportion of the activator, leading to

the quicker formation of CASH and NASH gels [39]. The opposite trend was noted in the W/P ratio optimization step, where the setting time increased with the increase in the W/P ratio. An increase in the initial setting time of 94% was recorded when the W/P ratio changed from 0.35 to 0.55 while an increase of over 100% was noted for the final setting time. This observation is owed to the dilution of the activator solution with increase in the W/P ratio.

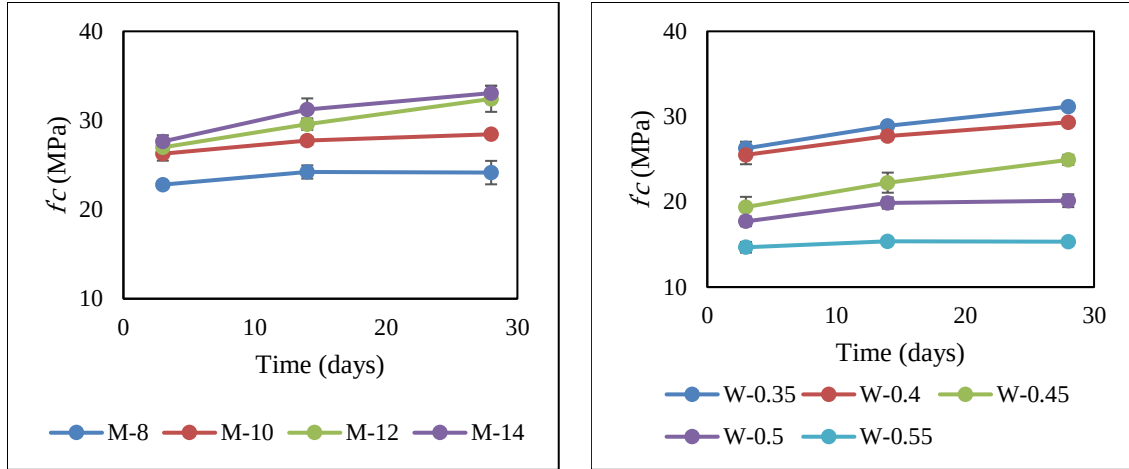
4.8.3. Compressive strength development

Figure 4-5 and Figure 4-6 show the variation of compressive strength of the mortar mixtures with age. While Figure 4-5 shows the effect of the activation parameters (A/P ratio, NS/NH ratio, NH molarity, and W/P ratio), Figure 4-6 depicts the effect of the curing regimes on the compressive strength. The standard deviations of the 3, 14, and 28-day compressive strength results shown in Figure 4-5 and Figure 4-6 varied between 0.5 to 3.0 MPa, 0.7 to 2.5 MPa, and 0.4 to 2.9 MPa, respectively.



(A: Optimization of A/P ratio)

(N: Optimization of NS/NH ratio)



(M: Optimization of NH molarity)

(W: Optimization of W/P ratio)

Figure 4-5 : Optimization of activation parameters

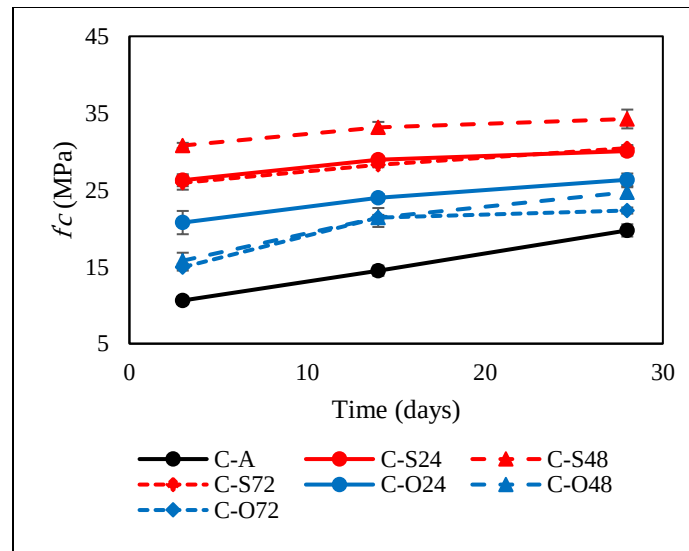


Figure 4-6: Optimization of curing regime

The compressive strength increased with age regardless of the activation parameters values and curing regime, which is expected since more polymerization products are formed with age, which results in a denser and stronger microstructure. However, the rate of strength development slowed down after three days, with over 80% of the strength being developed by that age except for the case of ambient air-cured mixture (C-A) where the strength

significantly increased after 3 days due to relatively slower polymerization. It is evident from Figure 4-5 and Figure 4-6 that the optimum mixture in terms of the compressive strength, flow, and setting time is mixture C-S48 which has A/P, NS/NH, Molarity of NaOH, W/P, and curing regime of 0.5, 2, 10, 0.4, and 48-hour steam curing with mixture C-S24 being the second most optimum which shares the same mixture characteristics with C-S48 but with 24-hour steam curing rather than 48. The influence of each factor on strength development is discussed in the following section.

4.8.3.1. Influence of the activation and curing factors on strength development

4.8.3.1.1. *A/P ratio*

The 28-day compressive strength increased from 26.7 to 31.99 MPa with the increase in the A/P ratio from 0.3 to 0.5 indicating a relatively minor effect of A/P ratio on the compressive strength. Further, the increase in the A/P ratio beyond 0.5 did not result in a significant increase in the compressive strength particularly at the after 14 and 28 days, however, the compressive strength was relatively higher at 3 days (27.4 MPa for 0.5 A/P and 30 MPa for 0.6 A/P). It is hypothesized that this increase in the early age strength comes as a result of the increase in the polymerization of the reactants (precursor materials) that are consumed at a higher rate initially due to the higher concentration of the alkaline activator at higher A/P ratios. However, as time goes by, the reaction rate slows down due to the depletion of the activators, leading to a plateau in the strength gain profile. Nasir et al. [176] reported an opposite trend from their study on the effect of the A/P ratio on the compressive strength of an AAB composed of GGBFS and SMF (as precursor materials) that were activated with a mixture of NH and NS and varying the A/P. They postulated that

an increase in the A/P ratio increased the free water in the mixture that diluted the alkaline activator solution and resulted in a weaker binder. In the present study, the A/P ratio was varied while maintaining the same water content in the mixture. This was done to ensure a more precise illustration of the effect of the A/P ratio.

4.8.3.1.2. NS/NH ratio

As observed from Figure 4-5 showing the effect of the NS/NH ratio (i.e., silica modulus), the compressive strength increased steadily with increase in the amount of NS in the activator solution. The compressive strength increased from 24 MPa at NS/NH of 1.0 to 30 MPa at NS/NH of 2.0, however, by increasing the silica modulus beyond 2.0 resulted in a minimal effect on the compressive strength while shortening the setting time. Therefore, it can be concluded that the optimum silica modulus for the precursor considered in this study may be taken as 2.0 from the point of view of compressive strength and setting times. Numerous studies have reported that the combined usage of NS and NH yields significantly stronger AABs with sturdier internal structures compared to the binders activated by NS or NH alone [177]–[179]. Furthermore, precursors activated with NH alone produce highly crystalline aluminosilicate hydrate products, while those activated by NS are mainly amorphous, so the use of both activators results in a mixture of amorphous and crystalline polymers, which increases the mechanical properties significantly. However, information on the optimum NS/NH ratio in the literature is limited. Some researchers reported the optimum NS/NH ratio as 2.5 [176], while others reported different values [42].

4.8.3.1.3. *NH molarity*

The compressive strength increased with the increase in the NH molarity at all ages. The relatively low molarity of 8 M had a 28-day compressive strength of 24 MPa, while mixtures made with NH molarities of 10, 12, and 14 M had compressive strengths of 28.5, 32, and 33 MPa, respectively. The increase in the NH molarity increases the pH, increasing the ratio the alkaline $[\text{OH}]^-$ to the acidic $[\text{H}_3\text{O}]^+$ ions, which in turn expedites and magnifies the dissolution of the aluminosilicate monomers (calcium, silicate, and aluminate) in the precursors resulting in the condensation of a more connected and sturdy network of polymeric gels and highly crystalline CSH thus resulting in higher compressive strength as shown in Figure 4-5. However, previous studies reported a degradation in the compressive strength with age for mixtures with NH molarities higher than 10 M [180], thus indicating that an NH molarity higher than 10 M is not necessarily advantageous. Considering the given results, an NH molarity of 10 M is recommended.

4.8.3.1.4. *W/P ratio*

As expected, the increase in the W/P ratio resulted in a significant decrease in the compressive strength, as shown in Figure 4-5, due to the dilution effect created by the addition of extra free water and increase in the porosity in the mortar matrix. A decrease of over 50% was noted when the W/P ratio increased from 0.35 to 0.55. This trend was similar to that reported in the literature for traditional and nontraditional binders [176], [181]. However, the use of an excessively low W/P ratio is not preferable since it would impart adverse effects on the setting time, workability, and pumpability. Therefore, a balance between the fresh and mechanical properties of the mixtures should be ensured before recommending a certain W/P ratio for an AAB.

4.8.3.1.5. Curing regime

The effect of three curing regimes that were considered in the present study included ambient air curing, stream curing, and oven curing, on the compressive strength can be observed from the plots shown in Figure 4-6. Ambient air cured specimens exhibited the lowest compressive strength, with an average 28-day strength of 19.7 MPa. This is expected since the polymerization reaction is highly influenced by temperature and alkalinity, as reported in the literature [182].

Mixtures cured in the oven at a temperature of 60°C exhibited signs of deterioration, especially as the curing period exceeded 24 hours, as shown in Figure 4-7. Surface cracks caused by temperature effect appeared and deepened as the curing duration increased, which reflected negatively on the compressive strength, where the specimens were cured for longer durations. The specimens cured for 24 hours had a compressive strength of 26.3 MPa at 28 days, while specimens cured for 48 and 72 hours exhibited compressive strengths of 24.7 and 22.3 MPa, respectively, indicating a significant loss of strength. The decrease in the compressive strength at longer durations of oven curing is attributed to the loss of moisture and damage to the specimens.



Oven-cured for 24 hours



Oven-cured for 48 hours



Oven-cured for 72 hours

Figure 4-7 Cracking of mortar specimens after oven curing

On the other hand, specimens cured with steam had the highest compressive strength values among the three curing regimes considered. However, it was noted that curing the specimens beyond 48 hours negatively impacted their compressive strength. Specimens that were steam-cured for 24 and 48 hours had 28-day compressive strengths of 30.1 and 34.24 MPa, respectively, while specimens cured for 72 hours had a 28-day compressive strength of 30.5 MPa. The decrease in the compressive strength beyond 48 hours of curing can be owed to the leaching of the alkaline activators from the specimens as evident from the increase in pH of the water in the chamber used for steam curing, which hinders the polymerization by removing $[\text{OH}]^-$ ions from the specimens thus resulting in a reduction in the denseness of the polymeric matrix.

4.8.3.2. Selection of optimum activation parameters and curing

For the selected optimum precursor composition (i.e., P9 containing 20% OPC, 10% LSP, 40% NP, 10% SMF and 20% RM), the following criteria were adopted to select optimum activation parameters and curing based on the results of the flow, setting time, and compressive strength tests conducted on the specimens of trial mortar mixtures:

- 1- The 28-day compressive strength of the mortar should be higher than the minimum targeted value of 28 MPa ($\approx$ 4000 psi) which is suitable for a cementitious composition exposed to aggressive conditions.
- 2- An initial setting time of the mortar equal to or greater than 45 minutes is targeted since it satisfies the ASTM C150 criterion for minimum initial setting time.
- 3- A workability of the mortar around 200 mm (flow value) is targeted which is satisfactory for pumping and consolidation from a practical implementation point of view.

- 4- In case two mixtures have satisfactory performance, the more economically efficient mixture is chosen.

By applying the above criteria to the results presented in Figure 4-4, Figure 4-5, and Figure 4-6, the following activation parameters and curing regime were optimally selected in a step-by-step manner:

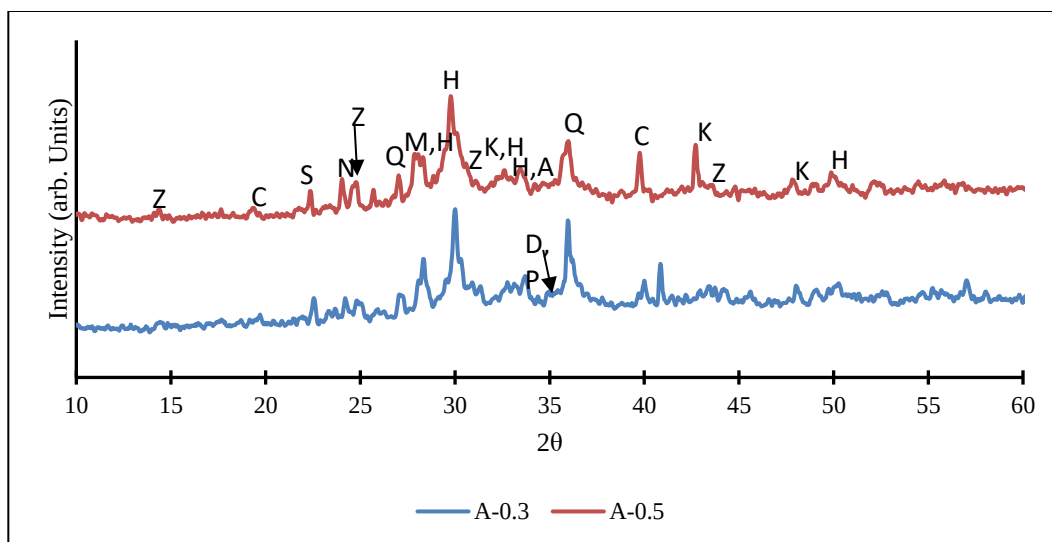
- 1- **A/P ratio of 0.5** was chosen since it had an f'_c value of 32 MPa (>28 MPa) at 28 days while having an initial setting time more than the mortar with the A/P ratio of 0.6.
- 2- **NS/NH ratio of 2.0** was chosen since it had an f'_c value of 30.7 MPa (>28 MPa) at 28 days while having an initial setting time more than the mortar with the NS/NH of 2.5.
- 3- **NH molarity of 10 M** was chosen since it had an f'_c value of 28.5 MPa (>28 MPa) at 28 days while having an initial setting time more than the mortar mixtures with NH molarities of 12 and 14 M as well as being more economical since higher NH molarity would entail the consumption of more NaOH pellets.
- 4- **W/P ratio of 0.4** was chosen since it had an f'_c value of 29.3 MPa (>28 MPa) at 28 days while having an initial setting more than 45 minutes and a flow greater than 200 mm.
- 5- **Steam curing for 24 hours** was chosen to be optimum since it satisfied the compressive strength criterion while being more economical than mixtures cured for 48 and 72 hours. While the ambient air curing regime is not recommended due to slow evolution of strength, the oven curing regime is not suitable due to cracking and loss of strength.

However, the other developed mixtures could be utilized if the applications demand different criteria. For example, mixtures with shorter initial setting times could be used for quick-setting repair materials, precast applications, and 3-D printing, while mixtures with lower compressive strength could be used in non-structural members or in controlled low-strength materials applications.

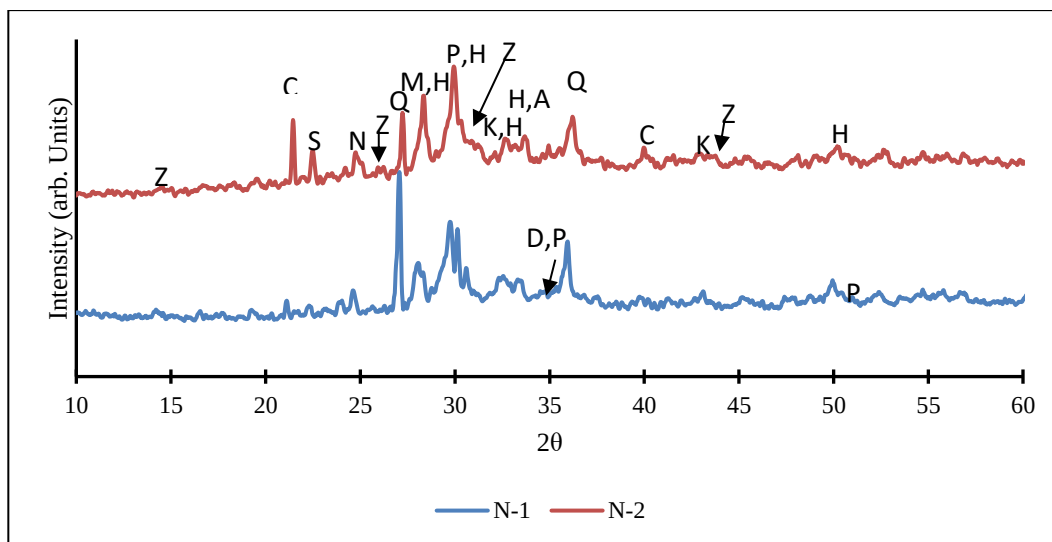
4.8.4. Microstructure

4.8.4.1. XRD analysis

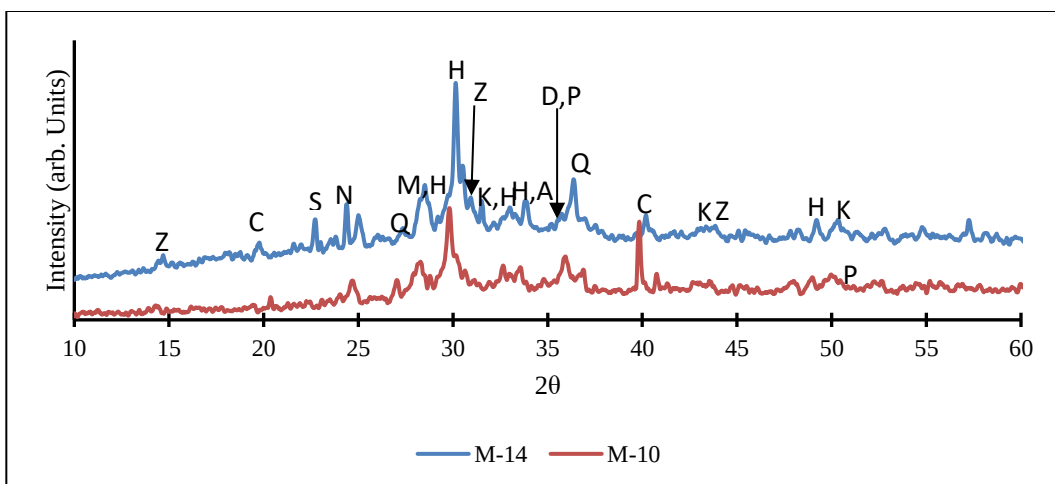
As mentioned previously, two paste specimens belonging to each activation parameter were chosen for XRD analysis to study the effects of each factor on the developed mineral phases. Figure 4-8 shows effects of each activation parameter on the crystalline structure after polymerization. All of the specimens showed similar key mineral phases which included: Stratlingite ($\text{Ca}_2\text{Al}_2(\text{SiO}_2)(\text{OH})_{10}\cdot 2.5\text{H}_2\text{O}$) [183], Nchwaningite ($\text{Mn}_2\text{SiO}_3(\text{OH})_2\cdot \text{H}_2\text{O}$) [184], calcium silicate hydrate (CSH) [42], [54], Potassium or K-Feldspar (K-A-S-H) [184], Manganese calcium hydrate (Mn-C-H) [184], Portlandite (CH) [186], Calcite (CaCO_3) [183], [185], Quartz (SiO_2), Anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) [187], Sodium aluminosilicate hydrate (NASH) [187], and Hydrotalcite ($\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3\cdot 4\text{H}_2\text{O}$) [183], [184]. The peaks of the calcite at $2\theta = 22^\circ$ can be owed to the carbonation of the specimens during pulverization and storage before testing as well as the addition of the LSP in the precursor, which consists mainly of calcite.



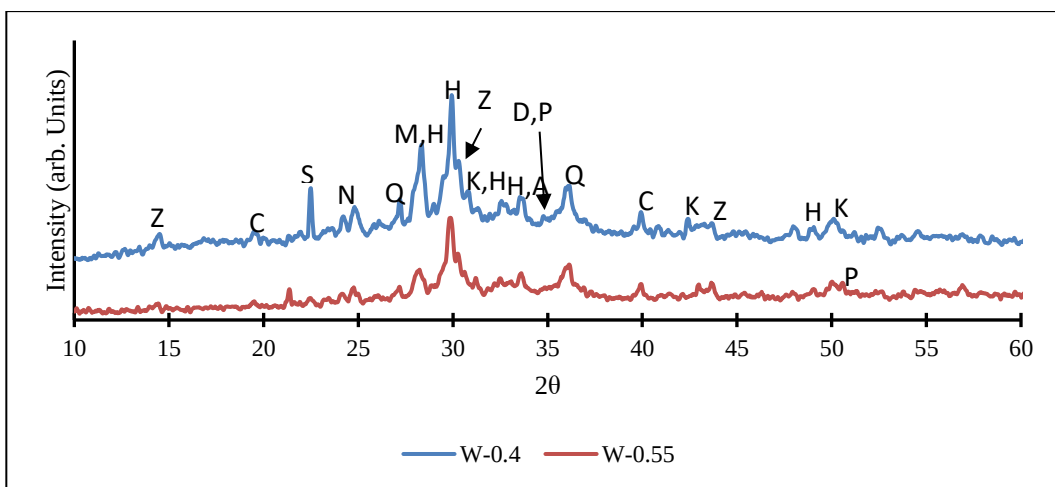
(A: Effect of A/P ratio)



(N: Effect of NS/NH ratio)



(M: Effect of NH molarity)



(W: Effect of W/P ratio)

Figure 4-8 XRD diffractograms of the developed AABs (C: Calcite, S: Stralingite, N: Nchwaningite, Q: Quartz, M: Manganese-Calcium-Hydrate, H: CSH, K: Feldspar, A: Anorthite, D: Hydrotalcite, P: Portlandite, Z: NASH)

The increase in the A/P ratio from 0.3 to 0.5 resulted in the diminishing of the quartz peaks and increasing the sharpness of the peaks of CASH and NASH as well as the peak of the K-feldspar which indicates that the increasing the A/P ratio leads to the consumption of silica and the condensation of more crystalline products. Furthermore, there was an increase in the sharpness of the manganese products (Nchwaningite and Mn-C-H) peaks which indicates a transformation towards a more crystalline structure as well as consumption of the manganese carrying oxides in the raw precursor. The formation of more

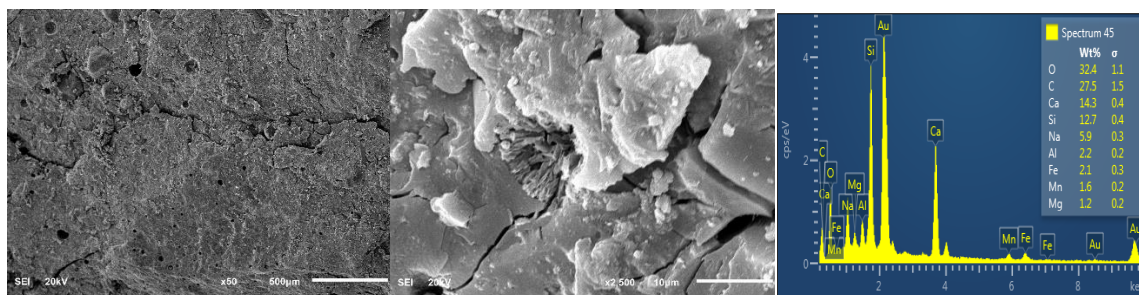
crystalline products results in a stronger microstructure, as reflected by the increase in compressive strength with the increase in A/P ratio, as discussed earlier. The same observation regarding the quartz consumption and the more crystalline products applies to the effect of the NS/NH ratio where increasing the silica modulus positively impacted the strength. Furthermore, The increase in NH molarity from 10 M to 14 M had a similar effect where sharper CASH, Stratlingite, Nschwanningite, KASH and NASH peaks were observed which is in agreement with what was reported by Nasir et al. [183] and Das and Shrivastava [188] who observed that increasing NH molarity led to the consumption of more silica phases and the formation of more crystalline NASH and CASH phases. Finally, as expected, increasing the W/P ratio from 0.4 to 0.55 led to the dilution of the alkaline activators, which in turn hindered the dissolution of aluminosilicate monomers. It negatively impacted the condensation of CASH, NASH, and feldspar which is also reflected by the decrease in the compressive strength with the increase in W/P ratio, as discussed earlier. In addition, increasing the free water at a higher W/P ratio might have led to leaching of the calcium and sodium phases, which are reported to be prone to leaching [189], thus reducing the compressive strength.

4.8.4.2. SEM-EDS analysis

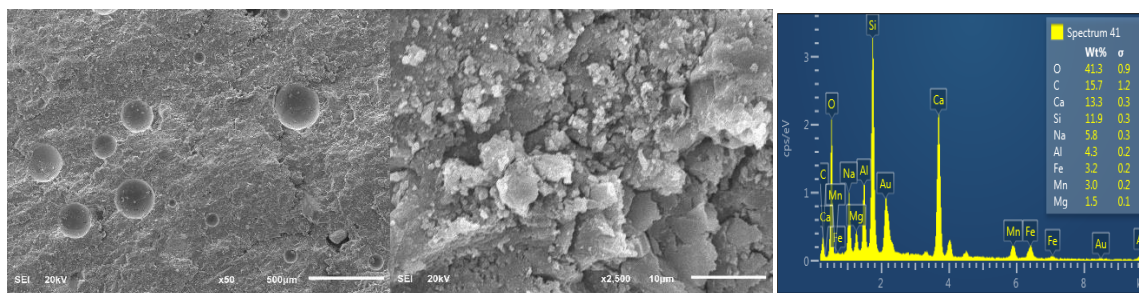
4.8.4.3. Morphology

Figure 4-9 shows the scanning electron microscopy (SEM) images at varying magnification levels in addition to the energy dispersive spectra of the developed AABs. These images show the formation of random and non-uniform polymerized surfaces as affected by the activation parameters. The surface includes parts of filled/partially-filled pores in addition to microcracks. The increase in the A/P ratio shows less partially filled

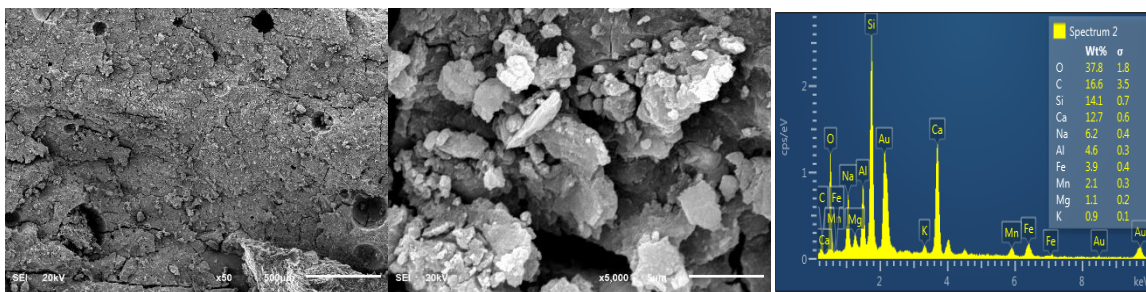
cracks, indicating a denser microstructure that coincides with the reported compressive strength results and the XRD results as discussed earlier. In addition, the specimen with A-0.5 (i.e., A/P ratio = 0.5) shows the surface with more distributed gel formations that minimize the pores compared to the specimen with A-0.3, thus leading to a more uniform surface. Similar observations can be made for the effects of the NS/NH ratio and NH-molarity, where the micrographs show an overall improved structure with the increase in both variables confirming the observations made with regard to the compressive strength results as well as results reported in the literature [41], [176], [180], [183], [188]. The opposite trend is noted in the specimens with varying W/P ratio (W-0.40 and W-0.55) where the increase in the W/P ratio led to the formation of major cracks and an overall more porous microstructure, which also agrees with the observations made previously.



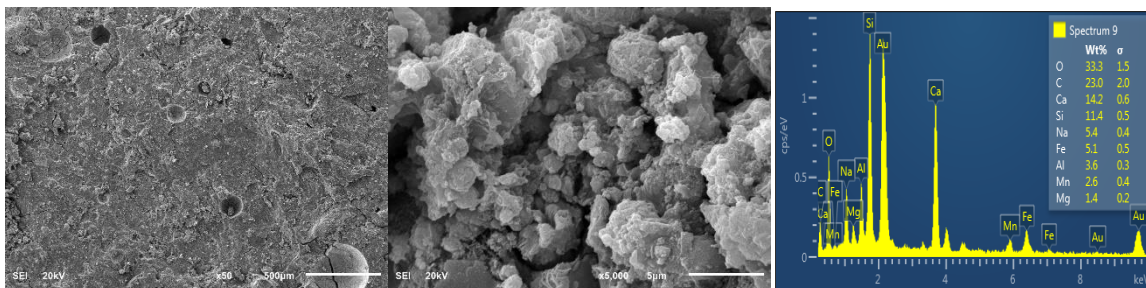
(A-0.3)



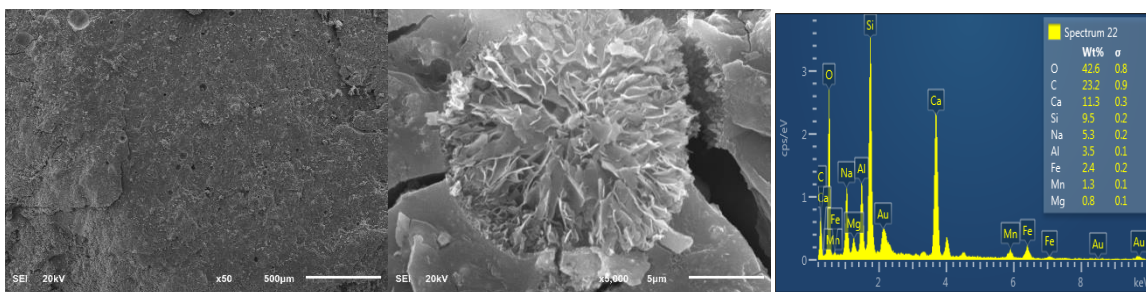
(A-0.5)



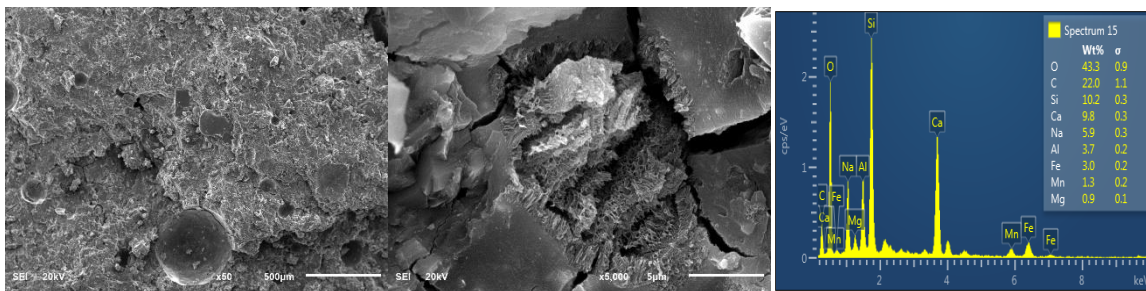
(N-1)



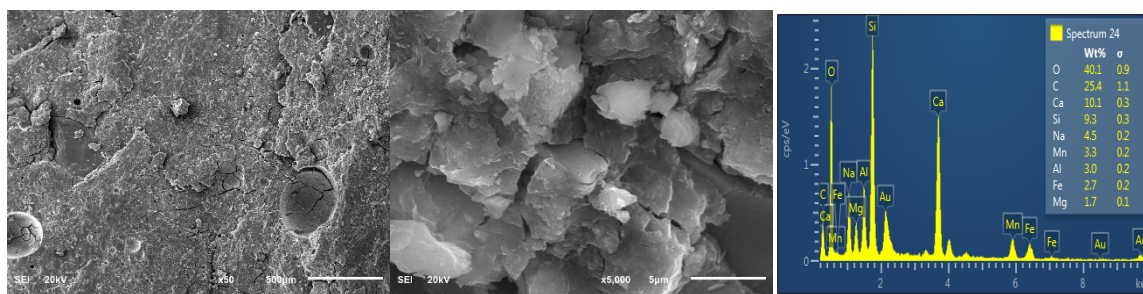
(N-2)



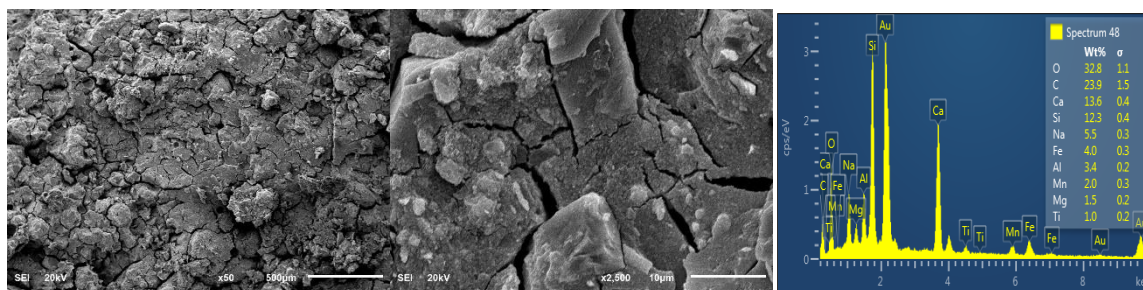
(M-10)



(M-14)



(W-0.40)



(W-0.55)

Figure 4-9 SEM and EDS spectra of the AABs showing the effects of activation parameters (A: A/P ratio, N: NS/NH ratio, M: NH molarity, W: W/P ratio)

4.8.4.4. Elemental composition

The elemental compositions of the developed AABs, as presented in Table 4-6, were deduced from the respective EDS spectra shown in Figure 4-9. The major elements detected were calcium, silicon, aluminum, iron, and manganese, with average percentages of 31.1, 28.6, 8.9, 8.2, and 5.4%, respectively. Sodium being sourced from the alkaline activators, it was detected in addition to traces of magnesium and potassium.

Table 4-6 EDS elemental composition of the developed AABs (without C and O)

Element	A-0.3	A-0.5	N-1	N-2	M-10	M-14	W-0.40	W-0.55	Raw-p9
Ca	35.6	30.9	27.8	32.5	33.2	28.1	29.3	31.4	33
Si	31.6	27.8	30.9	26.1	27.8	29.3	26.9	28.3	16.8
Al	5.6	9.9	10.2	8.3	10.3	10.6	8.6	7.9	6.3
Mn	4.1	7	4.6	5.9	3.8	3.9	9.5	4.7	7.2

Fe	5.3	7.4	8.4	11.6	7.1	8.5	7.8	9.2	27.3
K	-	-	1.9	-	-	-	-	-	0.6
Na	14.8	13.4	13.6	12.4	15.5	16.9	13.1	12.8	3.6
Mg	3.1	3.6	2.5	3.1	2.4	2.6	4.9	3.4	2.4
Ti	-	-	-	-	-	-	-	2.3	1.4

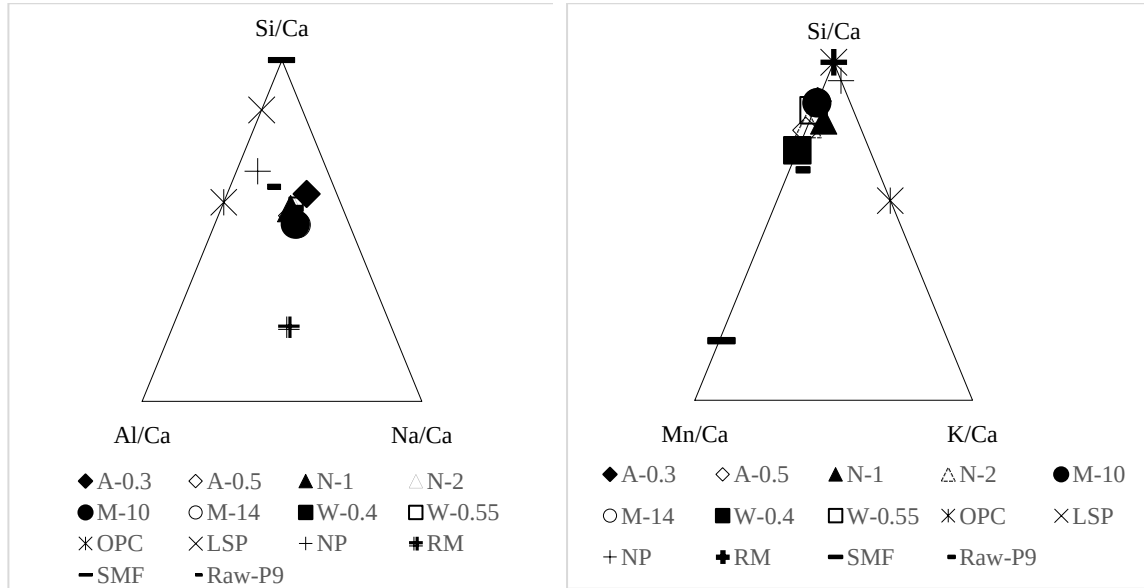


Figure 4-10 Ternary Diagram of the elemental composition for Si, Al, Na, K, and Mn normalized to Ca

Two ternary diagrams were prepared to visually illustrate the changes in the elemental compositions of the developed AABs as their activation parameters varied, as shown in Figure 4-10. The apexes of the diagrams represent some of the major elements detected normalized to calcium. The chosen precursor (P9) was located between the apexes of Si/Ca and Mn/Ca and near the border of Al/Ca and Si/Ca, indicating the predominance of Al, Mn, Si, and Ca. After the polymerization, the binder compositions moved more towards the center of ternary diagram with a decrease in Mn/Ca ($\approx 50\%$) and considerable increases in Na/Ca ($\approx 300\%$), Si/Ca ($\approx 100\%$), and Al/Ca ($\approx 50\%$) indicating that higher Ca and Al in the precursor as well as higher Si and Na from the activators leads to the formation of denser microstructures while also indicating that the role of Mn is less significant than Ca and Al.

4.8.4.5. FTIR analysis

Figure 4-11 illustrates the FTIR spectroscopy spectra of the developed AABs in addition to the raw precursor. A summary of the observed bands with references from the literature is provided in Table 4-7. In the raw precursor, the IR peaks detected were at wavenumbers 3645, 2978, 2881, 1454, 1385, 1134, 964, and 547 cm^{-1} . The first peak coincided with the stretching vibration in sulfates, confirming the detection made by XRF and EDS. The peak at 2978 cm^{-1} corresponds to symmetric and asymmetric stretching of the carbon-hydrogen bond found in traces of organic impurities coming mainly from RM. Furthermore, the peak at 1454 cm^{-1} coincided with the stretching vibration of the double carbon-oxygen bond found in carbonates, mainly calcite from LSP as well as the carbonation of the precursor during storage and testing. The remaining peaks detected were from the stretching vibration of the silicon-oxygen-silicon bond found in quartz and silicate minerals, the silicon-oxygen-aluminum bond found, and the hematite stretching in NP, SMF, and RM.

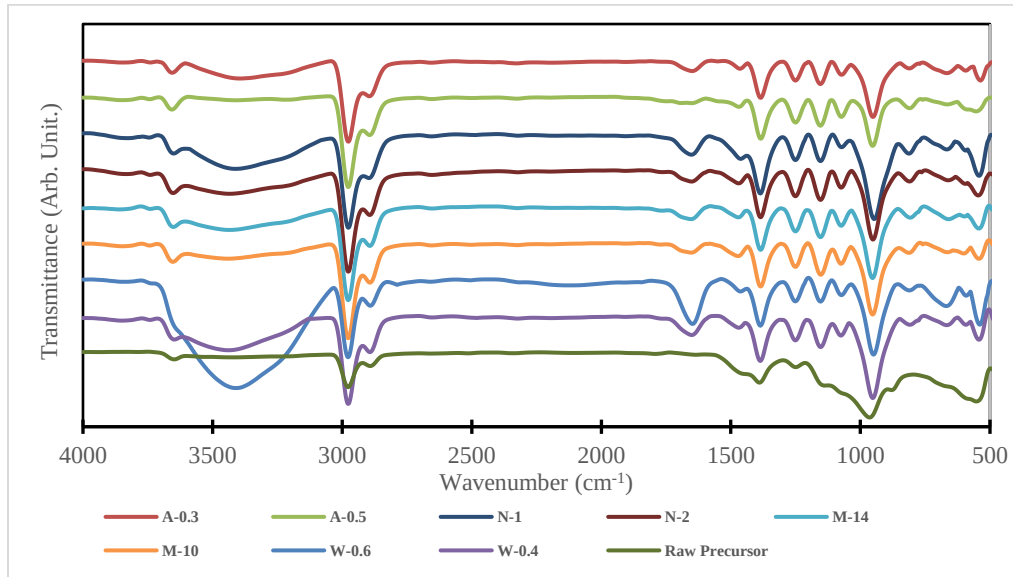


Figure 4-11 FTIR spectra of the developed binders and raw precursor

Table 4-7 Summary of the observed bands in FTIR

Band (wavenumber)	Bond	Vibration type	Ref.
3600-3700	X-O-H (X = Ca or S)	Stretching in Portlandite or sulfates	[190]
3500-3300	H-O-H	Stretching in free and surface adsorbed water	[190]– [197]
2800-3000	C-H	Asymmetric and symmetric stretching	

1600-1700	H-O-H	Bending in structural water	
1350-1460	C=O	Stretching in carbonates	
1100-1300	Si-O-Al	Stretching in geopolymers	[197]
1100-1050	Si-O-Si	Stretching in silicates	[190]– [197]
850-1050	Si-O-M (M→Si, Al or Mn)	Stretching in geopolymers	
850-750	Si-O-Si	Stretching in quartz	
600-500	Fe-O-Fe	Stretching in hematite	[195]
500-400	O-Si-O	stretching in quartz	[190]– [197]

There were some noticeable changes after the activation of the precursor in all specimens. The first change was the flattening of the carbonate peak at 1454 cm^{-1} , which indicates that the calcite was partially consumed. The consumption could either be in the form of leaching during steam curing or by activating the precursor, which the authors have reported in previous studies [198], [199]. Another change was the creation of the peaks at 1643 cm^{-1} which coincided with the bending vibration of water molecules in structural water (i.e., water that is chemically bound in the binder matrix), thus indicating that water was consumed during polymerization/hydration to form CSH, Mn-C-H and MnSH thus supporting the results indicated by XRD. Finally, the sharpening and intensification of the peaks at 925 cm^{-1} and the diminishing of the peaks at 1040 cm^{-1} indicate the formation of amorphous and crystalline geopolymeric chains and the consumption of the free silicates to form those products. The flattening of the peaks at 1643 cm^{-1} in binder A-0.5 compared to A-0.3 as well as the magnification of the peak at 925 cm^{-1} , implies that increasing the A/P ratio favors the formation of the previously mentioned polymeric products rather than the formation of CSH by hydration. The same observation applies for increasing the NS/NH ratio from 1 to 2 in the case of specimens N-1 and N-2 and increasing the molarity from 10 to 14 M, as was the case with specimens M-10 and M-14. On the other hand, specimen W-0.55 showed a remarkable increase in the peaks at 3405 and 1643 cm^{-1} , which indicate that the additional water is adsorbed on the surface and free to evaporate, leaving larger voids behind and weakening the internal structure.

4.9. Summary

This chapter illustrated the influence of the activator to precursor ratio, alkaline activator composition and concentration, water to precursor ratio, and curing regime on the physical, microstructural, mineralogical, and chemical properties of a novel and sustainable alkali-activated binder containing OPC, limestone powder, natural pozzolana, red mud and silicomanganese fume. An optimum precursor composition that satisfies the flow, compressive strength, and setting time was selected followed by the systematic optimization of the activation parameters were. The following conclusions could be drawn based on the observations made through the chapter:

- 1- The chemical investigation of the precursor materials revealed that SMF, RM, NP, and LSP were rich in reactive manganese and silica, alumina, and calcium oxide, respectively, as indicated by XRF and EDS. Furthermore, the optimally selected precursor (P9) contained 10% LSP, 40% NP, 20% RM, 10% SMF, and 20% OPC. The precursor chemical composition, loss on ignition, and moisture content satisfy the ASTM C618 criteria for being a pozzolanic material, thus allowing the blend to be used as supplementary cementitious material as well.
- 2- The activation parameters (A/P and NS/NH ratios, NH molarity, and W/P ratio) significantly influenced the compressive strength and setting time. The flow was affected substantially only by the W/P ratio.
- 3- The evolution of strength in case of ambient air curing was slow and oven curing caused the formation of cracks that lowered the strength, while steam curing increased the strength significantly. Increasing the duration of steam curing beyond 48 hours resulted in a retrogressive behavior where the strength decreased.
- 4- An AAB-based mortar mixture with, a flow of 201 mm, an initial setting time of 46 minutes, a final setting time of 77 minutes, and a 28-day compressive strength of 30 MPa can be considered as having the most optimum activation parameters and curing regime. The optimum A/P and NS/NH ratios, NH molarity, W/P ratio, and curing regime were found to be as follows: 0.5, 2, 10 M, 0.4, and 24-hour steam

curing, respectively. However, for applications requiring lower strength and/or different setting times, the other developed trial mixtures can be used.

- 5- XRD analysis showed the formation of various aluminosilicate-based polymers such as NASH, CASH, and KASH in addition to CSH, Mn-SH, and Mn-CH with A/P, NS/NH, NaOH molarity having a proportional influence on their formation while W/P had the opposite effect. FTIR confirmed the formation of those phases. SEM micrographs showed the formation of uniform hydration products, resulting in a sturdy and dense microstructure with the hydration product filling the microcracks. The observations made through these microstructural examinations validated the trends observed in the compressive strength results with variation in the activation parameters.

CHAPTER 5. PHYSICAL, MECHANICAL, DRYING SHRINKAGE, AND ACID AND SULPHATE ATTACKS PROPERTIES

5.1. Overview

This chapter investigates the properties of alkali-activated concrete (AAC) mixtures prepared using the optimum combinations of four precursor materials (limestone powder, red mud, silicomanganese fume, and natural pozzolana) and four activation parameters (activator to precursor ratio, silica modulus, sodium hydroxide molarity, and water to precursor ratio) that were obtained by initial investigation highlighted in the previous chapter. In order to examine the beneficial effects of inclusion of ordinary Portland cement (OPC) and curing regimes on the properties of AAC, three dosages of OPC (in the range of 10 to 30% by weight) and two curing regimes (steam and ambient-air curing) were considered. Tests were conducted on the mixtures of AAC to determine different properties that included the density, void ratio, water absorption, compressive and tensile strengths, modulus of elasticity, drying shrinkage, and loss of weight and strength after exposure to acid and sulfate salt solutions. Additionally, microstructural investigations (XRD and SEM-EDS) were conducted on the alkali-activated binders to justify the trends of the experimental data pertaining to different properties of the AAC mixtures.

5.2. Materials

The same raw precursor materials, activators and fine aggregates that were used for the initial optimization were used in the development of the AAC and OPC mixtures. Calcareous limestone aggregates from the Riyadh Province of Saudi Arabia that has a

specific gravity of 2.55, absorption of 1.6%, and moisture content of 0.98% were utilized. A gradation conforming to the ASTM C33 standard was chosen (Figure 5-1) with a maximum aggregate size of 12.5 mm ($\frac{1}{2}$ inch). The gradation of the fine aggregate is also presented in Figure 5-1. All materials used were kept in sealed containers to maintain the same moisture properties and avoid oxidization.

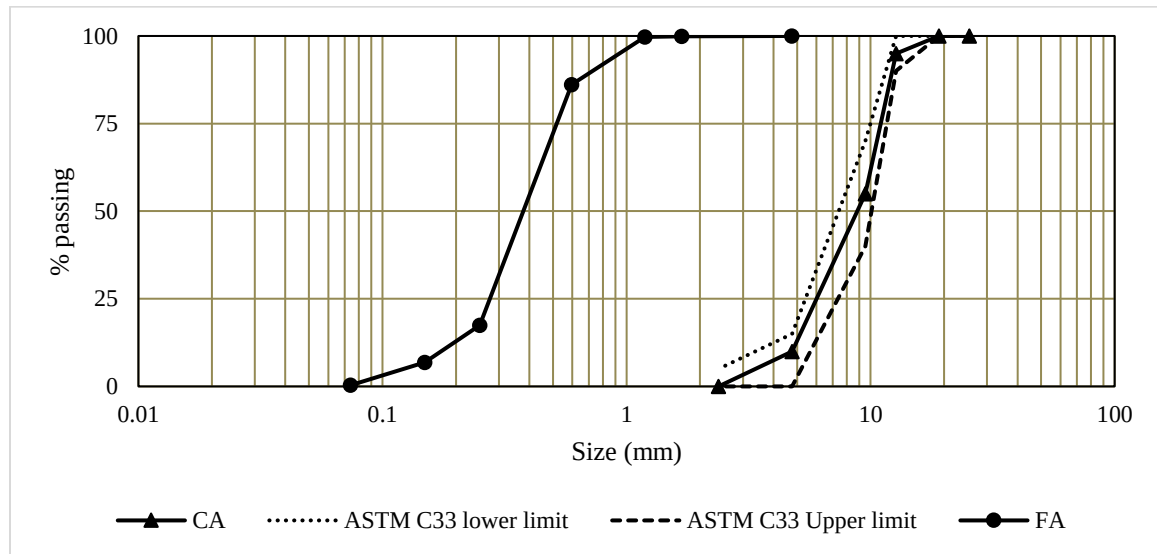


Figure 5-1 CA and FA gradation

5.3. Mixture optimization and design

Unlike OPC mixtures, AACs have multiple factors that influence their performance. These factors include precursor composition, activation parameters, and curing regime. The key activation parameters include the A/P ratio, NS/NH ratio, NH-molarity, and W/P ratio. Firstly, the precursor composition (i.e., proportioning of PMs) was optimized based on the results of the flow, setting times and compressive strength tests on trial mortar mixtures. Three optimum precursor compositions were considered and then the optimum levels of the activation parameters were determined through trial experiments. In total, 6 AAC mixtures were selected (3-optimum precursor compositions $\times$ 2-curing regimes $\times$ 1-

optimum set of activation parameters) for evaluation of their physical, mechanical, shrinkage and durability characteristics, as shown in Table 5-1. The optimum levels of activation parameters were selected as follows: the A/P ratio of 0.5, NS/NH ratio of 2.0, NH-molarity of 10 mol/liter, and W/P ratio of 0.40.

Table 5-1 Optimum AAC mixtures under investigation

ID*	Curing regime	Proportion of PMs (% by wt.)				
		OPC	NP	LSP	SMF	RM
10CA	Ambient air curing	10	50	10	10	20
20CA		20	40	10	10	20
30CA		30	30	10	10	20
10CS	Steam curing for 24 hours	10	50	10	10	20
20CS		20	40	10	10	20
30CS		30	30	10	10	20
*Naming followed the formula (a ₁)C(a ₂), where a ₁ represents the OPC content expressed as a percentage of the precursor and a ₂ represents the curing regime where “S” is used for steam curing for 24 hours and “A” is used for ambient air curing. For example, 10CS is the label of the mixture with 10% OPC in its precursor that was steam cured for 24 hours.						

The proportioning of all six AAC mixtures, as shown in Table 5-1, was carried out using a modified version of the ACI’s mixture design method. The absolute volume equation, used for determining the quantities of the AAC’s ingredients, is as follows:

$$V_C = V_P + V_{NS} + V_{NH} + V_{CA} + V_{FA} + V_{Wa} + V_{air} \quad \text{Equation 5-1}$$

Where V_C , V_P , V_{NS} , V_{NH} , V_{CA} , V_{FA} , V_{Wa} , V_{air} , are the absolute volumes of concrete, precursor, NS, NH, CA, FA, additional water, and air, respectively. Considering the volume of the concrete as 1 m³, absolute volume of each ingredient can be converted to their respective weights (W) in kg divided by their absolute densities ($\rho = \text{unit weight of water} \times \text{specific gravity}$) in kg/m³, as follows:

$$1 = \frac{W_P}{\rho_p} + \frac{W_{NS}}{\rho_{NS}} + \frac{W_{NH}}{\rho_{NH}} + \frac{W_{CA}}{\rho_{CA}} + \frac{W_{FA}}{\rho_{FA}} + \frac{W_W}{\rho_W} + V_{air} \quad \text{Equation 5-2}$$

The absolute density of the precursor (containing five different PMs) can be calculated as follows:

$$\rho_P = W_P \left(\frac{W_{OPC}}{\rho_{OPC}} + \frac{W_{LSP}}{\rho_{LSP}} + \frac{W_{NP}}{\rho_{NP}} + \frac{W_{RM}}{\rho_{RM}} + \frac{W_{SMF}}{\rho_{SMF}} \right)^{-1} \quad \text{Equation 5-3}$$

The precursor's content per cubic meter of concrete (W_P) and the coarse aggregate ratio to total aggregate (CA/TA) were chosen to be 400 kg/m³ and 0.6 (by weight), respectively.

The air content was assumed to be 3% based on the nominal maximum aggregate size.

The six AAC mixtures (10CS, 20CS, 30CS, 10CA, 20CA, and 30CA) and a control OPC mixture labeled “100C” (since the binder was composed of OPC alone as a binder in order to compare the performance of AACs to traditional OPC mixtures) were considered for casting and testing. The proportions of all seven mixtures, as obtained from the calculations using the absolute volume method described above, are presented in Table 5-2.

Table 5-2 Mixture proportioning

Mixture Group	Mixture ID	Proportion (kg/m ³ concrete)										
		OPC	LSP	NP	RM	SMF	NS	NH	Water	FA	CA	Curing
Steam group	10CS	40	40	200	40	80	133	67	33	677	1016	Steam for 24 hours
	20CS	80	40	160	40	80	133	67	33	678	1017	
	30CS	120	40	120	40	80	133	67	33	679	1018	
Ambient air group	10CA	40	40	200	40	80	133	67	33	677	1016	Ambient air
	20CA	80	40	160	40	80	133	67	33	678	1017	
	30CA	120	40	120	40	80	133	67	33	679	1018	
Control	100C	400	-	-	-	-	-	-	161	705	1058	Standard

5.4. Casting and curing

The molds were assembled and coated with oil using a soft brush, and any excess oil was allowed to drain. Then, the coarse aggregate, fine aggregate, and dry precursor materials were mixed thoroughly in the basin of a wheelbarrow until a homogenous dry mixture was achieved. The activator solution and additional water were then added in thirds and mixed for 2 minutes between each addition of the liquids. When the final third was added, the concrete was mixed for an additional 4 minutes and then was cast in the prepared molds in three layers while being vibrated for 20 seconds between each pour. The top surface was then leveled using a trowel, and the specimens were covered with plastic sheets until setting to prevent moisture loss. The specimens were demolded after 24 hours of casting and cleaned with a soft vinyl paintbrush to remove any loose debris and excess oil on the surface. The same mixing and demolding procedures were followed for mortar and paste specimens (mortar used for drying shrinkage monitoring and paste used for sulfate and acid attacks evaluation, and for microstructural analysis) except for adding the coarse and fine aggregate, respectively.

Ambient-air curing specimens (i.e., mixtures 10CA, 20CA, and 30CA) were wrapped in plastic cling-film, kept inside polyethylene bags, and sealed under room temperature conditions (23 ± 5 °C and 60% relative humidity) until testing. As for the steam-cured mixtures (i.e., 10CS, 20CS, and 30CS), the specimens were placed after demolding and cleaning inside a chamber that was provided with a resistance-heating element. The specimens were suspended inside the chamber using a screen, and the chamber was half-filled with potable water. The heating element was set to boil the water, and the chamber was covered with a lid to allow condensation. Steaming was carried out for 24 hours, and

then the specimens were allowed to cooldown to room temperature inside the chamber. They were then wiped with a microfiber cloth and sealed inside bags under the same conditions as the ambient-air specimens until testing. Finally, the control mixture specimens (i.e., 100C) were demolded and cured by submersion in potable water for 28 days at room-temperature, after which the specimens were allowed to air-dry and then sealed inside bags to minimize carbonation until testing.

Table 5-3 Summary of tests conducted on the AAC, mortar, and paste specimens

Test		Standard	Specimen type	Specimen size	Number of samples	Age at test	Duration
Physical properties	Density, Void and Absorption	ASTM C642	Concrete	75 mm dia. cylinder	3	28 days	-
Mechanical properties	Compressive strength	ASTM C39	Concrete	75 mm dia. cylinder	3	28 days	-
	Modulus of elasticity	ASTM C469	Concrete	75 mm dia. cylinder	3	28 days	-
	Split tensile strength	ASTM C496	Concrete	75 mm dia. cylinder	3	28 days	-
Shrinkage	Drying Shrinkage	ASTM C596	Mortar	25 mm × 25 mm × 250 mm prism	3	28 days	180 days
Acid and sulphate Attack	Acid attack	ASTM C1898	Paste	25 mm cube	3	28 days	90 days
	Sulphate attack	ASTM C1012	Paste	25 mm cube	3	28 days	180 days
Micro-structure	XRD	-	Paste	25 mm cube	1	28, 118, 208 days	-
	SEM-EDS	-	Paste	25 mm cube	1	28, 118, 208 days	-

Specimen size and type varied based on the test to be conducted. Acid and sulphate attack, mineralogical and morphological tests were conducted on paste samples, while the remaining tests were conducted on concrete specimens except for the drying shrinkage, which was conducted on mortar samples, as mentioned previously. Table 5-3 summarizes

the specimen size, the number of samples, the standard followed, and the type of specimen for each test.

5.5. Evaluation

5.5.1. Density, void ratio and water absorption test

Three 75 mm-diameter cylindrical concrete specimens were used to determine the density, void ratio, and water absorption by conducting a test on the specimens of AAC mixtures in accordance with the ASTM C642 standard. This test estimates the density, surface-connected and permeable voids (expressed as a percentage of the total volume), and water absorption capacity (expressed as a percentage by mass of concrete) by measuring the weight of specimens at different moisture and buoyancy conditions. The specimens were first oven-dried at a temperature of 110°C for 48 hours, and their dry weights (W_D) were recorded. Then the specimens were submerged in boiling water for 6 hours, after which they were allowed to cool down while submerged in the water for a further 18-hour period, and their weights were monitored until no change in the weight was observed so as to ensure saturation. The final weight recorded during saturation was taken as the saturated-surface dry weight (W_S). After that, the specimens were suspended in water, and their suspended weights (W_U) were recorded. Finally, the dry density (ρ_D), saturated-surface dry density (ρ_S), apparent density (ρ_A), void ratio (ν), and water absorption (ω) were calculated using the following equations (Equations 5-4 through 5-8):

$$\rho_D = [W_D / (W_S - W_U)] \times \rho_W \quad \text{Equation 5-4}$$

$$\rho_S = [W_S / (W_S - W_U)] \times \rho_W \quad \text{Equation 5-5}$$

$$\rho_A = [W_D / (W_D - W_U)] \times \rho_W \quad \text{Equation 5-6}$$

$$v = [(W_S - W_D) / W_D] \times 100 \quad \text{Equation 5-7}$$

$$\omega = [(W_S - W_D) / (W_S - W_U)] \times 100 \quad \text{Equation 5-8}$$

Where, ρ_W is the density of water (i.e., 1000 kg/m³).

5.5.2. Mechanical properties

5.5.2.1. Compressive strength (f'_c)

Following the ASTM C39 standard, three 75 mm in diameter and 150 mm in length concrete cylindrical specimens were tested at 3, 7, and 28 days to determine the compressive strength. The specimens were tested using a Matest C088-11N Servo-plus Progress compression testing machine at a loading rate of 0.25 ± 0.05 MPa until failure. The specimens were taken out from the curing basin 12 hours before testing for the OPC control mixture. The maximum load before failure was used to calculate the compressive strength (f'_c) following Equation 5-9. The fracture pattern was also recorded following the standard. The average and standard deviation of the three specimens were calculated.

$$f'_c = 4P / \pi D^2 \quad \text{Equation 5-9}$$

Where P is the maximum applied load and D is the diameter of the specimen.

5.5.2.2. Split-tensile strength

Unlike the direct tensile strength test, where concrete is subjected to a uniaxial tensile load, the split-tensile strength test consists of applying tensile stress on the concrete along one plane while applying considerable compressive stresses around that plane. The split-tensile strength is lower than the modulus of rupture (flexural strength of concrete) and higher than the direct tensile strength. Three 75 mm in diameter and 150 mm in length cylindrical

specimens were tested for the split-tensile strength in accordance with the ASTM C496 standard. The specimens were tied to 25 mm wide stainless-steel strips at the top and bottom faces, subjected to loading via paper tape, and then subjected to compression (Figure 5-2). The specimens were stressed until failure at a loading rate of 0.1 kN/sec.



Figure 5-2 Split-tensile strength test setup

The maximum load (P) before failure was recorded, and the split tensile strength (T) was calculated using the following equation:

$$T = 2P/\pi ld \quad \text{Equation 5-10}$$

Where l and d are the length and diameter of the specimen, respectively.

5.5.2.3. Modulus of elasticity (E_c)

The modulus of elasticity was determined after 28-day for each AAC mixture. The specimen, used for the compressive strength test, was attached to two linear variable displacement transducers (LVDTs) parallel to the loading direction of the specimen to record the deformation during compression loading. The LVDTs were fixed to the specimen by a steel ring mechanism (Figure 5-3). The LVDTs were connected to a data logger, and a calibrated load-sensing cell that was placed under the specimen. The data

logger recorded the load versus displacement data at 1-second intervals until failure. The normal strain was then calculated from the displacement, while the normal stress was calculated from the load values. A stress-strain curve was plotted, and the static modulus of elasticity was calculated based on the ASTM C469 chord method (Equation 5-11).

$$E_c = 1000 \times (\sigma_{40\%} - \sigma_{50}) / (\varepsilon_{40\%} - 50) \quad \text{Equation 5-11}$$

Where E_c is the static chord modulus of elasticity (in GPa), $\sigma_{40\%}$ and $\varepsilon_{40\%}$ are stress (in MPa) and strain (in microstrain) at 40% of f'_c , respectively, and σ_{50} is the stress (in MPa) at a strain of 50 microstrain.



Figure 5-3 Modulus of elasticity setup showing LVDTs and load cell

5.5.3. Drying shrinkage

Three prism specimens with dimensions: 25 mm × 25 mm × 250 mm, cast using mortar having a sand-to-precursor (S/P) ratio of 2 following the casting and curing procedures illustrated previously, were used for monitoring the drying shrinkage. At the age of 28 days, the specimens were removed from storage, and the initial length was measured by a length comparator using an LVDT connected to a data logger following the ASTM C596

standard. The specimens were then allowed to dry in air, and the change in length was frequently recorded for 180 days to determine the drying shrinkage. Length readings were taken daily for the first 14 days, every two days until 30 days, weekly until 60 days, and monthly until 180 days.

5.5.4. Acid and sulfate attacks

Nine cubical paste specimens 25 mm in size were cast for each mixture. Specimens were first conditioned in water for 48 hours before exposure to acid and sulfate solutions. Three specimens were submerged in water as control. Another three specimens were placed in a container filled with 3% sulfuric acid solution (pH=1.23) for evaluating the effect of the acid attack for a duration of 90 days. Last three specimens, used for evaluating the effect of sulfate attack, were placed in a container filled with a solution of sodium sulfate and magnesium sulfate at a combined concentration of 20% (10% MgSO₄ +10% Na₂SO₄) for an exposure duration of 180 days. The specimens exposed to acid and sulfate solution were weighed before exposure. The pH of the acid exposure solution was measured bimonthly, and extra sulfuric acid was added to maintain the pH around the targeted value of 1.23. The specimens were washed after each exposure with tap water, and loose material, if any, was removed from the surface using a soft nylon brush. The specimens were visually inspected, weighed, and the residual compressive strength was determined. By comparison to other specimens that were kept in water for the same exposure period, the strength and weight losses were calculated using the following equations:

$$\Delta f'c = (f'c_w - f'c_E)/f'c_w \times 100 \quad \text{Equation 5-12}$$

$$\Delta m = (W_w - W_E)/W_w \times 100 \quad \text{Equation 5-13}$$

Where $\Delta f'_c$, Δm are strength loss (%) and weight loss (%), respectively while f'_c , W_w , f'_c , and W_E are the compressive strength and mass for specimens placed in water and acid/sulfate solution, respectively.

5.5.5. Microstructure

5.5.5.1. Mineral composition

The mineral composition of the steam-cured binders was studied by extracting a portion from the center of paste specimens that were pulverized and analyzed by XRD using a Rikagu Miniflex II diffractometer. After an exposure of 180 days in sulfate solution and 90 days in acid solution, portions of paste from the peripheries of the specimens were also pulverized and studied using XRD.

5.5.5.2. Morphology

The effects of the OPC content of the precursor, curing regime, acid exposure, and sulfate exposure were studied by SEM imaging using a JEOL microscope at a 20-mA current and high vacuum conditions. Samples were extracted from the core of the paste specimens to highlights the influence of the OPC content and curing regime while samples extracted from the peripheries of the paste specimens exposed to sulfuric acid and sulfate salts were used to study the influence of the exposures on the morphology. The samples were held by a double-sided copper tape during testing, and a sputter gun sprayed a 20-nm layer of gold on the surface of the samples.

5.6. Results and discussion

5.6.1. Density, void ratio and water absorption

Figure 5-4 and Figure 5-5 show the results of densities (dry, saturated-surface dry, and apparent), void ratio and water absorption test.

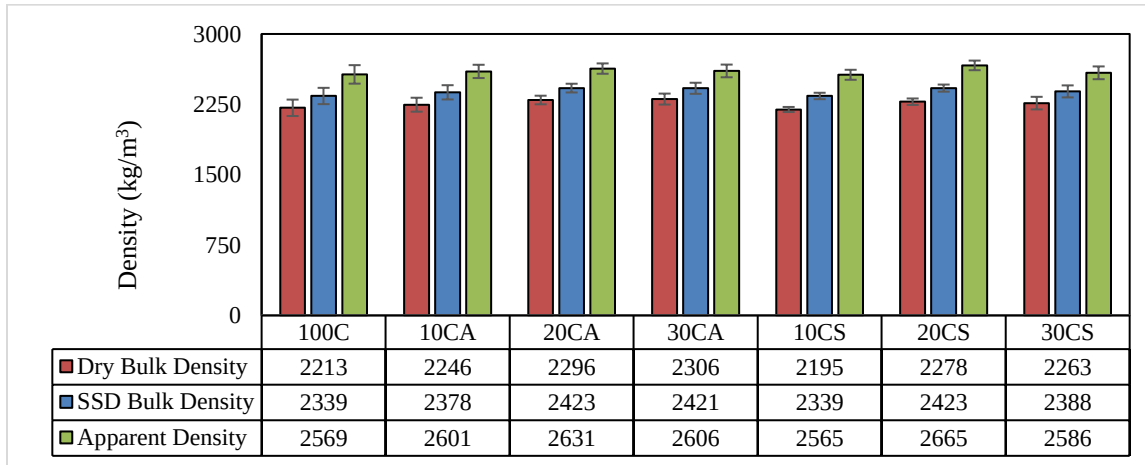


Figure 5-4 Densities of the concrete mixtures at 28 days

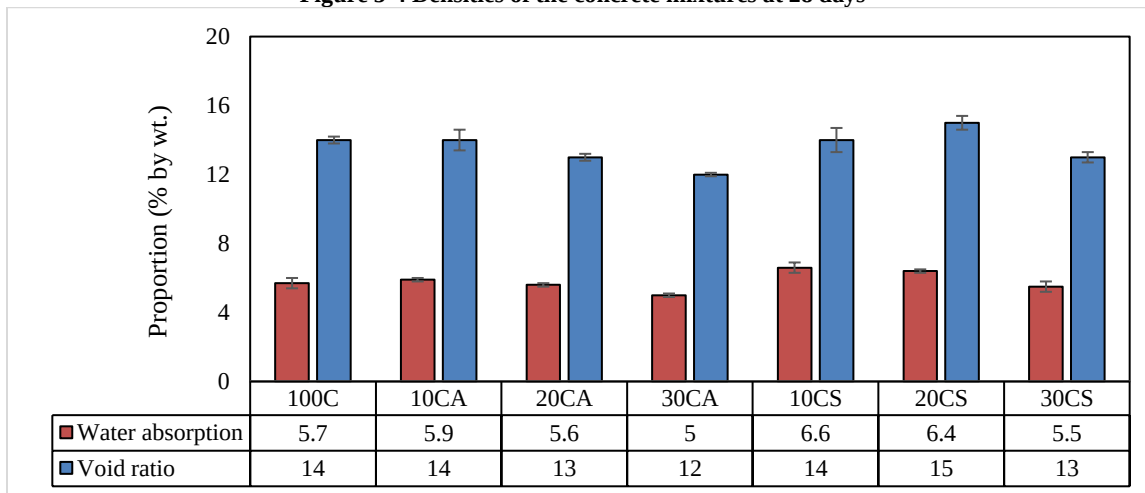


Figure 5-5 Water absorption and void ration of the concrete mixtures at 28 days

Both the AAC mixtures and control mixture exhibited insignificant variations in their density, void ratio and water absorption values. The variations in density, water absorption, and voids were less than 90 kg/m³, 1.1%, and 3%, respectively. This can be owed to the minimal variation in the densities of the constituents used in the preparation of AAC and

control mixture (specific gravities ranging from 2.88 to 3.1) as well as all mixtures possessing the same water, fine aggregate, and coarse aggregate contents which constitute more than 75% of the weight of the concrete.

5.6.2. Mechanical properties

5.6.2.1. Compressive strength

The compressive strength development with age is shown in Figure 5-6. Type 3 fracture pattern (i.e., columnar vertical cracking through both ends of the specimen with no well-formed failure cones) was observed in all specimens according to the ASTM C39 standard. The control mixture reached a maximum compressive strength of 29.4 MPa at 28 days. Its rate of strength development trend seems to agree with results reported in the literature for OPC mixtures with similar mixture characteristics [5]. Regarding the compressive strength of the AACs, steam-cured mixtures exhibited higher compressive strengths at all ages compared to their ambient-air cured counterparts. The increase in the compressive strength in the steam-cured mixtures is more pronounced at the early age (i.e., three days) where increases of 100%, 75%, and 44% were observed for 10CS, 20CS, and 30CS compared to 10CA, 20CA, and 30CA, respectively. Higher compressive strength for the steam-cured AAC mixtures may be attributed to the formation of more polymerization products due to increasing the temperature during curing. The temperature highly influences the polymerization reaction, which has been reported by other researchers [171], [182], [188]. In addition, it is worth noting that around 90% of the ultimate compressive strength for the steam-cured AAC mixtures was reached during the first seven days, indicating its

feasibility for applications where rapid strength gain is necessary such as for precast concrete members.

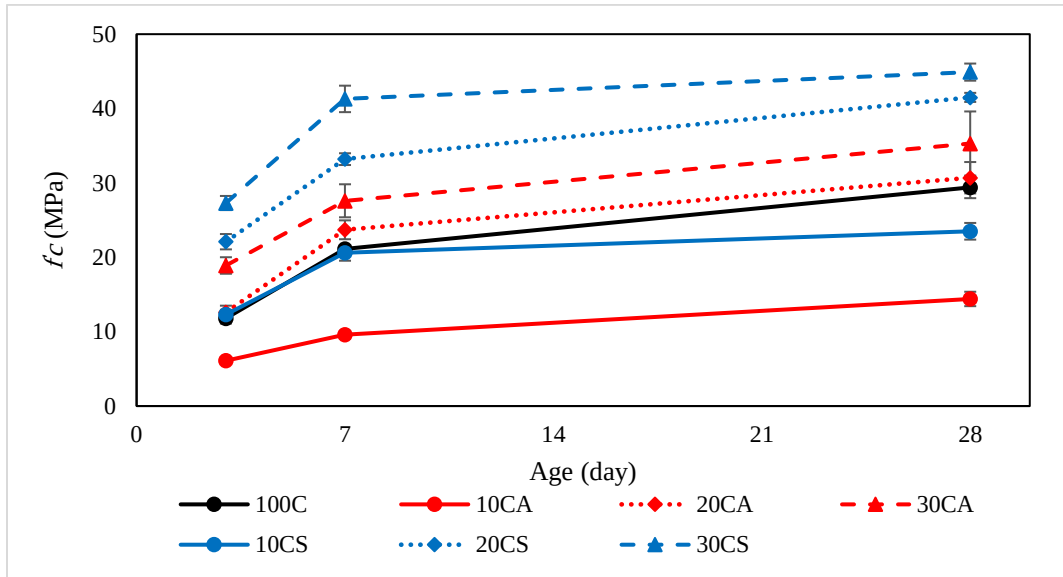


Figure 5-6 Compressive strength development of the AACs

The compressive strength increased with the increase in OPC content of the AACs. More significant increase in the compressive strength (113% for the air cured mixtures and 44% for the steam cured mixtures) was observed when the OPC content of the precursor increased from 10 to 20%. The developed AACs (except for 10CA and 10CS) had higher compressive strength than the control mixture even under ambient curing conditions at all ages. At 28 days, 20CA, 30CA, 20CS, and 30CS exhibited compressive strengths of 30.7 MPa, 35.3 MPa, 41.5 MPa, and 44.9 MPa, which is higher than the requirement for standard concrete ($f'_c > 27.6$ MPa [4000 psi]) and higher than the control mixture. In addition, 20CS and 30CS exhibited compressive strength beyond 41.4 MPa (6000 psi) required for the high-strength concrete classification. Higher strength indicates a more tightly-packed microstructure where voids are filled with polymerization products.

5.6.2.2. Split-tensile strength

Figure 5-7 shows the plots of the split-tensile strength results of the developed six AAC and control OPC mixtures. The tensile strength values ranged from 1.11 to 3.3 MPa. The control mixture had an average split tensile strength of 2.8 MPa, which is higher than all the AAC mixtures except for the AAC mixtures containing 30% OPC in the precursor (i.e., 30CA and 30CS), which were higher than that of control mixture (100C). The steam-cured AAC mixtures exhibited higher tensile strengths than the ambient-cured mixtures, a trend that has been observed for the compressive strength as well. Further, the tensile strength increased with increasing OPC content in the precursor, which was also observed in case of the compressive strength.

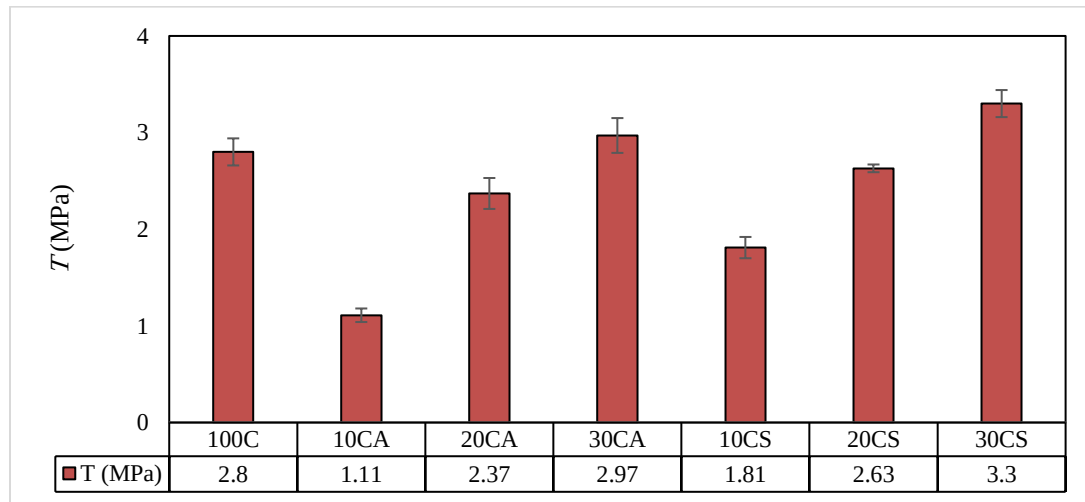


Figure 5-7 Split tensile strength results

The split-tensile can be used as a conservative estimate of the flexural strength of concrete. Researchers have reported split tensile strengths that are 50-60% lower than flexural strength. The flexural strength is an important design parameter for prestressed concrete where the tensile stresses are designed to be less than the modulus of rupture (i.e., flexural strength) of concrete. The split-tensile strength test results were used to develop an

empirical model to correlate the split-tensile strength with the compressive strength. The best-fitted model obtained is as follows (Equation 5-14):

$$T = 3.409\sqrt{f'_c} - 4.902 \quad \text{Equation 5-14}$$

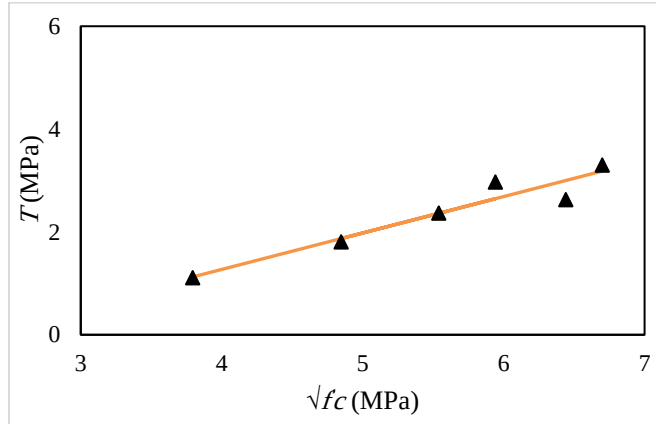


Figure 5-8 Regression results of the split tensile strength data

A high value of the coefficient of determination, $R^2 = 0.933$, indicates an excellent fit of the data, as also evident from Figure 5-8.

5.6.2.3. Modulus of elasticity

Figure 5-9 shows the plots of the results of 28-days static modulus of elasticity for the developed AAC mixtures.

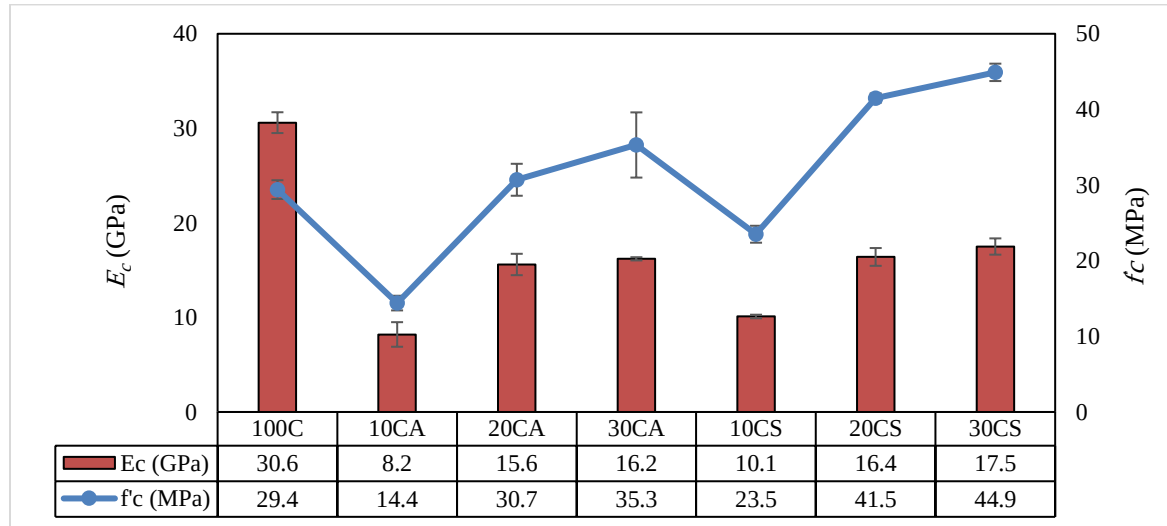


Figure 5-9 Modulus of elasticity and compressive strength of the developed concretes

Out of the six AACs, mixtures 30CS and 30CA showed the highest chord modulus of elasticity, followed by the 20CS and 20CA indicating the positive effect of increasing the dosage of OPC in the precursor. Mixtures 10CS, 20CS, and 30CS exhibited modulus of elasticity values larger than their ambient air cured counterparts (10CA, 20CA, and 30CA), which indicates the evolution of more tightly-packed microstructure due to steam curing.

It is very interesting to note that unlike the case of the compressive strength, the control mixture 100C showed a significantly higher value of modulus of elasticity as compared to those exhibited by all six AAC mixtures. Similar observations to the one made under the present study, i.e., lower modulus of elasticity and higher compressive strength values of AAC mixtures as compared to that of conventional OPC concrete, are reported in the literature [200], [201]. The reason behind higher values of the compressive strength and lower values of the modulus of elasticity of AAC mixtures may be attributed to the higher

ductility of the major polymerization products acting as binders (i.e., CASH, NASH and Mn-SH) as compared to the CSH which is the main component of the binder in case of conventional OPC concrete mixtures. Although, the bond between aggregates and binder matrix in AAC mixtures is better resulting in a higher compressive strength, the higher ductility of the binder matrix in AAC mixtures allows higher normal strain under the influence of the same compressive stress thereby decreasing the modulus of elasticity. Therefore, considering the fact that the AAC mixtures possess relatively lower modulus of elasticity without compromising the strength, they can be utilized in walls, slabs, and foundation of the buildings and structures where the deflection is controlled mainly by larger cross-sections unlike the case of slender members such as beams and columns where the deflection is governed by both cross-section and modulus of elasticity.

The American Concrete Institute (ACI) provides an empirical model to estimate the modulus of elasticity based on the compressive strength of conventional OPC concrete mixtures. However, the same model is unsuitable for AAC mixtures since they present lower moduli of elasticity as discussed previously. Hence, statistical analysis of the compressive strength versus modulus of elasticity data, generated for the AAC mixtures in the present study, was carried out and an empirical model based on the least squares method was obtained, as follows:

$$E_c = 3.409\sqrt{f'_c} - 4.902 \quad \text{Equation 5-15}$$

A high value of $R^2 = 0.936$ indicates that the developed model (Equation 5-15) had the high degree of fit of the data. The plots of the model developed in the present study was compared to the ACI-318 [202] model for normal OPC concrete mixtures, as well as to the

models developed by Noushini et al. [200] and Ibrahim et al. [201] for AAC mixtures, as shown in Figure 5-10. It can be observed from the plots shown in Figure 5-10 that, as expected the ACI model overestimates the modulus of elasticity for the same compressive strength values as compared to the models for the AAC mixtures, which supports the discussion on the reason behind lower modulus of elasticity of AAC mixtures presented previously.

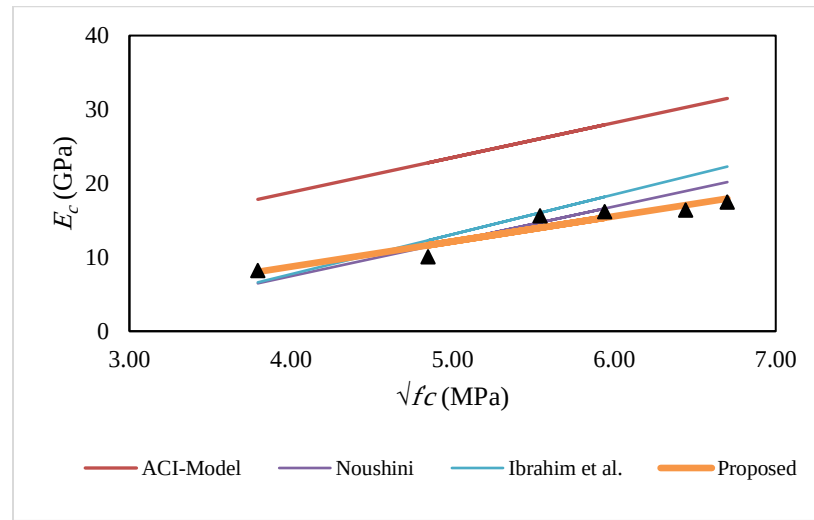


Figure 5-10 E_c models from the literature and the proposed model

5.6.3. Drying shrinkage

Drying shrinkage occurs when free water evaporates causing contraction of the concrete that develops tensile stress resulting in the cracking of concrete. Figure 5-11 shows the plots of the drying shrinkage versus age, up to 180 days, for the mixtures under the present study. The shrinkage rate was the highest during the first 30 days for all mixtures, after which a noticeable plateau in the shrinkage curves can be observed. Mixture 10CA had shrunk the most, followed by the control OPC mixture during the first 45 days, after which the latter surpassed it in shrinking. In addition, as OPC content increased in the precursor,

the drying shrinkage decreased significantly. This can be owed to the consumption of free water during hydration of OPC. Furthermore, as OPC content increased the pore structure was refined and filled by the polymerization/hydration products which further decreased the shrinkage exhibited by mixtures with higher OPC content irrespective of the curing method.

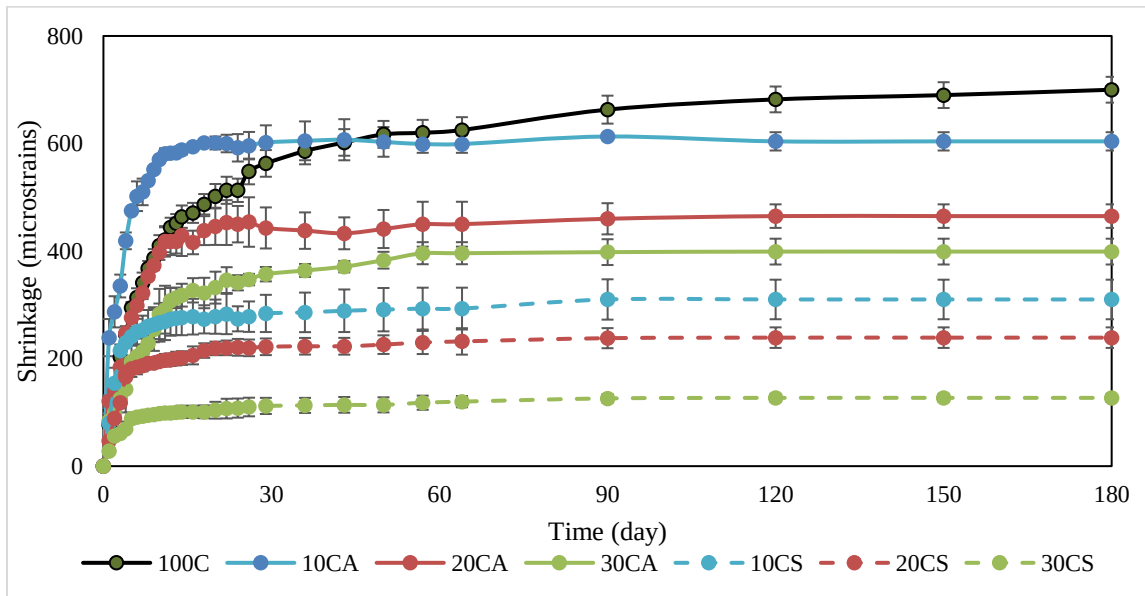


Figure 5-11 Drying shrinkage of the developed concretes

The maximum overall drying shrinkage was observed in case for the control mixture (100C), followed by the ambient-air cured and steam cured mixtures, respectively. At seven days, a maximum shrinkage of 510 microstrains (i.e., $\mu\text{m/m}$) was observed for mixture 10CA, representing an increase of 49.6 % compared to the control mixture, which had a drying shrinkage of 341 microstrains. Mixtures 20CA, 30CA, 10CS, 20CS, 30CS shrank by 322, 213, 253, 187, and 93 microstrains at 7 days which represent decreases of 5.6, 37.5, 25.8, 45.2, and 72.7%, respectively, compared to the control mixture (Figure 5-12). The limit for drying shrinkage at 28 days is 0.05% (i.e., 500 microstrains) which

was exceeded by mixtures 100C (563 microstrains) and 10CA (602 microstrains). The other developed mixtures showed significantly lower drying shrinkage values of 443, 357, 284, 222, and 112 microstrains for 20CA, 30CA, 10CS, 20CS, and 30CS at 28 days which represent decreases of 21.3, 36.6, 49.6, 60.6, and 80.1%, respectively. At the end of the experiment, the control mixture (100C) exhibited the maximum shrinkage of 700 microstrains compared to that of all six AAC mixtures, which were significantly lower. There was an overall decrease in the maximum drying shrinkage of 12.4, 34.9, 43.0, 55.7, 65.9, and 81.9% for mixtures 10CA, 20CA, 30CA, 10CS, 20CS, 30CS, respectively, at 180 days, which indicates that the AAC mixtures developed stronger microstructures with refined pores that were able to resist and limit the shrinkage caused by the loss of moisture.

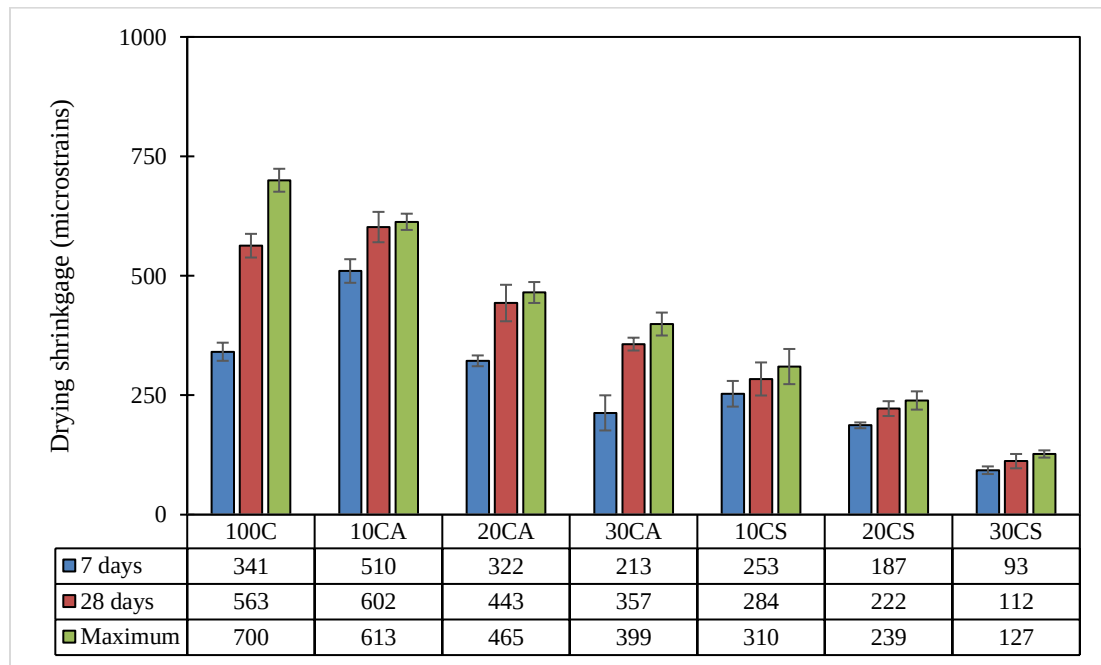


Figure 5-12 Drying shrinkage summary

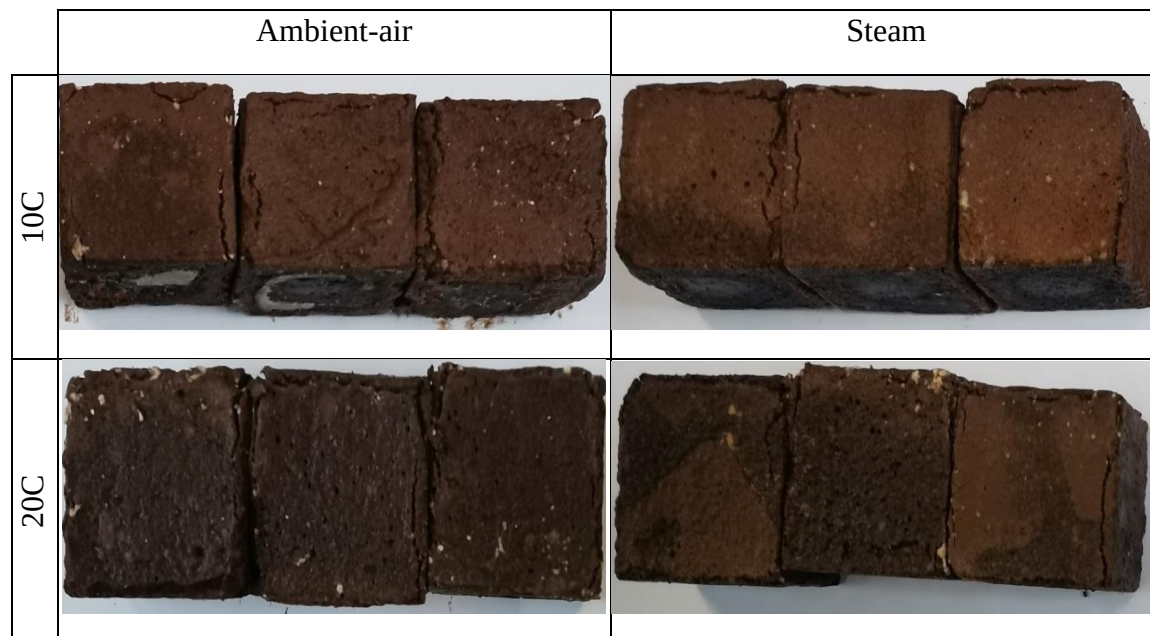
In addition, similar to the observed beneficial effect on the mechanical properties, the steam-cured AAC mixtures exhibited drying shrinkage values less than their ambient-air cured AAC mixture counterparts at all ages indicating that the microstructure of the prior

was more tightly-packed and refined than the latter, thus restricting the shrinkage caused by the loss of moisture.

5.6.4. Durability

5.6.4.1. Acid attack

Figure 5-13 shows the physical condition of the AAC paste specimens after exposure to 3% sulfuric acid for 90 days. The specimens showed minimal signs of damage despite the low pH of the exposure medium (≈ 1.23). After exposure, the surface had changed color to a brighter brown and had become covered with a soft calcium sulfate dihydrate layer. The edges of the paste specimens had begun to show signs of cracking and detachment, especially in the case of the low OPC content mixtures (i.e., 10CS and 10CA). Furthermore, the outermost layer of paste of those specimens had started to show signs of detachment as the acid had penetrated the underlying binder causing depolymerization and deterioration. Specimens with higher OPC content showed less signs of visual deterioration.



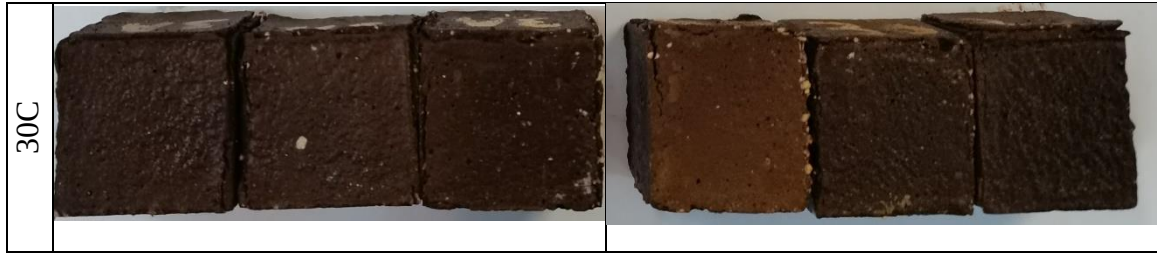


Figure 5-13 AAB specimens after 90 days of exposure to 3% sulfuric acid

Figure 5-14 shows the weight loss measured at the end of acid exposure. It ranged from 1.05 to 7.53% compared to specimens kept in water. The control mixture (100C) had lost 3.12 % of its mass, while the ambient-air cured specimens had lost 7.53% for 10CA, 2.11% for 20CA, and 1.05% for 30CA of their masses. The steam-cured specimens lost 3.36% for 10CS, 2.48% 20CS, and 1.35% for 30CS of their respective average masses.

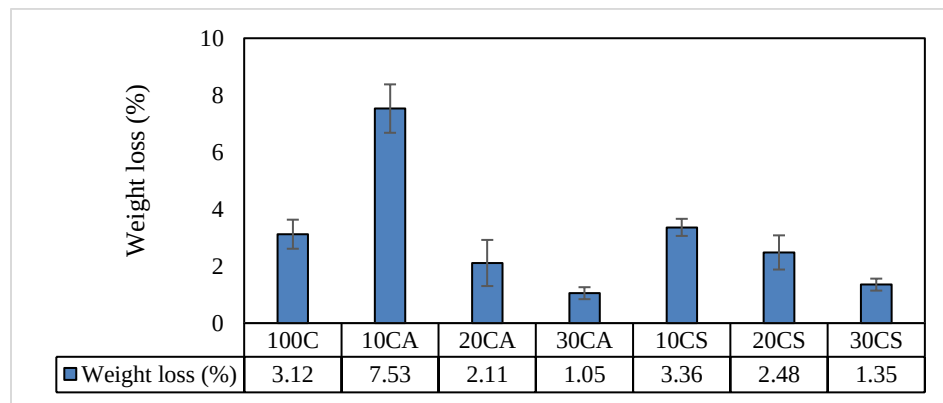


Figure 5-14 Weight loss after 90 days of exposure to 3% sulfuric acid

Figure 5-15 shows the strength loss and residual strength of the control OPC and AAB paste specimens after exposure to sulfuric acid for 90 days. The control mixture lost a third of its compressive strength after exposure and had a residual compressive strength of 30 MPa. All of the AAB specimens showed residual strengths lower than the control except for 30CS and 30CA, which had residual strengths of 34 MPa and 31 MPa, respectively. It is worth noting that the steam-cured mixtures showed greater compressive strength losses (as a percentage of their initial compressive strength) compared to the ambient-cured specimens. However, their residual strengths were still higher than the ambient-cured

specimens. This indicates that steam curing can be both an advantage in terms of higher overall residual strength and a disadvantage in terms of more susceptibility to damage in acidic environments.

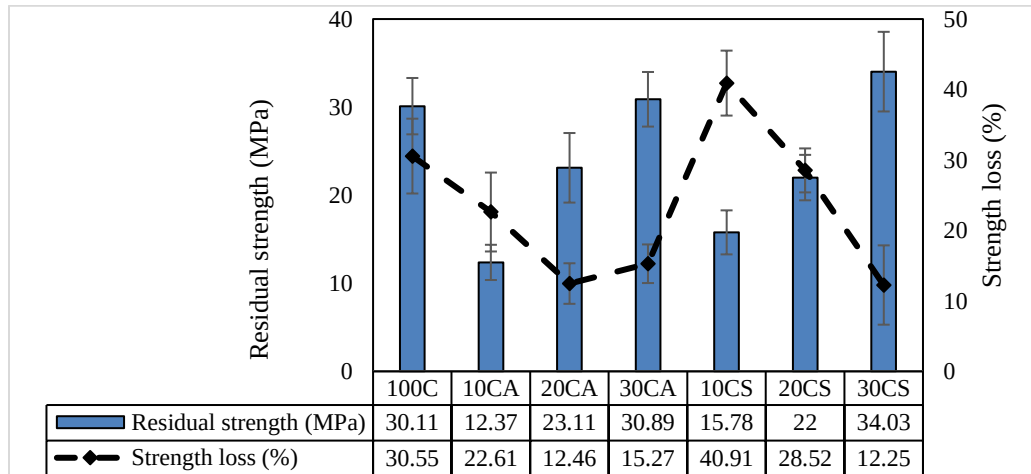


Figure 5-15 Residual strength and strength loss after 90 days of exposure to 3% sulfuric acid

5.6.4.2. Sulfate attack

Figure 5-16 shows the physical condition of the AAB paste specimens after 180 days of exposure to a mixture of sodium and magnesium sulfates at a combined concentration of 20% by weight. The specimens showed moderate to severe damage after exposure to the sulfate solution. Similar to the behavior of the specimens exposed to acid, mixtures with low OPC content (i.e., 10CA and 10CS) exhibited the most severe signs of damage where the majority of specimens (all of the specimens in the case of 10CA) had expanded and cracked into several pieces. The surface of the specimens had become covered with a mushy white precipitate which is thought to be a mixture of gypsum and calcite. The other specimens (i.e., 20CA, 20CS, 30CA, and 30CS) showed varying signs of expansion and delamination. Specimens with higher OPC content showed less sign of visual deterioration, especially 30CA and 30CS, which showed damages around the outermost layer along the edges only.

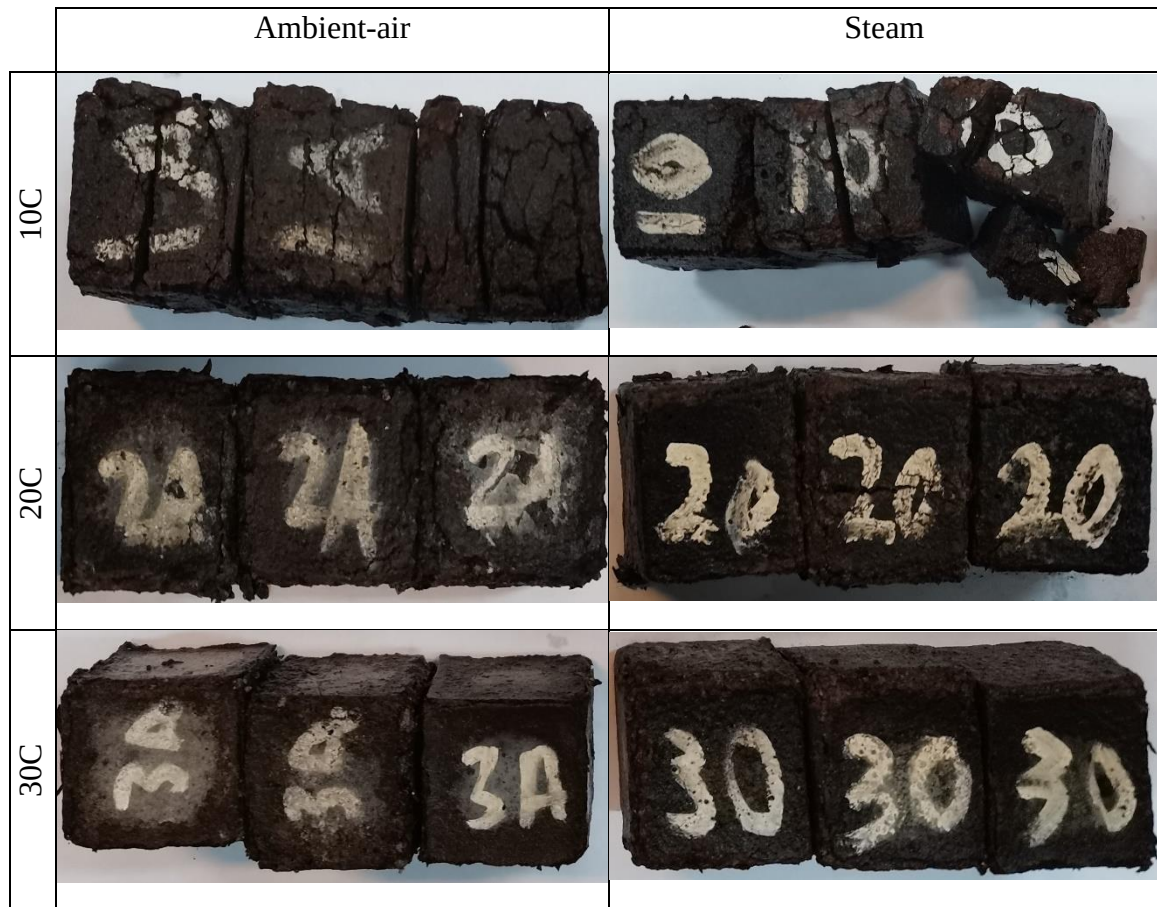


Figure 5-16 Sulfate attack specimens after 180 days of exposure

Figure 5-17 shows the weight loss of the specimens at the end of sulfate exposure. It ranged from 0.78 to 8.63% compared to specimens kept in water. The control mixture had lost 2.06% of its mass, while the ambient-air cured specimens had lost 2.37% for 20CA and 1.95% for 30CA. On the other hand, the steam-cured specimens lost 8.63% for 10CS, 1.85% 20CS, and 0.78% for 30CS of their respective average mass.

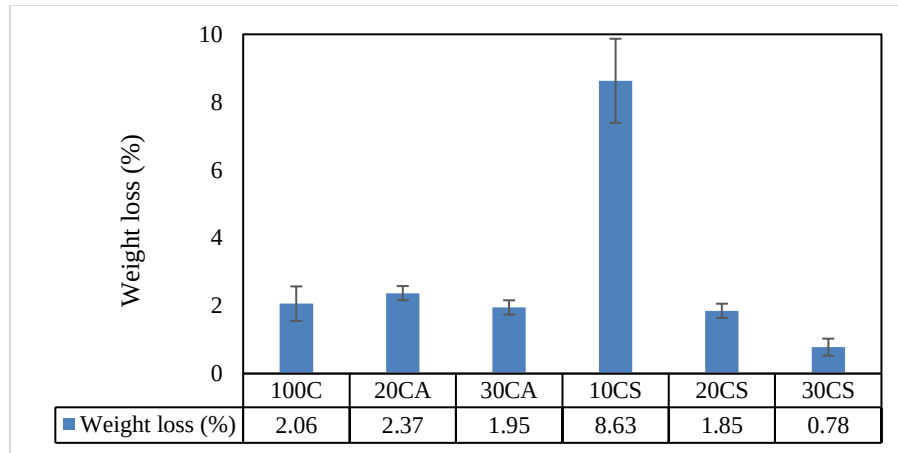


Figure 5-17 Weight loss after 180 days of exposure to 20% sulfate salts (Note: 10CA was not available since all of the specimens were severely damaged by the exposure and could not be tested)

Figure 5-18 shows the percentage strength loss and residual strength of the paste specimens at the end of the 180-day exposure to sulfate solution. The control mixture lost 44% of its compressive strength after exposure and had a residual compressive strength of 24.3 MPa. All of the AAB paste specimens showed residual strengths lower than the control except for 20CS, 30CS, and 30CA, which had residual strengths of 26.04 MPa, 38.6 MPa, and 27.99 MPa, respectively, higher than the residual strength. This indicates that increase in the dosage of OPC in precursor beyond 10% significantly improved the resistance to damage caused by sulfate attack. Further, the residual strengths of the steam-cured mixtures were higher than the ambient-cured mixtures of equal OPC content. This observation is in agreement with the observations made earlier in case of the mechanical properties, shrinkage and acid attack which supports the hypothesis that steam curing led to denser microstructures that possess superior properties at the same OPC content.

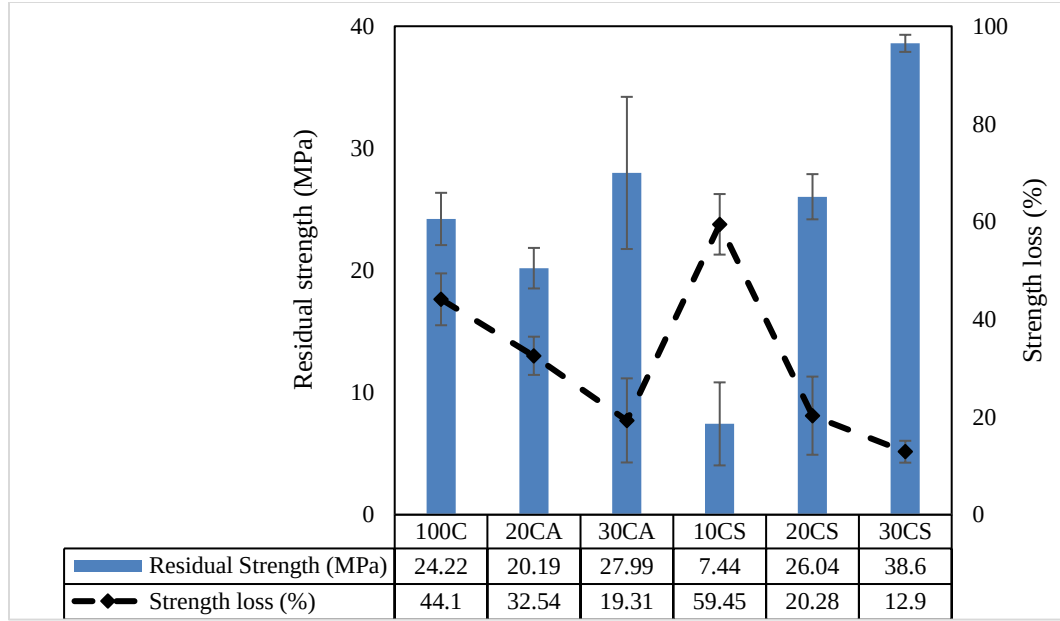


Figure 5-18 Residual strength and strength loss after 180 days of exposure to 20% sulfate salts (Note: 10CA is not available since all of the specimens were severely damaged by the exposure and could not be tested)

5.6.5. Microstructure

5.6.5.1. Mineral composition

5.6.5.1.1. Influence of OPC content and curing regime

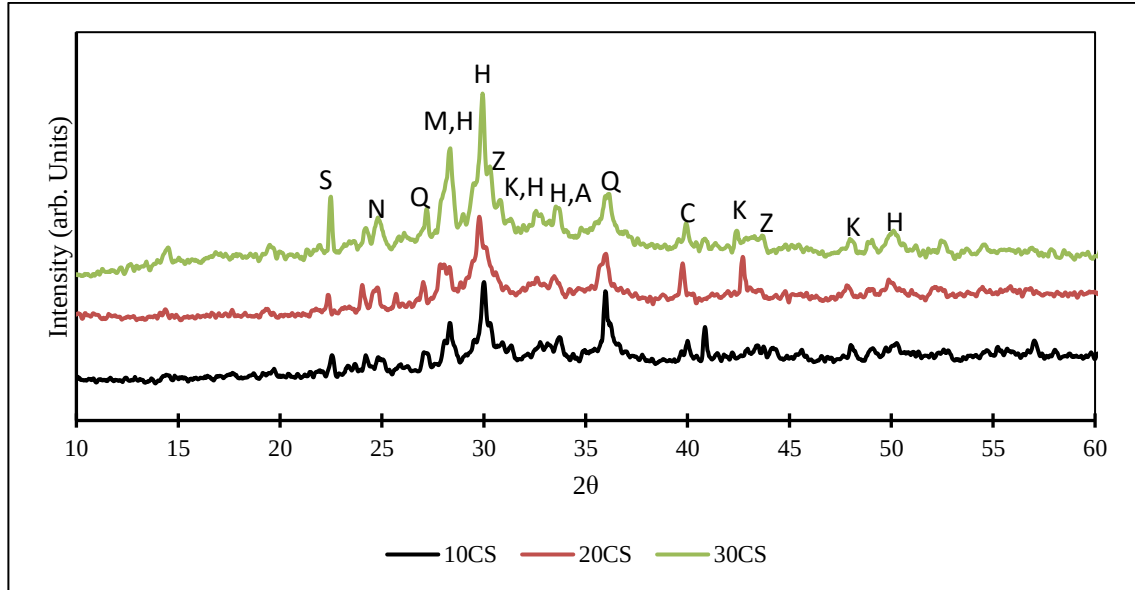
Figure 5-19 shows the XRD diffractograms of the AAB paste specimens of the mixtures under the present study. All of the specimens showed similar key mineral phases which are summarized in Table 5-4. The peaks of calcite at $22^\circ 2\theta$ can be owed to the carbonation of the specimens during pulverization and storage before testing, as well as the addition of the LSP in the precursor, which consists mainly of calcite.

Table 5-4 Summary of the phases identified by XRD

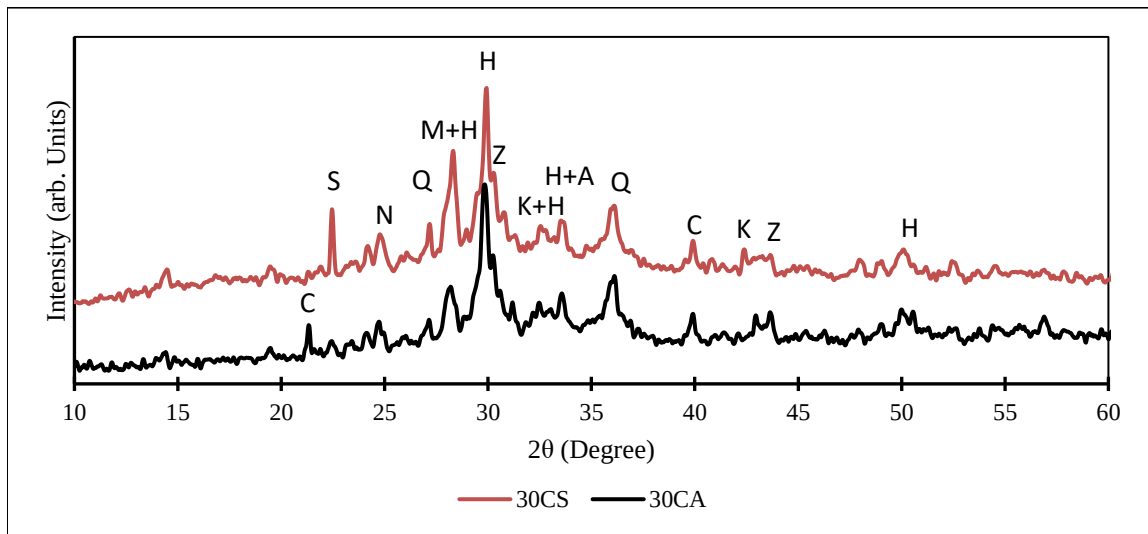
Mineral phase	Reference
Stratlingite ($\text{Ca}_2\text{Al}_2(\text{SiO}_2)(\text{OH})_{10}\cdot 2.5\text{H}_2\text{O}$)	[183]
Nchwaningite ($\text{Mn}_2\text{SiO}_3(\text{OH})_2\cdot \text{H}_2\text{O}$)	[184]
CSH	[183]
K-Feldspar (K-A-S-H)	[184]
Manganese calcium hydrate (Mn-C-H)	[184]
Portlandite (CH)	[186]
Calcite (CaCO_3)	[183], [185]
Quartz (SiO_2)	[184]
Anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$)	[187]
Sodium aluminosilicate hydrate (NASH)	[187]
Hydrotalcite ($\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3\cdot 4\text{H}_2\text{O}$)	[183], [184]

As shown in part (a) of Figure 5-19, as the OPC content increased in the precursor, the peaks of CASH, CSH, and Stratlingite increased in sharpness, indicating the formation of more crystalline polymerization products. Further, the peaks of quartz decreased, indicating that more silica phases were consumed in mixtures with higher OPC content leading to a more refined microstructure. Furthermore, the peaks of calcite and hydrotalcite increased when OPC decreased which indicates that there was an abundance of calcium-carrying and aluminum-carrying phases that were not consumed in the polymerization process which then were free to react with air and magnesium to form calcite and hydrotalcite. The same observations apply in the case of the ambient-cured specimens [Figure 5-19 (b)] where the absence of the heat generated by steam curing slowed down the polymerization process leading to less crystalline polymerization products, as evident

by the less intense polymerization products peaks and more intense peaks of the unreacted phases that formed calcite and hydrotalcite.



(a)



(b)

Figure 5-19 XRD diffractograms showing (a) influence of OPC content and (b) influence of curing method, (C: Calcite, S: Stralingite, N: Nchwangingite, Q: Quartz, M: Manganese-Calcium-Hydrate, H: CSH, K: Feldspar, A: Anorthite, D: Hydrotalcite, CH: Portlandite, Z: NASH)

5.6.5.1.2. Influence of acid and sulfate

The influence of acid and sulfate attacks is illustrated in Figure 5-20. The main binder matrix deterioration, in the case of acid immersed specimens, manifested in the formation of calcium sulfate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) via the reaction between the sulfuric acid and calcium ions as shown in Equation 5-16, which had peaked at 12° , 23.5° , 29.4° , 40.9° , 42.6° , and 48° [203], [204]. The source of calcium ions could be either from the unreacted calcium phases or from the calcium-carrying polymerization/hydration products (CASH, CSH), which have been reported to be susceptible to this form of dissolution [205], [206]. It is worth mentioning that other polymerization products, such as Mn-CSH, KASH, and NASH, are also susceptible to depolymerization by H_2SO_4 , similar to CSH and CASH [204]. Furthermore, minor peaks of natrite (Na_2CO_3), dolomite ($\text{CaMg}(\text{CO}_3)_2$), portlandite, and calcite were detected, which resulted due to the carbonation of the calcium, sodium, and magnesium ions liberated by sulfuric acid from their respective polymers as well as unreacted raw PMs as shown by Equation 5-17. The formation of the calcium sulfate dihydrate mentioned above led to the binder matrix's disintegration and subsequently loss of strength due to its expansive nature. Furthermore, the formation of sulfate products in the empty spaces in the voids of the binder matrix leads to the creation of internal stresses that contribute further to the disintegration of the binder matrix and further propagation of sulfate ions that start the cycle of attack again.

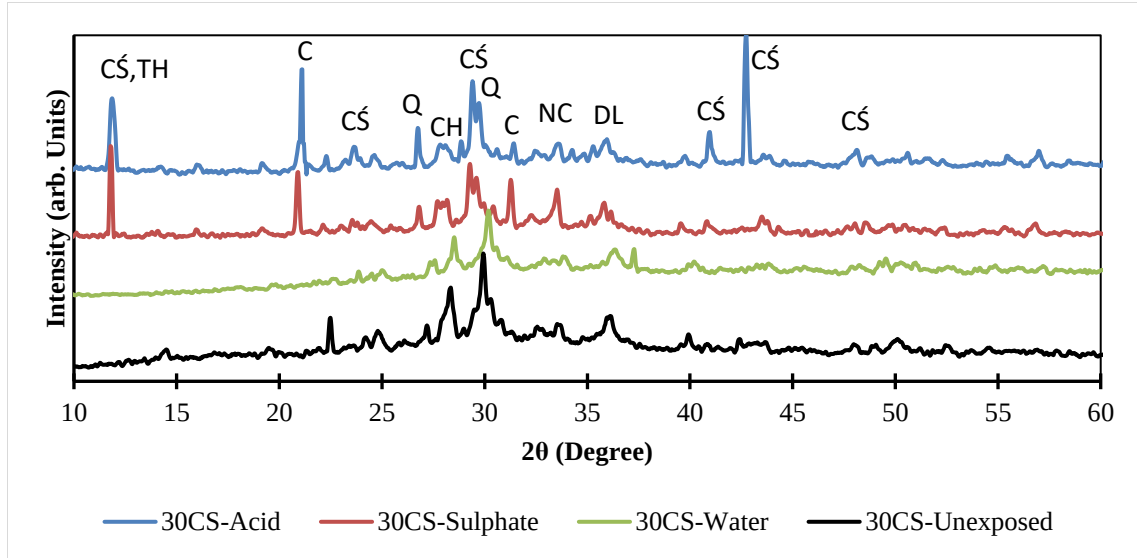
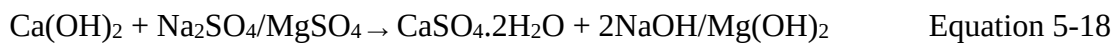
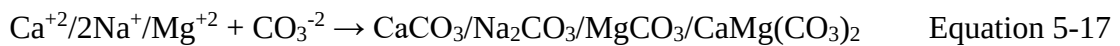
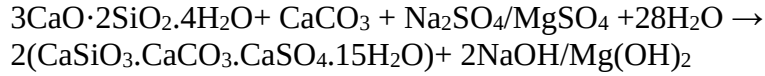


Figure 5-20 XRD results showing acid and sulphate exposure (C: Calcite, Q: Quartz, CH: Portlandite, CS: Calcium sulphate dihydrate, NC: Natriite, DL: Dolomite, TH: Thaumasite)

On the other hand, sulfate attack diffractograms (Figure 5-20) shows the formation of calcium sulfate dihydrate and concomitant thaumasite ($\text{CaSiO}_3 \cdot \text{CaCO}_3 \cdot \text{CaSO}_4 \cdot 15\text{H}_2\text{O}$) at 12.5° , 23.5° , 29.4° , 40.9° , 42.6° , and 48° [183], [207]. Their formation occurs as a result of the reaction between sulfate ions and calcium ions from calcium-carrying polymerization products in the case calcium sulfate dihydrate (Equation 5-18) and as a result of the reaction between carbonated phases, sulfates and CSH (Equation 5-19). The relatively low temperature and high relative humidity favor the formation of thaumasite. Radial needle-like thaumasite was observed in SEM imaging of some specimens, as will be discussed in the following section, which confirms the mechanism of formation of thaumasite mentioned previously. The formation of calcium sulfate dihydrate and thaumasite are expansive and cause expansion and cracking as discussed in earlier sections.





Equation 5-19

5.6.5.2. Morphology

5.6.5.2.1. Influence of OPC content and curing regime

Figure 5-21 shows the surface morphology and EDS spectrum of a typical ambient-air cured specimen compared to that of a typical steam-cured specimen at the same OPC content at two magnification levels.

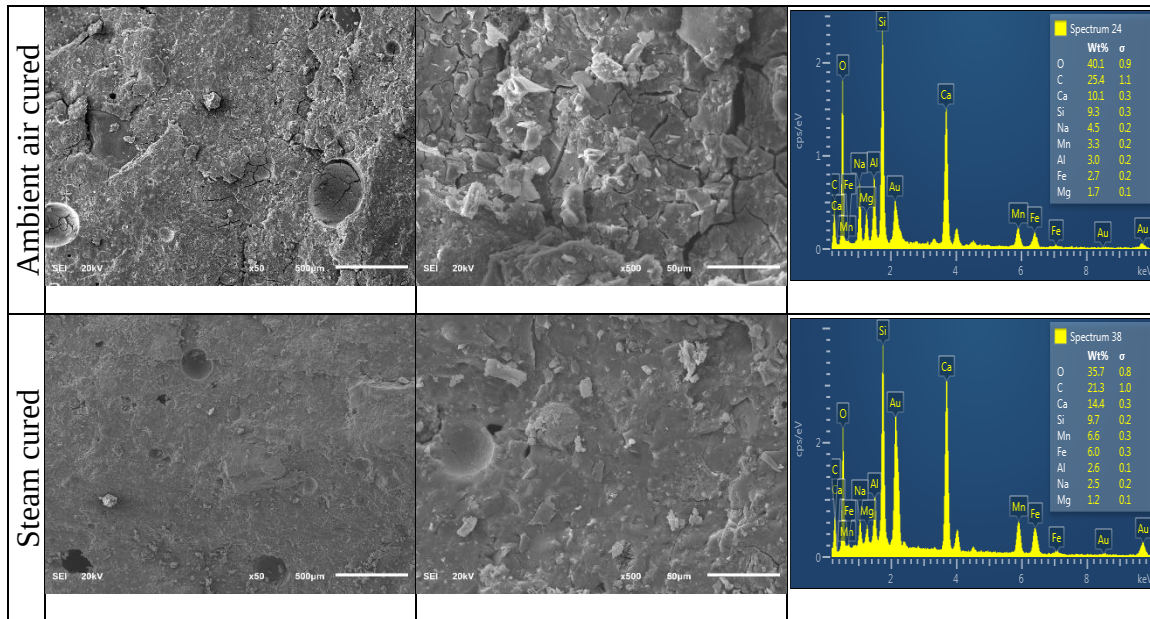


Figure 5-21 SEM micrographs and EDS spectra showing influence of curing on morphology

Steam-curing showed a noticeable improvement in the microstructure where fewer cracks were visible compared to the ambient-air cured sample. Further, the steam-cured specimen showed fewer unhydrated particles, a denser microstructure with fewer voids, and a more homogenous microstructure where the voids and cracks are filled with a network of polymerization/hydration products. On the other hand, the increase in OPC content showed a similar influence on the microstructure, as shown in Figure 5-22. As OPC increased, the

microstructure had fewer voids, cracks, and unhydrated particles, resulting in a denser microstructure.

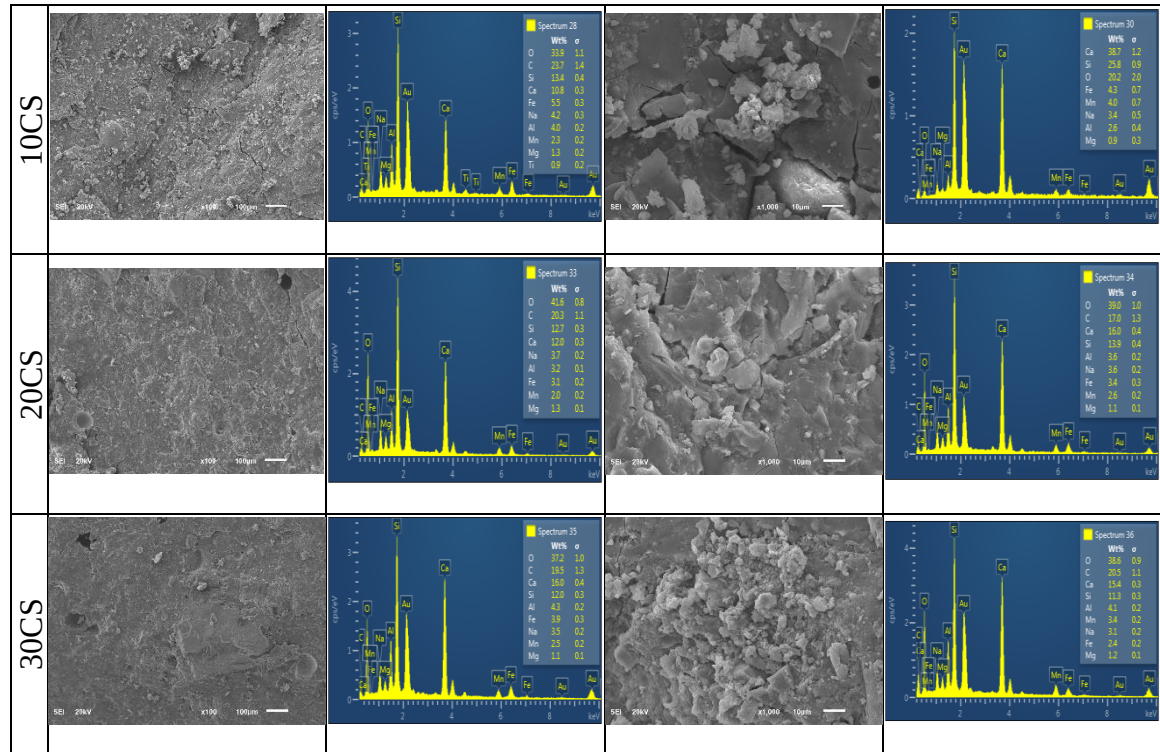


Figure 5-22 SEM micrographs and EDS spectra for AAB specimens with different OPC content

5.6.5.2.1. Influence of acid and sulfate

Figure 5-23 and Figure 5-24 show the microstructure of specimens after 90 days of exposure to 3% sulfuric acid, and after 180 days of exposure to a mixture of sodium and magnesium sulphate solution, respectively. The micrographs show uneven surfaces with cracks, pits, and loose materials, especially in the case of 10CS. The cracks seem more intensive and pervasive within the binder matrix in the case of the specimens exposed to sulfate which could indicate a higher susceptibility of the AAB mixtures under the present study to sulfate attack. However, since the duration of the sulfate attack exposure was considerably more than that of the acid exposure in addition to the concentration of the exposure medium being significantly higher than that of the acid attack medium, no direct

comparison of severity could be established between the two exposures. As the OPC content increased, the surface was less damaged, and the cracks were less prevalent in the binder matrix resulting in better durability and better longevity for AAB mixtures with higher OPC content in corrosive environments.

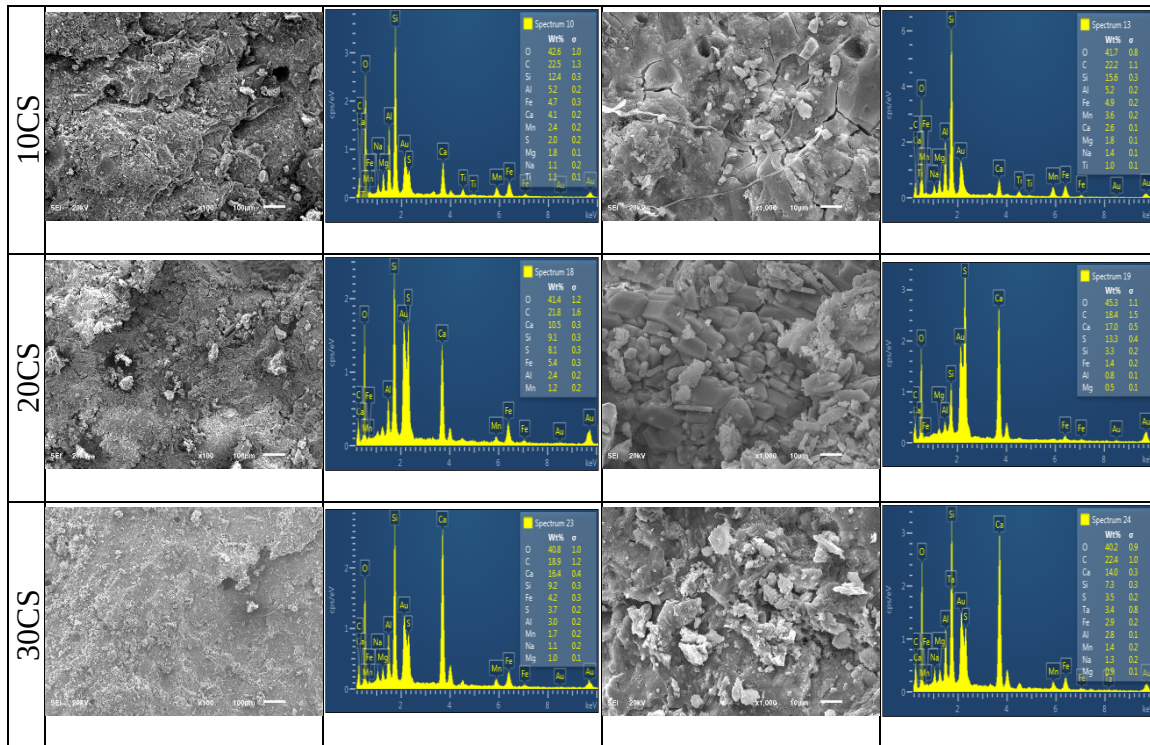


Figure 5-23 SEM micrographs and EDS spectra for specimens exposed to sulfuric acid

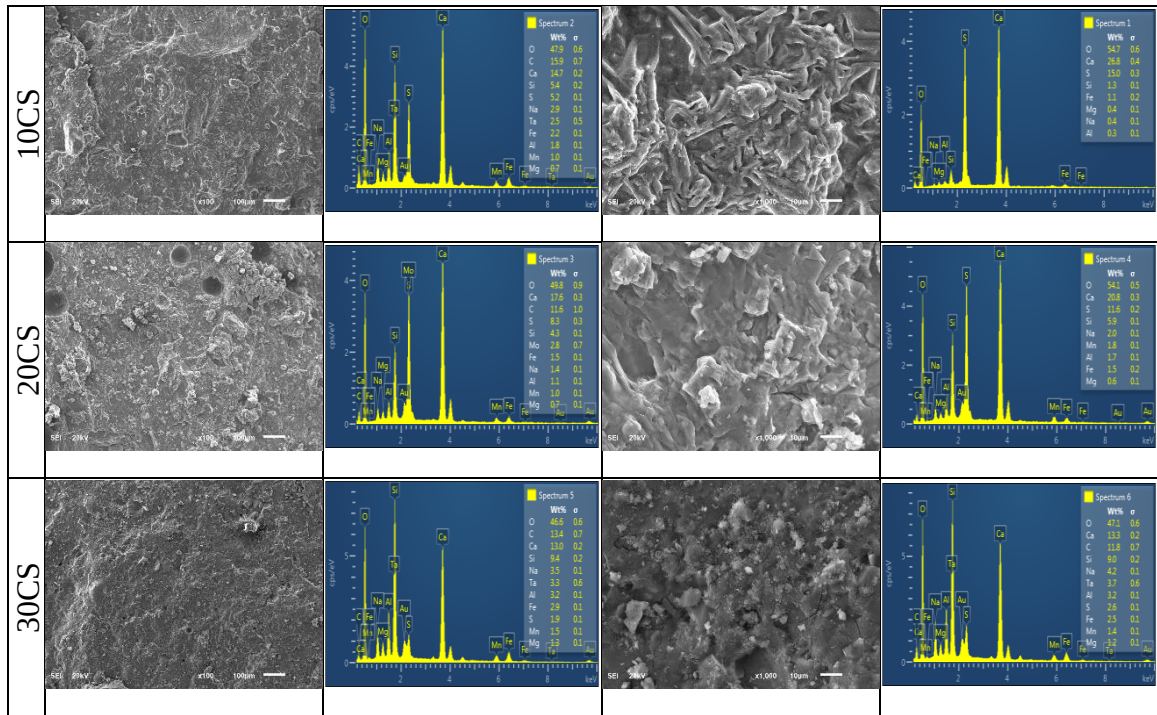


Figure 5-24 SEM micrographs and EDS spectra of specimens exposed to sulfate salts

Figure 5-25 shows some of the main deterioration products observed in the developed binders, including platelets of portlandite, flakes of calcite, radial needles of thaumasite, and crystals of calcium sulfate dihydrate, which supports the XRD results discussed earlier.

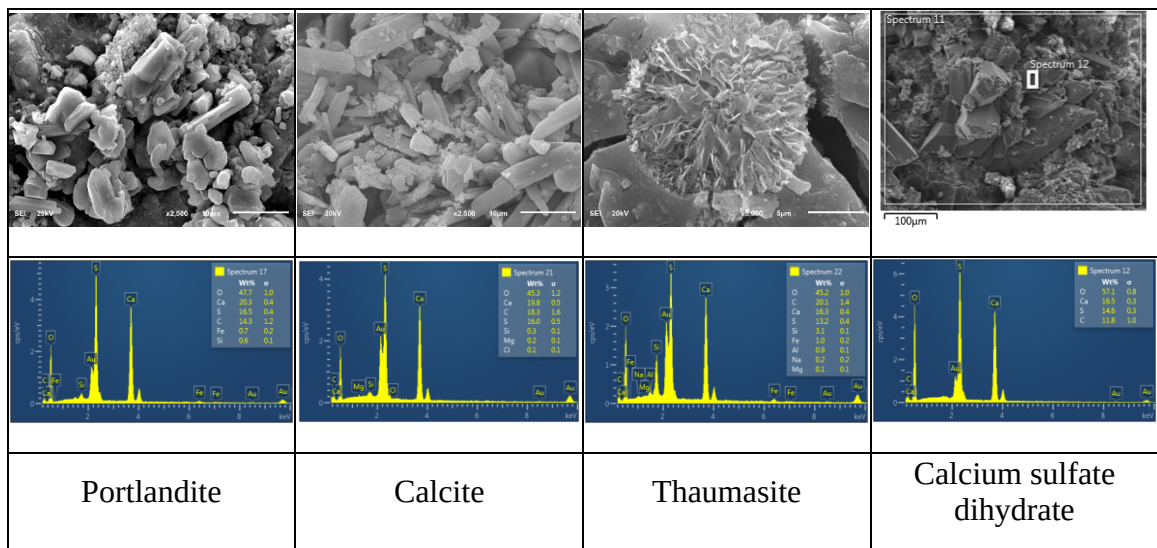


Figure 5-25 SEM micrographs of sulfuric acid and sulfate exposure products and their EDS spectra

5.7. Summary

The physical and mechanical properties, drying shrinkage, durability, and microstructural analyses of alkali-activated concrete (AAC) mixtures containing LSP, NP, RM, and SMF with varying OPC content, as precursor materials, and different curing conditions were studied. The following conclusions can be made:

- 1- The increased OPC content and steam curing led to the formation of more crystalline hydration/polymerization products such as CSH, CASH, NASH, Mn-SH, and KASH, which resulted in a denser and more resilient structure that produced better mechanical properties. Maximum compressive strength of 44.9 MPa and splitting-tensile strength of 3.3 MPa were achieved at 28 days by an AAC mixture containing 30% OPC and cured using steam (i.e., 30CS), which were significantly higher than of the control mixture (conventional OPC concrete, i.e., 100C). These observations were validated by the microstructural investigation via XRD and SEM-EDS analyses. However, the modulus of elasticity of all AAC mixtures were lower than the control OPC mixture which can be attributed to the higher ductility of the polymerization products that have higher binding capacity but lower resistance against compressive strain.
- 2- AAC mixtures exhibited lower drying shrinkage than the control mixture at all ages except for mixture 10CA. Furthermore, the drying shrinkage was mostly unchanged after the first 28 days for the AAC mixtures. A maximum drying shrinkage of 399 microstrain for 30CA and 127 microstrain for 30CS was recorded at 180 days compared to the 700 microstrain observed for the control OPC mixture.
- 3- AAC mixtures with OPC content higher than 10% exhibited resistance against acid and sulfate attacks similar or better than the control OPC mixture in terms of weight loss and strength reduction.
- 4- Calcium sulfate dihydrate was mainly formed as a result of acid and sulfate exposures due to the disintegration and depolymerization of the calcium-carrying polymerization products, as evident by XRD spectroscopy and SEM-EDS imaging. In addition, calcite, dolomite and natrite were observed in XRD due to the

carbonation of the calcium, magnesium and sodium ions liberated by the sulfuric acid and sulphate attacks. Furthermore, thaumasite formation, as radial needle-like crystals, was observed in SEM imaging in the case of the sulfate exposure due to the low temperature and high relative humidity in the exposure environment which favors the formation of thaumasite over rod-like crystals of ettringite.

- 5- The increase of the OPC content from 10 to 20% as a proportion of the precursor led to a significant improvement in all aspects of the concrete mixture performance that were able to surpass the control OPC mixture, irrespective of the curing regime, while the increase in OPC content beyond 20% resulted in marginal improvements.

CHAPTER 6. CHLORIDE TRANSPORT AND REINFORCEMENT CORROSION PROPERTIES

6.1. Overview

A large number of studies that were conducted earlier focused mainly on the mechanical properties and some durability aspects of industrial waste-based AABs. However, chloride migration and diffusion causing reinforcement corrosion in AAB-based concrete (AAC) have not been thoroughly investigated. This chapter presents the tests focused on the durability of AAC produced using multiple precursors that included natural minerals and industrial waste materials such as natural pozzolan (NP), limestone powder (LSP), red mud (RM), and silicomanganese fume (SMF) activated by alkali. The AAC mixtures were prepared and cured under different conditions and the performances of the mixtures were evaluated in terms of their durability characteristics related to chloride permeability, chloride migration, chloride diffusion, and chloride-induced reinforcement corrosion.

6.2. Background

The reaction process and performance of AABs containing the previously-mentioned precursor materials is dependent upon the mix characteristics which has been the subject of numerous studies in recent years. However, the durability of such binders in harsh chloride-laden environments is yet to be fully investigated given the recent emergence of such proposed binders as construction materials in lieu of OPC. This problem is also exacerbated by the unique nature of AABs having variable microstructure, physical, and durability characteristics with different precursors, activators and mix characteristics. In

order for AABs to be fully integrated and adopted in the construction industry, such understanding of its durability is essential, particularly in chloride-laden environments which is the primary cause of reinforcement corrosion of steel embedded in concrete.

Diffusion of chloride ions through the binder matrix depend on the chemistry of pore solution and microstructure of the developed binder which in turn depend on the composition of the precursors as well as the concentration and type of activators used in the synthesis of such AABs [208]. Compared to traditional OPC binders, AABs are more complex in terms of their diffusion characteristics and chloride-induced reinforcement corrosion mechanism since they have more factors that influence their chemistry thus leading to the conclusion that the diffusion and reinforcement corrosion behavior may as well be significantly different than that of concrete made using conventional OPC binders [209], [210].

The literature on chloride diffusion and chloride-induced reinforcement corrosion is conflicted. For example, Kupwade and Allouche [211] claimed that AABs with low calcium exhibited lower chloride diffusion than that of high calcium AABs and similar OPC mixes. On the contrary, other researchers claimed that the diffusion properties and chloride-induced reinforcement corrosion is highly dependent on the composition of the precursor materials as well as mix design parameters [208]. Ibrahim et al. [210] studied the chloride diffusion properties of AAB-based concrete (AAC), using pozzolana as a sole precursor, in terms of rapid chloride permeability, chloride migration and chloride bulk diffusion. They also studied chloride-induced reinforcement corrosion in terms of reinforcement corrosion potential (half-cell potential), reinforcement corrosion current density (I_{corr}), and accelerated reinforcement corrosion through impressed current. In

addition, they conducted gravimetric weight loss of the corroded reinforcement to compare the results with electrochemically measured I_{corr} . Half-cell potentials indicated that the AAC mixtures were in a state of severe reinforcement corrosion while I_{corr} values indicated that the reinforcement corrosion current density was in the moderate reinforcement corrosion range (i.e., $0.3 \mu\text{A}/\text{cm}^2 < I_{corr} < 0.5 \mu\text{A}/\text{cm}^2$) only after 30 days of exposure to 5% sodium chloride solution. After 150 days of chloride exposure, I_{corr} reached the high reinforcement corrosion range (i.e., $0.5 \mu\text{A}/\text{cm}^2 < I_{corr} < 1 \mu\text{A}/\text{cm}^2$). However, gravimetric analysis conducted on the bars extracted from concrete were found to be in good condition with no sign of significant reinforcement corrosion even after 400 days of chloride exposure. This finding was also in agreement with what was reported by Babaei and Castel [212] who studied the reinforcement corrosion in concrete produced using binary FA and GGBFS AABs that were activated by a combination of sodium hydroxide (NH) and sodium silicate (NS). They reported half-cell potentials that indicated more than 90% probability of reinforcement corrosion and values of I_{corr} in high reinforcement corrosion range. However, physical examination of the reinforcing bars (rebars) did not show signs of significant reinforcement corrosion. The reason behind the conflict between the results of electrochemical measurement and visual observation was attributed to the fact that the half-cell potential readings and the reinforcement corrosion readings were influenced by the lower pH of concrete in presence of AABs, which ranged from 11 to 11.5, and to the lack of oxygen at the rebar interface due to the improved microstructure of the developed AACs. Furthermore, some researchers reported reinforcement I_{corr} values as high as $2 \mu\text{A}/\text{cm}^2$ after 6 months of chloride exposure and $5 \mu\text{A}/\text{cm}^2$ after 12 months which if true would have resulted in concrete cracking due to the internal tensile stresses caused by expansion

of the reinforcement corrosion products. However, imaging of the rebars showed minor signs of reinforcement corrosion [213].

Analysis of the available data on the resistance of AABs to chloride diffusion and chloride-induced reinforcement corrosion clearly indicates that there are some discrepancies in the experimental results. For instance, factors such as chemistry of precursor and alkaline activator, type and duration of curing, and variety of other factors may significantly influence the interaction of chloride ions with the rebars in AACs. Hence, the mechanisms of reinforcement corrosion in AACs, either due to lower pH or due to chloride ion diffusion, may differ from those typically identified in OPC-based materials [209], [214]. As the deterioration of reinforced concrete structures due to reinforcement corrosion is the main cause of premature deterioration and involve expensive repair and rehabilitation, it is highly necessary to establish the durability performance of variety of AACs when exposed to chloride-laden service environment.

The literature review presented above indicates that various studies are reported about different aspects of AACs, however, there is a dearth in the information regarding chloride permeability, chloride migration, chloride diffusion, and chloride-induced reinforcement corrosion in AACs. Furthermore, the durability of AACs that contains multiple waste materials and minerals as precursors is not yet fully covered. In this chapter, AAC mixtures were considered for studying the effects of utilizing AABs, that were prepared by mixing four different minerals and industrial byproducts and OPC as precursors, on chloride permeability, chloride migration, chloride diffusion, and reinforcement corrosion. The AACs mixtures with optimum combinations of precursors were prepared and underwent different curing regimes before subjecting them to chloride solution to allow the migration

and diffusion of chloride inside concrete. After starting the chloride exposure, half-cell potential and corrosion current density (I_{corr}) were monitored frequently for a total duration of one year. Gravimetric weight loss test was also conducted on the rebars extracted from the reinforced concrete specimens after completion of the chloride exposure and electrochemical testing. Important conclusions were withdrawn based on the analysis of the experimental test results that would be useful in adopting the AACs in lieu of conventional OPC concrete as a durable concrete option for chloride exposures.

6.3. Materials, casting, and curing

The same PMs, activators, and aggregates that were used in the previous chapters were used to study the chloride transport and chloride-induced reinforcement corrosion properties of AACs. Furthermore, the AAC and control OPC mixtures were cast and cured in a similar manner to the one explained in the previous chapter.

6.4. Evaluation

6.4.1. Chloride transport properties

Chloride is responsible for reinforcement corrosion, mostly pitting type that is more catastrophic than the uniform type, in the majority of reinforced concrete structures subjected to the chloride-laden exposures [5], [11], [12]. The durability characteristics of a concrete exposed to chloride is evaluated in terms of chloride migration and diffusion properties. In the present work, rapid chloride permeability test (RCPT), chloride migration test, and chloride bulk diffusion test were conducted on the specimens of AACs and control mixture.

6.4.1.1. RCPT

The RCPT provides a qualitative assessment of the concrete's resistivity against chloride diffusion. However, the available ASTM standard (C1202) is not suitable for AACs due to the high applied voltage during the test that leads to overheating and subsequent failure. Noushini and Castel [215], studied the efficacy of ASTM C1202 for traditional and AACs made with GGBFS and metakaolin. They came up with a modification for the test in which the samples are subjected to a voltage of 10 V instead of 60 V as described in ASTM C1202 while maintaining the same sample conditioning regime and experiment duration of six hours. They showed good correlation between their modified test and the test described in ASTM C1202 as well as good correlation between their test and the chloride diffusion coefficient described in ASTM C1556 thus their modified test was followed in the present study.

After curing and aging for 28 days, the 100 × 200 mm cylindrical specimens were sliced into 45 mm-thick discs. The discs' curved surfaces were then sealed with a commercial epoxy sealant. Specimens were then conditioned and tested following the modified test conforming to ASTM C1202. The conditioning and testing was previously described in earlier research [12]. A Germann PROOVE'it power supply and multimeter was used to measure the charges passed through the specimens during testing. The total charges passed at the end of the test were used to give a qualitative grade of the concrete's ion permeability using the grading criteria, as shown in Table 6-1.

Table 6-1 Modified ASTM C1202 permeability grade

Charges passed (Coulombs)	Permeability
< 38	Negligible
38-120	Very low
120-220	Low
220-350	Medium
>350	High

6.4.1.2. Chloride migration test

Chloride migration is defined as the movement of chloride ions under an electrical potential differential. NT Build 409 standard provides a procedure using which the non-steady state chloride diffusion coefficient (D_{nssm}) is calculated that provides a quantitative evaluation of the chloride resistance of concrete. A 100 mm-diameter cylindrical specimen for each concrete mixture was cast, cured, aged for 28-days, and then sliced into three discs having 50 mm thickness after discarding the top 20 mm layer of the main cylinder. The curved sides of each disc was coated with a commercial epoxy sealant. The discs were then exposed to a saturated calcium hydroxide [$\text{Ca}(\text{OH})_2$] under vacuum for 20 hours. After that, they were installed in a Germann PROOVE'it sample cell that had a cathode and an anode connected to a reservoir at each end of the sample. The catholyte reservoir was filled with 10% NaCl solution and the anolyte reservoir was filled with a 0.3 mol/liter solution of NaOH. The cell was then connected to the power source and a 10 V current was applied for 24 hours. The cell's initial and final temperatures were recorded, and the sample was extracted after the test. The extracted sample was then split in half along its length after which the sawn face was sprayed with a 0.1 mol/liter solution of silver nitrate (AgNO_3)

which led to the formation of a white precipitate of silver chloride indicating the chloride penetration depth. The representative chloride penetration depth was determined by taking the average of 10 readings of the white precipitate along the diameter of the sawn sample. Finally, the D_{nssm} (in $\times 10^{-12} \text{ m}^2/\text{s}$) was then calculated using the following Equation 6-1:

$$D_{nssm} = \frac{0.0239 (T + 273)l}{(U - 2)t} \left(x - 0.0238 \sqrt{\frac{(T + 273)lx}{U - 2}} \right) \quad \text{Equation 6-1}$$

Where, T is the average of the initial and final temperatures in degree Celsius, l is the disc's thickness = 50 mm, U is the applied voltage = 10 V, t is the experiment duration in hours = 24 hours, and x is the average chloride penetration depth in mm.

6.4.1.3. Chloride diffusion

Diffusion is the propagation of dissolved ions under a concentration differential from a higher chemical potential (concentration) towards a lower one. The diffusion of chloride in concrete is assumed to follow Fick's second law of diffusion. At the age of 28 days, the specimens were conditioned following the ASTM C1556 standards and epoxy sealant was applied on all faces except the top finishing surface. The specimens were then exposed to sodium chloride at a concentration of 165 g/l of solution for 180 days after which the specimens were sliced perpendicular to their height at 5 mm intervals. The slices were then pulverized to pass #100 sieve after which a portion was digested in nitric acid to find the acid-soluble chloride content (i.e., total chloride) in accordance with ASTM C1152 and another portion was digested in deionized water to find the water-soluble chloride content (i.e., free chloride) in accordance with ASTM C1556. For each depth, the powder of three samples per concrete mixture was mixed together before digestion to get the average

results. The concentration in both cases was analyzed by potentiometric titration against silver nitrate. Chloride concentration and depth were used to model the chloride profile following Equation 6-2 by the method of least squares.

$$C(x, t) = C_s - (C_s - C_i) \cdot \operatorname{erf}(\sqrt{x/4tD_a}) \quad \text{Equation 6-2}$$

Where $C(x, t)$ is the chloride concentration as a function of time and depth expressed as a percentage of the concrete's weight, C_s is the surface chloride concentration, C_i is the initial chloride concentration before exposure, D_a is the chloride apparent diffusion coefficient (m^2/s), and erf is the Gauss error function.

6.4.2. Reinforcement corrosion monitoring

In order to assess the resistance of a concrete mixture against propagation of reinforcement corrosion in post-initiation phase, the half-cell potential (i.e. corrosion potential E_{corr}) and corrosion current density (I_{corr}) are monitored during chloride exposure. For reinforcement corrosion monitoring, cylindrical reinforced concrete specimens having 75 mm-diameter and 150 mm-height were cast. Each reinforced concrete specimen had a 12 mm-diameter steel bar centrally embedded inside the concrete. The end point of the rebar embedded in the specimen was coated with epoxy as well as the area of the bar at the surface of the specimen in order to avoid crevice reinforcement corrosion, as shown in Figure 6-1. After curing and aging for 28 days, the “lollipop” concrete specimens were immersed in a 125 mm-deep 5% NaCl solution.

6.4.2.1. E_{corr} monitoring

E_{corr} was monitored weekly during the first 60 days of exposure and then monthly for the remaining 300 days. This was achieved via a digital multimeter and a saturated calomel

reference electrode (SCE) following the procedure given in ASTM C876. The SCE was suspended in the exposure medium and connected to one terminal of the multimeter while the rebar was connected to the other terminal, as shown in Figure 6-2.

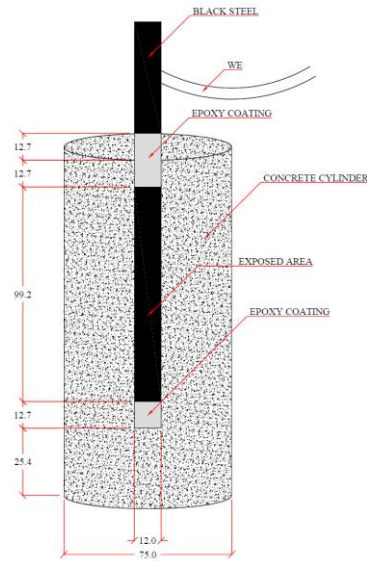


Figure 6-1 Configuration of reinforced concrete specimen for electrochemical tests

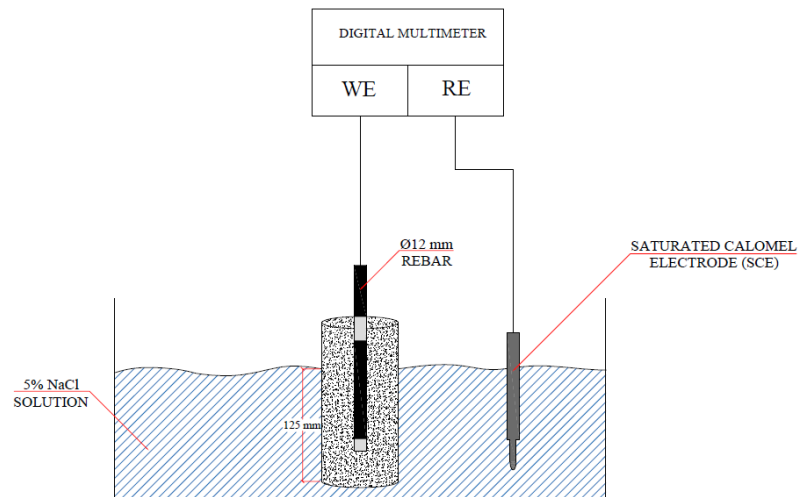


Figure 6-2 Half-cell potential monitoring setup

6.4.2.2. I_{corr} monitoring

I_{corr} was monitored via the linear polarization resistance (LPR) method using a 3-electrode setup (Gamry Reference 3000 Potentiostat), as shown in Figure 6-3. The rebar of the specimen was connected to the working electrode terminal while a stainless-steel panel suspended in the exposure medium was connected to the counter electrode terminal. The SCE was connected to the reference electrode terminal. The Potentiostat was connected to a personal computer provided with the Gamry framework software. The software was setup to run the LPR test under a scan rate of 0.2 mV/s within the linear polarization range of ± 20 mV from the open circuit potential ($E_{oc} = E_{corr}$). Reinforcement corrosion current density was then calculated using the Stern-Geary formula given in Equation 6-3 and Equation 6-4. LPR was carried weekly for the first 60 days and then monthly up to 360 days.

$$I_{corr} = \frac{B}{R_p} \quad \text{Equation 6-3}$$

$$B = \frac{\beta_a \cdot \beta_c}{2.303(\beta_a + \beta_c)} \quad \text{Equation 6-4}$$

Where, I_{corr} is the reinforcement corrosion current density ($\mu\text{A}/\text{cm}^2$), R_p is polarization resistance ($\text{k}\Omega \cdot \text{cm}^2$), B is the Stern-Geary constant, β_a and β_c are the anodic and cathodic Tafel's slopes (mV), respectively.

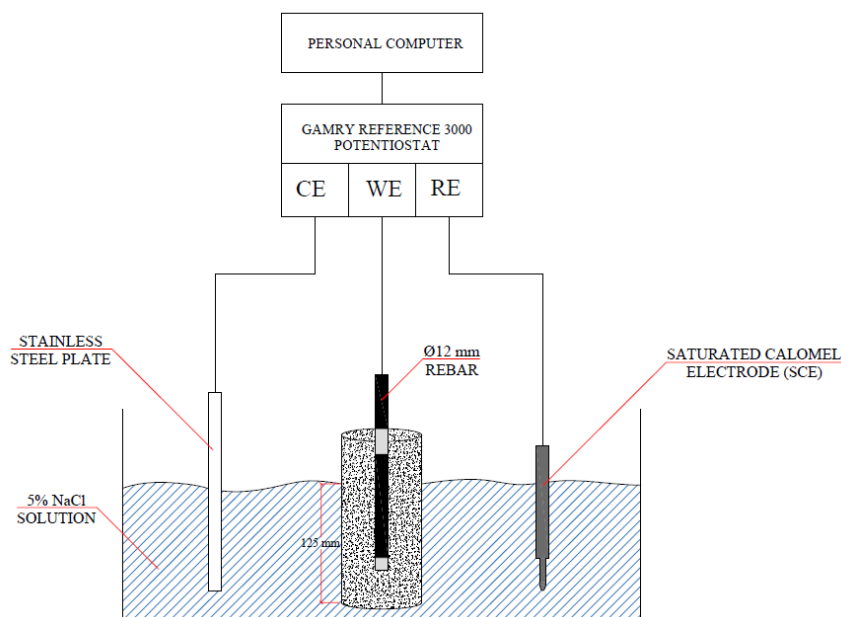


Figure 6-3 Reinforcement corrosion current density monitoring setup

6.4.2.3. Gravimetric weight loss test

Weight loss testing was conducted on rebars extracted from the specimens used for reinforcement corrosion monitoring at the end of the exposure period. Two rebars extracted from each concrete mixture were used for the gravimetric test which was conducted following the procedure stated in ASTM G1.

6.5. Results and discussion

6.5.1. Chloride transport properties

6.5.1.1. RCPT

Figure 6-4 illustrates the results of the modified rapid chloride permeability test (RCPT) and the subsequent chloride permeability classification of the mixtures considered under the present study. A lower RCPT value indicates a more compact microstructure that has the ability to hinder the movement of ions through it. The maximum passed charges of 402

Coulombs was recorded for the control mixture (100C) which belonged to the ‘high permeability’ class while the AAC mixture 30CS had the least passed charges of 99 Coulombs which belonged to the ‘very low’ chloride permeability class indicating high resistance of the AAC mixtures against chloride penetration.

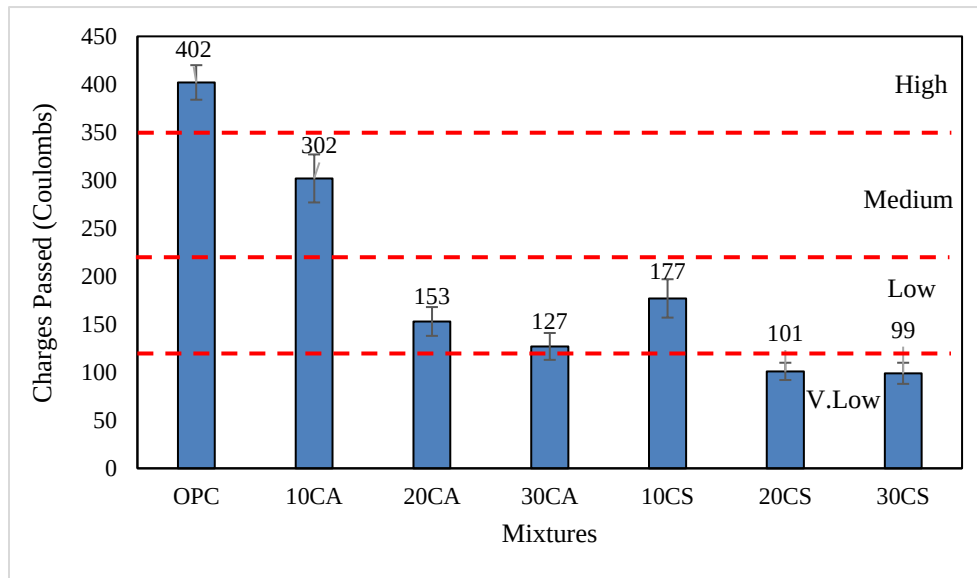


Figure 6-4 Modified RCPT results

As compared to the control mixture, reductions of 24.9, 61.9, and 68.4% in the charges passed were observed for the AAC mixtures 10CA, 20CA, and 30CA, respectively. A similar trend was observed in the steam-cured AACs also where reductions in the charges passed were found to be 56, 74.5, and 75.4% for 10CS, 20CS, and 30CS, respectively, as compared to the control mixture. Similar to the case of compressive strength, major reductions in the chloride permeability were recorded when the OPC content in the precursor was increased from 10 to 20%. This is due to the fact that the increase in the denseness of the microstructure of the AACs showed beneficial effects on both the compressive strength as well as resistance against chloride permeability. Furthermore, this correlation was also reflected when the RCPT results of all concrete mixtures in the present

study were plotted against their respective 28-day compressive strengths, as shown in Figure 6-5. An exponential model (Equation 6-5) was obtained with a coefficient of determination (R^2) of 0.86 by statistically fitting the f'_c versus RCPT data. A high value of R^2 indicates a strong correlation between the compressive strength and chloride permeability.

$$RCPT = 757.75e^{-0.048f'_c} \quad \text{Equation 6-5}$$

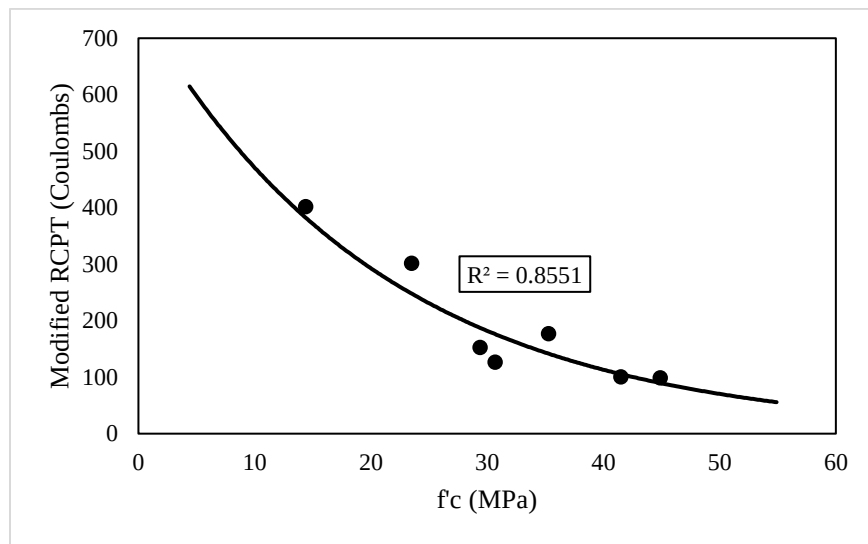


Figure 6-5 RCPT vs compressive strength at 28 days

6.5.1.2. Chloride migration

Figure 6-6 shows the plots of chloride migration test results measured in terms of the chloride penetration depth and the non-steady state migration diffusion coefficient (D_{nssm}). A concrete mixture that has a porous microstructure with interconnected voids is more prone to chloride migration reflected by higher values of D_{nssm} and chloride penetration depth. The D_{nssm} and chloride penetration depth values ranged from $37.85 \times 10^{-12} \text{ m}^2/\text{s}$ and 29 mm to $19.1 \times 10^{-12} \text{ m}^2/\text{s}$ and 16.8 mm, respectively. Similar to the RCPT results, the control mixture (100C) exhibited the highest D_{nssm} and chloride penetration depth while

AAC mixture 30CS exhibited the lowest values. Increase in the OPC content of the precursor resulted in a significant decrease in the D_{nssm} and chloride penetration depth irrespective of the curing method. However, as compared to the ambient air curing the steam curing had a better resistance against chloride migration.

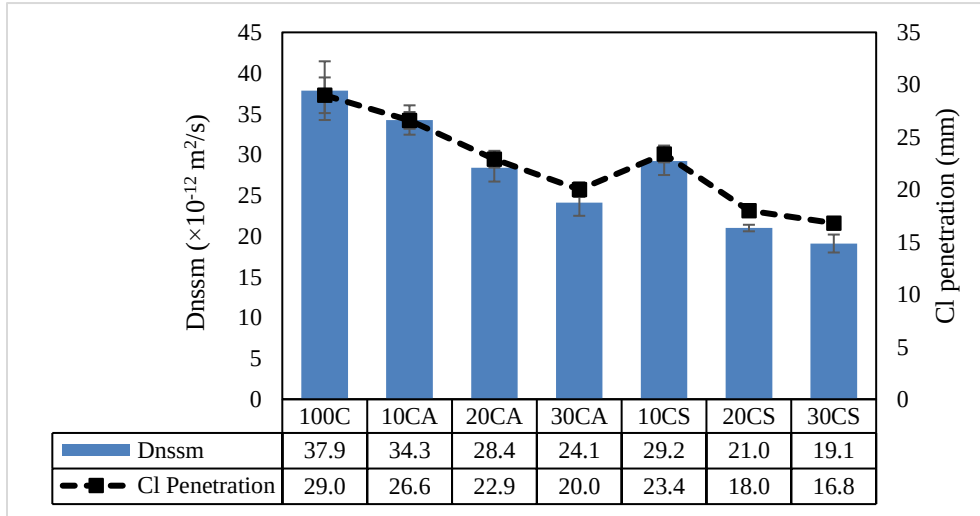


Figure 6-6 Chloride migration test results

The D_{nssm} values were plotted against the RCPT values, as shown in Figure 6-7, to observe if a correlation exists between these two chloride transport parameters. The plot shown in Figure 6-7 confirmed a strong correlation between D_{nssm} and RCPT and therefore an exponential model (Equation 6-6) was obtained with a very high value of R^2 (0.98) by fitting the data. However, more data that cover a larger range of RCPT and D_{nssm} values is required to establish a more reliable correlation between these two parameters.

$$RCPT = 19.187e^{0.0782D_{nssm}} \quad \text{Equation 6-6}$$

Where RCPT is in coulombs and D_{nssm} is in $\times 10^{-12} \text{ m}^2/\text{s}$.

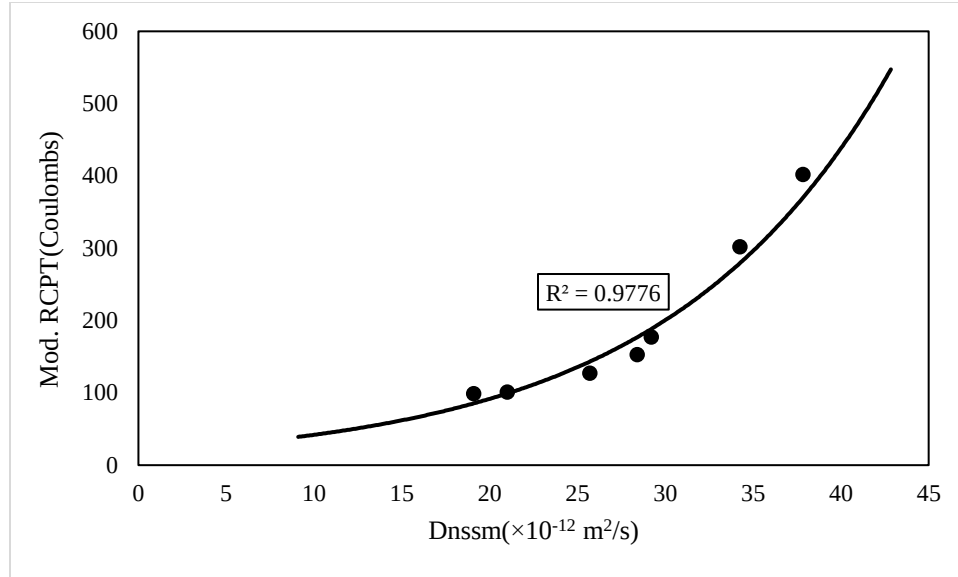
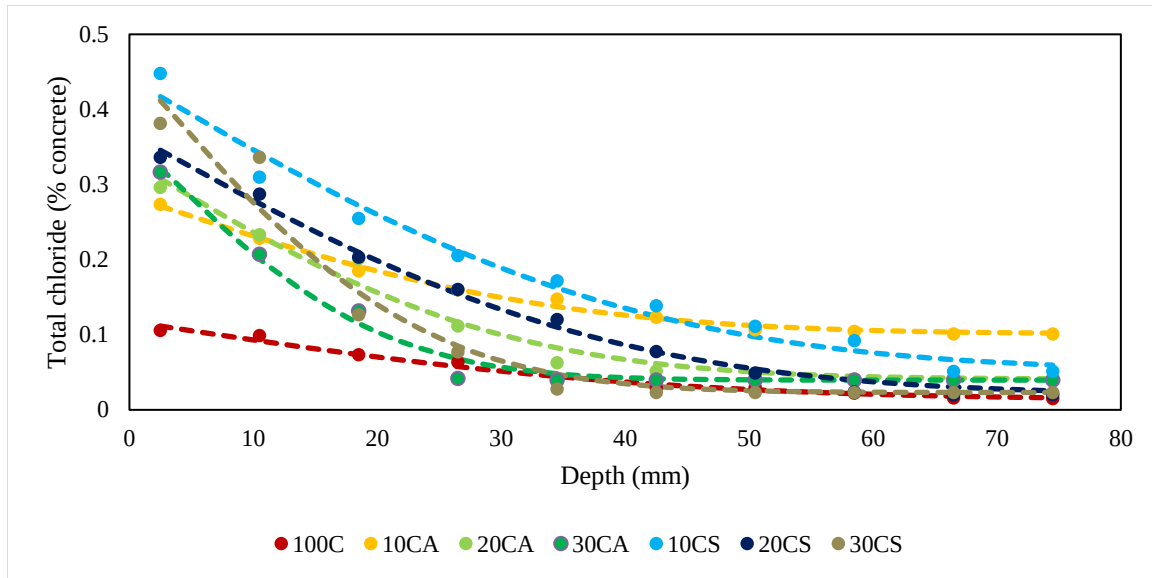


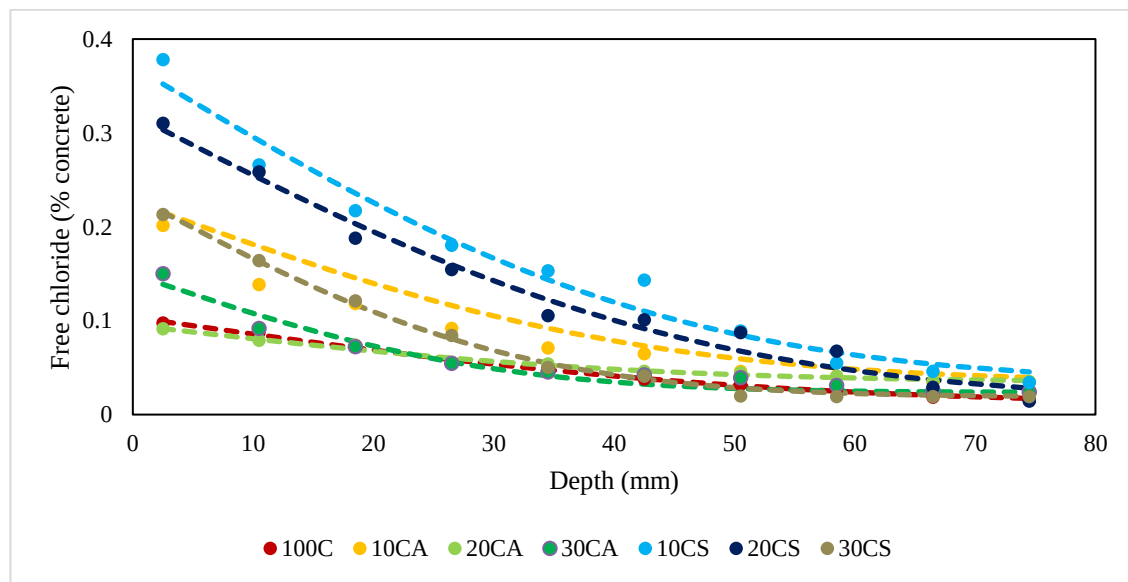
Figure 6-7 RCPT vs D_{nssm} plot

6.5.1.3. Chloride diffusion

Figure 6-8 presents the total and free chloride profiles of the developed mixtures after an exposure for 180 days in sodium chloride solution (165 g/l). The chloride concentration decreased as the depth increased following Fick's law of diffusion. The fitted data were used to estimate the surface chloride concentration (C_s) and apparent chloride diffusion coefficient (D_a) for both free as well as total chlorides. The values of C_s and D_a for all concrete mixtures are presented in Table 6-2.



(a)



(b)

Figure 6-8 Total chloride profile (a) and Free chloride profile (b) of the mixes under study (dots are the observed chloride and the dashed line is the fitted model)

Figure 6-9 shows the correlation between the total and free chloride concentrations. A linear model (Equation 6-7) was best-fitted with an R^2 value of 0.82 indicating a fairly good

correlation between the free and total chloride. Equation 6-7 can be used to calculate the total chloride using the measured value of free chloride.

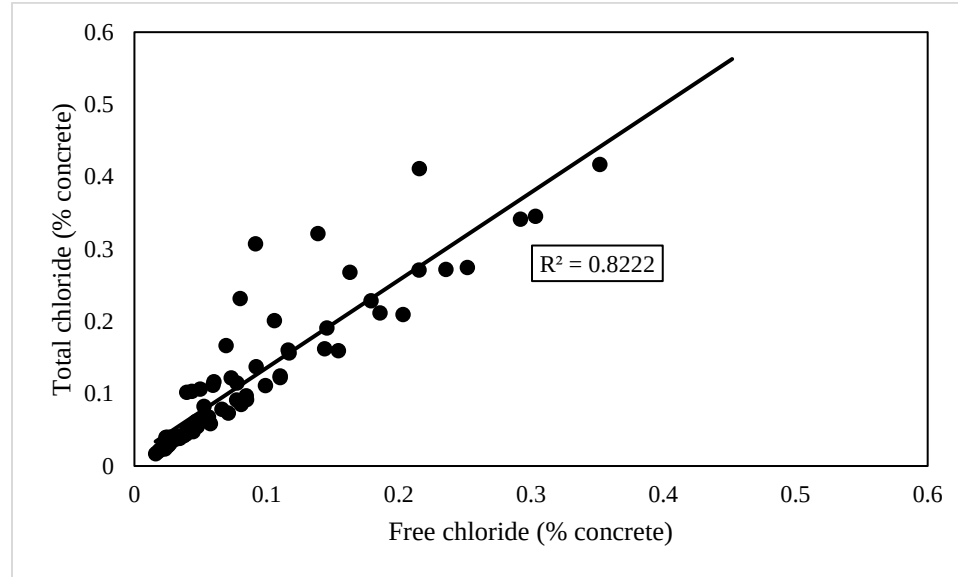


Figure 6-9 Total vs free chloride concentrations

$$C_{total} = 1.2129 C_{free} + 0.0144 \quad \text{Equation 6-7}$$

The chloride diffusion coefficient, D_a , represents an evaluation of the ease of diffusion of chloride through concrete. A higher value indicates faster and easier diffusion of chloride, and the opposite is true. In the present study, D_a ranged from 53×10^{-12} to $27.6 \times 10^{-12} \text{ m}^2/\text{s}$ for the free chloride and from 35.1×10^{-12} to $7.8 \times 10^{-12} \text{ m}^2/\text{s}$ for the total chloride, as shown in Table 6-2. In both cases, the control mixture showed the highest D_a value followed by ambient-air cured mixtures and then the steam-cured mixtures. The D_a value decreased significantly with increasing OPC content of the precursor in the ambient air cured mixtures as well as the steam-cured mixtures. There was a decrease in D_a by 4.6, 14.5,

70.1, 34.2, 49.3 and 77.8% for the total chloride and 16.03, 25.3, 62.1, 33.2, 35.3, and 66.8%, for the free chloride for mixtures 10CA, 20CA, 30CA, 10CS, 20CS, and 30CS, respectively, compared to the control mixture.

The surface chloride concentration, C_s , represents an estimation of the maximum chloride content which exists at the interface between the concrete and exposure medium (i.e., chloride solution) hence the name. In addition, it represents the maximum chloride content after exposure and can be used to estimate the binding capacity. It is expressed as a percentage of either concrete or equivalent paste. The C_s values for the total chloride ranged from 0.118% to 0.49% (by weight of concrete), as shown in Table 6-2. Further, it increased with increasing OPC content of the precursor in the AACs. The curing method also influenced the C_s values with steam-cured mixtures having higher C_s values than that of ambient-air cured mixtures indicating more binding capacity of the former mixtures. The same trends were observed for the free chloride C_s values which ranged from 0.104 to 0.371% (by wt. of concrete).

Table 6-2 Total and free surface chloride (C_s), and chloride diffusion coefficients (D_a) after 180 days of exposure to NaCl

Mixture	Total chloride		Free chloride	
	C_s (% weight of concrete)	D_a ($\times 10^{-12} \text{m}^2/\text{s}$)	C_s (% weight of concrete)	D_a ($\times 10^{-12} \text{m}^2/\text{s}$)
100C	0.118	35.1	0.104	53.0
10CA	0.285	33.5	0.227	44.5
20CA	0.332	30.0	0.211	34.3
30CA	0.460	10.5	0.232	20.1
10CS	0.491	23.1	0.371	34.3
20CS	0.368	17.8	0.202	29.6
30CS	0.363	7.8	0.149	17.6

Chloride exists in concrete in the form of free chloride and bound chloride with the latter being in the form of complex alumina-chloride salts such as Friedal's salt [11]. As the alumina hydration products increase, the binding capacity increases which limits the amount of free chloride that initiates reinforcement corrosion in reinforced concrete structures [216]. The chloride binding capacity for all the concrete mixtures were calculated using the values of total and free chloride concentrations at surface by subtracting the surface chloride values of the free chloride from those of the total chloride. Figure 6-10 shows the values of bound chloride (i.e., chloride binding capacity) of all concrete mixtures. The binding capacity ranged from 0.014% (by wt. of concrete) for control mixture to 0.228% for 30CS. Further, the binding capacity increased with increasing OPC content in the precursor of the AAC mixtures. Furthermore, the steam curing regime increased the binding capacity as compared to that of the ambient air-cured mixtures. Both observations can be owed to the formation of more alumina-carrying polymerization products such as CASH, NASH, and Mn-ASH which results in higher binding capacity that can increase the service life of structures by delaying reinforcement corrosion initiation. Furthermore, alumina-rich mixtures have been reported to increase the threshold at which reinforcement corrosion is initiated, which is also known as the chloride threshold. For example, Ann and Song [216] reported increases in the chloride threshold ranging from 55 to 213% with the addition of 10% calcium aluminate cement to OPC.

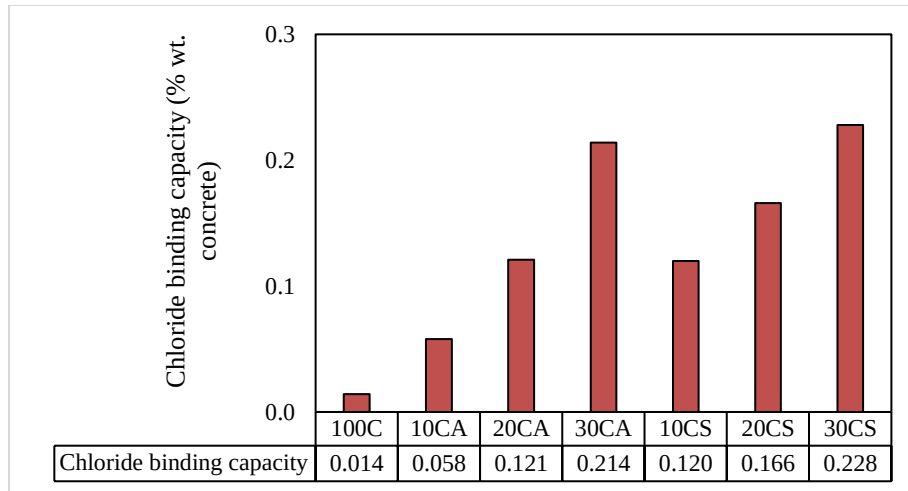


Figure 6-10 Chloride binding capacity of the concrete mixtures

Table 6-3 presents the free chloride concentration at a depth of 75 mm which is equivalent to the minimum concrete cover recommended by the ACI-318 code for concrete exposed to external chlorides. Table 6-3 also presents the free chloride limits for C1 and C2 types of exposure for reinforced concrete as well as prestressed concrete structures. Mixtures 30CA, 20CS, and 30CS showed chloride contents that pass the ACI-318 criteria for reinforced concrete structures in both exposure conditions C1 and C2. As for the prestressed concrete structures, all mixtures failed to meet the chloride content criterion set by the ACI-318. However, research have shown that the suggested criteria to be too conservative for AACs [212], [217].

Table 6-3 Free chloride concentration at 75 mm depth

Mix	Free chloride (% concrete) at 75 mm	Chloride threshold (ACI-318)			
		RC		Pre-stressed	
		C1 exposure	C2 Exposure	C1 exposure	C2 Exposure
100C	0.0149	0.05	0.025	0.01	0.01
10CA	0.0348				
20CA	0.0350				
30CA	0.0237				
10CS	0.0341				
20CS	0.0144				
30CS	0.0190				

6.5.2. Reinforcement corrosion monitoring

6.5.2.1. Electrochemical methods

Figure 6-11 shows the variation of the half-cell potential (i.e., reinforcement corrosion potential, E_{corr}) of the specimens exposed to the chloride-laden environment for 360 days. Initially, all of the mixtures started in the uncertain reinforcement corrosion status range ($-270 \text{ mV} > E_{corr} > -420 \text{ mV}$) or the $>90\%$ reinforcement corrosion probability range ($E_{corr} < -420 \text{ mV}$) according to the criteria set by the ASTM C876 standard. E_{corr} for all AACs increased significantly within the first 60 days to reach -700 mV for 10CA and 20CA, -610 mV for 30CA and 20CS, -670 mV for 20CS, and -570 mV for 30CS compared to the control mixture which exhibited an E_{corr} value of -420 mV at that time. Beyond the 60 days exposure period, E_{corr} values remained relatively stable until the end of the exposure period

which indicates that the status of the rebar inside concrete did not experience much change beyond the 60 days mark.

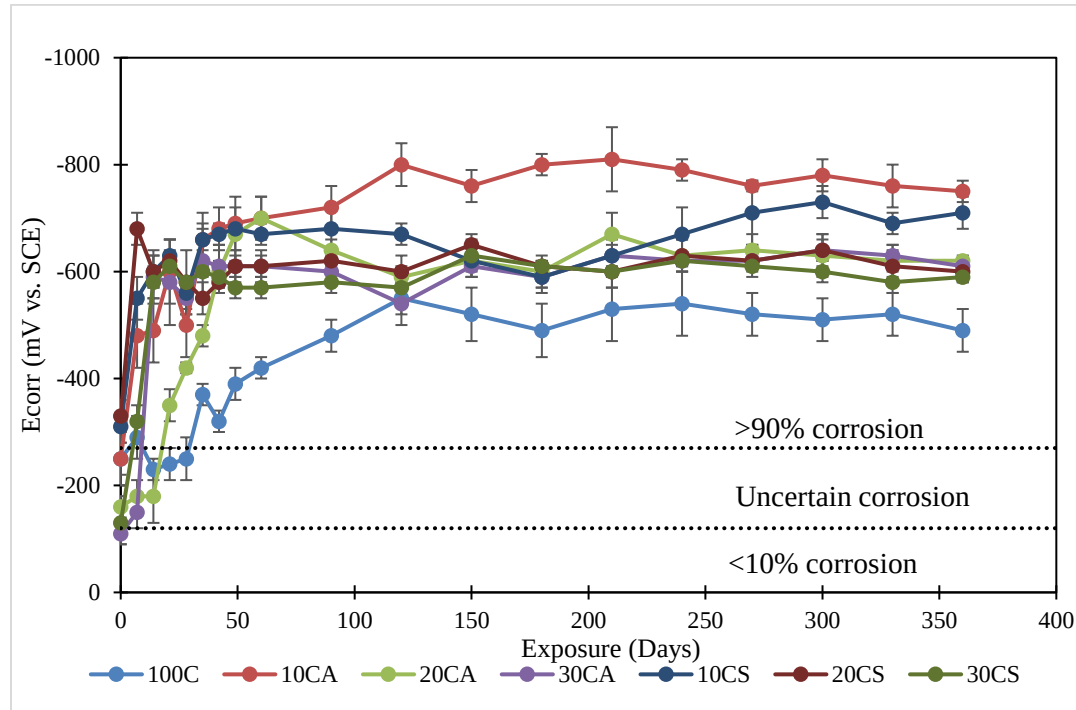


Figure 6-11 Half-cell readings of the steel embedded in the developed concretes

Overall, the AAC mixtures showed more negative E_{corr} values compared to that of the control mixture at every exposure stage. It was noted that the steam-cured mixtures exhibited marginally lower reinforcement corrosion potentials compared to their ambient-air cured counterparts. In addition, the E_{corr} values decreased as the OPC content of the precursor in the AACs increased. However, given the qualitative nature of the ASTM C876's criteria, a more negative E_{corr} value does not necessarily indicate a worse reinforcement corrosion condition of the embedded rebar or an active reinforcement corrosion status at all, since the thresholds provided by the ASTM C876 indicate only a probability of reinforcement corrosion and the actual reinforcement corrosion status itself is not known. The fact that a highly negative value of E_{corr} does not necessarily indicate an

active reinforcement corrosion in AACs mixtures was observed in the literature. Tennakon et al. [218] reported E_{corr} values more negative than -700 mV within the first 30 days of exposure for AABs with varying fly ash and slag content while the rebars indicating such potentials were found to be in good condition (i.e., uncorroded). Furthermore, they analyzed the chloride content at the level of the rebar and found that chloride has not reached the reinforcement corrosion initiation threshold. In addition, Ibrahim et al. [210] studied reinforcement corrosion in pozzolana-based AACs with varying nano-silica content and reported a similar trend where the rebars in the AACs showed E_{corr} values more negative than -550 mV while the rebars themselves were found to be in good conditions despite the more negative potentials compared to OPC concretes. The higher negative values were found to be a result of three factors which are: the lower pH of alkali-activated concretes, the lack of oxygen at the rebar level especially in the cathodic region due to the refined and more tortuous pore structure of AACs, and the interference with the measurement that is caused by the ionic accumulation in AACs. The measured pH at the rebar level was found to be 11.6 for the AAC mixtures and 12.8 for control mixture (100C) which might be in fact causing the more negative reading despite the rebar being in a passive status.

Figure 6-12 shows the plots of I_{corr} , measured electrochemically using the LPR method, at different times of the chloride exposure for a total duration of 360 days. The classification of the state of reinforcement corrosion, based on the value of I_{corr} [passive/very low reinforcement corrosion range ($I_{corr} < 0.3 \mu\text{A}/\text{cm}^2$), low to moderate reinforcement corrosion range ($0.3 \mu\text{A}/\text{cm}^2 < I_{corr} < 0.5 \mu\text{A}/\text{cm}^2$), high reinforcement corrosion range (0.5

$\mu\text{A}/\text{cm}^2 < I_{corr} < 1 \mu\text{A}/\text{cm}^2$), and very high reinforcement corrosion range ($I_{corr} > 0.3 \mu\text{A}/\text{cm}^2$)] is also shown in Figure 6-12.

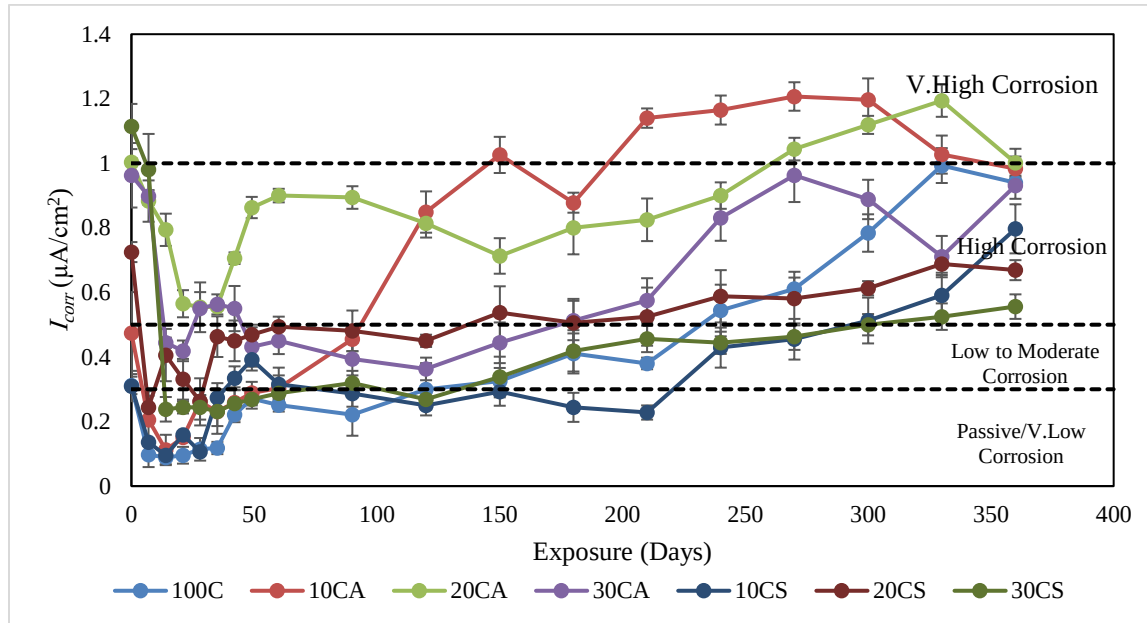


Figure 6-12 I_{corr} by the LPR method for 360 days

All concrete mixtures exhibited a trend where the values of I_{corr} was initially high and then it dropped within the first 60 days which could be attributed to the formation of the passive layer on the surface of the rebar. At the 60-day mark, all concrete mixtures (except for 20CA) exhibited I_{corr} values in the ‘low to moderate’ reinforcement corrosion range which is in disagreement with the probability of reinforcement corrosion based on the E_{corr} values that indicated a state of active reinforcement corrosion. For all mixtures, I_{corr} trended in an increasing manner after the 60-day mark until the end of the exposure unlike E_{corr} which, as mentioned previously, stabilized after 60 days of exposure. After a year of exposure to 5% NaCl, I_{corr} values of 0.984, 1.001, 0.931, 0.797, 0.669, and 0.556 $\mu\text{A}/\text{cm}^2$ were measured for mixtures 10CA, 20CA, 30CA, 10CS, 20CS, and 30CS, respectively compared to an I_{corr} value of 0.94 $\mu\text{A}/\text{cm}^2$ measured for the control mixture which classifies

all of the mixtures in the ‘high’ and ‘very high’ reinforcement corrosion states. In addition, studies reported cracking of the concrete specimens due to internal tensile stresses caused by the expansion of the products of reinforcement corrosion when I_{corr} values exceeded $0.9 \mu\text{A}/\text{cm}^2$, which was not observed in the present study. The performance of the AACs in general was comparable to the control mixture in terms of the measured I_{corr} values. It was also noted that the steam-cured mixtures exhibited I_{corr} values lower than their counterparts from the ambient-air curing group and even lower than the control mixture for 20CS and 30CS in particular. This can be owed to the denser microstructure that hinders the dissolution of the rebar as well as the diffusion of oxygen required for the reinforcement corrosion reaction.

Similar to the case of the present study, numerous researchers have reported discrepancies between the indication of the state of reinforcement corrosion based on E_{corr} values and that indicated by I_{corr} values of the same specimens [210], [211], [218], [219]. Despite the relatively comparable performance of AACs and OPC in those studies in terms of the measured E_{corr} and I_{corr} values, researchers have claimed that AACs performed more superiorly compared to OPC mixtures in chloride-laden environment due to their higher binding capacity which is what was observed in the chloride binding results discussed previously. The dichotomic nature of the values of E_{corr} and I_{corr} requires the confirmation of the actual status of reinforcement corrosion using the gravimetric weight loss method, as conducted in the present work.

6.5.2.2. Gravimetric method

Two specimens belonging to each concrete mixture containing centrally embedded reinforcement bars were picked up after one year of exposure to 5% NaCl. The bars were

exposed for observing the status of reinforcement corrosion by splitting the specimens along their length, as shown in Figure 6-13 for a typical specimen.



Figure 6-13 Rebar condition in a typical specimen after 360 days of exposure to 5% NaCl

The rebars embedded in the AAC mixtures were observed to be in good condition with no signs of active, pitting, or crevice reinforcement corrosion were visible on the rebars. The rebars were extracted from the specimens and cleaned following the procedure stated in ASTM G1. The condition of the rebars after cleaning is illustrated in Figure 6-14. After cleaning the rebars, the percentage weight losses were determined, as shown in Table 6-4. After one year of exposure, all of the mixtures showed minimal weight loss. The average weight loss was 2.532, 1.709, 1.329, 1.646, 0.633, and 0.570% for AAC mixtures 10CA, 20CA, 30CA, 10CS, 20CS, and 30CS, respectively. The steam-cured mixtures showed significant reduction in the weight loss due to chloride-induced reinforcement corrosion compared to their ambient-air cured counterparts.

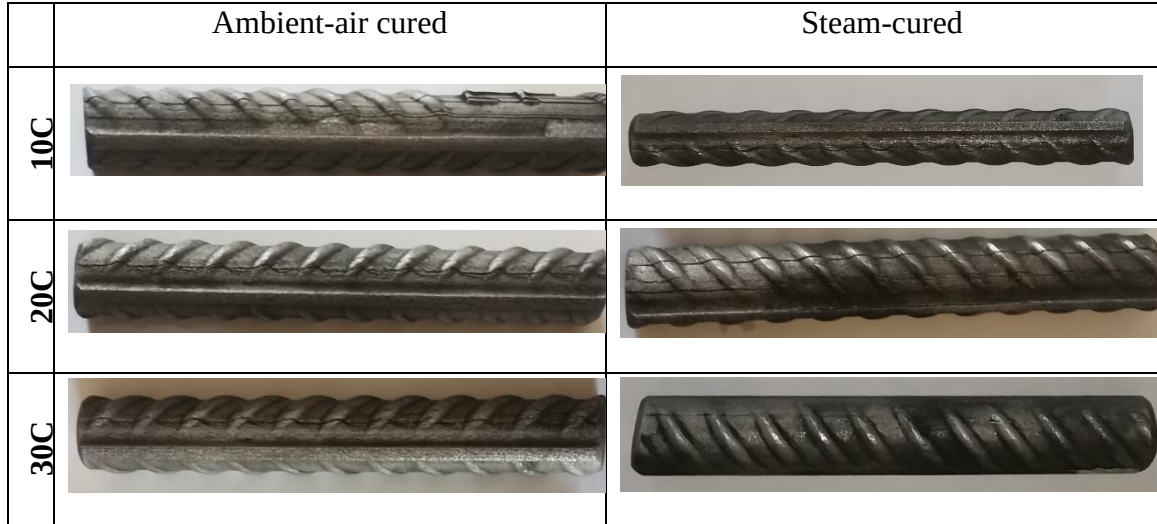


Figure 6-14 Cleaned rebar condition after 360 days of exposure to 5% NaCl

The equivalent corrosion current density, I_{corr} values, shown in Table 6-4, were calculated by substituting the measured value of the weight loss and other parameters to the Faraday's law, as given by Equation 6-8:

$$W = \frac{I_{corr} \cdot t \cdot M_w \cdot A}{n \cdot F} \quad \text{Equation 6-8}$$

Where, W is the weight loss (g), I_{corr} is the reinforcement corrosion current density ($\mu\text{A}/\text{cm}^2$), t is the time (s), M_w is the atomic weight of the steel rebar (g/mol), A is the surface area of the rebar (cm^2), n is the number of electrons involved in the reaction, and F is the Faraday's constant = 96500 Coulomb/mol. M_w is assumed to be equal to that of Iron (atomic weight = 55.85 g/mol) to ease the calculation, n is equal to 2 from the anodic half-cell reaction $\text{Fe} \rightarrow \text{Fe}^{++} + 2\text{e}^-$, and t is equal 31.104×10^6 s (360 days).

Table 6-4 Gravimetric test results and the equivalent I_{corr} (σ is the standard deviation)

Mixture	Weight loss (%)	σ	Equivalent I_{corr} ($\mu\text{A}/\text{cm}^2$)
10CA	2.532	0.127	0.582
20CA	1.709	0.063	0.393
30CA	1.329	0.190	0.305
10CS	1.646	0.127	0.378
20CS	0.633	0.127	0.145
30CS	0.57	0.064	0.131

The values of equivalent I_{corr} , determined using gravimetric test results after one-year exposure to 5% NaCl (Table 6-4), could be considered as true representation of the status of reinforcement. Figure 6-15 shows the plots of both I_{corr} values measured using the LPR method and equivalent I_{corr} values from the gravimetric test results. It can be observed from Figure 6-15 that the status of reinforcement corrosion for all AAC mixtures (except 10CA) were in the range of ‘very low/passive’ to ‘low/moderate’, based on the curve obtained using equivalent I_{corr} values that is in agreement with the status of reinforcement corrosion of rebars noticed through the visual observation of the rebars before conducting the gravimetric test. Therefore, it is confirmed that the electrochemical measurements (half-cell potential and LPR tests) yielded misleading values of E_{corr} and I_{corr} . Hence it can be noted that the electrochemical tests cannot be reliably used to monitor corrosion of rebars embedded in AAC mixtures due to the previously mentioned reasons associated with the compositions of AACs. In order to pave the way for application of electrochemical measurements in case of AACs, there is a need for research to develop corrective measures.

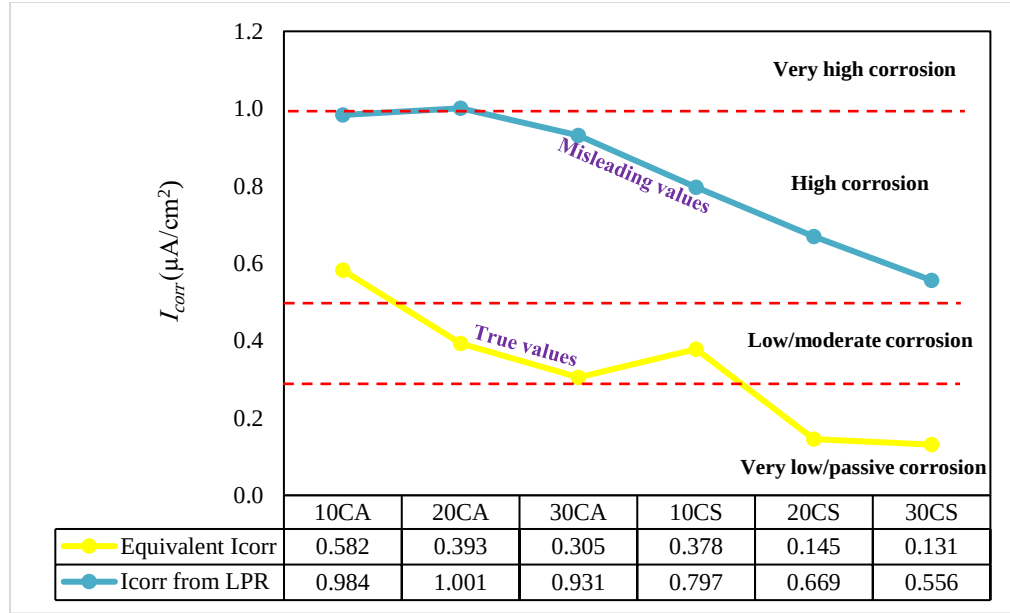


Figure 6-15 Plots of I_{corr} values after 360 days of exposure to 5% NaCl

Considering the gravimetric (i.e., actual) I_{corr} plot shown in Figure 6-15, the beneficial effect of the increase in the OPC content of precursor on resistance against reinforcement corrosion can be observed for both groups of the AAC mixtures. A sharp decrease in I_{corr} can be observed for both ambient-air cured as well as steam-cured AAC mixtures when the OPC content of the precursor increased from 10 to 20%. The resistance against reinforcement corrosion marginally increased for increase in the OPC content from 20 to 30%. Further, like other durability characteristics the performance of steam-cured AAC mixtures against reinforcement corrosion was better than that of the ambient-air cured AAC mixtures.

6.6. Summary

A detailed experimental investigation into the chloride transport properties and the chloride-induced reinforcement corrosion behavior of AACs made with industrial byproducts and mineral additives was undertaken. The durability tests such as the chloride

permeability, chloride migration, and chloride diffusion were conducted. Furthermore, the chloride-induced reinforcement corrosion of rebars embedded in the AAC mixtures was studied by means of electrochemical methods that included monitoring of reinforcement corrosion potential and corrosion current density in addition to the gravimetric method. The following conclusions can be drawn based on the results of this investigation:

- 1- AAC mixtures that were ambient-air cured exhibited a chloride permeability that classified them in the ‘moderate’ to ‘low’ chloride permeability classes while the steam-cured AAC mixtures exhibited RCPT values that classified them in the ‘low’ to ‘very low’ chloride permeability classes, compared to the OPC control mixture which was classified in the ‘high’ chloride permeability class. The non-steady state chloride migration coefficient (D_{nssm}) was in the range of 17.5 to $29.6 \times 10^{-12} \text{ m}^2/\text{s}$ for the AAC mixtures with the lowest being exhibited by steam-cured AAC mixture (30CS), compared to the control OPC mixture which had a D_{nssm} value of $34.75 \times 10^{-12} \text{ m}^2/\text{s}$. The apparent chloride diffusion coefficient (D_a) ranged from 53×10^{-12} to $27.6 \times 10^{-12} \text{ m}^2/\text{s}$ for the free chloride and from 35.1×10^{-12} to $7.8 \times 10^{-12} \text{ m}^2/\text{s}$ for the total chloride. In both cases, the OPC control mixture showed the highest D_a value followed by ambient-air cured mixtures and then the steam-cured mixtures. The chloride binding capacity of the AACs was found to be much higher than the OPC control mixture and varied from 0.014 to 0.248 % by weight of concrete which can be owed to the higher alumina phases which react with the chloride and bind it to form complex chloride-alumina salts such as Friedel’s salt.

- 2- Good correlations were observed between compressive strength and RCPT, and D_{nssm} and RCPT indicating the dependency of both strength and durability characteristics on the microstructure of the concrete mixtures.
- 3- The indication of the status of reinforcement corrosion in AAC mixtures using electrochemically measured E_{corr} and I_{corr} values were found to be misleading as confirmed by visual inspection of the extracted rebars and the gravimetric test results. The reason behind ineffectiveness of the electrochemical measurements in reflecting the true status of reinforcement corrosion in AAC may be attributed to the lower pH of AACs, the lack of oxygen at the rebar level especially in the cathodic region due to the refined and more tortuous pore structure of AACs, and the interference with the measurement that is caused by the ionic accumulation in AAC binder matrix. Therefore, before using electrochemical measurements in case of AACs, there is a need for research to develop corrective measures.
- 4- The equivalent I_{corr} (i.e., actual corrosion current density) values calculated using Faraday's law based on the weight loss due to chloride-induced reinforcement corrosion demonstrate a high resistance of AAC mixtures against reinforcement corrosion. After one year of 5% NaCl exposure, no significant corrosion was observed.
- 5- The results of strength as well as durability characteristics tests including corrosion current density indicate that there is a sharp increase in the performance of the AAC mixtures when the OPC content of the precursor was increased from 10 to 20%, irrespective of the curing method. Therefore, an optimum dosage of the OPC in the precursor can be considered as 20% allowing 80% waste materials and natural

minerals in the precursor with much higher strength and durability characteristics than traditional OPC concrete thus saving energy and reducing environmental pollution leading to a cleaner production of concrete.

CHAPTER 7. CONCLUSION

Low carbon/non-carbonate binders were developed utilizing indigenous natural minerals and industrial waste materials in the form of an alkali-activated binder composed of a precursor containing an optimum proportioning of limestone powder, natural pozzolana, red and silicomanganese fume, in addition to minor quantities of OPC. The raw precursor materials were procured and characterized in terms of their physical, chemical, and microstructural properties. In addition, the study was successful in studying the hydration/polymerization products of the developed AABs as well as their physical, mechanical, drying shrinkage, acid and sulphate attack resistance, chloride transport, and chloride-induced reinforcement corrosion properties as alkali-activated concretes. A reduction in the consumption of OPC ranged from 70 to 90% while maintaining an overall performance and properties comparable to and even better than traditional OPC concrete.

The following conclusions can be drawn based on the results of this comprehensive study:

- 1- The chemical investigation of the precursor materials revealed that SMF, RM, NP, and LSP were rich in reactive manganese and silica, alumina, and calcium oxide, respectively, as indicated by XRF and EDS. Furthermore, the optimally selected precursor (P9) contained 10% LSP, 40% NP, 20% RM, 10% SMF, and 20% OPC. The precursor chemical composition, loss on ignition, and moisture content satisfy the ASTM C618 criteria for being a pozzolanic material, thus allowing the blend to be used as supplementary cementitious material as well.
- 2- The activation parameters (A/P and NS/NH ratios, NH molarity, and W/P ratio) significantly influenced the compressive strength and setting time. The flow was affected substantially only by the W/P ratio.

- 3- The evolution of strength in case of ambient air curing was slow and oven curing caused the formation of cracks that lowered the strength, while steam curing increased the strength significantly. Increasing the duration of steam curing beyond 48 hours resulted in a retrogressive behavior where the strength decreased.
- 4- An AAB-based mortar mixture with, a flow of 201 mm, an initial setting time of 46 minutes, a final setting time of 77 minutes, and a 28-day compressive strength of 30 MPa can be considered as having the most optimum activation parameters and curing regime. The optimum A/P and NS/NH ratios, NH molarity, W/P ratio, and curing regime were found to be as follows: 0.5, 2, 10 M, 0.4, and 24-hour steam curing, respectively. However, for applications requiring lower strength and/or different setting times, the other developed trial mixtures can be used.
- 5- XRD analysis showed the formation of various aluminosilicate-based polymers such as NASH, CASH, and KASH in addition to CSH, Mn-SH, and Mn-CH with A/P, NS/NH, NaOH molarity having a proportional influence on their formation while W/P had the opposite effect. FTIR confirmed the formation of those phases. SEM micrographs showed the formation of uniform hydration products, resulting in a sturdy and dense microstructure with the hydration product filling the microcracks. The observations made through these microstructural examinations validated the trends observed in the compressive strength results with variation in the activation parameters.
- 6- The increased OPC content and steam curing led to the formation of more crystalline hydration/polymerization products such as CSH, CASH, NASH, Mn-SH, and KASH, which resulted in a denser and more resilient structure that

produced better mechanical properties. Maximum compressive strength of 44.9 MPa and splitting-tensile strength of 3.3 MPa were achieved at 28 days by an AAC mixture containing 30% OPC and cured using steam (i.e., 30CS), which were significantly higher than of the control mixture (conventional OPC concrete, i.e., 100C). These observations were validated by the microstructural investigation via XRD and SEM-EDS analyses. However, the modulus of elasticity of all AAC mixtures were lower than the control OPC mixture which can be attributed to the higher ductility of the polymerization products that have higher binding capacity but lower resistance against compressive strain.

- 7- AAC mixtures exhibited lower drying shrinkage than the control mixture at all ages except for mixture 10CA. Furthermore, the drying shrinkage was mostly unchanged after the first 28 days for the AAC mixtures. A maximum drying shrinkage of 399 microstrain for 30CA and 127 microstrain for 30CS was recorded at 180 days compared to the 700 microstrain observed for the control OPC mixture.
- 8- AAC mixtures with OPC content higher than 10% exhibited resistance against acid and sulfate attacks similar or better than the control OPC mixture in terms of weight loss and strength reduction.
- 9- Calcium sulfate dihydrate was mainly formed as a result of acid and sulfate exposures due to the disintegration and depolymerization of the calcium-carrying polymerization products, as evident by XRD spectroscopy and SEM-EDS imaging. In addition, calcite, dolomite and natrite were observed in XRD due to the carbonation of the calcium, magnesium and sodium ions liberated by the sulfuric acid and sulphate attacks. Furthermore, thaumasite formation, as radial needle-like

crystals, was observed in SEM imaging in the case of the sulfate exposure due to the low temperature and high relative humidity in the exposure environment which favors the formation of thaumasite over rod-like crystals of ettringite.

10- The increase of the OPC content from 10 to 20% as a proportion of the precursor led to a significant improvement in all aspects of the concrete mixture performance that were able to surpass the control OPC mixture, irrespective of the curing regime, while the increase in OPC content beyond 20% resulted in marginal improvements.

11- AAC mixtures that were ambient-air cured exhibited a chloride permeability that classified them in the ‘moderate’ to ‘low’ chloride permeability classes while the steam-cured AAC mixtures exhibited RCPT values that classified them in the ‘low’ to ‘very low’ chloride permeability classes, compared to the OPC control mixture which was classified in the ‘high’ chloride permeability class. The non-steady state chloride migration coefficient (D_{nssm}) was in the range of 17.5 to $29.6 \times 10^{-12} \text{ m}^2/\text{s}$ for the AAC mixtures with the lowest being exhibited by steam-cured AAC mixture (30CS), compared to the control OPC mixture which had a D_{nssm} value of $34.75 \times 10^{-12} \text{ m}^2/\text{s}$. The apparent chloride diffusion coefficient (D_a) ranged from 53×10^{-12} to $27.6 \times 10^{-12} \text{ m}^2/\text{s}$ for the free chloride and from 35.1×10^{-12} to $7.8 \times 10^{-12} \text{ m}^2/\text{s}$ for the total chloride. In both cases, the OPC control mixture showed the highest D_a value followed by ambient-air cured mixtures and then the steam-cured mixtures. The chloride binding capacity of the AACs was found to be much higher than the OPC control mixture and varied from 0.014 to 0.248 % by weight of concrete which can be owed to the higher alumina phases which react with the chloride and bind it to form complex chloride-alumina salts such as Friedel’s salt.

- 12- Good correlations were observed between compressive strength and RCPT, and D_{nssm} and RCPT indicating the dependency of both strength and durability characteristics on the microstructure of the concrete mixtures.
- 13- The indication of the status of reinforcement corrosion in AAC mixtures using electrochemically measured E_{corr} and I_{corr} values were found to be misleading as confirmed by visual inspection of the extracted rebars and the gravimetric test results. The reason behind ineffectiveness of the electrochemical measurements in reflecting the true status of reinforcement corrosion in AAC may be attributed to the lower pH of AACs, the lack of oxygen at the rebar level especially in the cathodic region due to the refined and more tortuous pore structure of AACs, and the interference with the measurement that is caused by the ionic accumulation in AAC binder matrix. Therefore, before using electrochemical measurements in case of AACs, there is a need for research to develop corrective measures.
- 14- The equivalent I_{corr} (i.e., actual corrosion current density) values calculated using Faraday's law based on the weight loss due to chloride-induced reinforcement corrosion demonstrate a high resistance of AAC mixtures against reinforcement corrosion. After one year of 5% NaCl exposure, no significant corrosion was observed.
- 15- An optimum dosage of the OPC in the precursor can be considered as 20% allowing 80% waste materials and natural minerals in the precursor with much higher strength and durability characteristics than traditional OPC concrete thus saving energy and reducing environmental pollution leading to a cleaner production of concrete.

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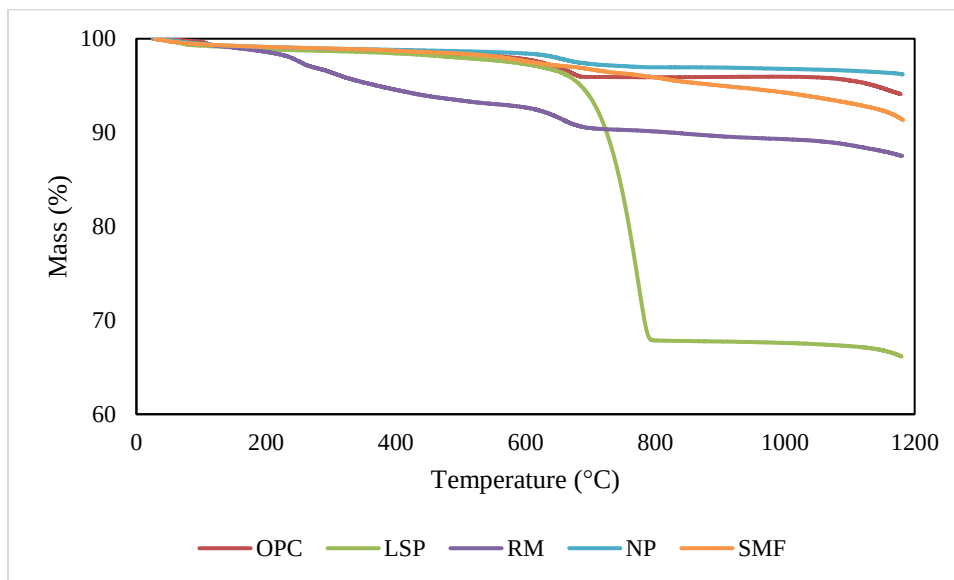
Taguchi method,” *Mater. Des.*, vol. 36, pp. 191–198, Apr. 2012.

APPENDIX A: TGA/DTG OF THE RAW PMS

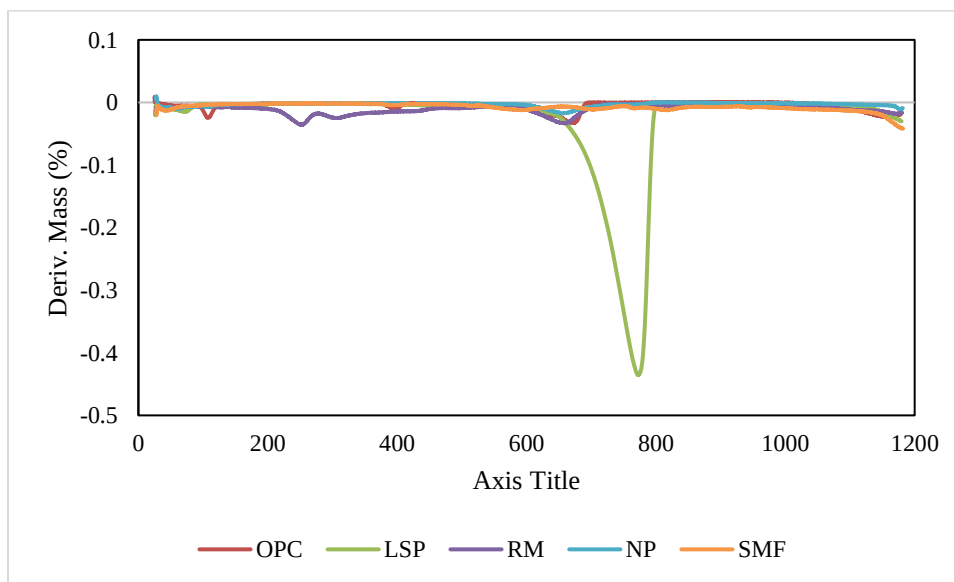
Conditions:

Temperature: 25 – 1200 °C, Environment: Nitrogen, Temp. increase rate: 10 °C per minute

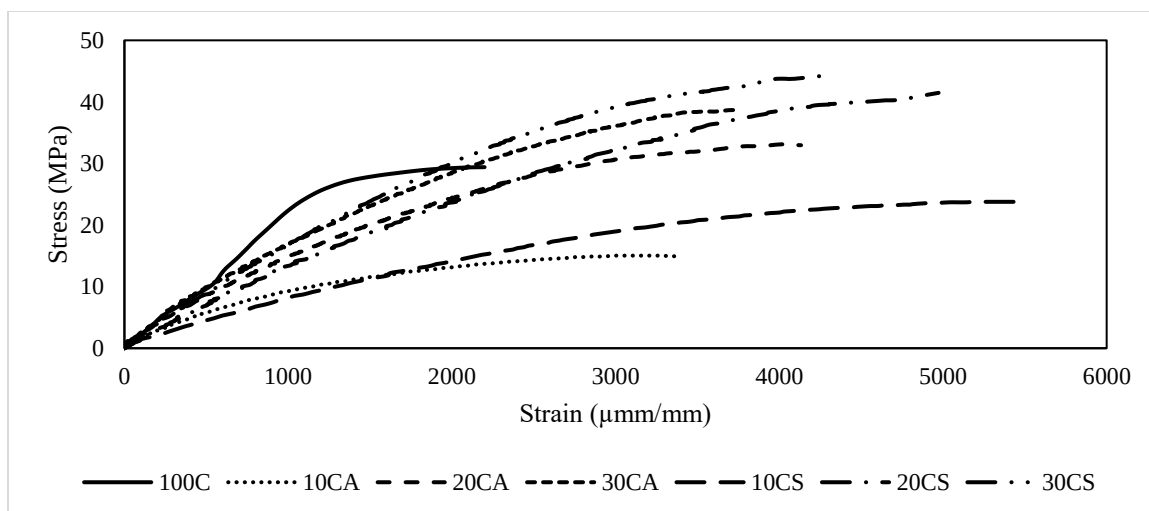
1- TGA



2- DTG



APPENDIX B: STRESS-STRAIN CRUVES

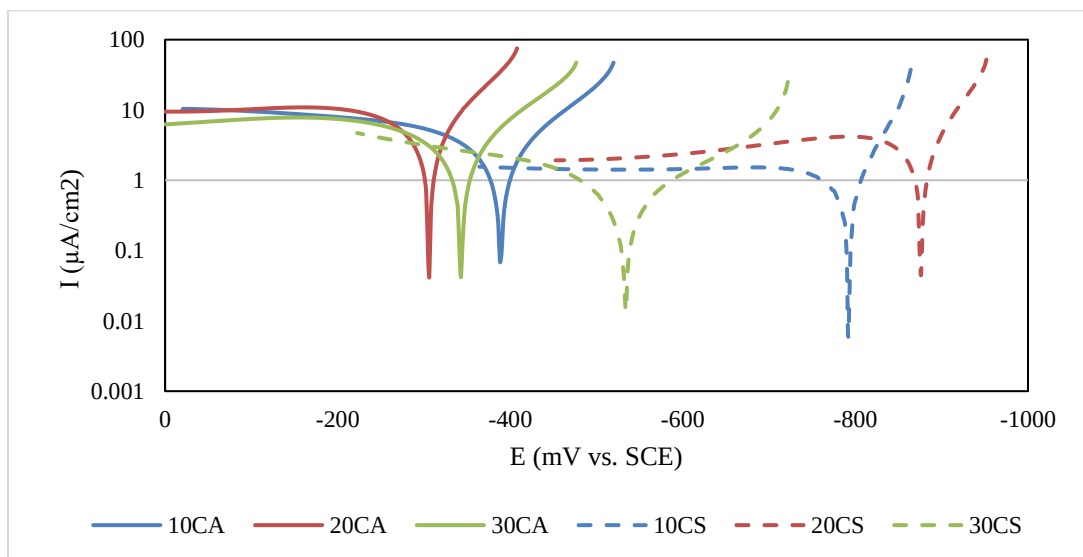


APPENDIX C: POTENTIODYNAMIC POLARIZATION

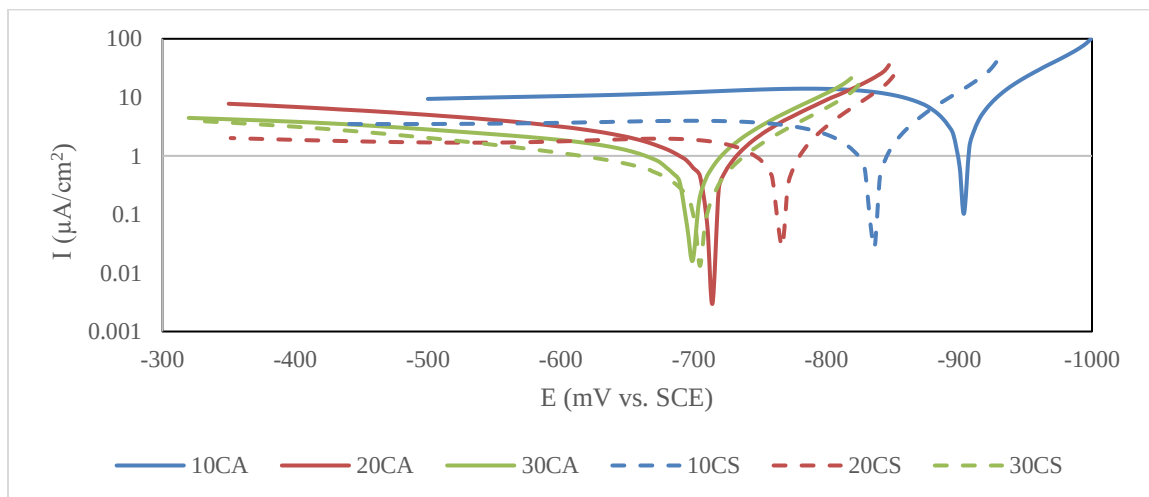
Conditions:

Polarization range: ± 200 mV from E_{corr} .

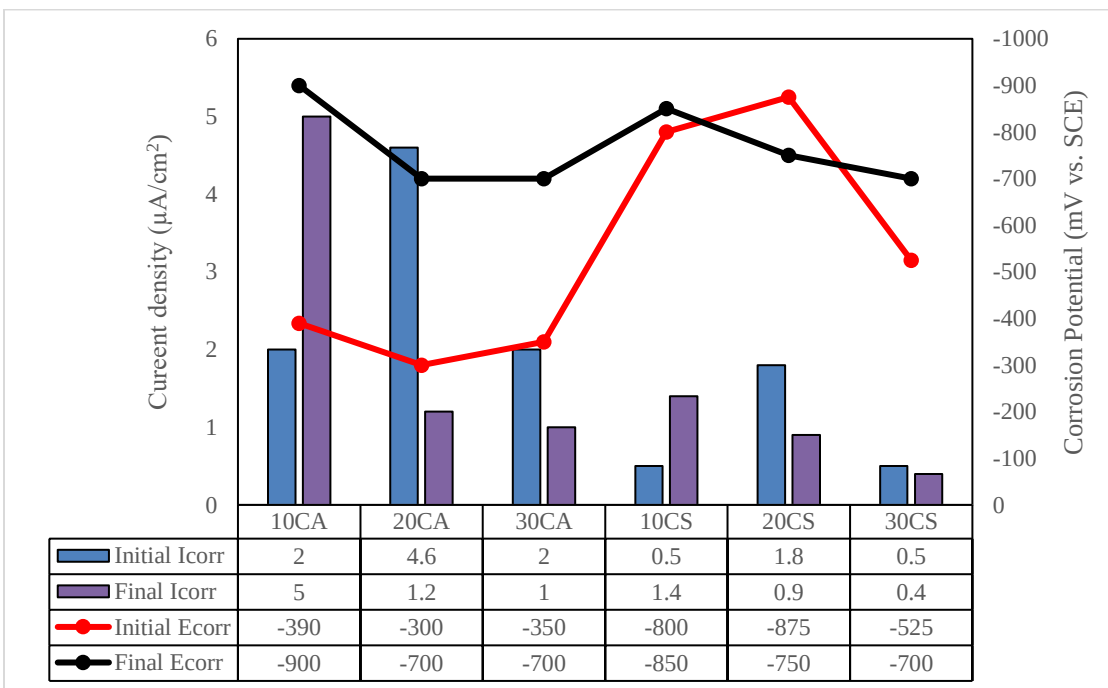
1- Initial PDP (Exposure day 0)



2- Final PDP (Exposure day 360)



3- Summary



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Publications:

A) Published

- [1] A. M. Abd El Fattah and **I. N. A. Al-Duais**, “Modeling of Chloride Binding Capacity in Cementitious Matrices Including Supplementary Cementitious Materials,” Crystals, vol. 12, no. 2, p. 153, 2022. (**Q2; IMPACT: 2.589, Citations: 1**)
- [2] A. Ali, K. Irshad, M. F. Khan, M. M. Hossain, **I. N. A. Al-Duais**, and M. Z. Malik, “Artificial intelligence and bio-inspired soft computing-based maximum power plant tracking for a solar photovoltaic system under non-uniform solar irradiance shading conditions—A review,” Sustain., vol. 13, no. 19, 2021. (**Q1, IMPACT: 3.889, Citations: 6**)

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- [4] A. A. El Fattah, **I. Al-Duais**, K. Riding, M. Thomas, S. Al-Dulaijan, and M. Al-Zahrani, “Field validation of concrete transport property measurement methods,” *Materials (Basel)*., vol. 13, no. 5, pp. 1–19, 2020. (**Q1, IMPACT: 3.623, Citations: 7**)
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B) Submitted/Planned

- [1] **I. N. A. Al-Duais**, A. Shamsad, M.A. Al-Osta, M. Maslehuddin, and T. A. Saleh “Properties of Alkali-Activated Concrete Made using the Optimum Combinations of Precursor Materials and Activation Parameters” submitted to *Construction and Building Materials* (**Q1, IMPACT: 6.141**)
- [2] **I. N. A. Al-Duais**, A. Shamsad, M.A. Al-Osta, M. Maslehuddin, T. A. Saleh, and S.U. Al-Dulajan “Optimization of Alkali-Activated Binders Using Natural Minerals and

Industrial Waste Materials as Precursor Materials” submitted to Journal of Building Engineering (**Q1, IMPACT: 6.331**)

[3] **I. N. A. Al-Duais**, A. Shamsad, M.A. Al-Osta, M. Maslehuddin, T. A. Saleh, and M. Ibrahim “Durability of Alkali-Activated Concrete made using Natural Minerals and Industrial Waste Materials as Primary Binders” submitted to Journal of Cleaner Production (**Q1, IMPACT: 9.297**)

[4] **I. N. A. Al-Duais**, Al-Shugaa.A. Shamsad, M.A. Al-Osta, M. Maslehuddin, and T. A. Saleh “A review on the use and availability of indigenous mineral and industrial byproducts in the development of low-carbon/Non-carbonate binders” to be submitted to the Arabian Journal of Science and Engineering (**Q2, IMPACT: 2.621**)