Towards understanding the influence of metakaolin in the prevention of alkali-silica reaction

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Abstract. The role of supplementary cementitious materials (SCM) in the prevention and mitigation of the Alkali-Silica Reaction (ASR) in concrete materials and structures is becoming increasingly significant and relevant in the civil engineering. The use of SCMs in South Africa is limited to Ground Granulated Blast-Furnace Slag (GGBS) and Fly Ash (FA) as they are readily available. With recent advancements in concrete technologies, it has been found that calcined clays such as Metakaolin (MK) have been useful in concrete to improve the chemical, mechanical, and physical properties of concrete material. Deposits of MK have been found in some regions of South Africa and are now available for consumption with various applications but have not yet been widely accepted as conventional SCM within the concrete ready-mix industry. This article aims to summarise state-of-the-art and existing knowledge gaps in the application of SCMs in concrete material and identify the feasibility and benefits of extending the use of SCMs with MK in a comparative study with FA Class F and SF. The performance of MK with respect to the key variables such as exposure conditions, reaction mechanisms and pore solution composition in the prevention of ASR in concrete material relative to the mentioned SCMs is discussed.

1 Introduction

The durability of concrete structures subjected to alkali-silica reaction (ASR) is compromised, thereby affecting the serviceability of its intended use [1]. This can result in unforeseen maintenance and capital costs on concrete structures. ASR is a reaction in concrete where alkalis found in cement reacts with silicas present in natural aggregates, which causes concrete material to expand as the reaction between alkalis and silica takes place. The reaction is sustained with sufficient exposure to moisture, and as the alkalis and silica are hydrated, they form an alkali-silica gel in the pores of the concrete and begin to expand [2].

With structures being subjected to ASR, their intended serviceability period is reduced, resulting in unforeseen overhead costs in maintenance. Therefore, the mitigation of ASR is important to ensure the durability of concrete structures is preserved in the built environment. Supplementary cementitious materials (SCMs) have been found to be effective in the mitigation of ASR in concrete [3].

With the introduction of SCMs such as metakaolin (MK) into concrete, an overall increase in the performance of the mechanical and physical properties of concrete has been reported. The use of SCMs is limited to fly ash (FA), ground granulated blast-furnace slag (GBBS) and silica fume (SF) in South Africa. However, with an increase in the demand for more sustainable and cleaner energy sources, an inevitable decline in FA production in the near future is foreseen. This emphasises the need for the sustainable development of SCMs.

With the availability of MK in South Africa, extending the use of SCMs with MK can be beneficial to the concrete ready-mix industry in South Africa, as MK is not yet commercially accepted. Furthermore, with concrete technology advancing and the use of calcined clays being promoted, the use of MK can prove to be a commercial success and improve concrete properties in South Africa.

2 The role of supplementary cementitious materials in concrete production

Engineering methods and technology are becoming increasingly more advanced and efficient as time progresses. The need for more efficient and durable concrete needs to complement advancements in engineering methodologies and technologies. Ensuring concrete structures' longevity by investing in concrete technology advancements is of utmost importance. This will help improve the durability and serviceability of civil engineering infrastructure and lowers capital costs associated with construction and maintenance [4].

Extending the use of SCMs with MK can reduce the impact on the environment by reducing the cement and concrete industry's carbon footprint [5]. Kaolinite clay is available globally; once it undergoes the calcination process, the reactivity of the product – MK is notable as a

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partial replacement of the total binder content in concrete [6].

The role of SCMs in ASR mitigation is to provide more siliceous material to react with alkalis in ordinary Portland cement (OPC). Therefore, SCMs with low calcium and high silica content are more effective in mitigating the expansion induced by ASR. In addition, they can be used in lower replacement levels in the total cementitious content [2].

2.1 Limitations of supplementary cementitious materials in South Africa

South Africa boasts a wide variety of power generation plants over a wide geographical area. Power generation sources range from Coal Power, Nuclear Power, Hydro Energy, Solar Energy and Wind Energy. The production of FA in South Africa is a derivative of coal power production. Coal power plants are predominantly found in the provinces of Gauteng, Limpopo and Mpumalanga. Due to the bituminous coal used in power generation, Class F FA is found in South Africa [7, 8]. As there is an abundance of FA in South Africa, costs incurred on transportation of FA to other regions of South Africa increase the cost of ready-mix concrete in the coastal regions of South Africa.

Slag is a by-product of the iron and steel manufacturing process [9]. Previously in the Western Cape Province, South Africa, GGBS and ground granulated corex slag (GGBCS) were produced at the Saldanah Steel Plant by ArcelorMittal South Africa; however, the plant was shut down in 2020. This shutdown came after ArcelorMittal faced financial difficulties. This meant that the slag could no longer be locally procured within the Western Cape as ArcelorMittal South Africa no longer produced it.

The application of SF in South Africa calls for special applications and is not seen as a conventional SCM. In addition, the use of SF requires the material to be imported as it is not manufactured locally.

2.2 Metakaolin as a sustainable supplementary cementitious material in South Africa.

MK is a calcined clay derived from kaolinite clay and is a natural pozzolan. Its chemical composition is made up of silica and alumina ($Al_2Si_2O_7$). MK is produced by the process of calcination and is heated up to temperatures of 900 ºC in a kiln, removing any traces of hydrogen and the crystalline structure of the clay [10].

MK is a topic of numerous studies in the effort to promote sustainable use of SCMs globally. The physical, mechanical, and durability properties of concrete are influenced by MK addition. At optimum MK content, increased compressive and tensile strength, reduced permeability, and overall improvement in durability properties have been reported.

A study done by Ekosse [11] identified kaolin deposits in the African continent and set out to quantify individual deposits of raw kaolin. It was found that most deposits were found in Western and Southern Africa, namely, Nigeria, Cameroon and South Africa, with 40, 27 and 20 deposits, respectively. The locations of the 20 deposits in South Africa are shown in Table 1.

Table 1. Locations of kaolinite deposits in South Africa. Reproduced from Ekosse [11].

Province	Location
Western Cape	Fishhoek Noordhoek Valley
Western Cape	Kommetjie
Western Cape	Brakenfell
Western Cape	Somerset West
Western Cape	Gansbaai
Western Cape	Albertinia
Western Cape	Riversdal
Western Cape	George
Western Cape	Mossel Bay
Western Cape	Vanrhynsdorp
Western Cape	Bitterfontein
Northern Cape	Garies
Kwa-Zulu Natal	Inanda
Kwa-Zulu Natal	Ndwedwe
Mpumalanga	Nelspruit
Eastern Cape	Grahamstown
North West	Koster
North West	Potchefstroom
Limpopo	Polokwane
Gauteng	Bronkhorspruit

In the study conducted by Ekosse [11], 55% of deposits identified within South Africa are in the Western Cape Province.

3 Characterisation of metakaolin

3.1 Oxide composition

The oxide composition is obtained by conducting an X-ray fluorescence (XRF) test on the powder samples. Table 2 shows the oxide composition reported by some authors. From the results, the major compounds are SiO_2, Al_2O_3, and Fe_2O_3, with a total of over 96%-98% [12-14]. These oxides are those required for the pozzolanic reaction.

3.2 Surface morphology of metakaolin

The surface morphology determined through Scanning Electron Microscopy (SEM) of MK is shown in Figure 1. The particles of the MK are mostly angularly shaped. Hence, using MK will increase friction within the matrix and thereby decreasing the flowability of the mix. However, this can be mitigated by using an appropriate high-range water-reducing agent.

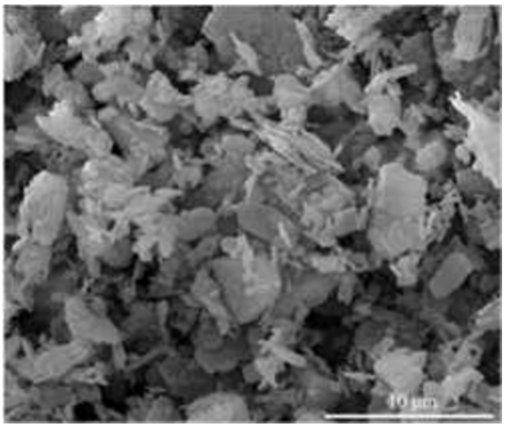

Fig. 1. Surface morphology of MK [15]

3.3 X-ray diffractometry (XRD)

The mineralogy of MK is typically determined from an X-ray diffractometry (XRD) analysis. The spectral analysis of the MK shown in Figure 2 indicates that quartz is the dominant mineral among others [16]. Other authors have also reported the dominance of quartz in MK [17].

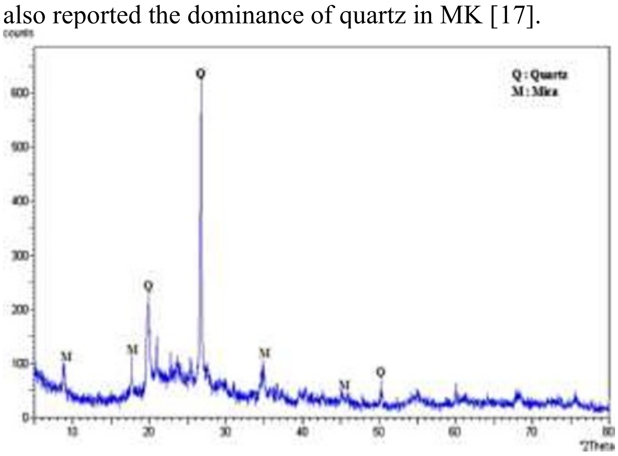

Fig. 2. X-ray diffractometry of MK [16]

4 Fresh state properties of metakaolin concrete

As with other pozzolanic materials, MK influences the setting times of cement-based materials. The addition of MK will increase both the initial and final setting times [18], which is good for the ready-mix industry. However, care must be taken to add accelerating admixtures to the mix when temperatures are low (winter season). Typically, the fresh properties (slump, slump flow) of concrete containing MK decreases as the content of the MK increase in the mixture, irrespective of the MK type. This is influenced by several factors such as the fineness, particle shape, and water/cement ratio [19]. Also, the rheological properties, yield stress, and plastic viscosity are influenced by the addition of MK in cement-based materials (paste, mortar, concrete). The impact of MK on the fresh properties of cement-based materials with different content, as reported by [18], is presented in Figures 3 (a) and (b). A high-range water reducer would enhance the fresh properties when substituting MK for cement.

5 Hardened state properties of metakaolin concrete

The hardened state properties, compressive, flexural, and splitting tensile strength of concrete containing MK are influenced by MK. Generally, when MK is substituted for cement, it improves the strength of cement-based composites up to an optimum content of 15-20%, beyond which the strength could decrease. However, strength properties increase at later ages, up to 90 days. MK acts as a filler within the matrix (physical effect) and also the chemical effect when the hydration kinetics densifies the microstructure of concrete. As the MK reacts with calcium hydroxide from the reaction of cement with water, more calcium-silicate hydrate, calcium-aluminate hydrate, and calcium-silicate-aluminate hydrate are produced; hence, enhancing strength [20]. Figure 4 (a) and (b) show the compressive strength performance of mortar and concrete at varying ages and MK content. Depending on how the mixture is engineered, high compressive strength concrete (up to 90 MPa at 28 days) can be achieved, as shown in Figure 4 [21]. Also, significant flexural and split tensile strength can be achieved at varying ages and MK content (Figure 5 (a) and (b)). For a mixture containing crumb rubber and modified with SF, MK concrete attained an elastic modulus of approximately 40 MPa, as shown in Figures 6 (a) and (b). Overall, these results indicate that the MK-based concrete performs equally well as the control tested, and even higher strength was achieved where the mixture was adequately engineered for optimum performance. Hence, the South African construction industry should capitalise on the abundance of MK and adopt its usage as an alternative to FA.

6 Durability of concrete containing Metakaolin

With the advancements in the sustainable development of construction materials such as concrete, the durability performance of this material can be addressed with new concrete technologies. Understanding the need for infrastructure is important when addressing the issue of concrete durability, and by understanding that need, the identification of infrastructure requirements can be done. Furthermore, maintaining the durability and the quality of concrete structures is important when ensuring that our intentions and actions are sustainable in society and the environment [27].

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Table 2. Chemical compounds of metakaolin and OPC

Compounds (%)	CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	MgO	K_2O	Na_2O	LOI	$^{*}O_{sum}$
MK [12]	0.39	54.30	40.26	2.28	–	0.08	0.50	0.12	–	96.84
MK [13]	0.20	52.10	42.8	1.60	–	0.21	0.32	0.11	–	96.50
MK [14]	–	51.13	47.69	–	–	–	–	–	–	98.82
OPC [14]	4.37	19.06	4.37	3.51	3.50	1.75	0.65	0.21	–	26.94

$^{*}SiO_2 + Fe_2O_3 + Al_2O_3$

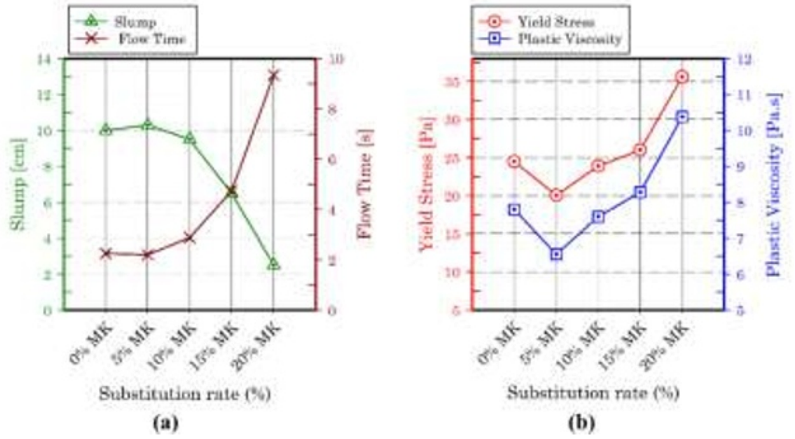

Fig. 3. Impact of MK on the (a) slump and flow, (b) yield stress and plastic viscosity of mortar [19]

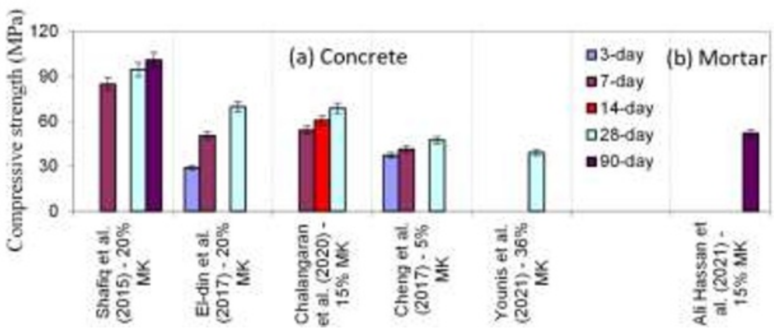

Fig. 4. Compressive strength development of metakaolin-cement (a) concrete and (b) mortar [21-26].

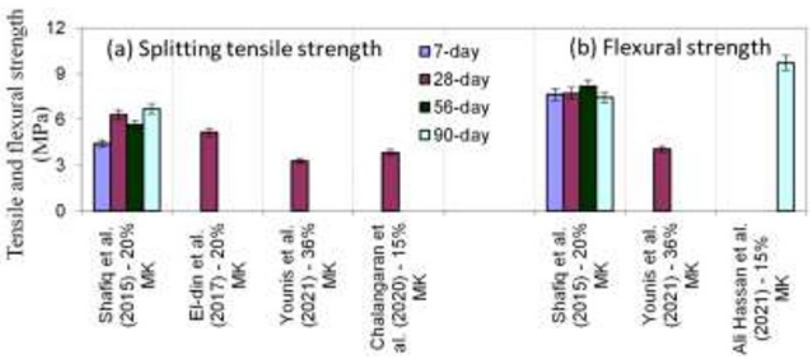

Fig. 5. Effect of metakaolin on (a) splitting tensile and (b) flexural strength of concrete [21-23, 25, 26].

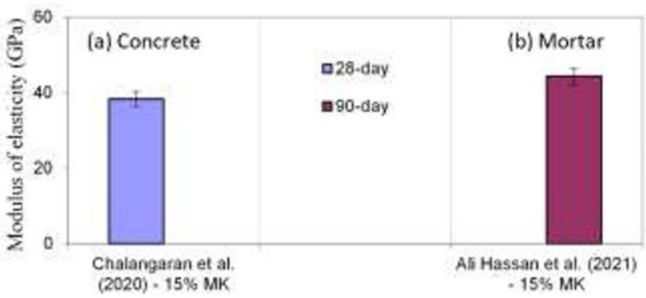

Fig. 6. Modulus of elasticity of metakaolin-cement (a) concrete and (b) mortar [23, 26]

6.1 Factors influencing concrete durability

Concrete structures subjected to the elements and aggressive chemicals will generally see much more rapid degradation depending on the type of exposure. The durability of concrete is affected by the transport mechanisms such as ingress of water, oxygen and chlorides. Concrete durability is the ability of the concrete to resist the penetration of gases and liquids. Some durability indices of importance are water sorptivity index (WPI), oxygen permeability index (OPI), chloride conductivity index (CCI) and resistance to sulphate attack.

Concrete structures or elements whose durability has been affected can generally be attributed to the type of concrete structure and exposure. For example, reinforced concrete water retaining structures for freshwater would need to be very resistant to oxygen and water permeability. Concrete waste-water structures and foul sewer systems would need to be resistant to oxygen permeability, water permeability and sulphate ingress. Reinforced concrete structures such as bridges and their components in coastal regions would have an emphasis on resistance to chloride ingress. These durability indices are important when designing concrete for a specific purpose and ensuring durability and performance [28].

6.2 Use of supplementary cementitious materials to improve concrete durability

Extending the use of SCMs in concrete will yield positive results in improving hardened concrete's durability. Conventional SCMs used globally are GGBS, SF and FA, with FA being the more efficient in enhancing durability properties [29].

Malhotra [29] proved that FA is more efficient between SF and GGBS, whereas Naik [30] later showed that Class F FA is the more effective FA between Class C and Class F. Malhotra [29] sampled cores taken from a 10-year-old concrete block, and conducted a Rapid Chloride Penetration Test (RCPT). Table 3 shows the concrete's resistance to chloride ingress, where FA shows more resistance to chloride-ion resistance.

With a similar approach to Malhotra [29], Naik [30] focused on Classes C and F FA at various replacements and found that Class F FA is more effective in improving the durability of concrete, as shown in Table 4.

Table 3. Resistance to chloride penetration of concrete after 10 years outdoor exposure [29].

Mix	SCMs	Cementitious Content (kg/m^3)	W/C	Resistance to chloride-ion penetration (Coulombs)
1	7% SF + 28% Slag	485	0.29	100
2	35% Slag	484	0.28	235
3	8% SF	488	0.27	565
4	12% SF	486	0.27	120
5	57% FA	350	0.29	0
6	100% OPC	485	0.27	380

Table 4. Chloride-Ion penetration of concrete cores [30].

Mix	FA Class C	FA Class F	Cementitious Content (kg/m^3)	W/C	Resistance to chloride-ion penetration (Coulombs)
A-1	70%	-	335	-	113
B-5	50%	-	350	0.26	217
C-4	19%	-	350	0.29	566
D-2	-	67%	400	0.31	65
E-3	-	53%	389	0.31	77
F-6	-	35%	416	0.31	155

Where the addition of SCMs can be beneficial to concrete with respect to the durability of concrete, the performance of FA is superior to GGBS and SF, more specifically Class F FA. Sujjavanich [31] conducted a study on the effect of MK and FA on the durability of concrete. This study replaced OPC partially with a blend of MK and FA up to 20% in increments of 5% at 0%, 5%, 15% and 20%. Sujjavanich [31] measured the resistance to chloride-ion penetration at 28 days and 56 days of concrete age. The result of this study is shown in Figure 7. The study demonstrated that MK is more resistant to chloride attack.

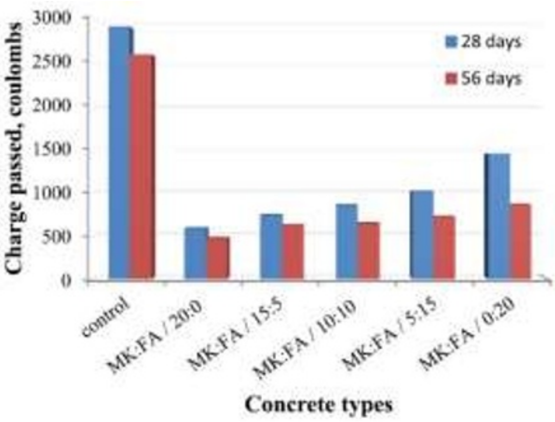

Fig. 7. Resistance to chloride penetration of concrete after 28 days and 56 days [31].

6.3 Improving South African concrete durability with Metakaolin

With concrete structures in South Africa subjected to various types of exposures due to climatic and industrial diversity, there is a need to ensure more durable concrete to ensure the sustainability of South African infrastructure. Previous studies by Bakera [10], Mackechnie [32] and Pillay [33] have outlined the advantages of incorporating MK into concrete, as well as the durability of hardened concrete containing MK.

These studies show an overall improvement in the OPI, WPI and CCI for samples with MK. This improvement in durability can be beneficial to the improvement and development of South African infrastructure, where the longevity and sustainability of future projects can be assured.

7 Influence of metakaolin in the mitigation of the alkali-silica reaction in concrete structures

ASR-exposed concrete structures pose a problem for the concrete's durability, compromising its suitability for its intended purpose [34]. This can also result in unforeseen maintenance and capital costs on concrete structures. ASR is a reaction in concrete where alkalis found in cement paste reacts with siliceous phases as present in natural aggregates forming a gel layer on reactive aggregate. The potassium and sodium ions in cement paste then react with the gel to form an alkali-silica gel filling up the microstructural pores. This causes the concrete to expand and crack over time with sufficient exposure to alkalis and moisture [35]. The mitigation of ASR is important in concrete to ensure the enhancement of durability of concrete structures.

The mechanism of ASR can be attributed to the chemical composition of the constituents of the concrete material, where concrete with lower alkalinity will not be able to dissolve silicas in the aggregates [36]. Alkali-silicate gel formed in the pore solution by the hydration of cement with alkalis and hydroxide ions. This may lead to swelling as the gel is hydrated by sustained exposure to moisture, causing the aggregate to crack. The failure in the concrete's matrix ultimately causes a structure to lose its integrity due to ASR [37].

A study conducted by Hong & Glasser [38] shows that decreasing the Ca/Si ratio increases the amount of free sodium (Na) and potassium (K) in the Calcium-Silicate-Hydrate (C-S-H) gel. This reduces the pore solution's alkalinity and silica's dissolution in the aggregates. A further study by Hong & Glasser [39] suggests that silica-rich cementitious material or pozzolana will alter the Ca/Si ratio within the cement paste.

By introducing MK, a pozzolan with a higher silica content and lower calcium content, the Ca/Si ratio was adjusted. As suggested in the studies conducted by Hong & Glasser [38] and Hong & Glasser [39], reducing the Ca/Si ratio will reduce the amount of alkalis in the C-S-H gel. This reduces the amount of siliceous material that the alkalis can absorb.

Wei et al. [40] investigated the combined effect of alkalis and aluminium in the pour solution on the alkali-silica reaction using Portland cement (PC) and MK as cementitious materials. The study investigated the effects of alkali ions and aluminium in the pour solution of ASR through an accelerated mortar bar test (AMBT), partially replacing 100% PC with 5% MK with various amounts of NaOH to increase the Na_2O_{eq} from 0.65%, 1.25%, 2.25% and 2.75%.

The AMBT test was conducted and carried out for 200 days, as seen in Figure 8. This figure shows that with the introduction of MK, a reduction in expansion induced by ASR can be observed where results are evident at 14 days, 28 days and 40 days of age, respectively.

With previous studies showing that the introduction of MK can lead to a reduction in ASR activity, the need to understand the effects of MK is of great importance to improve the functionality of concrete structures and components that form part of South African infrastructure.

8 Conclusion

This paper on the role of SCMs in mitigating the ASR outlines the importance of the sustainable development of SCMs for concrete and the use of concrete in civil engineering infrastructure. As South Africa can see a decline in the production of conventional SCMs such as FA, GGBS and SF, seeking new sustainable sources of SCMs becomes inevitable.

Introducing MK as a sustainable SCM will help produce better-performing concrete and reduce the environmental impact by curbing the cement and concrete industry's carbon footprint.

The characteristics of MK satisfies the pozzolanic requirements for the natural SCMs. These requirements are investigated using a number of international standards and petrographic analysis such as XRF, XRD and SEM.

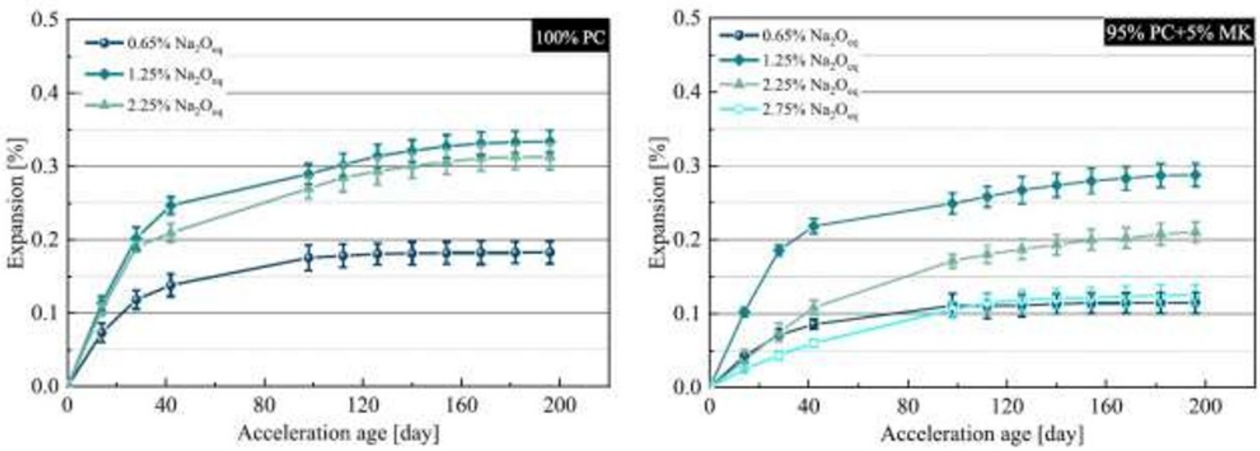

Fig. 8. Expansion of mortar bars accelerated at 38 °C [40].

It is reported that the addition of MK into concrete samples, will generally lead to a decrease in workability. This can be enhanced using water reducing admixtures.

The addition of MK to the concrete typically enhances the hardened properties such as compressive and tensile strength and modulus of elasticity of concrete up to optimal content of 20 %.

By reducing the permeability of the concrete, it is observed that the amount of water, oxygen, chloride and sulphate ingress is decreased. With the introduction of MK into the concrete an overall improvement of the durability of concrete by controlling the underlined transport mechanisms can be achieved. MK has a low calcium content, thereby lowering the Ca/Si ratio and mitigating of occurrence of the ASR in concrete structures.

This research highlighted the importance of using MK in reduction of ASR in concrete material. In order to understand the role of concrete samples with MK in the physical and mechanical performance of concrete material in South African context, a set of experimental studies have been planned and implemented at the Cape Peninsula University of Technology (CPUT) in collaboration with Stellenbosch University (SU). It is foreseen that the results of these studies would increase the knowledge in using MK in future civil engineering application both locally and internationally.

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