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Use of metakaolin as a supplementary cementitious material in concrete, with a focus on durability properties

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Abstract

Numerous research efforts on metakaolin as a supplementary cementitious material (SCM) have been undertaken in the past 20 years. This material, while relatively expensive mainly due to low production volumes worldwide, nevertheless has a significantly lower production cost than Portland cement. However, the industry remains tentative in considering metakaolin in concrete. This paper takes the view that industry should consider investing in the production and application of metakaolin in appropriate concrete projects, particularly in aggressive environments where plain Portland cement may be inadequate, and where other SCMs may not be readily available. A major contribution of the paper is a global review of recent studies on the use of metakaolin in different types of concrete. This international experience is then compared with results from a study on the durability performance of metakaolin concrete using local materials in the Western Cape province of South Africa, as a means of concrete performance improvement. The study investigated concrete durability properties: penetrability (sorptivity, permeability, conductivity and diffusion), mitigation of Alkali-Silica Reaction (ASR), and carbonation resistance. The concretes were prepared with three water-binder ratios (0.4, 0.5 and 0.6), and with metakaolin replacement levels of 0% (control), 10%, 15% and 20%. Performance results show that, with increasing metakaolin content, the transport properties of concrete are considerably improved, ASR expansion due to a highly reactive local aggregate decreases to non-deleterious levels, while no detrimental effect on carbonation is observed. Thus, metakaolin could serve as a valuable SCM to enhance the durability performance of concrete in local aggressive environments.

Keywords: Metakaolin; Concrete penetrability; Alkali-Silica Reaction; Carbonation

1 Introduction

Metakaolin, also referred to as highly reactive calcined clay, is manufactured by calcining high-grade kaolinite clay at temperatures between 600 °C and 900 °C [1,2]. The kaolinite structure consists of a 1:1 layer of combined tetrahedral silicate sheets bonded to octahedral aluminium oxide sheets continuously and alternatively by an interstitial layer of bound water molecules [3]. During calcination, the bound water is expelled, and the material structure collapses, followed by the formation of an amorphous phase (metakaolin). Metakaolin being neither a by-product nor a naturally occurring material is used as a Supplementary Cementitious Material (SCM) conforming to natural pozzolan in ASTM C 618 and natural calcined pozzolana (Q) in EN 197-1.

Kaolinite clay is abundant in various locations worldwide, as depicted by Ito and Wagai [4] in their global soil distribution map. This clay is used in various industrial applications such as manufacturing of paper, plastics, adhesives, rubber, paint, refractories, cement, bricks and ceramics. However, all these applications, except those related to construction purposes, require high-grade kaolinite clay. Therefore, considering its relative abundance, particularly in those areas of the world that are rapidly developing, and in terms of mitigating the effect of global warming attributed to Portland cement production, the construction industry is urged to focus on the benefits of using this clay.

Metakaolin is applied in the construction industry as either a clinker substitute in cement production [5] or as an SCM in concrete. However, it is more commonly used at concrete level in binary or ternary blends with plain Portland cement. Its application as an SCM has captured the attention of researchers due to its high effectiveness in enhancing concrete properties. Likewise, its potential in producing more cohesive and dense concrete, provided that a proper dosage of superplasticiser is used, has generally contributed to its popularity in innovative concretes (lightweight concrete,

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high-strength concrete, Ultra-High Performance Concrete (UHPC), and Self-Compacting Concrete (SCC)) [6–10].

Metakaolin is also considered as a sustainable and environmentally-friendly material due to its limited CO_2 emissions during production [11]. The calcination process emits no aggressive gases that lead to environmental pollution. However, it requires energy that involves burning fossil fuels such as oil or coal, which in turn emits CO_2 gas. Thus, as shown in Figure 1, to reduce emissions, alternative sources such as natural gas should be emphasised since they emit lower CO_2 compared to other fossil fuels, while wood is not advisable due to the massive amount of waste ash. Wang et al [12] stated that the Global Warming Potential (GWP) for metakaolin ranges between 0.09 and 0.7 kg CO_2 eq./kg, which seems to be a conventional basis for comparison with CEM I with 0.8 to 1.0 kg CO_2 eq./kg. Nevertheless, the exploitation and processing of the raw material for metakaolin, if sustainable development practices are not implemented, may also lead to the environmental destruction such as soil erosion, water pollution, and destruction of natural reserves [13].

Even though research has revealed the high potential of metakaolin in concrete, there has been limited response in the cement and concrete industry to incorporate it in construction. This paper aims to provide knowledge about metakaolin to increase awareness and interest in its production and application in concrete construction, specifically in aggressive environments where plain Portland cement may be inadequate.

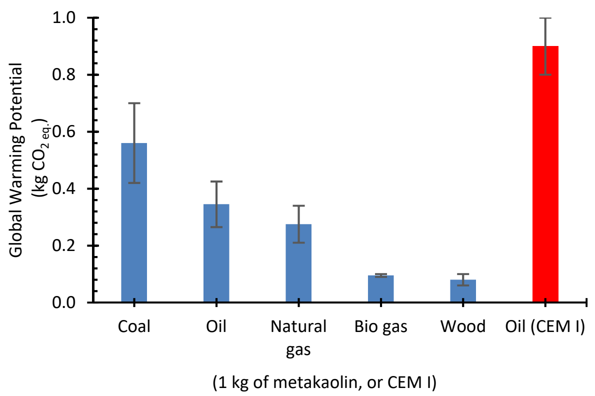

Figure 1. Global Warming Potential in kg CO_2eq to produce 1 kg of metakaolin depending on the type of fuel used for calcination [14] in comparison to CEM I production.

2 Economic comparison of metakaolin and Portland cement

Production of metakaolin requires lower calcining temperatures (600 °C-900 °C), compared to Portland cement (1450 °C) [5]. This lower calcination temperature leads to lower energy consumption, and consequently, lower production cost. It is estimated that to manufacture one tonne of metakaolin requires about 2950-3300 MJ [15, 16], while cement needs about 3000-6500 MJ/tonne of clinker, depending on the manufacturing process [17]. Surprisingly, the commercial cost of metakaolin is still higher than that of cement. The current cost of metakaolin ranges between $600-$700/tonne [18], while that of cement is about $130/tonne [16]. This high cost is attributed to various reasons including; i) a limited number of production plants; thus low production rate, ii) poor response from the construction industry, iii) environmental restrictions related to exploring kaolinite clay deposits, and iv) competition from other high-value industrial applications of kaolinite clay. The likelihood is that, with increased number of production plants and sufficient uptake of this material as an SCM in concrete, the production costs would reduce substantially.

Globally, kaolinite clay exploitation and metakaolin production plants exist in the US, China, and India, while limited in Africa [19], despite the continent's abundant availability of kaolinite clay deposits [4]. This limitation is associated with the lack of production skills and capital, as well as confidence in marketing and advertising the product.

Lack of response from industry on using metakaolin is also observed in regard to other SCMs such as fly ash and slag, in certain regions. This is associated with a low emphasis on the importance of sustainable practices, and political barriers that lead to lack of government-level regulation. For instance, the United Arab Emirates (UAE) implemented new regulations in May 2015, that all major infrastructure projects and sub-structures must use at least 60% slag or ash-containing cement. Such regulation, if introduced in many countries, especially in Africa, will assist the response of industry in adopting metakaolin.

Environmental consequences related to kaolinite clay mining also impact the metakaolin market. For example, surface mining, the most desirable mining method for kaolinite clay, if poorly implemented, carries a risk of technogenic mineral wastes which may cause environmental pollution, biodiversity loss, as well as encroachment on areas of human habitation. These consequences may lead to environmental restrictions, which subsequently affect the metakaolin economy.

There is also a growing demand for kaolinite clay by other industrial applications such as paper, plastics, adhesives, rubber, paint, refractories, and ceramics, which might affect its availability for construction. According to a Market Research Future report, the global kaolinite clay market is projected to reach $9.83 billion by 2025, expanding at a Compound Annual Growth Rate of 8.8%. This market growth is primarily influenced by the growing demand for use in ceramics and paper, followed by penetration into the paints and coatings industry. This may indicate possible metakaolin scarcity for the construction industry, especially where there is rapid infrastructure development [20], but considering the global resources of kaolinite clay [4], this may not necessarily always be the case.

To summarise, with increased metakaolin production and application in the construction industry, exploiting its technological and environmental merits could potentially decrease its production costs. In general for metakaolin to be widely used, its cost must approach that of Portland cement [16].

3 Influence of metakaolin on concrete durability properties – a review

The development of concrete microstructure and resulting properties is critical in determining the durability performance of concrete. The hydration of Portland cement results in large quantities of portlandite (calcium hydroxide (CH)), which is susceptible to various types of chemical and physical attack. In this regard, the incorporation of metakaolin in concrete is very beneficial, since it reacts readily with CH, improving the concrete microstructure, thereby reducing concrete vulnerability to various aggressive attacks. Use of metakaolin in concrete positively influences durability properties such as penetrability (water absorption, gas permeability and chloride ingress), and helps mitigate ASR. The consumption of CH by SCM may render the concrete more susceptible to carbonation; however, in some cases, metakaolin has been noted to improve carbonation resistance. These aspects are discussed below, from the current literature. Table 1 provides a convenient overview of the different research findings discussed below.

3.1 Water absorption and sorptivity

The water absorption of concrete can be expressed in terms of two parameters: bulk absorption, which is the total uptake of water into an unsaturated sample, and sorptivity, which is the rate of water uptake by capillary suction and can be regarded as an index of moisture transport into unsaturated concrete. Both water absorption and sorptivity are influenced by the concrete pore size distribution and capillary pore interconnectivity [21]. Various studies [22]–[24] show that incorporating metakaolin in concrete tends to refine concrete pore size, reduce the interconnectivity, but may increase the total porosity.

Khatib and Clay [25] reported a consistent and significant reduction of water absorption by capillary suction and a slight increase of absorption by total immersion, with increasing metakaolin content in concrete up to 20%. Razak et al [21] showed that the inclusion of 10% metakaolin in concrete significantly decreased the sorptivity value compared to the control, measured in terms of initial water absorption, and also reduced the water absorption of concrete (i.e. the accessible pore volume in concrete) under different curing regimes, contrary to [22].

Badogiannis and Tsivilis [26] made similar observations, where metakaolin contents of 10% and 20% decreased the sorptivity by an average of 30%, in comparison with control concrete at a 0.5 w/b ratio. Güneyisi et al [27] reported a maximum reduction in sorptivity of about 29% for concrete with 15% metakaolin at both 0.25 and 0.35 w/b ratios.

Ramezanianpour and Bahrami Jovein [28] studied the influence of metakaolin at contents of 10%, 12.5% and 15%, and w/b ratios of 0.50, 0.40, and 0.35, on the water sorptivity of concrete. They concluded that, for their materials, the optimum metakaolin replacement rate for sorptivity was 10%, irrespective of w/b ratio and curing age. This observation was supported by the findings of Siddique and Kaur [29], who proposed that increasing metakaolin content beyond 10% may adversely affect the durability of the interior mass of concrete.

Thus, the optimum metakaolin replacement rate, in respect of water absorption and water sorptivity, depends on concrete mix parameters such as w/b, curing and age, as well as the nature of the cement and metakaolin; a universal optimum replacement rate cannot be defined.

3.2 Gas permeability

Gas permeability of concrete indicates the potential for resisting the permeation of harmful gases such as CO_2 and H_2S. While the literature on the influence of metakaolin on gas permeability of concrete is limited, available evidence indicates the important influence of metakaolin on this performance aspect.

Badogiannis and Tsivilis [26] used a modified triaxial cell to determine nitrogen (N_2) permeability in 100 mm diameter x 50 mm thick concrete specimens. They reported gas permeability reductions of 54% and 50% for concrete with 10% and 20% metakaolin respectively. Güneyisi et al [27] observed maximum permeability reductions of 52% and 58% for concrete with 15% metakaolin replacement at 0.25 and 0.35 w/b ratio, respectively. Shekarchi et al [30] reported a decrease in gas permeability with the use of metakaolin, the maximum reduction being 37% for 15% metakaolin replacement and 0.38 w/b ratio.

Nicolas et al [31] studied the performance of a wide range of concretes (from very stiff to self-compacting concretes, and from low to high-performance concretes) with 25% metakaolin replacement, in relation to a control mix. They observed that metakaolin concrete had lower oxygen permeability, despite the high metakaolin content used, over the wide range of concretes studied.

Therefore, the inclusion of metakaolin shows a positive influence in reducing the gas permeability of concrete. As expected, concrete permeability also depends on w/b ratio and curing age (refer to Table 1).

3.3 Chloride ingress

The influence of metakaolin in resisting chloride ingress in concrete, by diffusion or electro-migration, is important in view of chlorides being a major cause of lack of durability in reinforced concrete structures by causing rebar corrosion. Boddy et al [32] studied the influence of metakaolin (0%, 8% and 12% replacements) in concrete with 0.3 and 0.4 w/b, in resisting chloride penetration, using bulk diffusion, rapid chloride permeability (RCPT), resistivity, and chloride migration tests. Their results indicated that with increasing metakaolin content and reducing w/b ratio, chloride diffusion, permeability, and conductivity decreased, while resistivity increased, as might be expected.

Table 1. Durability properties of concrete with metakaolin from the literature

Durability properties	Metakaolin replacement rate	References cited (in square brackets), and their salient results			
Water sorptivity in $mm^3/mm^2/min^{0.5}$ ##	Description	[21] w/b = 0.3; water cured for 7 to 90 days	[26] w/b = 0.5, cured in lime-saturated water for 90 days; commercial and locally made metakaolin, respectively	[27] w/b = 0.25 and 0.35, water cured for 28 days; respectively	[28] w/b = 0.5, 0.4 and 0.35; water cured for 28 days, respectively
	0%	0.060 to 0.040	0.114	0.064 and 0.081	0.091, 0.033 and 0.030
	10%	0.040 to 0.020	0.097 and 0.080	-	0.070, 0.023, and 0.027
	15%	-	-	0.046 and 0.058	0.091, 0.036, and 0.030
	20%	-	0.089 and 0.067	-	-
Gas permeability in 10^{-16} m^2	Description	[30] w/b = 0.38; nitrogen gas as per RILEM-TC 116	[26] w/b = 0.5; nitrogen gas; commercial and locally made metakaolin, respectively	[27] w/b = 0.25 and 0.35, respectively; Oxygen gas as per RILEM TC 116	[55] w/b = 0.4; oxygen gas as per RILEM TC 116 at 28- and 90-days, respectively;
	0%	1.20	2.94	2.00 and 3.45	2.78 and 2.50
	10%	0.94	1.68 and 1.35	-	1.89 and 1.76
	15%	0.75	-	0.95 and 1.45	1.72 and 1.40
	20%	-	1.45 and 1.60	-	1.67 and 1.28
Chloride ingress, using RCPT, in Coulombs	Description	[55] w/b = 0.4; ASTM C1202; 28- and 90-days concrete specimens, respectively	[26] w/b = 0.5; AASHTO T277 (ASTM C1202); 90-days concrete specimen of 200 mm diam. x 50 mm thick; using commercial and locally made metakaolin, respectively	[28] w/b = 0.5, 0.4 and 0.35 respectively; ASTM C1202; 90-days concrete specimens	[41] w/b = 0.4; ASTM C1202; 90 days concrete specimens
	0%	2778 and 1986	2460	3956, 2196, and 2075	≈1100
	10%	1250 and 914	730 and 690	2953, 1212, and 1045	≈850
	15%	1056 and 755	-	1524, 998, and 924	≈700
	20%	1000 and 636	240 and 760		≈600
Alkali-silica reaction	Description	[56] as per CSA* A23 5-98 and ASTM C1260#; Aggregates: siliceous limestone and greywacke aggregate, respectively	[38]as per ASTM C1260# and C1567; three metakaolin (M1, M2, and M3), respectively; Aggregate used: highly reactive	[57] ASTM C1260#; Aggregate: reactive opal	[58] ASTM C1260#; Aggregate: reactive volcanic basalt
Accelerated mortar bar test	0%	>0.30% and ≈ 0.30%	0.36% very reactive	0.73%	0.45%
	10%**	≈0.13% and ≈0.12%	0.23 %, 0.09% and 0.03%	0.18%	0.20%
	15%***	≈0.05% and ≈0.03%	0.06%, 0.05%, and 0.01%	0.06%	0.07%
	20%***	≈0.03%[2] and N/A	0.03%, 0.00%, and 0.01%	0.01%	0.06%
Carbonation using Accelerated carbonation test	Description	[41] w/b = 0.25; No pre-conditioning; carbonation chamber at 5% CO_2, 60% RH, and 20°C; carbonation depth measured at 28- and 56-days exposure, respectively	[59] w/b = 0.5 and 0.6 respectively; wet cured for 3 days, pre-conditioned by oven drying for 2 weeks at 40°C and 20% RH; carbonation chamber at 5% CO_2, 60% RH, and 20°C; carbonation depth measured at 28 days exposure	[46] w/b = 0.6; wet cured for 28 days and 365 days, respectively; pre-conditioned at 50% RH and 20°C for 14 days; carbonation chamber at 5% CO_2, 60% RH, and 20°C; carbonation depth measured at 70 days exposure	
	0%	3.9 mm and 4.2 mm	≈4.5 mm and ≈11.0 mm	9.5 ± 2.3 mm and 8.9 ± 1.5 mm	
	10%	4.3 mm and 7.5 mm	≈5.5 mm and ≈10.0 mm	-	
	15%	9.0 mm and 10.0 mm	≈8.0 mm and ≈13.0 mm	16.5 ± 2.1 mm and 14.8 ± 2.1 mm	
	20%	11.5 mm and 14.0 mm	-	17.6 ± 1.4 mm and 11.8 ± 2.2 mm	

Unit converted from $m/s^{0.5}$ to $mm^3/mm^2/min^{0.5}$

*CSA: Canadian Standard Association **use with precaution such as limiting alkalis in concrete or protecting against external moisture [60];

***use without precaution mentioned at **

#expansive aggregate ≥0.30%, safe level ≤ 0.10% at 14 days of testing

Badogiannis and Tsivilis [26], using the RCPT, found that replacement of 10% to 20% metakaolin reduced the RCPT value of the 90-day control concrete by between 60% and 90%. Using the same mix design, but concrete immersed in chloride solution for the bulk diffusion test (ASTM C1218), they observed significantly lower chloride profiles of concrete with metakaolin compared to the control. After 3 months of immersion, the chloride content at 15 mm depth for 10% to 20% metakaolin varied from 0.01% to 0.07%, while the control had 0,24% [33].

Al-Alaily and Hassan [34] studied long-term chloride diffusion of concrete with 0 to 25% metakaolin and 0.3 to 0.5 w/b, over an extended period. After two years of immersion, concrete with metakaolin was found to have significantly reduced chloride ingress, indicating a lower chloride diffusion coefficient. This was attributed to the high chloride binding capacity of metakaolin, which increased with its content, as also noted by Thomas et al [35].

Metakaolin is, therefore, an excellent SCM in resisting chloride ingress into concrete, and offers possibilities for use in marine concretes and concretes used in de-icing salt conditions.

3.4 Alkali-silica reaction (ASR)

The potential for metakaolin to suppress ASR was studied by Ramlochan et al [36] and Gruber et al. [37], on concretes incorporating two types of Canadian aggregates: a highly reactive siliceous limestone from Spratt Quarry in Ottawa, and a lesser reactive greywacke-argillite gravel from Sudbury, Ontario. Their results showed that with increasing metakaolin content, the ASR expansion of concretes with both aggregates decreased, with the highest reduction at 20% and 15% metakaolin content, respectively. With these contents, both aggregates could be used in concrete without other precautions (refer to Table 1).

Ballard et al [38] evaluated the potential of metakaolin from different manufacturers for suppressing ASR. They concluded that, despite the different sources, metakaolin contents of 10% to 20% were able to substantially suppress ASR expansion to below the safe level of 0.01%. Shekarchi et al [30] measured reductions of ASR expansion of 70% and 80% for 10% and 15% metakaolin replacement in mortars, respectively, while metakaolin below 5% had an insignificant influence on mitigating ASR in mortar.

Sarfo-Ansah et al [39] recorded average reductions in expansion of 45% for mortar bars (modified ASTM C1260) with 10% to 15% metakaolin, and 70% for mortar bars with 20% to 30% metakaolin. They indicated that the higher reduction was associated with the formation of secondary calcium silicate hydrates due to pozzolanic reaction of metakaolin. Sabir et al [40] explained further that the role of metakaolin in suppressing ASR was in reducing the freely available CH and the CH/silica ratio, consequently depleting the formation of swelling gel.

Generally, the mechanisms by which metakaolin suppresses ASR in concrete was ascribed to its properties of pore structure refinement, consumption of CH, and entrapment of alkalis in silica-rich hydration products [39].

3.5 Carbonation

Considering that, in general, metakaolin significantly reduces permeability to gases in concrete, its potential to reduce carbonation also needs to be reviewed, in light of the fact that carbonation influences rebar corrosion in reinforced concrete structures.

Kim et al [41], using the phenolphthalein indicator method on concrete with metakaolin contents up to 20% (without pre-conditioning, concrete subjected to accelerated carbonation of 5% CO_2, 60% RH, and 30°C temperature for 7 to 90 days), found that carbonation depth increased with increasing metakaolin content and exposure time. The largest increase of 70% was observed at 56 days of exposure for concrete with 20% metakaolin.

McPolin et al [42] performed a similar test on concrete with 10% metakaolin content, but initially pre-conditioned for 2 weeks in an oven at 40°C, followed by polythene sheet-wrapping for 6 weeks, then exposed in the carbonation chamber at 5% CO_2, 60% RH, and 20°C temperature for 6 weeks. Their results showed that metakaolin concrete had a carbonation depth of 50% higher than the control.

Nicolas et al [31] used the French recommended procedure (AFPC-AFREM) [43] in a carbonation chamber at 20°C and 65% RH with 50% CO_2 to assess the potential of 28-day old concrete with 25% metakaolin content in resisting carbonation. After 28 days of exposure, they found a higher carbonation depth for metakaolin concrete, ascribed to decreasing CH content in the pore solution due to the pozzolanic reaction. Shi et a. [44] also associated the phenomenon with the metakaolin pozzolanic reaction, which consumed CH responsible for slowing the carbonation rate. A similar argument was provided by Saillio et al [45], who showed a trend of CH decrease and carbonation depth increase with increasing metakaolin content and exposure time.

Bucher et al [46] showed that 10% to 25% metakaolin replacement of CEM I led to increasing carbonation depth, while 15% metakaolin replacement of CEM II/A-LL (16% limestone filler) reduced carbonation with respect to concrete with only CEM II/A-LL. They inferred this synergy between metakaolin and limestone filler to the formation of hemicarboaluminates which limit CO_2 ingress.

The general conclusion is that metakaolin tends to increase the carbonation depth of concrete, despite reducing the gas permeability of concrete. The carbonation is also influenced by the w/b ratio and the curing duration (refer to Table 1). On occasion, however, metakaolin concretes did not suffer an increase in carbonation.

3.6 Synergistic behaviour of metakaolin and its wider range of usage

Research shows that metakaolin appears to work synergistically with other SCMs. Sujjavanich et al [47] observed that a ternary blend of cement, metakaolin and fly ash at a ratio of 80:10:10 yielded a more uniform fresh mix with good workability and a denser microstructure, with better performance in the hardened state in terms of durability, abrasion resistance, chloride permeability and steel corrosion risk. Vance et al [48] observed the synergistic effect of a blend of 10% limestone and 10% metakaolin, resulting in improved concrete compressive strength and significantly reduced CH content.

Modern concrete types with metakaolin also perform well. Hassan et al [9] compared the durability performance of SCC with metakaolin and silica fume in terms of drying shrinkage, freeze-thaw, salt scaling, and rapid chloride permeability. They found that SCC mixtures with 20% metakaolin outperformed those of silica fume up to 11%. A similar observation was reported by Vejmelková et al. [6], studying the rheological, mechanical and durability properties of SCC with a ternary blend of metakaolin and blast furnace slag. Perlot, Rougeau, and Dehaudt [49] found that a mixture of metakaolin blended with limestone filler is suitable for SCC and precast concrete manufacturing.

Tafraoui, Escadeillas, and Vidal [10] confirmed that UHPCs containing 25% metakaolin have good durability performance in terms of oxygen permeability, diffusion and chloride ion migration, and carbonation. Muhd Norhasri et al [7] found that the inclusion of up to 10% nano-metakaolin in UHPC exhibited low workability in the fresh-state while having early compressive strength similar to plain UHPC, but which increased gradually with time.

In shotcrete operations, Bindiganavile and Banthia [50] found that a ternary blend of silica fume and metakaolin positively impacted the rheology and mechanical properties of fibre reinforced dry-mix shotcrete. Yun, Choi, and Yeon [51] reported that metakaolin outperformed fly ash and slag, leading to a satisfactory pumpability and substantial increase in the build-up thickness of the wet-mix shotcrete with crushed aggregates.

In addition, metakaolin is used in modern binders as a means of reducing environmental impact related to Portland cement, and to produce alternative binders [52]. When metakaolin is blended with limestone, it can be used as a clinker substitute in the production of Limestone Calcined Clay Cement (LC^3) [53], albeit in this case, as a high grade calcined clay. Metakaolin is also used in the production of alkali-activated binders [54]. Both binders illustrate good performance, especially under acid, seawater, and sulphate attack, and in suppressing ASR.

3.7 Summary

This brief review of the use of metakaolin in concrete has shown that metakaolin has a high potential for enhancing the durability properties of concrete, inter alia, as summarised in Table 1 and schematically in Figure 2. Metakaolin pozzolanic reaction and filler effect lead to a reduction in pore connectivity and pore sizes, while increasing total porosities. These characteristics lead to concrete matrix densification, which in turn, alter durability parameters such as ASR mitigation, gas permeability, water sorptivity and water absorption. However, other durability properties such as carbonation resistance and chloride ingress are attributed to w/b ratio and the pozzolanic reaction. The reduction of w/b impacts the permeability of concrete and incorporating metakaolin influences both the permeability and the depletion of concrete alkalis, which proportionally have competing influences on the carbonation rate. With reducing w/b ratio, chloride ingress also reduces, while metakaolin, with its high alumina content, is able effectively to bind chloride ions and hinder their penetrability.

The following section describes an experimental study on the influence of metakaolin in comparison to Ground Granulated Corex Slag (GGCS), which was conducted to stress that metakaolin can be a reliable and alternative SCM to incorporate in concrete subjected to aggressive environments.

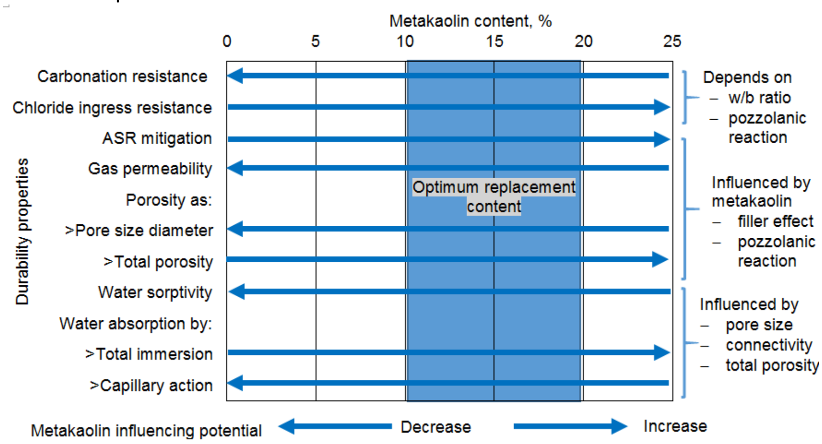

Figure 2. Schematic diagram showing the influence of metakaolin on concrete durability properties.

4 Experimental study on the durability potential of metakaolin concrete

A local metakaolin in the Western Cape province of South Africa was studied in regard to its potential to enhance the durability of concrete, in comparison with another locally available additive, Ground Granulated Corex Slag (GGCS) [61]. Local greywacke aggregate (potentially alkali-silica reactive) and a Portland cement were used. The study evaluated the durability of concrete in respect of penetrability (sorptivity, permeability, conductivity and diffusion), mitigation of ASR, and carbonation resistance. (The corresponding mechanical properties of metakaolin concrete in comparison with GGCS concrete are presented in [62])

GGCS differs from Ground Granulated Blast-furnace slag (GGBS) in the process to produce iron; the Corex process with two reactors (reduction shaft and melting gasifier reactor) is employed for iron production, with GGCS as a by-product. GGBS emanates from the traditional blast furnace process for iron production.

4.1 Materials and methodology

CEM II/A-L 52.5 N and GGCS from PPC Cement, and metakaolin (mk) from the Kaolin Group were used for concrete preparation. The chemical composition of the cement, metakaolin and GGCS, and the concrete mix designs and compressive strength at 28 days, are shown in Table 2 and Table 3, respectively. The proportions of metakaolin replacement were 0% (control), 10%, 15% and 20%, while the replacement for GGCS was 50%. Greywacke coarse aggregates with a maximum size of 19 mm, and a blend of dune sand and greywacke crusher sand at a ratio of 3:2 were used. Concrete mixes of w/b ratio 0.4, 0.5 and 0.6 were cast, and the target slump of 100 mm was regulated using a superplasticiser (CHRYSO® Plast Omega 103).

Durability Index (DI) tests were used to assess concrete penetrability. The DI tests include Oxygen Permeability Index (OPI), Water Sorptivity Index (WSI), and Chloride Conductivity Index (CCI), which were conducted as per SANS 3001-CO3-1 and 2 and the UCT DI Manual [63–65]. As part of the WSI test, the water penetrable porosity of the concrete is obtained, and this is also reported. The ASR accelerated mortar bar test (ASTM C1567-13 [66]) was used to determine the potential for metakaolin to suppress ASR expansion of greywacke aggregates.

Carbonation potential was assessed using an accelerated carbonation testing protocol according to Salvoldi [67], on 28-day wet cured concrete cubes (100 mm). The cubes were preconditioned at 65% RH and 20 ± 3°C for 60 days, sealed with epoxy on four sides, followed by placing in the carbonation chamber at 20 ± 3°C, 65 ± 5% relative humidity, and 2 ± 0.1% CO_2 concentration. Carbonation depth was determined at 28, 56, and 90 days as per RILEM CPC-18 [68].

Table 2. Chemical composition of cement, metakaolin and GGCS

Chemical formula	Chemical composition, %		
	CEM II A-L 52.5N	**Metakaolin (mk)**	**GGCS**
SiO_2	19.77	52.81	31.32
Al_2O_3	3.24	42.02	17.04
Fe_2O_3	3.11	0.32	1.00
Mn_2O_3	0.06	0.03	0.05
TiO_2	0.19	1.30	0.58
CaO	63.84	0.02	35.15
MgO	1.28	0.07	11.76
P_2O_5	0.14	0.09	0.03
SO_3	2.55	0.00	3.04
K_2O	0.61	0.06	0.63
Na_2O	0.22	0.00	0.00
LOI	4.63	1.16	-

Table 3. Concrete mix proportions – kg/m^3

w/b	Mixes	Cement	Metakaolin or Corex slag		Water	Coarse Aggregate	Fine Aggregate		Total	Compr str. at 28 days	SP dosage, % by mass binder
		CEM II/A-L	mk	GGCS	Potable	Greywacke	Dune Sand	Crusher sand			
		kg/m^3								MPa	
0.4	0% mk	463	-	-	185	1000	544	305	2497	63.7	0.56
	10% mk	416	46	-	185	1000	534	300	2481	77.0	0.67
	15% mk	393	69	-	185	1000	529	297	2474	81.2	1.12
	20% mk	370	93	-	185	1000	524	294	2466	86.7	1.34
	50% GGCS	231	-	231	185	1000	533	299	2479	61.0	0.50
0.5	0% mk	370	-	-	185	1000	597	335	2487	52.7	0.42
	10% mk	333	37	-	185	1000	590	331	2475	63.3	0.57
	15% mk	315	56	-	185	1000	586	328	2469	66.7	0.85
	20% mk	296	74	-	185	1000	582	326	2463	74.8	0.94
	50% GGCS	185	-	185	185	1000	589	330	2474	48.7	0.42
0.6	0% mk	308	-	-	185	1000	633	355	2481	42.2	0.04
	10% mk	278	31	-	185	1000	626	351	2471	51.3	0.13
	15% mk	262	46	-	185	1000	623	350	2466	55.0	0.26
	20% mk	247	62	-	185	1000	620	348	2461	57.0	0.34
	50% GGCS	154	-	154	185	1000	626	351	2470	43.2	0.08

Concrete penetrability in terms of chloride diffusion was determined using the chloride bulk diffusion test, ASTM C1556 (derived from Nordtest Build 443) [69], using two 100 mm diam. x 300 mm concrete cylinders per mix, wet cured for 56 days. Two test specimens of 75 mm height, together with a 25 mm disc for initial chloride content, were cut from each cylinder, while discarding the part near the finished surface. The specimens were then epoxy-coated on their cylindrical surfaces, preconditioned in saturated calcium hydroxide solution (3 g/L) for 48 h, and then immersed in sodium chloride solution (165 g/L) for 90 days prior to determining the chloride-ion (Cl^-) profile. The Cl^- content by mass of binder at different depths was measured using auto-titration. The surface concentration and apparent chloride diffusion coefficient were determined by fitting equation (1) to the measured Cl^- contents by means of non-linear regression analysis using the method of least squares.

$$C(x,t)=C_s-(C_s-C_i).\mathrm{erf}\left(\frac{x}{\sqrt{4.D_a.t}}\right) \quad (1)$$

Where:

C(x,t) Chloride concentration, measured at depth x and exposure time t, mass %,

C_s Projected chloride concentration at the interface between the exposure liquid and test specimen that is determined by the regression analysis, mass %,

C_i Initial chloride-ion concentration of the cementitious mixture prior to submersion in the exposure solution, mass %,

x Depth below the exposed surface (to the middle of a layer), m,

D_a Apparent chloride diffusion coefficient, m^2/s

t Exposure time, s, and

erf Error function described in ASTM C 1556

4.2 Results and discussion

4.2.1 Durability index (DI) test results

A summary of DI test results for oxygen permeability, water sorptivity and chloride conductivity of concrete with metakaolin and GGCS is presented here (with details given in [62]). Note that the DI results for concrete with 0.4 and 0.5 w/b were cast with material batches different from that for 0.6 w/b. This may have led to some inconsistency in the results. The error bars in the figures signify ± one standard deviation. The criteria in Table 4 were used for judging the quality of concrete.

Table 4. Criteria to judge the quality of concrete from the results of durability index (DI) tests [70]

Qualitative description	Oxygen permeability Index (OPI) log scale	Water sorptivity index (WSI) $mm/h^{0.5}$	Chloride conductivity index (CCI) mS/cm
Excellent	>10	< 6	< 0.75
Good	9.5 – 10	6 – 10	0.75 - 1.50
Poor	9.0 - 9.5	10 - 15	1.50 - 2.50
Very Poor	< 9	> 15	> 2.50

Despite having different amounts of SCMs and w/b ratios, the OPI results in Figure 3 show that all concretes had values above 10 (log scale) which signified "excellent" quality (Table 4). At all w/b, the OPI values increased with metakaolin content, with the highest values at 20% metakaolin, implying increasing impermeability of these mixes. Similar behaviour was observed by Güneyisi et al [27] and Shekarchi et al [30]. In comparing the influence of metakaolin with GGCS, concretes with metakaolin showed higher OPI values than GGCS, implying higher gas impermeability.

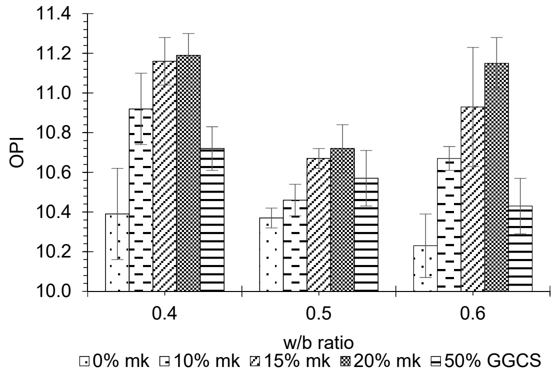

Figure 3. Oxygen Permeability Index (OPI) of concrete at different w/b ratios.

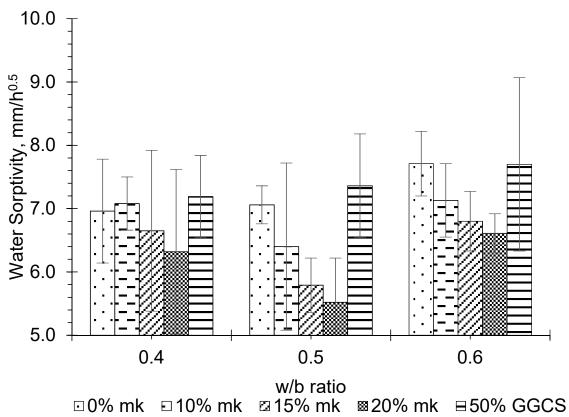

Figure 4. Water sorptivity index of concrete at different w/b ratios.

The WSI results in Figure 4 showed that all concretes had sorptivity values below 10 $mm/h^{0.5}$, which indicated 'good' to 'excellent' concrete quality (Table 4). At all w/b ratios, the sorptivity values decreased with increase in metakaolin content, with the lowest values at 20% metakaolin content. Metakaolin also had the potential to reduce water penetrable porosity across all the chosen w/b, as observed in Figure 5. At 0.5 and 0.6 w/b, GGCS reduction in water penetrable porosity was equivalent to roughly the 15% metakaolin concretes. This indicates that GGCS acts as a filler and reduces porosity without reducing its interconnectivity.

The CCI results in Figure 6 show that all concretes had CCI values less than 0.75 mS/cm, which implied 'excellent' quality concrete, except the control at 0.6 w/b (Table 4). The CCI values decreased with increasing metakaolin content and w/b ratio. The best performance in resisting chloride ion migration was observed at the highest metakaolin replacement rate of 20% at all w/b ratios, but was more significant at a low w/b.

This potential was attributed to the chloride binding capacity of metakaolin as indicated in [35]. In comparing metakaolin to GGCS, GGCS concrete generally was comparable to 10% metakaolin at 0.4 and 0.5 w/b ratios, and 15% metakaolin at 0.6 w/b. Generally, 20% metakaolin at all w/b outperformed 50% GGCS concrete. The relatively high CCI values of the plain control concretes are notable, indicating that such binders are not appropriate for chloride-laden environments.

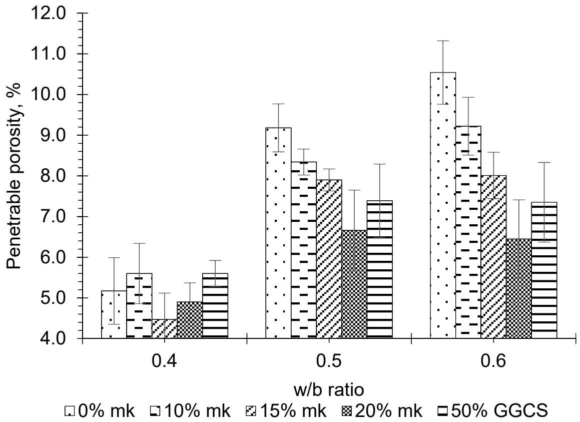

Figure 5. Water penetrable porosity of concrete at different w/b ratios.

Generally, the durability index test results indicated that all metakaolin-containing concrete had 'excellent' quality, with the best performance at 20% replacement, as also observed in [71]. Metakaolin had a substantial influence on reducing gas permeability, although its influence with w/b ratio was somewhat obscured due to the difference in material batches for concrete with 0.4 w/b and 0.5 w/b, and 0.6 w/b ratio. Its potential in simultaneously reducing water sorptivity and porosity was notable, while it showed a marked reduction in chloride conductivity even at low metakaolin contents. The improved performance of metakaolin concrete is ascribed to improvement in concrete microstructure, related to its chemical (pozzolanic) and physical (filler effect) actions. Comparing metakaolin and GGCS (at 50% replacement) for gas permeability and chloride conductivity, the potential for GGCS to improve these transport properties was equivalent to that of metakaolin at 10% replacement.

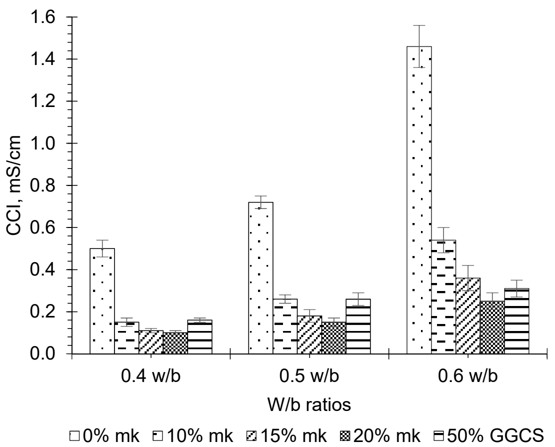

Figure 6. Chloride conductivity index (CCI) values of concrete at different w/b ratio.

4.2.2 Alkali-Silica Reaction (ASR)

The ASR test results in Figure 7 indicate that ASR expansion using greywacke aggregate decreased with increasing metakaolin content, with the lowest expansion at 20% metakaolin content. Approximately 61% of ASR expansion was suppressed with 10% metakaolin, while the maximum reduction of 89% was observed at 20% metakaolin. The results correlate well with the literature (Table 1 and Figure 2); this suggests that the suppression might be related to the effect of alkali dilution and of immobilisation of the alkalis in the pore solution, thus reducing the ASR.

It was concluded that metakaolin has excellent potential in mitigating ASR expansion, although the optimum replacement rate depends significantly on the nature of the reactive aggregate (as observed in Table 1). It is recommended that before using metakaolin to suppress ASR, an effective replacement level must be established in combination with the given aggregate.

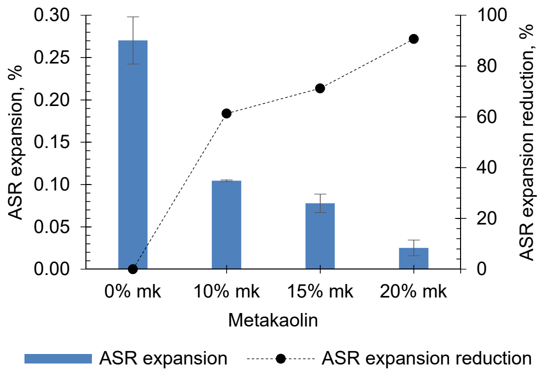

Figure 7. ASR expansion at 14 days and metakaolin potential for reduction expansion (ASTM C1567-13).

4.2.3 Accelerated carbonation test results

The carbonation results for concrete with metakaolin and GGCS at 0.5 and 0.6 w/b are presented in Figure 8, with the error bars signifying ± standard deviation of the carbonation depth measurements. At 90 days of exposure, concretes with 0.4 w/b ratio had no measurable carbonation regardless of the type and quantity of SCMs. This was attributed to the low w/b ratio in combination with metakaolin, yielding concretes with high resistance to gas penetration, as also observed in Figure 2, and the OPI results in Figure 3.

The rate of carbonation for concrete with 0.6 w/b was higher than that with 0.5 w/b. This was associated directly with the influence of porosity for higher w/b (Figure 5) that facilitated more easily the penetration of CO_2. At 0.5 w/b, the carbonation depths, at all exposure ages, decreased with increasing metakaolin, with the lowest depth at 20% replacement. At 0.6 w/b, at 56 and 90 days of exposure, all concretes with or without metakaolin had similar carbonation depths; at 28 days, carbonation depths decreased with metakaolin content. This observation was in contrast with results presented from the literature in Table 1 and implied that, in the current work, metakaolin had a less detrimental carbonation effect. This relates to a balance between the chemical process, which tends to increase carbonation, and the physical process, where a denser and less penetrable microstructure reduces carbonation. Thus, matrix densification and improved impermeability are important factors in metakaolin concrete.

The results also show that concrete with GGCS had substantially higher carbonation. It must, therefore, be inferred that matrix densification of GGCS concretes was not as marked as for metakaolin concretes. Also, GGCS concretes, with 50% replacement ratio, would tend to have less cabonatable material than the metakaolin concretes. The OPI test results also show that the GGCS concretes permitted greater gas permeability. Therefore, metakaolin performed better than GGCS in resisting accelerated carbonation up to at least 90 days, provided that low permeability of concrete was ensured.

4.2.4 Chloride bulk diffusion results

Chloride bulk diffusion tests were conducted only on metakaolin concretes with 0.4, 0.5 and 0.6 w/b. The results are presented in Figure 9 in terms of Cl^- profiles and apparent chloride diffusion coefficients. As expected, lower w/b ratios produce lower Cl^- contents. At 0.4 w/b, the metakaolin concretes had overlapping profiles, with the control having significantly higher Cl^- contents, associated with the low concrete penetrability of the metakaolin concretes at low w/b. At 0.5 and 0.6 w/b, the Cl^- values decreased with increasing metakaolin content, with the lowest diffusion at 20% metakaolin.

The apparent chloride diffusion coefficients of concretes also decreased with metakaolin content. At all w/b ratios, the controls had the highest apparent chloride diffusion coefficients, but with increasing metakaolin content, the coefficients decreased significantly. For example, the diffusion coefficient for 0.6 w/b ratio metakaolin concrete was similar to the control at 0.5 w/b. The influence of metakaolin on chloride bulk diffusion is also supported by the CCI results in Figure 6. Metakaolin has the potential to reduce chloride ingress, which is likely a combined effect of matrix densification and chloride binding capacity.

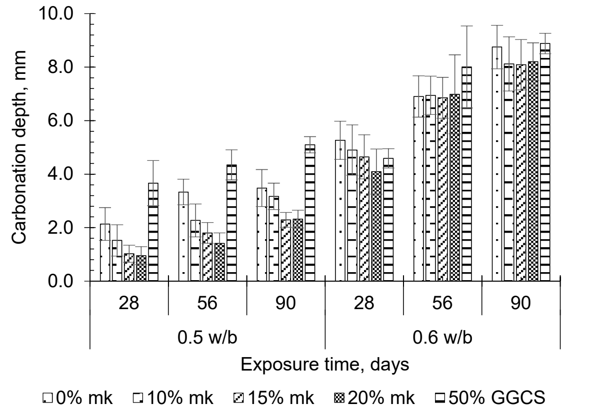

Figure 8. Carbonation depths of concrete at 0.5 and 0.6 w/b ratio, after 28, 56, and 90 days of accelerated carbonation.

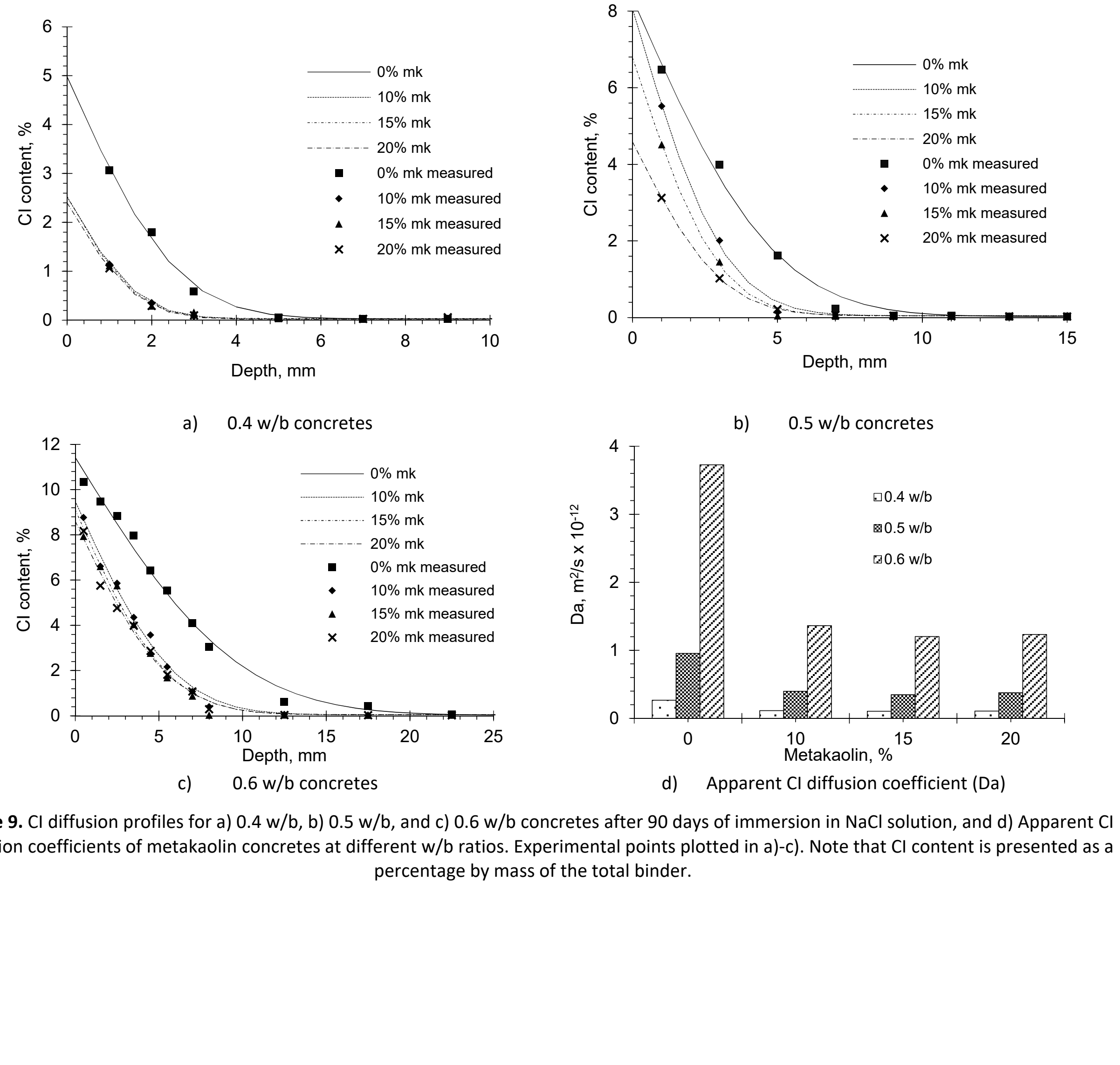

Figure 9. Cl diffusion profiles for a) 0.4 w/b, b) 0.5 w/b, and c) 0.6 w/b concretes after 90 days of immersion in NaCl solution, and d) Apparent Cl diffusion coefficients of metakaolin concretes at different w/b ratios. Experimental points plotted in a)-c). Note that Cl content is presented as a percentage by mass of the total binder.

4.3 Conclusions from experimental work

The present results show that inclusion of metakaolin in concrete significantly improves its potential durability in terms of penetrability (sorptivity, permeability, conductivity and diffusion), mitigation of ASR, and carbonation resistance. The results indicate that use of metakaolin can produce concretes with enhanced quality, which generally improves with metakaolin content up to 20%. This is attributed to the potential of metakaolin to alter the concrete microstructure, both chemically and physically. The following conclusions should be noted from the test results.

i. In term of the DI test results, metakaolin generally produced excellent quality concrete, which improved with metakaolin content. This potential is associated with its pozzolanic and filler effects that densify the concrete microstructure, thereby reducing gas permeability, water sorptivity and chloride conductivity.

ii. The potential of metakaolin in mitigating ASR improved with increasing metakaolin content, with the highest expansion reduction occurring at 20% replacement. Before considering the use of metakaolin for suppressing ASR for any given potentially deleteriously reactive aggregate, the most effective replacement rate should be established.

iii. In this work, metakaolin did not have a detrimental effect on carbonation rate; the effect depended on w/b ratio. The improved physical microstructure seemed able to compensate for the reduced buffer capacity in metakaolin concretes.

iv. With increasing metakaolin content and decreasing w/b ratio, chloride ion penetration and chloride bulk diffusion coefficient decreased. This effect is most likely due to its chloride binding capacity and its ability to alter or refine the concrete microstructure. (However, in the current study, the chloride binding capacity of metakaolin was not directly assessed).

v. In comparing the potential of GGCS and metakaolin to effect improvement in terms of durability index values, metakaolin generally showed excellent potential; in terms of carbonation, GGCS increased carbonation depth, attributed largely to its lower buffer capacity and higher gas penetrability, in comparison with metakaolin.

5 Closure

The work reported in this paper found that incorporating metakaolin up to 20% in concrete improves its potential durability performance. Metakaolin can safely be used for water-retaining structures since it is non-toxic and reduces permeability. In locations where non-reactive aggregates are scarce, metakaolin can be used to suppress ASR. Likewise, in cases where control of carbonation is needed, metakaolin can be used to slow the rate of ingress of carbon dioxide, provided the physical improvement to microstructure that it brings about more than compensates for the reduced buffer capacity.

From an economic perspective, the cost of metakaolin is not directly associated with its production cost or raw material availability. The high cost is related to insufficient production plants, lack of supportive government policy, and the competition from other kaolin industrial applications. Great benefits could be gained by use of this material in concrete, and it is recommended that industry should invest in its production and application. It must also be ensured that the means of raw material exploitation and metakaolin production should be such as to reduce environmental impact and promote sustainability.

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