



Key durability characteristics of GGBS-cement kiln dust based concretes

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ABSTRACT

With the advent of global warming, the concrete industry has the potential to drive the future of construction through sustainable cement technologies. These technologies rely on activation of industrial waste materials, such as Cement Kiln Dust (CKD) and Ground Granulated Blast Furnace Slag (GGBS) while Portland cement (PC) content is maintained at a minimum, resulting in concrete products of reduced embodied carbon footprint. This work reports on the durability of mixes made from PC, GGBS and CKD at incremental contents of 40-75% and 0-35% for GGBS and CKSD, respectively, in an attempt to identify durable formulations while maintaining blends at low embodied CO₂ emissions in the Sultanate of Oman. Dimensional changes, sulfate and chloride resistance, as well as surface resistivity were determined and compared to those of a PC-based concrete formulation. The results suggest that, when GGBS and CKD were incorporated within the mix at an optimum content of 55% and 20% respectively, the concretes appeared to have exhibited promising durability characteristics which could lead towards the material's implementation within a greater context.



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Introduction

The cement industry is faced with an increasing pressure to reduce cement production towards minimizing the environmental impact associated with the limestone calcination during cement manufacturing. For every tonne of Portland cement (PC) produced at the plants, there are approximately 930 kg of CO₂ emitted into the atmosphere; and, with almost 4.5 billion tons of cement produced annually around the globe, there is a clear need to tackle the concerns of embodied CO₂ emissions (eCO₂) through strategic sustainability levers [1]. With US and China being the predominant providers in worldwide cement manufacture, the Sultanate of Oman seems to be further away from the spotlight, contributing to almost less than 1% of the world's total cement production, i.e. a merely 8-10 million metric tons. Nevertheless, Oman has been witnessing an appreciable growth in the demand for concrete during the last 30 years, and this is due to the strategic reform initiated by His Majesty Sultan Qaboos bin Said; triggering, essentially, the need for raising sustainability awareness within the industry. Indeed, annual concrete production in Oman showed an upward trend since 2011 where initially, concrete volumes have been well below 200,000 m³ during that period. Within less than 6 years, however, the productions quadrupled at approximately 860,000 - 880,000 m³ and continued to increase at an exponential rate from 2016 to 2020 [2, 3]. In addition, such a high demand was reflected on the increase in the number of new construction projects that initiated in the country, resulting in almost current demand that is almost 15-fold compared to that of previous years [3, 4]. In this light, it is reasonable to assume that concrete productions in the country will most likely continue to increase, which now assigns a clear challenge on the Omani concrete industries to address the infrastructural needs, and at the same time tackle the environmental barriers associated with cement manufacture. It is evident that there are numerous challenges that the cement industry will face towards decarbonization, however ongoing research approaches include but not limited to using alternative cementitious materials, such as fly ash and slag, incorporating biomass fuels in cement kilns, improving energy efficiency in cement kilns etc. [5].

An effective strategy approach towards minimizing the environmental impact of cement in concrete is the partial replacement of cement with industrial by-products, thereby yielding blends of a reduced overall embodied carbon footprint. Well known examples of such industrial waste/by-products are cement kiln dust (CKD) and ground granulated blast furnace slag (GGBS). These

materials are locally available within Oman as they are extracted mainly from the kiln plants as well as the steel industries respectively, particularly in the areas of Sohar and Muscat. GGBS is a versatile byproduct of iron and steel manufacturing process, which comprises of mineralogical composition including silicate and aluminosilicate of molten calcium and has high amounts of calcium, silica, and alumina [6]. Hence it is considered as promising substitute for cement. As the granules are powdered to fine glassy substance, it helps to fill voids in concrete, reducing the penetration of chloride ions which eventually prevents corrosion of reinforcement [7]. CKD is a fine powder byproduct obtained from cement production plants. It is collected from the exhaust gases to prevent air pollution and collected in particulate matter control devices. CKD is rich in mineralogical composition comprising calcium oxide and silica, hence can act as an effective binding agent reducing the reliability on traditional materials [8].

However, there appears to be an insufficient body of research output that focuses on the properties of concretes made from PC-GGBS-CKD blends, especially when such blends are utilized in a locally commercial scale. Therefore, the industries of Oman may lack confidence on the reliability of such blends when considering a commercial context and a long-term implementation. An appreciable number of previous studies suggests that both GGBS and CKD indeed improve the mechanical and durability characteristics of concrete when incorporated within mixes individually, provided that they are added at the respective optimal amounts by mass [9, 11-13]. The compressive strength of cement mortar mix formed with varying GGBS/CKD ratios proved to have an increase in compressive strength with age and eventually reaching values comparable to that of the control mix [9]. GGBS is an industrial by-product with an embodied carbon footprint of merely 52 kg CO₂ for every tonne of GGBS produced [10]. GGBS can enhance the durability and lifespan of concrete structures in harsh environments by reducing the vulnerability to deteriorating mechanisms [11]. Because of having a denser microstructure, GGBS significantly improves the chloride resistance compared to OPC. [11] GGBS is known to be "latent hydraulic", hence depending on the amount of GGBS incorporated there can be a possibility in delaying the setting time of concrete but the previous studies have shown that it will gain strength over period of time based on the manufacture conditions [13]. Even though the reaction at the beginning is rapid, it slows down during the CSH gel formation phase as it forms thin film over the GGBS particles. [14] GGBS acts as an alkalinity buffer in

concrete as it can effectively mitigate alkali-silica reaction by lowering the overall alkalinity of the mix [14]. It possesses an almost identical mineralogy to that of conventional Portland cement and it yields from the 2Mt/year steel manufacture with the current figure being 25% higher than that witnessed in 2014 [15]. While production volumes of steel and iron are forecasted to be increasing within Oman, it follows that GGBS will also continue to be derived as a by-product in the country. Meanwhile, CKD, is considered as a highly alkaline, lime-based material yielded from the manufacturing of cement in the plants [16, 17]. The amount of CKD produced for every tonne of Portland cement produced can vary, but it is estimated that between 54 and 200 kg with other studies indicating approximate 0.13 tons CKD per ton of CKD is produced per ton of cement. The production of one ton of cement involves the comminution of about 2.6 to 2.8 tons of raw materials, and approximately 75 percent of the kiln dust particles are finer than 0.030 mm. CKD is having relatively uniform particle size range and having fineness in the range of 460-1400 m²/kg [18]. The high fineness can enhance CSH formation although this could possibly lead to higher water demand as well as tendency to agglomerate due to its fineness [19]. Previous research on use of CKD as partial substitute of cement suggests that replacements on the range of 0-40% are feasible, however, the predominant volume of previous work reported better performing concrete mixes when CKD replacement was approximately 5-30% [20]. Every cement company in Oman generates, between approximately 22,000-31,000 tonnes of CKD per annum, while partial amounts of the material are mainly being re-fed into the process. Such re-feeding may lead to an increase in the alkaline content of cement if the re-fed amount of CKD reaches beyond certain limits [17]. Hence, the majority of the by-product is disposed, leaving no scope whatsoever, for any possible reclamation or even reutilization [21]. The majority of CKD has been dumped in landfills causing threats to surroundings, which consequently leads to the essential need to identify sustainable means of disposal practices [22]. By providing a sustainable reuse for CKD can reduce the wastage, carbon footprint and environmental impact. Considering, on the other hand, the CKD's capability of activating industrial waste additions (as of its high pH value), then exploring GGBS-CKD cementitious combinations in concrete would appear to be a promising approach towards improving concrete properties and utilizing potential candidate formulations for a long-term implementation. Due to inherent alkali content in CKD which hinders strength development, incorporation of GGBS together with CKD can result in significant strength enhancement [18]. Both GGBS and CKD materials could therefore provide a

promising leeway towards attaining a balance between durability, environmental impact and cost within the Oman's construction industry.

The research presented in this paper explores the potential of utilizing Oman's local industrial by products (GGBS and CKD) within concrete, towards developing low carbon, optimally proportioned and high performing formulations for long term durability. Continuing from the author's previous work [23], an experimental investigation on key durability properties of concretes developed from blends of Portland cement (PC), GGBS and CKD at strategically incorporated ratios (by mass) was conducted, in pursuit of establishing ideal mix designs that yield competent durability characteristics.

Materials and Characterization

Conventional Portland cement (PC) of type CEM I 42.5N was utilized in this study provided from 'Oman Cement Company'. The cement was conforming to the standard BS EN 197-1:2011 [24]. A 4.75mm alluvial and commercially available fine sand to BS EN 12620:2002 [25] was used as the fine aggregate. Limestone (crushed) was utilized as coarse aggregate (CA), having 20mm maximum size to BS EN 12620:2002 [25]. CKD was directly obtained from a cement plant in Muscat; whereas GGBS was collected from a local steel factory in Sohar. All the above-mentioned materials were characterized prior to commencing the experimental program. Particle density tests were conducted on fine aggregates, as well as on CKD and GGBS materials in accordance to ASTM C128 [26]. For the coarse aggregates, the guidelines as per ASTM C127 [27] were adopted. Physical properties of all used materials are presented in Table I. In addition, sieve analysis was carried out in all materials, based on ASTM C136/C136M [28].

Experimental Program

Mix Design

Proportioning of all investigated formulations is shown in Table I, and the design was conducted based on the Building Research Establishment (BRE) method [29]. For all mixes, a water-to-cement (w/c) ratio of 0.5 was used. The control or reference mix (PC100) was produced using 100% Portland cement (PC), while the remaining mixes were developed by replacing the PC content with the GGBS and CKD at the percentages defined in Table I. The convention used for the particular mixes was BFSXXKDY, where XX refers to the GGBS replacement content, which was introduced at contents of 40-75% by weight, and YY referring to the percentage amounts of CKD incorporated at 0-35% by weight.

Experimental

Drying shrinkage of 7-day water cured 300x75x75 mm concrete specimens was determined by monitoring the length changes of samples placed in air-cured conditions (20°C, 65% RH) at weekly intervals for a duration of 20 weeks.

The sulfate resistance of 28-day water-cured 300x75x75mm concrete specimens was determined by monitoring the change in length of the samples immersed in 5% Na₂SO₄ solution at 20°C for a period of 40 weeks. Length-change measurements were obtained at 10, 20 and 40 weeks of age. The solution was replaced

every 28 days to maintain the sulfate ion concentrations throughout the immersion period. The chloride resistance of 28-day water-cured 100 mm concrete cube specimens immersed in 3% NaCl solution for 90 days was determined in accordance to EN 12390-11 [30]. Powdered layers of the samples were obtained by drilling the samples at specified interval depths and chloride contents were obtained by mixing 5g of the sample with 5g of 1M nitric acid, then slowly introducing anhydrous sodium carbonate to the mixture and immersing Quantab® strips on the extracted solution.

Physical Properties of Materials And Proportioning[23]

	CEM I	Sand	CA	GGBS	CKD
Specific gravity	3.11	2.63	2.71	2.81	3.02
Percentile d ₁₀ (µm)	1.6	203.4	1911	1.9	1.7
Percentile d ₉₀ (µm)	41.5	892.7	16430	49.3	47.8
Water absorption (%)	-	0.65	1.47	-	-
	Concrete mix proportions (kg/m ³)				
Water (l/m ³)	Binder*	Sand	CA		
210	420	705	1055		
	*Binder constituents (% by mass)				
Nomenclature	CEMI	GGBS	CKD		
PC ₁₀₀	100	0	0		
BFS ₇₅ KD ₀₀	25	75	0		
BFS ₇₀ KD ₀₅	25	70	5		
BFS ₆₅ KD ₁₀	25	65	10		
BFS ₆₀ KD ₁₅	25	60	15		
BFS ₅₅ KD ₂₀	25	55	20		
BFS ₅₀ KD ₂₅	25	50	25		
BFS ₄₅ KD ₃₀	25	45	30		

The non-steady state diffusion coefficients D_{nss} and surface chloride concentration contents were then determined using linear regression based on Fick's law, by approximating the data to the equation below:

where,

C_x is the chloride concentration at depth x and time t ,

C_i is the initial chloride content,

C_s is the surface concentration,

'erfc' is the complementary error function,

D_{nss} is the apparent, non-steady state diffusion coefficient at transient condition.

To verify the experimental results of the diffusion coefficients, electrical surface resistivity measurements were additionally taken at 9 points on the surface of 90-day water-cured cylindrical samples of 200 mm height and 100 mm diameter. The surface resistivity test was conducted in accordance to AASHTO T 358 [31], using a 38 mm-probe surface resistivity meter by applying a low frequency alternating current to the sample's surface and obtaining the potential difference ($k\Omega \cdot cm$) between its equally spaced outer probes.

All experimental procedures involved water cured specimens where applicable, until the specified ages of testing, and with the average result of at least three test measurements being obtained. The results of consistence, compressive strength, splitting tensile strengths, density, sorptivity of all the aforementioned samples can be found in the authors' previous work [23], where it was observed that when GGBS and CKD was incorporated in specific percentages by weight, minimal impact on rheological characteristics with good workability comparable to reference concrete.

Results And Discussion

Dimensional Changes

The evolution of drying shrinkage strains of the investigated formulations across the 20-week period is shown in Fig. 1.

Dimensional changes of the investigated formulations across a period of 20 weeks.

All mixes incorporating GGBS or CKD, regardless of their content, had evidently exhibited higher strains compared to those of the reference mix. Samples containing high CKD amounts (> 30% by mass) exhibited approximately twice the shrinkage compared to the reference PC100, whereas those containing high GGBS contents were still at high regimes. However, BFS55KD20

appeared to display a significantly less shrinkage effect compared to any other formulation, which is about 25% less than the worst exhibiting mix, i.e. the BFS40KD35.

It is commonly established that drying shrinkage in concrete occurs due to a mechanism of evaporation/loss of capillary water within the pores (and to a lesser extent on the loss of adsorbed water on the C-S-H phase). Such loss leads to development of internal stresses and eventually results in contraction, micro cracks and moisture-dependent deformations. In concretes with high amounts of GGBS and/or CKD, the C-S-H formation rates are significantly slower than those in PC-based concretes due to the low reactivity of the GGBS' mineralogical compounds (low Ca/Si ratios) or due to phase instabilities caused by high CKD amounts. Combined with the absence of activator, weaker exothermic reactions occur during mortar volume changes. This leads the setting of the paste to be surrounded by large amounts of free water as it is not utilized for hydration, which is precisely what can be observed in Fig. 1 for the samples with high GGBS mixes. When considering the BFS55KD20 concrete, however, it appeared that optimal amounts of both GGBS and CKD were present to initiate pozzolanic reactions promptly to form stable C-S-H phases, by engaging higher volumes of free water which would have otherwise evaporated and which would have caused internal stresses/deformations. Such dense microstructure of the particular combination was also reflected on the mechanical properties investigated in agreement to the author's previous work [23].

Resistance to Sulfate Attack

Sulfate expansion strains of all investigated concretes across a 40-week period are shown in Fig.2. Undoubtedly, the incorporation of GGBS and CKD in concrete had significantly improved the sulfate resistance of all developed formulations compared to the reference PC100, regardless of the amount of the two materials added. When considering the addition of 55% GGBS and 20% CKD by mass, it was observed that the sulfate resistance was enhanced by 75% against the PC100. All formulations achieved a minimum of 50% improvement in the sulfate resistance as their expansion strains were ranging merely within a regime of $45-60 \times 10^{-6}$.

Sulfate resistance of the investigated formulations across 40 weeks of immersion.

The main causes underpinning such an improvement is due to a combination of benefits provided by GGBS and CKD in the mixes, which are discussed below. The mechanism of sulfate attack is based on the presence of

available tricalcium aluminates (C_3A) and $Ca(OH)_2$ from PC (and/or CKD in this study) to form expansive ettringite when Na_2SO_4 reacts with the abovementioned phases. Ettringite occupies larger volume than its parent initial compounds prior to hydration; therefore it leads to dimensional volume changes in the matrix and eventually causes expansion cracks. As GGBS is a material containing no C_3A , then the overall C_3A amounts present would be significantly less in those high GGBS mixes, therefore providing no opportunity for any reactions and/or formation of expansive ettringite. Additionally, as part of the pozzolanic reaction, the GGBS would have reacted with all available $Ca(OH)_2$ that was yielded from PC and CKD; thus, no $Ca(OH)_2$ would be available for allowing a possibility for expansive ettringite formation. The absence, therefore, of expansive ettringite is reflected on the insignificant strains observed in Fig.2.

Chloride Resistance

The electrical surface resistivity values measured at 9 points on the surface of 90-day water-cured cylindrical samples for different formulations are given in Fig. 3. The surface resistivity is influenced by the water cement ratio, the immersion period and mode, as well as the addition of GGBS and CKD. It is evident that only the formulation BFS₅₅KD₂₀ yielded 22% higher resistivity than that of the reference concrete PC₁₀₀, thus decreasing the flow of chloride ions.

Surface resistivity of investigated formulations at 90 days of age

The non-steady diffusion coefficient D_{ns} , which represent the overall movement and distribution of chlorides ions in both bound and free state present in the samples for different formulations are given in Fig. 4

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Non-steady diffusion coefficient of investigated formulations at 90 days of age

The relationship between non-steady state diffusion coefficients and surface resistivity profiles of the investigated formulations is given in Fig. 5. An inversely proportional relationship can be clearly seen from the trend, indicating that the addition of both GGBS and CKD caused a decrease in chloride resistance of the investigated formulations. Particularly, the combination suffering from the poorest chloride resistance was observed to be the one where CKD was incorporated at 35% (i.e. BFS₄₀CKD₃₅), with diffusion coefficients being more than 52% higher than that of the reference concrete PC₁₀₀. Formulations containing CKD up to 25% by mass

exhibited a more controlled behaviour with somewhat minimized ingress of chlorides, although their coefficients were still higher than the reference. Interestingly, however, the BFS₅₅KD₂₀ combination yielded the lowest coefficient combined with its equivalent resistivity value, reaching 12% lower than that of the reference; essentially indicating that an optimally dense and impermeable microstructure was formed through proper hydration of the phases and at quick rates, preventing the chloride ion penetration in the pores. The particular combination would also have contributed to increased chloride binding capacity thereby reducing their mobility. When considering combinations with either high or zero CKD contents, the development of insufficient amounts of C-S-H probably led to a more porous microstructure, either due to the characteristic inability of GGBS towards yielding sufficient hydration products (i.e. BFS₇₅KD₀₀), or due to the high CKD contents which promote matrix instabilities. In this light, and based on the overall results, there would be two key issues to be taken into consideration when developing optimally enhanced formulations based on CEM I, GGBS and CKD: firstly, it would be essential to determine an ideal GGBS percentage content to be incorporated, keeping in consideration the unavoidable effects of slow hydration and the risks of reduced performance; and secondly, to determine and incorporate precise amounts of CKD within a specified content threshold, allowing for complete activation and proper C-S-H phase development and without causing matrix instabilities. Based on the results, the long-term durability characteristics of the formulations are evidently sensitive to the variations of GGBS and CKD amounts incorporated within the concrete and therefore a careful approach needs to be adopted for the optimum balance between the constituent contents.

Chloride resistance of investigated formulations at 90 days of age.

Conclusions

Significant amounts of GGBS and CKD are generated every year in the Middle East region annually, with, however, no applied context of measures for utilizing, re-using or reclaiming those materials towards developing eco-friendly construction materials for the industry. The objective of this research was to provide insights on two promising by-products currently available within the country, blast furnace slag (GGBS) and cement kiln dust (CKD), by exploring their long-term potential to be utilized in concrete towards sustainable and optimally proportioned products. An experimental investigation on

the long term durability of concretes based on blends of Portland cement (PC), GGBS and CKD at strategically incorporated ratios and contents was conducted. Formulations were prepared based on PC/ GGBS/ CKD blends at strategically incorporated contents and at a w/c ratio of 0.5. The PC content was kept at 25% by weight throughout the experimental, while the remaining 75% of the binder weight was allocated to 40-75% and 0-35% by GGBS and CKD respectively and at 5% step increments for each of the two constituents. The objective was to assess and identify an optimum formulation, which offers the best possible long-term performance [23]. The following conclusions were drawn from this paper:

When GGBS or CKD were incorporated at relatively high volumes, the formulations appeared to be enduring high shrinkage values and low chloride resistance due to the slow formation of hydration products, large amounts of unengaged evaporable free water and matrix instabilities. Such behavior was also in agreement with the mechanical properties of the same formulations investigated in the author's previous study [23].

Sulfate resistance of concretes containing any amount of GGBS and/or CKD was significantly improved, compared to the reference concrete (100% PC), regardless of the proportions. The reason underpinning such behavior is the absence of the high-risk phases that contribute to the formation of expansive ettringite. This denotes that the permeability and porosity of the formulations were not significant factors dictating the risk of sulfate attack, as hydration products do not engage with the sulfates to produce dangerous expansive phases. Rather, the presence of alkali ions in the concrete matrix would be more of a key indication that sulfate attack is imminent.

A formulation consisting of 25% PC, 55% GGBS and 20% CKD exhibited interesting durability characteristics compared to those of the other formulations, and even better chloride resistance profiles compared to the reference concrete (100% PC). This particular formulation seems to offer a promising potential for utilization in the industry, most probably due to the formation of a dense, impermeable microstructure at prompt hydration rates and within optimally proportioned constituents. As stated before, the particular findings were also coherent with the results of the author's previous study [23]. It is the authors' judgement that, ideally, the formulation may potentially be utilized and implemented in structural applications having C_{20/25} strength requirements; as well as in non-structural applications of no apparent risks.

For an equivalent strength target and comparing to CEM I concrete, the savings potentially achieved in embodied

CO₂ emissions may be more than 53% compared to a purely PC-based concrete used for the same application. This calculation is made considering the embodied carbon of each individual constituent incorporated within the concrete mix.

Overall, the results of this experimental investigation offer insights on determining a balance between high performing, low cost and reduced carbon footprint based on strategically incorporated contents of CEM I/GGBS/CKD. The authors, in addition, suggest that a more robust and stringent framework should be established, so as to define and stipulate upper and lower thresholds of the contents of the two materials (GGBS as well as CKD) when considering the long-term durability results of the formulations. The results of this study could indeed contribute towards the establishment of such framework, which may then serve as a leeway for introducing specifically, the BFS₅₅KD₂₀ formulation within a larger scale, or at least on a commercial context within the Sultanate of Oman.

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