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Effect of chemical composition of slag on chloride penetration resistance of concrete

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Three ground granulated slags (FeMn arc-furnace (GGAS), Corex (GGCS) and blastfurnace (GGBS) slags) of varying chemical composition, and from different sources were used to make concretes using two w/b ratios (0.40 and 0.60) and three slag replacement levels (20%, 35% and 50%). The effect of chemical composition and replacement level of slags on the chloride penetration resistance of the concretes was assessed using the chloride conductivity test. The results showed that the chloride penetration resistance of concrete increases with decreasing w/b ratio and increasing slag replacement level. In the GGAS concretes, despite having relatively low SiO_2 and high MgO content, its significantly high Mn_2O_3 and low Al_2O_3 content was found to have a negative effect on the chloride penetration resistance of the concrete. The significantly high chloride penetration resistance of GGCS concretes was partly attributed to both its high CaO content and particle fineness. Only GGCS concretes showed a trend of increasing chloride penetration resistance with increased particle fineness; GGBS and GGAS concretes did not show any trend between particle fineness and chloride penetration resistance. The slag activity index was found to be a better indicator of chloride penetration resistance in concrete than the slag hydraulic index.

1. Introduction

The use of supplementary cementitious materials (SCMs) such as slag, fly ash, silica fume and metakaolin to make blended cement concretes instead of plain CEM I (PC) concretes is common because of the positive attributes associated with their use, which generally relate to improved economic, durability and sustainability properties. From a chloride-induced reinforcement corrosion perspective, the use of blended cement concretes is usually preferred to plain PC concretes mainly due to their improved resistance to chloride penetrability [1], extended time-to-corrosion initiation [2,3], and relatively low corrosion rates [4,5]. The improved chloride penetration resistance and decreased corrosion rate in blended cement concretes has been observed in both cracked and uncracked concretes [6,7]. This publication focuses on the chloride penetration resistance of slag-blended cement concretes and examines the influence of chemical composition of various granulated slags.

Slag is a non-metallic by-product of the iron manufacturing process. It has a relative density of approximately 2.9, with its bulk density varying in the range of 1200–1300 kg/m^3. It generally has a higher particle fineness (>350 m^2/kg Blaine) than PC (approximately 310 m^2/kg Blaine) [8–10]. Its primary constituents are silica (SiO_2), alumina (Al_2O_3) and quicklime (CaO). Lime is added as a fluxing agent [9]. It typically replaces 20–50% of PC in concrete but higher replacement levels have been used in the past [1,9,11]. On the practical side, high levels of slag replacement may result in excessive delays in setting times and slower rate of strength development but by contrast, lower replacement levels may not produce all of the technical benefits possible with slag concrete, for example those relating to improved durability. The commonly used replacement level in the South African construction industry is 50%.

The hydraulic activity of slag as a cementitious material is influenced by (i) its chemical composition, (ii) the alkali concentration (pH) of the reacting system, (iii) its glass content, (iv), its particle fineness, and (v) the temperature during the early phases of the hydration process [12,13]. Compounds that increase its hydraulic activity include CaO, MgO and Al_2O_3 while SiO_2 reduces its hydraulicity [14,15]. These compounds (CaO, MgO, Al_2O_3 and SiO_2) are used to assess the suitability of a slag as a partial cement replacing material in concrete. This is done by calculating the slag *hydraulic index* (HI) which can be used as a first indicator to assess the potential of a slag to form cementitious hydration products in an alkaline medium such as concrete i.e. it can be regarded as the slag's cementitious potential [16]. A number of formulae have been proposed in the literature to predict the HI of slag (see [17]) but the most commonly used one is the ratio of the sum of oxides

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known to increase slag hydraulicity (CaO, MgO and Al_2O_3) to SiO_2 which decreases its hydraulicity [14,15]. However, these formulae have been criticized for their inadequacy to sufficiently predict the hydraulic activity of a slag since the hydration reactions that occur are far more complex than indicated by these formulae [3]. Furthermore, even though the type of PC used has also been shown to have a significant effect on hydraulic activity of a slag [17], this is not reflected in these formulae.

Even though the hydration product formed when slag is blended with PC and water is essentially the same as the principal product formed when PC hydrates, i.e., calcium silicate hydrate, C–S–H [18], the properties of hydrated paste systems incorporating slag such as strength, porosity and heat of hydration are influenced by the properties of the slag such as chemical and mineralogical composition, glass content, particle fineness, and the type of activation provided [8,19].

Partial replacement of PC with slag has been shown to lead to significant reduction in chloride ion penetrability by densification of concrete microstructure [20–22]. In its hydration process, it reacts not only with calcium hydroxide ($Ca(OH)_2$) but also with water to form calcium aluminates and C–S–H [23]. The latter product, additional to that formed by hydration of PC, contributes to refinement of pores and blocking of chloride diffusing paths [24]. An optimum slag replacement level to maximize concrete resistance to chloride penetration has so far not been established. The commonly used replacement level of 50% is based solely on compressive strength considerations [9], and some studies have reported increased chloride resistance as the slag replacement level increases from 40% to 65% by mass of total cementitious material [25].

The presence of slag in concrete also influences the chemical chloride binding capacity of the hardened cement paste [26]. This affects chloride transport in concrete through (a) partial blocking of pores in concrete, which results from the formation of calcium chloro-aluminates (Friedel's salt), (b) demobilization of chloride ions, or (c) both [24,27]. The main compounds in cement which take part in chloride binding are tricalcium-aluminate (C_3A) and tetracalcium-aluminoferrite (C_4AF) [28]. In the case of plain PC concrete, its chloride binding capacity can be predicted by applying the Bogue formulae to estimate the quantity of these compounds [29]. In the case of blended cements, suitable chloride binding isotherms are used e.g. Langmuir and Freundlich isotherms [27,30]. However, the applicability of these isotherms is usually limited to the chloride contents in the concrete and the SCM replacement levels used in their derivation. Furthermore, they do not take into account the chemical composition of the blended cement. Factors that affect the chloride binding capacity of slag-blended cement concretes include slag replacement level, w/b ratio, temperature, pH, carbonation, chloride desorption, sulphate content and particle fineness of the blended cement [30]. A summary of past literature on selected factors (relevant to this publication) affecting the chloride binding capacity of slag blended concretes is presented here:

(i) *Slag replacement level:* Chloride binding capacity increases with increasing slag replacement level [31]. This trend is attributed to the dilution effect of sulphates by slag [32]. The net effect of SCM on the binding capacity of a blended cement mainly depends on the resulting types and amounts of calcium–aluminate–hydrate (C–A–H), C–S–H and calcium–aluminate–silicate–hydrate (C–A–S–H) in the cement paste [30]. These hydrates are influenced by the chemical composition of the blended cement and the SCM replacement level.

(ii) *Water-to-binder (w/b) ratio:* Even though previous researchers have reported conflicting results with respect to the influence of w/b ratio on chloride binding capacity, with some reporting significant increase [33,34] and others reporting insignificant increase [35] with increase in w/b ratio, the general consensus is that the chloride binding capacity of a slag-blended cement concrete increases with increasing w/b ratio [36]. This trend is attributed to the higher porosity at higher w/b ratios which makes potential binding sites more exposed and more accessible to chloride ions [30].

2. Research significance

Even though the partial replacement of PC with slag can result in significant benefits with respect to chloride penetration resistance of concrete, differences in composition and reactivity of the slag, depending on the source, in addition to variations in slag replacement levels can affect its efficacy. An understanding of the effects of both the chemical compositions and physical characteristics of slag on the durability performance of concrete is therefore important, and can help in the development of more durable concretes. This study is specifically important in the South African context. As more types of slags are produced, it is necessary that their durability performance is investigated so that the extent of their strengths and weaknesses are known. A separate publication by Beushausen et al. [19] investigated the early-age properties, strength development and heat of hydration of concrete containing three types of slags. This publication reports on the same slags, and focuses on the influence of chemical composition and replacement level of slags on the chloride penetration resistance of concrete.

3. Experimental details

Three types of slags produced in South Africa were used in this research:

(i) *Ground granulated blastfurnace slag (GGBS):* This is the most common type of slag used in concrete in South Africa. It is produced when pig iron is manufactured in a blastfurnace. In the manufacturing process, the iron oxide is reduced to metallic iron using, as a fluxing agent, limestone or dolomite, which combines with the silica and alumina constituents in the ore to form a molten slag, which is then further treated to produce the finely ground slag used in the manufacture of concrete.

(ii) *Ground granulated Corex slag (GGCS):* This slag is produced in the Corex process which is a more environmentally friendly process to produce iron. In the Corex process, coke ovens and a blastfurnace are replaced with a direct reduction shaft and a melter-gasifier. This process yields a quenched slag, called GGCS, as a by-product. Changes in the manufacturing process inevitably result in subtle differences in chemical and physical properties of slags produced by the Corex process in comparison with the blastfurnace slags.

(iii) *Ground granulated FeMn arc-furnace slag (GGAS):* Recently, trials in South Africa have shown that modified basic oxygen furnace steel and arc-furnace steel slags can be granulated successfully to comply with the requirements of granulated blastfurnace slag for use in concrete [37]. One of these slags, namely a ground granulated FeMn arc furnace slag was included in this investigation. The ground granulated FeMn slag is a "Processed Air-Cooled FeMn Arc Furnace Slag", which was re-melted on a pilot plant scale (800 kg) with the addition of dolomitic limestone to obtain the same composition as GGBS. At the same time, the MnO content was reduced from ca. 20% to between 4% and 6%. The slag complies with all of the requirements for GGBS in terms of SANS 1491-1 [37] and BS EN 15167-2 [38].