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Physico-mechanical characteristics and durability of calcium aluminate blended cement subject to different aggressive media



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HIGHLIGHTS

• Compressive strength of CAC pastes is lower than CAC-WCS and CAC-ACS pastes.

- 20 mass% of CAC-WCS or CAC-ACS improve the physico-mechanical properties of CAC-blended pastes.
- Compressive strength of CAC-WCS pastes are higher than those of CAC-ACS pastes.
- Compressive strength of CAC in aggressive solution increases at 90 days, then decrease up to 120 days.
- The thin flaky-plate like of C₂ASH₈ reflects the closed and compact texture in aggressive solutions.

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ABSTRACT

Three mixes were prepared from calcium aluminate cement (CAC) and 20 mass% water-cooled (WCS) slag or air-cooled slag (ACS). The pastes were prepared with the required water of standard consistency, cured under tap water until time of testing (1, 3, 7 and 28 days). The durability of calcium aluminate blended cement was investigated by immersing the samples under tap water for 7 days (zero time), and then immersed in 5% sodium chloride, 5% magnesium sulphate and 5% ammonium sulphate as aggressive media. Compressive strength, bulk density and apparent porosity were measured. X-ray diffraction analysis and scanning electron microscopy were studied to reveal their mineralogical and microstructural features. Compressive strength of neat CAC pastes are lower than those of CAC–WCS and CAC–ACS blends. Compressive strength of CAC pastes immersed in 5% NaCl, 5% MgSO₄ or 5% (NH₄)₂SO₄ increases with curing time up to 90 days and then shows a slightly decrease up to 120 days immersion time. The presence of Cl⁻ or SO₄^{2–} ions activates the hydration rate of CAC, CAC–WCS and CAC–ACS. The SEM micrographs of CAC–WCS and CAC–WCS indicate the presence of the thin flaky-plate like morphology of C₂ASH₈ and thin fibrous particles of C–S–H I,II, which reflects closed and compact texture.

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1. Introduction

CAC is a versatile special cement that is used in high performance applications, due to fast hardening and excellent resistance to chemical attack, high early strength, refractory, resistance to abrasion, and/or low ambient temperature placement. CAC is advantageously used for repair work of highways, airport's runways, internal and external building surfaces [1–8].

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Hydration products formed in hardening depends considerably on curing temperature. The main hydration products of CAC are crystalline hydrate CAH₁₀, which forms at <21 °C, crystalline hydrate C₂AH₈ and amorphous AH₃ (21–35 °C), crystalline hydrates C₃AH₆ and AH₃ (> 35 °C). CAH₁₀ and C₂AH₈ are metastable, when subjected to various conditions (temperature, W/C ratio, etc.) can change into C₃AH₆ and AH₃. Concreting in winter conditions mostly results in formation of hydrates CAH₁₀, while in summer – C₂AH₈ and C₃AH₆ [9–10]. One interesting way to reduce the conversion of hexagonal hydrates and the decreasing of strength, this is due to replace some of the CAC by pozzolans cured at either 20–60 °C, the compressive strength increased continuously, whereas the compressive strength of neat CAC decreased, due to the conversion reaction. Stratlingite (C₂ASH₈) is formed in the mixes incorporating WCS

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or SF [11–16]. Initially, silica inhibits the formation of C_2AH_8 , and C_3AH_6 after conversion reaction as well as reflecting the role of WCS and ACS, preventing the conversion reaction occurring during hydration of CAC [13].

CAC have a long history of successful well documented and well understood use in corrosion-resistant waste water applications and seawater around the world. CAC is very expansive and losses its ultimate strength at high curing temperature during conversion reaction, so, many efforts had been directed to solve this problems. Replacement of WCS by CAC improves the mechanical and physical properties at room temperature 20 up to 60 °C, this is due to the formation of the more stable and dense structure stratlingite phase (C_2ASH_8) [11–14,17].

The conversion process results a change in the morphology, mineral nature and physico-mechanical properties of the cement pastes. It was found that the physico-mechanical properties was adversely affected by the conversion process and this well be very dangerous for building structures made from CAC concrete as was found in the failure of the beams at the swimming pool at the sir John Case and Red-Coat School at Stepnay, England [18,19]. It is well known that the CAC is highly resistant against attack if it is cured safely but if the conversion process was stacks, cracks will be formed as well as the hydrogarnet (C_3AH_6) will be formed which will decrease the chemical resistivity of CAC to sulphate attack [20,21]. Midgley [22] stated that the hydrogarnet formed as a result of the conversion process has lower resistance to sulphate attack than CAH₁₀. Curing of CAC paste in the presence of chloride salts results in the lower pH values inside the pores than that of hydrate OPC, which perhaps decrease the resistivity against these solutions [23]. However, the great possibility of the formation of Friedel's salt, which results in the increase of the concentration of free chloride ions in the medium, which will be very dangerous for the steel reinforcement. Goni and Guerrero studied the stability of Friedel's salt during the carbonation process [24]. Free Cl⁻ ion is one of the more aggressive for steel embedded in concrete, many corrosion studies have been carried out on hydrated calcium aluminate cement (CAC) [25–27].

This work aimed to utilize water cooled slag (WCS) or air cooled slag (ACS) produced in Egypt with calcium aluminate cement as a blended system. Durability of these blended cements was studies using 5% sodium chloride, 5% magnesium sulphate and 5% ammonium sulphate as an aggressive media. Compressive strength, bulk density and apparent porosity were measured. X-ray diffraction analysis, and scanning electron microscopy were studied to reveal their mineralogical and microstructural.

2. Materials and methods of investigation

2.1. Materials

The starting materials used in this investigation were calcium aluminate cement (CAC), Egyptian water cooled blast-furnace (WCS) and air-cooled (ACS) slags provided from Iron and Steel Company. The chemical analyses of the starting materials are given in Table 1. The appropriate proportions from these starting materials were dried and mixed in a porcelain ball mill for 2 h till complete homogenization. The mix compositions were mixed separately with the CAC to prepare the two optimum mix compositions that containing 20 mass% of both slag types. The fineness was checked using the Blaine air-permeability apparatus, according to the ASTM method (ASTM Designation C204–79) [28].

Figs. 1 and 2 illustrate the XRD of WCS and ACS, it is clear that the WCS is nearly completely vitreous with an amorphous structure. X-ray diffraction (XRD) pattern of ACS indicates that the ACS is completely crystalline and consists of mullite, Quartz and gehlenite (C_2AS).

2.2. Preparation of cement pastes

The cement blends were mixed in a rotary mixer to give complete homogeneity. To the prepared blended pastes, the required amount of mixing water was mechanically mixed for three minutes and the paste was then poured into one-inch cube

Table 1

Oxides	CAC	AS	WS
SiO ₂	4.59	32.69	37.21
Al ₂ O ₃	53.68	8.17	10.45
Fe ₂ O ₃	1.24	1.89	1.27
CaO	35.52	33.57	35.70
MgO	n.d	1.35	2.05
SO ₃	n.d	0.01	0.15
L.O.I	n.d	-	-
K ₂ O	n.d	0.43	0.71
Na ₂ O	n.d	1.47	1.60
TiO2	2.92	0.46	0.35
MnO	Nill	4.48	3.50
BaO	-	6.63	3.11
S	Nill	0.01	3.62
Blaine surface area, cm ² /g	3,500	3,500	3,500



Fig. 2. XRD of ACS.

molds, which were compacted several times, and their surfaces smoothened. The required water of normal consistency was determined in accordance with ASTM Specifications (ASTM Designation: C–150, 2007). The required water of normal consistency of CAC, CAC–WCS and CAC–ACS were 24.5, 25.1 and 25.4%. The pastes were moulded in 2.5x2.5x2.5x2.5 cm stainless steel molds. The molds were placed in a humidity cabinet having about 100% RH at 25 ± 1 °C for 24 h. After demoulding, the cubes were placed under water until time of testing (1, 3, 7 and 28 days). The resistivity of the hydrated cement pastes against aggressive media was investigated by immersing the required number of cement samples hydrated for 7 days (zero time), respectively in 5% NaCl, 5% MgSO₄ and 5% (NH₄)₂SO₄ solutions for different curing periods (7, 28, 60, 90 and 120 days).

2.3. Methods of investigation

The strength measurements were conducted for a set of at least 3 cubes of each mix at a given curing period. The rate of loading was fixed at a thrust of 50 kg/min. The mean value was taken into consideration. Representative samples were used to determine bulk density (BD) and apparent porosity (AP) [29,30].

The X-ray diffraction analysis was carried out on some selected samples with the aid of a Philips PW 1390 apparatus between $5-50^{\circ}$ 20 and a scanning speed of °20/min. The crystalline phases present were identified using X-ray diffraction

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