Research Article

Feasibility study of dealuminated kaolin utilization in marine constructions

Hazem I. Bendary1, Mohamed Heikal2, Mohamed A. Ali3*, Djamel Ghernaout4,5, Noureddine Elboughdiri4,6*

1 Chemical Engineering Department, The Higher Institute of Engineering, Cairo (Egypt), Hazemibrahem31@yahoo.com
2 Chemistry Department, Faculty of Science, Benha University, Benha (Egypt), mohamed.heikal@fsc.bu.edu.eg
3 School of Biotechnology, Badr University in Cairo (BUC), Cairo (Egypt), Mohamed.ahmed.ali@buc.edu.eg
4 Chemical Engineering Department, College of Engineering, University of Ha’il, Ha’il (Saudi Arabia), dj.ghernaout@uoh.edu.sa, n.elboughdiri@uoh.edu.sa
5 Chemical Engineering Department, Faculty of Engineering, University of Blida, Blida (Algeria), djamel_andalus@yahoo.fr
6 Chemical Engineering Process Department, National School of Engineers Gabes, University of Gabes, Gabes (Tunisia)

*Correspondence: ghilaninouri@yahoo.fr, Mohamed.ahmed.ali@buc.edu.eg

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Abstract: In the marine environment, the resistance of cement structures to salts is the most critical factor affecting their life span. We investigated the sulfate attack of ordinary Portland cement (OPC) and dealuminated kaolin (DK) blended cement in the marine environment. The performance of this cement was assessed by immersing the mortar specimens in fresh seawater for one year and measuring the strength development, reduction in compressive strength, expansion due to (SO₄²⁻) penetration, and weight change of the mortar specimens using the standard test methods. The results proved clearly that 7.5% (DK) blended cement mortar specimen is the best achieved the lowest reduction in compressive strength (10%), a relatively small weight gain (0.62%), and expanded to less than 0.10% at 1-year exposure so it is considered sulfate resistant.

Keywords: Marine environment, sulfate attack, blended cement, dealuminate.

1. Introduction

Concrete permeability allows for the ingress of ions from seawater into the concrete structure, or the leaching of the constituent components of concrete into the seawater. The process of fluid and ion transport through concrete can be attributed to four fundamental mechanisms, including capillary suction, which occurs due to capillary action within the cement paste's capillaries, permeation driven by pressure gradients, diffusion caused by concentration gradients, and migration induced by electrical potential gradients (Bertolini, Elsener, Pedferri, Redaelli, & Polder, 2013). Concrete that is exposed to seawater is subject to various influencing factors, such as the seawater composition, climate, wave action, and marine zones, including immersion, tidal, splash, or spray zones. Seawater is primarily comprised of Na⁺, Mg²⁺, Cl⁻, and SO₄²⁻ ions, along with small amounts of K⁺, Ca²⁺, HCO₃⁻, and Br⁻ (Skalny, Marchand, & Odler, 2003). The salinity of seawater can vary widely, but it can be generally assumed to have an average dissolved salt concentration of 3.5% (35 g/L) (Thomas, 2016). The permeability of
concrete and the composition of its hydrated cement phases are the primary factors that govern sulfate reactions in concrete materials. The hydrated products of tricalcium aluminate (C3A) are known to be susceptible to sulfate attack (Lamond & Pielert, 2006). The mechanisms of sulfate attack include (Lamond & Pielert, 2006; Skalny et al., 2003):

\[
\begin{align*}
\text{Na}_2\text{SO}_4 + \text{Ca(OH)}_2 + 2\text{H}_2\text{O} & \rightarrow \text{CaSO}_4\cdot\text{H}_2\text{O} + 2\text{NaOH} \\
\text{MgSO}_4 + \text{Ca(OH)}_2 + 2\text{H}_2\text{O} & \rightarrow \text{CaSO}_4\cdot2\text{H}_2\text{O} + \text{Mg(OH)}_2
\end{align*}
\]

(1) (2)

The gypsum produced by those reactions is believed to damage concrete by increases in overall solid volume.

\[
\begin{align*}
3(\text{CaSO}_4\cdot\text{H}_2\text{O}) + 4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot1.9\text{H}_2\text{O} + 8\text{H}_2\text{O} & \rightarrow 3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot3\text{CaSO}_4\cdot32\text{H}_2\text{O} + \text{Ca(OH)}_2 \\
2\text{Na}_2\text{SO}_4 + 3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaSO}_4\cdot12\text{H}_2\text{O} + 2\text{Ca(OH)}_2 + 2\text{H}_2\text{O} & \rightarrow 3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot3\text{CaSO}_4\cdot32\text{H}_2\text{O} + 4\text{NaOH}
\end{align*}
\]

(3) (4)

The formation of ettringite (eq. 3, 4) causes volume expansion, hence generating cracks (Merida & Kharchi, 2015; Robbins & Lebel, 2016; Rozière, Loukili, El Hachem, & Grondin, 2009). However, interactions with chloride prevent ettringite from forming (Skalny et al., 2003).

\[
\begin{align*}
3\text{MgSO}_4 + 3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot3.6\text{H}_2\text{O} + 6\text{H}_2\text{O} & \rightarrow 3(\text{CaSO}_4\cdot2\text{H}_2\text{O}) + 3\text{Mg(OH)}_2 + 2\text{Al(OH)}_3 \\
3\text{MgSO}_4 + 3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaSO}_4\cdot12\text{H}_2\text{O} + 2\text{H}_2\text{O} & \rightarrow 4(\text{CaSO}_4\cdot2\text{H}_2\text{O}) + 3\text{Mg(OH)}_2 + \text{Al}_2\text{O}_3\cdot3\text{H}_2\text{O} \\
3\text{MgSO}_4 + 3\text{CaO}\cdot2\text{SiO}_2\cdot\text{nH}_2\text{O} + z\text{H}_2\text{O} & \rightarrow 3(\text{CaSO}_4\cdot2\text{H}_2\text{O}) + 3\text{Mg(OH)}_2 + 2\text{SiO}_2\cdot4\text{H}_2\text{O} \\
4\text{MgSO}_4 + \text{Ca(SiO}_2\cdot\text{H}_2\text{O} + (4 - x)\text{Ca(OH)}_2\cdot\text{nH}_2\text{O} & \rightarrow 4\text{MgO}\cdot\text{SiO}_2\cdot8\text{H}_2\text{O} + 4\text{CaSO}_4\cdot2\text{H}_2\text{O}
\end{align*}
\]

(5) (6) (7) (8)

The low resistance of concrete structures against sulfate and acid attacks has direct financial and environmental consequences. To seal the concrete surface physically against an aggressive environment, effective coatings were introduced by several scientists (ACI, 2013; Aguiar, Camões, & Moreira, 2008; Almusallam, Khan, Dulaikan, & Al-Amoudi, 2003; Aygörmez & Canpolat, 2021). Such effective coatings should protect the concrete structure by stopping the penetration of aggressive ions; however, they are expensive and labor-dependent (Tahri, Abdollahnejad, Mendes, Pacheco-Torgal, & de Aguiar, 2017).

Based on the fact that both Ca (OH)\(_2\) and 4CaO·Al\(_2\)O\(_3·13\)H\(_2\)O involved in sulfate reaction are the major products for C\(_3\)S, C\(_3\)S, and C\(_3\)A in cement hydration, any approach that inhibits the formation of both Ca (OH)\(_2\) and 4CaO·Al\(_2\)O\(_3·13\)H\(_2\)O should improve the resistance of concrete to the sulfate attack.

Numerous investigations have been conducted to enhance the impermeability of concrete, such as incorporating clay brick powder (Castillo, Hernández, Rodriguez, & Eyzaguire, 2020), adjusting the water-to-cement ratio (Kuhail & Shihada, 2015), substituting fly ash (Dinakar, Babu, & Santhanam, 2008) (Nath & Sarker, 2011) (Moffatt, Thomas, & Fahim, 2017) or blast furnace slag (Choi, Choi, & Yang, 2016), and utilizing silica fume to reduce porosity and enhance chemical resistance (Alam et al., 2013).

Efforts to decrease porosity in concrete have also been made by introducing inhibitors based on natural ingredients. Bambusa Arundinaceae has been identified as having the potential to replace nitrite and amine-based corrosion-inhibiting admixtures in the construction of durable concrete structures, due to its ability to block pores and reduce porosity (Abdulrahman, Ismail, & Hussain, 2011).
Nowadays, a lot of industrial by-products and agricultural residues are being used as a partial substitute for cement in concrete structures but are not abundant such as silica fume, rice husk ash, iron slag, and fly ash (Arunkumar, Muthukannan, Suresh Kumar, Chithambar Ganesh, & Kanniga Devi, 2023).

On the other hand, quite abundant sustainable dealuminated kaolin (DK) in Egypt is a waste by-product formed during the extraction of aluminum from calcined kaolin using sulfuric acid (Eq. 9).

\[ 3\text{H}_2\text{SO}_4 + \text{Al}_2\text{O}_3\cdot2\text{SiO}_2 = \text{Al}_2(\text{SO}_4)_3 + 2\text{SiO}_2 + 3\text{H}_2\text{O} \]  

Such treatment leaves behind a silicate-rich acidic paste, which upon exposure to air dries intensively. The dealumination process of the calcined kaolin increases the surface area of the resulting material. The amount of increase in the surface area is related to the type of dealuminated chemical reactants used (HCl, H_2SO_4 and Na_2HSO_4), also to the reaction time and the amount of aluminum extracted. Generally, the dealumination of calcined kaolin by acid leaching produces amorphous silica with a high surface area expected to be highly reactive with lime. The main effect of the acid attack on the calcined kaolin is the dissolution of the aluminum from its octahedral and tetrahedral sites and the formation of free silica (Colin & Llorens, 2007).

This waste is particularly problematic because of its acidic nature, and the large amounts generated, which are normally landfilled, have a negative effect on aquifers. The use of DK as a cement replacement material was introduced by (Abdelaziz, Abdelalim, Ghorab, & Elsayed, 2010). They compared the specific surface area and pozzolanic activity of silica fume and DK, and the result was in favour of the latter, as well as the effect of adding each one on the initial setting time and they had the same effect in delaying it. These authors found that the use of up to 10% cement replacement by DK resulted in an improvement in tensile and compressive strengths.

The pozzolanic activity of alum waste (i.e., DK) and calcined kaolin (CK) activated by cement kiln dust (CKD) was investigated by Abo-El-Enein et al. (Abo-El-Enein, Heikal, Amin, & Negm, 2013). Various proportions of both activators and binders were hydrated. Chemically combined water, as well as free CaO, were assessed instrumentally at various ages of hydration using differential scanning calorimetry (DSC), X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FTIR). The results showed that DK has a higher pozzolanic character due to the lack of free lime compared to other binders such as CK and silica fume. On the other hand, Mostafa et al. (Mostafa, Mohsen, El-Hemaly, El-Korashy, & Brown, 2010) concluded that DK blended cement had a more rapid gain in compressive strength as compared to silica fume blended cement due to the high pozzolanic activity of DK, which accelerates Ca(OH)_2 consumption in pozzolanic reaction. Abdelmawla et al. (Abdelmawla, Abdelaal, Beheary, Abdullah, & Razek, 2020) mixed DK with metakaolin (MK) in various proportions to produce eco-friendly and economical geopolymer concrete. Full characterization of DK showed that it is a good pozzolanic material.

The feasibility to use DK was evaluated by measuring the compressive strength at 1 and 4 weeks. MK with added proportions of DK up to 40% of MK is recommended. DK was also mixed with dead burnt calcined magnesite, and then sintered for the manufacture of forsterite-type refractories (Mg_2SiO_4) that showed excellent refractoriness (Khalil, 2001). Besides their excellent refractory properties, these forsterite-type refractories were recommended to be used in the clinkering zone of cement rotary kilns and regenerators of the steel furnaces owing to their basic character. During their recent research, Salam et al. (Salam, Ghaly, Abadir, & Amin, 2022) produced geopolymer bricks using DK activated by sodium hydroxide solution (with concentrations ranging from 2 to 14 M). The effect of curing time and molarity of the alkaline activator solution on the degree of geopolymerization, bulk density, water absorption and 28 days compressive strength were evaluated. The results stipulated that to achieve a 90% degree of geopolymerization at 28 days it is recommended to use an alkaline activator solution up to 8-10 M. Water absorption decreased considerably with ranging the sodium hydroxide concentration from 4 to 14 M. The minimum allowable value of 28 days compressive strength for building bricks (8.7 MPa) was achieved by using a 12 M alkaline activator solution, ASTM C 62, (ASTM International, 2012).

It is not the best for silica fume and fly ash, which produced stronger results for salt resistance (Zahra, 2014), but it is more economically feasible. Finally, we can clearly say that all pozzolana mixtures resist salts to a higher degree than that which
was prepared with Portland cement only (Chatveera & Lertwattanaruk, 2009; De Sensale, 2010; Venkatanarayanan & Rangaraju, 2014).

Studying the effect of seawater on samples prepared by combining dealuminated kaolin with other types of industrial waste such as silica fume or wastewater treatment sludge is recommended for future work. This research aimed to study the durability of ordinary Portland cement (OPC) and DK cement blended mortars in seawater. It has been motivated by the growing economic and environmental concerns over the disposal of wastes as well as the increased value associated with their use in the economic production of some engineering components, in the present case, high-performance concrete.

2. Experimental methods

2.1. Characterization of raw materials

2.1.1. Fine aggregate (FA)

In the present work, natural sand was used. Its physical and mechanical characteristics are listed in Table 1, as well as its particle size gradation pattern is shown in Figure 1.

<table>
<thead>
<tr>
<th>Table 1. Physical and mechanical characteristics of natural sand in this research.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Physical and mechanical properties</strong></td>
</tr>
<tr>
<td>Specific gravity</td>
</tr>
<tr>
<td>Unit weight</td>
</tr>
<tr>
<td>Void ratio</td>
</tr>
<tr>
<td>Fineness modulus</td>
</tr>
<tr>
<td>Fine matter and clay</td>
</tr>
<tr>
<td>Water absorption</td>
</tr>
</tbody>
</table>

![Figure 1](image.jpg)

*Figure 1. Particle size distribution pattern of fine aggregate (FA) and dealuminated kaolin (DK).*

2.1.2. Water

In this study, two types of water were used: (1) freshwater was employed mainly for mixing to obtain the appropriate texture required for casting and then curing the mortar specimens until testing, (2) red seawater, which was brought from the beach of Ain Sukhna (Suez Governorate, Egypt) for curing and verification of the resistance of mortar specimens to its salts as specified in Figure 2.
2.1.3. Ordinary Portland cement (OPC)

The study employed Ordinary Portland cement of class CEM I 42.5 N produced by the Suez Cement Company. The cement was tested in accordance with Egyptian standards (ESS4756-1 2009) and American specifications (Cement, 2013). Its chemical composition as kindly supplied by the parent company is shown in Table 2.

<table>
<thead>
<tr>
<th>Item</th>
<th>DK</th>
<th>OPC</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>71.86</td>
<td>21.16</td>
</tr>
<tr>
<td>TiO₂</td>
<td>2.95</td>
<td>-</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>7.48</td>
<td>5.32</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.51</td>
<td>3.52</td>
</tr>
<tr>
<td>MgO</td>
<td>0.08</td>
<td>1.32</td>
</tr>
<tr>
<td>CaO</td>
<td>0.31</td>
<td>63.8</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.11</td>
<td>0.2</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.08</td>
<td>0.13</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.05</td>
<td>-</td>
</tr>
<tr>
<td>SO₃</td>
<td>5.28</td>
<td>2.01</td>
</tr>
<tr>
<td>Cl</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>0.2</td>
<td>-</td>
</tr>
<tr>
<td>L.O.I</td>
<td>10.98</td>
<td>2.52</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>99.91</td>
<td>100</td>
</tr>
</tbody>
</table>

2.1.4. Dealuminated kaolin (DK)

Waste from the alum industry was kindly supplied by the Alum Factory of “El-Nasr Company for Intermediate Chemicals (NCIC)”, Egypt. DK was dried at 105°C for 24 hours to eliminate the humidity/water content, then the waste was sieved to exclude large-size particles through a 600-micron sieve.
2.2 Chemical analysis

X-ray fluorescence (XRF) analyses were run on an AXIOS, analytical 2005, Wavelength Dispersive (WD-XRF) Sequential Spectrometer. Table 2 summarizes the chemical composition of alum waste samples as analyzed using XRF to check whether the materials are pozzolan (Bendary H.A., Abadir M.F., Moselhy H., 2017). Table 2 reveals the predominance of silica (SiO2) in a proportion exceeding 70%. The presence of alumina (Al2O3) is due to a minor amount of unreacted kaolinite and aluminum sulfate. This is emphasized by the presence of slightly more than 5% sulfate ion. As the sum of silica and alumina contents exceeds 70%, the material can be classified as pozzolanic (American Society for Testing and Materials Annual, 1992). The amount of silica present in unreacted MK can be deduced from that of free silica. This was determined using the Trostbl method (Trostbl & Wynne, 1940) and found to be equal to 66.4%, meaning that only about 5.5% of silica was in combined form.

2.3 Mineralogical analysis

The raw material’s mineralogical composition was determined using X-ray diffraction (XRD) Brukur D8 advanced computerized X-ray diffractometer apparatus with monochromatic CuKα radiation, operated at 40 kV and 40 mA (Ahmed, Abadir, Yousef, & El-Naggar, 2021). The mineralogical analysis of DK, shown in Fig. 3, displays the main peaks of quartz with minor peaks of titanium oxide (anatase). No peaks for amorphous MK appeared, as expected.

2.4 Microscope analysis

The raw as-received DK powder was subjected to two types of microscopic observations, namely, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The first one was used to assess the morphology of the fired samples. A JEOL-JSM 6510 apparatus (zoom magnification power up to 300,000) was used to generate SEM images for some selected fired specimens (El-Naggar, Amin, El-Sherbiny, & Abadir, 2019). The obtained SEM and TEM micrographs shown in Figs. 4 and 5, respectively, explained the presence of large quartz grains to which adhered smaller particles and anatase particles that possess nano-sized diameters seem embedded in larger quartz particles.

Figure 3. X-ray diffraction (XRD) pattern of dealuminated kaolin (DK).
2.5 Microscope analysis

Screen analysis is used to sort granular solids into definite-size fractions with the standard sieving procedure described by (Materials, 1998). The cumulative analysis, presented in Fig. 1, can be used to determine the particle’s median diameter of 0.21 mm at a 50% fraction passed. It was possible to use the cumulative graph, shown in Fig. 1, to predict the specific surface area of the as-received powder $A_w$ (m$^2$.kg$^{-1}$). To that aim, Eq. (10) was used (McCabe, Smith, & Harriott, 1993):

$$A_w = \frac{6}{\sigma} \sum_{i=1}^{n} \frac{x_i}{D_{av_i}}$$

where:
- $\sigma$ Sphericity of powder.
- $\rho_p$ Density of powder (kg.m$^{-3}$).
- $x_i$ Fraction retained between sieves $i$ and $i+1$.
- $D_{av_i}$ Mean sieve opening of sieves $i$ and $i+1$.

The powder’s true density was determined using the conventional density bottle technique according to (ASTM, 2002). It was found to be equal 2820 kg.m$^{-3}$. The particle’s sphericity is taken as that of quartz (0.82) (Wadell, 1935). Then, the powder’s specific surface area was determined and found to be equal ~ 22.3 m$^2$.kg$^{-1}$.

True density of DK powder was determined using the density bottle and found to be equal 2.8 g/cm$^3$. 
2.6 Mix preparation

Cement was gradually substituted by waste keeping the ratio \( \frac{\text{Cement} + \text{Waste}}{\text{Sand}} \) constant at 1:2.75. (Cement, 2013). Table 3 shows the designation of different mixes (wt. %) used, where the sand mass was fixed at 275 g and the ratio (Water/Cement) maintained at 48.5.

<table>
<thead>
<tr>
<th>Specimen identity</th>
<th>Replacement (%)</th>
<th>Cement</th>
<th>DK</th>
<th>Sand</th>
<th>Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>A₀</td>
<td>0</td>
<td>100</td>
<td>0</td>
<td>275</td>
<td>48.5</td>
</tr>
<tr>
<td>A₁</td>
<td>7.5</td>
<td>95</td>
<td>5</td>
<td>275</td>
<td>48.5</td>
</tr>
<tr>
<td>A₂</td>
<td>10</td>
<td>90</td>
<td>10</td>
<td>275</td>
<td>48.5</td>
</tr>
</tbody>
</table>

2.7 Specimen casting, demolding and curing

The different mixes were weight, batched, and mixed; then, a number of thirty-six 50 mm cubes and six 25 × 25 × 285 mm bars of mortar specimens for each mix were cast and placed at room temperature till 24 hours. Following that, the specimens were demolded and cured in tab and seawater containers until testing at the specified time (28, 56, 90, 180, 365 days).

2.8 Testing procedures

2.8.1 Mortar bar length change

A common test procedure was employed to evaluate the length change in the mortar bars submerged in seawater Figure. 6. to determine the resistance of DK mortars (ASTM C1012/C1012M-15, 2015).

Figure 6. The standardized test method ASTM C1012 was employed to evaluate mortar bars that contained Ordinary Portland Cement (OPC) and blended dealuminated kaolin Cement (DK).

After demolding, the mortar bars were cured in lime water together with cube specimens until the specimens obtained a compressive strength of 20 MPa, which was accomplished for A1 and A2 samples in about 3 days, but took about 4 days for DK-free samples. To measure the SO42- resistance of the DK mortars, the length of the mortar bars was then measured before being exposed to seawater. Then, from the first day of immersion in seawater, the length of the mortar bars is set at 365 days. Eq. (11) was applied to that object.

\[
\Delta L (\%) = \frac{(L_2-L_1)}{L_1} \times 100
\]  \hspace{1cm} (11)

where: \( \Delta L \) indicates the percentage of length (%) gained in mortar bars.
L1: is the mortar bar's original length.
L2: stands for the length of the mortar bars as measured after 365 days in the sea.
Up to the completion of the curing period, the seawater was regularly replaced every 60 days.
2.8.2 Compressive strength

In this test, the mortar cubes, prepared previously during casting, needed to measure the expansion of the cement mortar as a result of the penetration of the salt in seawater. The mortar cubes' mechanical compressive strength was measured at different curing periods (28, 56, 180, and 365 days) in seawater. These results were used in calculating the percentage loss in compressive strength and comparing them to standard rates. For that aim, a standard test procedure was used (Cement, 2013).

2.8.3. Weight changes

Weight change was found using Eq. (12):

$$\Delta W(\%) = \frac{W_t - W_i}{W_i} \times 100$$  \hspace{1cm} (12)

where: \(w_i\): Initial weight for water primed cube, and \(w_t\): weight of mortar cube after any exposure time.

2.8.4. Loss of compressive strength

For that purpose, Eq. (13) was used.

$$\Delta S(\%) = \frac{S_2 - S_1}{S_1} \times 100$$  \hspace{1cm} (13)

where: \(\Delta S\) indicates the reduction percentage in compressive strength due to \(SO_4^{2-}\) penetration.

\(S_1\): Mortar cubes of compressive strength in MPa cured in lime water for a certain time (curing time in days to obtain \(\sim 20\) MPa, compressive strength + 28 days curing in saturated lime water) for all mixtures, which are approximately equal to 31 days.

\(S_2\): Strength of mortar cubes at any time interval from the beginning of immersion in seawater.

3. Results and interpretations

3.1 Mortar bars expansion

The formation of -aluminate hydrate, otherwise known as ettringite or Candlot's salt, due to the reaction between sulfate and hydrated aluminate phases, results in the expansion of plain and blended cement mortar specimens. The length change results for mortar bars soaked in seawater for one year is shown in Figure. 7. After a period of 4 months of exposure, the OPC mortar bars exhibited bending and cracking, with the appearance of white deposits on their surfaces. The cracks were predominantly observed near the corners and edges of the bars, as well as along the sides adjacent to the finished surface. As the test progressed, a network of cracks developed along the long sides of the bars near the end of the experiment. In contrast, the DK mortar bars showed the emergence of fine horizontal cracks in the region close to the finished surface and cracks along the ends and corners of the bars after approximately 6-12 months of exposure. Moreover, The OPC mortar bars exposed to seawater exhibited a higher total length change of approximately 0.121%, as opposed to the 0.078% total length change observed for DK mortars.
The results strongly proved that DK utilization in concrete structures as cement replacement material increased its resistance to sulfate ingress by inhibiting the expansive phases (ettringite) production. This phenomenon can be attributed to the weakening of the reactivity of cement phases, particularly C3A and C3S, due to their dilution. It is considered that A1 and A2 specimens are sulfate resistant as the expansion does not exceed 0.10% during one year (ASTM Committee C01.10, 2011).

3.2. Change in weight

The change in the mortar cube's weight exposed to seawater is presented in Fig. 8. All the specimens recorded an increase in weight throughout the exposure. A marginal weight gain in all of the mortar specimens was noticed due to the formation of calcium sulfate compounds. Specimen A0 gained the maximum increase in weight, and the least gain in weight was achieved by specimen A1. Till up to 28 days of exposure, there was a rapid gain in weight for all the specimens. Thereafter, an increase in weight was gradually observed; after 180 days, a stable trend was observed for all the specimens. A relatively small weight gain for all the specimens ranged from 0.62% to 1.07%. White deposits within the surface pores were observed during the early age of curing in the seawater, which agrees with Rendell and Jauberthie (Rendell & Jauberthie, 1999).

3.3. Compressive strength

Figure 9 demonstrates the influence of curing age on the development of compressive strength in all mortar cubes cured in fresh water, which can be attributed to the ongoing hydration process of Portland cement and pozzolans. The illustrated curves proved that the maximum compressive strength was reached in specimens A1 and A2, which exceeded A0 by 21.8% and 12.6%, respectively, after 365 days of curing. The enhanced performance of DK mortars can potentially be attributed to the formation of C-S-H gel with a low C/S ratio resulting from the pozzolanic reaction. This gel formation leads to low permeability of the mortars, which effectively hinders the ingress of sulfates into the cementitious matrix.
There was an increase in the mechanical compressive strength for all the mortar cubes exposed to sea water till three months; then, it started to decrease along the exposure period as depicted in Fig. 10. This phenomenon can be explained by the filling of pores through the expansive reaction products, resulting in the densification of the hardened mortar mix, and subsequently increasing its weight and strength (Montemor, Simoes, & Salta, 2000).

The change in compressive strength versus curing age for all mortar specimens placed in seawater is plotted in Fig. 11. A 10% reduction in the compressive strength was achieved by A1, which is the lowest one followed by 14% attained by A2 compared to 21% registered by A0 after one year of exposure to seawater. It is hypothesized that the addition of waste material in the specified amount is adequate to counteract the presence of calcium hydroxide in the mortar pores, which leads to the formation of C3S2.xH2O crystals through the reaction with free silica present in the waste. Further addition beyond the specified amount is deemed unnecessary, as it would only act as an inert filler that decreases rather than enhances the strength of the mortar. While the results obtained using this waste material as an additive are promising, its efficacy is still inferior to that of using silica fume as an additive (Mohamadien, 2012). Nevertheless, the economic advantage of using the waste material as an alternative is substantial, given that it is practically cost-free.

Figure 9. Compressive strength development of mortar specimen immersed in fresh water.

Figure 10. Compressive strength development of mortar specimen immersed in seawater.
4. Conclusions

Considering the results obtained, the following points can be deduced:

1. A1 and A2 specimens are sulfate resistant as the expansion did not exceed 0.10% at 1 year.
2. A relatively small weight gain for all the specimens ranging from 0.62% to 1.07% was obtained.
3. A 10% reduction in the compressive strength was achieved by A1, which is the lowest one followed by 14% attained by A2 compared to 21% registered by A0 after one year of exposure to seawater.
4. The pozzolanic reaction progress of DK in mortar cubes is similarly developed in fresh and seawater curing conditions, consuming the hydration product (Portlandite) and blocking the ions ingress due to pore size refinement.
5. The durability of DK concrete increased with a 7.5% replacement of DK with cement and then started decreasing gradually to 10%.
6. Finally, we can conclude that replacing cement partially with DK improved the resistance of cement constructions against the marine environment.

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References


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