Engineering Properties of Mortar Containing Calcined Local Clay as a Supplementary Cementitious Material

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Abstract. The use of natural and artificial cementitious and pozzolanic materials is gaining importance and become an essential component in today’s cement-based materials. Supplementary cementitious materials are recognized to provide an added value to concrete/mortar both for mechanical and durability performances as well as to their sustainability with reduced environmental impacts of the construction industry. Developing locally produced natural pozzolans is vital in the efforts towards enhancing the construction industry’s sustainability. Locally extracted raw soil from Nizwa city (NZS) in Oman was ground, calcined, characterized, and used at 10%, 25%, 35%, and 50% as partial replacement of ordinary Portland cement (OPC) in mortar mix. The blend mortar was assessed with regard to compressive strength and durability properties. The obtained results indicate a slight reduction in the flow of the blended mixes. An insignificant effect of the NZS replacement on the hardened mortar’s density was observed while slightly reduced strength at 1-day and 28-day for some replacement levels. Meanwhile, around a 1% reduction in the porosity and absorption. Blended cement mortar with NZS demonstrated adequate resistance to sulphuric acid and (sulphate + chloride) exposure with lower weight and strength losses compared to the control mortar.

1. Introduction
Portland cement concrete/mortar is the primary building material used in several construction projects due to its affordable cost, availability of components, and properties. The main component of mortar and concrete is the general use ordinary Portland cement (OPC). This concrete and mortar component is not only the most expensive one but also the most pollutant due to the large quantity of carbon dioxide (CO₂) generated during the burning process of the raw materials used. A process that consumes a vast amount of energy, realizing a considerable amount of greenhouse gases (GHG) and raising the final product’s cost (clinker cement). To overcome these economical and environmental issues, and promote sustainability in the concrete industry, several alternative binding materials such pozzolanic and supplementary cementitious materials (SCMs) are broadly used at this time in concrete as a partial replacement of clinker cement. These pozzolanic and SCMs could not only enhance concrete’s sustainability but also mechanical properties and durability performances of concrete/mortar material [1-5]. Pozzolanic and SCMs might be natural or artificial. Although the artificial ones derived from industrial by-products may contribute more to sustainability, the natural ones, including calcined clays may also reduce energy consumption, reducing both the GHG released and the cost. Recent studies by the authors demonstrated that clays procured from identified locations within the Sultanate of Oman have an impressive potential to be used as a cementitious/pozzolanic materials in mortar production as a partial replacement of OPC [5-7]. Although the sultanate of Oman is very rich with natural minerals, it is fully depending on artificial pozzolans that are imported with all the economic and environmental consequences. There is a need to explore the local richness of minerals and develop
new local pozzolans.

2. Materials and experimental methods

2.1. Materials

Natural standard sand with all particles passing sieve No. 30 (600 μm) and retained on sieve No. 100 (150 μm) that fulfils the grading requirements of ASTM C778 [8] was used for the production of hydraulic cement mortar. The sand used has a water absorption and specific gravity of 1.41% and 2.84, respectively. General use ordinary Portland cement (OPC) locally manufactured fulfilling the ASTM C150 [9] Type I cement requirements was used in the production of all mortar mixes. To maintain an acceptable mortar’s workability, polynaphtalene sulphonate superplasticizer (PNS) was used at a fixed amount in the control, 10%, 25%, and 35% blended mortar mixes. The mortar mix with 50% NZS was too stiff and not flowable at all when the same amount of PNS was used. For this reason, the 50%NZS mix was produced with polycarboxylate (PCE) superplasticizer.

Raw clay locally procured from Nizwa province in the Northeast of Oman was the subject to a series of mechanical and thermal treatments to turn it into a pozzolana for cement mortar production. The collected raw clay was ground and sieved on a sieve No. 200 (75 μm). The resulting powder with all particles passing 75 μm was then subjected to burning in an automatic electric furnace at a temperature of 950 °C for a duration of 4 hours and at a rate of 10 °C/min. This burning temperature was selected based on the differential thermal analysis (DTA) and thermogravimetric analysis (TGA) results conducted on a representative sample of the raw clay.

The chemical composition of both Portland cement and the raw clay used to produce a natural pozzolan that is partially replacing cement is given in Table 1.

Table 1. Chemical composition of OPC, and raw NZS clay

| Compounds | OPC (%) | NZS (%) |
|-----------|---------|---------|
| SiO₂      | 21.60   | 40.6    |
| Al₂O₃     | 4.3     | 8.2     |
| Fe₂O₃     | 3.4     | 4.7     |
| CaO       | 62.9    | 36.1    |
| MgO       | 1.7     | 7.1     |
| SO₃       | 2.5     | 0       |
| LOI       | 2.2     | 26      |

2.2. Mixtures proportioning and testing

All mortar mixes were designed using a constant water-to-cement (w/c) ratio of 0.485 and prepared in a standard pan type concrete mixer as per ASTM C305 standard test method [10]. The mortar mix design consists of the following proportions 1:2.75:0.485 (cement:sand:water). Following the mixing operations, the temperature and flow of mortar were measured on a freshly mixed mortar as per ASTM C1437 standard [11]. After casting, mortar specimens were kept in a laboratory environment covered with a plastic sheet and then demolded after 24 h. The specimens were then cured under water till the time of testing. Mortar mixes were tested for hardened density and compressive strength at 1, 7, and 28 days using 50mm-cubes. Porosity and water absorption, thermal conductivity, and ultrasonic pulse velocity were all conducted on 50mm-cubes after 28 days of wet curing. The Durability of mortar was assessed on 50 mm-cubes after 28 days of moist curing in terms of resistance to acid and (sulphate + chloride) under wet and dry conditions. Weight and strength changes were recorded after 12 weeks of exposure. Permeability to chloride ions was assessed through a rapid chloride permeability test (RCPT) using mortar discs measuring 100 × 50 mm.
3. Results and discussion

3.1. Materials characterization
In addition to the thermal treatment done to the raw clay, materials used to produce mortar were exposed to a series of physical, chemical, and microstructural characterizations. The chemical composition (Table. 1) of the NZS clay at raw and calcined states indicate a variety of different chemical compounds. The sum of silico-alumino-ferrite (SiO$_2$ + Al$_2$O$_3$ + Fe$_2$O$_3$) compounds for the NZS clay equals 53.5%. This amount of the three compounds does not meet the requirement of natural pozzolans class N (minimum 70%) as per ASTM C618 [12], but it meets the requirements for class C (minimum 50%) and more than 18% of Calcium oxide (CaO). This class is described as having some pozzolanic properties in addition to the cementing properties. The XRD pattern of the calcined NZS clay at 950 °C is shown in Figure 1. Although the pattern presents some sharp peaks, mainly of quartz, but mostly it shows a high degree of amorphousness. The SEM images showed that the clay particles are mostly angular and irregular shape, as shown in Figure 2.

![Figure 1. XRD pattern of NZS clay calcined at 950 °C.](image)

![Figure 2. SEM micrograph of NZS clay powder.](image)

3.2. Mortar’s flowability
All mortar mixes were assessed in terms of flowability using a flow table. The results are shown in Figure 3. The mortar's flow reduces at a constant superplasticizer content and when partially replacing OPC with the calcined ground clay pozzolan. The higher the replacement amount of OPC by the calcined NZS clay, the lower the mortar's flow. Up to 25% replacement level, the reduction in flow is slightly more than a half compared to the control mix while at 35% the reduction reached 66%.
Meanwhile, replacing 50% of OPC by the NZS calcined clay has resulted in a non-flowable stiff mix with 0% flow. As such, the 50% NZS mix was produced with polycarboxylate instead of polynaphtalene, which led to an acceptable flow that is very close to the flow of the control mixture. The observed decrease in the mortar’s flowability when OPC is partially replaced with NZS is due to the intrinsic properties of the clay. As mentioned above and shown in Figure 2, the clay particles have an angular and irregular shape and rough surface, which contributes to reducing the flowability of the mortar. The absorptive and adsorptive nature of the clay have also accentuated the workability reduction of the blended cement mortar.

![Figure 3. Effect of NZS proportions on the mortar’s flow.](image)

### 3.3. Hardened density and Compressive strength

The hardened density and the compressive strength of the control and blended mortar mixes was measured at different ages 1, 7, and 28 days of moist curing, and the results are displayed in Figures 4 and 5, respectively. At all testing ages, the partial substitution of OPC by the NZS clay pozzolan did not significantly impact the hardened density of the mortar. Meanwhile, only minor reduction in the compressive strength of mortar was observed at early-age (1 day) when NZS replaces OPC up to 35%. Large replacement level up to 50% has resulted in a significant early-age (1 day) strength reduction, but the later age (7 and 28 days) strength was very similar to the control mix. Although the 7-day strength was nearly unaffected by the presence of NZS as a partial substitution (10% to 50%) of OPC, the 28-day strength suffered a certain reduction at replacement levels of 10, 25, and 35%. Overall, a minor negative impact on strength was observed when replacing part of the OPC with this NZS calcined clay pozzolana. Long-term strength is expected to develop certain enhancement as the calcined clay reacts slowly over time.
Porosity is one of the main properties that significantly affects mortar and concrete durability performances. Figures 6 and 7 show the effect of using NZS calcined clay pozzolan on mortar porosity and water absorption. The results showed that up to 35% replacement level, a slight drop in the porosity was recorded due to the slight improvement in the hardened density (Figure 4). In fact, the pozzolanic reaction produces additional C-S-H gel that not only refines the pore network but also reduces the total porosity of the mortar. On the other hand, the water absorption results showed a good agreement with the porosity results for the 10%NZS mix with an important reduction in the absorption capacity. The other mixes showed a certain discrepancy between the porosity results and the corresponding absorption. This might be due to the factor of intrinsic water absorption of the clay particles themselves.
3.5. Ultrasonic pulse velocity (UPV)

Ultrasonic pulse velocity technique is considered as a non-destructive method that could qualitatively assess the mortar. The UPV values for all mixes studied are shown in Figure 8. The results indicate that introducing various proportions of NZS calcined clay as a partial replacement of OPC did not affect the UPV values of the mortar mixes investigated. Although a very slight increase in the UPV values was recorded but the indication that this pozzolana does not negatively impact mortar quality. The UPV values are a qualitative indicator of the presence of defects, cracks, and pores in the mortar samples. The blended mortar mixes showed a similar even slightly higher UPV values than the control mortar.
Figure 8. Effect of NZS proportions on the UPV values of mortar.

3.6. Chloride ions permeability
The chloride ions permeability of different mortar mixes was assessed after four months of wet curing using the rapid chloride permeability test (RCPT), and the obtained data are shown in Figure 9.

Figure 9. Effect of NZS proportions on the total charge passed of mortar.

The inclusion of various proportions of the NZS calcined clay up to 25% has increased the chloride permeability of blended mortar. At 35% replacement level, the blended mortar achieved a similar chloride permeability as the control mix. However, a large increase (up to 50%) of the NZS pozzolana replacing OPC has resulted in an important decrease of the chloride permeability. The obtained results indicate that the low substitution level of NZS (10% & 25%) induced a negative impact on the mortar’s chloride impermeability, while the high replacement level (50%) exhibited a large improvement in the mortar’s chloride impermeability. This could be explained by the slow and low reactivity of this natural
pozzolana (NZS). The contribution of this natural pozzolana both in strength enhancement and permeability to chloride reduction is more expected at longer term than at earlier ages.

3.7. Chloride and sulphate attack, and acid attack
Mortar exposure to aggressive environment agents such as chloride ions and sulphates may lead to progressive deterioration of the structural element. To assess the resistance of blended mortar when exposed to marine environment, mortar specimens were exposed to a combination of 5% of Na\textsubscript{2}SO\textsubscript{4} and 5% of NaCl solution. The tested specimens were stored in the combined solution for one week, and the next week were exposed to a dry environment for a total period of 12 weeks. Similarly, the mortar specimens were exposed to a solution with 5% sulfuric acid (H\textsubscript{2}SO\textsubscript{4}) for 12 weeks.

The results displayed in Figure 10 show the weight change resulting from possible degradation of the mortar. It can be seen that exposing both control and modified mortar specimens to the combined solution (5% of Na\textsubscript{2}SO\textsubscript{4} + 5% of NaCl) has led to a weight increase of around 2% compared to the water-cured specimens. However, the exposure of mortar specimens to 5% sulfuric acid solution has resulted in a large loss of weight of around 3% for the control mix, while the blended mixes with 25% and 35% NZS clay have exhibited an increase in the weight of about 1.7% and 1%, respectively. The 10% NZS mix seems to have the best performance, with only a negligible weight loss of around 0.1%. The increase in weight of mortar specimen exposed to either sulphate or sulfuric acid solutions is due to the formation of gypsum resulting from the reaction of sulphate (Na\textsubscript{2}SO\textsubscript{4}) or H\textsubscript{2}SO\textsubscript{4} with portlandite Ca(OH)\textsubscript{2}. Meanwhile, the weight loss of the control mix when it is exposed to sulfuric acid is a result of mass degradation due to the leaching of Ca(OH)\textsubscript{2}. These results indicate the good resistance acid of blended cement with NZS pozzolan compared to the plain cement mortar.

Similarly to the weight change, compressive strength was tested at the end of the exposure period and compared to the strength of water cured samples. The results displayed in Figure 11 indicate some decrease in the compressive strength of the submerged samples compared to that of the control mix. The strength drop for mortar samples exposed to sulfuric acid was more than in the case of (sulphate + chloride) solution. Nevertheless, the blended mortar showed less strength reduction compared to a large reduction recorded in the control mix (around 48%). This performance proves the contribution of the NZS pozzolan in the improvement of the resistance to acid compared to the plain cement mortar.
3.8. Thermal conductivity
The effect of the introduction of NZS pozzolan as a partial substitute of OPC in mortar on the thermal conductivity is schematized in Figure 12.

The results indicate no effect to a slight increase in the thermal conductivity of mortar when partially substituting OPC by various contents of NZS. This increase in the thermal conductivity may due to the reduction in porosity, as shown in Figure 6, and the enhanced compactness of mortar. The lower the porosity of mortar, the higher the thermal conductivity. Although the pure natural pozzolana is known to have lower thermal conductivity than the plain cement, the presence of this natural pozzolana (NZS) in the cement mortar enhanced its density and compactness and hence, increased its thermal conductivity.

4. Conclusion
Based on the obtained experimental results, the mains conclusions are given below:

- The investigated clay has both cementitious and pozzolanic properties based on its chemical composition.
• Calcination at 950 C seems to reduce crystallinity of the clay but did not transform completely the clay into an amorphous powder.
• The inclusion of calcined NZS clay reduced the flowability of mortar.
• Although the hardened density, the 28-day UPV values, and thermal conductivity were unaffected, the 1-day compressive strength slightly reduced while the 7-day strength was similar to the control or slightly enhanced depending on the NZS content.
• Porosity and water absorption were slightly reduced when adding NZS pozzolan.
• Although most of the mortar mixes are ranked as moderate chloride permeability, the resistance to chloride permeability slightly reduced with 10%NZS and 25%NZS mixes but improved with 50%NZS compared to the control mix.
• Blended mortar mixes with NZS showed a better resistance to sulphate and acid with less weight and strength losses compared to the plain mortar.

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