Effect of volcanic ash pozzolan or limestone replacement on hydration of Portland cement

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abstract

The replacement of Portland cement (PC) with either supplementary cementitious material (SCM) or fillers, such as natural pozzolans (NP) or limestone powder (LP) respectively, is known to affect the chemical properties of concrete, thus influencing its fresh and hardened properties. This study investigated the effects of volcanic ash NP or LP on setting time, normal consistency, hydration, and strength properties of cement paste and mortar while following the chemical changes that were a direct result of the substitution. While both materials were found to increase water demand, NP at 30% and 50% replacement levels increased setting time whereas LP at 15% replacement level insignificantly influenced the property. At a proportion lower than their replacement levels, both materials reduced the ultimate compressive strength of mortar. Thermal, chemical and microstructural analyses confirmed the participatory roles of NP and LP in controlling reaction kinetics and forming new hydration products.

1. Introduction

About 2000 years ago, the Romans produced concrete from volcanic ash and hydrated lime, which still remains intact today [1]. The extraordinary longevity of Roman concrete is attributed to an elevated curing temperature, mineralizing effects of seawater, and alkali- and alumina-rich volcanic ash [2]. Unfortunately, the technology was lost with the downfall of the Roman Empire. In 1824, Portland cement (PC) of calcined lime and clay was patented [3], and that marked the technological and commercial commencement of modern cement. Ever since the use of concrete with PC as the main binder has been prevalent, and it is undeniable that concrete has become the main building block of our modern society. However, its extensive use and pervasiveness have also raised concerns about its impact on the environment. One major concern is that production of cement is not sustainable. PC is energy- and emissions-intensive to produce with an energy requirement of 4 GJ/tonne of cement and an average carbon intensity of 900 kg CO₂/tonne [4,5]. In 2016 when the annual global production of blended and unblended cement reached 4.1 billion tonnes [6], the cement industry was estimated to emit approximately 3.0 billion tonnes of CO₂ (assumed 80% clinker), representing 6% of the 49.3 billion tonne total anthropogenic CO₂ emissions [7]. Billions of tonnes of water and aggregates are also required to produce concrete to satisfy the need of our society [8], thus aggravating the consumption of natural resources and associated adverse impacts on the ecology. Notably, although PC production has similar or even better environmental impacts per unit weight relative to steel production [9,10], the high recycling rate of more than 97% for structural steel [11] makes concrete inferior on a complete life cycle basis. Hence, immediate actions need to be taken by technology,
business, and government stakeholders to ensure long-term sustainability for the construction industry.

With the highest impact intensity per unit volume of concrete, cement is logically a priority to effectively resolve the environmental issues of concrete. Over the past years, various efforts to reduce CO₂ emissions from cement related activities have been undertaken within the research and business communities through: (i) partial replacement of cement by supplementary cementitious materials (SCM), such as ground granulated furnace slag (GGBS) and fly ash (FA), (ii) alternative binding materials with smaller environmental footprints, (iii) improved energy efficiency in production, and (iv) renewable energy sources [12–17]. However, due to their nascent state, high cost or lack of governing regulations, implementation of alternative binding materials in place of PC will be a challenge in the short term. The use of SCMs as partial PC replacement, on the other hand, has been favored and become a common practice in construction due to its benefits in CO₂ and cost reduction, long-term strength and durability enhancement [18–20]. Yet, as the world transitions to cleaner energy sources [21], the availability of suitable SCMs is not expected to meet the ever-increasing demand for concrete and new alternatives are needed.

With vast available resources [22], limestone powder (LP) and natural pozzolan (NP) represent attractive potential options for PC replacement. LP up to 30% as PC replacement has been shown to produce concrete of good mechanical performance [23]. LP was also revealed to accelerate the reaction rate of PC [24]. When used with fly ash as PC replacement, LP accelerated and amplified the early-age hydration reactions by serving as nucleation sites, thus mitigating delayed setting times induced by high-volume fly ash [25]. Likewise, incorporation of 15% NP was demonstrated to produce concrete of similar properties as compared to reference mixes with 100% PC or 20% fly ash as cement replacement [26]. High-volume basaltic ash as NP was incorporated into concrete to achieve comparable strength and durability properties to those of reference mixes [27]. Recently, finely-ground LP and NP with a combined replacement level of 45% was formulated for self-compacting concrete with superior long-term strength and permeability coefficients to composites with 100% PC [5].

Initially, LP was generally considered as an inert filler [23]. Yet, it was demonstrated that calcium carboaluminate hydrates as hemicarbonate and monocarbonate are formed in the presence of LP as cement replacement [23,28–30]. Carboaluminate hydrates are products from the reaction between various calcium aluminate hydrates of cement hydration and calcium carbonates of limestone [28]. The two main carboaluminate hydrates are hemicarbonate (C₃A·0.5CaCO₃·12H₂O) with one half CO₃²⁻ anion and monocarbonate (C₃A·CaCO₃·11H₂O) [30]. Both exhibit a highly variable composition of interlayer water and ions [28]. Similarly, NP participates in reactions to form additional C-S-H that is coexistent with C-A-S-H, which leads to enhanced matrix densification [31,32].

In this laboratory study, the effects of LP and NP on reaction kinetics, reaction products, fresh and hardened properties were comprehensively investigated. PC was replaced with 15 wt% of LP or 30 and 50 wt % of basaltic volcanic ash as NP. Experimental techniques including X-ray diffraction (XRD), isothermal calorimetry, thermogravimetric (TGA) and differential thermal analysis (DTA), and scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS) were implemented. Integrating these complementary techniques helped the understanding of the fresh and mechanical performance of the mortar samples and brought new insight into the effects of both LP and NP on the hydration of PC. The ultimate pursuit of the research is the ability to produce highly durable concrete with minimal environmental impact, similar to what the Romans did thousands of years ago.

### 2. Materials and methods

#### 2.1. Materials

PC, basaltic ash as an NP and LP were used in powder form to produce blended cementitious material for the production of mortar and cement paste. NP was obtained by finely grinding volcanic ash from Jabal Kadaha in Harrat Rahat, Saudi Arabia. The mean particle diameters of PC, NP, and LP as determined by laser granulometry (Malvern Mastersizer) are 15 μm, 17 μm, and 19 μm, respectively, and are summarized in Table 1. Corresponding size distributions are also given in Fig. 1. A recent work showed that replacing cement by smaller sized volcanic ash (6 μm) enhanced microstructural development of the matrix through the formation of secondary C-S-H and calcite, thus leading to a higher compressive strength [32]. In this study, the mean particle size of NP was chosen as 17 μm which was similar to the ones of PC and LP to investigate the effects of fine materials on the reaction mechanism and chemico-mechanical properties of cement.

The chemical compositions of PC, NP, and LP determined by X-Ray Fluorescence (XRF) are shown in Table 2. The sum of silicon oxide (SiO₂), aluminum oxide (Al₂O₃), and ferric oxide (Fe₂O₃) for the raw NP is 73.4% (greater than 70% limit), indicating that the material is a Class N-type ash in accordance with ASTM C618 [33].

XRD measurements on the raw materials were performed using a PANalytical X’Pert PRO Materials Research Diffractometer. The procedures for sample preparation and diffractometer configuration are given in Section 2.2.2.3. XRD patterns taken at ambient conditions and schematic diagrams for relevant phases are presented in Fig. 2 for NP and LP on the same intensity scales. The NP was rich in anorthite.

#### Table 1

<table>
<thead>
<tr>
<th>Material</th>
<th>Mean (μm)</th>
<th>Median (μm)</th>
<th>Mode (μm)</th>
</tr>
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<tbody>
<tr>
<td>PC</td>
<td>14.8</td>
<td>21.7</td>
<td>18.5</td>
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<tr>
<td>NP</td>
<td>17.4</td>
<td>13.8</td>
<td>18.6</td>
</tr>
<tr>
<td>LP</td>
<td>18.9</td>
<td>15.5</td>
<td>14.2</td>
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#### Table 2

<table>
<thead>
<tr>
<th>Oxide</th>
<th>PC (%)</th>
<th>NP (%)</th>
<th>LP (%)</th>
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</thead>
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<tr>
<td>SiO₂</td>
<td>20.44</td>
<td>46.48</td>
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</tr>
<tr>
<td>Al₂O₃</td>
<td>3.97</td>
<td>14.74</td>
<td>0.50</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>4.07</td>
<td>12.16</td>
<td>0.12</td>
</tr>
<tr>
<td>CaO</td>
<td>62.90</td>
<td>8.78</td>
<td>47.40</td>
</tr>
<tr>
<td>MgO</td>
<td>2.42</td>
<td>8.73</td>
<td>6.80</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.37</td>
<td>3.39</td>
<td>–</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.43</td>
<td>1.27</td>
<td>–</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.16</td>
<td>0.63</td>
<td>–</td>
</tr>
<tr>
<td>TiO₂</td>
<td>2.33</td>
<td>0.01</td>
<td>–</td>
</tr>
<tr>
<td>MnO</td>
<td>0.32</td>
<td>0.19</td>
<td>–</td>
</tr>
<tr>
<td>LOI</td>
<td>4.69</td>
<td>1.32</td>
<td>44.48</td>
</tr>
</tbody>
</table>
Composition of binders in mortar specimens.

2.2 Methods

2.2.1 Mortar samples

2.2.1.1 Mortar mixture proportions. Mortar cubes (40 × 40 × 40 mm³) with a binder–sand–water proportions of 1/3/0.5 by weight were prepared in accordance with ASTM C305-12 [34]. The percentages of cement replacement levels by weight were denoted and mixed to normal consistency by adjusting the amount of added water, and the final time of setting in accordance with ASTM C191 [36]. To this end, the pastes whose binder compositions described in Table 3 were proportioned and mixed to normal consistency by adjusting the amount of added water, and thereafter the Vicat needle penetration test was conducted to obtain the initial and the final time of setting in accordance with ASTM C191 [36].

2.2.1.2 Normal consistency and setting time. The reference and blended cement mixtures were tested for normal consistency in accordance with ASTM C187 [35]. To this end, the pastes whose binder compositions described in Table 3 were proportioned and mixed to normal consistency by adjusting the amount of added water, and thereafter the Vicat needle penetration test was conducted to obtain the initial and the final time of setting in accordance with ASTM C191 [36].

2.2.1.3 Compressive strength test. The compressive strength of the samples was determined on three mortar prisms at 1, 3, 7, 28, and 56 days according to ASTM C109/C19M [37]. The reported strength results are the average of three mortar cubes (40 mm³) with a water/binder ratio (w/cm) of 0.50 and compositions as described in Table 3. All pastes were mixed in a vacuum mixer (Twister evolution) at 450 rpm. The first step involved dry mixing of all the powder ingredients for 30 s. In the next step, 90% of the water was added and mixed for another 1.5 min. Lastly, the rest of the water was added and the pastes were mixed further for 3 min.

2.2.2 Cement pastes

2.2.2.1 Mixture proportions of cement pastes. To study the time-dependent hydration process, XRD, TGA, isothermal calorimetry (IC) and SEM were performed on the selected specimens at 7, 28, and 91 days. To isolate the interference of aggregate process, XRD, TGA, and SEM were performed on the selected specimens at 7, 28, and 91 days. To isolate the interference of aggregate ingredients, pastes were adopted in the study and proportions of powder materials were based on Table 3. Accordingly, sample annotations were retained. It is also noted that 50P–50NP was tested only for isothermal calorimetry. All the powder materials were homogenized by dry mixing.

2.2.2.2 Mixing and casting of cement pastes. A water-binder ratio (w/cm) of 0.50 was adopted for all samples. The paste samples were prepared by manually mixing distilled-water with the homogenized powders, then casting in plastic cylindrical molds measuring 62.54 × 2.54 cm, and storing at 23 ± 2 °C until testing. After hydration for 24 h, vacuum-dried, and kept under carbonation-free conditions until testing with XRD, TGA, and SEM.

2.2.2.3 X-ray powder diffraction (XRD). XRD spectra of both raw materials and hydrated cement paste specimens were obtained using a PANalytical X’pert PRO with X’celerator™ position sensitive detector. The finely-ground samples of cement paste were loaded into metal sample holders and placed into the diffractometer. XRD measurements were operated with Cu Kα radiation (wavelength of 1.5405 Å) at 40 mA and 40 kV. XRD acquisition was carried out in a continuous scan mode with 2θ range of 5 and 65°, a step width of 0.0170° (i.e. 3527 steps) and a counting time of 4.08 s, corresponding to a total acquisition time of 4 h. PANalytical X’pert HighScore Plus was used to analyze the data.

2.2.2.4 Isothermal calorimetry (IC). The hydration kinetics of the cement pastes were investigated by calorimetry. A series of cement pastes was prepared with w/cm of 0.50 and compositions as described in Table 3. All pastes were mixed in a vacuum mixer (Twister evolution) at 450 rpm. The first step involved dry mixing of all the powder ingredients for 30 s. In the next step, 90% of the water was added and mixed for another 1.5 min. Lastly, the rest of the water was added and the pastes were mixed further for 3 min.

The heat flow was measured with a Thermometric TAM Air conduction calorimeter, capable of eight parallel measurements in eight separate measuring cells. Approximately 5.4 g of freshly mixed paste were weighed into glass vials with 25.4 mm internal diameters, corresponding to about a 5-mm thick paste layer. The glass vials were sealed and placed into the calorimeter and the heat flow was measured for approximately 162 h. During the experiment, isothermal conditions (20 ± 0.02 °C) were maintained in the measuring cells. The hydration heat flow and the cumulative hydration heat, normalized to the PC weight in the samples, are shown in the resulting plots.

2.2.2.5 Thermogravimetric analysis (TGA). TGA of the pastes described in Table 3 was used to determine the amount of calcium hydroxide (CH) and the presence of other phases in the cement pastes, and to quantify the level of pozzolanic reactions. With a high content of Al₂O₃ and MgO in NP, the pozzolanic reactions refer to the formation of secondary C-S-H, C-A-S-H, magnesium silicate hydrate (M-S-H) and even crystalline brucite Mg(OH)₂ as the results of interaction between the NP particles and cement reaction products [32]. The use of CH to gauge the level of pozzolanic reactions will hence be limited to the formation of C-S-H and C-A-S-H, and not magnesium-based products. Eq. (1) was used to calculate the amount of bound water (H) in the paste where w₂05 and w₅50 are the weights of isopropanol-dry sample at 40 °C and 550 °C, respectively. The bound water indicates decomposition of hydrates such as Aft and AFt phases, and C-S-H in cement paste [38]. The amounts of portlandite and calcite were found by the weight losses between 400 °C and 550 °C, and 600 °C and 900 °C, respectively. A tangent method was used to quantify the weight changes [39].

\[ H = \frac{W_{205} - W_{550}}{W_{550}} \] (1)

The ground samples of 15 ± 1 mg were placed in an alumina crucible. TGA and DTA were subsequently performed with an SDT Q600 under nitrogen gas at a flow rate of 100 ml/min. The temperature was ramped from 30 to 1000 °C at a heating rate of 20 °C/min.

2.2.2.6 Scanning electron microscope (SEM). SEM with EDS was performed on 200 μm thick slices of hardened paste, dried via solvent exchange using isopropanol before being resin impregnated with EPO-TEK 301-2 from Epoxy Technology. The resin-impregnated pastes were then ground and polished until level and smooth using a Dayton Mico –3 μm and 1/4 μm before being carbon coated to a thickness of approximately 15 nm to prevent charging under the SEM beam. The anhydrous material was placed on carbon tape for the same reason. An EDAX TSL energy dispersive x-ray spectrometer on the Zeiss EVOMA10 Scanning Electron Microscope was operated with a beam energy of 15 keV, beam current of 850 pA, and counting time of 10 s with 3500 counts per second, reported as relative atomic concentrations. The working distance was set between 6 and 9.5 mm for backscattered (BSE) imaging and 10–15 mm for EDS analysis for signal optimization. For microstructural morphology, magnifications ranging from 2 k to 20 k on BSE–SEM images were chosen.

Table 3

<table>
<thead>
<tr>
<th>Composition of binders in mortar specimens.</th>
<th>Proportions (by wt)</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PC</td>
<td>NP</td>
<td>LP</td>
<td>Sand</td>
<td>Water</td>
</tr>
<tr>
<td>100PC</td>
<td>1.00</td>
<td>–</td>
<td>–</td>
<td>3</td>
<td>0.5</td>
</tr>
<tr>
<td>85PC–15LP</td>
<td>0.85</td>
<td>–</td>
<td>0.15</td>
<td>3</td>
<td>0.5</td>
</tr>
<tr>
<td>70PC–30NP</td>
<td>0.70</td>
<td>0.30</td>
<td>–</td>
<td>3</td>
<td>0.5</td>
</tr>
<tr>
<td>50PC–50NP</td>
<td>0.50</td>
<td>0.50</td>
<td>–</td>
<td>3</td>
<td>0.5</td>
</tr>
</tbody>
</table>
3. Results and discussion

3.1. Mortar samples

3.1.1. Normal consistency and setting time

The water to cementitious material ratios needed for normal consistency are shown in Fig. 3 along with initial and final times of setting of the cementitious mixtures. The water demand of 70PC–30NP and 50PC–50NP was 6% and 10% higher than that of the control 100PC, respectively. This highlighted that the inclusion of NP in the blends increased the water requirement in the cement paste. In 85PC–15LP, however, the 15% LP replacement of PC slightly increased the water demand of mixture.

The results shown in Fig. 3 demonstrate that the variation in mixture proportions of NP had a significant effect on the initial and final times of setting. The blends of binary cementitious material with NP had longer times of setting as compared to the control specimen. With an increase in NP content, both initial and final times of setting increased in binary mixtures. The final times of setting for 70PC–30NP and 50PC–50NP were 22% and 57% longer than that of 100PC, respectively. Lastly, the addition of 15% LP did not have a significant influence on the times of setting.

3.1.2. Compressive strength of mortar specimens

The results for the compressive strengths of mortar specimens incorporating LP or NP at different ages are shown in Fig. 4. The control sample 100PC shows greater strength as compared to 85PC–15LP whose strength at 1 day and 3 days was 40% and 28%, respectively, lower than that of 100PC. At 7 days, the strength of 85PC–15LP was just 2% lower. This is a favorable early age strength development, but 85PC–15LP produced 15% lower strength than 100PC mixture at 91 days of hydration.

All proportions of NP in the mortars had adverse effects on the strength evolution of the mortars at relatively early ages of curing. When compared to the control 100PC mortar, the binary 70PC–30NP mortar produced significantly lower strength through 91 days; whereas, it produced only 6% lower strength at 91 days as the strength development continued. As expected, the binary 50PC–50NP showed lower strength than the control 100PC and the binary 70PC–30NP at all testing ages despite its upward strength development rate. While 50% replacement of cement by NP (50PC–50NP) produced a mixture with lower strength than the binary 85PC–15LP through 91 days of hydration, 30% NP replacement led to a higher strength than 15% LP replacement by 91 days of hydration. This phenomenon can be attributed to the significant-strength recovery due to pozzolanic reactions of 30% NP replacement after 28 days of hydration [5]. After 28 days, the strength reduction was observed to be generally less than the replacement levels of LP and NP, indicating their beneficial effects on cement hydration reactions.

3.2. Cement paste samples

3.2.1. X-ray powder diffraction (XRD)

XRD patterns with the same intensity scale of 100PC, 85PC–15LP and 70PC–30NP at different ages of hydration are shown in Fig. 5. It is observed that in all samples, belite and ferrite as anhydrous phases were still present after 91 days of hydration. Calcite was also present in 85PC–15LP at 91 days. The hydration products of 100PC were ettringite, monosulfate, and portlandite, while the addition of 15% LP produced hemihydrate and monocarbonate in 85PC–15LP. In 100PC, the ettringite peak, visible at 7 days, had significantly declined by 28 days and disappeared by 91 days, at which time monosulfate peaks became clearly visible. However, in agreement with prior research [40], the amount of ettringite did not decline, and monosulfate was not observed over time in 85PC–15LP. The underlying reason for the disappearance of ettringite and appearance of monosulfate in 100PC over time is that at the time of depletion of calcium sulfate and in the absence of calcite, the ettringite will begin to dissolve and react with calcium, aluminum and iron ions from the dissolution of phases such as aluminates, ferrite, and portlandite to form monosulfate [29].

Portlandite was present in both 100PC and 85PC–15LP samples, and the peaks of portlandite increased at later ages due to the hydration reaction of silicates [41]. Fig. 5b shows that carboaluminate hydrates were precipitated at 7 days (Hc at 12.2° and 25.2° 2ϴ; d-spacing (d) = 8.4 Å and 4.1 Å, and Mc at 13.6° and 27.3° 2ϴ; d = 7.5 Å and 3.8 Å) in 85PC–15LP, indicating that the calcite in the composition led to its reaction with aluminate and ferrite to form hemihydrate and monocarbonate after all gypsum was consumed [29], thus hindering the decomposition of ettringite to form monosulfate. However, hemihydrate disappeared by 91 days of hydration while monocarbonate peaks increased prominently by 91 days due to its higher thermodynamic stability [30].

In comparison, Fig. 5c reveals that monosulfate was observed in 70PC–30NP at 28 days and 91 days. This shows that ettringite became unstable sometime after 7 days of hydration in binary blends of 70% PC and 30% NP, and the unreacted aluminates, ferrites, and NP reacted with ettringite to produce monosulfate. While monosulfate was first observed at 91 days in 100PC, it was detected at 28 days in the sample 70PC–30NP. The earlier detection of monosulfate in 70PC–30NP can be attributed to an increased amount of aluminum available in the system. After calcium sulfate depletion,
Fig. 5. Phase composition observed by XRD in a hydrated cement paste at 7, 28 and 91 days a) 100PC b) 85PC–15LP c) 70PC–30NP. The main peaks of ettringite (Ett), monosulfate (Ms), portlandite (CH), hemicarbonate (Hc), monocarbonate (Mc), muscovite (M), quartz (Q), calcite (Cc), dolomite (D), forsterite (F), diopside (Di) and anorthite (A) are designated. The XRD measurements are plotted with the same intensity scales.
additional aluminum coming into solution from aluminite, ferrite, or NP dissolution will produce aluminum-rich and sulfate-poor hydrates, such as C-A-S-H and monosulfate. Eq. (2) shows the conversion of ettringite to monosulfate in the presence of calcium hydroxide and aluminum oxide [29,42,43].

\[ \text{C}_4\text{A}_2\text{S}_3\text{H}_{12} + 2\text{A} + 6\text{CH} \rightarrow 3\text{C}_4\text{A}_2\text{S}_3\text{H}_{12} + 2\text{H} \]  

(2)

3.2.2. Isothermal calorimetry (IC)

Fig. 6 shows the heat flow normalized to PC and the cumulative heat flow normalized to both PC and total binder of blended cement containing LP or NP. The heat flow in Fig. 6a reveals that the induction period, which is the period after the first release of heat once the cement came into contact with water, was not changed when PC was substituted by LP at 15% (85PC–15LP); however, the slope of the heat evolution curve was slightly steeper during the acceleration period as compared to 100PC. Between 10 h and 20 h, the heat flow graphs of Fig. 6a exhibit two peaks which will be called the main peak (or first peak) and the second peak and are associated with the reaction of silicate and aluminates phases, respectively. The second peak was visible only as a shoulder for 100PC in Fig. 6a. Both peaks of 85PC–15LP were increased as indicated by amplitifying and broadening of peaks and slightly accelerated as indicated by the peaks being shifted to the left-hand side with respect to 100PC. Appropriately, the cumulative heat per mass of PC was higher for 85PC–15LP than 100PC at 160 hr (Fig. 6b). The cause of acceleration and amplification of the heat flow when 15% limestone powder was blended with PC is attributed to (i) the filler effect created by the limestone powder, which means that there were more spaces for the reaction of PC at the same water to binder ratio, assuming that the limestone powder did not produce more hydration products, but instead created more nucleation sites for the hydration products of PC [19], (ii) the higher water to Portland cement ratio. It was also observed that the second peak of 85PC–15LP was higher than the main peak of 85PC–15LP, while in contrast the main peak of 100PC was higher than its second peak. This phenomenon can be attributed to the filler effect of limestone powder and the participation of aluminates phases [19,44] in chemical reactions resulting in the formation of carboaluminates hydrates in the mix of 85PC–15LP [24,25,29]. Fig. 6c shows that the cumulative heat per mass of cementing material was lower for 85PC–15LP than for 100PC at 160 hr due to the dilution effect of limestone powder on the clinker. Even so, the cumulative heat of blended cement (85PC–15LP) per gram of binder at 24 hr was about 91% of the cumulative heat of 100PC.

Despite a slight delay in induction period when PC was substituted by 30% and 50% natural pozzolan (70PC–30NP and 50PC–50NP), the slope of heat evolution was steeper during the acceleration period as compared to the control mix 100PC. The second peaks of 70PC–30NP and 50PC–50NP were higher than their respective first main peaks. The peaks were more amplified and slightly accelerated as compared to the ones of 100PC. Consequently, the cumulative heat flow per mass of PC at 160 hr was higher for 70PC–30NP and 50PC–50NP than 100PC as shown in Fig. 6b. The observed acceleration period, the peaks and the cumulative heat per unit PC were increased as the replacement of PC with NP was increased from 30% to 50%. The data suggest that the replacement of PC by finely-ground natural pozzolan promoted the filler effect and nucleation sites at early ages and thus enhanced acceleration period and heat flow. Other researchers showed that the inclusion of fine natural pozzolan (14.5 μm) reduced self-diffusion of water as a result of the formation of multiphase cementitious gels (C–S–H and C-A-S-H) [45] and with an even finer particle size (6.4 μm), the pozzolan could potentially react with PC and thus enhance gel formation as revealed by an increase in surface area observed with X-ray scattering [32]. Nevertheless, the same studies also indicated that at replacement levels greater than 30% and with a larger particle size (17.14 μm), the pozzolan was not observed to participate in the hydration or pozzolanic process during an early stage of reaction. This leads to a conclusion that the filler effect dominated the acceleration period and the corresponding heat flow of this study. This is in agreement with a previous study by Kocaba [39]. The cumulative heat per mass of binder, however, was lower as replacement of PC with NP increased due to the dilution of PC clinker. The cumulative heat emitted per gram of binder during the first 24 hr was about 77% for 70PC–30NP and 60% for 50PC–50NP of the cumulative heat of hydration of 100PC (Table 4).

![Fig. 6. Isothermal calorimetry of cement blends containing PC and LP/NP](image-url)
3.2.3. Thermogravimetric analysis (TGA)

TGA was performed on the cement pastes at 7, 28, and 91 days to determine the effect of PC replacement with LP or NP on the contents of bound water (H), calcium hydroxide (CH) and calcium carbonate (Cc). Fig. 7 shows the TGA results of all blended cement pastes at 7 days (Fig. 7a), 28 days (Fig. 7b), and 91 days (Fig. 7c) of hydration. It is observed that 100PC and 70PC-30NP exhibited similar mass loss curves with changes in slopes at 400 °C and 550 °C, and 600 °C and 900 °C attributable to the decomposition of portlandite and calcite, respectively. At the final scanning temperature, 100PC showed higher total mass losses due to a higher content of bound water (H) in the system. A more prominent mass loss at 600 °C and 900 °C occurred for 85PC-15LP due to a higher content of calcite in the matrix. The results for H along with CH and Cc are summarized in Figs. 8–10, respectively.

Fig. 8 shows that 100PC had the highest amount of bound water yet the lowest amount of normalized bound water as compared to the blended cement pastes at all corresponding tested ages. Replacing 15% of PC with LP or 30% with NP resulted in an increase in the amount of bound water per PC (Fig. 8b), which is in agreement with the results of other studies [29,38,46]. The increase in bound water per PC can be attributed to the filler effect and more nucleation sites accelerating the hydration of PC (as previously discussed) and additional hydration reactions like the formation of hemicarbonate and monocarbonate in 85PC–15LP, pozzolanic reactions in 70PC–30NP. In addition, having more normalized bound water in 70PC–30NP as compared to 85PC–15LP indicates that the NP is better able to participate in hydration reactions than LP, which is expected since PC has a limited amount of aluminum to produce carboaluminate phases yet relatively more calcium carbonate. The thermogravimetric analysis (TGA) results for all blended cement pastes are summarized in Table 4.

Table 4
Cumulative heat per gram of binder during the first 24 h and normalized cumulative heat to PC100.

<table>
<thead>
<tr>
<th></th>
<th>Cumulative heat (J/g binder)</th>
<th>Normalized cumulative heat (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100PC</td>
<td>199.2</td>
<td>100.0</td>
</tr>
<tr>
<td>85PC–15LP</td>
<td>180.5</td>
<td>90.6</td>
</tr>
<tr>
<td>70PC–30NP</td>
<td>152.9</td>
<td>76.7</td>
</tr>
<tr>
<td>50PC–50NP</td>
<td>119.5</td>
<td>60.0</td>
</tr>
</tbody>
</table>

![Fig. 7](image-url) TGA data of blended cement pastes containing LP or NP at (a) 7 days, (b) 28 days (c) 91 days of hydration.

![Fig. 8](image-url) The bound water contents (H) a) per binder b) per PC after 7, 28 and 91 days of hydration.
hydroxide from the reaction of calcium silicates to participate in pozzolanic reactions with NP. Accordingly, 100PC and 85PC–15LP had increasing amounts of calcium hydroxide at each age tested; however, calcium hydroxide decreased from 28 to 91 days in 70PC–30NP. An enhanced incorporation of aluminum into hydration products to form C-A-S-H under the presence of pozzolanic materials [29] could also explain the increase in bound water in 70PC–30NP. The presence of aluminum in C-S-H was shown to increase water uptake of the gel structure [47] possibly due to an increase in zeolitic content (Ca<sup>2+</sup> and water) in the interlayer space [48].

Fig. 9 shows that the amount of CH in the cement pastes 100PC and 85PC–15LP increased with time up to 91 days of hydration. However, replacing 30% of PC with NP resulted in a slight increase in the amount of CH at 28 days of curing yet a decrease at 91 days of curing. The observed reduction in CH confirms the pozzolanic activity of NP with time. The normalized CH content of all binary blended cement pastes containing LP or NP was greater than the level in 100PC at 7 days of hydration. This is because of an increase in nucleation sites and reaction space for PC grains due to filler effects under the presence of mineral admixtures. At later ages, the normalized CH of 85PC–15LP was higher than that of 100PC. However, the CH per PC of binary cement pastes incorporated with 30% NP was similar to the CH level in 100PC at 28 days of curing and became lower at 91 days of hydration. This suggests that the reduction of CH in the binary cement pastes containing 30% replacement is due to the pozzolanic reaction of NP.

The content of Cc calculated from the thermal analysis is given in Fig. 10, and it is revealed that Cc was present in all samples. The samples that did not contain limestone powder in the blended cement pastes had less than 3% of Cc by weight, indicating the existence of no carbonation at all tested ages as the Cc content of the anhydrous cement was 2.84%. The Cc content decreased with time in the cement pastes incorporating LP. The reduction in the Cc content suggests that Cc from limestone was consumed with the reaction of aluminates resulting in the formation of calcium carboaluminates [28,40] which prevents the formation of monosulfate [42].

3.2.4. Scanning electron microscope (SEM)
The paste samples of 100PC and 70PC–30NP were analyzed after 28 days of hydration with SEM/EDS. Three regions of interest (unreacted PC, C-S-H/C-A-S-H, and NP glassy rims and relicts) [5] are presented in both CaO-(Na<sub>2</sub>O + MgO + Al<sub>2</sub>O<sub>3</sub> + Fe<sub>2</sub>O<sub>3</sub>)-SiO<sub>2</sub> and CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> ternary composition diagrams in Fig. 11. Compositional differences exist among the three regions. Unreacted PC has the highest CaO content, while NP glassy rims and relicts have the lowest CaO content (Fig. 11a and b). It should be noted that calcium content of C-S-H/C-A-S-H gels were in the medium range with the value of 0.26–0.72 in the ternary plots, consistent with findings by previous studies [49,50]. This observation could be due to limited interaction between NP and PC at the relatively early age. It is known that reactions between OH<sup>–</sup> ions from PC pore solution and SiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> from NP are time-dependent [39,51]. In addition, as medium calcium C-A-S-H gels are associated with lower porosity than high calcium C-A-S-H gels [31], the lower Ca/Si in C-(A-)S-H could be one of the underlying reasons for enhanced durability against chloride migration of concrete containing 30% NP (70PC–30NP) [27].

As shown in Fig. 11a, the content of silicon and the metal oxides such as Na<sub>2</sub>O, MgO, Al<sub>2</sub>O<sub>3</sub>, and Fe<sub>2</sub>O<sub>3</sub> were found to be much greater in natural pozzolan-integrated samples than the level in 100PC. The SiO<sub>2</sub> and metal oxides concentrations of the C-S-H/C-A-S-H phase are in between the levels found in unreacted PC and NP glassy rims and relicts, confirming the interaction of the neighboring gel-palagonite with the PC pore solution leading to the incorporation of dissolved species in alkali-rich cementitious hydrates that was previously reported by authors of this work [5].

4. Overall discussion
A combination of techniques including normal consistency and setting time test, compressive test, XRD, isothermal calorimetry,
The results presented so far confirm the beneficial role of NP as a PC replacement in influencing physiochemical properties and in enhancing long-term mechanical properties of the matrix with a strength reduction that is less than the replacement levels. Interaction of NP with PC hydration products and the resulting formation of more stable medium-calcium C-(A-)S-H phases could potentially lead to tailoring and design of more durable concrete for construction without a compromise on other required properties. Indeed, finer NP was used as cement replacement and was shown to be involved in early hydration processes [32] and could consequently contribute to early strength development. Nevertheless, as the construction industry is moving toward a more ecological age, the sustainability characteristics of the composite should be assessed. A life-cycle approach adopted by Celik et al. [18] could be implemented in assessing environmental impacts per cubic meter of concrete by taking into account the additional energy used in the production of the fine NP. The technique could be further refined with a normalization of the impacts to both mechanical and durability properties of concrete [52].

5. Conclusions

This work investigated the effects of limestone powder (LP) and basaltic volcanic ash (NP) as partial replacement of Portland cement (PC) on fresh, mechanical and physicochemical properties of mortars and cement pastes. Both materials were found to increase water demand. NP significantly increased the setting time, whereas LP did not. Both materials reduced the mortars' ultimate compressive strengths but at a proportion lower than their replacement levels, signifying their participatory and influencing roles in hydration reactions. Isothermal analyses confirmed their accelerating effects on PC reactions by promoting filler effects and providing nucleation sites to give steeper heat flow curves with more distinguished peaks. Consistently, an increase in the amount of bound water per gram of PC calculated from thermal gravimetric analyses also indicated their roles in enhancing reactions in the blended cement pastes. XRD confirmed that blended cement pastes with LP formed hemicarbonate and monocarbonate as secondary hydration products and NP participated in pozzolanic reactions as indicated by a reduction of calcium hydroxide with time. In addition, both materials were found to alter the formation of ettringite and monosulfate and alter the chemical composition of hydration products. NP was found to promote the dissolution of ettringite and monosulfate and alter the chemical composition of hydration products. NP was found to promote the dissolution of ettringite and monosulfate at earlier ages compared to the PC paste, while LP was found to stabilize ettringite and promote the metastable formation of hemicarbonate followed by the formation of stable monocarbonate. The results brought new insight into the effects of LP or NP as partial cement replacements on hydration kinetics and products. The findings set forth would contribute to microstructural and composition designs of durable concrete with lower cost and environmental impact.

Conflict of interest

None.

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