Effect of limestone on engineering properties of alkali-activated concrete: A review

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**ABSTRACT**

Alkali-activated concrete (AAC) is a promising sustainable alternative to cementitious materials concerning its environmental benefits and satisfactory engineering properties. Given the growing use of limestone and other forms of calcium carbonate as an additive or supplementary precursor in AAC, this review summarises the effect of limestone on the engineering properties of AAC synthesised from various precursors such as fly ash, slag, metakaolin, and blends of them. Due to the underlying mechanisms including filler effect, additional nucleation and dilution effect, and chemical reaction of limestone, the incorporation of limestone with physical and chemical modifications into AAC can result in changes in reaction kinetics, microstructure, fresh properties, and hardened properties of AAC, which are quantitatively discussed and compared. In addition, the sustainability and environmental impact of AAC containing calcium carbonate are also assessed, whilst the research gap and opportunities for the future are identified.

**1. Introduction**

The Portland cement (PC) industry is a major contributor to global environmental impact with approximately anthropogenic 8% CO₂ emissions [1]. Hence, the replacement of PC material in a form of alkali-activated concrete (AAC), also known as geopolymer, has been a topic of interest for academia and industry in recent decades. AAC is commonly synthesised through the reaction of aluminosilicate precursor and alkaline activator as the dissolution agent, which has been regarded as a sustainable alternative to conventional cementitious materials with similar binding properties [2,3]. The main constituents of AAC are generally sourced from industrial by-products (e.g., fly ash and ground granulated blast-furnace slag) or calcined clay (e.g., metakaolin) that are rich in alumina and silica to produce the precursor [4-6]. The CO₂ emission rate is about 55-75% lower when exploiting AAC as the substitute for conventional concrete with the same compressive strength, which varies with the alkali activator type, amount and concentration [7]. AAC can be tailored to have equivalent or better performance in hardened properties of AAC, which are synthetically discussed and compared. In addition, the sustainability and environmental impact of AAC containing calcium carbonate are also assessed, whilst the research gap and opportunities for the future are identified.

Depending on the nature and composition of raw materials, various reaction mechanisms, microstructure evolution and property development present in AAC with different characteristics. Unlike cement hydration which gives the main reaction product of C–S–H, the principal product in AAC formed by low-calcium raw materials (e.g., fly ash and metakaolin) is an amorphous gel composed of hydrated aluminosilicate chains with negative charges balanced by alkaline ions, e.g., aluminosilicate silicate hydrate (N–A–S–H) [4,13]. Meanwhile, the activation of calcium-rich precursors like slag produces calcium silicate hydrate (C–S–H and/or C–A–S–H) as the dominant binder phases with a denser matrix [14-16]. Despite the superior durability and mechanical properties demonstrated by AAC with various precursors, some drawbacks of these systems remain to be solved. While heat curing is suggested to accelerate the early-strength development of low-calcium systems with more N–A–S–H gels [17-20], applying high-calcium raw materials can transform the reaction products from N–A–S–H to C–A–S–H gels that improve the mechanical properties of AAC [21]. However, exploiting high-calcium precursors could result in other problems such as low workability, fast setting and large shrinkage [8,22-26]. To conquer the limitations of AAC and adapt to engineering applications, different approaches have been adopted for enhancing the mechanical properties as well as alleviating low workability and high shrinkage. These include the use of blended precursors [27,28], optimising alkaline activator [29,30], adjusting curing conditions [31], reinforcing with fibres [32], and adding chemical and mineral additives [33].

Calcium carbonate (CaCO₃, usually in the form of limestone) has
been widely regarded as an additive in cementitious systems because of the economic benefits, chemical-mineralogical composition, no calcination needs, broad availability, and preferable grindability [34]. The reciprocal actions of limestone can be explained by several mechanisms, namely filler, dilution, nucleation, and chemical reaction effects, which are governed by the dosage and fineness of limestone [35]. These physical and chemical modifications of limestone consequently affect the properties of cementitious materials. It has been anticipated that the interaction of limestone or other forms of CaCO₃ could demonstrate a certain level of resemblance in AAC. As a result, more studies have been actively performed regarding the impact of limestone on the properties of AAC with a range of precursors recently. Table 1 summarises all related studies of additive effects included in this paper with the aspects of precursors, alkali activators, additives, curing conditions, conducted tests, types of samples, variables, and major underlying mechanism of additives. The increasing attempts of using limestone as an additive or replacement in AAC necessitate a thorough understanding about the impact of limestone addition on the behaviour of products. In addition, the technology of applying alkaline solid wastes to mineralise and utilise CO₂ has been a subject of global CO₂ reduction, which creates end products of carbonates. It was estimated that 4.02 Gt CO₂ could be fixed per year by this approach, thereby exploring the potential use of CaCO₃ as can provide an extra sustainable choice and further minimise the environmental impact [36]. Thus, a systematic review of the role of limestone (and CaCO₃) as a substitute of precursor is needed to identify the possible applications and understand the role of CaCO₃ in AAC.

This review summarises previous research on exploiting CaCO₃ as a partial replacement of precursors in AAC, identifies knowledge gap and suggests future research opportunities. The synergistic effects of CaCO₃ (mainly limestone) on the behaviour of AAC are documented with respect to reaction kinetics, microstructure, fresh and hardened properties, and sustainability. First, the influences of additions on the reaction kinetics of sole and blended systems are presented. The modifications of additives on the microstructural aspects are then given, with a special focus on the reaction products and pore structure of AAC. These are to provide necessary insight into the mechanisms of which varies the properties of AAC discussed follows, namely workability, setting time, compressive strength, flexural and splitting tensile strengths, as well as durability-related properties. Finally, the sustainability performance of different systems is comparatively discussed with the potential development prospects proposed.

2. Effect of limestone on reaction kinetics of AAC

Isothermal calorimetry and thermogravimetric analysis (TGA) are the commonly employed tools to assess the reaction kinetics of AAC in the literature. The former is adopted to monitor the heat release over a certain continuous period as a measure of reaction rate, whereas the latter quantifies the composition of products that decompose at different temperatures during heating in terms of weight loss [37]. This section presents the effects of additives on the reaction kinetics of AAC with sole and blended precursor systems.

2.1. Sole precursor systems

2.1.1. Fly ash-based AAC

The reaction kinetic results obtained from isothermal calorimetry can be used compare and quantify the reaction process of AAC in terms of peak heights and times to peaks on the flow curves. The typical reaction process of AAC can be divided into five periods (Fig. 1), including the initial, induction, acceleration, deceleration, and slow continuous reaction. The initial reaction is sometimes not fully recorded due to the instability of instrument, which can be ascribed to the wetting and dissolution of raw materials [38]. In general, the presence of CaCO₃ in fly ash-based AAC led to a more intense and accelerated reaction than that without additives [39]. As seen in Fig. 2, the exothermic peak related to large reaction product formation of paste with 10% calcite appears at around 1.2 h, while that of paste with 0–5% positions at 1.0–1.6 d. With 0–5% calcite, there are third peaks in the deceleration stage at around 2.4 d owing to the further reaction products precipitation in AAC [39]. These suggest that CaCO₃ can largely accelerate the geopolymerisation process since CaCO₃ can act as nucleation sites for the reaction products [40,41] and improve the precipitation of them [39]. Meanwhile, the reaction degree can be enhanced with the CaCO₃ content, as indicated in the higher peaks [39,42]. For instance, the addition of 2% nano-CaCO₃ led to an 11% higher peak of reaction rate in the NaOH activated fly ash-based AAC cured at 60 °C [42]. Moreover, the weight loss measured in TGA increases with CaCO₃ addition due to the decomposition of carbonates and the structural water released from binding phases (e.g., C-S-H), as presented in Fig. 3 [39,43].

2.1.2. Slag-based AAC

The influences of limestone and other CaCO₃ on the reaction kinetics of slag-based AAC systems with different types of activators have been more explored [44–49]. The reaction process of sodium carbonate-activated slag-based AAC regardless of lignites follows similar patterns with five stages, although the induction periods are relatively long with CaCO₃ because of the initial precipitation of CaCO₃ [44,49]. With a small dosage (5%) of limestone incorporation, the reaction was slightly accelerated [44]. Then, increasing limestone content to 10–50% resulted in the delayed times to peaks due to the reduced slag content (i.e., dilution effect) [49,50]. Nevertheless, the inclusion of up to 40% limestone improved the reaction degree of slag and intensified the activations, as indicated in Fig. 4a and b, showing the increased normalised heat that took the slag mass into account [49]. The particle size of limestone plays a key role in the reaction process in this system that finer particles accelerate the progress. This effect can be promised when >39% of the particles were <5 μm [51]. Again, the acceleration and intensification of reaction can be explained by the fact that limestone grains act as nucleation sites for the generation and development of reaction products [44,49–51].

2.1.3. Metakaolin-based AAC

The reaction kinetics of metakaolin-based AAC systems with additives have been rarely studied. Only a few researchers have conducted TGA and differential scanning calorimetry (DSC) that measures heat flows as a function of temperature in the samples [40,52,53]. Similar to slag-based systems, two distinct weight losses at 50–200 °C and around 550–800 °C are presented in the NaOH activated metakaolin-based AAC with limestones [40]. The first loss corresponds to free or physically bound water, while the second loss is related to unreacted limestone and rises with its content up to 70%, irrespective of the concentration of activator and curing procedure [40,53]. This observation agrees with the DSC results presented in Ref. [52]. Furthermore, the reaction of limestone was found to be higher in the heated AAC with 3 M NaOH solution than that in the ambient cured samples. This was the opposite when AAC was activated with a 5 M solution because of the additional gels, carbonate phases, and modified C–A–S–H [40].

2.1.4. Other sole precursor systems

The existing studies on the reaction kinetics of AAC with other precursors and limestone are relatively limited [54,55]. According to the heat release results, the replacement of up to 50% limestone retarded the reaction rate due to the decreased reactive phases in the calcined marl system activated by hydrous sodium metasilicate (NSH₂). By incorporating 25% limestone into this AAC, the first peak related to aluminosilicate dissolution dropped by 0.5 °C and shifted to 30–70 min from 20 to 30 min. Then, the second peak linked to the polymerisation process was reduced by 2 °C and shifted to 400–660 min from 310 min. Like other AAC, there were endothermic peaks at 50–150 °C and 630–780 °C in the marl system containing limestone on the DSC curves due to the presence of N–A–S–H/C–A–S–H gels along with evaporable gel water
Table 1
Summary of precursor, activator, additives information, curing temperature, measured properties, type, variables, and major mechanisms of additives collected from studies on AAC containing limestone and CaCO$_3$.

<table>
<thead>
<tr>
<th>Ref</th>
<th>Precursor</th>
<th>Additive type</th>
<th>Additive content (wt % of precursor)</th>
<th>Fineness</th>
<th>Curing temperature</th>
<th>Measured properties</th>
<th>Type</th>
<th>Variables</th>
<th>Major mechanisms of additives</th>
</tr>
</thead>
<tbody>
<tr>
<td>[39]</td>
<td>Fly ash (0.06%Na$_2$O)</td>
<td>Natural CaCO$_3$</td>
<td>1, 3, 5, 10</td>
<td>Sieved with a 300 µm mesh (before further mechanical activation)</td>
<td>22 ± 2 °C</td>
<td>XRD, FTIR, SEM/EDS, CS, TGA, HF</td>
<td>P</td>
<td>Time of mechanical activation, CaCO$_3$ content</td>
<td>Filler, nucleation</td>
</tr>
<tr>
<td>[43]</td>
<td>Fly ash</td>
<td>Nano-CaCO$_3$</td>
<td>1, 2, 3</td>
<td>Average particle size = 15–40 nm</td>
<td>80 °C for 24 h and then at ambient temperature</td>
<td>SEM, 3 PB, CS, charpy impact tester, rockwell hardness test, XRD, FTIR, TGA</td>
<td>P</td>
<td>Nano-CaCO$_3$ content</td>
<td>Filler, nucleation, chemical, dilution</td>
</tr>
<tr>
<td>[65]</td>
<td>Fly ash</td>
<td>Nano-CaCO$_3$</td>
<td>1, 2, 3</td>
<td>Average particle size = 15–40 nm</td>
<td>80 °C for 24 h and then at ambient temperature</td>
<td>FRC</td>
<td>Nano-CaCO$_3$ content</td>
<td>Filler, chemical</td>
<td></td>
</tr>
<tr>
<td>[42]</td>
<td>NaOH (8, 10, 12% Na$^+$)</td>
<td>Nano-CaCO$_3$</td>
<td>1, 2, 3</td>
<td>Average particle size = 50–70 nm</td>
<td>60, 75, or 90 °C for 24, 48, or 72 h, then 23 ± 2 °C</td>
<td>M, P</td>
<td>Na$^+$ % of activator, nano-CaCO$_3$ content</td>
<td>Filler, nucleation, dilution</td>
<td></td>
</tr>
<tr>
<td>[92]</td>
<td>NaOH + waterglass (SiO$_2$/Na$_2$O = 0.5 &amp; 5%Na$_2$O)</td>
<td>LS</td>
<td>15, 30</td>
<td>$d_{50} = 1.5$ µm</td>
<td>Mini-slump, initial ST, rheology, influence of extrusion process on rheology of printed material, CS, FS, effect of extrusion and overburden pressure on pore structure</td>
<td>P</td>
<td>LS/Slag content</td>
<td>Filler</td>
<td></td>
</tr>
<tr>
<td>[51]</td>
<td>Slag</td>
<td>LS</td>
<td>10–70 at 10 intervals</td>
<td>200, 200–400, 400–600 m$^2$/kg (Blaine)</td>
<td>Room temperature</td>
<td>CS, HF, XRD, SEM</td>
<td>P</td>
<td>Three types of LS with 90, 33, and 100% calcite content, LS content, fineness, composition LS content</td>
<td>Filler, nucleation, dilution</td>
</tr>
<tr>
<td>[68]</td>
<td>Slag</td>
<td>LS</td>
<td>15, 30, 45, 60</td>
<td>600 m$^2$/kg (Blaine)</td>
<td>45 ± 1 °C</td>
<td>FS, CS, water absorption, rapid chloride-permeability, DS, XRD, TGA/DTG, SEM</td>
<td>P</td>
<td>Filler, nucleation, dilution</td>
<td></td>
</tr>
<tr>
<td>[44]</td>
<td>Slag</td>
<td>LS</td>
<td>5, 10, 15, 30</td>
<td>$d_{50} = 10.30$ µm, 546 m$^2$/kg (Blaine)</td>
<td>20 ± 1 °C</td>
<td>Mini-slump, HF, CS, XRD, TGA/DTG, FTIR</td>
<td>P</td>
<td>LS content</td>
<td>Filler, nucleation, dilution</td>
</tr>
<tr>
<td>[45]</td>
<td>Slag</td>
<td>LS</td>
<td>10, 20</td>
<td>$d_{50} = 15$ µm</td>
<td>23 °C</td>
<td>CS, ANOVA, XRD, TGA/DTG, MIP, trial concrete brick production and tests</td>
<td>P</td>
<td>LS content, activator types</td>
<td>Chemical, promoted slag dissolution</td>
</tr>
<tr>
<td>[46]</td>
<td>Slag</td>
<td>LS</td>
<td>5–50 at 5 intervals</td>
<td>400 m$^2$/kg</td>
<td>20 ± 2 °C</td>
<td>Mini-slump, ST, DS, TGA/DSC, N$_2$ adsorption test, XRD, FTIR, SEM/EDS, CS, FS, mass loss</td>
<td>M, P</td>
<td>LS content</td>
<td>Filler, chemical, dilution</td>
</tr>
<tr>
<td>[47]</td>
<td>Slag</td>
<td>PCC</td>
<td>5, 10, 20, 30, 40, 50 (of the whole mix)</td>
<td>$d_{50} = 4.74$ µm</td>
<td>23 ± 2 °C</td>
<td>CS, MIP, XRD, TGA, SEM</td>
<td>P</td>
<td>PCC content</td>
<td>Filler, promoted slag dissolution</td>
</tr>
<tr>
<td>[48]</td>
<td>Slag</td>
<td>LS</td>
<td>5</td>
<td>486 m$^2$/kg (Blaine)</td>
<td>20 ± 1 °C</td>
<td>Mini-slump, CS, XRD, TGA/DTG, SEM, DS</td>
<td>P</td>
<td>Additive types (SF/PC/Fly ash/hydrated lime)</td>
<td>Activator types</td>
</tr>
<tr>
<td>[69]</td>
<td>Slag</td>
<td>LS</td>
<td>55</td>
<td>$d_{50} = \text{approx.} 150$ µm</td>
<td>20 ± 5 °C</td>
<td>FAC</td>
<td></td>
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</tr>
</tbody>
</table>

(continued on next page)
<table>
<thead>
<tr>
<th>Ref</th>
<th>Precursor</th>
<th>Activator</th>
<th>Additive type</th>
<th>Additive content (wt % of precursor)</th>
<th>Fineness</th>
<th>Curing temperature</th>
<th>Measured properties</th>
<th>Type</th>
<th>Variables</th>
<th>Major mechanisms of additives</th>
</tr>
</thead>
<tbody>
<tr>
<td>[49]</td>
<td>Slag</td>
<td>Metakaolin + diatomaceous earth + NaOH, Na₂CO₃, diatomaceous earth + Na₂CO₃</td>
<td>LS</td>
<td>10–50 at 10 intervals, 1.33 m²/g (BET)</td>
<td>20 ± 1 ºC</td>
<td>Flow, CS, HF, shrinkage, N₂ adsorption test</td>
<td>P</td>
<td>LS content</td>
<td>Nuclearization, dilution</td>
<td></td>
</tr>
<tr>
<td>[50]</td>
<td>Slag</td>
<td>MgO + NaOH (8%Na₂O)</td>
<td>LS</td>
<td>20</td>
<td>23 ± 2 ºC</td>
<td>XRD, TGA, chloride exposure</td>
<td>P</td>
<td>With/without LS</td>
<td>Filler, nuclearization, chemical, dilution</td>
<td></td>
</tr>
<tr>
<td>[53]</td>
<td>Metaamol</td>
<td>H₂PO₄</td>
<td>LS</td>
<td>1, 2, 3, 4, 5</td>
<td>460 m²/kg (Blaine)</td>
<td>50 ºC for 3 h and then 90 ºC for 21 h</td>
<td>P</td>
<td>LS content</td>
<td>Foaming agent</td>
<td></td>
</tr>
<tr>
<td>[60]</td>
<td>Metaamol</td>
<td>NaOH + waterglass (SiO₂/Na₂O = 2.94, 5.26, 2.22 &amp; 21.76, 12.02, 21.76%Na₂O)</td>
<td>LS</td>
<td>20, 60</td>
<td>1.895 m²/g (BET)</td>
<td>60 ºC for 24 h and then 20 ºC</td>
<td>P</td>
<td>Comparing optimal mix with Metakaolin, based-AAC and OPC</td>
<td>Filler, nuclearization, chemical</td>
<td></td>
</tr>
<tr>
<td>[72]</td>
<td>Metaamol</td>
<td>NaOH + waterglass (SiO₂/Na₂O = 3.73 &amp; 4.7% Na₂O)</td>
<td>LS</td>
<td>80</td>
<td>d₅₀ = 11.30 μm</td>
<td>60 ± 3 ºC for 24 h and then 20 ± 3 ºC</td>
<td>CS, XRD, SEM/EDS</td>
<td>P</td>
<td>LS content, Na₂O/Al₂O₃, SiO₂/Al₂O₃</td>
<td>Filler, nuclearization, chemical, dilution</td>
</tr>
<tr>
<td>[61]</td>
<td>Metaamol</td>
<td>NaOH + waterglass (SiO₂/Na₂O = 5.28, 2.94 &amp; 12.02, 6.01, 21.76, 10.88% Na₂O)</td>
<td>LS</td>
<td>20, 60</td>
<td>d₅₀ = 11.30 μm, 1.895 m²/g (BET)</td>
<td>60 ºC for 24 h and then 20 ºC</td>
<td>P</td>
<td>CS, XRD, FTIR, MAS NMR, weight changes</td>
<td>Filler, nuclearization, chemical, dilution</td>
<td></td>
</tr>
<tr>
<td>[73]</td>
<td>Metaamol</td>
<td>NaOH + waterglass (SiO₂/Na₂O = 1.2, 1.5, 2.0)</td>
<td>CaCO₃</td>
<td>20–100 at 20 intervals</td>
<td>Average particle size = 17.13 μm</td>
<td>40 ºC for 24 h and 25 ºC</td>
<td>CS (90 &amp; 540 d), shrinkage, XRD, SEM, EDS</td>
<td>M</td>
<td>P</td>
<td>CaCO₃ content, CaCO₃/dolomite, modulus of activator</td>
</tr>
<tr>
<td>[40]</td>
<td>Metaamol</td>
<td>NaOH + waterglass (SiO₂/Na₂O = 3, 5 M NaOH)</td>
<td>30, 50, 70</td>
<td>Average particle size = 10.7 μm, specific surface area = 2.0 × 10⁴ cm²/g</td>
<td>80 or 20 ºC for 24 h then 20 ºC (dry or wet)</td>
<td>CS, 3 PB, XRD, TG, leaching test, ESEM</td>
<td>P</td>
<td>Concentration of NaOH, LS content, curing condition</td>
<td>Filler, nuclearization, chemical, dilution</td>
<td></td>
</tr>
<tr>
<td>[74]</td>
<td>Metaamol</td>
<td>KOH + NaOH + waterglass</td>
<td>CaCO₃</td>
<td>2–12 at 2 intervals</td>
<td>–</td>
<td>40 ºC for 12 h</td>
<td>XRD, rheology, 3 PB, Vicker hardness, SEM, FTIR, CS</td>
<td>P</td>
<td>CaCO₃ content</td>
<td>Filler</td>
</tr>
<tr>
<td>[52]</td>
<td>Metaamol</td>
<td>KOH + NaOH + waterglass</td>
<td>CaCO₃</td>
<td>2–12 at 2 intervals</td>
<td>d₅₀ = approx. 6 μm</td>
<td>40 ºC for 12 h</td>
<td>XRD, DSC, SEM, thermal performance of a wall</td>
<td>P</td>
<td>CaCO₃ content</td>
<td>Filler</td>
</tr>
<tr>
<td>[75]</td>
<td>Metaamol</td>
<td>NaOH + waterglass</td>
<td>LS</td>
<td>25, 50, 75</td>
<td>&lt; 63 μm</td>
<td>60 ºC for 72 h</td>
<td>CS, FS, STS, UPV, porosity ratio, weight losses after abrasion, XRD, SEM</td>
<td>M</td>
<td>LS content, other filler content</td>
<td>Filler, chemical</td>
</tr>
<tr>
<td>[76]</td>
<td>Metaamol</td>
<td>12.5 M KOH + potassium silicate (SiO₂/K₂O = 2.0)</td>
<td>LS</td>
<td>10, 15, 20, 30</td>
<td>&lt; 11 μm</td>
<td>20 ºC</td>
<td>CS, ST, XRD, FTIR, optical microscope images</td>
<td>P</td>
<td>LS content</td>
<td>Filler, nuclearization, dilution</td>
</tr>
<tr>
<td>[79]</td>
<td>Halloysite clay</td>
<td>5, 8, 10 M NaOH: waterglass (SiO₂/Na₂O = 2.06) = 1:1</td>
<td>LS</td>
<td>15, 30, 45, 60</td>
<td>26.1517 m²/g (BET)</td>
<td>24 ± 2 ºC</td>
<td>Linear shrinkage, water absorption, apparent density, CS, ST, XRD, FTIR, optical microscope images</td>
<td>P</td>
<td>LS content, molarity of activator</td>
<td>Filler, chemical, dilution</td>
</tr>
<tr>
<td>[78]</td>
<td>Laterite</td>
<td>NaOH + waterglass (SiO₂/Na₂O = 1.6–2.2)</td>
<td>CaCO₃</td>
<td>2–10 at 2 intervals, 20</td>
<td>d₅₀ = approx. 10 μm</td>
<td>25 ºC</td>
<td>XRD, FTIR, SEM/EDS, TGA/DTA, CS</td>
<td>P</td>
<td>CaCO₃ content</td>
<td>Filler</td>
</tr>
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<tr>
<th>Ref</th>
<th>Precursor</th>
<th>Additive type</th>
<th>Additive content (wt % of precursor)</th>
<th>Fineness</th>
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<th>Type</th>
<th>Variables</th>
<th>Major mechanisms of additives</th>
</tr>
</thead>
<tbody>
<tr>
<td>[54]</td>
<td>Marl</td>
<td>NSH₄ (SiO₂/Na₂O – 1)</td>
<td>LS</td>
<td>0, 25, 50 (strength tested with 10-70 at 10 intervals)</td>
<td>3700 cm²/g (Blaine)</td>
<td>Room temperature</td>
<td>CS, HF, XRD, TGA/DSC, FTIR, SEM</td>
<td>P</td>
<td>LS content</td>
</tr>
<tr>
<td>[55]</td>
<td>Natural pozzolan</td>
<td>4, 6, 8, 10, 12, 14 M NaOH: waterglass (SiO₂/Na₂O = 3.3) – 1</td>
<td>LS</td>
<td>60</td>
<td>d₅₀ = 4.63 μm, 0.6 cm²/g (Blaine)</td>
<td>20 ± 2°C for 24 h then 75°C for 24 h; and then 20 ± 5°C</td>
<td>Flow, ST, CS, STS, FTIR, SEM, DSC, XRD, TGA/DTG, DSC</td>
<td>M</td>
<td>NaOH concentration</td>
</tr>
<tr>
<td>[81]</td>
<td>Natural pozzolan</td>
<td>10 M NaOH: waterglass (SiO₂/Na₂O = 3.3) – 1</td>
<td>LS</td>
<td>20–100 at 20 intervals</td>
<td>d₅₀ = 4.63 μm, 0.6 cm²/g (Blaine)</td>
<td>20 ± 5°C for 24 h then 75°C for 24 h; and then 20 ± 5°C</td>
<td>ST, flow, CS, XRD, SEM/EDS, FTIR</td>
<td>M</td>
<td>LS content</td>
</tr>
<tr>
<td>[86]</td>
<td>Urban waste glass</td>
<td>NaOH, Na₂CO₃, NaOH + Na₂CO₃ (9%/NaO)</td>
<td>LS</td>
<td>30, 100</td>
<td>Milled to pass through #325 sieve</td>
<td>40°C for 24 h then 20, 40, or 60°C</td>
<td>CS, XRD, DTA/DTG, SEM</td>
<td>P</td>
<td>CaO/SiO₂, % NaO, curing temperature</td>
</tr>
<tr>
<td>[85]</td>
<td>Waste glass</td>
<td>NaOH, 15% CaO + NaOH (6, 8% NaO)</td>
<td>LS</td>
<td>15, 45</td>
<td>675 ± 20 m²/g, kg (Blaine)</td>
<td>20 ± 3°C</td>
<td>CS, XRD, SEM/EDS, NMR, underwater evolution index</td>
<td>M, P</td>
<td>Activator types, LS content</td>
</tr>
<tr>
<td>[82]</td>
<td>Volcanic ash</td>
<td>NaOH + waterglass, 10 M NaOH (SiO₂/Na₂O – 0.52, 0.72, 0.89, 2.05, 1.18)</td>
<td>LS</td>
<td>60</td>
<td>d₅₀ = 4.63 μm, surface area = 0.60 kg/L</td>
<td>25 ± 5°C for 24 h then at room temperature, 45, 60, 75, or 90°C</td>
<td>Flow, CS, XRD, FTIR, SEM/EDS</td>
<td>M</td>
<td>Waterglass, NaOH, curing temperature</td>
</tr>
<tr>
<td>[77]</td>
<td>Bottom ash</td>
<td>NaOH + waterglass (5, 6, 7%/NaO)</td>
<td>LS</td>
<td>10, 20, 30</td>
<td>&lt; 50 μm</td>
<td>23 ± 2°C for one day and then 20 ± 2°C</td>
<td>CS, XRD, MIP, toxicity characteristic leaching procedure, SEM/EDS, water absorption</td>
<td>P</td>
<td>NaO content, LS content, fly ash content</td>
</tr>
<tr>
<td>[85]</td>
<td>Fly ash + slag</td>
<td>12 M NaOH: waterglass (SiO₂/Na₂O – 0.52, 0.72, 0.89, 2.05, 1.18)</td>
<td>CaCO₃</td>
<td>0, 2, 4, 6</td>
<td>Natural medium fine with a packed density of 1.4</td>
<td>21°C</td>
<td>CS, STS, 4-point bending, XRD, SEM, water absorption</td>
<td>C</td>
<td>CaCO₃ content</td>
</tr>
<tr>
<td>[86]</td>
<td>Fly ash + synthetic-based mud</td>
<td>8 M liquid NaOH, sodium waterglass, solid waterglass (SiO₂/Na₂O = 0.12, 0.24, 0.48 &amp; 0% Na₂O)</td>
<td>LS</td>
<td>1, 1.5, 3, 5 by weight of fly ash</td>
<td>70, 125, or 170°F</td>
<td>CS (1 &amp; 3d), rheology, thickening time</td>
<td>P</td>
<td>LS dust content, activator types, fly ash types, fly ash/mud ratio</td>
<td>Stability enhancing</td>
</tr>
<tr>
<td>[87]</td>
<td>Fly ash + slag</td>
<td>NaOH + waterglass (solid and liquid; SiO₂/Na₂O = 2 &amp; 4% Na₂O)</td>
<td>LS</td>
<td>5, 10, 20</td>
<td>1.6018 m²/g (BET)</td>
<td>20 ± 1°C</td>
<td>Yield stress, plastic viscosity, SEM/EDS, CS, DS</td>
<td>P</td>
<td>LS content, solid/liquid waterglass</td>
</tr>
<tr>
<td>[58]</td>
<td>Fly ash + slag</td>
<td>NaOH + waterglass (SiO₂/Na₂O = 1.2 &amp; 5%/Na₂O)</td>
<td>White mud</td>
<td>10-50 at 10 intervals</td>
<td>d₅₀ = 7.569 μm, 4.626 m²/g (BET)</td>
<td>20 ± 2°C</td>
<td>XRD, TGA/DTG, FTIR, SEM/EDS, CS, elastic modulus and hardness</td>
<td>P</td>
<td>White mud content</td>
</tr>
<tr>
<td>[41]</td>
<td>Fly ash + slag</td>
<td>NaOH + waterglass (SiO₂/Na₂O = 1.4 &amp; 5%/Na₂O)</td>
<td>LS</td>
<td>10, 20, 30</td>
<td>d₅₀ = 10.12 μm</td>
<td>20°C</td>
<td>Slump flow, ST, HF, FTIR, XRD, TGA/DSC, CS</td>
<td>M, P</td>
<td>Fly ash and LS content</td>
</tr>
<tr>
<td>[56]</td>
<td>Fly ash + slag</td>
<td>NaOH + waterglass (SiO₂/Na₂O = 0.4, 1.2 &amp; 5% Na₂O)</td>
<td>LS</td>
<td>10-50 at 10 intervals</td>
<td>d₅₀ = 3.9 μm, specific surface area = 6.53 m²/cm³</td>
<td>20°C</td>
<td>Rheological tests, HF, ICPOES, SEM/EDS, XRD</td>
<td>M</td>
<td>Modulus of activator solution</td>
</tr>
<tr>
<td>[86]</td>
<td>Fly ash + slag</td>
<td>12 M NaOH: waterglass (SiO₂/Na₂O = 2.7) – 1</td>
<td>LS</td>
<td>25, 50, and 75 replacing river sand</td>
<td>2500 cm²/g (Blaine)</td>
<td>80°C for 24 h and then at ambient condition</td>
<td>FS, CS, STS, weight loss after abrasion, UPV, SEM</td>
<td>M</td>
<td>LS content</td>
</tr>
<tr>
<td>[89]</td>
<td>Slag + Metakaolin</td>
<td>NaOH + waterglass (SiO₂/Na₂O = 4)</td>
<td>LS</td>
<td>5-20 at 5 intervals</td>
<td>d₅₀ = 5 μm, specific surface area</td>
<td>25 ± 2°C</td>
<td>ST, CS, XRD, FTIR, SEM</td>
<td>P</td>
<td>LS content</td>
</tr>
</tbody>
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promoted and accelerated due to the high amount of limestone content (up to 50%) that provided higher specific surface and additional ash and slag systems with limestone addition, the reaction process was the calcite decarbonation, respectively. At the same time, the weight loss went up with limestone content [54]. Similar peaks in the natural nucleation sites facilitated the precipitation and growth of reaction products, implying that limestone can introduce apparent physical modifications and slight chemical effects that are further discussed in the next section [41,56]. In TGA, the two significant weight losses below 250 °C and around 600–800 °C identified in slag-based AAC can be observed in the fly ash and slag blends with additives [41,58]. Besides these peaks, the fly ash-slag based AAC with white mud (mainly containing CaCO$_3$) exhibited an endothermal peak at around 300–450 °C, attributed to the removal of water and CO$_2$ from hydrotalcite, which appeared in sodium carbonate activated slag systems as well. Another similar aspect in these systems was that the addition of white mud reduced the reactive precursors and led to fewer gels. However, given the difference in weight loss ratio of 0.8 between the control sample (fly ash/slag) = 50/50) and the blended mix (fly ash/slag/white mud = 25/25/50), the reaction degree was enhanced, which again indicated the acceleration and facilitation effects of CaCO$_3$ [44,58]. By contrast, the presence of limestone caused a clear dilution effect in the slag and waste glass blends that prolonged the induction period and retarded the reaction product formation by acting as an inert filler. The first peak in the reaction evolution (temperature rise) of the slag and waste glass blends
presented at 30 min (18.7 °C), whilst those of blends with 10% and 40% limestone retarded to 60 min (18.2 °C) and 120 min (17.02 °C), respectively, as shown in Fig. 4c. Afterwards, the time to reaction peak within 7 d was delayed to 126 h and 162 h from 40 h when 10% and 40% slag was replaced with limestone [57].

3. Effect of limestone on microstructure of AAC

This section discusses the effects of limestone powder on the assemblage of reaction products and pore structure characteristics of AAC, which are the primary mechanisms behind the changes in AAC performance. The microstructural characteristics of AAC are generally studied through different techniques, as listed in Table 1. X-ray diffraction (XRD) was adopted to obtain an understanding of potential transformation ongoing, while Fourier-transform infrared spectroscopy (FTIR) analysis can be employed to identify the chemical composition and acquire the bonding information of amorphous aluminosilicates, indicating high heterogeneity [59]. In a few studies [60–62], solid-state magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy was used to further evaluate the tetrahedral network structure of AAC binding gel at a smaller scale. Moreover, scanning electron microscopy (SEM) analysis was widely performed to elucidate the effect of additives on the microstructural improvement of AAC by capturing the surface micro-morphology of reaction products, which was sometimes implemented together with energy-dispersive X-ray spectroscopy (EDS) to characterise the chemical features of samples. Mercury intrusion porosimetry (MIP) and nitrogen sorption methods were implemented to quantitively characterise the pore structure of AAC in terms of porosity and pore size distribution [63,64].

3.1. Reaction products

3.1.1. Fly ash-based AAC

Several studies [39,42,43,65] have investigated the effect of CaCO₃ with a dosage of up to 10% and various sizes ranging from nanoscale on the geopolymerisation products of low-calcium (Class F) fly ash-based AAC. Without the addition of CaCO₃, the generation of amorphous phases (i.e., N–A–S–H) and certain crystalline phases like quartz, mullite, hematite, and magnetite, could generally be found in fly ash-based AAC activated with sole NaOH or a mixture of NaOH and waterglass solution. When a small amount of additive (5% or less) was added in fly ash-based AAC, these crystalline phases in AAC remained present with no new mineral phases formed except calcite. These non-reactive minerals mostly behaved as fillers or micro-aggregates embedded in AAC matrix. However, Kalinkin et al. [39] reported the transformation of calcite to vaterite in the XRD patterns when 10% calcite was blended in AAC, which can be obtained by the recrystallisation in NaOH solution based on the Ostwald’s step rule [66,67]. In terms of amorphous phases, the additional formation of calcium-
containing phases, e.g., C-S-H or calcium hydroxide, can be found besides N-A-S-H due to the dissolution of CaCO₃ within fly ash systems [43].

3.1.2. Slag-based AAC

Unlike low-calcium fly ash-based AAC, the main binding phase of alkali-activated slag system is generally known to be amorphous C-A-S-H gel that cannot be revealed using XRD analysis [51]. This C-A-S-H phase remains stable and unchanged regardless of the limestone content in slag-based AAC activated with sodium carbonate, MgO and NaOH, or combined NaOH and waterglass solution, as supported by other forms of analysis, e.g., FTIR [44,46,50]. Overall, independent of the CaCO₃ replacement and activator type, the C-S-H peaks in XRD patterns are normally noted in slag-based AAC. Furthermore, it is generally agreed that the intensity of calcite increases with the limestone content [45–48,51,68,69]. In addition to C-S-H and calcite, gaylussite (Na₂Ca(CO₃)₂⋅5H₂O) was commonly identified in the sodium carbonate activated slag-based AAC containing limestone [44,49,51]. However, Rakhimova et al. [51] found that limestone up to 60% did not contribute to chemical reaction with the binder gel, while Yuan et al. [44] reported that the decrystallisation of gaylussite led to the generation of natron (Na₂CO₃⋅10H₂O) when limestone replacement exceeded 15%. Gaylussite as a secondary reaction product released CO₂ anions and transferred to hydrocalcite-like phases in the sodium carbonate activated system. When limestone content was high, there were not enough ions released from slag to react with CO₂ and thus formed natron.

Regarding the MgO and NaOH activated slag-based AAC, carbonate-AFm phases that can increase chloride binding were induced by incorporating 20% limestone [50]. For slag-based AAC activated with NaOH and waterglass, it was indicated that no additional phase can be observed in the 60% limestone replaced AAC due to the unavailability of reaction between limestone and binder [68]. However, another study [46] noted that dolomite (CaMg(CO₃)₂) was detected in conjunction with C-S-H, calcite, Mg-Al layered double hydroxide (LDH), and akermanite (CaMgSi₂O₆) phases when 40% slag was replaced with limestone. Akermanite originated from slag and reduced as limestone dosage increased. Meanwhile, they suggested that the reaction products of this system can be altered by the waterglass solution modulus (Ms) with C-S-H gel being the major product when Ms is ≥1.0. A similar conclusion was achieved in pure limestone-based AAC with reaction products that were governed by silicate chains, including C-S-H, N-C-S-H, N-S-H, and silica gels, along with carbonates. Limestone was dissolved with carbonates such as thermonatrite (Na₂CO₃·3H₂O) and pirossonite (Na₄Ca(CO₃)₂·2H₂O) formed when Ms = 1.0 and 1.5, whilst portlandite (Ca(OH)₂) was generated when Ms = 0 [70]. Similar products including crystalline pirossonite and portlandite were detected in AAC with sole limestone to provide the cohesive capacity of AAC [71]. Moreover, limestone was capable to remove Ba(OH)₂·8H₂O and convert some Ba (OH)₂ to Ca(OH)₂ in the Ba(OH)₂ activated slag-based AAC [45]. Apart from limestone powder, the incorporation of up to 20% precipitated calcium carbonate (GCC) can lead to the formation of hemi-carboaluminate (Ca₆Al₂(OH)₁₀(CO₃)₂·4H₂O) in the calcium oxide and calcium sulphate activated slag-based AAC [47].

3.1.3. Metakaolin-based AAC

In regard to the compatibility between metakaolin and limestone, more studies [60,61,72–75] have been conducted to explore the composition of reaction products of AAC synthesised from metakaolin and up to 80% limestone. The microstructure of sole metakaolin-based AAC is predominantly composed of amorphous N-A-S-H gel with unreacted particles such as quartz and anatase [40,72]. With the partial replacement of limestone, the studies have identified the coexistence of N-A-S-H with other phases containing calcium, including N-(C)-(A)-S-H [60,61], (C) Na-A-S-H [72], C-S-H [72,75], and C-A-S-H [40,60,72,75] gels, in metakaolin-based AAC activated with combined NaOH and waterglass or sole NaOH.

Limestone can be an active precursor that enables the alteration of chemical composition and reaction products, along with the reduction of alkali consumption in metakaolin-based AAC. As reported in Ref. [60], limestone released calcium ion (Ca²⁺) that was incorporated into N-(C)-(A)-S-H as a result of the ion-exchange mechanism between Na⁺ and Ca²⁺ in the NaOH and waterglass activated system. Besides, some Ca²⁺ reacted with Si and Al from metakaolin and waterglass to form other calcium-containing secondary phases. This agrees well with a previous work [40] that the limestone dissolution in the NaOH activator resulted in the formation of layered calcium carboaluminate phases and likely C-A-S-H. The secondary phases in the NaOH and waterglass activated AAC included gismondine (CaAl₂Si₄O₁₀·4H₂O) and laumontite (Ca₆Al₂O₁₀·16H₂O) identified by XRD, as well as C-A-S-H revealed by MAS NMR, alongside other zeolites [60,61]. Meanwhile, the 3D-network structure of main products, i.e., N-A-S-H and N-(C)-(A)-S-H, was maintained. However, increasing the limestone content from 20% to 60% did not alter the metakaolin dissolution rate and 3D-network structure, although Ca²⁺ up taken in N-(C)-(A)-S-H was increased [60]. An optimal mix with 80% limestone, Na₂O/Al₂O₃ of 0.94, and SiO₂/Al₂O₃ of 3.54 was proposed [72]. Similar reaction products were detected, namely, N-A-S-H intermixed with (C-N) A-S-H, C-A-S-H, or C-S-H that depends on the Al content, along with partly dissolved limestone particle. Besides, the unreacted limestone can be filler [74] or nucleation sites for new reaction products [40].

Regarding metakaolin-based AAC activated with sole NaOH solution, the addition of limestone promoted the released Si and Al ions from metakaolin, while the dissolution of limestone was higher than that in NaOH solution with a lower concentration. The products in this system cured at 20 °C included gel, unreacted metakaolin, limestone particles, zeolite A, and AFm phases, while faujasite-like and hydrosalolite phases presented in that with 80 °C heat treatment. Moreover, it was noted that the limestone fineness played a more important role than limestone ratio (30–70%) in the properties of the phases in such AAC [40]. In contrast to the discussion above, some studies [52,53,73,74,76] stated that CaCO₃ is not actively involved in the chemical reactions without newly formed crystalline products except calcite. It is possible that calcium is integrated into the amorphous phases eventually or promoted the crystalline precipitates, e.g., Ca(OH)₂, that were undetectable with XRD [73].

3.1.4. Other sole precursor systems

The reaction products of AAC synthesised from other precursors, including bottom ash [77], laterite [78], halloysite clay [79], marl [54], waste glass [62,80], and natural pozzolan [55,81,82], have been studied. Limestone was reported to have minor influences on the reaction process in the bottom ash-based and laterite-based AAC, though more C-A-S-H gels were shown in the former with higher Na₂O content [77,78]. Moreover, crystallised C-S-H and amorphous C-A-S-H existed in halloysite clay-based AAC with 45% limestone confirming its apparent dissolution [79]. The limestone addition in marl-based AAC activated with NSH₅ could lightly dissolve in the fresh paste, increase the Al and Si ions released from the precursor and usefulness of activator-to-aluminosilicate ratio, act as nucleation sites for products and in turn, increase formed gels (N-A-S-H/C-A-S-H) [83,84]. In the waste glass-based AAC, a common reaction product is silica gel in different activators [62,80]. The molecular structure of gels can be modified with the dosage, fineness, and %CaO of limestone, resulting in the presence of C-S-H and various types of silica gels [62]. Alunitite (CaAl₂Si₂O₈) and gehlenite (CaO·Al₂O₃·SiO₂) that are similar to C-A-S-H compound and positive to strength development were found in the natural pozzolan-based AAC with the limestone incorporation, depending on the alkali concentration [55,81,82]. This can be attributed to the Ca²⁺ from limestone that bonds with O-Si-O, O-Al-O, and the OH⁻ to form skeletal frameworks [81].
3.1.5. Blended systems

A few studies have investigated the effect of limestone on the microstructural characteristics of blended binders, namely fly ash and slag [41,56,58,85–88], slag and metakaolin [89], along with slag and waste glass [57]. C-(A)–S–H gel was observed in fly ash-slag systems with limestone that exhibited slight chemical modifications (releasing Ca\(^{2+}\)) and did not introduce new crystalline phases [41,56]. However, the main product was C-(N)–A–S–H type gel coexisted with hydrotalcite as the secondary phase when white mud was added into the same system. The formation of hydrotalcite was promoted with the increasing white mud content, whilst strength-giving products were reduced [58]. Regarding slag-metakaolin systems, limestone acted as a non-active phase with minimal changes in reaction products [89]. It was considered unreactive in slag and glass powder system as it reduced the amorphous phases and the formation of reaction products without newly formed products [57].

3.2. Pore structure

3.2.1. Fly ash-based AAC

Overall, the inclusion of a small amount of CaCO\(_3\) (<10%) in fly ash-based AAC can lead to a more compact and denser microstructure [39,42,43,65] that eventually improves the strength of AAC, as illustrated in the SEM images (Fig. 5) [39]. This is associated with the filler effect of unreacted particles and the more geopolymerisation products due to the nucleation sites provided by CaCO\(_3\) and other calcium-containing phases [39,42,43,65]. However, extra nano-CaCO\(_3\) impaired the microstructure and thus other properties probably because of the hindered reaction product formation due to excessive fillers, the weakened zones created by the agglomeration of particles, and the dilution effect [43].

3.2.2. Slag-based AAC

The effect of additives on the pore structure of slag-based system with up to 70% limestone has been studied with results depending on the dosage [68] and other factors like fineness [51] and activator [45]. The presence of a small amount of limestone generally refines the pore structure, whereas higher content can contribute to a more coarsened microstructure [46,48,49,68]. For example, Rashad et al. [68] reported that replacing 15% slag with limestone densified the microstructure with improved compactness because of the filler effect and better packing density that disappeared with 30% limestone, whilst 45–60% limestone led to a looser and heterogeneous microstructure (Fig. 6). With the same activator of NaOH and waterglass, the incorporation of up to 25% limestone was found to reduce the pore volume and pores < 15 nm, whereas 40% limestone significantly increased the porosity from nano- to micro-scale, as obtained using the nitrogen sorption method. C-A-S-H gels were not enough to fill the voids between unreacted limestone due to reduced slag and hindered polycondensation reactions, resulting in more pores after evaporation [46]. This partially agrees with a study on the sodium carbonate activated system that 10% and 30% limestone raised the pore refinement and pores > 15 nm, respectively [49]. However, this study found that the addition of 10% limestone resulted in more pores within the range of < 15 nm (i.e., more C-A-S-H gel) due to intensification of reaction, while raising limestone content to 30% led to a reduction in this range and increase in the larger range. Similarly, with the increasing addition of PCC from 0% to 50%, the pore size was refined with total porosity reduced at 28 d due to filler effect accompanied by more reaction products that filled pores. Moreover, Rakhimova et al. [51] observed higher packing density and lower porosity when the limestone particles were grinded to the distribution with sizes < 20 \(\mu\)m and 5 \(\mu\)m reached 77% and 39%. When limestone was added in Ca(OH)\(_2\) activated AAC, the total porosity and pore diameter dropped with capillary pores (>50 nm) vanished. The pore structure of Ba(OH)\(_2\) activated system with the addition of limestone was more complex, suggesting that the pore size distribution depended on the activator type in this case. All these support that the limestone addition can undoubtedly affect the pore structure with levels depending on limestone content in the slag-based system.

3.2.3. Metakaolin-based AAC

The pore structure of metakaolin-based AAC with the application of any form of CaCO\(_3\) has been rarely discussed. As demonstrated in the SEM images (Fig. 7a-d), a few studies [60,72,75] have stated that the addition and increment of limestone resulted in a dense and compacting structure with more limestone particles dispersed in the matrix. Meanwhile, Kabirova et al. [75] reported that substituting 25% and 50% river sand with limestone powder as a filler material reduced the porosity by 4% and 5%, although further replacing 75% river sand increased by 2%. Conversely, the total porosity of metakaolin-based AAC went up with the addition of limestone (up to 5%) as a forming agent. Rising the limestone powder in this H\(_2\)PO\(_4\) activated AAC as a thermally insulating material led to more expansion and thus pores in the specimen (Fig. 7e and f) [53].

3.2.4. Other sole precursor systems

On the whole, the inclusion of limestone is beneficial to the matrix densification in a wide range of AAC produced from different precursors, namely halloysite clay [79], marl [54], natural pozzolan [81], waste glass [62], and bottom ash [77]. This can be captured in the micrographs (Fig. 8) showing a denser microstructure [79,81] or MIP results indicating a lower volume of pores and voids [77]. Such positive outcome is again attributed to the pore filling effect [54,55,62,77,79,81] and the promoted reaction degree induced by limestone [77]. Nevertheless, excessive limestone can adversely affect the density that more capillary pores were observed in the halloysite-based AAC containing 60% limestone as opposed to those with 45% or less limestone (Fig. 8d and e) [79].

3.2.5. Blended systems

The detailed studies related to the influence of CaCO\(_3\) on the pore structure of AAC with blended precursors are very limited. In a similar manner to the effects mentioned above, limestone particles filled the micropores and provided better packing in fly ash-slag based AAC [41,87]. The cumulative pore volume ranges from 1 nm to 100 nm in the liquid NaOH and waterglass activated AAC was reduced with the

Fig. 5. Pore structure of fly ash-based AAC with various calcite content: (a) 0%, (b) 5%, and (c) 10% [39].
addition of up to 20% limestone. This effect was less obvious in the solid mix activated AAC due to the large particles of waterglass [87]. However, adding white mud in such system (Fig. 9) [58] resulted in a looser microstructure due to the angular shape of white mud that reduced the packing density and increased pores created after evaporation since more water was added to achieve sufficient consistency [90,91]. Meanwhile, the slag and waste glass-based mortar with limestone (Fig. 10) had a heterogeneous, porous, and less compact structure with a high degree of cracking, which shows an agreement with the slag-based AAC with 45–60% limestone discussed above [57,68].

4. Effect of limestone on fresh properties of AAC

4.1. Workability

The workability of fresh mixtures is the relative ease of the placement, which is widely characterised by spread flow or rheological behaviour (i.e., yield stress and viscosity) of AAC. This section presents the effect of limestone on the workability of AAC which is mainly revealed by the change of flow values obtained from the mini-slump or flow tests in the literature. Fig. 11 illustrates the effects of limestone and nano-CaCO$_3$ on the spread flow of different AAC, including fly ash [42,92], slag [44,46,48,49], metakaolin [76], natural pozzolan [81], fly ash and slag [41,88], as well as slag and waste glass blends [57]. More studies have been conducted on the slag-based AAC with up to 50% limestone, whilst limited data has been collected from the studies of other AAC with fewer ranges of limestone. Overall, the addition of limestone can positively affect the flowability of various AAC. However, the reported effects of additives in AAC with fly ash are rather inconsistent [42], whilst excessive limestone can reduce the flow of metakaolin-based AAC [76]. The effect of limestone on the rheological behaviour of the blended AAC with fly ash has been also studied in Refs. [56,86,87].

4.1.1. Fly ash-based AAC

The effect of limestone on 3D-printable fly ash-based AAC was investigated with a special focus on extrudability and buildability (i.e., printability) [92]. Although increased slump flow and reduced yield stress along with plastic viscosity were observed when limestone content raised, the discrepancy was primarily related to the different activator concentrations. Nonetheless, there was an evident improvement in printability when 15% (5% NaOH) and 30% limestone (10% NaOH) were applied as fillers (d$_{50}$ of 1.5 μm) with a constant liquid-to-binder ratio of 0.27 (Fig. 12). This was ascribed to the increased number of interparticle contacts by the fine particles that improved the rigidity of fresh AAC and resisted the overburden pressure. Moreover, with the inclusion of nano-CaCO$_3$ (average size = 50–70 nm), the flowability of NaOH activated fly ash-based AAC slightly went up with an 8% Na$^+$ ratio and reduced with 10/12% Na$^+$ ratios due to the high surface area that absorbed more water [42]. Given the lack of studies in this aspect, it is not possible to confirm the influence of additives on fly ash-based systems.

4.1.2. Slag-based AAC

There is a general agreement that incorporating limestone in slag-based AAC improves the fresh behaviour of mixtures. As reported in the literature (Fig. 11), the replacement of 5–50% limestone increased the spread flow by around 3–50% [44,46,48,49]. The better flowability can be explained by various reasons. The mixture packing is enhanced when the added limestone particles are finer than slag particles [44]. Furthermore, the dissolution of limestone requires less water than slag in sodium carbonate activator by acting as an inert material during early reaction [44]. When the replacement level is higher, as discussed in Section 2.1.2, the reduction in slag content delays the initial reaction since the dissolving process of slag is quicker than limestone in alkaline solution [44,46].

4.1.3. Metakaolin-based AAC

The rheological properties or workability of metakaolin-based AAC

Fig. 6. Pore structure of slag-based AAC with various limestone content: (a) 0%, (b) 15%, (c) 30%, (d) 45%, and (e) 60% [68].
with limestone have been rarely studied [74,76]. Replacing 0–15% of precursor with limestone in metakaolin-based AAC resulted in a 15.6% rise in the mini-slump spread, while the further addition to 30% led to a decline, which can be ascribed to the filler effect of limestone, leading to more released free solution when limestone was added to the metakaolin-based paste [76]. This in turn resulted in a thicker water film formed from the excess water (other than void water between particles) coating and separating particles, which led to reduced particle interaction and higher workability [93].

4.1.4. Other sole precursor and blended systems

The beneficial effect of limestone on the flowability of AAC has been shown in other sole precursor and blended systems. The micro-filler effect of limestone contributed to the improved flowability of mortar made from natural pozzolan with high silica content (required higher water demand) and angular shape. The spread flow of this type of AAC led to a gradual increase of up to 125% when 100% natural pozzolan was replaced by limestone [81]. In the ternary mixtures with slag and waste glass, replacing slag with up to 40% limestone greatly improved the spread flow from 135 mm to 184 mm. This can be explained by the large Blaine surface area of limestone powder (4390 cm²/g) compared to that of slag (2759 cm²/g) and waste glass powder (2876 cm²/g) which enhanced the particle packing. As a result, pores were filled with more water available to rise the spread flow [57]. By contrast, the decrease in flowability was found in fly ash-slag based system (with 13% slag) that the rising limestone content from 0% to 75% reduced the flow value from 224 mm to 145 mm [88]. Moreover, the rheological performance of fly ash and synthetic-based mud as well as fly ash-slag based systems containing limestone has been reported. When a small amount of limestone dust (up to 3%) was added to the fly ash and synthetic-based mud paste, the shear stress at different shear rates went up with limestone dosage because of the fine particles with d₅₀ of 3 μm. The rheology of this system was negatively affected by limestone that was used as a stability-enhancing modifier under atmospheric conditions, while the rheological properties of fly ash-slag blends activated by waterglass and NaOH demonstrated different trends [86]. The overall yield stress and plastic viscosity dropped with the replacement of precursors with 5–20% limestone, which can be attributed to the fine limestone powder that filled the micropores and allowed more water to lubricate the mixtures [87]. However, Dai et al. [56] found that the dynamic yield stress decreased with limestone using an activator with Ms = 1.2 and reversed for the mixes with a solution of Ms = 0.4 in a similar system. Moreover, the substitution of fly ash with limestone reduced the water film thickness, and meanwhile the viscosity went up with the increase of limestone content. The former phenomenon was ascribed to the lower water

Fig. 7. Pore structure of metakaolin-based AAC with limestone dosage of (a) 20%, (b) 60% [60], (c) 80% (optimal mix), and (d) 0% limestone (pure metakaolin AAC) [72]; and (e) 0%, (f) 5% as foaming agent [53].
retention capacity of limestone compared to fly ash even though excess water was increased. The latter was related to the enhanced inter particle contacts that in turn raised the viscosity. Overall, these ternary mixtures fitted well with the Bingham model.

4.2. Setting time

The setting time of AAC reflects the stiffening process of AAC, which can be classified into initial and final setting time based on the penetration depth of the needle into fresh samples. They are usually measured with a Vicat needle apparatus, according to the standard test methods such as EN 196–3 [94] and ASTM C191 [95]. Fig. 13 shows the limited literature data on the effect of limestone on the setting time of AAC, which reveal that the incorporation of limestone decelerates the setting process in most of AAC, mitigating the quick setting to some extent. Although a study demonstrated the delayed initial setting time in the fresh fly ash-based AAC with 15% and 30% limestone, the increment of time was mainly due to the increased alkaline activator with minimal evidence showing the effect of limestone [92]. The influence of limestone replacement in AAC with slag about setting behaviour is more obvious because of the high activity of slag. For instance, limestone (up to 50%) was effective in extending the initial setting time in slag-based AAC, even though it was still too short for practical applications with values below 40 min. The slower calcium dissolving process in limestone compared to slag is the reason for the prolonged setting time [46].

Moreover, for a constant slag content, the effect of limestone in the ternary mixtures (with fly ash and slag) on both initial and final setting time was negligible. The setting time was then increased when limestone replaced slag with a consistent fly ash content [41]. This agrees with the other study that the initial and final setting time went up by 53.06% (77.55%) and 34.52% (24.83%) respectively when substituting 10% (40%) slag with limestone in slag and waste glass-based AAC [57]. All these results suggested that limestone plays a key role in resolving the fast setting in AAC with slag. A similar effect was found in the thermally activated halloysite-based AAC that up to 60% limestone retarded the initial setting time [79]. Nevertheless, opposite trends can be seen in Fig. 13 that the increase in limestone content reduced the initial and final setting time of natural pozzolan-based AAC because of early integration and formation of C–S–H induced by limestone powder [81].

5. Effect of limestone on hardened properties of AAC

5.1. Compressive strength

The compressive strength of AAC containing additives that were produced from different precursors has been extensively studied. This section quantitatively discusses the effects of additive amount and fineness on the strength of AAC, in relation to the physical and chemical interactions that can manifest in filler, dilution, nucleation, and chemical reacting modifications.

5.1.1. Fly ash-based AAC

Fig. 14 presents the 28 d compressive strength of different kinds of AAC as a function of limestone content. In general, the presence of CaCO$_3$ positively contributes to the compressive strength of fly ash-based systems, which is dependent on the content and fineness of limestone. The incorporation of 10% calcite increased the compressive strength by nearly 100% in fly ash-based paste, which was confirmed by the acceleration of reaction process, greater polymerisation, and denser gel microstructure as discussed in Sections 2 and 3. The mechanical activation of fly ash and calcite mixtures (180 s milling) was effective to enlarge particle surface area (fineness) and hence accelerated the gelation process, which was additionally beneficial to the strength gain [39]. As mentioned, CaCO$_3$ can act as nucleation sites in the reaction process of AAC and speed up the formation of reaction products while these
nanoparticles distribute in the matrix and denser the microstructure (filler effect) [39,42,43,65]. This in turn resulted in the improved strength development that applying 1.0% CaCO$_3$ in fly ash-based paste increased almost 40% of the compressive strength [43]. Similar results were reported in PVA fibre reinforced AAC. A 33% strength gain was achieved by adding 1% nano-CaCO$_3$ which compacted the microstructure and improved the fibre–matrix interfacial bonding [65]. A similar improvement in strength was observed in AAC with the addition of other type of nanoparticles, e.g., nano-silica [96]. However, an excessive amount of additive can cause dilution effect and deteriorate the strength or create more voids and worsen the cohesion of elements and binder [42,43]. Therefore, an optimal dosage of 1.0–2.0% is recommended in fly ash-based paste to achieve the desired compressive strength improvement.

5.1.2. Slag-based AAC

Independent of the additives, the slag-based AAC paste typically exhibits a higher compressive strength compared to fly ash-based AAC paste given by the C–A–S–H or C–S–H phases (Fig. 14(b)) [97,98]. Despite the slight increment induced by small limestone dosage, the greater content of limestone contributes to the descending trend in compressive strength [44,47,51,68]. As discussed, the mechanisms induced by additives that are favourable to the strength development of slag-based paste include providing nucleation sites [44,51,68], boosting slag dissolution/reaction degree [45,49,50], improving pore refinement [44–47,50,68], providing higher packing density [51], intensifying

![Fig. 10. Pore structure of slag and waste glass-based AAC with various limestone content: (a) 0%, (b) 10%, and (c) 40% [57].](image)

![Fig. 11. Effect of limestone on flowability of AAC made from different precursors and activators [42,44,46,48,49,57,76,81,88,92].](image)

![Fig. 12. Effect of limestone on printed hollow cube geometry with fly ash-based AAC paste: (a)-(b): 100% fly ash, (c) replaced with 15% limestone, (d) replaced with 30% limestone (abstracted from [92]).](image)

![Fig. 13. Effect of limestone on setting time of AAC made from various precursors [41,46,57,79,81,92].](image)
reaction degree [46,49], and increasing gel products [49]. Meanwhile, the reversed influence of limestone on the strength development of slag-based paste can be ascribed to the dilution effect due to the reduced slag content [44] and coarsened microstructure [46,47,68]. Various optimal contents have been reported in this regard. The optimal mixes for compressive strength were those with 15% and 25% limestone in the combined NaOH and waterglass activated slag paste and mortar, respectively [46,68]. The sodium carbonate activated paste with 10% limestone dosage presented the peak compressive strength along with the heat release (Fig. 4b [49]) when up to 50% limestone was included, achieving values of above 50 MPa and 60 MPa at 28 d and 91 d, respectively [44,49]. In a similar manner, the strength of slag-based paste raised with the increase of PCC content up to 20% and reached value of approximately 55 MPa prior to the decline [47]. Furthermore, slight increases in compressive strength were found when 5% and up to 20% limestone were employed in the Na$_2$SO$_4$ and Ca(OH)$_2$ activated slag paste. Conversely, more complex performance was observed with the Ba(OH)$_2$ activation that the strength clearly reduced when 20% limestone was added [45,48]. Apart from dosage, the effects of limestone type and particle size on the compressive strength of slag-based paste were studied where different types of limestone were ground to a Blaine fineness of 200, 400, and 600 m$^2$/kg [51]. It was reported that regardless of the types of limestone with various calcite contents, the inclusion of 30–40% limestone with 400 m$^2$/kg and 600 m$^2$/kg increased the strength by 18.3–48.8%, which acted as the physical modifier. The better effect of limestone with 100% calcite content was resulted from the higher bonding strength of calcite with gel compared to those of quartz and dolomite.

Fig. 14. Effect of additive content on 28-d compressive strength of AAC paste made from (a) fly ash [39,43,65], (b) slag [44,45,47–49,51,68], (c) metakaolin [40,52,53,60,61,74], (d) others [54,62,77–79], and (e) blends [41,58,87,89]; and (f) AAC mortar (LS-limestone) [41,46,56,57,60,62,73,75,81,88,99].
5.1.3. Metakaolin-based AAC

Overall, the addition of limestone in metakaolin-based AAC led to inconsistent alterations in terms of compressive strength, as displayed in Fig. 14c and f. Many studies have confirmed that limestone or CaCO₃ can be detrimental to the compressive strength of metakaolin-based AAC [53,60,61,73–75], though some positive effects have also been reported when a certain amount of additive was applied [40,73–76]. The advantageous influences are mostly ascribed to the filler effect (better packing density), extra nucleation sites, and refined gel structure (N–A–S–H) provided by the additives, while the adverse impacts can be attributed to the more porous structure, reduced reactive aluminosilicate content, unstable gel microstructure, and higher degree of shrinkage/cracking. The early age (7 d) strength was improved by 17.43% when 10% limestone powder was added to the potassium silicate content, unstable gel microstructure, and higher degree of shrinkage/cracking. The early age (7 d) strength was improved by 17.43% when 10% limestone powder was added to the potassium silicate content, N–A–S–H) provided by the additives, while the adverse impacts can be attributed to the more porous structure, reduced reactive aluminosilicate content, unstable gel microstructure, and higher degree of shrinkage/cracking. The early age (7 d) strength was improved by 17.43% when 10% limestone powder was added to the potassium silicate content, N–A–S–H) provided by the additives, while the adverse impacts can be attributed to the more porous structure, reduced reactive aluminosilicate content, unstable gel microstructure, and higher degree of shrinkage/cracking. 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5.1.5. Blended systems

Fig. 14e summarises the literature data about the effect of limestone on the compressive strength of AAC with mixed binders. Most of the studied blends including the slag and fly ash or metakaolin blends exhibited positive trends in compressive strength when limestone was partially incorporated [41,87–89]. However, additives could be harmful to the mechanical strength of blended systems in some cases, depending on the role and contributing mechanisms of additives [56–58,85,99]. Adapting <50% limestone leads to a greater compressive strength as it can physically and chemically modify the performance of mixed AAC. For example, the replacement of fly ash and slag with 20% limestone slightly increased the strength by 3.2 MPa because of the physical filler effect [87]. With a constant slag content, the addition of up to 30% limestone was also positive to the strength since it offered pore refinement and nucleation sites in conjunction with the light chemical effect as detailed in Sections 2 and 3. The maximum 28 d strength of 64.2 MPa was found for the mixture with 60% slag, 30% limestone, and 10% fly ash [41]. With constant fly ash and slag, the addition of 25% and 50% limestone as a substitute of river sand exhibited an improvement in the strength of 2.2% and 8.3% by dissolving in the activator and yielding a better packing [88]. The strength increment was also observed in the metakaolin-slag based system that replacing 15% precursors (with 80% metakaolin and 20% slag) with limestone caused a slight increase. Higher content of limestone can have negative effects on the hydrated gel structures and resulted in a significant reduction of <5 MPa [89]. By contrast, the strength was considerably reduced by around 40% when 50% white mud replaced fly ash and slag, though this strength was still comparable to that of PC 42.5. Moreover, the strength dropped by about 20% when 50% of fly ash was replaced with limestone in the fly ash-slag-based system. As mentioned, it can be ascribed to the dilution effect caused by reduced reactive precursors and lower reactivity of CaCO₃ in the former and latter systems, respectively [56,58]. As an unreactive filler, the presence of 10–40% limestone in the slag-glass powder-limestone mixture harmed the strength development due to the heterogeneous and porous structure with more cracking. Nonetheless, the use of 10% and 20% limestone in this system was a good alternative for CEM I PC 52.5 and alkali-activated slag materials [57].

5.2. Flexural and splitting tensile strengths

The flexural strength of AAC with limestone is normally measured using three-point bending test (e.g., ASTM C293 [100], ASTM D790 [101], and EN 196-1 (94)) [42,43,46,57,65,68] and four-point bending test [85]. Overall, the change trend of flexural and tensile strengths of AAC associated with the additives are akin to those presented in compressive strength because they share the same influencing factors, as depicted in Fig. 15.

5.2.1. Fly ash-based AAC

As seen in Fig. 15a, the addition of nano-CaCO₃ caused similar effects to the flexural and compressive strengths of fly ash-based AAC paste [43]. Assaeed et al. [43] proposed an optimal quantity of 2% CaCO₃, which led to a 58% rise in flexural strength compared to that without additives. In addition, the improved flexural strength can be attributed to the enhanced amount of gel as discussed in Section 3.1.4, along with the satisfactory limestone-matrix adhesion, chemical–mineralogical affinity, and improved paste structure [54]. A similar strength trend relative to the limestone content was shown in the natural pozzolan-based mortar. The optimal dosage of limestone was 60% in this binary mixture, leading to a 200% rise in the strength that was given by anorthite and gehlenite as well as the pore-filling effect [81]. Moreover, owing to the pore filling effect of limestone and higher reactivity of calcined clay, the compressive strength of bottom ash-based AAC was threefold with the 30% limestone-calcined clay addition [77]. In comparison, the effect of CaCO₃ substitution on the strength of laterite-based AAC was insignificant, although strengths lying between 30 MPa and 40 MPa were reached [78].
to the nanoparticles that had higher strength than the matrix. These particles can prevent the crack initiation and growth by creating a bond with geopolymerisation products and absorbing robust energy in the crack extension direction. Unlike the findings about compressive strength, the flexural strength of PVA fibre reinforced fly ash-based AAC yielded the maximum flexural strength of 9.08 MPa (3.5 times the original strength) when 2% CaCO$_3$ was incorporated. This suggests that 2% nano-CaCO$_3$ contributed to the better interfacial bonding and fibre distribution that may be due to greater workability [42,65]. It was also reported that up to 3% nano-CaCO$_3$ dosage went up with the flexural rigidity and stiffness from 1.70 Nm$^2$ to 2.17 Nm$^2$ and 1.09 N/m to 1.63 N/m, respectively.

5.2.2. Slag-based AAC

The incorporation of limestone powder affects the flexural strength of slag-based systems in a similar vein to compressive strength, with reinforcing mechanisms explained in Section 5.1.2. As illustrated in Fig. 15a, the partial replacement of 15% limestone increased the flexural strength of 9.08 MPa (3.5 times the original strength) when 2% CaCO$_3$ was incorporated. This suggests that 2% nano-CaCO$_3$ contributed to the better interfacial bonding and fibre distribution that may be due to greater workability [42,65]. It was also reported that up to 3% nano-CaCO$_3$ dosage went up with the flexural rigidity and stiffness from 1.70 Nm$^2$ to 2.17 Nm$^2$ and 1.09 N/m to 1.63 N/m, respectively.

5.2.3. Metakaolin-based AAC

As expected, the flexural, splitting and compressive strengths of metakaolin-based systems performed similarly with the rising limestone content as they were altered by the same contributing factors discussed [53,75,76]. For example, the 28 d peak flexural and splitting tensile strengths of 11.87 MPa (Fig. 15a) and 5.96 MPa (Fig. 16) were achieved when 50% limestone replaced the sand in metakaolin-based AAC mortar [75]. The same trend in compressive strength was noted in the splitting tensile strength when 5% limestone was adopted as a foaming agent in metakaolin-based paste due to the increased porosity [53]. However, the trend in flexural strength variation was unclear when up to 12% CaCO$_3$ was incorporated into the metakaolin-based pastes, which can be related to the random defects in the samples [74].

5.2.4. Blended systems

A similar tendency of effect regarding the flexural and compressive strengths of blended systems can be observed by comparing Fig. 15a and b. In particular, the positive effect provided by 50% limestone was more effective on the flexural strength (29.9%) than compressive strength (8.27%) in the fly ash-slag based AAC, whilst a moderate enhancement of around 15% in the splitting tensile strength was observed [88]. For the slag-waste glass powder based system, the generally negative impact of limestone on the flexural strength was similar to that on the compressive strength with > 1 MPa reduction when 40% limestone was added [57].

5.3. Durability-related properties

5.3.1. Drying shrinkage

The shrinkage of AAC, particularly for slag-based systems, was found to have a higher rate than that of ordinary PC concrete [102–104]. It was reported that the shrinkage of slag-based AAC can be 2–6 times higher than that of ordinary concrete [25,105]. The shrinkage of AAC can be affected by various factors, including alkaline and precursors properties [30,102,104], curing conditions [106,107], reaction products, and pore structure [108–110]. The shrinkage of AAC mainly occurred due to the autogenous and drying shrinkage. The autogenous shrinkage is a result of chemical shrinkage and self-desiccation while drying shrinkage is associated with the evaporation of water in the exposing environment and hardening process [111]. These volume changes can cause defects and uneven stresses in AAC elements, leading to cracking and penetration of harmful substances that reduce the durability of AAC. Therefore,
different approaches such as using shrinkage-reducing and mineral admixtures have been proposed to mitigate shrinkage [112-114], while only very few studies have explored the role of limestone in the shrinkage of AAC, mostly focusing on the slag-based systems as discussed below. Fig. 17 presents the influence of additive content on the drying shrinkage of AAC.

For the Na$_2$SO$_4$ activated slag pastes, the addition of 5% limestone increased the drying shrinkage of pastes at 28 d, followed by a reversed trend afterwards. The drying shrinkage was decreased by 3.24 times at 200 d, showing an average reduction of 5.6% between 1 month and 200 d compared to that without additive. Among different additives, limestone was more effective than silica fume, yet less useful than fly ash, hydrated lime, and PC in alleviating drying shrinkage [48]. Furthermore, the use of limestone to mitigate drying shrinkage of waterglass and NaOH activated slag systems is promising. This is mainly related to two factors that can affect the drying shrinkage of slag-based AAC, namely the gel product deformation (C–A–S–H) associated with binder content and the capillary pressure related to pore structure [106,108,111]. Limestone exhibits lower reactivity compared to slag and thereby resulting in fewer gels that experience volume changes [70]. Meanwhile, some limestone particles remain unreacted and are more stable in volume in the system when high content of limestone is included. They can better resist the capillary forces because of the higher elastic modulus than C–A–S–H. In addition, the pore volume would be increased as reaction products are inadequate to fill the gaps between particles, while more large pores would be generated from the evaporated redundant activator. All these mechanisms were suggested to mitigate the shrinkage in the slag-based AAC, depending on the limestone content included [46,68]. As seen in Fig. 17, the drying shrinkage of waterglass and NaOH activated slag pastes reaches the peak at a 25% limestone ratio and reduces at higher limestone content. It suggests that low limestone content can be detrimental to the shrinkage of AAC due to pore refinement (<15 nm) and beneficial because of the mechanisms mentioned above [46]. This study agrees with another research [68] that 60% limestone reduced the drying shrinkage of slag-based AAC systems by ~70%. Likewise, up to 50% limestone decreased that of fly ash-slag based AAC by around 7–45% because of the capillary pores reduction.

Fig. 18 indicates the relationship between drying shrinkage and mass loss measured in the slag-based AAC systems with various content of limestone. The mass loss of AAC exhibits a direct relationship with the drying shrinkage of slag-based AAC and the limestone content. However, the above studies appear to contradict the observation about the effect of limestone powder on sodium carbonate activated slag system. The autogenous shrinkage increased when limestone content was low (<30%) due to intensified and accelerated reaction, which can be directly linked to the heat release within 7 d (Fig. 19). Then, it dropped with higher limestone content due to the dilution effect. Despite the positive effects on autogenous shrinkage, the drying shrinkage was increased with the limestone in this system even binder content dropped. The enlarged drying shrinkage was primarily attributed to the release of chemical water from the dehydration of reaction products (gypsum and natron mentioned in Section 3.1.2), together with the increased porosity (especially meso- and macro-pores) [46,49]. The studies about limestone effect on the shrinkage of other systems are very limited. The shrinkages of metakaolin [73] and halloysite clay-based [79] systems activated with waterglass and NaOH went up with the rising CaCO$_3$ and limestone content, which could reduce other properties.

5.3.2. Chloride ingress resistance

One of the causes of steel reinforcement corrosion in concrete is the external chloride ingress, which is a serious concern regarding the durability of reinforced concrete structures exposed to chlorides (e.g., marine environment) [115]. The chloride ingress of AAC is dependent on the physical transport process linked to capillary pores and micro-cracks within the specimens, along with the efficient binding of chloride ions related to the reaction products that chemically or physically uptake chloride ions [17,50,116,117]. Slag-based AAC containing limestone has chloride binding capability due to the presence of hydrocalcite and AFm phases that are LDH with ion exchange and surface adsorption ability [118,119]. As seen in Fig. 20, the waterglass and NaOH activated slag paste exhibited a charge pass of 2500 Coulombs (moderate permeability to chloride) and 1940 Coulombs (low permeability to chloride) at 28 d and 90 d, respectively. The charge pass dropped by 22.4% from ‘moderate’ to ‘low’ with the replacement of 15% limestone. This was regarded as the optimal content in restraining chloride ingress since higher limestone content resulted in more pores and higher chloride permeability [68]. Furthermore, as compared to other samples in Fig. 21, the 20% limestone led to an approximate 50% higher chloride binding capacity when the slag-based AAC was exposed to a high chloride concentration of 2.0 M. The improved chloride binding capability was attributed to the CO$_3^-$-AFm phases that can transit into Friedel’s salt and its polymorphs [50].

5.3.3. Water absorption

The water absorption of AAC with limestone has also been assessed as a measure of durability with standard tests (e.g., ASTM C642 [120]), which is related to the surface porosity and pore structure [121]. As shown in Fig. 22, different trends are presented with increasing limestone content. A similar observation on the chloride permeability test was demonstrated in the slag-based AAC. 15% limestone powder reduced the amount of water absorbed from 2.91% to 2.71%, whilst higher content of up to 60% resulted in a gradual increase [68]. Same effects were reported in the thermally activated halloysite pastes with limestone incorporation with different optimal content. Regardless of activator concentration, the pastes containing 45% limestone had a minimal water absorption and more limestone led to a slight increase [79]. It was attributed to the improved packing and densification by limestone which reduced capillary pores and prevented water molecules fixation. Then, the adverse effect resulted from more voids created after the unreacted water molecules evaporation induced by higher limestone content, as discussed in Section 3.2 [68,79]. However, the water absorption increased with the CaCO$_3$ addition in the fly ash-slag based AAC. In addition, it was found that more pores were left when CaCO$_3$ reacted with moisture and CO$_2$ to form soluble calcium bicarbonate [85].

**Fig. 17.** Effect of limestone content on drying shrinkage of different AAC systems [46,48,49,68,79,87].
5.3.4. Abrasion

Two studies have evaluated the effect of limestone on the abrasion resistance of metakaolin as well as fly ash-slag based AAC mortars. As displayed in Fig. 23, the weight loss after the abrasion test dropped when 25% and 50% limestone replaced the river sand as a filler material in both studies since the substance filled the pores and packing density of AAC. As the limestone content increased to 75%, the abrasion resistance was weakened due to the poorer adhesion and increased porosity [75,88].

5.3.5. High temperature performance

Few studies have evaluated the performance of AAC subjected to elevated temperatures. Perez-Cortes et al. [61] investigated the structural change of limestone and metakaolin-based AAC containing 20% and 60% limestone at 300, 600, and 900 °C. The remained compressive strength of this AAC after exposure to 300 °C was still above 50 MPa with no structural changes in N–A–S–H or N–(C)–A–S–H. This was followed by the depolymerisation of partial metakaolin network structures and N–A–S–H or N–(C)–A–S–H at 600 °C, along with the formation of C–(A)–S–H due to the involvement of limestone. However, the presence of higher limestone content improved the thermomechanical performance of AAC since limestone reduced the as-cured bonded water. After subjected to 900 °C, most strength losses occurred with the crystallisation of amorphous phases, decarbonisation of CaCO3, and breakdown of zeolite.
framework. Likewise, the reduction in strength was found when lime-stone was used as a filler material in the metakaolin and red mud-based mortars under the high temperature effects at 200–800 °C [99].

6. Sustainability analysis of AAC containing limestone

Since sustainability has been given a high priority, the approach of using AAC as an alternative has been suggested to mitigate the CO₂ and energy burden of ordinary PC. As a result, the environmental impacts of these materials have been assessed using different parameters such as embodied carbon and embodied energy. In comparison with ordinary concrete, AAC is generally considered to be more sustainable with lower greenhouse gas emissions from production and the utilisation of industrial by-products [122–124]. According to the life cycle assessment carried out by Ramagiri et al. [125], the global warming potential of AAC with an activator modulus of 0.7 is almost half of that of PC concrete. In terms of the impact on climate change of AAC with different bases, 1 kg fly ash-metakaolin based AAC was reported to have a larger impact with 1880 kg CO₂-e, compared with slag-based (615 kg CO₂-e), fly ash-based (487 kg CO₂-e), and fly ash-slag based AAC systems (372 kg CO₂-e) [126]. Despite using abundant materials as aluminosilicate sources, the production of AAC can still cause a certain level of environmental impact during the manufacturing of alkaline solution and precursors. For instance, the calcination involved in the metakaolin production and the grinding process in the blast furnace slag can increase the cost and energy demands of AAC that impeded its application. For example, the total CO₂ emission from 1 kg NaOH production was reported to be 1.915 kg CO₂-e, whilst that from 1 kg waterglass manufacture was 1.222 kg CO₂-e [129]. The contribution of waterglass in terms of environmental impact and climate change can account for 21–33% and 50–59%, as reported in the life cycle and environmental assessment of AAC [125,130].

In addition to the effect of limestone discussed above, limestone is considered a promising alternative to the common precursors with wide availability and no heating treatment required. Moreover, the energy consumption and CO₂ emission for grinding limestone were calculated to be 20.1 kW h/ton and 12.2 kg CO₂/ton, which were only around 43% of that for grinding slag [128]. In this regard, some environmental analyses have been carried out concerning the comparative energy consumption and CO₂ contribution of AAC with limestone.

Fig. 24 presents the estimated embodied carbon and embodied energy of reference ordinary PC concrete, AAC, and AAC containing limestone that had comparable and adequate compressive strength (>35 MPa) in the literature. These sustainability analyses were conducted on slag, metakaolin, slag-waste glass, and limestone systems. It should be noted that the discrepancy among these studies can be ascribed to the considered phases in the life cycle of products. In all cases, the emission and energy consumption of PC systems were higher than those of AAC, whilst similar strength was achieved with most cases showing values of above 50 MPa (Fig. 24). An optimised formula of sodium carbonate activated slag system with high limestone dosage was proposed by Moseson et al. [128], which demonstrates competitive cost and performance as typical ordinary PC system. The emitted CO₂ and consumed energy estimated were 97% lower as opposed to ordinary PC system, i.e., 20.1 kW h/ton and 12.2 kg CO₂/ton, which were only around 43% of that for grinding slag [128]. In this regard, some environmental analyses have been carried out concerning the comparative energy consumption and CO₂ contribution of AAC with limestone.

Fig. 23. Effect of limestone content on weight loss of AAC after abrasion test [75,88].
limestone (20–60%) incorporated pastes yielded high strength of 55–61 MPa and reduced the carbon emissions by up to 61% as opposed to blended PC. Nonetheless, as seen in Fig. 24b, the energy consumptions of AAC with 100% metakaolin and 20% limestone are higher than that of blended PC due to the higher content of alkaline activator. The activator and limestone in these pastes exhibited the highest and least contribution to CO$_2$ impact and energy demand, respectively. Thus, pastes with a higher amount of limestone resulted in minimised carbon footprint and energy consumed as limestone can reduce alkalis demand and did not involve calcination like metakaolin [131]. Further, the optimal mix presented in Ref. [72] with 80% limestone reduced the content of alkaline activator while remaining a sufficient chemical environment for reactions and providing the 28 d compressive strength of 51.86 MPa. The CO$_2$ emission and energy consumption were 75.1% and 41.1% lower than those of blended PC and were 51.6% and 53.8% less than those of sole metakaolin-based AAC, respectively.

The environmental impact of blended systems with limestone has been rarely studied. The slag or slag-waste glass system activated with waterglass and NaOH was much more environmental-friendly with comparable strength of > 50 MPa as the PC system. Besides, increasing the limestone content further dropped the carbon footprint, though the energy consumption and strength were negatively affected with 40% limestone addition [57]. It is noteworthy that the cost of product should be considered in conjunction with the embodied carbon and energy, which can be varied on a case-by-case basis. Furthermore, by comparing the carbon footprint of sole limestone binder (10% Na$_2$O and Ms = 1) and PC binder, a study [70] suggested the production of the former and latter would emit 71–90 kg CO$_2$/m$^3$ and 82–100 kg CO$_2$/m$^3$, respectively (Fig. 24c). However, the emission of limestone binder was mainly related to waterglass and NaOH production as mentioned, implying that a replacement of alkaline activator would further improve the sustainabilty of AAC.

It is evident that the use of limestone or CaCO$_3$ as secondary precursor or additive in AAC can provide the desirable documented performance and minimise environmental impact. However, conventional limestone used in cement production can lead to high electricity consumption and fossil depletion due to limestone grinding and quarrying [130]. To further address the environmental issues and combat climate change, the required CaCO$_3$ can be sourced from carbon mineralisation utilising alkaline solid wastes (e.g., slag [132] and fly ash [133]). As the steelmaking and cement industries are highly emission-intensive and release lots of alkaline solid wastes with high calcium oxide contents, the reaction between CO$_2$ and these active compounds can convert CO$_2$ to carbonates (i.e., direct CO$_2$ reduction) and meanwhile stabilise alkaline solid wastes [36,134–136]. These reacted products, namely CaCO$_3$, can therefore be adopted as an alternative of natural limestone that can partially replace the discussed precursors in AAC.

### 7. Conclusions

This review covers the effects of limestone and CaCO$_3$ on the main properties of AAC synthesised from a range of precursors, which is driven by the enhanced sustainability with additives. The underlying mechanisms of AAC properties alterations from the reaction kinetics and microstructural perspectives are discussed, followed by the analysis of the studies that examined the fresh and hardened properties of AAC containing additives. It is suggested that synthesising AAC with limestone/CaCO$_3$ along with other precursors exhibits a promising engineering application potential. Some main conclusions can be drawn as follows:

- The incorporation of fine additives leads to a more intensive and accelerated reaction process by offering sites for nucleation of reaction products in the fly ash, slag, and blended systems, while the higher content of limestone retarded the reaction in the calcium-rich system (e.g., slag) due to dilution effect, while the reaction degree of

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**Fig. 24.** Comparisons of (a) embodied carbon, (b) embodied energy, and (c) embodied carbon in terms of volumetric mass among PC, AAC, and limestone incorporated AAC with similar strengths (PC – Portland cement; LS – limestone; AAC – alkali-activated concrete) [46,57,70,72,128,131].
slag can be accelerated with the addition of limestone. The existing studies on reaction kinetics of AAC containing limestone are relatively limited with mostly only focusing on sole or blended fly ash and slag systems.

- The additives were sometimes reported to be unreactive in the fly ash, slag-waste glass, and slag-metakaolin systems. In most cases, limestone or CaCO$_3$ was dissolved in alkaline solution and released Ca$^{2+}$ to form new calcium-containing phases (e.g., C-S–H, C-A–S–H, and similar crystalline compounds) in the fly ash, metakaolin, halloysite clay, marble, waste glass, and natural pozzolan-based AAC. In the slag-based systems, new crystalline phases (e.g., glassyolite) were detected with limestone replacement, mainly depending on the alkaline activator types.
- A certain amount of additive can refine and densify the pore structure of AAC through the filler effect that filled micropores and improved packing as well as promoted reaction degree that formed more gels, while an excessive amount of additive can cause a more coarsened and looser pore structure. However, most studies only presented image-based analysis and thus more quantitative research is required.
- The flowability of AAC can be generally improved with limestone addition owing to enhanced packing and less water demand for limestone dissolution. In particular, the improvement in the flowability of slag-based AAC can be attributed to the reduced slag content with high activity that delayed initial reaction, implying that limestone can also alleviate the fast-setting problem of slag-based AAC. It is noted that there is a lack of detailed information about the effect of CaCO$_3$ on the workability and setting time of fly ash and other systems.
- A smaller amount of limestone or CaCO$_3$ can be positive to the compressive strength of AAC, including fly ash, slag, metakaolin, and fly ash-slag based systems. The beneficial effects are primarily ascribed to the pore refinement, higher particle packing, intensified reaction, increase in gel products by nucleation effect, and promoted reaction degree of the main precursor (e.g., slag). However, beyond the optimal content, the additives can have side effects on the mechanical strength of AAC due to reduced reactive phase, unstable gel structure, more porous structure, and higher degree of shrinkage. The flexural and splitting tensile strengths of AAC present similar responses to the compressive strength when additives are applied. Although it is apparent that additive fineness plays a key role in modifying the properties of AAC, quantitative investigation on this aspect is relatively insufficient as most studies are focused on the effect of additive dosage.
- The drying shrinkage of slag-based systems activated with NaOH and waterglass can be mitigated by the addition of limestone because of reduced gels, higher modulus of limestone than C-A-S-H resisting capillary forces, and the formation of larger pores and fewer capillary pores. This is reversed in the sodium carbonate activated system due to the dehydration of reaction products and increased porosity. Furthermore, the generation of hydrotalcite and AFm phases contributes to the chloride binding ability of slag-based AAC, while improved packing and densification resulted in the decreased water absorption of AAC when a certain amount of limestone is added. Few studies have used limestone as a filler material to increase the abrasion resistance of AAC due to the enhanced packing density. However, it is noticed that only slag-based systems have been studied regarding the effect of limestone on some durability-related properties. More experimental data on long-term durability (e.g., acid and frost resistance) of different AAC containing limestone are essential, which should also link to the reaction mechanisms and microstructure.

Overall, limestone can be considered a promising supplementary precursor to produce AAC with a low carbon footprint. In response to the challenge of Net Zero emission, it is vital to develop more sustainable engineering materials with less environmental impact. This can be achieved by employing CO$_2$ mineralisation technology with alkaline solid wastes to form CaCO$_3$ while solving the carbon emission and waste issues.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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