Reusing Ceramic Waste as a Precursor in Alkali-Activated Cements: A Review

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Abstract: Concrete and ceramic products are among the most widely used materials in the construction sector. The production of ceramic materials has significantly grown in recent years. Concrete is one of the most widely used materials worldwide and most of its carbon dioxide (CO2) emissions are attributed to Portland cement (PC) production. This review analyzed previous research works into the use of ceramic waste (CW) as a precursor in alkali-activated (AA) cements. The physico-chemical properties of different CW materials were analyzed, and the properties and environmental impact of three main categories of AA CW cements were explored: those developed solely with CW; hybrid cements combining CW with traditional binders (PC, calcium hydroxide or calcium aluminate cement); combinations of CW with other precursors (i.e., blast furnace slag, fly ash, fluid catalytic cracking residue, etc.). The results evidenced that CW can be successfully employed as a precursor in AA cements, particularly in the context of prefabricated products where thermal curing is a prevalent procedure. When enhanced mechanical strength is requisite, it is feasible to attain improvements by employing hybrid systems or by combining CW with other precursors, such as blast furnace slag. This new alternative reuse option allows progress to be made toward sustainable development by reducing not only CO2 emissions and embodied energy compared to PC but also PC consumption and CW accumulation in landfills.

Keywords: ceramic waste; sustainable construction materials; alkali activation; geopolymers; mechanical properties; microstructure; durability

1. Introduction

Ceramic products like bricks, roof tiles, wall/floor tiles or sanitary ware are generally used worldwide and as previously reviewed by Reig et al. [1], the amounts of manufactured ceramic products have substantially grown in recent years. Most ceramic companies reuse all clay waste generated before sintering ceramic products, and the ceramic sector is making many efforts to incorporate waste from the pieces fired during the manufacturing process [2]. However, the huge quantities of ceramic products manufactured worldwide (16,093 million m² of ceramic tiles globally produced in 2020 or 6.3 million tons of bricks/roofing tiles manufactured in Spain in 2021) [1] still imply significant volumes of ceramic waste (CW) because about 3–7% of ceramic products are commercially discarded due to technical imperfections. Additionally, large CW volumes come from construction and demolition waste (CDW) because, according to the European Environment Agency (EEA), more than one third of the waste generated worldwide is...
CDW, and a significant part of this comprises CW (from 8–54%) [3]. As observed by the EEA, most of this CW is landfilled or used in backfill applications, such as road bases [4].

Sustainable development, with lower natural resources and energy demands, would significantly contribute to minimizing climate change, which our planet is currently undergoing. The rapid growth of buildings and infrastructure has turned concrete into one of the most consumed materials worldwide, with around 13 billion tons produced annually [5]. As reported by Lasseguette et al. [3], most concrete CO₂ emissions (95%) are attributed to Portland cement (PC), whose production contributes 5–7% of the world’s total CO₂ emissions [6,7], with 530–940 kg of CO₂ per ton of produced clinker. These emissions are primarily due to CaCO₃ decomposition and to the energy consumed during the clinkerization process [8–11]. In addition, PC production is expected to increase by 45% by 2050 [7].

Several studies that have centered on these environmental challenges have focused on the development of more sustainable construction materials via the reutilization and valorization of CW. In the previous reviews by Reig et al. [1,12], using CW as a recycled aggregate in concrete [1], and as a supplementary cementitious material to partially replace PC [12], has been explored. This new review aims to complete previous ones by exploring and synthesizing previous findings on CW use as a precursor in alkali-activated (AA) binders. Its main findings will encourage the valorization and reutilization of CW, a material that is widely available all over the world, to develop more sustainable cementing systems. This would reduce the consumption of energy and natural resources, as well as CO₂ emissions associated with PC production, and would also minimize the amount of landfilled CW [9,13–15]. This review will also facilitate knowledge transfer to industry by allowing the identification of new research areas that complement existing knowledge.

The conducted bibliographic search is summarized in Figure 1. It focused on research works from 2010 to 2022, and only covered CW studies (any research into the AA of concrete waste or CDW was excluded). Following these criteria, 82 bibliographic references were found. After reading and summarizing them all, only the most significant and representative research works on the AA of CW were included. This review is divided into three main sections: (i) AA materials developed with only one ceramic precursor; (ii) hybrid materials with a ceramic precursor, plus a traditional binder; (iii) combinations of several materials as precursors in AA systems. Finally, a sustainability and carbon footprint analysis of CW AA binders was conducted. Therefore, this systematic study presents the main findings reported in the literature concerning the production and characterization of CW in alkali-activated systems. The research analyzes the variation of properties depending on the type and concentration of the alkaline activating solution, curing time and temperature. Additionally, the study identifies existing gaps and highlights potential future research topics in this field.

**Figure 1.** Review on the use of CW as a precursor in AA cements.
2. Physico-Chemical Properties of CW

The widespread use of ceramic products in construction generates large amounts of CW, which originate from both CDW and high ceramic production rates. To be used as a precursor in AA systems or as a supplementary cementitious material (SCM) [12], the particle size of CW can be easily adapted by crushing and milling. Scanning electron microscopy (SEM) images of milled CW powders that were previously used as precursors in AA systems or as SCM have been published in [12]. Table 1 summarizes the density and mean particle size of different types of CWP (tile ceramic waste, TCW; ceramic sanitary ware, CSW; and brick ceramic waste, BCW) previously used as SCM or as precursor in AA binders. Although the mean particle size of CWP widely varied, it generally came close to 20–30 µm [6,9,14–26]. This particle size is similar to that commonly reported for PC [8,12] and is appropriate for enhancing its dissolution. CWP density usually varied from 2.3 to 3.0 g/cm³.

Table 1. Density and mean particle size of the CWP used as SCM or as a precursor in AA binders.

<table>
<thead>
<tr>
<th>Pozzolan or AA Precursor</th>
<th>CW Density, g/cm³</th>
<th>Mean Particle Size µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCW</td>
<td>2.5–2.7</td>
<td>3.4–48.5</td>
</tr>
<tr>
<td></td>
<td>[5,16,18,21,24,25]</td>
<td></td>
</tr>
<tr>
<td>TCW</td>
<td>2.4–2.6</td>
<td>&lt;1–20</td>
</tr>
<tr>
<td></td>
<td>[9,16,17,22,23,25]</td>
<td></td>
</tr>
<tr>
<td>CSW</td>
<td>2.6</td>
<td>20–31.2</td>
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<tr>
<td></td>
<td>[5,9,16,19,26]</td>
<td></td>
</tr>
<tr>
<td>Not specified</td>
<td>2.3–3.0</td>
<td>2.3–35</td>
</tr>
<tr>
<td></td>
<td>[6,14,15,20]</td>
<td></td>
</tr>
</tbody>
</table>

CW reactivity is determined mainly by the chemical and mineralogical compositions of the ceramic product, which depends on the used clays and the sintering process applied during its manufacture [17,27]. Although the reactivity of clays is generally low, it normally improves when ceramic products are manufactured due to the dehydroxylation and amorphization of their microstructure [1,7,11,28]. As described by Jaskulski et al. [10], dehydroxylation of clays may occur from 350 ºC to 900 ºC, depending on clays’ composition, and new crystalline phases may form as of this temperature. However, studies like that conducted by Zanelly et al. [29] in porcelain stoneware tiles have also reported significant amounts of vitreous phases at above 900 ºC, which are originated by the partial fusion of crystalline phases. Pavesi et al. [30], who investigated the pozzolanic activity of several clays after being sintered from 400 ºC to 1000 ºC, also concluded that the pozzolanic activity of calcined clays strongly depends on their sintering temperature, whose optimum varies depending on their chemical and mineralogical compositions. As the sintering temperatures employed to manufacture ceramic products vary depending on the properties required for their use (tiles, bricks, sanitary ware, etc.), the ratio of amorphous/crystalline phases and, consequently, the reactivity of CW when employed as a precursor in AA systems, are also expected to vary. Table 2 summarizes the mineralogical compositions of the different CW materials used as either SCM or a precursor in AA cements. TCW, CSW and BCW were the major types of utilized CW. The main crystalline phases identified by X-ray diffraction were quartz (SiO₂), feldspars, such as anorthite (CaAl₂Si₂O₈), albite (NaAlSi₃O₈) or microcline (KAlSi₃O₈) and, in the CW obtained from ceramic products sintered at higher temperatures (i.e., CSW or some porcelain stoneware tiles), mullite (Al₆Si₂O₁₃).
Table 2. Mineralogical compositions of different CW materials.

<table>
<thead>
<tr>
<th>CW</th>
<th>Q</th>
<th>M</th>
<th>C</th>
<th>Ca</th>
<th>H</th>
<th>R</th>
<th>D</th>
<th>K</th>
<th>Z</th>
<th>T</th>
<th>m</th>
<th>A</th>
<th>B</th>
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<td>X</td>
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<td>-</td>
<td>-</td>
<td>[18]</td>
</tr>
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<td>-</td>
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<td>-</td>
<td>[31]</td>
</tr>
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<td>-</td>
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<td>[32]</td>
</tr>
<tr>
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<td>[16]</td>
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<tr>
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<td>-</td>
<td>[33]</td>
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<tr>
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<td>X</td>
<td>X</td>
<td>-</td>
<td>-</td>
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<td>PTCW*</td>
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<td>[36]</td>
</tr>
<tr>
<td>CSW</td>
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<td>-</td>
<td>-</td>
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<td>[19,39]</td>
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<td>X</td>
<td>X</td>
<td>-</td>
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<td>-</td>
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<td>-</td>
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<td>[40]</td>
</tr>
<tr>
<td>CSW</td>
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<tr>
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<td>X</td>
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<td>X</td>
<td>-</td>
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<td>[42–44]</td>
</tr>
</tbody>
</table>

Q: Quartz; M: Mullite; C: Calcite; Ca: CaO2; H: Hematite; R: Rankinite; D: Diopside; K: Muscovite; Z: Zircon; m: Microcline; A: Anorthite; B: Albite; S: Sanidine; O: Orthoclase. * PTCW: Polishing tiles ceramic waste.

Table 3 summarizes the chemical composition of the CW obtained from various ceramic product types. Although it varies depending on its origin (i.e., BCW normally contains larger quantities of calcium oxide than CSW or TCW), all CW shares high silica and alumina contents, with varying percentages of Na2O, K2O or CaO. Almost all the CW analyzed in this review met the UNE-EN 450-1:2013 specifications established for SCM such as type A fly ash (FA) [45], and the sum of SiO2, Al2O3 and Fe2O3 went over 70%, with loss on ignition (LOI) below 5%. Additionally, significant amounts of amorphous phases formed during the dehydroxylation or vitrification of clays, especially in CSW and some ceramic tile types. As reviewed in [12], the chemical and mineralogical compositions of the analyzed CW materials, their amorphous content and the particle size reduction performed in the studies that used CW as SCM resulted in the successful reutilization of this waste as a pozzolanic admixture. Similarly, these properties make CW materials perfect candidates to be employed as a precursor in AA systems, which would provide a new reutilization alternative for a significant amount of waste.
Table 3. Chemical composition of different CW types (percentage as mass).

<table>
<thead>
<tr>
<th>CW</th>
<th>SiO$_2$ %</th>
<th>Al$_2$O$_3$ %</th>
<th>FeO$_3$ %</th>
<th>CaO %</th>
<th>Na$_2$O %</th>
<th>K$_2$O %</th>
<th>LOI * %</th>
<th>Amorph %</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCW</td>
<td>49.9–64.6</td>
<td>16.6–20.0</td>
<td>5.6–14.2</td>
<td>0.6–11.5</td>
<td>0.5–5.2</td>
<td>2.3–4.4</td>
<td>0.2–2.4</td>
<td>20.1–46.7</td>
<td>[5,16,18,21,3,146–48]</td>
</tr>
<tr>
<td>TCW</td>
<td>55.8–78.3</td>
<td>14.4–20.0</td>
<td>1.1–7.9</td>
<td>0.1–9.6</td>
<td>0.2–4.7</td>
<td>1.4–3.5</td>
<td>0.1–1.1</td>
<td>46–60</td>
<td>[9,17,22,33,34,46,49–51]</td>
</tr>
<tr>
<td>CSW</td>
<td>66.0–70.8</td>
<td>19.0–24.1</td>
<td>0.6–1.3</td>
<td>0.1–1.2</td>
<td>1.3–2.7</td>
<td>2.8–4.6</td>
<td>0.2–1.1</td>
<td>45.6–46.0</td>
<td>[5,9,16,19,37,39]</td>
</tr>
<tr>
<td>Porcelain insulators</td>
<td>70.9–73.9</td>
<td>14.1–21.1</td>
<td>0.8–2.1</td>
<td>0.8–1.6</td>
<td>0.5–1.5</td>
<td>3.6–5.6</td>
<td>-</td>
<td>-</td>
<td>[49,52]</td>
</tr>
<tr>
<td>Flower pots</td>
<td>61.7</td>
<td>22.3</td>
<td>1.2</td>
<td>6.7</td>
<td>1.0</td>
<td>1.6</td>
<td>4.0</td>
<td>-</td>
<td>[36]</td>
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<tr>
<td>Not specified</td>
<td>28.8–78.3</td>
<td>9.8–45.2</td>
<td>0.5–16.6</td>
<td>0.02–25.2</td>
<td>0.2–13.5</td>
<td>0.2–13.5</td>
<td>0.0–7.5</td>
<td>-</td>
<td>[6,7,15,25,53–57]</td>
</tr>
</tbody>
</table>

* LOI: Loss on ignition.

3. Ceramic Waste as a Precursor in Alkali-Activated Cements

This section analyzes existing studies on the reutilization and valorization of CW as a precursor in AA systems. As summarized in Figure 1, it is divided into three subsections: (i) use of CW as the only precursor; (ii) combined with other binders (i.e., PC, Ca(OH)$_2$ or calcium aluminate cement, CAC); (iii) combined with other precursors (i.e., FA; metakaolin, MK; blast furnace slag, BFS).

3.1. AA Cement Using Only Ceramic Precursors

This section reviews the main research works that employed BCW, TCW or CSW as the only precursor in AA cements. BCW was the most commonly used CW in these AA systems. Its main oxides are SiO$_2$ and Al$_2$O$_3$, with about 50–65% and 16–20%, respectively. This CW type may be activated with only NaOH or KOH [57,58] or with combinations of these and other activators, such as sodium silicate (SS) [59,60]. BCW can be obtained from the production industry (discarded commercial pieces or residual dust) or from CDW. Komnistsas et al. [58] separated three different CDW fractions (concrete, tiles and bricks), which were activated with NaOH/SS solutions by varying both NaOH molarity and curing temperatures. The fact that the samples developed using BCW or TCW as a precursor behaved better than those made with the concrete fraction was attributed to the bigger amounts of SiO$_2$ and Al$_2$O$_3$ in CW, which enhanced geopolymeric reactions. The BCW pastes gave 45.9 MPa after being activated with 8 M NaOH solutions and cured for 7 days at 90 °C. Those developed by activating TCW with 10 M NaOH solutions gave 57.8 MPa when cured at 80 °C for the same period. Only 13 MPa was achieved after activating the concrete fraction with 14 M NaOH solutions after a 7-day curing period at 90 °C.

Bumanis and Vaičiukynienė [57] compared BCW activation to that of raw illitic clay calcined at three different temperatures: 700 °C, 750 °C and 800 °C. These authors used 6 M and 7 M NaOH solutions, and the AA solution content introduced into the mixture was determined by materials' fineness (smaller amounts with coarser fractions). Some samples were cured at 80 °C for 24 h and then tested under compressive strength, while others followed additional curing and were stored at room temperature at two different degrees of relative humidity: 50% and 95% RH. The main conclusion was that the BCW samples provided the highest compressive strength, and strength values hardly varied after the first 24 curing hours (16 MPa). Samples made with BCW mixtures exhibit faster strength development compared to those made with clay mixtures. The presence of zeolites and hydrosodalite was detected in BCW samples. Additionally, SEM images demonstrated that the BCW-activated samples had a higher density than the clay-activated samples. Regarding the original clay’s reactivity, the optimal sintering temperature was 700 °C,
which gave 5 MPa after the first 24 curing hours. This strength improved with curing time and reached 16 MPa after 28 days at 20 °C and 95% RH. Better mechanical strengths (about 10 MPa higher) were obtained when using 7 M than 6 M NaOH solutions.

An interesting option explored by Fort et al. [59] was to use the powder that derives from grinding thermal insulating bricks because this material does not need any treatment but only a sieving process to separate larger particles. The authors activated this powder with mixtures of NaOH/SS and different amounts of water. The paste prepared with the lowest concentrations of activators and the largest amount of water obtained 41.9 MPa and 11.9 MPa of compressive strength and bending strength, respectively, after 28 curing days. However, that mixed with the highest concentration of activators and the smallest quantity of water, respectively, gave only 10.3 MPa and 1.2 MPa. The microstructural studies of the activated pastes showed more macropores with smaller amounts of water. Additionally, some crystalline phases identified in the original material (i.e., quartz, muscovite and albite) remained in the activated pastes, which also contained 40–45% amorphous phases.

Scheinherrová et al. [60] studied the carbonation process in mixtures developed by AA with NaOH/SS solutions of powder waste obtained from cutting bricks (BCW). The quantities of BCW, SS and water remained constant and the NaOH concentration varied. This gave SiO2/Na2O ratios (Ms) of 0.8, 1.0, 1.2 and 1.4 (referenced as A, B, C, D, respectively). The authors compared the behavior of air-exposed mixtures cured at 20 °C to others exposed to accelerated carbonation (20% CO2 and 85% RH for 10 months) after being cured at 60 °C for 6 days (85% RH) and also at 20 °C for 21 days. Some efflorescence arose in mixture A (SiO2/Na2O ratio of 0.8) when cured at different temperatures and exposed to air, which was attributed to excess alkalis. As reported in Figure 2, in the samples cured at 20 °C, the compressive strength values generally improved with the Ms ratio and reached a maximum of 38.5 MPa for the 1.2 samples. This behavior was attributed to a uniform microstructure due to the partial dissolution of the precursor. Conversely, curing at 60 °C positively influenced the strength of the samples developed with lower SiO2/Na2O ratios (A and B) but negatively affected that of the pastes prepared with higher ratios (C and D). Consequently, the authors concluded that the Ms modulus had a stronger influence on the mechanical properties than the curing temperature. When exposed to accelerated carbonation, the main identified phases were calcite and vaterite, whose formation enhanced mortars’ compressive strength. This improvement was more significant in the samples cured at 60 °C than in those cured at 20 °C, which was attributed to a reduction of porosity due to CaCO3 crystallization. Unlike PC carbonation, however, where formed carbonates are generally insoluble, the authors stated that this improved strength in geopolymers may be temporary because the formed carbonates are soluble.

![Figure 2](image-url)
Pommer et al. [61] also studied the behavior of waste obtained from grinding red-clay brick blocks as a precursor in AA NaOH/SS mortars. They compared four different fractions (<125 µm, <500 µm, <1 mm and unsorted) and reported similar compressive strength values for smaller particle sizes, which released more heat (determined by isothermal calorimetry analysis) when dissolved in the activating solution. The authors noticed that removing particles larger than 0.5 mm improved the reactivity of the precursor, which was attributed to the larger surface specific area of the smaller particles. The coarse particles were less active in the geopolymeric reaction and resulted in mixtures with higher porosity. All the precursors exhibited a nearly equal polycondensation heat flow after their dissolution. The microstructural analyses showed that the crystalline products of the original waste were partially dissolved during the geopolymerization reaction. Hence, the percentage of amorphous phases in BCW (37%) rose to 56% when alkali-activated, and the binding matrix was composed of a mixture of N-A-S-H and C-A-S-H gels.

Gado et al. [62] studied the influence of SiO\textsubscript{2}/Na\textsubscript{2}O (0.5–2.5), H\textsubscript{2}O/Na\textsubscript{2}O (10–20) and liquid/solid ratios (0.25–0.40) on the properties of the pastes developed using BCW as a precursor and NaOH/SS as activators. BCW particles were milled for 1 h. Setting times were longer for lower SiO\textsubscript{2}/Na\textsubscript{2}O and H\textsubscript{2}O/Na\textsubscript{2}O ratios or a higher liquid/solid ratio. The variations in workability, viscosity or the degree of geopolymerization reactions also influenced the setting time. In relation to the properties in the hardened state, variation in compressive strengths, water absorption, apparent porosity and bulk density were analyzed. The authors concluded that the optimal SiO\textsubscript{2}/Na\textsubscript{2}O, H\textsubscript{2}O/Na\textsubscript{2}O and liquid/solid ratios were 1.25, 12.5 and 0.25, respectively. After 28 curing days, this combination provided compressive strength of 37.5 MPa, a bulk density of approximately 2.1 g/cm\textsuperscript{3}, an apparent density below 30% and a water absorption percentage of around 15%.

Reig et al. have published several articles using different CW types [31,37,46,63]. Their first work studied BCW employed as a precursor [31] and investigated the influence of the sodium concentration, the SiO\textsubscript{2}/Na\textsubscript{2}O ratio and the water/binder ratio on mortars cured for 3 and 7 days at 65 °C. BCW was crushed below 4 mm and then milled for 40 min in a ball mill. When activating BCW only with NaOH (2–5–7–10 mol.kg\textsuperscript{−1}), an optimum sodium concentration of 5 mol.kg\textsuperscript{−1} was obtained, which provided 15 MPa under compression after 7 curing days. These authors concluded that excess sodium may cause carbonate salt formation. In a second stage of the study, the influence of the Na\textsuperscript{+} concentration (5–6–7–8–9 mol.kg\textsuperscript{−1}) was once again studied by keeping the SiO\textsubscript{2}/Na\textsubscript{2}O ratio constant at 1.6. The best results (close to 28 MPa) in this study stage were recorded with 6 and 7 mols of Na\textsuperscript{+} per kg of solvent. The water/binder ratio, a dominant parameter, then lowered, and the activator/binder and SiO\textsubscript{2}/Na\textsubscript{2}O ratios remained constant. This further improved the compressive strength values insofar as the mortars prepared with a water/binder ratio of 0.35, a sodium concentration of 9 mol.kg\textsuperscript{−1} and an SiO\textsubscript{2}/Na\textsubscript{2}O ratio of 1.6 gave more than 40 MPa after 7 curing days at 65 °C.

In a later study [46], these authors compared the use of BCW as a precursor to that of CW obtained from porcelain stoneware tiles (a specific TCW type). The chemical analyses revealed that the employed TCW contained small amounts of CaO, which meant having to add an extra source of calcium to these mixes (2 wt.% of the TCW was replaced with Ca(OH)\textsubscript{2}). Following the aforementioned process in [31], the developed mortars were cured at 65 °C for 7 days. The study allowed the authors to conclude that both CW types behaved differently insofar as the TCW mortar required a lower water/binder ratio and provided better results for a higher Na\textsuperscript{+} concentration. A compressive strength of 30 MPa was obtained by the TCW mortar when activated with a water/binder ratio of 0.35, 9 mol.kg\textsuperscript{−1} of sodium and an SiO\textsubscript{2}/Na\textsubscript{2}O ratio of 1.6.
Tuyan et al. [64] also studied the influence of Na₂O addition, the SiO₂/Na₂O ratio and the water/binder ratio when using BCW as a precursor and reported similar conclusions to those of Reig et. al. [31]. The authors analyzed the influence of 4–10% Na₂O (% per binder weight) and observed improved compressive strength from the 6% additions, plus minor variations with larger quantities of sodium. The highest mechanical resistance was obtained in the mortars developed with an optimum SiO₂/Na₂O ratio of 1.6 and 10% Na₂O after being cured for 5 days at 90 °C at 40% RH. This was attributed to the denser microstructure and reduced porosity of the binder formed.

In the study by Zhang et al. [65], the mechanisms of reaction were investigated by FTIR and XRD when activating BCW with a mixture of NaOH/SS. The authors observed that the kaolinite, muscovite and illite identified in raw material participated in the activation process, while other minerals like quartz were not involved in reactions. The high curing temperature enhanced the activation of the reaction, which was divided into three stages: dissolution, precipitation and condensation. The Si-O and Al-O groups from the BCW reacted with the Si-O supplied by the alkaline solution to form a new aluminosilicate. These authors also observed that the solution’s excessive alkalinity could lead the dissolution and precipitation reactions to overlap.

Pasupathy et al. [66] published a research work on the development of a foam concrete employing BCW as a precursor, NaOH/SS as an activator and aluminum powder as an aerated agent. Samples were activated with different proportions of NaOH and SS and were cured for 7 days at 80 °C, which resulted in density values below 900 kg/m³. The lowest compressive strength (0.7 MPa) and thermal conductivity (0.225 W/m·K) values were recorded for the mixture prepared without NaOH, while these properties respectively rose to 2.42 MPa and 0.28 W/m·K when using the highest NaOH and SS contents.

Sassoni et al. [67] studied the possibility of utilizing BCW geopolymeric mixtures for masonry repointing. In culture heritage applications, properties like open porosity, pore size distribution or water vapor permeability are important. The authors compared these properties among the AA BCWs with different proportions of SS, NaOH, water and sodium aluminate. The influence of five different formulations (SiO₂/Al₂O₃ ratios between 1.4 and 0.4) was investigated on the AA BCW samples by comparing their behavior at room temperature and 50 °C. The main conclusions were that open porosity decreased when lowering the SiO₂/Al₂O₃ ratio because larger amounts of sodium aluminate progressively densified the binding matrix. The water absorption of all the AA BCW samples was approximately 30%, which was slightly higher than that commonly presented by other traditional mixtures like lime or lime/pozzolan (<22%).

The AA foamed mixtures investigated by Horvat and Ducman [68] were made using CW from the production of ceramic fuses as a precursor. After analyzing the influence of different proportions of NaOH/SS and aerated agents, the authors found that the optimum results to aerate samples (2.8 MPa compressive strength and density of 0.7 kg/L) when employing aluminum were obtained with 0.1% of this agent and 1% sodium dodecyl sulfate (SDS). Although similar density values were obtained in the mixtures made with hydrogen peroxide and sodium perborate, 4.6 MPa under compression was recorded when combining 1% hydrogen peroxide and 0.1% SDS and 5.1 MPa for the samples made with 0.6% sodium perborate and SDS.

In the study by Keppert et al. [69], two different industrial CW dust types, obtained during the calibration processes of brick blocks, were used as a precursor in geopolymeric mixtures. Both the CW types came from two different factories and were employed as received. This implies that they were not milled, and the only applied process was sieving to remove particles bigger than 1 mm. These CW materials were activated with different SS/NaOH proportions and samples were cured at room temperature. This research work is very interesting because both precursors had many crystalline phases, and amorphous content was only 27.8% in the CW called H and 47% in that named L. Regarding oxide content, both residues exhibited similarities in the amounts of SiO₂, Al₂O₃ and Fe₂O₃, with
SiO$_2$ being the predominant oxide (58.8% and 49.9% for H and L, respectively). The main difference was in the CaO content, which was significantly higher in the L waste (15.4%) in comparison to the H waste (6.9%). The two CW types had quartz, mullite, illite, microcline or muscovite. The L CW also contained portlandite and calcite, whose presence promoted C-S-H formation in the activated pastes. The results revealed that some crystalline phases were dissolved by the alkaline environment, while others remained stable and acted as fillers in the geopolymeric matrix. The obtained compressive and bending strength values fell within the 22.3–38.8 MPa and 4.1–9.5 MPa ranges, respectively. In a later study, Keppert et al. [70] analyzed the activation of a similar CW, which contained 37.4% amorphous phases and 15.2% CaO. These mixtures were activated with a set amount of SS and varying quantities of NaOH, which gave SiO$_2$/Na$_2$O ratios within the 0.8–1.5 range. Samples were cured at 60 °C and at ambient temperature. The best compressive strength results were obtained with a SiO$_2$/Na$_2$O ratio of 1.0, and lower values were recorded for the 1.5 mixture. Curing at high temperature only enhanced the strength of the mixtures prepared with the highest SiO$_2$/Na$_2$O ratio, while that of the 1.0 and 0.8 mixtures even decreased, which was attributed to crystallization of muscovite with thermal curing. The main reaction products were C-A-S-H and N-A-S-H gels.

Mendes et al. [71] activated clay CW by a different dosing system, in which the quantity of waste, NaOH and SS varied to complete 100 wt.% of paste. The optimum mixture contained 15% NaOH, 22.5% SS and 62.5% clay CW and provided a compressive strength of 16 MPa after 28 curing days at ambient temperature (precured at 45 °C for 72 h). They studied the possibility of enhancing the system’s mechanical properties by adding fiberglass. They observed that pastes’ strength improved by 35% when 0.1 mass % of fiberglass was added. After 133 curing days, however, compressive strength diminished, which was attributed to the degradation of the fibers inside the alkaline binding matrix.

A few articles have employed TCW as the only precursor in AA cements. Amin et al. [72] used a powder captured from cyclones during ceramic tile production. This powder was calcined at 800 °C for 2 h, which led to the transformation of kaolin into MK. Bricks were produced by mixing this calcined powder with NaOH, water and different proportions of slaked lime. The optimum results were obtained by combining 1% NaOH, 10% lime and 38% water, which gave a compressive strength of 9 MPa after 28 curing days at room temperature. The authors observed that curing at high temperatures was detrimental to compressive strength.

Reig et al. [63] combined the use of TCW powder as both a precursor (TCWP) and an aggregate (TCWA) in geopolymeric systems. The influence of different aggregate types was investigated: siliceous, calcareous, obtained from CSW waste (CSWA) and from red clay bricks (BCWA). As the siliceous and calcareous sands had particle sizes below 2 mm and 4 mm, respectively, the CW aggregates were prepared with two different particle size distributions: below 2 and 4 mm. All the aggregates were physically characterized. The relative density of the dry particles varied between 2.23 g/m$^3$ (BCWA2) and 2.73 g/m$^3$ (natural limestone). The water absorption values also varied within a wide range from 1.58 wt.% for CSWA2 to 11.64 wt.% for BCWA2. TCW was first used only as a precursor (TCWP), and mortars were prepared with natural siliceous and calcareous aggregates. TCW was AA with a NaOH/SS solution prepared with 10 mol/kg of sodium, a SiO$_2$/Na$_2$O ratio of 1.16 and a water/binder (w/b) ratio of 0.45. To improve the geopolymerization process, 5% Ca(OH)$_2$ was applied as a source of calcium in all the prepared samples. After 3 curing days at 65 °C, the mortars prepared with the siliceous and limestone aggregates gave compressive strength values of 9.45 MPa and 34.22 MPa, respectively (TCWA could not be employed under these conditions because workability was insufficient). Given the large differences between the water absorption values of aggregates, they were presaturated before the mixing process to maintain a constant effective w/b ratio of 0.45 for the precursor. Figure 3 (adapted from reference [63]) summarizes the compressive strength of the mortars prepared with all these aggregates cured at 65 °C for 3 days. As it
shows, the total w/b ratio (in brackets) varied depending on the water absorption of aggregates; thus, BCWA2 and BCWA4 exhibited the highest water demand. The best compressive strength results were obtained for natural limestone aggregates (LIM), and CW particles had better strength results than siliceous sand (SIL). The main conclusion drawn by this research was that CW aggregates can be used to replace natural aggregates if they are properly presaturated.

Figure 3. Compressive strength of the AA TCW mortars developed using different types of natural and CW recycled aggregates cured at 65 °C for 3 days. Adapted from Reig et al. [63].

Two of the references that used CW as the only precursor in AA systems employed CSW [37,73]. Öztürk and Atabey [73] reported that CSW was activated with different NaOH concentrations (10, 12, 14 and 16 M) and at w/b ratios of 0.45 and 0.50. Fresh mortars' workability improved with increasing w/b ratios and molarity values. Samples' flexural and compressive strengths were tested after being cured at 100 °C for 1 day and after being exposed to 400 °C and 800 °C. An improvement in mechanical properties was noted with lower w/b ratios and higher sodium concentrations, with the main change taking place when molarity increased from 10 to 12 M. Exposing mortars to high temperatures reduced their flexural and compressive strengths. This was explained by the formation of cracks in the interface region. By way of example, the mortar mixed with 16 M NaOH and a w/b ratio of 0.45 had a flexural strength of 6.4 MPa at 100 °C, which lowered to 3.6 MPa and 3 MPa after being exposed to 400 °C and 800 °C, respectively. Compressive strength followed a similar trend by decreasing from 36 MPa (obtained when cured at 100 °C) to 25.1 and 14.3 MPa recorded after being exposed to 400 °C and 800 °C. The microstructural studies revealed the formation of zeolitic products when exposed to high temperatures, together with a reduction in the intensity of the crystalline peaks attributed to quartz and albite.

Reig et al. [37] activated CSW with NaOH/SS solutions by adding 3.0 to 7.5 wt.% Ca(OH)₂ as a source of calcium to enhance geopolymerization reactions. Pastes and mortars were prepared at a w/b ratio of 0.4, the Na⁺ concentration varied between 2.5 and 12.5 mol/kg and the SiO₂ concentrations were within the 1.82–7.28 mol/kg range. The first step of the study was to analyze the influence of the Na⁺ and SiO₂ concentrations on the compressive strengths of the mortars cured for 3 days at 65 °C. The authors concluded that the optimum quantity of SiO₂ was 7.28 mol/kg. For this SiO₂ concentration,
compressive strength evolution depending on the Na\(^+\) concentration was investigated in the mortars cured for 3 and 7 days. After 3 curing days, better strength results were obtained with bigger amounts of Na\(^+\), and approximately 20 MPa was recorded for 7.5 to 12.5 mol/kg of sodium. However, after 7 curing days, the differences with increasing Na\(^+\) concentrations became more evident, and strength values of around 15, 27, 35 and 36 MPa were obtained with sodium concentrations of 5, 7.5, 10 and 12.5 mol/kg, respectively.

### 3.2. Hybrid Alkaline Cements

Hybrid alkaline cements consist of two primary components. The larger one, accounting for more than 70 wt.%, is formed by an aluminosilicate precursor which is activated by an AA solution, following a similar process to AA cements. The remaining component, less than 30 wt.%, is composed of binders commonly used in construction applications, such as PC, calcium hydroxide or calcium aluminate cement. During the AA reaction, C-A-S-H and N-A-S-H gels can simultaneously form, which enhances the microstructure of the resulting mortars and concretes [74,75].

Research into the production and characterization of hybrid alkaline cements dates back to 1974 [76]. However, it was not until the works performed by the A. Palomo research group [77] that hybrid alkaline cements gained broader attention. This type of cements solves some technical issues that are frequently associated with AA cements, such as severe shrinkage, setting problems and efflorescence [78]. Only a few papers used CW as a precursor during hybrid alkaline cements production [32,79]. This fact indicates the need for R&D in this research field. The main findings associated with using CW in the production, characterization and mechanical and durability properties of hybrid alkaline cements are summarized below.

In 2014, Reig et al. [34] assessed the influence of calcium hydroxide (0–5 wt.%) on the fresh and hardened properties of hybrid alkaline cements based on porcelain stoneware waste. Pastes and mortars at a w/b ratio of 0.4 and a sand/binder ratio of 3 were prepared by varying the Na\(^+\) and SiO\(_2\) concentrations within the 5–12 mol.kg\(^{-1}\) and 1.82–7.28 mol.kg\(^{-1}\) ranges, respectively. The setting time of these hybrid systems was prolonged up to 10 h with bigger amounts of Na\(^+\) (7–10 mol.kg\(^{-1}\)) and SiO\(_2\) (5.46–7.28 mol.kg\(^{-1}\)). This occurred because adding Ca(OH)\(_2\) alters the setting time. In mixtures with high alkalinity, the dissolution of Ca(OH)\(_2\) is hindered by higher OH\(^-\) concentrations, which prolongs setting time. Compressive strength was also enhanced (up to 36 MPa) with the sodium concentration and calcium hydroxide content when the silica concentration (7.28 mol.kg\(^{-1}\)) and the calcium modulus (Ca\(^+2\)/Na\(^+\) molar ratio) remained constant.

Murillo et al. [79] followed a statistical surface methodology (RSM) procedure to optimize the PC percentage (5–15 wt.%) and the SiO\(_2\)/Al\(_2\)O\(_3\) (7–8) and Na\(_2\)O/SiO\(_2\) (0.08–0.18) molar ratios of hybrid alkaline cements based on TCW. According to these authors, apart from obtaining the optimum parameters for the dose of these hybrid cements, RSM was able to predict their compressive strengths and acceptable values were found compared to the experimental results (about 30 MPa after 90 curing days).

The production of hybrid cements based on BCW waste and CAC has been reported by Reig et al. [32]. Pastes and mortars (sand/binder ratio of 3.0) were prepared using a set SiO\(_2\)/Na\(_2\)O molar ratio of 1.60, a w/b ratio of 0.40 and CAC percentages within the 0–50 wt.% range. Specimens were cured at 65 °C for 7 days and at room temperature for 3, 7, 14 and 28 days. Although the mortars without CAC addition did not harden at room temperature, the compressive strength values improved with increasing amounts of CAC, with up to 93 MPa after 7 curing days at 65 °C.

The influence of different calcium sources (calcium hydroxide, CAC and PC) on the mechanical properties and microstructure of AA CSW waste binders was assessed in [38]. The mortars and pastes developed with a w/b ratio of 0.4, a binder/sand ratio of 1:3 (only for mortars) and Na\(^+\) and SiO\(_2\) concentrations of 7.5 and 7.28 mol.kg\(^{-1}\), respectively, were cured at 65 °C for 3 and 7 days. CSW was partially replaced with Ca(OH)\(_2\): (4.5 wt.%, 6.0 wt.% and 8.0 wt.%), PC (5 wt.%, 10 wt.% and 15 wt.%) and CAC (5 wt.%, 10 wt.% and 15 wt.%), respectively.
20 wt.%, 30 wt.%, 40 wt.%, 50 wt.% and 100 wt.%). According to the XRD pattern, none of the typical phases commonly found during PC hydration (portlandite, ettringite), CAC hydration (hexagonal and cubic aluminate phases) or even calcium hydroxide were detected in the AA cements. Based on infrared spectroscopy, SEM images and TG analyses, the authors were able to identify the formation of both C-A-S-H and (N,C)-A-S-H gels. Regarding the compressive strength results, increasing the amounts of the different sources of calcium generally improved systems’ mechanical properties, with up to 80 MPa in the mortars containing 20 wt.% CAC.

Atabey [80] performed an experimental study on hybrid systems in which 0–25 wt.% CSW wastes were replaced with CAC. Mortars, which were cured in an oven at 90 °C for 24 h and held at 23 °C and 55 °C for up to 28 curing days, were prepared using a binder/sand ratio of 1:3, a w/b ratio of 0.50 and a set amount of Na2O (10 wt.% of the binder). It was observed that larger amounts of CAC increased the flow table values due to the lower water absorption of CAC compared to that of CSW. Improvements in mechanical strength were also achieved with up to 15 wt.% CAC (about 30 MPa after 28 curing days). The authors explained this by the densification of the microstructure with CAC addition, which led to the formation of both C-A-S-H and N-A-S-H gels. Compressive strength decreased for the samples exposed to high temperatures due to pore formation (Figure 4).

Figure 4. Compressive strength of hybrid mortars based on CSW containing different amounts of CAC: Effect of high temperatures. Adapted from [80].

3.3. Combination of Different Precursors

Different types of CW materials, such as TCW, porcelain, BCW or CSW, were combined with other precursors to produce AA mortars and concrete. These systems came to suppress some fundamental issues that can affect the production of AA systems, such as problems with setting and hardening at room temperature, severe shrinkage, etc. Although the precursor most commonly combined with CW is BFS [19,81–86], other materials like FA, MK or even tungsten mining waste have also been used [19,82,87]. The main findings on this topic are presented below.

Abdollahnejad et al. [81] reported a comparative analysis of AA mortars composed of BFS and porcelain CW (unfired and fired ceramic; up to 30 wt.%), which were activated using anhydrous sodium metasilicate and water (H2O/Na2O molar ratio within the 66.81–69.86 range and Na2O/SiO2 set at 0.06). The water/precursor ratio was set at 0.39 and a porcelain CW (0.5–4.0 mm) was used as a fine aggregate. According to the authors,
increasing amounts of CW (from 0 to 30 wt.%) reduced compressive strength from about 20 MPa to 10 MPa in the mortars containing fired CW and to about 6 MPa in that developed with unfired ceramics (7 thermal curing days).

Cosa et al. [39] assessed the mechanical and microstructural properties of AA binary systems developed by combining CSW and fluid catalytic cracking residue (FCC). The AA mortars and pastes were prepared by replacing 0 to 50 wt.% CSW with FCC and using an AA solution with a SiO$_2$/Na$_2$O molar ratio that varied from 0.78 to 1.94, constant 4 wt.% Ca(OH)$_2$ addition and a w/b ratio of 0.45. Mechanical tests were performed on the mortars cured at room temperature for 28 and 90 curing days and at 65 °C for 7 days. The compressive strength values improved with FCC addition regardless of the curing time. The obtained values went up to 70 MPa in the AA systems containing 50% FCC and cured for 90 days at room temperature (see Figure 5). According to the microstructural analysis, N-A-S-H/(N,C)-A-S-H gels were the main products to form and, depending on the SiO$_2$/Na$_2$O molar ratio, some minor crystalline phases were detected, such as anorthite, herschelite and zeolite type-A.

![Figure 5. Compressive strength development of AA mortars based on CSW with different amounts of FCC, activated at a constant SiO$_2$/Na$_2$O ratio of 1.94 [39].](image)

In another study, Cosa et al. [19] combined CSW with up to 50 wt.% BFS or class F FA to improve CSW AA mortars’ properties. Similarly to the above-mentioned study, the w/b ratio was set at 0.45 with a constant Na$_2$O/SiO$_2$ molar ratio of 1.94, and specimens were cured at 65 °C for 7 days and at room temperature for 28 and 90 days. The compressive strength results (Figure 6) showed that BFS addition led to significant improvement, with up to 40 MPa in the mortars containing 50% BFS and 50% CSW and over 50 MPa in similar mortars that contained 4% Ca(OH)$_2$. The mortars developed with FA and 4% Ca(OH)$_2$ yielded lower compressive strength values (up to 40 MPa). Although both BFS and FA improved the AA CSW mortars’ mechanical properties, the authors associated the better results obtained in the CSW/BFS systems with the higher reactivity and amorphous content of BFS and also with the fact that the alkaline activating solution was not optimized for FA systems. The main hydrated products that formed due to these reactions were C-S-H/(N-(C)-A-S-H gels in the CSW/BFS systems and N-A-S-H/(N-(C)-A-S-H gels in that containing FA. The XRD patterns also indicated the formation of carbonate compounds, such as natron (Na$_2$CO$_3$.10H$_2$O) and thermonatrite (Na$_2$CO$_3$.H$_2$O).
Huseien et al. [82] performed an interesting study about ternary AA systems' mechanical and durability properties based on 50 wt.% TCW (set for all the mixtures) and varying proportions of BFS:FA (from 50:0 to 10:40, in mass). The binder/sand ratio was set at 1:1, and the AA solution was composed of 188.6 kg/m$^3$ of Na$_2$SiO$_3$ and 251.4 kg/m$^3$ of NaOH. The increment in FA reduced the ternary system’s compressive strength from the 70 MPa recorded after 28 curing days in the 50:0 samples to about 42 MPa in those prepared with 10:40 proportions. On the contrary, after exposing these mortars to acid attack (10% H$_2$SO$_4$ solution) for 12 months, enhanced results were achieved with larger amounts of FA. In fact, the 50:0 sample presented a residual compressive strength of 67.8%, while that of the 10:40 sample was about 89.2%. According to the authors, the calcium present in BFS can react with SO$_4^{2-}$ ions to form gypsum, which results in expansion and cracking in AA systems.

In another study, Huseien et al. [88] evaluated the effect of TCW (up to 80 wt.%) on AA self-compacted concretes containing BFS. According to the obtained results, good fresh state properties (slump flow, passing ability, resistance to segregation) were obtained with up to 50 wt.% TCW. Although a significant reduction in mechanical strength occurred with increasing TCW contents, the self-compacting concretes mixed with 40–50 wt.% TCW yielded around 40–50 MPa after 28 curing days, which denotes the feasibility of this CW in this concrete type. The water absorption values progressively increased with CW addition and went from 6.5% in the reference sample to 50% in the concrete developed with 50 wt.% TCW.

Mahmoodi et al. [89] developed an optimized binary AA binder by combining ceramic tiles and concrete waste. The mix proportions were designed using a sequential algorithm, with TCW percentages varying from 20–80 wt.%, a liquid/solid ratio of 0.3, an SiO$_2$/Al$_2$O$_3$ molar ratio within the 11.4–12.5 range, and Na$_2$O/SiO$_2$ from 0.18 to 0.24. After 28 curing days, the highest compressive strength results (about 31 MPa) were obtained in the mixtures prepared with a Na$_2$O/SiO$_2$ ratio of 0.18, a SiO$_2$/Al$_2$O$_3$ ratio of 12.3 and 40 wt.% TCW. When the above-mentioned mixture was cured for 24 h at high temperature (100 °C), this AA paste had almost 90 MPa, which proved the positive effect of thermal curing on these AA systems’ mechanical properties. At this curing temperature, the XRD analyses revealed the dissolution of albite and anorthite and the relative consumption of the plagioclase phases of TCW and concrete waste, plus the consequent increment in amorphous gel formation.

Rashad and Essa [83] assessed the effect of TCW (0–50 wt.%) on the mechanical properties and microstructure of AA BFS exposed to high temperatures (200–1000 °C). All
the pastes were prepared with a set w/b ratio of 0.22 and a constant amount of SS (30 wt.% of the binder). Samples were cured for 90 days at 45 °C before being exposed to high temperatures for 2 h. According to the obtained results, TCW addition enhanced compressive strength due to a filler effect, which densified the microstructure. When exposed to temperatures within the 200–600 °C range, the dehydration of the matrix led to pores and microcracks forming in all the samples, which lowered their compressive strength. Nevertheless, mechanical strength improved in the samples exposed to 800–1000 °C (increments of up to 50%, yielding up to 68 MPa) compared to those cured for 90 days. This was attributed to the sintering and formation of stable phases, such as mullite, albite, nepheline and akermanite.

Zhang et al. [86] performed a systematic study about employing TCW (up to 30 wt.%) in BFS AA systems. Mortars and pastes were prepared by mixing a 2M NaOH solution with commercial SS at a constant w/b ratio of 0.46 and a Si2O/Na2O molar ratio of 1.2. The thermal calorimetry analyses showed that cumulative heat reduced over 72 h with increasing TCW contents, which was attributed to its slower reaction at early curing ages compared to BFS. Regarding the compressive strength results (Figure 7), although larger amounts of TCW caused a slight reduction at 3 and 7 curing days, no differences for the reference sample were observed after 28 curing days and all the strength values came close to 57 MPa.

![Figure 7](image-url)

Figure 7. Effect of TCW on the compressive strength of AA BFS mortars cured for different ages. Adapted from [86].

Mahmoodi et al. [90] reported an interesting study in binary AA systems based on TCW and BCW, where the amount of BCW varied from 20 to 80 wt.%. The solid/liquid ratio was set at 0.30, and different molar ratios of SiO2/Al2O3 (7.8–10) and Na2O/SiO2 (0.18–0.24) were applied. The best TCW/BCW proportion was employed to produce and characterize ternary systems using MK, BFS, class C FA and class F FA. The obtained results showed that the binary system containing 80% TCW and 20% BCW, together with a SiO2/Al2O3 ratio of 10 and a Na2O/SiO2 ratio of 0.24, led to enhanced mechanical properties (30 MPa after 28 curing days) compared to the other assessed mix proportions. The best mechanical results in the ternary system were achieved with 45 wt.% class C FA (45% FA/44% TCW/11% BCW), which yielded 57 MPa after 28 curing days. The increment of almost 100% in compressive strength with FA addition was explained by the enhanced dissolution process, which improved the formation of cross-linked aluminate and silicate tetrahedrals intermixed with C-A-S-H gels.
The study conducted by Hwang et al. [84] on binary AA mortars combined BCW with up to 50 vol.% BFS. It also used CW sand as a fine aggregate. Mortars were prepared using a binder/sand ratio of 1:2.75 and a w/b ratio of 0.4. The AA solution was prepared by mixing Na₂SiO₃ and a 10 M NaOH solution to achieve a Na₂O percentage of 5.5 and a SiO₂/Na₂O ratio of 1.25. The results showed that compressive strength lowered with BCW contents, with about 22 MPa obtained in the 90 vol.% BCW sample after 56 curing days and 93 MPa in that mixed with 50 vol.% BCW for the same curing age. The authors also reported a reduction in samples’ porosity (%) with increasing curing times (e.g., porosity of the 90 vol.% BCW mortars reduced from 15.3% to 12.83% from 7 and 56 curing days, respectively) and with higher BFS contents (porosity values of 12.83% and 8.38% with 10 vol.% and 50 vol.% of BFS, respectively). The presence of BFS densified the binding matrix, and C-S-H and C-A-S-H gels formed that covered both unreacted BCW and CW sand.

Rakhimova and Rakhimov [85] assessed the influence of different factors related to the precursor (fineness, mineralogical composition), AA solution (SS or sodium carbonate solutions) and processing parameters (separate or conjoint grinding, curing conditions) on binary systems with different BFS and BCW proportions (0/100 to 100/0). The alkaline activator was set at 5% Na₂O in all the prepared samples. For those containing SS, the SiO₂/Na₂O molar ratio was set at 1.5. According to the authors, low alkali contents were insufficient to promote minimal compressive strength in the systems developed using only BCW as a precursor. Higher compressive strengths (about 120 MPa) were obtained for conjoint grinding (about 22.6% higher than grinding separately). Fineness of around 600–700 m²/kg seemed to provide optimum compressive strengths and densities, together with the lowest water absorption values (about 140 MPa, 1.95 g/cm³ and 9%, respectively) when employing SS activating solutions.

In the study by Sedira et al. [87], up to 50% BCW was used in AA binary systems based on tungsten mining waste. The activating solution was prepared by mixing SS and 10 M NaOH solutions (2:1 in mass). According to the obtained results, 59 MPa was achieved in the 50–50% mixes (tungsten mining waste–BCW) cured for 28 days, which represents a gain of almost 140% compared to the sample prepared with 10% BCW. The increment in mechanical strength was explained by enhanced N-A-S-H/C-A-S-H gel formation due to BCW addition.

As evidenced by the reviewed literature, CW can serve as a suitable precursor for the synthesis of geopolymers. Although BCW can be activated using only NaOH, its performance can be enhanced by adding SS. BCW alkali-activated mortars presented compressive strengths of around 40 MPa and 45 MPa after 28 curing days at room temperature and 7 days at 80 °C, respectively. When thermally cured at 80 °C and activated with 10 M NaOH solutions, TCW mortars exhibited a compressive strength of 57.81 MPa after 7 days. On the other hand, CSW exhibited the lowest mechanical performance when used as the sole precursor. Typically, NaOH/SS solutions are used to activate this CW, and its mechanical properties can be significantly improved by incorporating additional sources of calcium. Hybrid mixes containing CAC or PC have been found to significantly enhance the performance of CW alkali-activated systems. These mixes have yielded compressive strength values of over 90 MPa after 7 curing days at 65 °C. Another way to improve the performance of CW systems is by mixing them with other traditional precursors such as FA or BFS. It has been reported that compressive strength values of up to 100 MPa can be achieved in such instances.

4. Sustainability and Carbon Footprint of AA CW Cements

AA cements are some of the most promising binders for solving the environmental problems generated by employing PC. However, several authors [91,92] reject AA binders due to some negative environmental issues, such as abiotic depletion, acidification, eutrophication and human toxicity. These parameters are strongly influenced by the chemical synthesis of the alkaline activators required to prepare AA cement. Contrarily, some authors [58,93] emphasize the advantages of reducing the greenhouse gas emissions
and embodied energy associated with AA cements. Environmental analyses must be accompanied by an assessment of some functional properties, such as the open porosity, bulk density, compressive strength or bending strength of AA composites.

Fořt et al. [59] prepared different pastes by activating brick powder waste (BCW) with SS and sodium hydroxide solutions (silicate modulus: 1.4). These authors considered the high energy use and CO2 emissions associated with both chemical reagents: 5462 MJ/ton and 15.24 kgCO2/ton for pure SS and 6965 MJ/ton and 1930 kgCO2/ton for pure sodium hydroxide. These values are significantly higher than those reported for PC, namely 2986 MJ/ton and 829 kgCO2/ton. The energy use of the BCW precursor was 135 MJ/ton and CO2 emissions were 28 kgCO2/ton. These values were related to the grinding process. The pastes prepared by activating BCW had a relative SS content of 35%, 40%, 45% and 50% in relation to the amount of the precursor (the precursor did not harden with 30% SS). Despite the high SS proportion, both energy use and CO2 emissions were much lower than those reported for PC: energy use and CO2 emissions lowered within the 63–50% and the 81–75% ranges, respectively. The best values were obtained for the mixture prepared with the smallest amounts of SS (40% of BCW). The combined functional (compressive strength) and environmental properties assessment is depicted in Figure 8. It is noteworthy that using high SS proportions is not a good solution from an environmental point of view because of the low compressive strength yielded after 28 curing days.

In order to improve AA materials’ compressive strength, some authors have attempted to blend ceramic waste powder (CWP) with other precursors, such as BFS and FA. Huseien et al. [82] prepared mortars with 50% CWP and 50% of a BFS and FA mixture (from 50:0 to 10:40). All these mixtures yielded compressive strengths over 40 MPa after 28 curing days. The CO2 emissions of the CWP mortars were lower than 110 kgCO2/m3, a significantly lower value than that obtained for the PC mortar (420 kgCO2/m3). Saxena and Gupta [94] tested the AA of TCW and FA mixtures. An FA geopolymer was used as the reference (activated with SS and sodium hydroxide, with a binder content of 445 kg/m3) and FA replacements of 5%, 10%, 15% and 20% with TCW were tested. Because the embodied energy values for FA and TCW were very low, the total embodied energies for mortars were alike (=1480–1490 MJ/m3). Similar results were also obtained for CO2 emissions, which fell within the 136–137 kgCO2/m3 range for all the developed samples.

Figure 8. Embodied energy and CO2 emission indices obtained using compressive strength values as a functional property for a PC paste and those obtained by activating BCW powder with different SS percentages (data taken from [60]).
Both functional and durability properties diminished when FA was replaced with TCW and, consequently, lower performance indices were obtained for the activated mortars containing TCW. Only the 5% replacement was considered acceptable.

Mahmoodi et al. [89,95] analyzed binary and ternary blends containing TCW. In the binary blends [89], several TCW and concrete waste (CRW) combinations were studied by varying the Na₂O/SiO₂ ratio of the activator (0.18, 0.21, 0.24). The CO₂ emissions of the activated cements fell within the 280–325 kgCO₂/ton range, whereas those for the PC cement were 769 kgCO₂/ton. The CO₂ intensity index for most of the AA TCW-CRW samples varied within the 9–18 kgCO₂/MPa-ton range and was significantly lower than that for PC (23.67 kgCO₂/MPa-ton). The ternary blends were prepared by mixing TCW, CRW and recycled clay bricks (BCW) [95]. Most of the ternary activated cements had less embodied energy and lower CO₂ emissions than the PC system. The optimal ternary composition had 20% BCW, 40% TCW and 40% CRW, which gave values of 18.61 MJ/MPa-ton for the embodied energy index and 5.58 kgCO₂/MPa-ton for the CO₂ emission index. These values dropped by 85.75% and 76.4% compared to the control PC paste.

Ground brick waste powder has also been used in geopolymeric foamed concrete [66]. Foam was prepared by a chemical method using aluminum powder. The CO₂ emissions associated with the preparation of 1 m³ of foamed concrete fell within the 45–143 kgCO₂ range (depending on the amount of activators, SS and sodium hydroxide). This value was 88–62% lower than that obtained for the PC foamed concrete.

Finally, hybrid systems, developed by combining AA cements and PC, have been studied in environmental impact terms [96]. Red clay brick waste (RCBW) was activated with NaOH and Na₂SiO₃ solutions and was then mixed with PC (in 10% and 20% proportions). The global warming potential of the hybrid system containing 10% PC was 265 kgCO₂/ton, which was approximately half that associated with the PC mortar (511 kgCO₂/ton). The developed hybrid mixture was proposed as a very good option for fabricating structural blocks and pavers.

5. Conclusions

This work reviewed using CW as a precursor in AA cements, and reached the following conclusions:

- Research into using CW as the only precursor in AA cements has shown that most CWs require high temperatures and moderately high concentrations of activators to initiate alkaline reactions;
- Sometimes the setting time of AA CW systems can be delayed at room temperature. Although this could be seen as a disadvantage, it can be resolved by using hybrid systems or combining CW with other precursors;
- Although the contribution of an additional source of calcium favors AA reactions, very few studies have developed AA hybrid cements that combine the use of CW precursors with traditional binders, such as PC, CAC or Ca(OH)₂;
- The mechanical properties of AA CW hybrid systems generally improve by incorporating different sources of calcium. Additionally, PC and CAC follow a different reaction mechanism than that generally observed when hydrated in water. Similarly, the combination of different precursors generally enhances AA CW systems’ mechanical properties;
- The growing demand for natural resources and energy has led to unsustainable development. This review evidences that CW can be successfully used as a precursor to develop more sustainable cements by AA, with appropriate properties to be employed in construction applications. This is a promising reutilization alternative for CW that would contribute to circular economy, helping to reduce not only PC consumption and its associated CO₂ emissions but also the amount of landfilled waste.
6. Future Trends

From the conducted review, the following research future trends are proposed:

- Given that the quality of CW materials significantly influences their behavior as a precursor in AA systems, separating CW materials when they are generated would facilitate their valorization;

- Although only one study has been found to combine the use of CW as an AA precursor and as a recycled aggregate, promising results with a wide variety of mechanical properties are reported [63]. The combined use of CW as both a recycled aggregate and a precursor in AA systems would allow larger amounts of CW to be reused, which would offer maximum environmental benefits;

- No previous studies have been found on the AA of CW with alternative activators to commercial SS. The viability of activating CW with more environmentally friendly activators derived from silica-rich waste materials, such as rice husk ash, diatomaceous earth or waste glass, should be explored;

- It is important to compare the AA of CW provided by the ceramic industry with that obtained from CDW, which may be mixed with other construction materials like cement mortar and gypsum. Although this review focuses only on the AA of CW with no impurities, it is necessary to investigate any potential differences in the activation process for both types of waste;

- An artificial neural network can be used to develop algorithms that allow the strength and properties of AA materials to be estimated depending on the CW employed as a precursor, the type of activator and the AA solution concentration;

- Standardization and long-term durability studies are required for real-scale applications.


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List of Abbreviations

Ceramic waste (CW); ceramic waste powder (CWP); brick ceramic waste (BCW); ceramic sanitary ware (CSW); tile ceramic waste (TCW); ceramic waste from polishing tiles (PTCW); construction and demolition waste (CDW); Portland cement (PC); supplementary cementitious material (SCM); calcium aluminate cement (CAC); fly ash (FA); blast furnace slag (BFS); metakaolin (MK); fluid catalytic cracking residue (FCC); ceramic waste aggregate (CWA); scanning electron microscopy (SEM); weight percentage (wt.%); volume percentage (vol.%); alkali activation or alkali-activated (AA); sodium silicate (SS).
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