Green Concrete: By-Products Utilization and Advanced Approaches

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Abstract: The popularity of concrete has been accompanied with dreadful consumptions that have led to huge carbon footprint in our environment. The exhaustion of natural resources is not yet the problem, but also the energy that is needed for the fabrication of the natural materials, in which this process releases significant amount of carbon dioxide (CO2) emissions into the air. Ordinary Portland Cement (OPC) and natural aggregates, which are the key constituents of concrete, are suggested to be recycled or substituted in order to address the sustainability concern. Here, by-products have been targeted to reduce the carbon footprint, including, but not limited to, fly ash, rice husk ash, silica fume, recycled coarse aggregates, ground granular blast-furnace slag, waste glass, and plastic. Moreover, advanced approaches with an emphasis on sustainability are highlighted, which include the enhancement of the hydration process in cement (calcium-silicate hydrate) and the development of new materials that can be used in concrete (e.g., carbon nanotube). This review paper provides a comprehensive discussion upon the utilization of the reviewed materials, as well as the challenges and the knowledge gaps in producing green and sustainable concrete.

Keywords: by-products; green concrete; recycling; sustainability

1. Introduction

For several decades, the demand of construction materials has been increasing, particularly, for concrete. Concrete, as a composite material, gained its status of applicability through its mechanical properties and economical price, especially when compared with other available materials. However, there is no ideal material, and concrete is not an exception. Concrete is responsible for a great impact on the environment by consuming large amount of natural resources and continually releasing approximately one ton of CO2 for each ton of Ordinary Portland Cement (OPC) produced [1]. It has been estimated that cement production will reach up to four billion tonnes each year by 2030 [2]. Additionally, more than 5% of the manmade greenhouse gas emissions originate from cement production [3]. Such harmful contribution on the environment paves the way for alternative materials that can either reduce the uncontrolled consumption of natural resources or recycle industrial and agricultural by-products. Accordingly, green concrete concept that came out at the end of the last century aims to fully or partially replace the components of the ordinary concrete for waste or recycled materials. In fact, the idea of green concrete has been extended to not only waste materials, but also to nano-engineered materials that can enhance concrete’s mechanical properties, and, as a result, its life-cycle sustainability.
Concrete is widely known to be composed of four ingredients, including: cement, aggregates, water, and additives. The carbon footprint of cement production on earth, in addition to the huge consumption of aggregates and water, is the key theme for engineers to find environmentally friendly solutions for. Figure 1 shows the companionship of CO$_2$ with all the processes of the production and application of OPC. This figure clarifies the sources of CO$_2$ during cement production starting from the limestone quarries, where considerable energy is needed for the excavation work. CO$_2$ emissions are mainly caused during the manufacturing process of OPC. These emissions are mostly attributed to: (a) burning of fossil fuels during the manufacturing process, which is required to heat raw materials up to 1400 °C in the rotating kiln [4,5] and (b) the chemical decomposition of limestone CaCO$_3$ (calcium carbonate), which is the main ingredient of cement, to lime CaO (calcium oxide) and CO$_2$ [6]. The challenge for these substitutes is to enhance the overall performance of concrete, or at least not to prejudice the current bottom line. Fortunately, there has been success in improving the fresh and hardened properties of concrete. For example, fly ash decreases the setting time for mass concrete structures without affecting the long-term strength [7–9] and even with better workability [9–11], rice husk ash reduces water absorption of concrete [12,13] and improves the durability properties [12–14], as well as chemical resistance [15–17], ground granular blast-furnace slag and municipal solid waste ash significantly reduce CO$_2$ emissions [18–20] and heat of hydration [21], and waste glass develops better compressive strength [22–24] and improves the resistance in both high and low temperature environments [24,25]. On the contrary, these by-products bring out some drawbacks, and the decision of using any of them depends on several criteria (i.e., mechanical and chemical properties, availability, and cost). A major and common advantage of the abovementioned by-products and many others is that they are waste materials anyway, and the disposal of these wastes brings up great cost of landfills and manpower [23,26–30].

**Figure 1.** Main processes for manufacturing and using OPC. From excavation works at quarries, to cement production in industries, which include burning fuels to heat kilns and calcination process in which limestone is broken down into calcium oxide and CO$_2$. Each step is accompanied by mitigating greenhouse gas emissions into the environment.

Sustainability is an approach to find balance in the environment by integrating available economic and social resources, and manipulating long-term development and endurance. The idea of sustainability can be seen in concrete through materials with long service life, like OPC and aggregates, but without carbon footprint in the environment. Green concrete incorporates materials that have been used before in either industries or farms. Nevertheless, the development of green concrete does not stop at the utilization of by-products, it goes further through more advanced approaches to investigate material systems at the nano-level to achieve the aim of sustainability [31]. Nano-engineering is simply understanding the behavior of a material at the nanoscale with a view to enhance the performance of the micro-level structure that is reflected, accordingly, on the macro-level of the material. By following
the bottom-up approach of nano-engineering, the chemical and physical properties of a material can be studied, understood, and enhanced [32]. New developments can also be seen in the near future, including smart concrete in sever conditions, eco-binders that aim to reduce the amount of OPC, therefore, CO$_2$ emissions, and self-healing concrete [33], to mention a few. The molecular dynamics (MD) atomistic simulation is a tool for studying the nanostructures and understanding the atomic behavior of materials. This method started long time ago to study the physical and chemical systems in order to solve problems in chemistry [34], but it was limited to a small number of particles due to memory capacity and processing speed. MD simulation is now being used for engineering applications to study the elastic properties of OPC [35], where the physical and chemical properties are the dominant concerns, and to study and develop new materials, such as carbon nanotube (CNT) [36,37], which is being effectively used in concrete nowadays.

This paper encapsulates the most common by-products that are used as substitutes for the major components of concrete. A review on the recyclable industrial and agricultural waste materials that are usable in concrete is provided, as well as the advantages and disadvantages of each candidate. Among the reviewed by-products, this paper clearly shows which substitute is appropriate for the three main ingredients of the ordinary concrete, alongside the optimum substitution ratio of each. Fly ash (FA), rice husk ash (RHA), silica fume (SF), and other pozzolanic ashes are introduced as cement replacements, while recycled coarse aggregates is an alternate of the virgin coarse aggregates. Ground granular blast-furnace slag (GGBFS), waste glass (WG), plastic (P), and several agricultural and aquacultural by-products are represented as both cement and/or aggregate substitutes afterwards. Figure 2 clarifies the concept of the classification that is used in this review by showing which by-product is substituted for. The materials listed above might form ternary systems, in which two by-products can work as a substitute in the same mixture. Thus, the most common ternary systems are also mentioned with their benefits. Furthermore, nano-engineered materials also carry out the aim of utilizing different by-products in concrete; in other words, sustainability in concrete industry in terms of nano-engineering is addressed. Finally, the difficulties that are faced for accepting either the reviewed by-products or the nano-engineered materials in concrete are stated with suggestions for surmounting their limitations. Each limitation of the abovementioned substitutes is a research area by itself, and a clear interpretation of such by-products is the first step towards the incorporation of these materials into the concrete industry and consummation a footstep for sustainability.

**Figure 2.** The most common by-products that are used as substitutes. This diagram clarifies the methodology of this review for the categorization system of the reviewed by-products used as concrete ingredients.
2. Materials Replacing Cement

Historically, the first development for the combination of lime and pozzolan was made by the Romans 2000-plus years ago [38]. Materials that can replace cement share the same chemical composition with cement. However, the amount of each component for the substitutes varies. This variation can also be found for the same substitute due to the change of the source for these by-products. For instance, GGBFS is obtained when water or steam is used to quickly cool the molten iron slag from a blast furnace [39]. Thus, it can be found with different chemical compositions depending on all factors that take role in this process. Table 1 lists the sizes and percentages of the main chemical compositions of OPC and its substitutes. All of the substitutes of cements have, more or less, the same compositions of cement. It is worth mentioning that the closer the chemical compositions of a substitute, the better it can replace the cement, even at high replacement ratios. Microscopic images of these candidates can explain some of their unique behavior. Therefore, their main features and references for the microscopic images are provided in Table 2.

### Table 1. Chemical composition and particle size of cement and its substitutes (%). The cement mentioned in this review is the OPC type-1.

<table>
<thead>
<tr>
<th>Size and Compounds</th>
<th>Cement</th>
<th>FA Class F</th>
<th>FA Class C</th>
<th>RHA</th>
<th>SF</th>
<th>WG</th>
<th>GGBFS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle size (µm)</td>
<td></td>
<td>5–60 [40]</td>
<td>2–20 [40]</td>
<td>&lt;75 [10]</td>
<td>0.3–2 [40]</td>
<td>≤70 [22,50]</td>
<td>0.1–200 [41,53]</td>
</tr>
<tr>
<td></td>
<td>0.1–110 [41]</td>
<td>0.05–100 [43]</td>
<td>av. 3.8 [45]</td>
<td>av. 11.5 [46]</td>
<td>av. 0.1 [48]</td>
<td>≤90 [24]</td>
<td>av. 45 [51,52]</td>
</tr>
<tr>
<td></td>
<td>1–200 [44]</td>
<td>av. 3.8 [45]</td>
<td>0.3–2 [40]</td>
<td>≤70 [22,50]</td>
<td>av. 45 [51,52]</td>
<td>0.1–200 [41,53]</td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
<td>20–22</td>
<td>50–68</td>
<td>38–46</td>
<td>75–91</td>
<td>85–97</td>
<td>64–72</td>
<td>34–42</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>4.0–6.0</td>
<td>17–28</td>
<td>16–22</td>
<td>0.3–9</td>
<td>0.2–1.1</td>
<td>1.0–10</td>
<td>7–16</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>2.4–3.5</td>
<td>4–14</td>
<td>6–14</td>
<td>0.1–1.1</td>
<td>0.4–2.0</td>
<td>0.1–1.6</td>
<td>0.3–1.5</td>
</tr>
<tr>
<td>CaO</td>
<td>61–65</td>
<td>1.6–9.3</td>
<td>19–25</td>
<td>0.5–3.8</td>
<td>0.3–0.7</td>
<td>8.5–15</td>
<td>32–45</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.1–0.4</td>
<td>0.1–1.6</td>
<td>0.03–1.6</td>
<td>0.1–1.1</td>
<td>0.1–0.7</td>
<td>12–18</td>
<td>0.2–0.4</td>
</tr>
<tr>
<td>K₂O</td>
<td>0–0.9</td>
<td>0.4–2.6</td>
<td>0.2–1.4</td>
<td>1.0–3.8</td>
<td>0.3–1.3</td>
<td>0.4–1.6</td>
<td>0–0.8</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0–0.24</td>
<td>1.4–1.6</td>
<td>6–14</td>
<td>0–0.1</td>
<td>0–0.1</td>
<td>0–0.1</td>
<td>0–0.1</td>
</tr>
<tr>
<td>MgO</td>
<td>1.0–2.6</td>
<td>1–5.2</td>
<td>3–7.8</td>
<td>0.2–0.8</td>
<td>0.0–1.6</td>
<td>0.9–3.9</td>
<td>3.2–15</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0–0.9</td>
<td>0.4–1.5</td>
<td>5–2.1</td>
<td>0–0.1</td>
<td>0–0.1</td>
<td>0–0.1</td>
<td>0–0.1</td>
</tr>
<tr>
<td>SO₃</td>
<td>2.0–4.7</td>
<td>0.2–2.0</td>
<td>1.6–3.3</td>
<td>0–1.2</td>
<td>0.0–1.3</td>
<td>0.1–0.4</td>
<td>0.01–1.0</td>
</tr>
<tr>
<td>Loss of ignition (LOI)</td>
<td>0.1–2.4</td>
<td>0.3–3.9</td>
<td>0.2–1.3</td>
<td>1.8–8.6</td>
<td>0.0–2.8</td>
<td>0.8</td>
<td>0.04–0.3</td>
</tr>
</tbody>
</table>


### Table 2. Main microscopic features of different candidates replacing cement, in addition to the relevant references for the SEM images.

<table>
<thead>
<tr>
<th>Material</th>
<th>Main Microscopic Feature</th>
<th>Reference for SEM Images</th>
</tr>
</thead>
<tbody>
<tr>
<td>FA</td>
<td>Most of particles have spherical shapes</td>
<td>[40]</td>
</tr>
<tr>
<td>RHA</td>
<td>Particles have irregular shapes with many micro-pores. This can explain the higher porosity of this material</td>
<td>[70]</td>
</tr>
<tr>
<td>SF</td>
<td>Particles are found smaller than FA and RHA in most of the reviewed cases, they can rarely be found at bigger sizes</td>
<td>[43]</td>
</tr>
<tr>
<td>GGBFS</td>
<td>Particles are angular in shape, and their surfaces are rough</td>
<td>[75]</td>
</tr>
<tr>
<td>WG</td>
<td>Particles appear to have angular shapes with narrow sizes</td>
<td>[50]</td>
</tr>
<tr>
<td>P</td>
<td>Particles are heterogenous in shapes and textures</td>
<td>[77]</td>
</tr>
</tbody>
</table>

2.1. Fly Ash (FA)

Luckily, there have been different standards that study and specify the types and properties of fly ash as supplementary material in concrete. American Society for Testing and Materials (ASTM) developed the first version of the standards for using fly ash more than 40 years ago, which was ASTM C 618. This confirms the importance and popularity of using fly ash as a pozzolanic material in concrete. According to ASTM C 618-17a [63], fly ash is mainly a residue fine material that is transported by air after powered or ground coal is burnt. Therefore, the properties of fly ash are greatly influenced by the raw coal. Fly ash is classified in ASTM C 618 into three different categories: Class N, Class F, and Class C. This classification is mainly based on the chemical composition of the resultant ash. Fly ash Class N is not commonly used in construction due to the existence of clay and shale, which requires more mixing water and increases the Loss on Ignition (LOI). Importantly, it has been found that a reduction of up to 30% in CO₂ emissions of concrete with fly ash classes C and F could be attained as compared to portland cement [78,79]. Moreover, ACI committee mentions that Class C fly ash reduces sulphate resistance when compared to Class F that increases the sulphate resistance of concrete [44].

When compared to cement, both classes of fly ash have different ratios of the controlling chemical compounds. The four main compounds that specify the concrete characteristics are: tricalcium silicate C₃S, dicalcium silicate C₂S, tricalcium aluminate C₃A, and tetracalcium aluminoferrite C₄AF. The increase of silica, alumina, and iron oxide in fly ash at the expense of calcium, which is the main portion in OPC, is the key element in changing the properties of concrete. Classes F and C of fly ash were compared to OPC and to each other physically and mechanically [9,11,40]. It was found that fly ash influences the setting time, where Class C with higher sulphate SO₃ content causes a great delay compared to Class F [9], this is due to the reduction in the active dissolution sites caused by the initial adsorption of the sulphate ions. Generally, fly ash class F retards setting time more than class C due to the higher calcium content [80]. However, fly ash Class C can produce a higher early-age (before 28 days) strength of concrete [11]. Although Class F is recommended when concrete is used in high sulphate ions environment, it delays the early-age strength of concrete for up to as long as 60 to 90 days [10], but it improves the workability of the concrete mixtures [81]. Furthermore, some fly ash types can also be pelletized and used as lightweight aggregates in concrete, as proposed by [82].

The pozzolanic activity of FA results in advantageous reactions with the free lime that results from the hydration process of OPC and water. It is well known that the increase of free lime in concrete reduces the total silicates produced during the hydration process. The strength of concrete is reduced, accordingly. In other words, more calcium-silicate-hydrate (C-S-H) is produced when FA is used in concrete [83]. The following illustration can be used to clarify the reaction:

\[
\begin{align*}
\text{OPC} + \text{water} & \rightarrow \left\{ \begin{array}{c}
\text{C-S-H} \\
\text{free lime}
\end{array} \right\} \\
\text{OPC} + \text{FA} + \text{water} & \rightarrow \left\{ \begin{array}{c}
\text{free lime} \\
\text{FA}
\end{array} \right\} \rightarrow \text{(C-S-H)}
\end{align*}
\]

There is almost no research related to concrete that does not mention the resistance of concrete for compression. Concrete is a mixture of aggregates and cementing materials that hydrate with the existence of water. Compressive strength of concrete is mainly controlled by the weaker component, which is the adhesion medium, cement. Accordingly, the substitution of cement for fly ash is controlled by the compressive strength that fly ash can produce. The compressive strength of concrete incorporating fly ash as a cement substitute has been thoroughly studied [8,40,43,55,60,62,84]. The substitution ratio has always been the key factor that researchers investigate in their studies. It was
found that the optimum ratio of substitution for the standard concrete was 8% to 20%. Table 3 shows how the substitution of cement for fly ash Class F at different substitution ratios affects the overall compressive strength of concrete. The ratio w/b herein identifies the water to binder ratio that is used in the mixtures. The binder is the cement matrix plus any other material used for substituting cement. While the ratio w/c used in later tables identifies water to only-cement ratios for different mixtures. The table clarifies that the substitution of cement should be limited to 15% by the weight of cement to obtain an increase of 20% of the compressive strength. Substitution ratios of 20% to 25% were also suggested for the common use of concrete [7]. Moreover, the early-age strength development is a drawback for fly ash, where the seven-day strength ratios are, most of the times, less than 1.0, which indicates a slower compressive strength as compared to the controlled samples (reference compressive strength), even at the recommended substitution ratios. In fact, this delay is not a problem for mass concrete structures that are not loaded until a while after casting [1], e.g., dams, especially since heat of hydration for fly ash is lower than that of the regular portland cement. Compressive strength of concrete incorporating fly ash Class C was also studied, and the trend was fairly the same, however the early-age strength was always higher compared to Class F. Even more, at 60% of substitution ratio for Class C, the early-age strength is considerably remarkable [62], but it gets weaker at 28 days as compared to the OPC concrete.

Table 3. The effects of different substitution ratios of cement for fly ash Class F at different ages.

<table>
<thead>
<tr>
<th>w/b</th>
<th>Cement Content (kg/m³)</th>
<th>Reference Compressive Strength at Different Ages (f'c/reference) (MPa)</th>
<th>Substitution Ratio of Cement (%)</th>
<th>Substitution Content (kg/m³)</th>
<th>f'c with substitutes/f'c reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>7</td>
<td>28</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>0.25</td>
<td>400</td>
<td>86.0</td>
<td>92.0</td>
<td>91.5</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8</td>
<td>15</td>
<td>60</td>
<td>0.97</td>
</tr>
<tr>
<td>0.35</td>
<td>64.0</td>
<td>66.0</td>
<td>79.0</td>
<td></td>
<td>8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15</td>
<td>60</td>
<td></td>
<td>0.94</td>
</tr>
<tr>
<td>0.40</td>
<td>352</td>
<td>33.2</td>
<td>47.5</td>
<td>55.1</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30</td>
<td>106</td>
<td></td>
<td>0.91</td>
</tr>
<tr>
<td>0.28</td>
<td>500</td>
<td>66.8</td>
<td>81.1</td>
<td></td>
<td>50</td>
</tr>
</tbody>
</table>

Notes: The data in the first and second rows, third row, and the last row are taken from the references [8,43,60] respectively.

2.2. Rice Husk Ash (RHA)

An agricultural by-product that is being popular as a cement substitute in rice-producing countries is Rice Husk Ash (RHA). The cementitious properties of RHA was not elaborately known until the detailed experimental studies in 1970s [85]. The production of RHA is relatively easier when compared to OPC, where rice husks are incinerated under particular conditions of time and temperature ranging from 30–120 min. and 500–700 °C [46,86,87], respectively. The burning process is recommended to be in a closed room to avoid high carbon content when burnt in an open field [88]. The burning conditions control the fineness of RHA, which represents the specific surface area that improves the pozzolanic activity when it increases [89]. Table 1 includes the chemical composition of RHA, and it can be noticed that RHA is at least three-fourths silica after incineration, and this is the reason for RHA to be a good candidate among other by-products that replace cement. The pozzolanic property of RHA makes it chemically active with calcium hydroxide and water during the hydration process [57].

The presence of RHA in concrete as a cement substitute has benefits and drawbacks. Compressive strength of concrete is one of the vital benefits of RHA. Researchers have found great merits of substituting cement for RHA at lower percentages [12,16,42,45,47,57,64,65,68,70]. Table 4 represents the overall trend of the effects of RHA in concrete according to the reviewed researches. The table shows that best results for the compressive strength of concrete after 28 days could be obtained at a substitution ratio lying in the range 10% to 20%. Within this range, reduction of CO₂ emissions
could be achieved with no effects on compressive strength [65]. Importantly, concrete incorporating RHA was found to reduce magnesium sulphate attacks [12] and chloride penetrability according to ASTM C1202 [16,17]. However, different researchers have produced conflicting mechanical results, such as compressive strength [56,69,90]. This can be referred to the degree of fineness, which RHA is very sensitive to, and the source and properties of rice husks than can vary from a place to another. A more serious drawback of RHA is noticed in Table 1, where the loss of ignition is as high as 8%, while it is limited to 3% in OPC. The high ratio of LOI indicates that there are enough components that might evaporate at elevated temperatures, which makes it uncertain to be a competitive for cement substitutes, especially when concrete is exposed to high temperature.

Table 4. The effects of different substitution ratios of cement for rice husk ash (RHA).

<table>
<thead>
<tr>
<th>w/b</th>
<th>Cement Content (kg/m³)</th>
<th>Reference Compressive Strength (f’c reference) (MPa)</th>
<th>Substitution Ratio of Cement (%)</th>
<th>Substitution Content (kg/m³)</th>
<th>f’c with substitutes/f’c reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.53</td>
<td>383</td>
<td>37.0</td>
<td>5</td>
<td>19</td>
<td>1.05</td>
</tr>
<tr>
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<td>10</td>
<td>38</td>
<td>1.16</td>
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<td>15</td>
<td>57</td>
<td>1.26</td>
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<td>20</td>
<td>77</td>
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<td>25</td>
<td>96</td>
<td>1.04</td>
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<td>134</td>
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<tr>
<td>0.35</td>
<td>571</td>
<td>56.0</td>
<td>10</td>
<td>57</td>
<td>1.09</td>
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<td></td>
<td></td>
<td>30</td>
<td>171</td>
<td>0.96</td>
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<tr>
<td>0.30</td>
<td>550</td>
<td>63.5</td>
<td>10</td>
<td>55</td>
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<td></td>
<td></td>
<td>20</td>
<td>110</td>
<td>1.23</td>
</tr>
</tbody>
</table>

Notes: The data in the first, second and third rows are taken from the references [45,64,65] respectively.

2.3. Silica Fume (SF)

Silica fume (SF) fits in the same category with by-products that result from industrial applications. SF can also be found as micro-silica, condensed silica fume, or volatilized silica [73,91]. They all originate from electric arc furnaces during the production of silicon metal or ferrosilicon alloys. The raw materials are high-purity quartz, coal or coke, and wood chips [92–95]. SF was firstly used during the industrial revolution in the mid of twentieth century in various countries to reduce the release of the material into the atmosphere [48]. Since then, there have been many researches and various applications of silica fume, especially in construction industry. This motivates governments and organizations to set up quality test and requirements for this material to control its production, storage, shipping, and mixing, such as ACI 234 [48], ASTM C1240 [92], AASHTO M 307 [95], and Silica Fume Association [49], to mention a few. The physical properties and resultant reactions of SF varies depending on raw materials and production processes of silicon metal and ferrosilicon alloys. Generally, the size distribution of a typical SF particles has to have an average size of 0.1 µm, where most of the particles (>95% [73]) are smaller than 1 µm [48]. The key feature of SF is its fineness that can be found as high as a hindered time more than OPC. This has great impact on the overall performance of concrete in both short- and long-term durability.

There are several advantages of adding SF to concrete. SF is able to improve the bonding between cement paste and aggregates [96], this is mainly due to the decrease of calcium hydroxide (Ca(OH)₂) at the interface of components by adding SF. The high surface area of SF allows for more particles of Ca(OH)₂ to react in the presence of water and it results in a better hydration process and higher density accordingly. It has been observed that 5% of SF content in concrete is enough to prevent
bleeding [49]. Other researchers [97,98] suggest a SF content of 5–10% to prevent the bleeding of concrete and increased protection against sulphate attacks and chloride ions. The bleeding of concrete normally happens when the concrete components settle under their own weight just after casting. Water, as a light material as compared to others in concrete, is forced upward or moves up to the surface through capillary channels, and then it evaporates [49]. These channels become exposed ways for aggressive chemicals to attack concrete and its reinforcement. Therefore, the existing of SF in concrete develops better resistance against aggressive chemical agents. The incorporation of SF into concrete increases the overall compressive strength [96,98–102], tensile strength, and modulus of elasticity [98,100,102]. The increase in these strengths varies depending on SF particle size, dimensions of specimens used in the tests, and testing procedures. Table 5 shows an example of the enhancement of compressive strength of concrete containing different portions of SF. Compressive strength is enhanced 10–45% as compared to the controlled samples at substitution ratios of 5–20% of cement by weight. Another key advantage of using SF in concrete is its ability to reduce permeability of concrete, this has been thoroughly investigated [49,103–105]. It was reported that the permeability of concrete reduces drastically as long as the SF content is beyond 8% [103]. The reduction of permeability of concrete diminishes gradually as SF content increases within the range 8–12%. Alkali-silica-reaction (ASR) reduces in the presence of SF as long as the silica content is within the specified standards [106].

<table>
<thead>
<tr>
<th>w/b Cement Content (kg/m³)</th>
<th>Reference Compressive Strength at Different Ages (f'c reference) (MPa)</th>
<th>Substitution Ratio of Cement (%)</th>
<th>Substitution Content (kg/m³)</th>
<th>f'c with substitutes/f'c reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.43</td>
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<tr>
<td></td>
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<td>74</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Notes: The data in the first, second and third rows are taken from the references [94,104,107] respectively.

Like other substitutes, SF requires more experienced labors to avoid its drawbacks. The workability of concrete reduces because of the high surface area of SF particles. Therefore, an increase in water demand has been observed [94,97,101]. Moreover, it has been reported that very high SF content reduces the long-term compressive strength due to the inhibition of hydration of cementitious materials in concrete [107]. In addition, a high content of SF increases the dry shrinkage of high-performance cementitious mixtures accordingly [94,107].

2.4. Other Pozzolanic Ashes

Wastes from different sources have always been research topics in terms of landfilling, decomposition, and environmental impacts. Sewage sludge ash (SSA) is an urban waste that can be used as a supplementary cementitious material. Although it is a result of waste water treatment, there are several advantageous applications that can profit from this waste. SSA is successfully used as fertilizer [108,109], and it is also being used as a cement substitute [110,111]. The reduction of carbon footprint caused by cement production can be reduced when replacing OPC by SSA [110,112,113]. The replacement ratio of OPC by SSA in a concrete mixture is limited by different researchers to an average of 20% [110–112,114], because phosphorous and sulphate become high in the mixture at higher substitution ratios. Another environmentally threatening by-product is saw dust ash (SDA), which is also known as wood waste ash. Generally, SDA satisfies the chemical requirements for pozzolanic materials [115,116], with adequate content of lime and silica compounds. Optimum substitution ratio of OPC for SDA varies depending on the source of the wood, combustion temperature, and treatment
processes. However, the suggested substitution ratios varies from 5% [116], 10% [117], and 20% [115]. Water demand of concrete mixtures increases as the portion of SDA increases in concrete [115–117], and the mechanical properties are generally reduced accordingly [117].

Furthermore, sugarcane bagasse ash (SBA) is a by-product that results from producing can sugar juice from sugar cane, where this requires crushing the stalks of the plants [91]. The incorporation of SBA into concrete reduces the temperature of hydration up to 33% when 30% of OPC was replaced by SBA [118]. In addition, water permeability significantly reduces when compared to controlled concrete samples [118,119]. In order to get higher compressive strengths, the suggested cement replacement varies from 15% [120], 20% [118], and 30% [119]. It was reported that SBA helps control ASR expansion in concrete by binding alkalies [121]. There are various agricultural by-products that can be used to replace cement. Bamboo fiber and leaf ash (BA) is also used to replace OPC. Bamboo is well-known for its high yielding strength, and it is widely used in some regions for construction purposes, mostly scaffoldings. Burning the bamboo fibers and leaves results in a grey ash with high content of silica [122–124]. The development of compressive strength of concrete containing BA witnessed different trends. While slight decrease was noticed when 10–20% of OPC was replaced [125], an increase was recorded when 5–10% of OPC was replaced [126]. On the other hand, it was found that water demand of concrete mixtures increases as BA increases in the concrete [125–128]. Moreover, a delay in the setting time was noticed during the hydration process, when 20% of BA was used [125]. Palm oil fuel ash (POFA) is another by-product that can be used to replace cement in concrete. It is a waste product of bio-diesel industry [91]. POFA has enough silica content that can react with calcium hydroxide [129]. Nevertheless, the optimum substitution ratio of cement for POFA is limited to 20% by some researchers [129–131] and 10% by others [132]. It was also noticed that 20% of POFA in concrete results in high strength with lower drying shrinkage concrete [131]. One drawback that can be found with POFA is the reduction of workability in fresh concrete mixtures [133,134]. Therefore, superplasticizers are needed with the addition of POFA [131,135,136].

3. Materials Replacing Aggregate

Aggregates in concrete have gained proper care in terms of classifications, tests, and applications. It is well-known that three-fourths of the volume of concrete is occupied by aggregates. Accordingly, it is crucial to guarantee the high quality of physical, chemical, and mechanical properties of aggregates. Fortunately, enough details for aggregates have already been provided by different manuals and standards, e.g., ACI E1 [137].

As construction continues at a rapid pace, the need for land areas for these constructions is high, which is not an easy option in some parts of the world, where space is a serious problem; e.g., Hong Kong and Japan. Therefore, the demolition of old constructions has always been a solution to find space for new ones; however, the disposal of the demolished construction wastes also needed space in landfills. It has been found that 200–300 million tons of demolition wastes is annually generated in America [1]. As a response, engineers and organizations have developed methods and standards, such as ACI 555 [28], to reuse the demolished concrete constructions in new concrete applications, and one of which is the recycled concrete aggregates (RCA).

The technical benefits of RCA incorporated into concrete mixes have been focused on environmental impacts, costs, and an ignorable reduction of mechanical properties of the resultant concrete. The use of RCA reduced the environmental impact and the cost paid off for all stages of virgin aggregate production [28,29,138]. Notwithstanding that high-quality concrete has to go through proper treatments and measures [139], the particle size distribution of RCA needs always to be carefully controlled to balance between fracture resistance and compressive strength of concrete [140]. The mechanical properties of concrete incorporating different percentages of RCA have been studied in details [141–149]. Table 6 shows the effect of substitution coarse aggregates for RCA at different substitution ratios. The results mentioned in the table represent the general pattern for the effect of incorporating RCA. In short, a substitution ratio within 25% to 30% led to a reduction in mechanical strengths by 5% only,
while the reduction could reach as high as 25% when 100% of natural coarse aggregates were replaced by RCA. The usage of RCA might be judged by an engineer for a project based on the aggregates’ availability and feasibility. For general practices, it was found that RCA did not have a significant effect when it replaced 25% of natural aggregates [148], and it was recommended for the “Moderate” exposure conditions defined in ASTM C1202 [150].

As a recycled material, RCA has some drawbacks because of the preceding use in concrete. Firstly, the old paste can still be found at the surface of the RCA, as a result, the specific gravity of the aggregate is reduced, and the porosity is increased [142]. In fact, not only does the existence of the paste affect the specific gravity, but it also becomes a foothold for water particles at the surface in addition to the water particles inside the aggregate. This is also the main reason for the reduction of workability in concrete that involves RCA [145,151]. It was concluded that, as the amount of RCA increases in concrete, the workability and mechanical performance of the concrete decreases. This is referred to the residual adhered mortar at the surface of the RCA that has high absorption capacity that is caused by its high porosity. The adhered mortar absorbs the designed amount of water added for new mixtures due to its lightweight and high porosity, as mentioned earlier, as compared to natural aggregates [152]. Using RCA requires more experience with water content because the dry condition is away different from saturated condition of RCA due to its high absorption [146,147]. Multi-recycled aggregate was also experimentally studied [151], and it was concluded that the mechanical properties of RCA continued to decrease as the number of recycling increased.

Table 6. The effects of different substitution ratios of coarse aggregates for recycled concrete aggregates (RCA).

<table>
<thead>
<tr>
<th>w/c</th>
<th>Cement Content (kg/m³)</th>
<th>Coarse Aggregates Content (kg/m³)</th>
<th>Reference Compressive Strength $f'_c$ (MPa)</th>
<th>Substitution Ratio of Coarse Aggregates (%)</th>
<th>Substitution Content (kg/m³)</th>
<th>$f'<em>{c</em>{with substitutes}}/f'<em>{c</em>{reference}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.43</td>
<td>430</td>
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<td>570</td>
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</tr>
<tr>
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<td>450</td>
<td>1179</td>
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<td>50</td>
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<td>0.89</td>
</tr>
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<td></td>
<td></td>
<td>100</td>
<td>990</td>
<td>0.81</td>
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<tr>
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<td></td>
<td>25</td>
<td>230</td>
<td>0.97</td>
</tr>
<tr>
<td>0.5</td>
<td>450</td>
<td>1100</td>
<td>41.5</td>
<td>50</td>
<td>460</td>
<td>0.92</td>
</tr>
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<td>920</td>
<td>0.83</td>
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<td>1361</td>
<td>34.6</td>
<td>100</td>
<td>1361</td>
<td>0.76</td>
</tr>
</tbody>
</table>

Notes: The data in the first row, second to fifth rows, and the last row are taken from the references [142,148,149] respectively.

4. Materials Replacing Cement and Aggregates

4.1. Ground Granular Blast-Furnace Slag (GGBFS)

A by-product that is currently enormously used in concrete, in industrial countries, is the ground granular blast-furnace slag (GGBFS). ACI 233 committee found out that production capacity of slag cement annually exceeded 2,000,000 metric ton in the northern part of America [53]. GGBFS is mainly a wasted product from steel industry that forms when molten blast furnace slag is cooled down in water [53]. Going back to Table 1, GGBFS is the most candidate whose chemical composition matches with those of OPC, especially for silica and calcium content. This match gets the optimum cement
replacement by mass for GGBFS to the tune of 60% to 70%, which is high when compared with other substitutes. GGBFS generates less heat during the hydration process [21]; therefore, no wonder that different mixtures with OPC and GGBFS are commonly used when it is required to minimize the temperature differentials during heat of hydration without installing cooling systems [18]. GGBFS can be used as a cement substitute and as an aggregates substitute. The particle size of the GGBFS that was used to replace fine aggregates is generally less than 5 mm [75]. While the size of GGBFS used as cement substitute can vary from 0.1 to 250 µm, which is the size distribution of typical cement particles. The size of GGBFS as a cement substitute depends on the milling time [41]. Therefore, it can be tailored to match the size distribution of cement. The chemical composition of GGBFS that is used to replace cement and aggregates is the same according to the reviewed articles.

The utilization of GGBFS as a cement substitute has advantages and disadvantages. It has been proven that greenhouse gas emissions are reduced when using GGBFS as a cement replacement [18,19]. On the other hand, the mechanical properties were also investigated regarding compressive strength and ductility [21,41,58,59,75,153–155]. Although GGBFS might develop lower early-age strength of concrete, an equivalent or even greater 28-day strength can be gained. Table 7 represents the trend of substituting cement for GGBFS. Fairly said, early-age strength was always lower when compared to the controlled samples, whilst the 28-day strength was equivalent or slightly better with substitution ratios of up to 50% and sometimes 70%. Importantly, concrete incorporating GGBFS continued developing strength in the long-term (90-day compressive strength) as high as 15% as compared to the controlled concrete. In fact, this was also valid for the flexure and modulus of elasticity [18]. Some drawbacks were spotted regarding the cohesive substance (C-S-H) production of concrete in the presence of GGBFS. Normally, OPC produces C-S-H in an alkaline medium (PH ≥ 9.5), while the GGBFS mixture requires higher values (PH ≥ 11.5) [39]. Moreover, the carbonation rate raises when GGBFS increases, but it can be reduced by controlling the wet curing time that is based on GGBFS content [156].

Table 7. The effects of different substitution ratios of cement for Ground Granular Blast-Furnace Slag (GGBFS) at different ages.

<table>
<thead>
<tr>
<th>w/b</th>
<th>Cement Content (kg/m²)</th>
<th>Reference Compressive Strength at Different Ages (f’c reference) (MPa)</th>
<th>Substitution Ratio of Cement (%)</th>
<th>Substitution Content (kg/m³)</th>
<th>f’c with substitutes/f’c reference</th>
</tr>
</thead>
<tbody>
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<td></td>
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<td>7</td>
<td>28</td>
<td>90</td>
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</tr>
<tr>
<td>0.3</td>
<td>400</td>
<td>73.8</td>
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<td>85.2</td>
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</tr>
<tr>
<td></td>
<td></td>
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<td>160</td>
<td>0.87</td>
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<td>0.79</td>
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<td>1.01</td>
</tr>
</tbody>
</table>

Notes: The data in the first three rows and the last row are taken from the references [38,59] respectively.

It is worth mentioning that GGBFS is also used as fine aggregates replacement, though not as much as cement replacement due to the chemical components mismatch. Compressive and tensile strengths were seen to be improved when the replacement level of fine aggregates for GGBFS did not exceed 60% [75]. However, using GGBFS with RCA in one mixture decreased the mechanical properties of concrete compared to a controlled sample, while the optimum substitution content was
recommended around 40% of GGBFS and 50% of RCA to guarantee less than 5% reduction in the mechanical properties [157]. The concept of mixing two materials, i.e., ternary systems, is explicitly addressed in the following section. Overcoming the limitation of one substitute being possible, and GGBFS is a common by-product for the ternary systems.

4.2. Waste Glass (WG)

Glass is considered one of the most brittle materials in construction, thus it is very likely to shatter and/or break. When glass breaks, it becomes useless and most of the times unmaintainable. To avoid using landfills for broken glass, countries have adopted the recycling of glass, since glass is 100% recyclable without any loss of its quality. For instance, the USA recycled 27% of broken glass in 2015 [158], while the European Union recycled an average of 74% in 2018 [159]. Hong Kong, on the other hand, produces around 300 tonnes of waste glass on a daily basis [160], but there is no local manufacturing units for recycling waste glass. Unfortunately, the rest of the broken glass ends in landfills. Like fly ash and rice husk ash, glass is a silica-based material (Table 1), which makes it a great competitor as a cement substitute. In fact, glass is also used to replace fine aggregates, but it is not used as a substitute for coarse aggregates due to the alkali-silica destructive reaction between the cement and the waste glass aggregates [161] and its brittleness that may lead to cracks and segregation [91]. Nevertheless, it can be found as a replacement for coarse aggregates for decoration purposes [162].

Despite the reduction of landfills needed for waste glass, the use of waste glass in construction has some other benefits. The presence of silica was noticed to contribute in forming C-S-H gel during the first seven days of the concrete age [23,25], and it occupied the space of hydration components in concrete [51]. Moreover, when glass was used as a powder for cement replacement, it was found to fulfill the limits of pozzolanic materials according to ASTM C 618 [22,23]. Freeze-thaw resistance of concrete containing glass was enhanced through the improvement of the pore system properties of the concrete structure [24,25,163]. Previous studies reported slight improvements in the compressive strength of concrete with glass if the replacement ratio was limited to 5% to 10% [22–24,50,163]. Table 8 summarizes the general effect on compressive strength of the glass replacing cement. As for compressive strength, it is concluded that the limits of substitution ratio for waste glass (5% to 10%) is low when compared to other substitutes. Waste glass might also be recommended for other purposes (e.g., glass recycling and CO₂ emissions reduction). On the other hand, when waste glass was substituted for 50% of natural fine aggregates, the resultant concrete samples recorded a reduction of 10% in compressive strength, and it might reach 15% to 20% if all of the natural fine aggregates were replaced by waste glass [163]. There are two studies in this table. The first row used glass powder of the size 1.5–70 µm [22], while the second row used glass powder passing through (#200 sieve) [23], which is 75 µm. The images show that the glass powder varies in size from hundreds of nanometers to several micrometers [22]. While, the images of coarse glass particles show that they have sharp edges and they need to be distributed based on the required sizes [163].

There are several concerns regarding the use of waste glass in concrete. Table 8 clarifies that a large amount of glass in concrete is not recommended, as it reduces the compressive strength of the resultant concrete. Additionally, the early-age strength was noted to be lower than the controlled samples [24]. When broken glass is collected for the use in concrete, it cannot be directly used. Therefore, the preparation of glass requires experience with specific particle size, otherwise glass would be more of a hindrance than a help with pozzolanic reactivity [25] as well as workability [162]. If the size of the glass powder is much larger than cement particles, the glass particles would fall between cement particles size and fine aggregates. Therefore, the pozzolanic reaction of the glass powder, which substituted cement, would not be reactive due to its bigger size as compared to cement particles. The replacement of fine aggregate by waste glass increased the air content of the concrete according to experimental results [163]. Therefore, it is not recommended to increase the substitution ratio for waste glass, even though the decrease in compressive strength is not significant.
Table 8. The effects of different substitution ratios of cement for waste glass (WG).

<table>
<thead>
<tr>
<th>w/b</th>
<th>Cement Content (kg/m³)</th>
<th>Reference Compressive Strength (fc’ reference) (MPa)</th>
<th>Substitution Ratio of Cement (%)</th>
<th>Substitution Content (kg/m³)</th>
<th>fc’ with substitutes/fc’ reference</th>
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Notes: The data in the first and second rows, and the last row are taken from the references [22,23] respectively.

4.3. Plastic (P)

As the name implies, plastic is a material that can keep new physical changes when deformed. From water bottles to space shuttles, plastic exists in our daily life in different types according to its application. It has advantageous features, including deformability, high strength-to-weight ratio, low density, and durability [164]. Therefore, the amount of plastic that is produced yearly is several millions of tonnes, in return, the catastrophe of waste plastic is frightening, unless it is recycled. The amount of waste plastic has triggered awareness among countries to go for recycling to save the environment, because most of the plastic consumed in the world does not get recycled. For instance, most of the plastic in the USA is not being recycled [164], while European Union countries are more likely to go for recycling and reusing [165]. Hong Kong, on the other hand, has recently started to take steps to cut down the use of plastic after a report talking about over 17 million pieces of plastic waste had been flushed into the sea each year [166]. Fortunately, the use of plastic in concrete is an option to post-consume plastic, and it became an attractive topic among the engineering society.

Plastic is mostly used in concrete as an aggregate substitute, and it leads to several benefits. Additionally, it has been utilized as a replacement for cement in a form of gamma-irradiated plastic [167]. Consequently, it reduced CO₂ emissions and decreased the porosity of the concrete samples. As an aggregate substitute, plastic was found to have favorable effects, including the reduction of the cost of concrete [168,169], improvement of the resistance to impact loadings [170], and changing the modes of failure of concrete from brittle to ductile [27,170–172]. One of the most common shapes in the reviewed researches is the shredded shape of waste plastic [173]. The size of the shredded waste plastic can be controlled according to the required size distribution. A comparison study of unreinforced plain concrete and recycled polyethylene terephthalate (PET) fiber reinforced concrete observed marked improvements in thermal resistance, mechanical strengths, and ductility of the latter [174]. It is important to mention that the partial replacement of aggregates for plastic meet the minimum strength criteria for standard concrete and, significantly, lightweight concrete [172]. PET strips were employed as reinforcement of different cement mortars [175], and they led to different beneficial effects on crack strengths. It has been noted that the regular PE types of plastic (e.g., water bottles) are the most consumed plastic in the world, and they can be recycled with different procedures [176].

On the contrary, there are several drawbacks that accompany the use of plastic in the concrete industry. The compressive strength of all concrete mixtures with plastic decreases as the plastic ratio increases [27,167,168,170,172,177,178]. When cement was replaced by irradiated plastic, only
1.25% replacement by volume led to around 30% reduction in compressive strength. While the use of shredded plastic as aggregate replacement by 5% and 15% led to a reduction in compressive strength of about 15% and 65%, respectively. Moreover, plastic reduces the abrasion resistance of concrete due to its plasticity nature [27]. Additionally, when applied to thermal cycles, concrete samples with plastic are inferior to that of controlling concrete samples [170,172]. Nonetheless, special treatments for waste plastic have been implemented in order to decrease the impact of the abovementioned drawbacks in concrete.

Plastic has been used in concrete for the aim of producing green concrete. Like any composite material, the interfacial transition zone between different materials is the controlling factor [179,180]. In the literature, there are different physical and chemical approaches to enhance interfacial bond between concrete and plastic. An improvement of the bond strength between plastics, as a replacement of aggregates, and concrete mixture prior to mixing was conducted successfully [181]. Two chemical compounds were used: (1) sodium hydroxide and sodium hypochlorite, (2) sodium hydroxide and sodium hypochlorite and water. The overall results, including compressive and tensile strengths, were not promising, especially when the plastic samples were not washed by water after the chemical treatment. Another approach was used through cutting the waste PET bottles to the size of 5–15 mm and then intruding them in a high temperature mixer with GGBFS to solidify the surface of the plastic samples [178]. The reactive GGBFS, which was used to solidify the plastic surface, was able to densely cover the plastic aggregates by C-S-H. The resultant pellets were then used in concrete mixtures and provided little drops in strengths, even when the new pellets replaced 50% of natural aggregates.

Moreover, a long treatment process was suggested for the waste PET bottles in order to solidify the surface of the plastic samples [182]. Plastics were crushed and washed first, and then dumped into a reactor power vacuum to be heated to the drying temperature. After that, the samples were extruded through several holes and then collected in a cooling bath. Finally, they were centrifuged to remove the excess water and then crystallized. When compared to the controlled concrete samples, and to the treatment procedure, the durability criteria of the final concrete with the treated plastic were moderate. Similarly, the same treatment method was proposed for plastics before using them as aggregates in concrete [183]. Their results verified the work that was done earlier [182], and the suggested replacement percentages are 5–10% of the fine aggregates in concrete mixtures. A simpler treatment method of plastics was suggested for the expanded polystyrene (EPS) foams [184], where different temperatures (100–150 °C) were applied to get plastic pellets. A relatively large decrease in compressive strengths of mixtures containing the treated EPS pellets was observed as compared to the controlled samples. Nonetheless, several types of EPS foams are highly toxic when exposed to elevated temperatures [185].

4.4. Miscellaneous Substitutes

There are plenty of agricultural and aquacultural by-products that can be used as either cement or aggregates substitutes. Coconut fibers and shells can be added into concrete as additives or as an aggregates substitute. The enhancement of compressive strength of concrete was noticed when shells were used as aggregates [186]. Whereas a slight decrease was recorded for both compressive and tensile strength of concrete [187,188]. Higher ductility was concluded with no effects on the tension strength of concrete [189]. On the other hand, water absorption was high when compared to controlled concrete samples [186,190], and interfacial bonding was weaker due to smooth textures of coconut fibers [190,191]. Wheat is another agricultural product that is planted extensively around the world. After harvesting, farmers normally burn wheat straw waste, which results in a threatening disaster [192]. Several researchers suggested that wheat straw waste can be involved in concrete as a pozzolanic material after being incinerated and ground [193]. Wheat straw ash (WSA) has been used as cement substitute. Compressive strength of concrete at a substitution ratio of 20% by WSA increased due to its pozzolanic and filler effects [194,195]. In addition, the enhancement of hydration reaction, as well as the improvement of microstructure of cement composite were reported [194]. This improvement
was also noted as a result of filling the voids by WSA that was caused by its fineness [196]. Therefore, better resistance against aggressive chemical agents (i.e., sodium and magnesium sulphates) was found even at low substitution ratio of cement [197]. Nonetheless, a decrease of workability and increase of setting times were noticed by the addition of WSA in concrete [198]. Other researchers [192,199] have used wheat straw waste as a replacement of fine aggregates. It was concluded that better durability and compressive strength of concrete can be gained at a 6% substitution ratio of fine aggregates for wheat straw waste [192]. A 15% replacement, thermal cycling resistance improvement of concrete was indicated [199].

Besides, oyster waste exists in large quantities. In China alone, around 10 million tonnes of waste seashells, including oyster shells, end up in landfills each year [200]. At a replacement ratio of 20% for oyster shells, a better strength development was noted for cement mortars for masonry and plastering [201]. Another study concluded that a few portions of oyster ash as a substitute for cement had no effects on the overall durability of the concrete [202]. However, in general, as the portion of oyster shells increases in the concrete mixtures, the compressive strength reduces accordingly [203–205]. One major harmful effect of oyster shells when used as a partial replacement of fine aggregates in concrete is that workability significantly decreases [202,203]. This is referred to two reasons: (a) water absorption of fine particles of oyster increases [203] and (b) irregular flat particles increases the friction in concrete mixtures [202]. Mussel is another aquacultural product that is known for its existence in salt and fresh water. Like oyster, mussel can provide better compressive strength when used to prepare cement mortars [201]. Moreover, the addition of mussel in concrete decreases thermal conductivity of cement mortars and plastering [201]. The substitution of fine or coarse aggregates for mussel should not exceed 25% [206], otherwise the mechanical strengths of concrete expressively reduces due to poor bonding caused by flat and flaky shapes of the particles of mussels [206,207], and the presence of organic polymers [206].

5. Materials Forming Ternary Systems for Concrete

The behavior of one single material might differ when it is used with other materials in a combination, as materials either affect or are affected by one another in the whole system. With this concept, researchers have been working on different ternary systems, including the abovementioned, to get the most benefits out of each, and overcome the shortfalls of each individual material. In fact, the ternary systems of concrete had been used, even before the term “green concrete” came out. The aim of searching for proper ternary, or even quaternary, systems is to enhance fresh properties (workability, setting time, heat of hydration, etc.), hardened properties (strength, shrinkage, permeability, sulphate attack resistance, etc.), serviceability, and sustainability.

One of the most common materials for ternary binders alongside with OPC is GGBFS. It has been mixed with FA, RHA, RCA, and P, to mention a few. Generally, a significant increase of compressive strength was noticed throughout the experimental studies [18,154,208,209], and the findings agreed with the predictions of the relevant codes and standards, e.g., ACI 318 [210]. Conflicting results for workability, flexural, and splitting tensile strength were observed due to the variety of elements that can be controlled, not only the source of ternary binders’ components, but also for the treatment and content of each material in the mixture. The combination of FA with GGBFS was found to be mechanically beneficial for lightweight concrete [155]. When RHA was mixed with GGBFS, compressive and split tensile strength were not significantly affected compared to the controlled samples [211,212]. More importantly, a reduction of CO₂ emissions was achievable in the reviewed researches for GGBFS with RHA [213]. RCA was also investigated with the presence of GGBFS, and it was concluded that the workability of concrete increased [157], while the mechanical properties (compressive strength, flexure, and split tensile strength) decreased. However, this ternary mixture met the minimum requirements for serviceability [157,214]. Finally, reduction in compressive strength and increase in workability and ductility have been deducted for a mixture of OPC with GGBFS and plastic [178]. Also for silica fume...
(SF) [72], GGBFS along with SF extended the curing time of concrete, but the early-age and long-term strengths increased and the shrinkage of concrete reduced at later ages.

FA was also studied in ternary mixtures with RCA, RHA, WG, and plastic. Regardless of the reduction in CO$_2$ emissions [215], RCA with FA results in great reduction of heat of hydration and early-age strength. It was observed that, at lower concrete grades, the mechanical properties were not tangibly affected [216]. Generally speaking, as the contents of FA and RCA increase, the mechanical properties generally decrease [217]. RHA has more pozzolanic activities than FA. Therefore, the implementation of both in one mixture (ternary system) results in overall better mechanical properties than using each one of them alone [218]. The benefits of this ternary system are limited to a substitution ratio of 50% or less for OPC by RHA and FA [219]. As high as 30% of FA and 15% of WG were found to be superior to the controlled samples in terms of compressive strength and freeze-thaw resistance [220]. The combination of 100% FA and different portions of WG was found to be promising with suitable durability and structural performance [221]. As for plastic, regular and irradiated plastic were used as cement and aggregates substitutes. The effect of irradiation process on the plastic was determined by calculating the amorphous and crystalline contribution of different dosages of irradiation of plastic. Additional C-S-H in different forms were observed with the addition of irradiated plastic, which indicates that a strength increase was gained by the irradiated plastic [167]. Furthermore, FA was also added with other materials, such as silica fume (SF) [71], and the resultant concrete samples perform better than the controlled samples, on the whole.

WG has also been investigated in ternary systems with RCA and RHA. The use of WG with RCA was a perfect way to overcome the high water-absorption of RCA, because the microstructure of the mortar got improved [222], and so did the bond between the binder and the surface of the aggregates. In other words, WG helped to form C-S-H gel better, which in turn contributed in warding off ASR reactions [25,222]. As for RHA, WG and RHA are both high pozzolanic materials, and they are recommended as cement substitutes at 15% and 5% [223], respectively. An improvement of compressive strength and tensile strength were noted. However, the early-age strength decreased as compared to the controlled concrete [224]. In addition, an enhancement of workability was observed due to the reduction of water absorption of concrete [224].

6. Advanced Approaches for the Sustainability of Concrete

Although the OPC concrete is the most widely used material in construction, there is still room for improvement of its chemical, physical, and, most importantly, mechanical properties [225]. Properties that are vital for the use of OPC concrete include: compressive and tensile strengths, consistency, durability, resistance against chemical attacks, and sustainability, to mention a few. Researchers have been devoting much effort for this purpose since the starting point of using concrete for construction purposes. Not only is the main reason for studying the ingredients of concrete to improve its properties, as mentioned before, but also to look for other alternatives that can be used without side effects. One of these alternatives that always evoke the curiosity of engineers is using the natural and industrial by-products as concrete ingredients, as discussed before, or developing new materials that can serve the purpose of sustainability. As methods for studying life problems are getting more innovative, materials are also being scrutinized at different scales while using advanced approaches. Hence, the modification and development of materials at the nano-level is being more effective with time, as it can enrich our comprehension of the hierarchical scaled-simulation of different materials, such as the nano- and mesoscale modeling of cement matrix [226]. Another successful example of bridging the stream of multi-scale research was conducted to study the new-to-old concrete interface [227]. This study used a special shrinkage reducing admixture at the interface to assimilate the development of stress concentration at the interface that leads to cracks.

The demand of concrete will not decrease, at least in the coming several years. Additionally, the development and research of concrete must cope with the current advanced technological means. Sustainability is an approach to meet the needs of today without sacrificing the ability to meet the
needs of future generations [228]. This cannot be achieved without the up-to-date techniques and tools from different scientific fields, because sustainability is not limited to one single aspect. All related scientific aspects deal with sustainability of materials, including concrete as the second most consumed material in earth, with the aim of reduction, reusing, and recycling [229]. Advanced approaches for improving concrete properties can either be like a sophisticated accurate way of modeling concrete components or a micro- and nano-scale study of atoms forming these components, where the latter is the most successful in terms of describing how properties originate.

6.1. Understanding and Developing C-S-H

The linking idea of nano-engineering and green concrete is that nano-engineering is not only about developing new materials or enhancing the properties of the existing ones, but it is rather about the significant reduction in energy consumption that is required for manufacturing the current materials. The idea of the term nano-engineering is crucially linked to the fulfillment of sustainability, and so is green, which is formed in responding to the current calls for reducing CO$_2$ emissions. For example, higher long-term compressive strength was obtained while using a new silica fume from waste glass to replace OPC in concrete [230]. The components of concrete exist in multiple length scales, from nano to macro, in which the properties of each component are dominated at the small scale [231]. A great example of this is the understanding and strengthening of the weakest component of concrete, C-S-H, which holds the other components of concrete together after hydration [232,233]. The understanding and enhancement of the performance of C-S-H gel is reflected to the properties of concrete, such as porosity, size of the pores, and permeability [32]. The porosity of cement matrix has been thoroughly studied [234] at a mesoscopic structure of C-S-H level that reflects the properties of the macroscopic structure. Silica nanoparticles have been experimentally investigated to modify the cement matrix [235–237]. It was concluded that the calcium leaching could be controlled by silica nanoparticles. Therefore, favorable improvements could be achieved: reduction of porosity, creation of C-S-H gel by pozzolanic reactions, and modification of the internal structure of C-S-H through increasing the silicate chain length. Additionally, it has been observed that nano-silica particles lessen the impact of the weak calcium hydroxide that forms at the surface of the aggregates after the hydration process. In fact, the understanding and improvement of the C-S-H gel could not have been achieved without nano-engineering, where the compressive strength of the cement paste increased up to 30%. This increase serves concrete’s sustainability. As for ternary systems, nano-engineering has been implemented through nano-silica with ordinary fly ash [8,238], such mix speeded up the pozzolanic reaction for concrete reaching its designed strength (95% of its ultimate strength) within two weeks is impressive for projects with tight construction time. Atomistic simulation, as well as experimental work, have been conducted to study the effect of triethanolamine dosage on the initial setting time of hydrated cement [239]. The molecular dynamic approach of the latter study explained the observed behavior in the macroscale and showed that the effect on the initial setting time was caused by the different dosage of the triethanolamine that formed the ettringite.

6.2. Investigating on New Materials for Different Sustainable Applications

CNTs are hollow tubes that are formed either by one-layer wall, and named single wall carbon nanotube (SWCNT), or multiple walls (MWCNT) [37], usually with diameters that ranged from a few nanometers to hundreds of nanometers. Generally, MWCNTs are more common than SWCNTs because of their affordable price and better performance [240]. CNTs is a nano-engineered cementitious composites additive known for its superb properties, including modulus of elasticity, compressive and tensile strengths, high surface area, and serviceability [36,241]. It is another perfect example of the nano-engineering applications that leads the construction industry to be more sustainable by enhancing the hydration process of cement and producing additional C-S-H gel. The effect of CNTs on the strength of composites has been investigated [242]. It was concluded that CNTs accelerated the hydration process of cement, resulting in higher early-age strength of concrete. The optimum dosage of CNT into
cement matrix was found to be 0.065% to 0.1% by the weight of cement [243], and sometimes up to 0.2% by weight [244]. Within these ratios, the maximum increase in compressive strength ranges from 10% to 25%, however it may reach 80% for ductility. In terms of thermal stability, a nano-branch of C-S-H with CNTs performed very well in flexural and compression at room and elevated temperatures [36]. The high cost of nano-engineered materials, including CNTs, is one of the biggest challenges for mass construction industry. Moreover, CNTs are not easy to be dispersed homogenously due to the strong van der Walls force between them that is caused by the large surface-area-to-volume (SA/V) ratio [245]. Furthermore, CNTs have a weak bond to the cement matrix due to the hydrophobicity of CNTs in the presence of water.

While researches have been carried on finding the optimum thicknesses of different materials to either isolate or conduct heat [246], advanced approaches have also been focused for isolation and thermal conductivity. In this area, two general points of view have been documented: sustainability in terms of saving energy required for air conditioners (i.e., isolation), and the sustainability of materials that are needed for better thermal conductivity. An experimental and finite element numerical study was conducted to assess the gained and lost heat between buildings’ walls and the surrounding environment [247]. This study presented a concrete wall that had a gypsum layer inside the concrete, in which the thermal insulation of the new wall system was enhanced. Another study was held by implementing titanium dioxide and hollow glass beads as coating materials [248]. In this study, experimental and finite-difference time-domain simulation approaches were used to observe the improvement efficiency of the reflective and insulation properties of the thermal coating implemented materials. The new coating films system was found to be superior in reducing the heat absorption and cooling energy for buildings, and therefore the invested initial cost of this system can be paid off through lower energy consumption during operation. Moreover, nanoparticle-based materials have been used in construction as thermal insulation in different micro- and macroscale applications [249]. This study concluded that the thermal resistance between nanoparticles increased rapidly as the particle contact radius decreased, and the presence/absence of chemical bonds between nanoparticles played an important role, while using molecular dynamics simulation. The importance of using macroscopic, mesoscopic, and microscopic studies of heat transfer and fire resistance were highlighted for fiber reinforced polymer (FRP) in concrete and wood structures [250]. However, it would be worth performing more exploratory multiscale researches, in which different nanoparticles are implemented in the macroscale of different structural materials/members to study heat isolation and conduction.

7. Summary, Prospects, and Challenges

All in all, the calls for the green constructions addressing the pillars of sustainability have been responded, not only by individual efforts, but also by the international society. The most common by-products that are applicable as concrete ingredients were discussed in three categories: fly ash, rice husk ash, silica fume, and several pozzolanic ashes as cement replacements, recycled coarse aggregates as an aggregate substitute, and waste glass, ground granular blast-furnace slag, plastic, and miscellaneous substitutes as both cement/aggregate replacements. Figure 3 concludes the advantages and disadvantages for the reviewed most common by-products that can replace concrete components for the most common by-products. The need for facing the current environmental problems has shed the light into: replacing some components (e.g., cement) by other environmentally friendly materials, recycling the most consumed natural resources (e.g., natural aggregates and water), improving the physical and chemical properties of concrete components, saving lands for more important projects rather than dumps, and lowering the overall cost of constructions. In fact, more and more governments have come to realize that the proceeding points are not an option anymore, but rather a necessity.
While several by-products have been investigated, particularly in the short-term, more research should be conducted in the long-term durability. More focus should be shed upon the alternatives for the natural resources, in which their consumption damages the land, sea, and air. Additionally, to get the benefits out of each by-product and overcome their individual limitations, more binary, ternary, and even quaternary mixtures ought to be comprehensively documented. The most important advantage of using these reviewed by-products is that they are waste materials anyway, and the other places for them are landfills where they require land space, money, and much effort. However, the main obstacle to extend the implementation of by-products, in general, is the need to control their quality before incorporating them in concrete, and this process requires experience and may differ depending on the source and application of these materials in construction. Additionally, the reliability of using some of these alternatives (e.g., plastic, waste glass, etc.) has not been high enough, because they have not been exposed to long-term field testing that must be conducted explicitly by researchers.

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