Chapter

Effect of Non-Traditional Supplementary Cementitious Materials in Concrete

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Abstract

Fly ash, silica fume, metakaolin and ground granulated blast furnace slag, etc. have been established as traditional supplementary cementitious materials (SCM) and cement replacement materials; however, other alternate materials such as palm oil fuel ash (POFA), palm oil clinker powder (POCP), eco-processed pozzolan (EPP) and rice husk ash (RHA) have emerged as non-traditional materials that would take a role in replacing some of those established SCM. With a closure of most of the coal-operated power plants and imminent closure of more plants, the search for alternate materials is on the rise. Thus, it is mandatory for the researchers and cement manufacturers to invest more time and efforts to apply sustainable development goals (SDG) on the replacement of virgin materials to achieve low-carbon materials. The suitability and the effect of the above-mentioned non-traditional materials are detailed and discussed. The oxide composition, particle size and shapes through multiple tests and investigations are outlined. The plentiful availability of such non-traditional materials not only paves way for more research interest, but a genuine means of execution of plans to vigorously utilize those materials. The concrete quality on using such materials such as pore refinement, creation of additional C–S–H and dilution effects has been discussed.

Keywords: non-traditional supplementary cementitious materials, palm oil fuel ash (POFA), palm oil clinker powder (POCP), eco-processed pozzolan (EPP), rice husk ash (RHA)

1. Introduction

It has been well established that origins of the present use of supplementary cementitious materials (SCM) in the construction industry date to the ancient Greeks between 750 B.C. and 600 B.C. The Greeks blended the volcanic ash with the hydraulic lime to develop mortar. The baton of the Greek's knowledge had been passed on to the Romans; this enabled Romans to engineer the Roman aqueducts and the Coliseum and these structures speak till today [1]. Due to the use of SCM, the properties of hardened concrete are improved through hydraulic or pozzolanic activity. It is unique to use the word 'pozzolan' linked to the town of Pozzuoli, Italy where a large deposit of volcanic ash from Mount Vesuvius was found.

Based on the chemical characteristics of the SCM, these can be used either as an addition to the cement or as a partial replacement of the cement. In most of the countries, it is imperative to use the SCM due to the compelling reasons of carbon dioxide emissions due to conventional cement. Further, the SCM is used to replace a portion of the cement content for economical or property-enhancement reasons. The SCM can broadly be divided into two classifications based on their type of reaction, either hydraulic or pozzolanic. It is well known that pozzolanic substances react with water to form cementitious compounds. ASTM C125 outlines the pozzolanic material as 'a siliceous or siliceous and aluminous material'. It also explains that the finely distributed particles react in the presence of water. On another note, SCM can be categorized based on: (i) source, (ii) chemical compositions and (iii) particle characteristics. The first term 'source' aligns the classification on the origin or source, and this provides an ideal way of creating a classification system. Normally, the label 'source' is not implicated with the location where the material is obtained, rather it is dealing with the formation or the process in which the material is attained. Generally, the SCM is split into two classes, namely natural and artificial SCM. The classification of the SCM is shown in **Figure 1** [2].

In general, naturally occurring SCMs are divided into two categories, namely sedimentary and volcanic materials. During the cooling of the molten materials, if the volcanic materials such as tuffs, zeolites and pumice cooled at a faster rate, then these materials can have pozzolanic properties. Furthermore, the faster cooling is essential for the silica to be in amorphous form.

The artificial SCM can be classified typically as industrial by-products and waste materials. In most of the Asian countries, rice is the major crop that produces millions of tons of rich hush. The burning of rice husk results in rice husk ash (RHA). The major oil producing crop, namely palm oil also produces large quantities of wastes that include palm oil fuel ash (POFA), palm oil clinker powder (POCP) and eco-processed pozzolan (EPP).

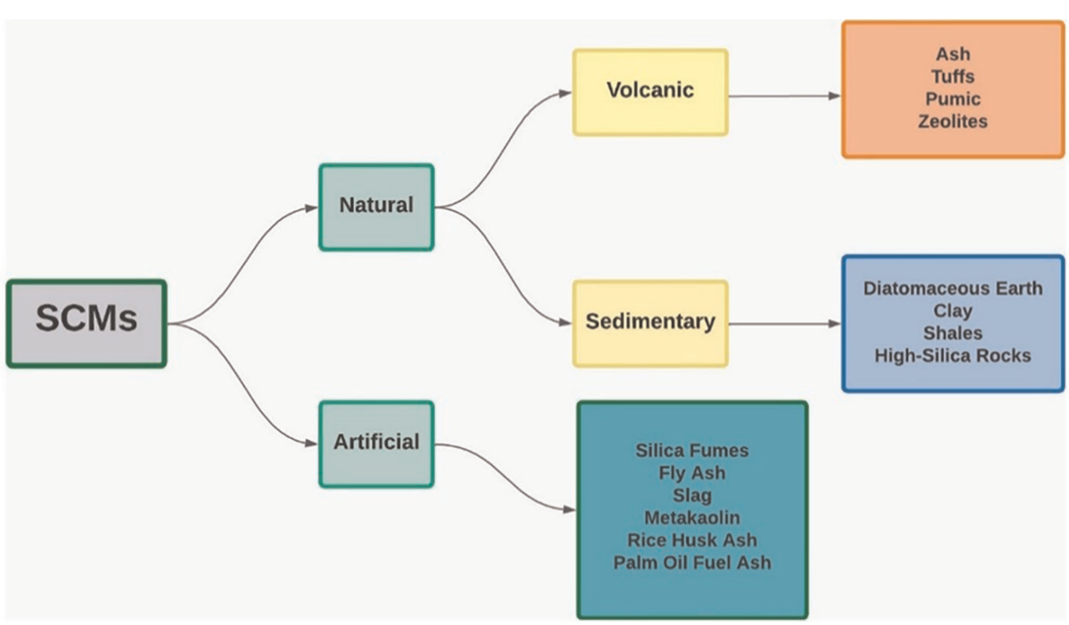

Figure 1.
Classification of SCM [2].

2. Properties of non-traditional supplementary cementitious materials

Different types of SCMs, namely, RHA, POFA, POCP and EPP from the by-products of two agricultural industries, namely rice and palm oil were inferred. Both the physical and chemical characteristics of the binders were determined including: (i) the particle size distribution, (ii) visualization of the morphology via scanning electron microscopy (SEM) imaging and (iii) the chemical composition via X-ray fluorescence (XRF). The physical appearance of the RHA, POFA, POCP and EPP along with OPC is shown in **Figure 2**.

Both the raw POFA and POCP are generally available in the palm oil mills; the available forms of POFA or POCP depend on the boiler used in the palm oil mills. The raw materials are normally sieved and then ground to 30,000 cycles in Los Angeles (LA) abrasion machine. The process of obtaining RHA is different from that of POFA or POCP. Some rice plants do use rice husk as fuel for processing the rice and the resulting RHA is further processed as RHA as pozzolans. There are processing plants that produce RHA. The raw materials such as POFA and POCP collected from the palm oil factories are to be processed before their use due to impurities of foreign materials and unburnt palm fibers, large particle size and moisture content. It is required to remove the moisture and larger particles more than 300 μm size; thus, POFA is oven-dried at 100 ± 5°C for 1 day and then sieved through 300 μm sieve. Finally, the sieved POFA particles are finely ground in a LA machine. Based on the requirement, the POFA particles are ground to 30, 000 to 60,000 cycles in the LA machine. To remove excessive unburnt carbon which will affect the potential pozzolanic properties, the POFA can be heated at 500°C for a certain period in a furnace. The same approach was previously employed and reported as to be effective in removing the excessive unburnt carbon in the POFA [3–6]. **Figure 3** shows the SEM image of OPC and RHA. Similarly, **Figure 4** shows the SEM image of POFA before and after grinding process.

In comparison to POFA, the processing of POCP involves a slightly different approach. The palm oil factories produce POFA or POC based on the boilers employed in the burning of palm wastes in their factories. Thus, the burnt by-products can be in the form of fine POFA or large chunks of POC. POC are very light due to porous in nature and have lower specific gravity. The POC chunks are collected from palm oil factories, and they are porous with sizes ranging from 100 to 250 mm. The collected

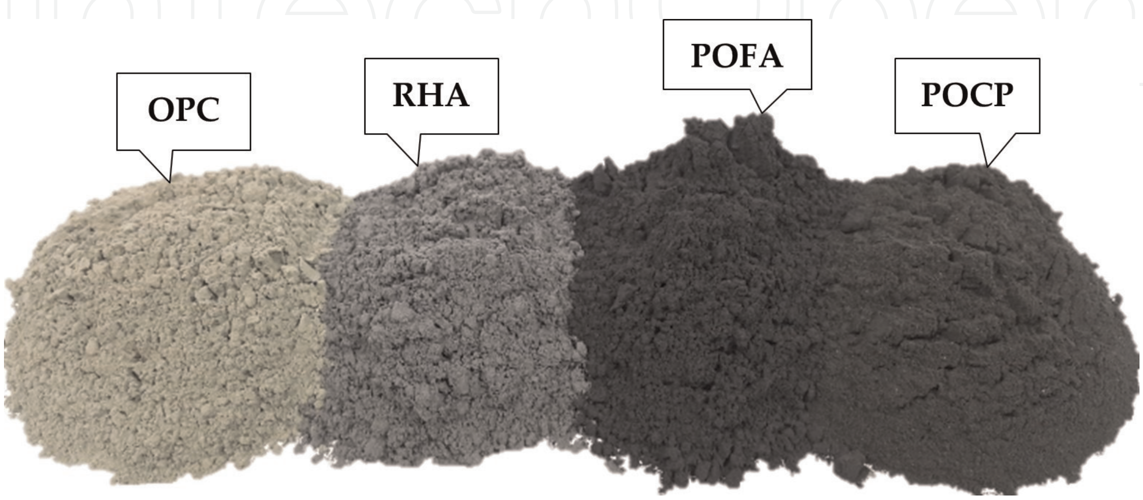

Figure 2.
Physical appearance of OPC, RHA, POFA and POCP.

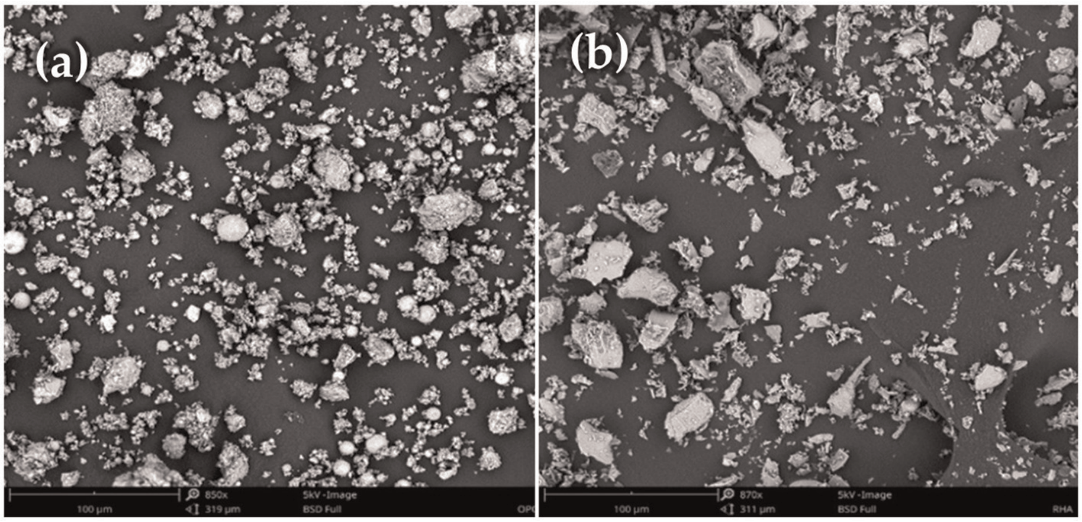

Figure 3.
SEM image of (a) OPC and (b) RHA.

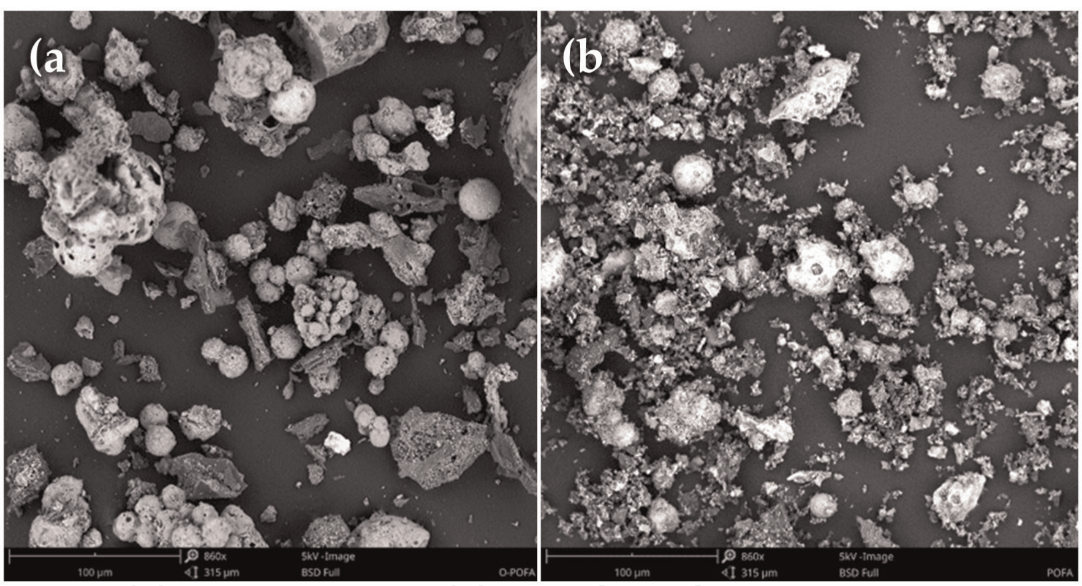

Figure 4.
SEM image of POFA (a) before and (b) after grinding.

POC are processed through a crusher to obtain coarse or fine aggregates; the finer part of POC which as less than 2.36 mm can be used to obtain POCP by grinding the finer POC in a LA machine. The SEM picture of the POCP is shown in the **Figure 5**.

The chemical and physical properties of the POFA, POCP and RHA are given in **Tables 1** and **2**, respectively. For the comparison, the properties of OPC are also outlined. The ground RHA has very fine size particles, with approximately 98% passing through a 45 μm sieve; furthermore, the lower specific gravity of 2.30 for the RHA particles makes it lighter compared to 3.15 for ordinary Portland cement. Another aspect of pozzolanic material is their S–A–F-silica (SiO_2), alumina (Al_2O_3) and iron oxide (Fe_2O_3) contents. Due to higher silica content in RHA, the SAF content was found about 92%. Based on the X-ray fluorescence (XRF) analysis, RHA falls within the requirements of pozzolanic material based on ASTM C618. On the fineness, the POFA and POCP particles were found to be coarser compared to RHA, as the

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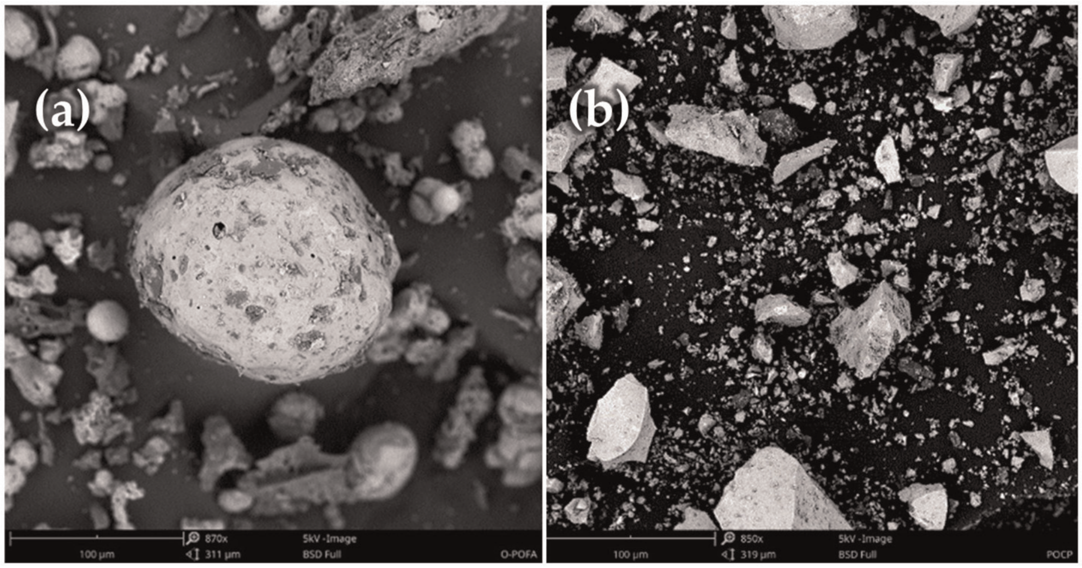

Figure 5.
SEM image of POCP (a) before and (b) after grinding.

Chemical compositions (%)	OPC	RHA	POFA	POCP	ASTM C618 class F
SiO_2	21.0	91	64.17	60.29	
Al_2O_3	5.9	0.35	3.73	5.83	
Fe_2O_3	3.4	0.41	6.33	4.71	
$SiO_2 + Al_2O_3 + Fe_2O_3$	30.30	91.76	74.24	70.83	70 (minimum)
CaO	64.70	0.49	5.80	3.28	
MgO	2.50	0.81	3.46	4.20	
SO_3	2.40	1.21	0.74	0.31	5 (maximum)
TiO_2	0.002	—	0.06	0.10	
Loss on ignition	0.9	4.81	11.56	5.23	12 (maximum)

Table 1.
Chemical properties of OPC, RHA, POFA and POCP.

Physical properties	Specific gravity	Retained on 45 μm sieve (%)	Median particle size (μm)
OPC	3.15	13.6	22.47
RHA	2.03	1.70	19.41
POFA	2.14	11.6	17.62
POCP	2.53	21.0	37.97
ASTM C618 class F	—	34% (maximum)	—

Table 2.
Properties of OPC, RHA, POFA and POCP.

amounts of retained particles on 45 μm sieve were found about 12% and 29%, respectively. Based on these results, both POFA and POCP confirmed the fineness requirement to be used as pozzolanic materials as per ASTM C618.

Figures 6–**9** illustrate the SEM image of the particle shape and surface texture of OPC, RHA, POFA and POCP. It is generally well established that the OPC particles are spherical in shape and solid. However, as noticed from the SEM images shown in **Figures 6**–**9**, the particles of RHA, POFA and POCP have some irregular and angular particles. Further, the SEM images also show the porous nature of POFA particles, and these porous particles must be considered in the mix design due to higher water absorption in these porous particles. Another significant aspect is the presence of the sharp edges in the RHA and POCP particles, and these sharp edges might hinder free movement whilst mixing and reduce the flowability of the mixes.

The particle size distribution of the binding materials is presented in **Figure 10**. It can be clearly seen from the curves that RHA and POFA have similar fineness of OPC, whilst POCP is relatively coarser than OPC. However, the fineness of these materials depends on the grinding time and process. In lab scale, there are restrictions for the

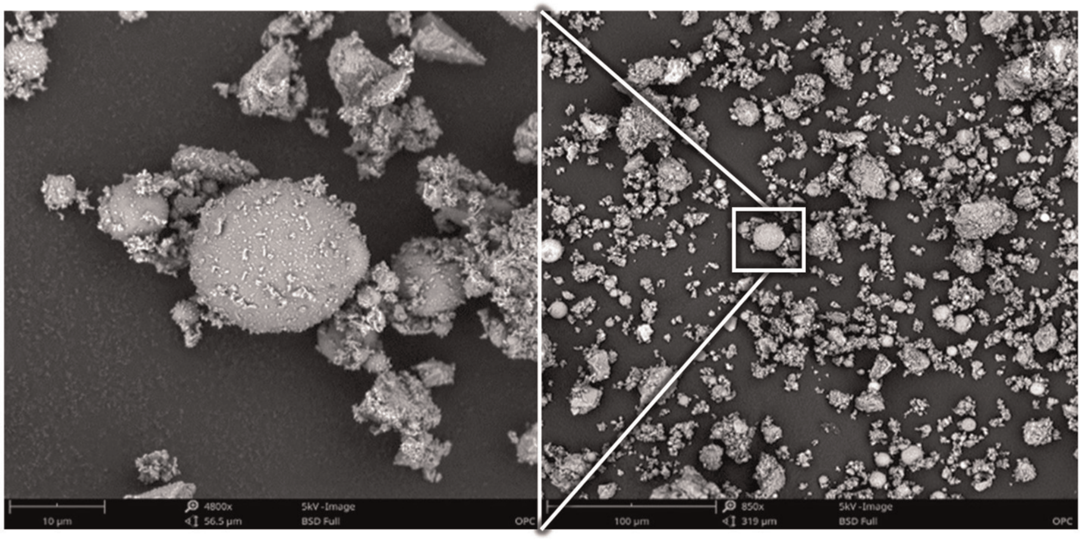

Figure 6.
SEM image of OPC.

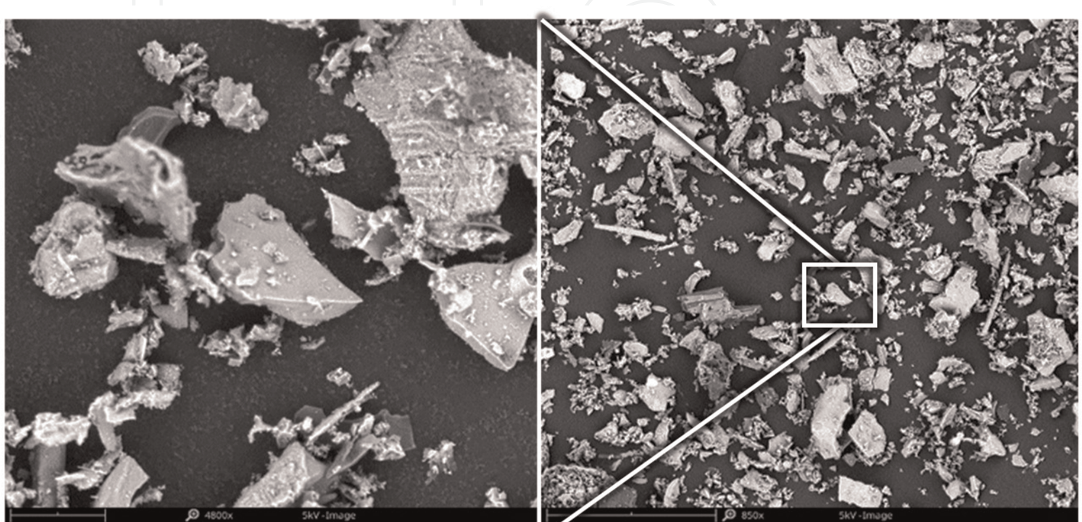

Figure 7.
SEM image of RHA.

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processing and if the methods adapted in commercial grinding are done, the fineness could be enhanced.

Like the POFA, POCP, RHA, another palm oil industrial by-products, namely EPP can also be considered as an SCM; it is produced from the spent bleach earth (SBE) used in the palm oil refineries. The oxide composition and physical properties of EPP are shown in **Tables 3** and **4**, respectively. **Table 3** compares the oxide composition of traditionally used pozzolan, fly ash with EPP. Based on the oxide composition outlined in ASTM C618–19, EPP can be classified as class N natural pozzolan. The SEM image of EPP as shown in **Figure 11** indicates the presence of pores with irregular shaped particles.

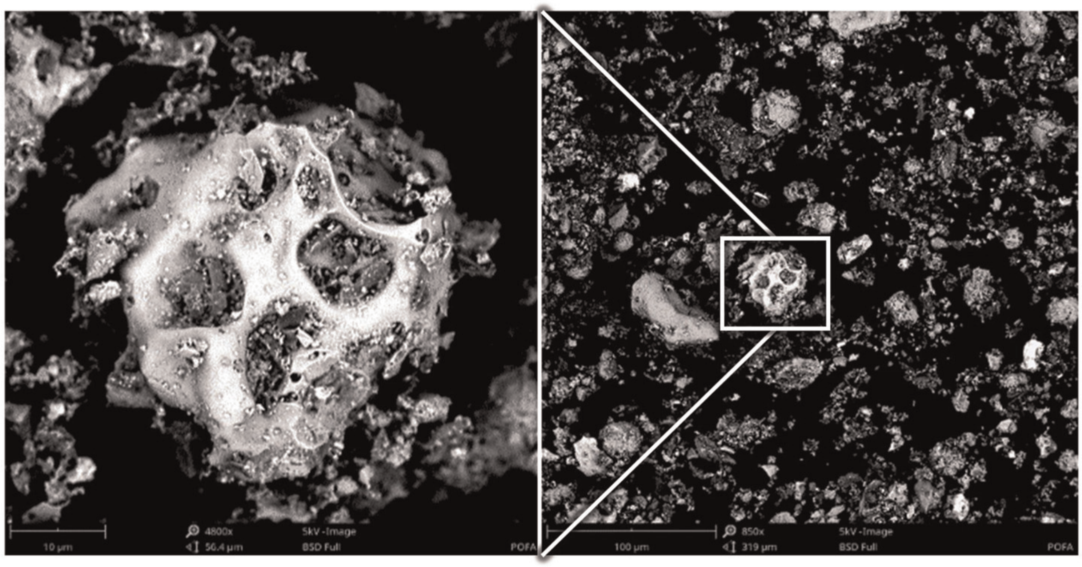

Figure 8.
SEM image of POFA.

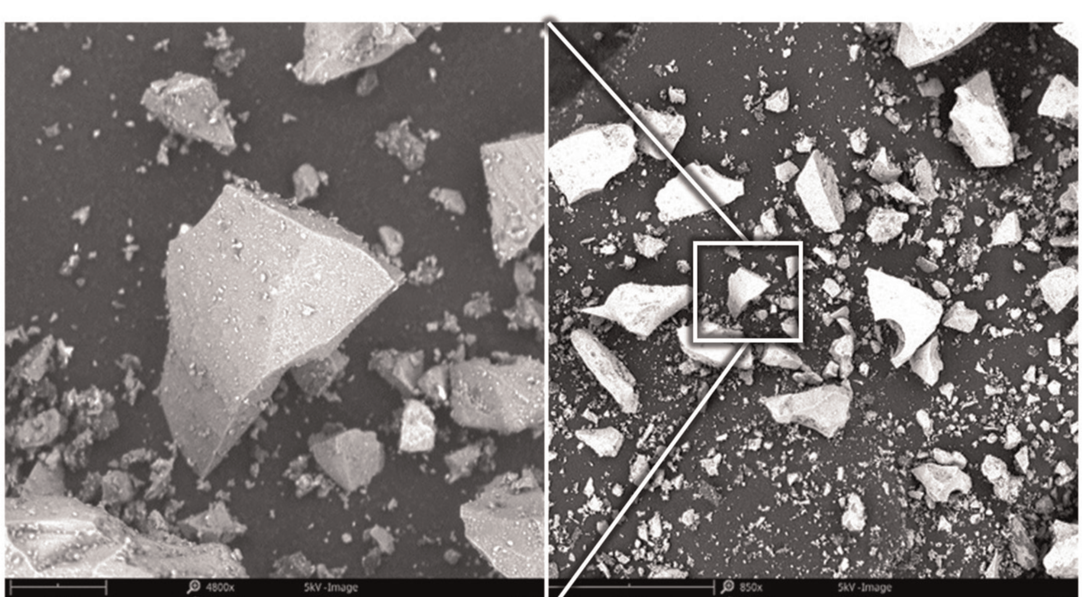

Figure 9.
SEM image of POCP.

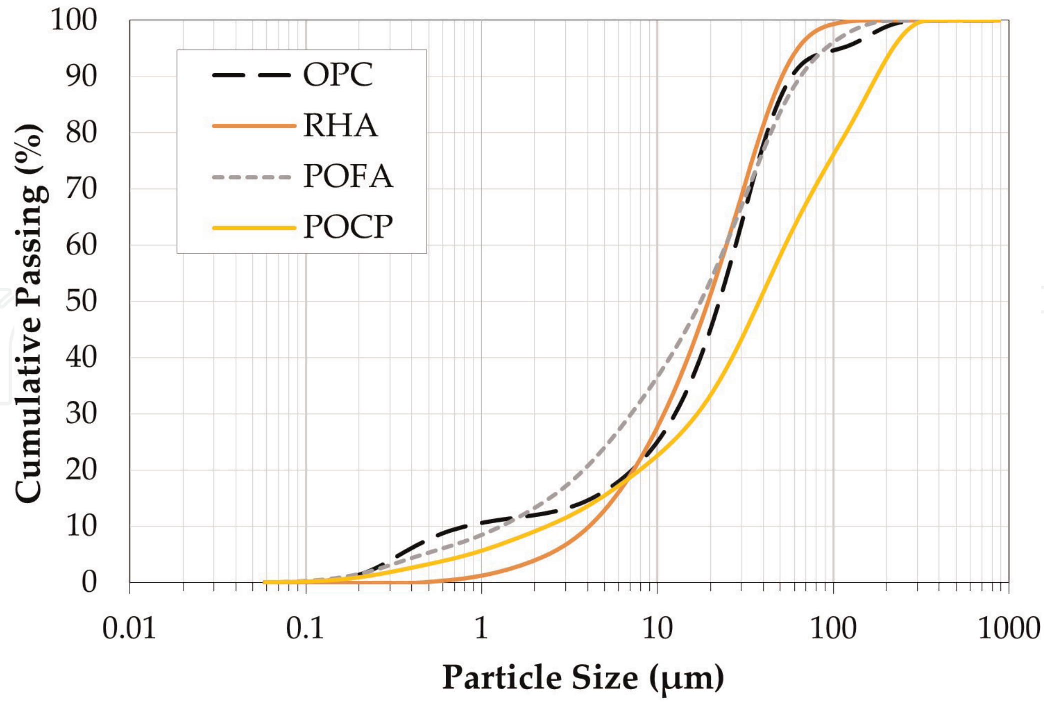

Figure 10.
Particle size distribution of ashes.

Chemical compositions (%)	FA	EPP
SiO_2	57.0	54.94
Al_2O_3	29.0	9.42
Fe_2O_3	5.8	9.28
CaO	0.2	8.73
MgO	0.9	5.81
SO_3	0.2	1.85
K_2O	0.9	1.41
Na_2O	—	0.34
$SiO_2 + Al_2O_3 + Fe_2O_3$	91.8	73.64

Table 3.
Oxides composition of FA and EPP.

Materials	Properties	
EPP	Color	Gray
	Shape	Irregular
	Specific gravity	1.9
	Particle passing on 45 μm sieve	73

Table 4.
Physical properties of EPP.

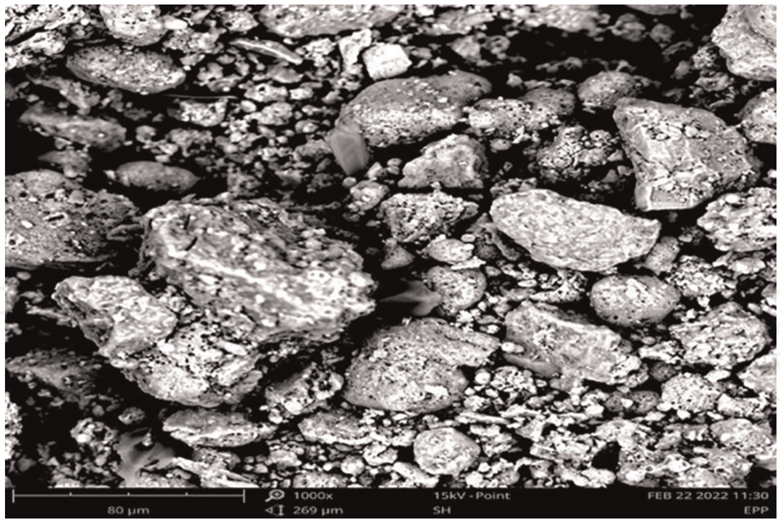

Figure 11.
SEM image of EPP.

3. Effect of SCM on concrete properties

The utilization of SCM from industrial by-products, such as silica fume, slag and fly ash has become more powerful in concrete industry; this is attributed to their significance in the sustainable aspect of low-carbon footprint material that enables the reduction of cement content, strength enhancement and durability. On the other hand, the research interest, and their potential commercial interest on the use of POFA, POCP, RHA and EPP as alternate non-traditional materials are gaining more momentum; numerous journals have been published and this shows the vigorous attempts on the interest of those new materials that are available in abundance in the countries. It is envisaged that the potential application of industrial and agro-based products in the concrete would enable the local industries to provide such pozzolanic materials without hindrance as these materials are regularly produced. If these products are not utilized or dumped in the vicinity of the factories, these materials will end up in the landfill, and that would cause land and air pollution; however, the utilization of such materials which have pozzolanic properties could enhance the properties of concrete. Researchers reported that the incorporation of up to 20% of RHA as SCM enhanced the mechanical behavior and developed resistance against chloride-ion penetration in comparison to the conventional OPC-based concrete [7].

It is envisioned that durability performance of SCM used in concrete is one of the prime factors that would draw attention of the concrete manufacturers in addition to their sustainable attributes. The use of SCM in concrete affects the strength development by the three known facts. The factors are filler effect, dilution and the reactivity. The type of SCM and the fineness and the replacement percentage have a significant effect on the strength and durability of concrete. It is to be taken into consideration that these factors are dependent on each other and hence the replacement level of SCM plays a major role. For instance, the replacement of SCM for the cement leads to the dilution, and this in turn could have a negative impact on hydration at the early age. On the contrary, the filler effect can have a positive impact as it decreases the voids in the concrete. As is known the presence of micro-pores creates an overall negative impact on the compressive strength and durability of the concrete. In contrast, the smaller particles of the SCM tend to have filler effect compared to that of cement.

Therefore, the addition of SCM increases the micro-filling and thus, enhances the packing capability and, this in turn effectively reduces the volume of voids.

If the SCM is used as an extra material, an enhancement in the concrete properties is expected due to the reduction in water-to-binder ratio [8]. In contrast, when SCM is used as a cement replacement material, a reduction in development of the strength occurs, more noticeable at early ages because of cement dilution as well as the slow nature of the pozzolanic reaction [9]. The replacement of cement with a SCM that has a lower reactivity will have a negative impact due to the dilution effect. This will result in a lower amount of hydration products, and as a result, it affects the pozzolanic reaction at the early ages. Also, the alkaline environment coupled with the reduction in cement could hinder the hydration of cement.

Researchers have reported that the addition of SCM might have some possible early adverse effects; however, at the later ages, the strength of concrete containing SCM could be at par with the normal concrete or even it could exceed the strength of the corresponding control concrete. Chao-Lung et al. [10] reported the quantity of RHA used in their research and expressed the opinion that incorporating up to 20% of RHA did not produce any negative impact on the strength and durability of the concrete. Further, researchers revealed that the addition of POFA reduced the early age strength, but the later strength was comparable to the control concrete, and they attributed this to the pozzolanic properties of the POFA [11]. Other group of researchers divulged that concrete containing up to 20% POFA produced comparable 28-day compressive strength to that of the control concrete; they also found out that the strength even after 28 days produced comparable strength [12]. Furthermore, researchers established the effectiveness of refinement of pore structure due to the addition of fly ash and silica fume; this in turn produced high mechanical performance by producing high compressive, tensile and bond strengths [13]. This is attributed to the presence of silica in the SCM as the pozzolanic reaction is proficient of taking part in a hydration.

It is a well-established fact that when cement is hydrated, the portlandite is produced which in turn creates an environment with a relatively high alkalinity in the cementitious paste and also acts as a reactant in the pozzolanic reaction, as shown in Eqs. (1) and (2) [2].

$$\begin{array}{l} 2Ca_2SiO_4 + 4H_2O \rightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O + Ca(OH)_2 \\ \text{(Belite)} + \text{(Water)} \qquad \text{(C–S–H phase)} + \text{(Portlandite)} \end{array} \tag{1}$$

$$2SiO_2 + 3Ca(OH)_2 \rightarrow 3CaO \cdot 2SiO_2 \cdot 4H_2O \tag{2}$$

It is well established that the addition of pozzolanic materials utilizes the calcium hydroxide and promotes the production of additional C–S–H; the additional C–S–H contributes to strength gain. This in turn reduces the concrete pores and improves the particle packing. The presence of SCM necessitates sufficient moisture and thus, the mix design should consider adequate water to facilitate pozzolanic reaction.

Though different SCMs are available, various aspects such as particle size, reactivity index, water requirement, etc. should be kept in mind whilst incorporating the specific type of SCM in the concrete mix; further, the inclusion of SCM can be related to the morphological and physical properties as not all SCM possess similar characteristics. Researchers experimented the impact of SCM obtained from different by-products on the mechanical properties of high-strength concrete [14]. Highly fine, ground pulverized coal combustion FA, ground RHA and ground POFA were used to partly substitute the conventional Portland cement and they discovered that concretes containing 10–40% ground FA and 10–30% ground RHA or POFA exhibited higher compressive strengths than that of the control concrete.

Another aspect on the implication of SCM in the properties is the optimum substitute level. It can be explained by the accomplishment of an optimum particle packing ability as well as the effect of cement dilution. When the very fine SCM are added to concrete, the particle packing increases, resulting in a decrease of the overall cavities or micro-pores. On the contrary, if too much fines are added, the water demand is higher and it may have a negative impact; further, the particle packing is disrupted and due to that the packing density decreases again [14, 15]. The dilution of cement can also have a negative effect in the strength development at the early ages such that the increase of replacement level leads to reduce the cement content, thus less hydration products will be produced namely C–S–H; it should be borne in mind that the C–S–H is the foremost constituent material that is predominant for strength contributing factor in the concrete [16].

4. Conclusions

The emphasis on utilizing non-traditional SCM is gaining momentum; this is mainly due to the implementation of low-carbon footprint materials by many governments, non-governmental agencies, cement manufacturers and construction industries. The significance on the implementation of sustainable development goals (SDG) as stipulated by the United Nations in achieving multiple attributes of sustainable development, is fueled by the vast availability of industrial by-products, pollution and the release of huge amount of carbon dioxide.

Thus, the topic summarized in this chapter on the non-traditional SCM is vital. The oxide compositions of the SCM of RHA, POFA, POCP and EPP point to a comparison with conventional OPC and the other established SCM, such as fly ash, silica fume, ground granulated blast furnace slag and metakaolin. Though the particle shapes vary, and some are porous in nature, the replacement of 10–20% of the conventional OPC and other traditional materials to move forward towards the sustainable development is the need of the hour. Another important consideration is the future availability of fly ash, which has been a trademark product in blended cement. Due to the implementation of cleaner energy and to achieve the climate change targets, many governments committed to a longer-term plan by closing most of their coal-fired power plants. This will necessitate the cement manufacturers to look forward to other non-traditional materials as a replacement for fly ash.

The other factors such as filler effect, strength development, refinement of pores and the enhancement of the durability properties assume a great significance. It is well established that the addition of SCM in concrete impacts the strength development. This depends on the SCM characteristics such as fineness, shape and their pozzolanic properties. The quantity of the SCM added in the concrete also defines the outcomes. It is also established that the use of SCM as an additional material would enhance the strength and durability. Furthermore, the secondary hydration responses also benefit to the strength development, as well as the fact that the water-to-binder ratio is efficiently reduced. However, based on cement replacement, the early age strength tends to be adversely affected. This is dependent on the replacement level and reactivity of the SCM used.

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