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Using Cementitious Materials to Enhance Concrete Properties and Improve the Environment: A Review

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Abstract

Cement production significantly contributes to carbon dioxide emissions, which increase global warming. Therefore, reducing cement consumption can support efforts to reduce that risk. On the other hand, the consumption of industrial wastes in concrete production contributes to improving the environment. Industrial waste can be used as supplementary cementitious materials (SCMs) to enhance concrete properties. This review study describes the effects of SCMs, such as silica fume, fly ash, metakaolin, and ground granulated blast furnace slag (GGBFS), on the properties of fresh and hardened concrete. The findings show that SCMs enhance packing density and reduce permeability. The impact of SCMs on concrete properties appears after a period of curing depending on the availability of calcium hydroxide and activity index. Calcium hydroxide produced from cement hydration reacts with silicates of SCMs to produce additional calcium-silicate hydrates that enhance concrete strength and minimize the relatively large size of calcium hydroxide, which lowers porosity. Silica fume and metakaolin raise water demands and reduce workability, while GGBFS and fly ash improve workability. Silica fume, metakaolin, and (10) µm particle size of GGBFS increase early-age strength, (10-45) µm particle size of GGBFS enhances strength after 28 days, while fly ash raises the strength after 90 days. For low cement content, 10 % or less silica fume, (10-30) % fly ash, (10-20) % GGBFS or metakaolin are considered the perfect percentage to arrive at best strength. For high cement content, (25-30) % silica fume or 40 % fly ash is considered the optimum ratio to reach the highest strength.

Keywords: Supplementary cementitious materials, Silica fume, fly ash, metakaolin, blast furnace slag

الخلاصة: يساهم إنتاج الأسمنت بشكل كبير في انبعاثات ثاني أكسيد الكربون، مما يزيد من ظاهرة الاحتباس الحراري. لذلك، فإن تقليل استهلاك الأسمنت يمكن أن يدعم الجهود المبذولة للحد من هذا الخطر. من ناحية أخرى فإن استهلاك المخلفات الصناعية في إنتاج الخرسانة يساهم في تحسين البيئة. يمكن استخدام النفايات الصناعية كمواد إسمنتية تكميلية (SCMs) لتعزيز خواص الخرسانة. تستعرض هذه الدراسة تأثيرات المواد الأسمنتية التكميلية، مثل دخان السيليكا، الرماد المتطاير، الميتاكولين، وخبث الفرن العالي الحبيبي (GGBFS)، على خواص الخرسانة الطرية والمتصلبة. تظهر النتائج أن SCMs تعزز كثافة التعبئة وتقلل من النفاذية. كما يظهر تأثير SCMs على خواص الخرسانة بعد فترة من المعالجة اعتمادا على توفر هيدروكسيد الكالسيوم ومؤشر النشاط التفاعلي. يتفاعل هيدروكسيد الكالسيوم الناتج من اماهة الأسمنت مع سيليكات المواد الإسمنتية التكميلية لإنتاج هيدرات سيليكات الكالسيوم الإضافية التي تعزز قوة الخرسانة وتقلل من الحجم الكبير نسبيا لهيدروكسيد الكالسيوم مما يقلل المسامية. يزيد دخان السيليكا والميتاكولين من الطلب على الماء ويقلل من قابلية التشغيل، في حين يعمل GGBFS والرماد المتطاير على تحسين قابلية التشغيل. يعمل دخان السيليكا والميتاكولين وخبث الفرن العالي بحجم جسيمات (10) مايكرومتر على زيادة القوة في عمر مبكر، ويعزز حجم جسيمات خبث الفرن العالي (10-45) مايكرومتر القوة بعد 28 يوما، بينما يزيد الرماد المتطاير من القوة بعد 90 يوما. بالنسبة لمحتوى الأسمنت المنخفض، فإن 10% أو أقل من دخان السيليكا، (10-30) % الرماد المتطاير، (10-20) % GGBFS أو الميتاكولين تعتبر النسبة المثالية للوصول إلى أفضل قوة. بالنسبة لمحتوى الأسمنت العالي تعتبر النسبة المثلى للوصول إلى أعلى قوة هي (25-30) % من غبار السيليكا أو 40 % من الرماد المتطاير.

1. INTRODUCTION

Concrete is a versatile and durable material frequently used in construction projects. The outstanding water resistance makes it ideal for use in various structures, besides being easily shaped to create a wide range of sizes and forms. Additionally, its prime components are abundant. Concrete primarily comprises a binding medium that surrounds aggregate particles to form a cohesive mass. The binding medium is a result of reactions between hydraulic cement and water. As such, the physical characteristics of hardened concrete, including porosity and strength, greatly depend on the arrangement of its ingredient particles and the internal binding forces, which are influenced by the amplitude of cement hydration products [1].

Concrete has experienced many stages of progress. Therefore, many types of concrete have evolved. The first and most widely used type is normal strength concrete (NSC), which has a compressive strength of up to 40 MPa, as stated by ACI Committee 211.1 [2]. NSC has been used for an extended period in various types of structures. However, the deficiencies, such as the ease of cracking and low strength-to-heavyweight ratio, encouraged the investigators and manufacturers to address these weaknesses. The efforts led to the evolution of some types of concrete. The developments included materials and mix proportions, using supplementary materials to enhance the properties of fresh and hardened concrete [1].

The advent of admixtures like superplasticizers in the 1960s led to lowering the w/c ratio and enhancing the concrete strength. Decreasing the water-to-cement (w/c) ratio by adding superplasticizers produced high-strength concrete (HSC). However, raising concrete strength causes brittle failure, i.e., no ductility occurs at concrete fracture and poor impact resistance [1].

A series of new generations of concrete occurred with the incorporation of fibers within the concrete by using it as a micro-reinforcement. Fiber-reinforced concrete (FRC) involving steel, glass, polyethylene, or other fiber types is utilized effectively in concrete structures to improve stiffness, ductility, and impact resistance besides tensile strength. Construction materials improvement led to the development of structural concrete over several generations.

In 2002, according to ACI Committee 363 [3], concrete having 55 MPa compressive strength or more is defined as HSC. It is characterized by a low water-to-cementitious materials ratio (w/cm) ratio ranging from (0.22-0.37) and relatively high cement content between (450-564) kg/m^3 solo or with cementitious materials such as silica fume, fly ash, metakaolin, marble powder, or blast furnace slag as a percentage of cement content or as supplementary materials. The mixtures of HSC contain coarse and fine aggregate, like NSC, but differ by w/cm and adding supplementary mineral admixtures. HSC is considered a type of high-performance concrete (HPC) because of its high strength and improved durability [4]. The quality of HSC is governed by the properties and uniformity of the constituents, as well as by mixing, placing, and curing conditions [1], [3].

The mixture proportion of HSC is widely demonstrated by ACI 211.4R [5]. Since HSC mixtures contain one or more cementitious materials such as fly ash, silica fume, blast furnace slag cement, or other cementitious materials, test age becomes the main feature to achieve considerable strength after 28 days. However, 56 days and 90 days or later may be considered to take advantage of this characteristic. Reactive powder concrete (RPC) is another type of concrete, although it does not contain coarse aggregate. RPC depends on enhancing homogeneity and compacted density by omitting coarse aggregates and using fine powders in the mix, besides heat treatment, to enhance the microstructure [6].

Cementitious materials describe a combination of Portland cement and other fine materials having cementitious characteristics, such as fly ash, silica fume, metakaolin, and ground granulated blast furnace slag. These materials have cementitious properties that can contribute to the hydration process to produce additional calcium silicate hydrates (C-S-H), which can reduce porosity and improve the strength of concrete. Table 1 illustrates the progressive generations of concrete with their major constituents and specific properties.

Based on Table 1, the density of the concrete is approximately consistent for all types. However, the compressive strength increases as the w/cm ratio decreases and the coarse aggregate content increases. Furthermore, the percentage of fine-to-coarse aggregates alters according to the required concrete type. For NSC, this ratio ranges between 0.4-0.63. In HSC, it is around 0.5, while in HPC, it is about 0.7. For FRC, the fine aggregate exceeds the coarse aggregate content, and the ratio between them is approximately 1.25. Finally, in self-compacted concrete (SCC), both fine and coarse aggregate content should be roughly equal.

The compressive strength increases with the increase of cement content, but not more than a specified limit, decreasing the maximum size of aggregate and using cementitious materials.

Cement is the prime binding material in different types of concrete. Therefore, it is excessively consumed in construction works and facilities worldwide. However, it is significant to note that cement production is also a major contributor to carbon dioxide (CO_2) emissions. Production of high amounts of cement requires large quantities of natural resources, besides releasing high doses of carbon dioxide into the atmosphere. The proportion of CO_2 emitted from the cement industry reaches (5-10) % of the total global industrial production. CO_2 is an influential greenhouse gas contributor to global warming [7]. Global warming results from the excessive emissions of gases to the atmosphere and the consequent depletion of the protective ozone layer. On the other hand, industrial waste can negatively affect the environment, causing pollution [8]. Therefore, embracing sustainability in concrete production can reduce gas emissions and improve the environment. Sustainable concrete minimizes cement consumption, addresses industrial waste issues, and reduces CO_2 emissions. Waste industrial materials can be used as supplementary cementitious materials (SCMs) for partial cement replacement to obtain concrete sustainability [7], [9].

Table 1 Proportion and Compressive Strength of Some Types of Concrete [1], [5], [3], [6]

Properties	**Concrete Type**					
	NSC	**HSC**	**HPC**	**SCC**	**FRC**	**RPC**
28-day f´c, MPa	**14 - 54**	**55-120**	**50-100**	**40-90**	**34-48**	**150-230**
w/cm ratio	**0.4 - 0.82**	**0.22-0.45**	**0.25-0.40**	**0.35-0.50**	**0.35-0.5**	**0.15-0.17**
Coarse aggregate, % by volume	**46 - 83**	**34-36**	**40-44**	**34-38**	**25-28**	**Nil**
Fine aggregate, % by volume	**29 - 34**	**16-18**	**27-31**	**30-41**	**32-36**	**22-44**
Cement content, kg/m^3	**≤ 400**	**450-565**	**450-580**	**400-465**	**300-593**	**955-1000**
Cement content, %by volume	**10 - 14**	**12-24**	**18-24**	**17-19.5**	**12.5-24.7**	**0.43**
Max. size of aggregate, mm	**150**	**38**	**19.05-25**	**25**	**10-19**	**0.6**
Silica fume, % by volume	**-**	**1-3**	**1.4-1.8**	**1.25-2.7**	**-**	**0.25**
Fly ash, % by volume	**20 - 35**	**11-18**	**2.5-5.5**	**5.0-8.6**	**5.8-6.2**	**-**
Admixtures type used	**AE‡** **WRA†**	**WRA†** **HRWRA⁑**	**SP#**	**SP#**	**AE‡** **WRA†**	**HRWRA⁑**
Fibers content, by volume %	**-**	**-**	**-**	**-**	**0.3-2.0**	**1.0-2.5**
‡ Air entrainment; † Water reducing admixture; ⁑ High-range water reducing admixture; # Superplasticizer						

In this paper, the positive effects of using industrial waste materials like silica fume, fly ash, metakaolin, and ground granulated blast furnace slag to improve the overall properties of concrete have been explored. By serving as cementitious substances, these materials can enhance the strength, porosity, acid and alkali resistance, and durability of the concrete. They can be used as a partial replacement for cement or added as an additive, which can alter the type of concrete. However, it is significant to note that there may also be some potential drawbacks that need to be addressed when using these materials.

2. Research Significance

The main contribution of this review is to study the effect of using supplementary cementitious materials (SCMs) as a replacement for cement or as additives on the properties of fresh and hardened concrete and to compare the results reached by researchers to arrive at the best proportions that can enhance the concrete, individually and in combination. In addition, it aims to show the importance of using those materials to reduce the cement alone in concrete and thus reduce its impact on the environment. The issues erected from the excessive use of these materials on concrete properties are also presented. Accordingly, the optimal proportions of these materials are determined to be used in concrete.

3. The Significance of Cementitious Materials

Supplementary cementitious materials (SCMs) represent inorganic substances that contribute to enhancing some of the concrete features. SCMs can be categorized as inert, potential hydraulic, or pozzolanic materials. Inert materials are crystalline hydraulically inactive materials [10]. It can be used as filler to densify the concrete microstructure and reduce porosity. Also, they act as a catalyst to speed up cement reactions, like limestone powder, quartz, and marble powder [7].

Potential hydraulics are materials rich in calcium or silicates that can react with water to form calcium-silicate-hydrates (C-S-H), such as ground granulated blast furnace slag (GGBFS). Pozzolanic materials are siliceous or siliceous aluminous substances that have no cementitious features themselves but are activated when they come into contact with calcium hydroxide $Ca(OH)_2$ yielded from the hydration of cement, like fly ash, silica fume as artificial Pozzolan, and calcined clay and metakaolin as natural Pozzolan [7]. Figure 1 illustrates the types of SCMs.

The prime reactions between cement and water to give the hydration products their binding features depend on the cement's chemical composition and the reaction period. Reactions mainly occur between calcium oxide, silicates, and water to produce calcium-silicate-hydrate (C-S-H) and calcium hydroxide ($Ca(OH)_2$), besides other little products. These products differ in percentage depending on the main constituents of the cement, the quantity of water, and the age. However, C-S-H has a dense needle shape that increases with the concrete age, while $Ca(OH)_2$ has a relatively large hexagonal shape, which becomes the main reason for enlarging internal voids. Therefore, reducing the percentage of $Ca(OH)_2$ is required to minimize the void size and number, which, in turn, minimizes the porosity and enhances the concrete strength. For reducing the proportion of $Ca(OH)_2$ in the concrete microstructure, interaction with substances that can react with alkali products is required. Silica fume, fly ash, metakaolin, and blast furnace slag have a composition that contains a high percentage of silicates. Silicates can react with $Ca(OH)_2$ in the presence of some agents to improve the mechanical properties of concrete and reduce the porosity [7], [9], [11]. Another benefit that SCMs can provide, which is reducing the impact of structures being exposed to high temperatures up to 400 ºC by improving the residual compressive and tensile strength [12].

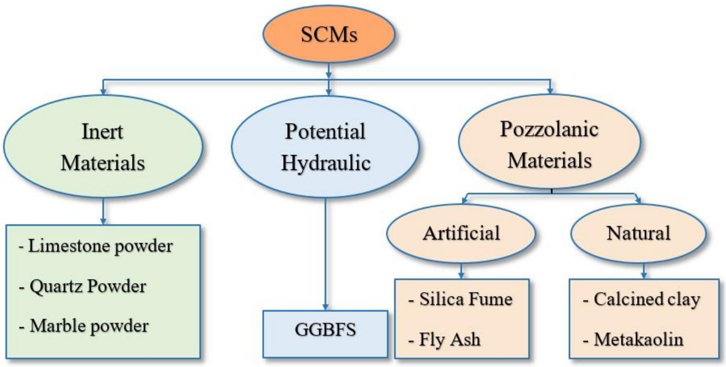


Fig. 1 Types of Supplementary Cementitious Materials

4. Chemical Composition of Cementitious Materials and their Impact on Concrete

The concrete composition can be modified from one region to another, depending on the availability and price of its ingredients [13]. Choosing the concrete compounds relies on the particle measurement to achieve the optimum packing density, i.e., a continuous gradation of the particles to minimize voids and attain dense microstructure to reduce porosity and improve the mechanical properties [14], [15]. However, the chemical composition of cement and SCMs is illustrated as follows:

4.1. Cement

Cement is the prime hydraulic binder for other ingredients of the concrete mix. The most significant feature of cement is its fineness (its surface area). The finer the cement powder, the faster the chemical reactions occur by hydration [13].

The particle sizes of cement, as measured by de Larrard [4] using a laser analyzer, range between (0.5-100) µm, whereas Graybeal [16], [17] assigned the average size of cement particles as 15 µm. However, the average particle size of cement is assumed to be 45 µm. Another feature that is considered significant is the chemical composition, which is represented by percentages of calcium, silicate, aluminates, and ferrite oxides (C_2S, C_3S, C_3A, C_4AF). Therefore, attention should be focused on cement composition. When cement contains a small percentage of C_3A, it becomes preferred because very little C_3A content minimizes water demand and reduces the w/c ratio [4]. Cement type affects the early age properties of concrete. The packing density of cement should be approximately 3150 kg/m^3, while bulk density is about 1440 kg/m^3, and specific gravity is about 3.15 [4], [18].

Previous studies [19] stated the cement type that could be utilized in the high-strength and ultra-high-strength concrete mixtures should have a low alkali content and low to medium fineness. The specific surface area should be more than 400 m^2/kg (Blaine). The prime components of cement that promote strength are C_3S and C_2S. Therefore, cement with a higher content of both C_3S and C_2S is regarded in mixes. On the contrary, tricalcium aluminate (C_3A) awards rapid hydration, which accelerates with increasing surface area, and hence, it raises water demand [13, 41]. Therefore, it was found that using cement with a percentage less than 8% C_3A is comfortable for concrete with high strength because of its low heat of hydration and delaying setting time [19].

ACI Committee 211.4R [3] mentioned that "there was an optimum cement content beyond which little or no additional increase in strength could be achieved by increasing the cement content." In this context, it was detected that boosting the cement content increased the strength, but after a cement content of 1700 kg/m^3 (in ultra-high performance concrete), the compressive strength decreased [20]. However, using cement alone as a binding to the other concrete ingredients was found to award a compressive strength of about 50 MPa after 28 days of moist curing [1]. A higher strength requires a low w/c ratio, which means diminishing workability, besides minimizing relatively large hydration compounds of calcium hydroxide. Thus, it is compulsory to use mineral or chemical admixtures in the concrete mix to achieve workable concrete and consume calcium hydroxide to reach a strength of more than 50 MPa [1].

4.2. Silica Fume

Micro-silica, condensed silica fume, or mere silica fume are terms used to describe the by-product of released gases from the ferrosilicon industry, silicon, or metal alloy industry, which has a high percentage of pozzolanic materials [10]. Silica fume is a very reactive Pozzolan; therefore, it can be used in concrete to enhance several properties due to its fineness, large surface area, and high content of silicon dioxide [21], [22]. It is used as an additive material or to replace a part of cement content. Silica fume performs two actions. The first enhances the packing density of concrete by filling the voids between cement particles and aggregate, thus reducing the permeability. The second action is the reaction between SiO_2 and the calcium hydroxide produced from cement hydration to form additional C-S-H compounds, which enhances concrete strength in compression and tension and increases the bonding force between concrete and steel rebars or fibers if they are used.

The characteristic properties of silica fume are their quite fine non-crystalline structure, high content of silicon dioxide, and extremely powdery spherical particles (0.01-0.2) µm diameter to be smaller than the largest cement particles by about 100 times [22], [23], [24]. Its surface area ranges between (15000-20000) m^2/kg, and the content of SiO_2 is determined to be (85-97) % according to ASTM C1240 and AASHTO M307 [17], [25], [26], [27]. It has a specific density of (2.2-2.5), and a bulk density of (130-430) kg/m^3 [22], Table 2 illustrates these properties.

At first using, silica fume was utilized to replace a part of cement and was determined to be less than 10% of cement weight [14]. However, a recent application is a supplementary component to create high-performance and ultra-high-performance concrete. That is due to its role in increasing compressive and tensile strength and improving durability.

Using silica fume in concrete usually raises the water demand, which means a reduction of fresh concrete workability because of the large surface area resulting from fine particle sizes and carbon content. Therefore, HRWRAs are used at a suitable dosage to get the desired workability of concrete, specifically concrete with a low w/cm ratio [10], [4], [23], [28].

To attain the best results of adding silica fume to the concrete mix, the concrete should be treated in hot water at about 90 °C. Hot water treatment can accelerate the reaction between calcium hydroxide erected from the hydration of cement and SiO_2 of silica fume to create more compounds of C-S-H, which, in turn, minimize porosity and increase concrete strength [29]. However, customary concrete curing in ordinary water minimizes compressive strength by about (10-20) % compared to heat-treated concrete strength. In the latter case, silica fume merely works as a filler substance [20], [28]. Figure 2 summarizes the influence of silica fume on concrete properties.

The silica fume/cement ratio significantly affects the strength gained at a later age. It was found that the proportion of 25 % yielded the highest compressive strength at w/cm of 0.20, while the strength decreased when the silica fume/cement ratio was higher than 0.25 [30]. The impact of silica fume on strength development can be explained by chemical and physical aspects. Chemically, silica fume begins to work upon presenting $Ca(OH)_2$ to react with it, to form extra calcium silicate hydrates. When the content of silica fume exceeds 0.25, the cement content decreases. Hence, the quantity of calcium hydroxide required to react with silica fume decreases. Therefore, this will cause a reduced strength [31]. Physically, the ultrafine size of silica fume particles participates effectively in optimizing the packing density of the composite [32].

Other studies stated that the best percentage of silica fume to use in HSC and UHPC mixes ranges between (15-30) % of cement weight relying on the other ingredients [4], [6], [16], [17], [19], [27], [33], [34], [35].

Arshad et al. [36] tested the effect of adding silica fume and bagasse ash on concrete properties. They found that increasing bagasse ash percentage from 0 % to 15 % decreased slump by more than 17 %. Therefore, the superplasticizer percentage should be increased to adjust the workability. Adding 8 % silica fume as a percentage of the cement weight increased compressive strength by 3.5 % and elastic modulus by 4.4 %. Adding bagasse ash at 5 %, 10 %, and 15 % besides 8 % silica fume increased compressive strength by 4.8 %, 10.3 %, and 2.43 %, respectively. Tayeh et al. [37] found that adding 7.5 % silica fume by cement weight boosted compressive strength more than the other percentages of 15 %, 20 %, and 25 %. However, adding silica fume at different percentages (7.5 % - 25 %) raised compressive strength at all ages (1-day, 7-day, 28-day, 56-day, and 90-day).

Silica fume mainly improves the performance of high-strength concrete in terms of compression, tension, and flexure. It may be associated with the increased concrete density because the concrete microstructure was about 5% denser when silica fume was added to the mixture. That is because the silica fume is rich in amorphous particles that can react with calcium hydroxide erected from cement hydration [38].

4.3. Fly Ash

Fly ash is a by-product of coal combustion, consisting of pozzolanic materials. It mainly consists of silicates, aluminates, and ferrite, besides other oxides that have cementitious characteristics [32], [39]. More than 250 million tons of fly ash are produced annually worldwide, but only 16 % of the amount is used in construction [39]. Therefore, the lack of fly ash consumption is regarded as a pollutant for the environment.

Fly ash can be used as filler to contribute to self-compact backfill material instead of compacted soil or granular filling. Fly ash is also used to replace a part of cement in the concrete mix due to its cementitious features or it may mix with cement clinker and grind by milling [40]. ASTM C618[41] defines fly ash as " the finely divided residue results from the combustion of ground and powdered coal and that is transported by flue gasses." Fly ash can be classified according to the degree of cementitious features. It can be classified into three classes: class N, F, and C, regarding the chemical composition [39]. However, ASTM C618 classified fly ash into two categories: class F and class C.

Class F is normally produced from burning anthracite or bituminous coal, whereas class C is produced from burning subbituminous coal and lignite. Class C is usually characterized by cementitious properties because it includes Pozzolan and free lime [42]. The use of fly ash in concrete improves workability and reduces long-term permeability. Also, it enhances the resistance to sulphate attack due to its reaction with the calcium hydroxide produced by cement hydration to form new products to fill the voids [43], [44].

Fly ash acts on lowering the heat of hydration, enhances rheological properties, and delays gaining early age strength. However, pozzolanic reactions between $Ca(OH)_2$ and SiO_2 in fly ash progress but slowly enhance the later-age strength. It was found that the 90-day compressive strength is 30 % higher than the 28-day strength [45], [46].

The particle sizes of fly ash range between (1-100) µm. The typical size is around 20 µm. The surface area is between (300-500) m^2/kg. The bulk density is between (540-860) kg/m^3. The packing density ranges between (1120-1500) kg/m^3 [47]. Table 2 illustrates the specifications of fly ash. Figure 2 summarizes the influence of fly ash on concrete properties. Several studies have been performed to explain the impact of fly ash on concrete properties in fresh and hardened cases. Johari et al. [48] stated that adding fly ash could increase concrete workability and minimize water demand. At early ages, fly ash does not contribute to strength gain due to dilution and slow pozzolanic reaction. Replacing cement with (10-30) % fly ash lowers 28-day compressive strength by (1-5) %. However, at 180 and 365 days, 10-30 % fly ash increases compressive strength by about 11 %. Arshad et al. [36] found that adding fly ash to a concrete mix of ultra-high-performance concrete (UHPC) reduced compressive strength at an early age but increased it at later ages. Adding fly ash to the concrete matrix minimizes heat of hydration at an early age because it disperses cement particles and delays hydration reactions; therefore, the strength gaining is reduced. However, the pozzolanic reactions between fly ash components and $Ca(OH)_2$ were activated at later ages, 90 days and over, to produce additional C-S-H compounds, which enhance the strength and reduce the porosity. The authors stated that 40 % fly ash awarded the better enhancement for UHPC strength.

4.4. Ground Granulated Blast Furnace Slag (GGBFS)

GGBFS, occasionally named slag, is a non-metallic product that has either a glassy amorphous granular composition, which is used as a cementitious substance, or may be formed as crystalline to use as aggregate [49]. It is produced through iron production when the molten blast-furnace slag is immediately cooled with water. It contains silicates and aluminosilicates of calcium and other ingredients [47], [50], [51]. It is ground to 45 µm or less in diameter as a white powder. Its Blaine surface area is between (400-600 m^2/kg), specific gravity is between (2.85-2.95), and the bulk density is between (1050-1375) kg/m^3 [47], [52], [53]. It is stated that when GGBFS particles are less than 10 µm, they contribute to an early strength gaining until 28 days, while particles in the range of 10-45 µm participate in hydration after 28 days and contribute to a later age strength. Particles larger than 45 µm exhibit little or no activity [49].

GGBFS has some cementitious characteristics. Therefore, it can be used as a supplementary material in concrete mixtures or a replacement for a part of cement content. Regardless of how it is used, slag can reduce cement content. The final reaction findings of GGBFS cement hydration are the same as those of Portland cement hydration [50], [54].

GGBFS usually minimizes water requirements by about (1-10) % according to the dosage used and also improves the workability, fluidity, and retards setting time. So that slag can enhance the strength and other mechanical properties [55].

Johari et al. [48] found that replacing cement with 20 % GGBFS content raised compressive strength by 9.2 %. However, a further raising of GGBFS content might reduce strength gaining. Mat Dom et al. [49] replaced cement with (10-60) % GGBFS in mortar to produce cement brick. The samples were cured for (7, 28, 56, and 90) days in water. Test results showed that the 10 % replacement of cement with GGBFS awarded the highest compressive strength at 7 and 28 days, while the percentage of 20 % gave the best compressive strength at 56 days and 30 % gave the highest strength at 90 days. However, the 50 % and 60 % replacement of cement with GGBFS awarded the lowest strength at all ages. Water absorption decreased at percentages of (10-40) % replacement cement with GGBFS at 7 days and later ages of 56 and 90 days.

Ayim-Mensah and Radosavljevic [56] studied the effect of replacing cement with GGBFS at 0 %, 20%, 40%, 60%, 75%, 90 % in UHPC mixture. The results showed that the flowability of the mixture increased with increasing GGBFS content up to 90 %. The 40 % and 20 % replacements of cement awarded the highest increase in 28-day compressive strength by 5.3 % and 2.5 %, respectively, while 60 % and 75 % caused a reduction in compressive strength by 15 % and 10 %, respectively. Also, the 40 % and 20 % replacements gave the highest increment in flexural strength. However, all percentages of cement replacement raised the flexural strength, where the lower the percentage of cement replacement with GGBFS, the higher the increment in flexural strength.

4.5. Metakaolin

Metakaolin is a non-industrial by-product having pozzolanic substances. Its activity exceeds the silica fume activity due to the thermal activation of aluminosilicates, which awards high pozzolanic activity. Metakaolin is manufactured by kaolin clay calcination at (650-800) ºC [57]. Therefore, it represents a distinctive type of calcined clay, which has an anhydrous form of clay mineral kaolinite, then ground to a fine powder. It consists of a high content of silica (50-63) %, alumina (28-40) %, and ferric oxide (1-4) %, besides other little oxides [57], [58]. The average particle sizes range between (1-2) µm. When metakaolin is used in the concrete mixture, it gives very low porosity and very high strength [47]. Metakaolin has many benefits for concrete by enhancing strength, resisting chemicals, and minimizing permeability and carbonation, therefore, increasing durability. It reduces autogenous shrinkage and improves workability [58].

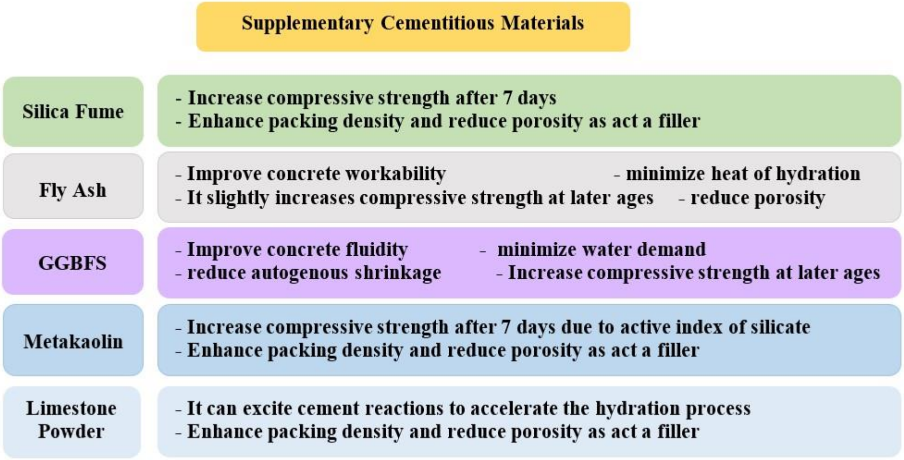
Due to its quite fine particle size, metakaolin can be used as an additive to concrete to ensure a dense microstructure [59], [60]. Its bulk density is about 1005 kg/m3, and the specific gravity is approximately (2.30). Chandak and Pawade [57] found that replacing 25 % of cement with metakaolin improved compressive, tensile, and flexural strength, besides enhancing durability and increasing concrete density due to filling action. Also, the authors stated that using metakaolin at any percentage could improve concrete workability. Wild et al. [61] studied the effect of metakaolin on compressive strength at different ages (1 -90) days. They replaced cement at (5, 10, 15, 20, 25, and 30) % with metakaolin. The results showed that the 20 % replacement awarded the best compressive strength at ages 14 to 90 days, and the activity of metakaolin occurred after 7 days of curing in enhancing the strength. Sasikala et al. [58] investigated the effect of replacing cement with metakaolin on concrete properties at different ages. Five percentages of metakaolin to replace cement were adopted by the authors; 0 %, 5 %, 10 %, 15 %, and 20 %. The results showed that the slump increases with increasing the replacement percentage from 0 % to 20 %. The 10 % replacement of cement with metakaolin was awarded the best compressive strength at all ages. The percent increment in compressive strength was 1.2 % at 7 days, 12.9 % at 14 days, 2.3 % at 28 days, 12.4 % at 56 days, and 10.8 % at 90 days. The 10 % also awarded the highest increment in tensile strength by 5.5 % at 28 days and 0.95 % at 90 days. However, 15 % and 20 % cement replacement with metakaolin reduced tensile strength at 56 and 90 days. 10 %, also increased flexural strength at 28 and 56 days, while 5 % raised strength at 90 days more than other percentages.

4.6. Limestone Powder

Limestone powder is made by crushing and grinding natural limestone, or it may be a by-product of a limestone quarry. The chemical composition of limestone relies on the raw materials. Generally, it consists of more than 50 % CaO as $CaCO_3$. It does not contain Pozzolan; therefore, no pozzolanic reactions occur. Consequently, it is called an inert filler. However, a study by Remizaniapour et al. [62] claimed that limestone is not an inert substance since there is little reaction between C_3S and $CaCO_3$. However, adding limestone powder to the concrete mix can excite cement reactions to accelerate the hydration process and enhance the formation of C-S-H [63].

Table 2 A Comparison Between Properties of Some Cementitious Materials [34], [24], [64]

Material	Particle size µm	Surface area m^2/kg	Bulk density kg/m^3	Packing density kg/m^3	Specific gravity
Fly Ash	**1-100 avg. $\leq$ 20**	**300-500**	**540-860**	**1120-1500**	**1.9-2.8**
Slag	**$\leq$ 45**	**400-600**	**1050-1375**	**1120-1940**	**2.85-2.95**
Silica Fume	**avg. $\approx$ 0.1**	**15000-20000**	**130-430**	**480-720**	**2.2-2.5**
Metakaolin	**1.0-2.0**	**11100-25400**	**$\approx$ 890**	**1005**	**2.3**
Cement type I	**1-100 Avg. (20-45)**	**300-500**	**1440**	**3150**	**3.15**
Cement type II	**1-100 Avg. (20-45)**	**500-600**	**1440**	**3150**	**3.15**


Supplementary Cementitious Materials

Silica Fume
- Increase compressive strength after 7 days
- Enhance packing density and reduce porosity as act a filler

Fly Ash
- Improve concrete workability - minimize heat of hydration
- It slightly increases compressive strength at later ages - reduce porosity

GGBFS
- Improve concrete fluidity - minimize water demand
- reduce autogenous shrinkage - Increase compressive strength at later ages

Metakaolin
- Increase compressive strength after 7 days due to active index of silicate
- Enhance packing density and reduce porosity as act a filler

Limestone Powder
- It can excite cement reactions to accelerate the hydration process
- Enhance packing density and reduce porosity as act a filler

Fig. 2 Effects of SCMs on properties of concrete

5. Impact of Binary and Ternary Cementitious Materials On the Properties of Concrete

Some researchers used two or three types of cementitious materials to replace cement in concrete mixes. The impact of these materials relies on their characteristics and proportions [65]. Mohammad et al. [66] studied the influence of replacing cement with fly ash alone, GGBFS alone, and a mix of them on rheological properties and strength of SCC. Test results showed that the workability increased by increasing fly ash content to 60 % replacement, slag content to 60 % replacement, and 30 % fly ash with 30 % slag replacement of cement. Regarding strength, there was a continuous decrease in compressive strength on replacing cement with fly ash up to 60 %, while on replacing cement by (10-40) % with slag alone, the compressive strength increased by about 7 % over the strength of solo ordinary cement concrete, which was 80 MPa. The binary replacement of fly ash and slag was more effective in raising the compressive strength by more than 7.3 %. It is clear that the supplementary cementitious materials can benefit the rheology of the mix besides other advantages to strength enhancement and minimizing porosity [67]. On the other hand, GGBFS and fly ash may contribute to reducing the heat of cement hydration at early ages.

Aghabaglou et al. [43] studied the influence of cement replacement by fly ash (class C), silica fume, and metakaolin on the mechanical properties and resistance of mortar mixes. The results showed that the mortar with 10 % silica fume presented the highest compressive strength, followed by the mortar with metakaolin, and then the one with fly ash. The fly ash mortar exhibited the lowest compressive strength for up to 180 days. However, after 300 days, the mortar with fly ash showed compressive strength more than that with silica fume and metakaolin by four and twice times, respectively. The pozzolanic activity index and the specific surface area of silica fume and metakaolin are higher than that of fly ash; therefore, the reaction between SiO_2 in silica fume or metakaolin started after 7 days of casting where a sufficient quantity of $Ca(OH)_2$ is available in the blend to form extra compounds of C-S-H and reduces the $Ca(OH)_2$ which has a relatively large size compared to C-S-H. That increases the strength from the age of 7 days and continues to rise until the materials are consumed, or the activity decreases. The activity of fly ash occurs after a long period of up to 180 days due to the relatively large size of particles and the role of dispersing cement particles. In addition, its activity index may be lower.

When silica fume, fly ash, and other cementitious materials are used as ternary additives in a concrete mixture, the increment in compressive strength of low-strength concrete is higher than that of high-strength concrete. In this context, Kumar and Prasad [68] inspected the impact of ternary mixes on three-graded concrete: 30 MPa, 50 MPa, and 70 MPa. The authors replaced cement with 15 % fly ash, 8 % silica fume, and 10 % lime sludge. The results showed that the increase in compressive strength was 42.95 %, 32.48 %, and 22.79 % for 30 MPa, 50 MPa, and 70 MPa concrete grades, respectively. Also, the workability of the mixture improved upon adding the mineral additives for all concretes' grades. On the other hand, the resistance to acid attacks of higher-strength concrete was more than that of lower-strength concrete.

Sharbatdar et al. [69] investigated the impact of replacing cement with silica fume alone, metakaolin alone, and a mix of them on the mechanical properties of SCC at various ages. The results indicated that 10 % metakaolin to replace cement provided the highest compressive strength at 7 days, while the 15 % percentage awarded the highest compressive strength at 14, 28, and 56 days. 10 % cement replacement with silica fume provided the best compressive strength at 7 and 28 days, while 5 % provided the highest compressive strength at 56 days. A mix of silica fume and metakaolin in equal proportion with a total of 10 % gave the highest compressive strength at (14-56) days. However, replacing cement with 20 % silica fume provided the highest increment in compressive strength at 56 days compared to 28 days, followed by a 20 % mix of metakaolin and silica fume. Mixtures in which cement was replaced with 20 % silica fume alone or a 10 % blend of silica fume and metakaolin awarded the highest increment in tensile strength. Furthermore, a mix with a 20 % blend of silica fume and metakaolin provided a better reduction in water absorption after 3 days.

Nasr et al. [65] inspected the effect of replacing 50 % of cement with binary combinations of silica fume and fly ash or metakaolin and fly ash on the properties of RPC. The findings illustrated that a blend of 20 % silica fume and 30 % fly ash raised the flowability more than the other mixes. However, a mix of 30 % silica fume and 20 % fly ash with 1 % steel fibers afforded the highest increment in compressive and flexural strength by 44 % and 11 %, respectively. Generally, the authors stated that " the silica fume and fly ash combinations mixtures revealed better performance than metakaolin and fly ash mixtures."

6. Impact of Supplementary Cementitious Materials On the Behavior of Structural Elements

Alghzali et al. [70] inspected the shear capacity of self-compacted concrete (SCC) beams containing a high content of fly ash. The results showed that the concrete rheology increased upon using a high proportion of fly ash, whereas a slight variation in the beam's shear capacity was noticed upon raising cement substitute proportions. Elsayed et al. [67] investigated the effect of GGBFS and fly ash as a substitution for cement content on the shear behavior of SSC beams. The results showed that GGBFS and fly ash negatively affect the mechanical properties of SCC, where adding them to the concrete decreased the maximum shear strength, durability, and toughness of the beams.

Arezoumandi et al. [71] studied the effect of replacing 70 % of cement content with fly ash as a high-volume fly ash concrete (HVFAC) on the shear behavior of (305 x 457) mm cross-section beams of (3-6) m clear span with a/d greater than 3. The compressive strength was 22 MPa for the mix with low cement content (92 kg/m^3 cement + 213 kg/m^3 fly ash) and 30-34 MPa for the mixture with high cement content (136 kg/m^3 cement + 317 kg/m^3 fly ash). Splitting tensile strength was between (1.6 – 3.1) MPa. Test results showed that there is no significant variation between the shear strength of both mixes. The experimental shear stress was lower than the ACI shear stress, but it was identical to the theoretical results of Australian specifications and Euro code 2.

Sushma et al. [72] studied the effect of metakaolin versus fly ash on the compressive strength of conventional concrete and the shear strength of identically reinforced concrete beams of (150 x 200) mm cross-section and 1.5 m length. The authors found that replacing cement with 10 % fly ash reduces compressive strength by 6.7 % and ultimate beam load by 16.7 %, whereas replacing cement with 10 % metakaolin increased compressive strength by 27.8 % and beam's load by 5.6 %.

7. Conclusions

This review paper focuses on the impact of using SCMs on some concrete types. The following conclusions can be withdrawn;

Cement production is a significant contributor to CO_2 emissions. On the other hand, industrial waste materials can harm the environment. Therefore, replacing cement with industrial waste as SCMs in concrete mixes can be beneficial for life and the environment.

The effect of SCMs on concrete properties appears after a period of curing where calcium hydroxide becomes available from cement hydration to react with silicates of SCMs. That depends on the activity index and fineness of the material. Silica fume and metakaolin are more active than GGBFS and fly ash. Also, upon replacing cement with silica fume or metakaolin, heat treatment can accelerate the reactions to enhance the microstructure and reflect positively on permeability and strength.

Silica fume enhances packing density and reacts with $Ca(OH)_2$ erected from cement hydration. However, using silica fume in concrete mix raises water demand. Thus, HRWRA should be used to moderate the workability in a low w/cm ratio. The perfect percentage of silica fume to replace the cement in the concrete mix depends on the cement content. For low cement content, a ratio of 10 % or less is perfect to increase the strength, while for high cement content, a percentage between (25-30) % is the optimum for increasing the strength.

Adding fly ash to concrete improves workability, minimizes water demand, reduces long-term permeability, and enhances resistance to sulfate attack. Fly ash also lowers the heat of hydration and delays gaining early-age strength. The effect of fly ash on strength occurs after 90 days. The 90-day compressive strength is 30 % greater than the 28-day strength. For low cement content, (10-30) % fly ash of cement weight is perfect to increase strength after 90 days, while for high cement content, 40 % fly ash of cement content could be the optimum ratio. However, the 60 % cement replacement with fly ash causes a continuous decrease in strength.

The activity of GGBFS depends on the size of its particles. Particles with a size less than 10 µm participate in strength gaining at early ages up to 28 days, while particles between (10-45) µm participate in strength after 28 days. Generally, GGBFS reduces water demand, improves workability, retard setting time, and enhances concrete strength. The lower the percentage of GGBFS, the higher the strength gained at early ages.

The activity of metakaolin exceeds the activity of silica fume. Using metakaolin in concrete mix significantly improves workability, reduces porosity, and enhances strength. The lower percentage of (10-20) % metakaolin to replace cement improves strength more than higher percentages.

Limestone powder can be used to enhance packing density to reduce permeability. However, the presence of limestone powder in concrete can excite cement hydration. Upon using ternary SCMs in a concrete mix, the increase in strength of low-strength concrete is higher than that of high-strength concrete. Furthermore, the resistance to acid attack of high-strength concrete is higher than that of low-strength concrete.

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