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Pozzolans: A review

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Abstract

Natural and artificial pozzolans are widely used in building materials and play an increasingly important role in minimizing costs and mitigating environmental effects in the manufacturing of building materials. These pozzolans can be obtained as by-products from various industries, generally they are wastes without any application or added value. However, when implemented in cement mixtures, their effectiveness is somewhat questionable. Therefore, it is necessary to determine the properties, characteristics, and behavior of these materials. This study aims to summarize the main pozzolans used in building materials. Volcanic pozzolans, pozzolans of sedimentary origin, fly ash, blast furnace slag, silica fume, metakaolin, ceramic wastes, demolition, and construction wastes, rice husk ash, bagasse ash, biomass ash, and paper sludge were considered. The chief characteristics studied were particle size, specific area chemical composition, and mineralogical composition. In addition, the impact on mechanical properties and durability in cement mixtures using pozzolans was analyzed. It was observed that the mechanical properties of cement mixtures change by increasing pozzolan replacement. The maximum percentage of replacement depends on the characteristics of the pozzolan. In the case of durability, pozzolans decrease absorption and permeability by reducing the porosity of the binder. This decreases acid diffusion and autogenous shrinkage, thus improving concrete durability. Finally, future studies are suggested to consider the implementation of artificial intelligence techniques and machine learning algorithms to improve the properties of the concrete mixtures.

Keywords: Pozzolan, Industrial wastes, Agro-industrial wastes, Calcined clays, Compressive strength, Concrete durability

1. Introduction

Construction is an industry that contributes greatly to the emission of greenhouse gases and is responsible for the depletion of non-renewable natural resources. A major negative impact on the environment is caused by concrete production [1]. The principal component of concrete is Portland cement, of which 4.1 billion metric tons were produced globally during 2019 [2]. Whereas, the production of concrete worldwide is almost 25 billion tons per year [3].

The cement industry causes 8-10% of greenhouse gas emissions [4] and 15% of global electrical energy consumption. Besides carbon dioxide emissions, the cement production process creates hazardous dust, which affects the surrounding environment, causing respiratory diseases in local inhabitants. The cement industry is also responsible for the exhaustion of non-renewable resources, such as limestone, clay, and fossil fuels [5].

Thus, it is extremely important to focus on the efficient use of resources by replacing conventional materials, used in cement production, with industrial by-products or waste materials. These alternative materials include construction and demolition waste [6-10], glass waste [11-13], plastic waste [14-16], sludge from wastewater treatment [17-19] and supplementary cementitious materials [20, 21]. Supplementary cementitious materials (SCMs) are inorganic materials that contribute properties to cementitious mixtures, through hydraulic activity, pozzolanic activity, or by both means [22].

A material is considered hydraulic if it shows a high dissolution when mixed with water and if it produces calcium silicate hydrate (CSH) and calcium hydroxide. In contrast, a material is considered pozzolanic, when it shows little dissolution concerning a hydraulic material, and in most cases, an activator is needed to speed up the initiation of the reaction [23]. Cementitious materials can be divided into those that can be used as cement replacement fly ash [24, 25], natural or artificial pozzolans [26-30], silica fume, and grainy blast furnace slag [31-34].

Different pozzolans of waste origin are being investigated as alternatives to existing ones, and the best-performing ones are: calcined clay, paper sludge, and different types of ash. These alternatives could reduce the total cement content by 20wt% whilst preserving given strength and also reducing the cost of concrete by 9%. Pozzolanic activity is the characteristic that determines the degree of reactivity in pozzolans. This mainly depends on the amount of amorphous silica and alumina in the composition of the pozzolanic material, specific surface area, and particle size distribution [35].

Pozzolans are incorporated into concrete to reduce the percentage of cement required and enhance durability. Pozzolans decrease absorption, permeability, and ion diffusivity by decreasing the binder porosity. The amount of pozzolan added varies from 5 to 40 wt.% of the cement [35]. This review aims to evaluate the performance of cement mixtures using natural and artificial pozzolans. Therefore, volcanic pozzolans, pozzolans of sedimentary origin, fly ash, blast furnace slag, silica fume, metakaolin, ceramic wastes, demolition and construction wastes, rice husk ash, bagasse ash, biomass ash, and paper sludge were studied.

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2. Pozzolans

Pozzolanic material was discovered, for the first time, in the form of volcanic soil of a reddish-brown color in the city of Pozzuoli, Italy, hence, the term pozzolan. It has been proven that Minoan, Greek, and Roman civilizations were using volcanic stone and pumice in construction many centuries ago. For example, the Pantheon and the Pont du Gard aqueduct were built using lime-pozzolan mortars and concrete, their longevity clearly demonstrating the remarkably durable properties of the binding materials employed [36]. Nowadays, different kinds of pozzolans are used as a substitute for cement content. These pozzolans are obtained from by-products of industrial and Agro-industrial processes and are used to reduce the energy required for clinker production and so reduce the harmful effects on the environment.

Pozzolan can be defined as a siliceous or siliceous and aluminous material that, in itself, possesses little or no cementitious value but, in the presence of water and when finely divided, can react with calcium hydroxide (lime), at room temperature, to form compounds with cementitious properties [37]. It is important to note that the definition of pozzolan does not depend on the origin of the material, but on its ability to react with lime and water. When pozzolan reacts with lime in the presence of water, OH- ions are released, causing an increase in the pH value (approximately 12.4). At that point, pozzolanic reactions occur, silicon and aluminum are combined with the available calcium, generating cementitious compounds called calcium silicate hydrates (CSH) and calcium aluminate hydrates (CAH). These reactions are represented in summary form below. One advantage of these compounds is that they improve the mechanical properties of the mixture due to the continuous development of pozzolanic reactions [38].

$$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^- \quad (Hydrolysis)$$
$$Ca^{2+} + 2OH^- + SiO_2 \rightarrow CSH \quad (Pozzolan\ with\ high\ silicon\ content)$$
$$Ca^{2+} + 2OH^- + Al_2O_3 \rightarrow CAH \quad (Pozzolan\ with\ high\ aluminum\ content)$$

Similarly, the presence of sulfate (SO_4^{2-}) in pozzolans generates a negative effect on pozzolanic reactions, since a highly hydrated mineral called ettringite is formed ($Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$). The conditions for ettringite formation are given by the presence of soluble aluminum, calcium, and sulfate, the presence of a high pH, and the amount of water. Also, the formation of ettringite is accelerated by the effect of high temperatures, and, depending on the environmental conditions, can form in a matter of seconds. In the reactions described, it can be seen that ettringite possesses some 26 water molecules; this shows that this compound is very expansive and, consequently, it can destroy cementitious materials produced by pozzolanic reactions [39].

$$CaO + H_2O \rightarrow Ca(OH)_2$$
$$Ca(OH)_2 \rightarrow Ca^{2+} + 2(OH)^-$$
$$Al_2Si_4O_{10}(OH)_2 \cdot nH_2O + 2(OH)^- + 10H_2O \rightarrow 2\{2Al(OH)_4^- + 4H_4SiO_4\} + nH_2O$$
$$M_xSO_4 \cdot nH_2O \rightarrow XM^y + SO_4 + nH_2O$$
$$where: x = 1, y = 2\ or\ x = 2, y = 1$$
$$6Ca^{2+} + 2Al(OH)_4^- + 4OH^- + 3(SO_4^{2-}) + 26H_2O \rightarrow Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$$

It is also worth mentioning that pozzolanic materials contain considerable amounts of silicon, iron, and aluminum oxide; in order that a material can be designated as pozzolan, the sum of these three oxides, as weight percentage, must be 70% [40]. Due to these chemical compounds, a cementitious gel (C-S-H) is produced. However, the amount of gel in the mixture is dependent on various factors, such as; the specific surface of the pozzolan, its characteristics, the chemical compounds present, the way the pozzolan is obtained, and the reactive silicon content. Considering this, pozzolans can be divided into two groups, natural pozzolans, and artificial pozzolans [41]. In the following section, some pozzolans shown in Table 1, which provides a general classification of pozzolans, will be discussed in more detail [42].

Table 1 General classification of pozzolans.

Pozzolans	
Natural pozzolans	**Artificial pozzolans**
Volcanic origin	Fly ash
Altered and unaltered pyroclasticmaterial	Blast furnace slag
Pumice stone and vitreous ashes	Silica fume
Zeolitic tuffs	Calcined organic matter residues
Sedimentary origin	Calcined clays and shales
Chemical sediments	Bottom ash from coal combustion
Diatomaceous earth	Steel industry slags
Detrital sediments	Municipal solid waste ashes
Naturally calcined clays	Glass wastes
Hydrothermal sintering of silicon	Fluid cracking catalyst residues

3. Classification of pozzolans

3.1 Natural pozzolans

Natural pozzolans can be divided into two major groups, one of volcanic origin and the other of sedimentary origin. The first group can be found in the form of tuffs (igneous rocks formed by the accumulation of volcanic ash), volcanic ash, volcanic slag, obsidian, and pumice stone (gray colored vitreous volcanic igneous rock). The second group, are found in the form of diatomaceous earth, cherts (sedimentary rock high in silica), opaline silica, and clays naturally calcined by the flow of burning lava [42]. Natural pozzolans are those that do not require any chemical treatment other than grinding to react with lime [26]. Likewise, natural pozzolans contain small amounts of non-reactive minerals (clay minerals, alkali feldspar, and quartz), and large amounts of reactive minerals (zeolite and volcanic glass) [27]. However, chemically, natural pozzolans are mostly composed of aluminum and silicon oxides. Table 2 shows the chemical composition of some natural pozzolans.

Table 2 Chemical composition of selected natural pozzolans

	Chemical composition (%)							
Chemical compound	Natural zeolite		Pumice stone		Diatomaceous earth		Volcanic tuffs	
	Iran [1]	Japan [2]	U.S.A. [2]	Turkey [3]	U.S.A. [2]	U.S.A. [2]	Italy [2]	Argentina [4]
SiO_2	67.79	71.65	65.74	77.52	85.97	60.04	54.68	62.53
Al_2O_3	13.66	11.77	15.89	12.99	2.3	16.3	17.70	10.76
Fe_2O_3	1.44	0.81	2.54	1.5	1.84	5.8	3.82	1.81
CaO	1.68	0.88	3.35	0.1	0.0	1.92	3.66	1.34
MgO	1.2	0.52	1.33	0.4	0.61	2.29	0.95	1.13
K_2O	1.42	0.0	1.92	0.95	0.21	0.0	0.0	3.67
Na_2O	2.04	1.8	4.97	0.12	0.21	0.0	3.43	5.66
SO_3	0.52	0.34	0.0	0.52	0.0	0.0	0.0	0.34

[1] [43], [2] [26], [3] [44], [4] [45]

3.1.1 Natural pozzolans of volcanic origin

Volcanic ash and pumice: are materials made up of a mixture of minerals and vitreous phases expelled during volcanic eruptions. Volcanic ashes are fine fragments of pyroclastic materials, which are usually less than 2 millimeters in size. This type of pozzolan has a high content of siliceous compounds [46]. In addition, pumice consists of 63% to 75% silicon oxide and is considered one of the major pyroclastic deposits next to volcanic slag. Pumice is derived from an acid magma; its pH is approximately 7.5. Also, it is a highly microvesicular compound, with a porosity ranging from 60% to 70%. Moreover, its density (700-1200 kg/m^3) varies depending on its formation and, in some cases, it can float on water. It is amorphous and is mainly composed of quartz, biotite, and feldspars [28, 47].

Volcanic slag: is a material of volcanic origin, with a low level of crystalline water and is porous. Its color ranges from black to dark brown. Volcanic slag is very similar to pumice but is derived from basaltic or andesitic magma. Compared to pumice, it has a lower silica content (40%-60%) and almost similar in pH (7.6) and density (500-1300 kg/m^3). In turn, it has a vesicular nature (with small spherical cavities) caused by of the escape of gases during eruptions. Its porosity is between 30% and 60% [47]. Sometimes, these vesicles contain zeolite, calcite, and quartz, minerals formed from fluids with high content of hot water. Similarly, slags contain vitreous phase and may contain phenocrysts such as feldspar and biotite [28, 42].

Zeolitic tuffs: these are volcanic ashes and lithified pumice stones. These rocks are composed of clay, zeolite, and carbonate minerals (filler materials). However, the most plentiful compound is zeolite, which occurs due to zeolitization. Zeolitization is the alteration of the vitreous phase in minerals of the zeolite group (clinoptilolite, paulingite, barrerite, among others) and occurs in a series of geologically controlled alkaline conditions. In addition to zeolite, tuffs include combinations of silicate minerals, such as quartz, feldspar, mica, clay minerals, and volcanic glass. The most abundant silicic zeolites are clinoptilolite and mordenite and the most widespread aluminous zeolites are phyllipsia, analcime, and heulardite [28, 48].

3.1.2 Natural pozzolans of sedimentary origin

Diatomaceous earth: also known as diatomite, is a sedimentary rock composed of fossilized remains of freshwater unicellular plants (diatoms). It is an amorphous siliceous pozzolanic material, containing carbonate and clay minerals, quartz, feldspar, and volcanic glass [49]. It is fine-grained, earthy, light-colored, finely porous, with low density, and chemically inert. The main applications of diatomites consist of filters, absorbents, fillers, and insulation material. Due to its special pore structure, it is used to prepare nanocomposites for filling voids in different substances. Likewise, it also serves as a pozzolanic material, either in natural or calcined form [50].

Sediments of detrital and mixed origin: detrital sediments are largely composed of minerals that appear as a result of weathering and erosion of rocks [51]. One of the sediments that can be used as a pozzolan is Sacrofano soil, of a mixed origin, found near Viterbo, Italy. This soil possesses a silicon oxide content of around 85% to 90% by weight. Diatoms, volcanic particles, and some crystalline minerals were drastically altered by acidic fluids that infiltrated through the top of the deposit. Other materials derived from detrital rocks are naturally burned clays, such as Trinidad porcelanite and Central Asian gliezh. Porcelanite is formed by spontaneous combustion of bituminous clays, and the second type is composed of shales burned by natural from underground coal fires [36]. Another kind of pozzolan of detrital origin is bentonite, which is an absorbent aluminum phyllosilicate clay mainly composed of montmorillonite [29].

Table 3 Chemical composition of some artificial pozzolans

Artificial pozzolan		Chemical compound									
		SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	SO_3	Ti_2O	Na_2O	Others
FA	FA [1]	11.8-62.8	2.6-35.6	1.4-24.4	0.5-54.8	0.1-6.7	0.1-9.3	0.0-12.9	0.0	0.1-3.6	0.0
	FA [2]	45-64.4	19.6-30.1	3.8-23.9	0.7-7.5	0.7-1.7	0.7-2.9	0.0	0.0	0.3-2.8	0.0
BFS	BFS [3]	32-42	6-19.3	0.0	35-48	3-14	0.0	1-4	0.2-2.1	0.3-1.2	0.0
	BFS [4]	35-40	10-15	0.3-2.5	30-42	8.0-9.5	0.0-0.3	0.0-1.3	0.0	0.0-1.4	0.8-8.3
SF	SF [5]	99.5	< 0.004	< 0.001	< 0.003	< 0.002	0.0	0.0	0.0	0.0	0.0
	SF [4]	85-97	0.2-0.9	0.4-2.0	0.3-0.5	0.0-1.0	0.5-1.3	0.0-0.4	0.0	0.1-0.4	0.0-1.4
MK	MK [6]	51.5	40.2	1.2	2.0	0.1	0.5	0.0	2.3	0.1	0.0
	MK [7]	52.17	44.5	0.45	0.01	0.0	0.15	0.0	1.42	0.0	0.12
	MK [8, 9, 10]	51.6	41.3	4.64	0.09	0.16	0.62	0.0	0.83	0.01	0.0
CW	CW [11, 12]	67.03	19.95	6.29	0.11	1.37	3.54	0	0	0.21	0
CDW	CDW [13, 14]	59.63	18.51	5.92	4.78	3.12	3.59	0.42	0.84	0.73	0.24
OMA	RHA [15]	82.13	4.27	0.38	0.16	1.65	1.23	0.0	1.23	0.14	1.44
	RHA [4]	87.0-87.3	0.1-0.8	0.1-0.8	0.5-1.4	0.3-0.6	2.4-3.7	0.0-0.3	0.0	0.1-1.1	1.8-5.2
	SCBA [16]	31.4-81.2	0.09-24.1	0.09-15.7	0.84-16.1	0.48-8.65	0.9-9.0	0.1-4.1	0.0	0.09-2.1	1.9-8.8
	SCBA [4]	78-78.4	8.6-8.9	3.5-3.6	2.1-2.2	0.0-1.7	3.4-3.5	0.0	0.0	0.0-0.1	1.2-3.0
	WA [17]	11.6	4.4	2.6	34.9	4.4	6.5	11.4	0.25	1.4	6.273
	WA [4]	1.9-68.2	0.12-15.1	0.37-9.6	5.8-83.5	1.1-14.6	2.2-32	0.36-11.7	0.06-1.2	0.22-29.8	0.66-13

[1] [24], [2] [25], [3] [32], [4] [29], [5] [34], [6] [52], [7] [53], [8] [54], [9] [55], [10] [56], [11] [57], [12] [58], [13] [59], [14] [9], [15] [60], [16] [61], [17] [62]

3.2 Artificial pozzolans

Artificial pozzolans are materials that have been produced or altered through an industrial process, and in many cases, they are the residue of production processes, for example, fly ash, obtained by burning coal [29]. Table 3 shows the chemical composition of some artificial pozzolans. Amongst these can be found, fly ash (FA), blast furnace slag (BFS), silica fume (SF), metakaolin (MK), ceramic waste (CW), construction and demolition waste (CDW), rice husk ash (RHA), sugarcane bagasse ash (SCBA) and wood ash (WA), and others [30]. Chemically, artificial pozzolans are mainly composed of aluminum, iron, and silicon oxides. In order to address the topic of artificial pozzolans as logically as possible, they will be divided into three groups; artificial pozzolans obtained from industrial processes, metakaolin, and pozzolans from calcination of organic matter.

3.2.1 Pozzolans obtained from industrial processes

Fly ash (FA): Fly ash is a by-product of the combustion of pulverized coal in power plants, generally thermal power plants. Coal combustion takes place at approximately 1500°C (2700°F), during combustion, the mineral impurities in the coal (clay, quartz, shale, and feldspar), melt and disperse with the exhaust gases. As the molten material rises with the gas flow, it cools and solidifies into spherical particles. This fine-grained material is collected by electrostatic precipitators or special filters [24]. Depending on its type and quality, fly ash contains different percentages of silicon, aluminum, iron, and calcium oxides. Table 3 shows the physical, mineralogical, and chemical properties of fly ash depend largely on the type, composition, and extent of pulverization of the coal, the combustion conditions, and the way it is collected, handled, and stored [25].

According to [40] fly ash can be divided into two classes, C and F. Class C fly ashes are generally produced from lignite or sub-bituminous coal. They are characterized by having between 10% and 15% calcium oxide in their chemical composition, this allows them to be hydraulic materials [25]. The crystalline phases of class C ashes include quartz, lime, mullite, gehlenite, anhydrite, tricalcium aluminate (C_3A), and dicalcium silicate (C_2S) [63]. Whereas, class F fly ashes, have a lower calcium oxide content, therefore they are considered pozzolanic materials. Generally, they result from the combustion of bituminous coal or anthracite. They have a high content of amorphous silica, which determines pozzolanic behavior. Among the crystalline minerals present in type F fly ash: are quartz, mullite, hematite, and magnetite [25]. Due to their chemical and mineralogical composition, fly ashes are widely used in cementitious mixtures.

As well as being an indicator for classifying fly ash, calcium content also effects several factors of cementitious mixtures; such as, fly ash reactivity, hardening rate, hydration evolution temperature, resistance at early ages, expansion due to alkali-silica reaction, and resistance to sulfates [64]. Nevertheless, other compounds such as alkalis (Na_2OyK_2O) and sulfate (SO_3), can affect the performance of fly ash. Fly ash particles are finer than those of Portland cement, their size ranges from 1 to 100 µm. The shape of the particles is predominantly spherical and some particles are massive. However, the vast majority are hollow [24]. Likewise, the color of fly ash depends on its chemical and mineral compounds. A dark brown color is associated with a higher amount of lime, a brownish color for those with higher iron content, and dark gray color for those with a high content of unburned coal [25].

Blast furnace slag (BFS): Blast furnace slag can be defined as a non-metallic product composed of calcium silicates and aluminosilicates; it is generated by the smelting of iron in the steelmaking process [65]. The melting of iron ore, coking coal, and limestone, at temperatures between 1300°C and 1600°C, produces pig iron and liquid slag. The slag, of lower density, floats, forming a layer on top of the pig iron. Depending on the cooling method, three types of slag can be obtained: granulated slag, air-cooled slag, and expanded slag. Granulated blast furnace slag is obtained by rapidly cooling the liquid slag using high-pressure water streams. The granular particles formed are glassy and usually have a particle size of less than 5mm. After being dried and ground, they are used as cement replacements in proportions between 30% and 85% [29, 64, 66].

When cooling of the molten slag occurs under atmospheric conditions, air-cooled slag is formed, which has a crystalline structure similar to that of rock. These slags are characterized by being hard and dense materials. They are used mainly as ballast in railways, as a roadbed stabilizer, and as aggregate in concrete [32]. However, expanded slag is produced using small amounts of water for refrigeration. The material obtained is dry, porous, rough, and light. It is usually used in lightweight building blocks, in the manufacture of bricks, and also as an aggregate in lightweight concrete mixtures [66]. The chemical compounds are quite similar in various types of slag. Table 3 indicates that some of these compounds are oxides of silicon, aluminum, lime, iron, and magnesium. Similarly, some minerals present in slags are melilite, merwinite, diopside, limestone, wustite, ferrite, monticellite, rankinite, and ancinamite [33].

Slags can also be classified by size and can be divided into fine and coarse slag. Finely granulated slag is amorphous and has the approximate size of coarse sand (11.5 mm). When finely ground, it exhibits hydraulic properties similar to cement. The particles can have subangular to sub rounded shapes [66] and have a pale white color. The specific surface area ranges from 400 to 600 m^2/kg [33]. Whilst, coarse granulated slag is pellet-shaped. Slags with sizes ranging from 4 to 15 mm are porous and partially crystalline and have been used as coarse aggregate in concrete. Coarse slag with sizes smaller than 4 mm are mostly glassy and are usually ground up for use as a hydraulic binder in Portland cement clinker [67].

Silica Fume (SF): silica fume, or microsilica, is created as a by-product of the smelting of silicon metal and ferrosilicon alloys used in the production of steel and aluminum [34]. Raw materials (quartz and carbon), are arranged in an electric-arc furnace and are melted at a temperature close to 2000°C. As the quartz is reduced to alloy, silicon monoxide vapor emanates. At the top of the furnace, this vapor is oxidized and condensed into amorphous silicon microspheres. This resulting fine powder is collected in bag filters and is packaged for further distribution [29]. The color of silica fume can be white, gray, or black. The color depends on the amount of carbon present in the production process [35].

Silica fume particles are spherical with a particle size of less than 1 µm and compared to Portland cement particles, they are approximately 100 times finer. Because of this, the density of silica fume is lower compared to cement, making it lighter. Moreover, the specific surface area of silica fume is between 15000 m^2/kg and 30000 m^2/kg, which is higher than Portland cement, resulting in a higher pozzolanic behavior. The mineralogical composition of silica fume consists mainly of amorphous silica (cristobalite), with very few crystalline particles [35]. Similarly, Table 3 shows that the chemical composition is of at least 85% silicon oxide, including small amounts of iron oxides, aluminum oxide, and alkalis [29].

Metakaolin (MK): clay is a clastic sedimentary rock, originating from the mechanical accumulation of rock fragments comprising clay minerals and quartz. Clay minerals are crystalline elements and are included in the phyllosilicates group due to their foliated form. Metakaolin is formed of silica and alumina and depending on the percentage of these compounds, it can present different colors, such as white, gray, brown, orange, or red. The minerals with the highest presence in clay are kaolinite, montmorillonite, illite, vermiculite, talc, and pyrophyllite [68]. Kaolinite is the main mineral present in clay, and when mixed with water, provides the characteristic plastic state of unfired ceramics. Structurally, kaolinite consists of octahedral alumina lamellae and tetrahedral silica lamellae stacked in interleaved form. [52].

When kaolinite is exposed to a temperature between 650°C and 900°C for a controlled time, its structure becomes disordered and collapses; this is due to de-hydroxylation, which is the elimination of the water ions that are present in the kaolinite. The resulting disorder, between the silica and alumina layers, produces a material called metakaolin [69]. This material is characterized as being amorphous and as having high pozzolanic and hydraulic reactivity [70]. In addition, metakaolin, whose chemical formula can be written as $Al_2O_3.2SiO_2$ or AS_2, differs from other pozzolans because it is neither completely natural nor the result of industrial processes. Although calcination is performed in rotary kilns or muffle kilns, the energy consumption of metakaolin production is much lower compared to that of cement production. [71].

The particle size of metakaolin is commonly 2 mm (smaller than cement particles). Metakaolin is white and, because of its controlled production process, it is a consistent material both aesthetically and operationally. The particle shape is layered and its specific area is 15000 m^2/kg [53]. Metakaolin has a high a content of silicon oxide (50%-55%) and aluminum oxide (40%-45%). Also, small amounts of other chemical compounds are present (Table 3). Mineralogically, metakaolin is composed of quartz, feldspar, mica, and calcite. The percentages of these minerals depend on the characteristics of the calcined kaolin [70].

Ceramic waste (CW) and construction and demolition waste (CDW): these wastes come from the construction and demolition of buildings and have been used as a replacement for cement, given that the particle size distribution of ceramic wastes is similar to cement. The color of ceramic wastes is gray or white [72]. The specific gravity is between 2.3 and 2.8. Ceramic waste can be substituted for cement and aggregates in cementitious mixtures. Its main compounds are silica, alumina, and iron oxide. Mineralogically, ceramic wastes are composed of quartz, hematite, muscovite, and microcline; in addition, the content of amorphous material is approximately 38% [73].

Construction and demolition waste (CDW) consists of waste generated from the construction, reconstruction, expansion, alteration, maintenance, and demolition of buildings and other infrastructure, in order for this waste to be used in cement mixtures their particle size must be reduced. Therefore, reducing the particles sizes of under 63 μm to be used as a cement substitute material is recommended. The mineralogical content of CDW is composed of illite, quartz, orthoclase, anorthite, calcite, dolomite, and hematite. Silicon oxide is the major component (75%), followed by alumina and iron oxide [74].

3.3 Pozzolans from organic matter (OMA)

About one billion tons of agricultural wastes are produced every year, approximately 80% of which are of organic origin [75]. Due to the low price of these residues, their economic value is lower than the cost of their collection, transportation, and processing. However, when these wastes are used in incineration, they become valuable materials. The incineration of agricultural residues to generate energy is called gasification. This process is carried out in a closed chamber and, as a by-product of the process, ash is generated [76]. Some of the wastes used are rice and rice husks, sugarcane bagasse, and wood sawdust. They are characterized by low inorganic content and high carbon content [77]. The composition of the ashes produced, as well as their origin, depends on the temperature and duration of incineration and accordingly they l have unique properties and applications.

Rice husk ash (RHA): Rice husk makes up about 20% of rice weight, in terms of production, is about 120 million tons annually. Its chemical composition consists mainly of cellulose (50%), lignin (25%-30%), silica (15%-20%) and water (10%-15%). In some regions, rice husk is used as fuel; and, although its incineration is neither complete nor controlled, its calorific value is half that offered by coal [78]. Large volumes of ash are generated as a result of calcination. It is estimated that, for every 100 kg of calcined husk, 25 kg of ash are produced. If the burning of rice husk is controlled, organic matter is removed and the resulting ash is composed of amorphous silica with a microporous structure, hence, the ash has high water absorption [60].

Rice husk ash is a fine material, with a specific surface area ranging from 20000 m^2/kg y 270000 m^2/kg. At the same time, the particle size ranges between 5 and 10 µm [29]. Because of this, ashes obtained by controlled processes have high pozzolanic activity. The color of the ashes obtained typically varies from gray to white. Likewise, their specific gravity varies between 2 and 2.1. whereas, the chemical composition depends on the temperature at which the ashes are calcined. It is recommended that rice husks be incinerated between 600°C and 700°C, to obtain ashes with better pozzolanity [60]. Table 3, shows the percentages of the most representative compounds. It can be observed that more than 80% of the ash is silicon oxide, as a result of the nutrients absorbed during the growth of the rice plant.

Sugarcane bagasse ash (SCBA): sugarcane is the largest crop by production quantity worldwide. As well, it is the raw material to produce sugar, bioethanol, some liquors, and brown sugar [61]. When juice is extracted from sugarcane, a large amount of wet bagasse is produced; approximately 30% to 40% by weight of collected sugarcane. The bagasse obtained, has a chemical composition consisting of; cellulose (45%-55%), hemicellulose (20-25%), lignin (18-24%), and ash (1%-4%) [79]. Sugarcane bagasse is used in the sugar process for the production of heat energy through combustion. As a result of this process, it generates ashes that are characterized by having a high silica content and an amorphous structure, which makes them highly pozzolanic materials. These ashes are characterized by their high silica content and amorphous structure, which makes them highly pozzolanic materials. The properties acquired by the ashes depend on the origin and processing, temperature, and time of incineration [80].

Recently calcined bagasse ash samples are comprised of different kinds of particles. The vast majority are completely burned fine particles; the rest are fibrous particles that have not been completely calcined. As a result, the ash is of low pozzolanity. Therefore, to increase its reactivity it is recommended to pass it through a 300 µm sieve and grind it to a fineness similar to that of cement (300-320 m^2/kg) [81]. In a controlled incineration process, reactive amorphous silica is formed as the main compound. Table 3, shows the various chemical compounds formed at different temperatures, which varies from 550°C to 1000°C [79]. It can be observed that the compound with the highest percentage is silicon oxide, followed by aluminum and calcium oxide. Similarly, minerals with high silica content can be found, such as quartz and cristobalite.

Wood ash (WA): is an inorganic residue generated by the combustion of wood (sawdust, bark, branches, and others), mainly to produce electricity. The temperature at which wood is calcined varies between 400°C and 1100°C. The most common trees, from which this wood used in power plants, comes from are pine and eucalyptus. Hardwood, bark, and leaves also produce a large amount of ash; on average, between 6% and 10% are recovered [82]. Furthermore, 70% of wood ash ends up as landfill waste, 20% is used as a supplement in agricultural crops, and 10% is used in construction, metal recovery, and pollution control. As always, the physical, and chemical properties of wood ash determine its application. Some factors that influence these properties are tree species, geographic location, growing conditions, and method of incineration, and the way the ash is collected [83].

Newly calcined wood ash is a heterogeneous mixture of particles of different shapes and sizes. Generally, at temperatures between 400°C and 600°C, calcination is not complete, so that partially burned wood particles appear. In addition, average particle size is 230 µm, whilst specific gravity ranges between 1.65 and 2.6, and density, between 490 kg/m^3 and 827 kg/m^3 [84]. Ash color, varies between black, brown, and gray. The chemical composition of wood ash is shown in Table 3. It is observed that the major components are oxides that must be present in a pozzolanic material. In the same way, the predominant crystalline form in this type of ash is quartz. Minerals such as calcite, rutile, mullite, gypsum, magnetite, among others, can also be found [62]. The presence of these minerals depends, to a great extent, on the nutrients absorbed during the growth of the tree.

Activated paper sludge (APS): is generated by the paper industry using recycled paper as raw material. When dry this sludge (35%-40% humidity) is composed of 30% organic matter, 35% calcite, and 20% kaolinite. To activate this residue and eliminate all the organic matter (80-90% reduction), it is necessary to calcine it at a temperature between 650°C and 700°C for two hours [85]. The product obtained has particles smaller than 90 mm with a brightness of more than 90%. The chemical composition of this activated sludge depends on the activation conditions, the nature of the recycled paper, and its chemical composition. This waste constitutes an alternative source of metakaolinite and is mainly composed of 30% silica, 30% lime, 18% alumina, and <5% magnesium [86].

4. Uses of pozzolans in cement blends

Some research into the uses of natural pozzolans in construction materials is mentioned below. [87] investigated the effects of volcanic ash on cement mortar. Mortar cubes (40×40×40 mm^3) with a binder/sand to water proportion of 1/3/0.5 by weight were prepared. The percentages of cement replacement levels by weight were 30% and 50% for volcanic ash, whilst the compressive strength of the samples was determined on three mortar prisms during 1, 3, 7, 14, 28, and 91 days. The reported strength results were the average of three mortar specimens. Volcanic ash reduced the mortars' ultimate compressive strengths but at a proportion lower than their replacement levels, signifying their participatory and influencing roles in hydration reactions. Similar research includes [42, 88].

In addition to natural pozzolans, artificial pozzolans have been used in construction materials. Fly ash, has been a highly implemented pozzolanic material. [89, 90] prepared three cylindrical samples of 100x200 mm to measure compressive strength. The compressive strength of the samples was determined at 3, 7, 28, and 91 days. The water/binder ratio for all mixes was 0.30. In the mixes, the cement content was replaced by 10%, 30%, 50% and 70% fly ash (by mass). It was found that the early compressive strength of the modified concrete was lower for all mixes than in the control concrete and that it generally decreased with the increase in the amount of fly ash. Similar research includes [24, 25].

Blast furnace slag is another pozzolanic material used in construction materials. [91] prepared three mortar cubic samples these were used for each age and curing condition. The dimension of the cubic samples was 70.6 mm×70.6 mm×70.6 mm the compressive strength was determined at 7, 14, 28, 90, 180, and 270 days. The binder/sand ratio was fixed at a 1/1 ratio. BFS was increased from 30% to 60% of total cement by weight with increments of 10%. A noticeable reduction in compressive strength was observed at all ages as the content of BFS reached 60%; thus, the maximum use of BFS is recommended to be 50% or less to achieve the best long-term compressive strength development of the mixture. Similar studies include [66, 67].

In similar tests, [92] designed two concrete mixes of M40 and M50 grades, with a w/c ratio of 0.36 and 0.33 respectively. In both cases, the cement was replaced with SF at increments of 5%, 7.5%, 10%, and 15%. Samples of standard cubes (150×150×150 mm) and standard cylinders (150 mm diameter×300 mm height) were used. A compression testing machine (CTM) was used to test 28-day compressive strength. The compressive strength of the two mixes, M40 and M50, with SF replacement, was increased gradually up to an optimum replacement level of 7.5% and then decreased over 28 days. Similar research includes [34, 93].

Additionally, [94] prepared cubic samples of 100 mm×100 mm×100 mm to measure compressive strength. A water/binder ratio of 4.0 and a sand ratio of 0.44 were selected. Two substitution rates of metakaolin (9% and 15% by mass) were used. The compressive strength was determined at 1, 3, 7, 28, and 90 days. The results showed that compressive strength increased as the metakaolin increased. Adding 15% metakaolin increased the compressive strength at 28 days by approximately 24%. Whereas, [95] showed that the high specific surface area and high reactivity of metakaolin decreased the workability of the mixture. However, the fineness of metakaolin decreased the porosity and obtained a more permeable concrete with higher resistance to acid attack. In addition, the compressive strength increased with the addition of metakaolin. However, the authors recommended adding up to 20% metakaolin by weight to the mix; thus, the compressive strength would be higher than the control sample. Similar research includes [54-56].

Likewise, [96] prepared samples with ordinary Portland cement, coarse sand, and crushed stone using three different w/c ratios (0.40, 0.50, and 0.60). To analyze the strength variation of concrete using RHA as partial replacement of cement specimens with 10% and 15%, RHA of the total cement content by weight was used. Specimens for the compressive strength test were cast using cylindrical molds of 100 mm diameter and 200 mm height. Tests were conducted after 7, 14, and 28 days of curing. Results showed that the increasing percentage of RHA, as a replacement of cement, caused a decrease in compressive strength. Replacement of 10% cement by RHA is optimum and considerable with respect to the compressive strength of concrete. The replacement of cement by RHA up to 15% caused a decrease in compressive strength of 10-12% on average. Similar studies include [97, 98].

Sugarcane bagasse ash (SCBA) is another type of agro-industrial waste used in the production of construction materials. [99] used a design mix for M20 grade concrete, based on the standards, castings of cubes were made with different ratios (5%, 10%, and 15%) and were tested at 7 and 28 days of curing. It was found that SCBA concrete provided more compressive strength than normal concrete. The maximum compressive strength obtained in M20 grade concrete was obtained with the addition of 10% SCBA. The compressive strength of 10% replacement of sugarcane bagasse gave improved strength when compared with 5% and 15%. Similar studies include [29, 100].

In addition, [101] replaced cement in mortar mixes with wood ash at 5%, 10%, and 15% by volume. A volumetric ratio of 1:4 (binder: aggregates) was chosen. Prismatic specimens (40×40×160 mm^3) were used to perform the mechanical behavior tests. The compressive strength was determined at 7, 28, 90, 180, 365, and 730 days. Mortar with 5% WA content presented an increment in compressive strength which was only discernible between 28 and 180 days. The remaining mortars presented a lower compressive strength than those of the reference mortar. In addition, at 730 days, the reduction of compressive strength was greater, between 29% and 45%. In fact, the incorporation of WA, decreased this strength when compared to a reference mortar. Similar research includes [82, 83]. Table 4 summarizes the highlights of pozzolans in cement blends.

Table 4 Summary of pozzolans in cement blends.

Pozzolan	High lights
Volcanic ash	The incorporation of volcanic slag in mortar and concrete increases properties such as durability, chloride permeability, and compressive strength. These properties increase with the age of curing and decrease with the content of volcanic slag in the mixture. This decrease is caused by the fact that pozzolanic reactions are retarded at room temperature [42, 87, 88].
Fly ash	Addition of fly ash in concrete improves workability, reduces runoff and linear shrinkage, decreases the amount of air in the mixture and the heat of hydration. Also, compressive strength increases with the age of curing [24, 25, 89, 90].
Blast furnace slag	Increases the compressive and flexural strength at mature ages. This depends to a large extent, on the fineness and percentages used in the mix. Also, the porosity decreases, increasing the resistance to sulfate attack and improving durability. Blast furnace slag decreases the heat of hydration but increases the bulk density [66, 67, 91].
Silica fume	Increases the compressive strength at mature ages, acid attack resistance, density, and durability of concrete [34, 92, 93].
Metakaolin	The recommended level of metakaolin as a cement substitute in concrete is between 10% and 20%. Within these percentages, higher flexural and compressive strengths in the mix are achieved. Similarly, the addition of metakaolin to this pozzolan reduces autogenous shrinkage and increases sulfate resistance and heat of hydration [54-56, 94, 95].
Rice husk ash	Improves compressive, tensile, and flexural strength. Moreover, rice husk ash reduces autogenous shrinkage. It also decreases the diffusion of acids in the mixture. The authors recommend a 20% substitution of cement for better results [96-98].
Sugarcane bagasse ash	Increases compressive strength at mature ages reduces permeability and increases resistance to acid attack. However, it has not yet been established how it affects concrete durability [29, 99, 100].
Wood ash	Workability and bulk density were not affected by this substitution. However, the mechanical performance was reduced by up to 45% compared to the reference samples. However, cement can be substituted with wood ash, up to 15%, without affecting the performance of mortars [82, 83, 101].

5. Conclusions

The conclusions that may be drawn from the present paper are set out below:

Compressive strength at early ages of concrete containing pozzolans is lower than the compressive strength of the reference concrete. Only metakaolin increase the early age compressive strength. However, all pozzolans increase their compressive strength at mature ages.

For optimum concrete performance, the percentage of cement substitution depends on the type of pozzolan. For example, the recommended level of metakaolin is between 10% and 20%, the suggested percentage of rice husk ash is 20%, the recommended level of blast furnace slag should not exceed 50%, and the suggested percentage of wood ash should not exceed 15%.

Pozzolans decrease absorption and permeability by reducing the porosity of the binder. This increases resistance to acid attack, reduces autogenous and linear shrinkage, and improves concrete durability.

6. Future works

The properties of concrete mixtures can be estimated by laboratory experiments. However, these tests are expensive, imprecise, and time-consuming. Besides, finding the best mix design and the exact quantity of materials is complicated. In order to improve mixtures, future work using artificial intelligence (AI) techniques and machine learning algorithms is suggested, as their capabilities for knowledge processing and pattern recognition are among the best methods for solving engineering problems.

As an example, [102] reviewed the available studies on the application of AI techniques to model the behavior of concrete elements and estimate the properties of concrete mixtures. Also, that paper provided recommendations on the selection of the appropriate input variables for developing the predictive models. In addition, two types of hybridized machine learning algorithms (Type-1) fuzzy inference system (T1FIS) and interval type-2 fuzzy inference system (IT2FIS) were used to develop predictive models for the compressive strength of recycled aggregate concrete [103]. The findings indicated that the importance of the variables, concrete age, total coarse aggregate to cement ratio, and water to binder ratio were of the first to third orders, respectively. It is hoped that this present review will provide the stimulus for further investigation.

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