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Alkali-Activated Hybrid Concrete Based on Fly Ash and Its Application in the Production of High-Class Structural Blocks

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Received: 1 October 2020; Accepted: 13 October 2020; Published: 17 October 2020

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Abstract: This article reports the production and characterization of a hybrid concrete based on the alkaline activation of a fly ash (FA) of Colombian origin, which was added with 10% Portland cement (OPC) in order to promote the compressive strength development at room temperature. The alkali-activated hybrid cement FA/OPC 90/10 was classified as a low heat reaction cement (type LH), according to American Society of Testing Materials, ASTM C1157; the compressive strength was of 31.56 MPa and of 22.68 MPa (28 days) at the levels of paste and standard mortar, respectively, with an initial setting time of 93.3 min. From this binder, a hybrid concrete was produced and classified as a structural type, with a compressive strength of 23.16 MPa and a flexural modulus of rupture of 5.32 MPa, at 28 days of curing. The global warming potential index (GWP 100), based on life cycle analysis, was 35% lower than the reference concrete based on 100% OPC. Finally, its use was validated in the manufacture of a solid block-type construction element, which reached a compressive strength of 21.9 MPa at 28 days, exceeding by 40.6% the minimum strength value established by the Colombia Technical Standard, NTC 4026 (13 MPa) to be classified as high class structural blocks.

Keywords: alkali-activated materials; geopolymers; hybrid cements; fly ash; concrete; structural blocks

1. Introduction

Alkali-activated materials (AAM) are obtained from chemical interaction between an aluminosilicate material (precursor), and a strongly alkaline solution. AAMs are produced at relatively low temperatures (25–90 °C) compared to the temperatures used in the clinkerization process (~1450 °C) of Portland cement (OPC), cementing material most used worldwide and responsible for 5–7% of greenhouse gases emitted into the atmosphere. One of the most commonly used precursors in obtaining AAM is fly ash (FA). FA is an industrial by-product, and its management and final disposal represents a major environmental problem for plants that use coal combustion as their main source of energy [1]. The large production volumes of FA (500–700 Mt/year in the world [2] and 600 Kt/year in Colombia) and its very limited (or null) use in Colombia, lead to its accumulation within these industries. This is generating an important environmental liability and the use of production spaces that translate into high storage costs for these industries. The use of FA in producing new materials through emerging technologies, such as alkaline activation or "geopolymerization", is therefore encouraged, as one of the most sustainable alternatives worldwide.

The industrial and technological difficulties that arise, however, in the synthesis and production of AAM are considered as barriers to achieving their introduction to the market as a possible replacement for OPC in some applications [3]. Particularly at the technological level, the need for heat treatments for the synthesis of AAM (low in calcium) makes their application on a large scale difficult [4]. Therefore, in the synthesis of AAM, sources of calcium have been introduced in small percentages (≤30%) that promote the formation of hybrid gels at room temperature, giving rise to materials that are known as hybrid cements [5].

In the case of hybrid FA–based cements, generally of high FA content (70–90%) and low OPC content (10–30%) [6], the clinker reaction products and reaction products from the glass phases of FA coexist [7]. As the curing time progresses, the Ca^{2+} and $Al(OH)^{4-}$ ions present in the aqueous solution begin to diffuse into the matrix structure. A small amount of Ca^{2+} ions that are not included in the calcium silicate hydrate gels (C-S-H) interact with sodium aluminosilicate hydrate (N-A-S-H) gels, leading to the formation of (N,C)-A-S-H type gels, called "hybrid gels". Simultaneously, the C-S-H type gels interact with $Al(OH)^{4-}$ ions, giving rise to aluminum-modified calcium silicate hydrate (C-A-S-H type) gels [8]. These gels, in combination, densify the cementitious matrix and are responsible for the mechanical performance of this type of material [9].

Most studies on hybrid materials have focused on the synthesis of binders (pastes), without going beyond the level of mortars and concretes on many occasions. This reveals the need to strengthen and validate research in these types of applications used mainly in the construction sector. With the incorporation of a source of calcium between 10–30% in FA–based AAM (≥70%), they have succeeded in replacing thermal curing processes [10], even achieving strengths of up to 55 MPa at 28 days of curing, at the concrete level [11]. At the paste level and at prolonged ages, 37% increases in compressive strength have been reported from 28 to 90 days, going from 40 to 55 MPa, respectively [12]. The sources of calcium that have been used successfully in these researches are blast furnace steel slag (GBFS) and OPC. This type of hybrid cements has also been characterized by releasing less heat of reaction compared to OPC, due to the nature of the reactions and the low levels (≤30%) of OPC dosing in these mixtures [7,13]. Setting time has been another property of interest in hybrid cements, since results very similar to those of OPC have been achieved—for example, initial setting times between 87 and 290 min for additions of 10% OPC and GBFS, respectively, with a tendency to decrease with addition contents greater than 10% [14]. The aforementioned results have been obtained with F-type ash (low in calcium) of variable origin and quality and activated with different solutions ($NaOH + Na_2SiO_3$ or Na_2SO_4).

The purpose of this article is to obtain and characterize a hybrid concrete based (90%) on the alkaline activation of FA (type F) of Colombian origin, supplemented with 10% (by weight) of OPC. Concrete production was based on the development and characterization of a hybrid cement, whose composition and synthesis were optimized by varying the content of alkaline activator ($NaOH + Na_2SiO_3$). The hybrid cement was characterized by evaluating its compressive strength and studying the reaction kinetics by determining the evolution and total heat of reaction, and the setting time. Using this cement, a hybrid concrete was designed and produced, which was characterized based on its physical-mechanical (compressive strength, flexural strength, density, absorption, and porosity) and microstructural properties (by scanning electron microscopy). Additionally, a preliminary analysis of its carbon footprint was carried out, determining the global warming potential (GWP) (LCA, life cycle analysis). Finally, to validate its application in the construction sector, solid hybrid concrete blocks were manufactured and characterized, which demonstrated the application potential of the developed material by complying with the standard specifications.

2. Materials and Methods

2.1. Materials

As a precursor of the hybrid cement, a mixture of 90% (by weight) of fly ash (FA) class F (ASTM C618), a by-product of an industry from the region (Cali, Colombia), and 10% of OPC type UG (General Use) was used—according to ASTM C1157, equivalent to NTC 121 in Colombia). The FA was ground in a ball mill for four hours in order to obtain a particle size similar to that of OPC (21.65 μm) to increase its reactivity. The mean particle size obtained by laser granulometry was 24.89 µm (Figure 1). Table 1 presents the chemical composition obtained from X-ray fluorescence (XRF) and loss on ignition (ASTM C140).

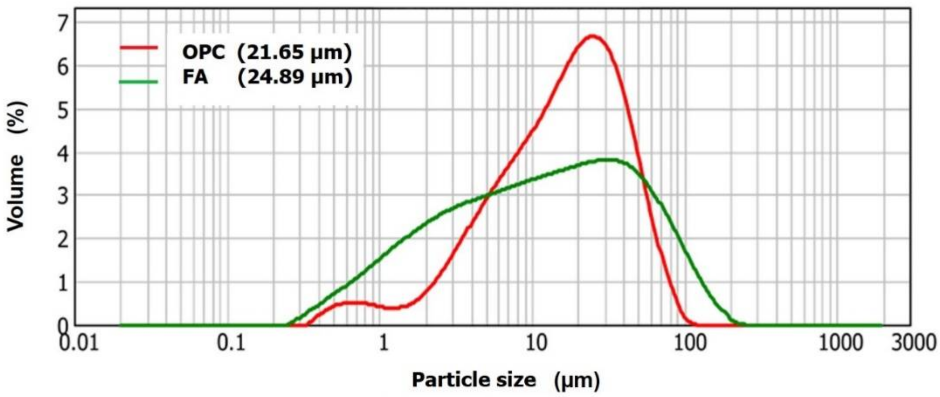

Figure 1. Particle size distribution curve of the fly ash (FA) and Portland cement (OPC).

Table 1. Chemical composition of the raw materials (%).

Material	SiO_2	Al_2O_3	Fe_2O_3	K_2O	CaO	SO_3	MgO	Na_2O	Others	LOI [1]	SiO_2/Al_2O_3 (Molar)
FA	59.03	23.97	5.98	1.21	0.74	0.55	0.31	0.19	1.66	6.35	4.19
OPC	17.99	3.88	4.76	0.32	62.28	4.03	1.71	0.23	0.66	4.14	-

[1] LOI: Loss on ignition.

Figure 2 shows the X-ray diffraction (XRD) pattern for the FA, where three main mineralogical compounds are observed—quartz (silica oxide), mullite (silica-aluminate), and hematite (iron oxide), whose composition is complemented and corroborated by the XRF results. Additionally, the pozzolanic activity of the FA was evaluated using the Frattini chemical test (NTC 1512 equivalent to International Organization for Standardization, ISO 863-2008; the results obtained were 14.2 millimoles of CaO/L and 47.5 millimoles of OH^- at 7 days and 10.7 millimoles of CaO/lt and 45.6 millimoles of OH^- at 28 days. These results do not permit FA to be classified as a pozzolanic addition. However, the mechanical test (ASTM C311) reported a strength activity index with Portland cement of 94.26% and 100% at 7 and 28 days, respectively, values that exceed the lower limit (75%) established by ASTM C618 to classify an addition as reactive (pozzolanic). The density of the FA, determined according to the procedure established by ASTM C329, was 2396 kg/m^3.

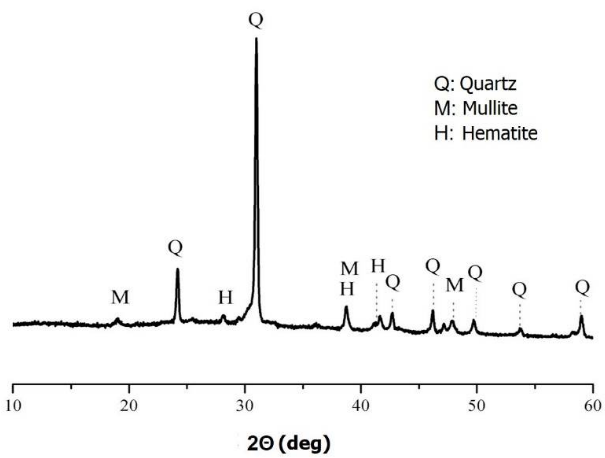

Figure 2. X-ray diffraction (XRD) of the FA.

As alkaline activator, a solution composed of sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_3) (32.09% SiO_2, 11.92% Na_2O and 55.99% H_2O), both of industrial grade, was used. Natural aggregates were used in the production of the concrete and the mortar: crushed gravel of maximum size 19 mm and siliceous sand with a fineness modulus of 2.6.

2.2. Methodology

2.2.1. Design and Obtaining of Mixtures

The hybrid cement was obtained by defining a response surface methodology (RSM) type experiment design using the Minitab 15 software, in which a total of 15 mixtures were fixed, varying the SiO_2/Al_2O_3 (Si/Al) and Na_2O/SiO_2 (Na/Si) molar ratios in the ranges of 4.0–5.5 and 0.05–0.35, respectively. Compressive strength was defined as response variable. Additionally, workability and setting time were taken into account. The liquid/solid (L/S) ratio was kept constant at 0.30 for all pastes.

The pastes were produced in a Hobart mixer with a total mixing time of 5 min. They were subsequently molded into 20 mm cubes on each side, which were vibrated for 30 seconds to remove the air naturally trapped during mixing. The specimens were cured in a humid chamber at room temperature (25 °C) and relative humidity greater than 90%, to then be tested at 7 and 28 days.

Once the hybrid cement was optimized, the reaction kinetics were studied by means of isothermal calorimetry and setting time tests. For the calorimetry, three mixtures were made: (1) standard mixture (100% OPC); (2) mixture (90% FA + 10% OPC) + activator (NaOH + Na_2SiO_3); and (3) mixture (90% FA + 10% OPC) + water. To study the effect of the inclusion of OPC on setting time, the Vicat test was carried out according to ASTM C191 for mixtures with 5, 10, and 20% addition of OPC. Additionally, pastes (optimal activator content) were prepared with 5 and 10% OPC to evaluate the effect of the OPC content on the evolution of compressive strength at ages 1, 3, 7, 14, 28, and 90 days.

Subsequently, three mortar mixes were produced to evaluate the effect of the incorporation of the fine aggregate, i.e., to verify that the hybrid cement fulfills the function of binder. In the mixtures, the precursor:sand ratio (by weight) varied, at 1:1, 1:2, and 1:2.75. These mixtures were molded into cubes of 50 mm on each side, according to the procedure described in ASTM C305, and compression tested at 7 and 28 days of curing. Curing of the specimens was carried out in a humid chamber at room temperature (25 °C).

Finally, based on the definition and characterization of the optimal hybrid cement, three concrete mixes were made. For these, the effect of precursor content (FA + OPC) was evaluated at 300, 400, and 500 kg/m^3 in order to obtain a minimum compressive strength of 21 MPa after 28 days of curing. It should be noted that according to American Concrete Institute, ACI 318, a concrete is classified as structural if the compressive strength is >17.5 MPa. Taking workability and compressive strength into account, a content of 400 kg/m^3 of cementitious material was selected for the final design. The dosage of the mixture was carried out by adapting the "absolute volume method" proposed in ACI 211.1, considering the density of all the materials in the mixture, including the alkaline activator. The optimal granulometric combination, calculated by the Fuller-Thompson method, was 45% sand and 55% gravel (% by weight). The L/S ratio of the concrete was 0.33. Table 2 presents the dry weight dosage of the hybrid concrete.

The concrete mixes were obtained in a CreteAngle horizontal mixer with a mixing time of approximately 7 min. First, the aggregates were homogenized and presaturated. The hybrid cement (previously prepared) was then incorporated. The mixtures were molded in cylinders and beams on a vibrating table following the procedure of the ASTM C192 standard. Curing of the specimens was carried out in a humid chamber at room temperature (25 °C).

The hybrid concrete was characterized by tests of compressive strength (7, 28, and 90 days), density, absorption and porosity (28 days) and scanning electron microscopy (28 days). Additionally, solid concrete blocks measuring 80 mm × 100 mm × 200 mm (height × width × length) were manufactured and characterized. All the results of the physical-mechanical characterization represent the average of three specimens tested.

Table 2. Dry dosage per cubic meter of concrete (1 m^3).

Material	Dry Weight (kg)	Density (kg/m^3)	Volume (m^3)
FA	360.0	2395.8	0.150
OPC	40.0	3100.0	0.0120
Activator *	288.8	1407.4	0.205
Sand	722.6	2570.0	0.281
Gravel	883.2	2520.0	0.350
Total	2294.6		1.000

* Activator: NaOH + Na_2SiO_3 + mixing water.

2.2.2. Instrumental Techniques

- Chemical composition. It was determined by X-ray fluorescence (XRF) using a Phillips PANalytical MagiX PRO PW 2440 spectrometer (Tollerton, United Kingdom) equipped with a rhodium tube, whose maximum power is 4 kW.
- Particle size and distribution. These properties were evaluated by the Laser Granulometry technique (ISO 13320 standard) in a Mastersizer 2000 (Malvern Instrument, UK) equipment coupled to a Hydro 2000MU dispersion unit, using distilled water as dispersion medium.
- Mineralogical and morphological characteristics. X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques were used. XRD and SEM were performed on a PANalytical X'Pert MRD X-ray diffractometer with Cu k-α radiation, where the diffraction angle 2θ was varied between 10 and 60° with increments of 0.020°, and a JEOL JSM-6490LV microscope with an acceleration voltage of 20 kV. The specimens were examined in low vacuum mode. An Oxford Instruments INCAPentaFETx3 X-ray spectrometer (energy-dispersive X-ray spectroscopy, EDS) was attached to the microscope. For the SEM test on the samples of 90% FA–10% OPC concrete after 28 days of curing, a 1 cm^3 sample was extracted from the concrete, which was subsequently encapsulated in epoxy resin and finally the observation surface was polished. DRX information processing was performed using the X´pert HighScore Plus software package, version 2.2.5.
- Heat of reaction and setting time of the pastes. The heat of reaction and heat evolution were evaluated using an I-Cal 8000 isothermal calorimeter (Calmetrix) at a temperature of 25 °C (ASTM C1702), and the setting time was determined with a Vicat apparatus (Humboldt) following the procedure of ASTM C191 (method B).
- The physical properties of density, absorption and porosity of the hybrid concrete and the solid concrete blocks were determined according to the ASTM C642 standard.
- Mechanical properties. The compressive strength of each paste was measured using an INSTRON 3369 universal machine (50 kN capacity) at a test speed of 1 mm/min. The compressive strengths of the mortars (ASTM C109), hybrid concrete (ASTM C39) and solid concrete blocks (ASTM C140) were determined in an ELE International hydraulic press, with 1000 kN capacity. The diameter of the concrete cylinders was 76.2 mm and the dimension (height × width × length) of the solid blocks was 80 mm × 100 mm × 200 mm. The flexural strength or modulus of rupture of the hybrid concrete was determined by a 3-bearing flexural test (ASTM C293) using beams of 300 mm × 75 mm × 75 mm (length × width × height). This test was carried out on a Tinius Olsen H50KS universal machine with a capacity of 50 kN at a loading speed of 1 mm/min.

3. Results and Analysis

3.1. Characterization of Hybrid Cement

3.1.1. Optimization of Alkaline Activator Content

Figures 3 and 4 show the effect of the Si/Al and Na/Si molar ratios on the compressive strength of the hybrid cement (paste) at 7 and 28 days of curing, respectively. In agreement with Rangan [15] and He et al. [16], the results demonstrate how the presence of sodium silicate promotes the development of mechanical strength, due to the increase in the species of soluble silica (Si-O) provided by the activator, which create the appropriate conditions for the development of a more resistant structure, improving the interface between the reaction products. The highest strengths were obtained for the mixtures with a low content of sodium hydroxide (NaOH) and a high content of sodium silicate (Na_2SiO_3), i.e., Na/Si and Si/Al ratios of 0.10–0.15 and 5.12–5.5, respectively. The optimum paste was selected using the Minitab 15 statistical program, resulting in values of 0.14 for Na/Si and 5.5 for Si/Al, with compressive strengths of 20.60 and 31.54 MPa at 7 and 28 days of curing, respectively.

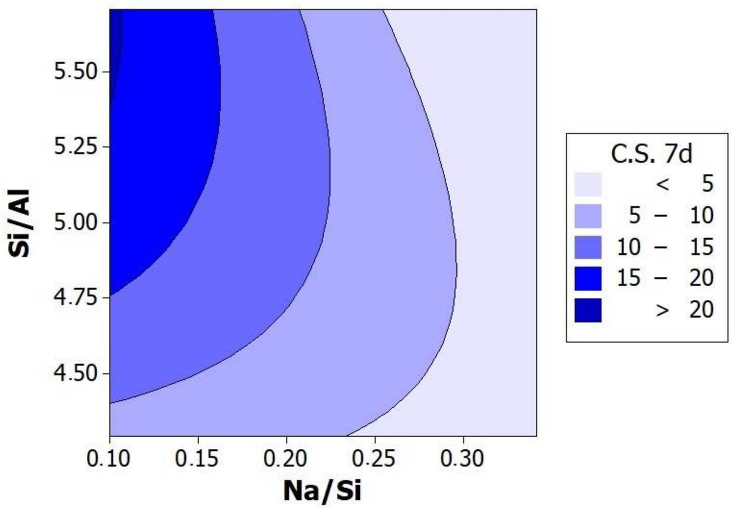

Figure 3. Effect of the molar ratios of Na/Si and Si/Al on the compressive strength (C.S.) of hybrid cement (paste) after 7 days of curing: the contours represent the strength levels.

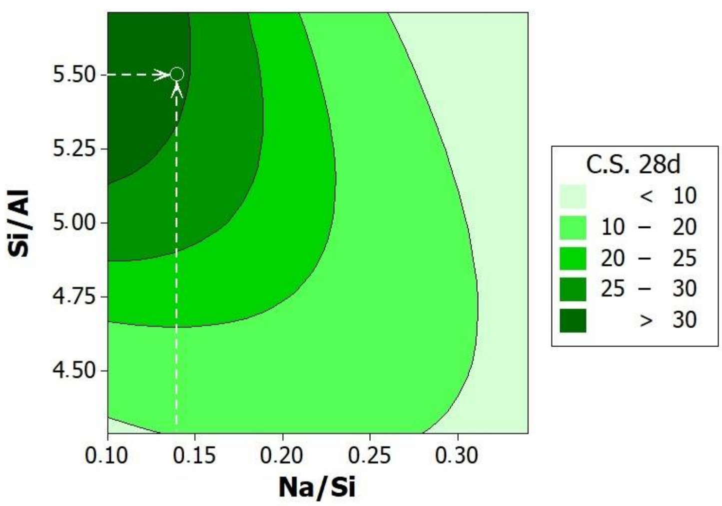

Figure 4. Effect of the molar ratios of Na/Si and Si/Al on the compressive strength (C.S.) of hybrid cement (paste) after 28 days of curing (C.S. 28d): the contours represent the strength levels.

3.1.2. Reaction Kinetics of the Hybrid Cement

The reaction kinetics of the hybrid cement was evaluated using isothermal calorimetry (ASTM C1702) and setting time techniques (ASTM C191). The heat of reaction released from the alkaline-activated hybrid cement (90% FA–10% OPC + Activator) was analyzed, compared to a reference mixture of OPC (100% OPC + H_2O) and a mixture of the hydrated precursor (90% FA–10% OPC +H_2O). In Figure 5, the presence of a single peak for the hybrid mixtures can be observed, which is quickly dissipated, corresponding to the initial release of heat, in contrast to the paste exclusively based on OPC, for which a large release is observed of heat associated with the hydration process of the constituent phases of the Clinker. Likewise, a slight increase in total heat of reaction is observed (Figure 6) promoted by the presence of the alkaline activator in the hybrid cement. The total heat of reaction values (70 h of testing) are presented in Table 3. On comparing the alkaline-activated hybrid cement (90% FA–10% OPC +Activator) with the reference mixture (100% OPC + H_2O), an 85% reduction in the total heat of reaction of this mixture is noticed, which is considered a technological advantage.

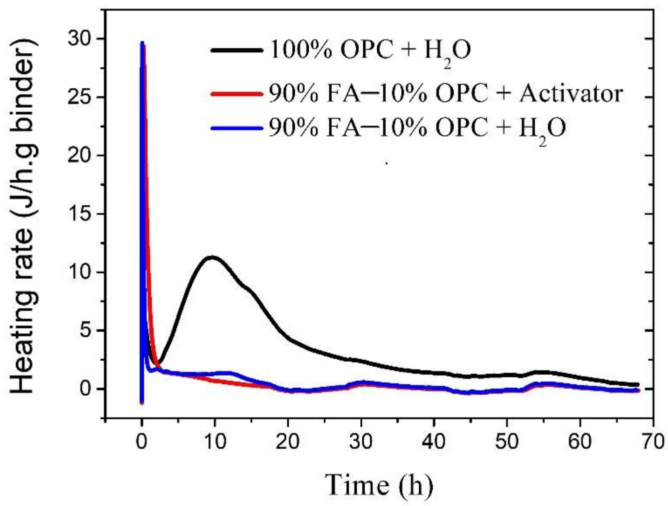

Figure 5. Evolution of the heat of reaction of the pastes.

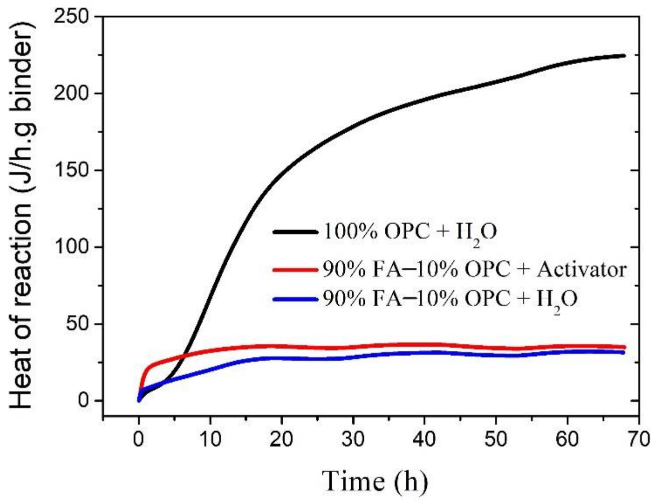

Figure 6. Total heat of reaction of the pastes.

Table 3. Total heat of reaction of the pastes up to 70 h of testing.

Mix (Paste)	Total Heat of Reaction (70 h) (kJ/kg of Paste)
90% FA–10% OPC + H_2O	31.49
90% FA–10% OPC + Activator	34.85
100% OPC + H_2O	224.6

In the setting time evaluation, three alkaline-activated hybrid cements were used, in which the percentage of OPC was varied at 5, 10, and 20% with respect to the total weight of the precursor (FA + OPC), keeping the content of activator constant. Chindaprasit et al. [17], Robayo-Salazar et al. [18], and Valencia-Saavedra et al. [19] carried out similar studies. The results obtained showed that the incorporation of calcium sources of a GBFS or OPC type reduces the setting time of alkaline-activated hybrid cements. This same effect can be seen in Figure 7, where the paste with the lowest OPC content (5%) obtained an initial setting time greater than 4.5 h, in contrast to that with the highest OPC content (20%) which began to set after 30 min. The initial and final setting times of each mix can be seen in Table 4.

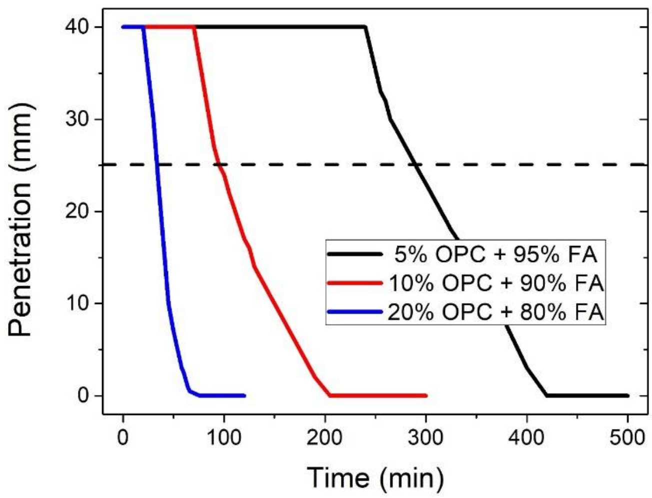

Figure 7. Binder (paste) setting times (initial and final) (ASTM C191).

Table 4. Initial and final setting times of the pastes.

Mix (Paste)	Setting Time (min)	
	Initial	Final
95% FA + 5% OPC	293	420
90% FA + 10% OPC	93	200
80% FA + 20% OPC	33	80

3.1.3. Compressive Strength and Classification of the Hybrid Cement

The evolution of compressive strength using cement pastes as a function of curing time can be observed in Figure 8. A direct relationship between compressive strength and the percentage of OPC inclusion was found, i.e., the higher the content, the greater the strength. The results at 7 and 28 days were 14.41 and 21.58 MPa for the 95% FA–5% OPC paste and 20.60 and 31.56 MPa for the 90% FA–10% OPC paste, respectively. This represents an increase of up to 46% in compressive strength (at 28 days) with an OPC increase of only 5%. This is in agreement with the results reported by previous studies [8,20–22] that associate the gain in strength to a greater densification of the cementing matrix promoted by the formation of C-A-S-H and (N,C)-A-S-H type “hybrid gels”. An increase in strength on aging longer was also noted. In the 90% FA–10% OPC paste, an increase of 63% was reported between the results at 28 and 90 days (the latter of 51.49 MPa), while from 7 to 28 days the increase was 53%. These results are comparable with those reported by other researchers [12,23].

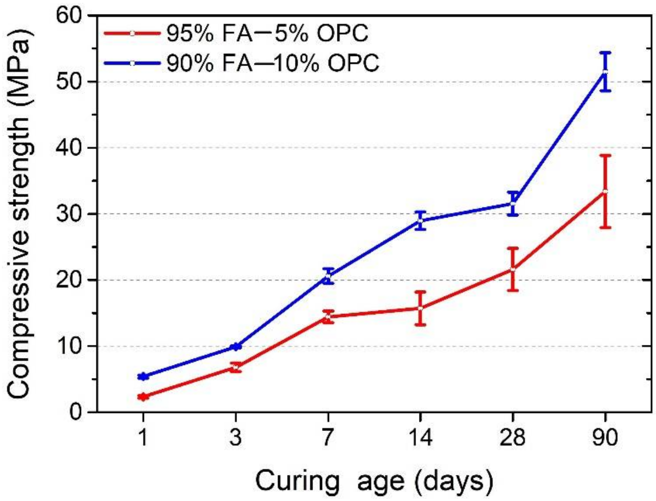

Figure 8. Evolution of compressive strength of optimal hybrid cement (Si/Al 5.5 and Na/Si 0.14): effect OPC content (5 and 10%).

Figure 9 shows the compressive strength results for three mortar mixtures based on the optimal hybrid cement (90% FA–10% OPC, Si/Al 5.5 and Na/Si 0.14), in which the sand content was varied (precursor:sand ratio). The decrease in strength corresponds to the increase in aggregate content, since the zones of interface also increase. However, a notable increase in strength can be seen with the evolution of curing time (7 vs. 28 days).

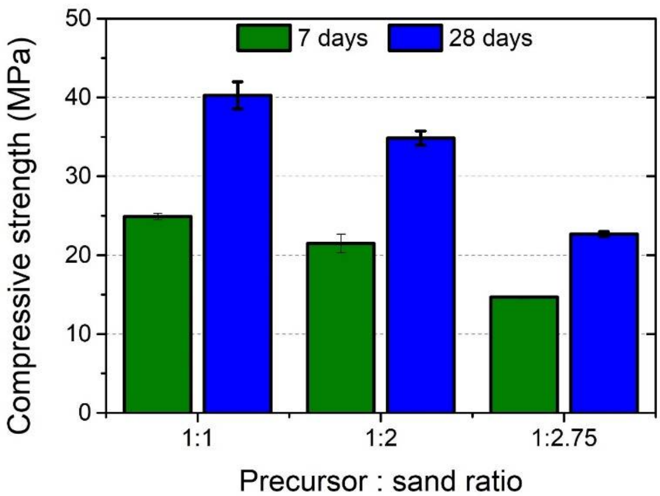

Figure 9. Compressive strength of mortars based on the optimal hybrid cement (90% FA–10% OPC, Si/Al 5.5 and Na/Si 0.14): effect of precursor:sand ratio.

Currently, the Colombian Technical Standard NTC 121, equivalent to ASTM C1157, classifies the cements according to their performance and not their composition. This represents a positive advance relating to the inclusion of such materials (AAM) on the market. Compressive strength is one of the most important parameters for their classification. The hybrid cement mortar with a precursor:sand ratio of 1:2.75 achieved a strength of 14.67 and 22.68 MPa at 7 and 28 days, respectively. Taking into account the results of isothermal calorimetry, setting time and compressive strength, the hybrid cement could be classified, according to ASTM C1157 and NTC 121, as a low heat of hydration cement (LH type) as can be corroborated in Table 5.

Table 5. Compressive strength required by the ASTM C1157 (NTC 121) standard for a LH type cementitious material and results obtained by the 1:2.75 hybrid mortar (90% FA–10% OPC).

Curing Age	LH Cement (ASTM C1157)	Hybrid Mortar (1:2.75)
7 days	11 MPa	14.67 MPa
28 days	21 MPa	22.68 MPa

3.2. Physico-Mechanical and Microstructural Characterization of Hybrid Concrete

3.2.1. Physical-Mechanical Characterization

In accordance with the results reported by Robayo et al. [24] and Valencia-Saavedra et al. [19], using other precursors, the hybrid concrete showed a high level of workability, associated with a high fluidity (24 cm settlement) (Figure 10a), without the presence of segregation phenomena (Figure 10b) due to the adequate cohesiveness of the mixture, mainly promoted by the presence of sodium silicate.

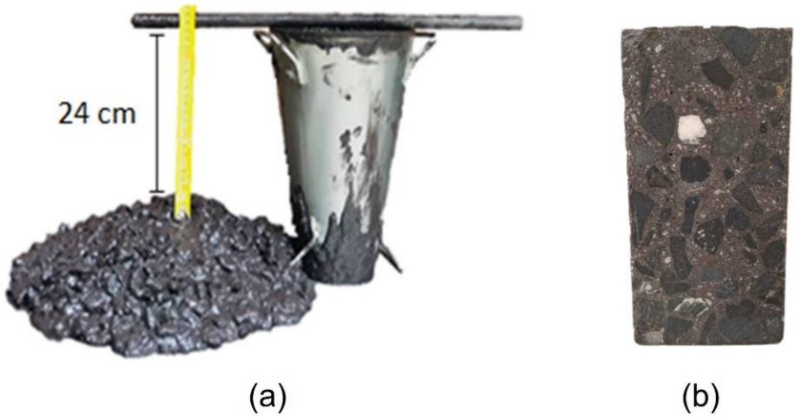

Figure 10. (**a**) Slump test; and (**b**) internal appearance of aggregates distribution in the hybrid concrete

Figure 11 shows the development of compressive strength of the hybrid concrete as a function of curing age. The tests were carried out for the ages of 7, 28, and 90 days, achieving values of 14.26, 23.16 and 29.15 MPa, respectively. In this regard, the regulation requirements for structural concrete (ACI 318) (equivalent to Colombian Regulation for Earthquake Resistant Construction (NSR–10) in Colombia), establishes a value of 17.5 MPa as the minimum compressive strength (28 days) that a concrete must meet to be considered structural. The strength reported by the hybrid concrete was thus found to exceed by 36% the minimum limit established by the standard.

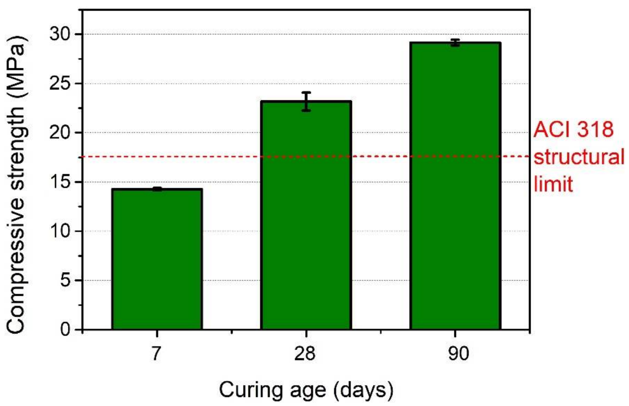

Figure 11. Evolution of compressive strength of the hybrid concrete.

Additionally, the modulus of rupture (MR) of the material was determined by means of the flexural strength test. The value obtained at the age of 28 days was 5.32 MPa, highlighting an adequate relationship with the compressive strength, equivalent to 23%. Some physical properties of the concrete such as density, absorption, and porosity are expressed in Table 6.

Table 6. Physical properties of the hybrid concrete (28 days).

Physical Properties	
Density	2665 kg/m^3
Absorption	8.69%
Porosity	18.80%

3.2.2. Microstructural Analysis of Hybrid Concrete

Through SEM analysis of the hybrid concrete (Figure 12) it was possible to detect a solid, dense surface, with low porosity and homogeneity, associated with the presence of (N,C)-A-S-H type hybrid gels formed by the coprecipitation and interaction of N-A-S-H type gels (product of alkaline activation of FA) and C-S-H gels (products of hydration of OPC) [6,13,25]. Additionally, the presence of unreacted FA particles is observed, corresponding to the crystalline phases of the FA, well adhered to the matrix through a homogeneous interface. These unreacted particles fulfill the function of a micro-aggregate, favoring the mechanical behavior of the compound (hybrid concrete) [24]. Finally, an optimal interface that ensures mechanical cohesion between the matrix phase and the aggregates (fine and coarse) was observed, very much in keeping with the good behavior obtained.

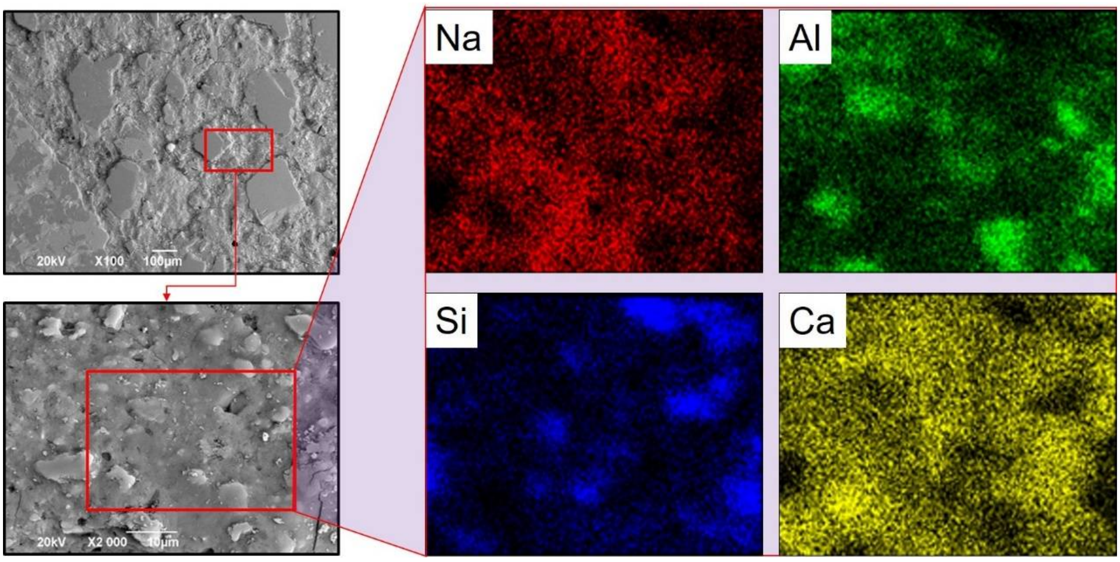

Figure 12. Composition and microstructural analysis (elemental chemical composition (EDS)-SEM) of the hybrid concrete.

Figure 12 shows the elemental chemical composition (EDS) analysis corresponding to the hybrid concrete at 28 days of curing. The analysis illustrates, through colors, the content and distribution of the elements as follows: Na (red), Al (green), Si (blue), and Ca (yellow). It is observed that the microstructural composition is based mainly on silica and alumina, elements provided in a greater proportion by the primary precursor (90% FA). However, the distribution of calcium and sodium over the entire area analyzed corroborates the presence of the hybrid type gels mentioned above.

3.3. Production of Solid Blocks from the Hybrid Concrete

The compressive strength results for the solid hybrid concrete blocks are presented in Figure 13. It can be seen that at 28 days the blocks achieved a strength of 21.89 MPa, a value that represents a 51% increase in the strength obtained after 7 days of curing. In this regard, the ASTM C1790 standard establishes the technical specifications that solid blocks manufactured from the alkaline activation of FA must meet. Additionally, the standard recognizes the implementation of alkaline-activation technology in the production of this type of application. Some physical characteristics of the blocks, such as density, absorption, and porosity are shown in Table 7.

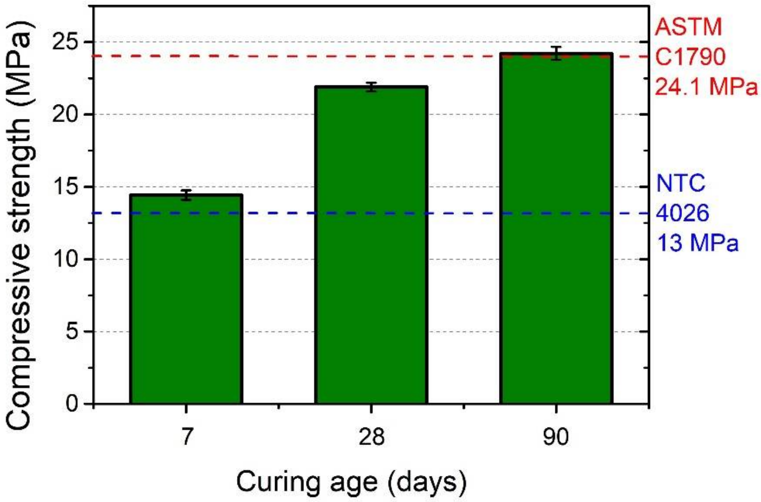

Figure 13. Compressive strength of the hybrid concrete solid blocks.

Table 7. Physical properties of the hybrid concrete solid blocks in relation to the specifications established by the standards as high-class structural blocks.

Physical Properties	Hybrid Concrete Solid Block	NTC 4026 Specifications	ASTM C1790 Specifications
Density (kg/m^3)	2183	Greater than 2000 (normal weight)	Greater than 2000 (normal weight)
Absorption (%)	9	≤9	≤10
Porosity (%)	19.67	Not applicable	Not applicable

In this regard, the ASTM C1790 and NTC 4026 standards (structural masonry) require a minimum compressive strength (24.1 and 13 MPa respectively) depending on the dry density of the precast elements. The standards also require a maximum absorption percentage equivalent to 9.0% and 10.0% for NTC 4026 and ASTM C1790, respectively, when the density is greater than 2000 kg/m^3 (normal weight). According to the results obtained, the solid blocks produced from the hybrid concrete exceeded by 40.6% (21.9 MPa) the value of compressive strength stipulated by NTC 4026 at 28 days (13 MPa), allowing them to be classified according to this regulation as high class structural blocks. Moreover, the minimum value of compressive strength established by the ASTM C1790 standard (24.1 MPa), which must be met at the time of delivery to the buyer, was achieved by the hybrid concrete solid blocks at the age of 90 days of curing.

3.4. Analysis of the Life Cycle of the Hybrid Concrete: Global Warning Potential

The aim of carrying out a life cycle analysis (LCA) was to compare the alkaline-activated hybrid concrete (90% FA–10% OPC) with a conventional concrete based exclusively in Portland cement (100% OPC as binder). The unit used for the analysis was 1 m^3 of concrete, taking as reference the same amount of cement (400 kg/m^3) as is shown in Table 8. In order for the mix designs of both concretes to respond to the same level of mechanical strength (≈21 MPa at 28 days), a water/cement ratio of the OPC concrete of 0.64 was set. The analysis was based on the comparison of the global warming potential indicator (GWP 100), which corresponds to the "carbon footprint" of the material measured in kilograms of CO_2 equivalent (Kg·CO_2·eq).

Table 8. Inventory of emissions and impacts associated with raw materials of alkali-activated hybrid concrete (90% FA–10% OPC) compared to a conventional concrete based 100% on OPC.

Raw Materials		GWP100 (kg·CO_2·eq)	Alkali-Activated Hybrid Concrete (90% FA + 10%OPC)		Conventional Concrete (100% OPC)	
			Input Values (kg)	Output Values (kg·CO_2·eq)	Input Values (kg)	Output Values (kg·CO_2·eq)
Primary precursor	FA	5.26×10^{-3} [a]	360	1.894		
	OPC	9.10×10^{-1} [b]	40	36.39	400	363.9
Alkaline activator	NaOH	1.36×10^{0} [b]	20.2	27.45		
	Na_2SiO_3	7.92×10^{-1} [b]	207.8	164.7		
Water	Water	4.29×10^{-4} [b]	60.8	0.026	256.8	0.110
Aggregates	Sand	4.47×10^{-3} [b]	722.6	3.22	691.74	3.09
	Gravel	1.11×10^{-2} [b]	883.2	9.79	845.46	9.37
		Total		243.5		377.8

[a] [26]; [b] [27].

As a limit of the analysis, the "cradle to gate" model was used, which covers variables ranging from the extraction phase, transport, drying, crushing, grinding, and homogenization of the raw material, to the adaptation processes and concrete production. The GWP unit of measurement was kg·CO_2·eq/m^3 of concrete, with a projection of 100 years. Figure 14 shows the phases (stages) associated with the treatment of the raw materials that make up each concrete. It is worth highlighting that only 10% OPC is used in the case of the hybrid concrete, thus, avoiding the clinkerization process by 90%.

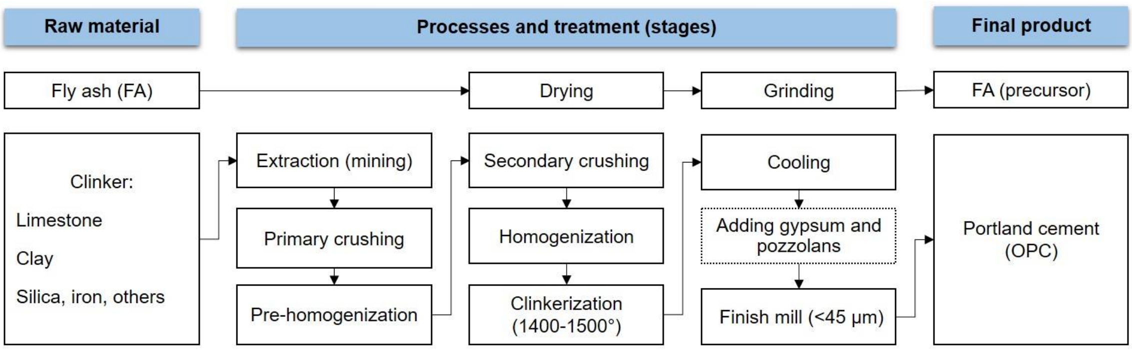

Figure 14. Processes and treatment (stages) of fly ash (FA) vs. Portland cement (OPC).

Figure 15 represents the production process of each of the mixtures. In general, the environmental impact of each concrete will ultimately depend on the design of the mixtures or proportion of the materials used. The inventory of emissions and impacts associated with the raw materials of each type of concrete are presented in Table 8. Secondary data extracted from the Ecoinvent 3.4 database, developed by the Swiss Centre of Life Cycle Inventories, were used [26,27]. Input values represent the mix proportions of each concrete expressed as kg/m^3 of concrete, and Output values represent the proportion of kg.CO_2.eq associated to the raw materials used in the concrete production.

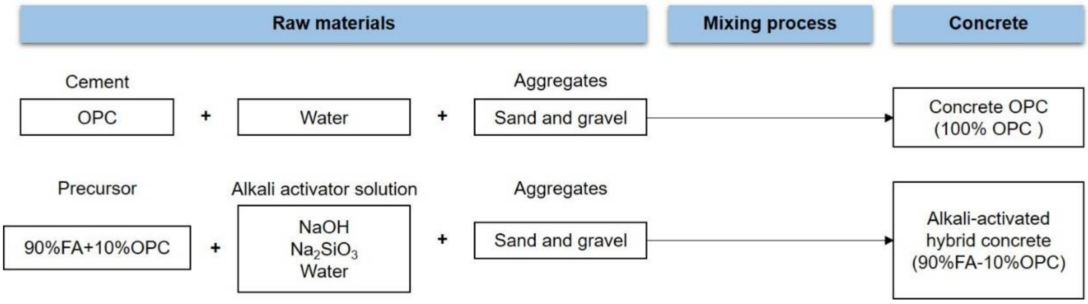

Figure 15. Production process of alkali-activated hybrid concrete (90% FA–10% OPC) vs. 100% OPC-based conventional concrete.

Several authors have reported that, in general, alkali-activated concretes have a significantly lower carbon footprint than conventional OPC-based concrete. Robayo-Salazar et al. [27] reported a 44.7% reduction for a binary concrete based on a natural pozzolan (70%) and blast furnace slag (30%), as well as Salas et al. [28] and Teh et al. [29] with values of 64%, 32%, and 43% for concrete based on natural zeolite, fly ash and blast furnace slag, respectively. Figure 16 shows the GWP values for the hybrid concrete (90% FA–10% OPC) (243.5 kg·CO_2·eq/m^3) and conventional concrete (100% OPC) (377.8 kg·CO_2·eq/m^3), where a decrease in the carbon footprint of the alkali-activated concrete of 35% was achieved compared to conventional OPC concrete.

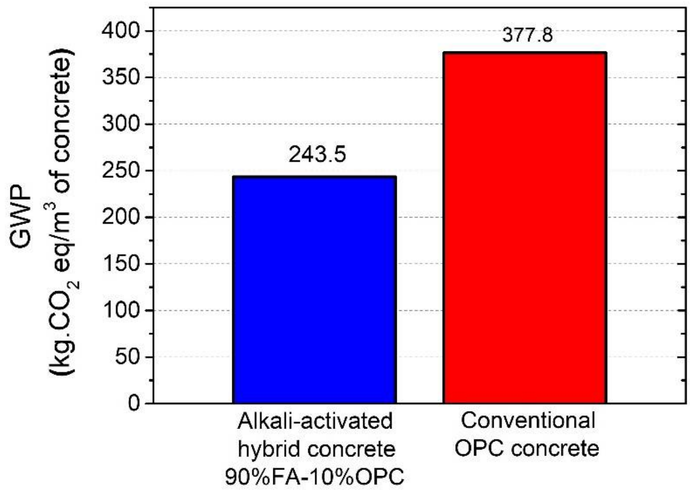

Figure 16. Impact of global warming potential index (GWP) projected over the next 100 years for alkali-activated hybrid concrete compared to conventional OPC concrete.

Additionally, through life cycle analysis it was possible to corroborate that the content of alkaline activators has an important influence on the GWP of the 90%FA–10%OPC hybrid concrete, mainly the content of sodium silicate, with a contribution of 67.6% in total GWP (Figure 17). Regarding the high carbon footprint (CO_2/kg) associated with alkaline activators (NaOH and Na_2SiO_3), these chemical reagents are based on natural raw materials and involve industrial processes with high energy costs and high CO_2 emissions. Sodium hydroxide (NaOH) is prepared mainly by electrolytic methods using an aqueous solution of sodium chloride. Sodium silicate (Na_2SiO_3) is initially obtained by mixing sodium carbonate (Na_2CO_3) and silica (SiO_2). Then, the mixture is cast at a temperature range between 1100 °C and 1200 °C, producing an amorphous solid which is then converted into an aqueous solution called "waterglass". To lessen the impact of industrial sodium silicate activators, alternative sources of silica such as rice husk, glass residue, silica fume, and diatomaceous earth have been proposed [27].

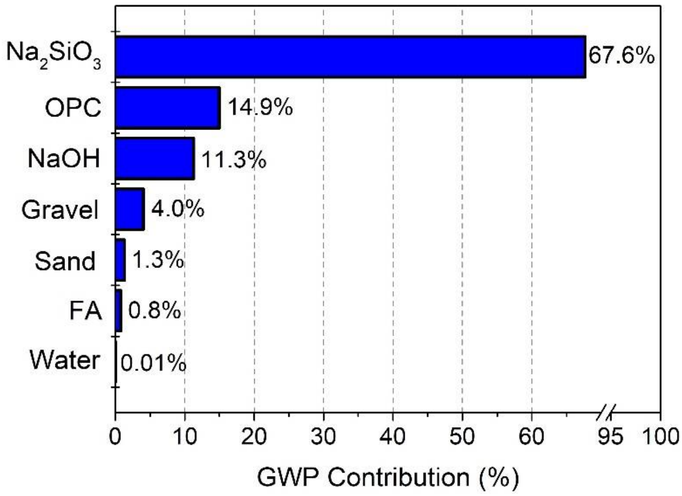

Figure 17. Percentage contribution of raw materials to the GWP of the alkali-activated hybrid concrete (90% FA–10% OPC).

Relating to conventional concrete (100% OPC), the main contribution to the GWP is Portland cement, with 96.31% (Figure 18), mainly due to the high temperatures (1400–1500 °C) required for the clinkerization process. In this sense, the results obtained highlight the feasibility of using alkali-activated hybrid concretes as a measure to mitigate CO_2 emissions caused by the high demand for OPC, considering them as low-carbon footprint concretes.

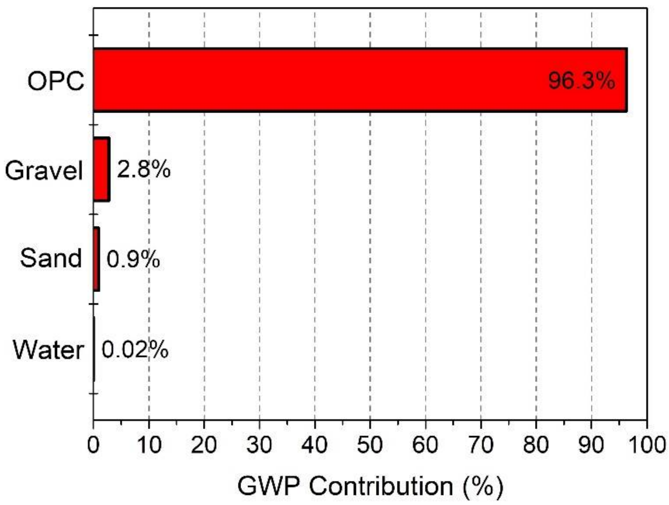

Figure 18. Percentage contribution of raw materials to the GWP of the conventional 100% OPC-based concrete.

4. Conclusions

In this research, the feasibility of obtaining an alternative concrete based on a high content (90%) of fly ash using alkaline-activation technology or "geopolymerization" was demonstrated, with the advantage of having a global warming potential (GWP) or carbon footprint 35% less than conventional concrete based on Portland cement (OPC). From the results obtained it can be concluded:

- The addition of 10% OPC to the hybrid cement allowed the curing and development of strengths at room temperature (~25 °C). This aspect is considered an advantage from a technological point of view since no additional hydro-thermal curing processes are necessary. The optimization of this percentage of OPC addition was carried out taking into account the compressive strength reached at 28 days (31.56 MPa) and the initial setting time (93.5 min), achieving a balance between mechanical strength and workability of the material.
- The results of the setting time test indicated that the addition of OPC has a catalytic effect on the reaction kinetics of the hybrid cement, proportionally accelerating the hardening of the mixture.
- The 85% decrease in the total heat of reaction of the hybrid cement (90% FA–10% OPC) compared to a 100% OPC–based paste represents one of the main advantages from the point of view of application. The hybrid cement, in fact, complies with the specifications of ASTM C1157 (equivalent to NTC 121) to be classified as a low reaction heat cement (type LH), taking into account the properties of compressive strength, setting time, and heat of hydration (cement hybrid: 34.85 kJ/kg vs. 200 kJ/kg specified by ASTM).
- The compressive strength of the hybrid concrete (23.16 MPa at 28 days) exceeds the minimum limit established by ACI 318 for classification as a structural concrete. Furthermore, the modulus of rupture (5.32 MPa) represented 23% of the compressive strength.
- The application of the hybrid concrete in the manufacture of solid block type masonry elements was validated. These blocks are commonly used in the construction of one and two-level houses, under the construction and design method of confined masonry walls. The compressive strength of the blocks at 28 days (21.9 MPa) exceeds the minimum mechanical performance limit established by NTC 4026 (13 MPa) to be classified as high-class structural blocks. The compressive strength specified in ASTM C1790 is reached at 90 days of curing.
- The carbon footprint (GWP) allowed the hybrid concrete to be classified as an environmentally sustainable alternative to conventional 100% OPC-based concrete, with a 35% decrease compared to the GWP of conventional concrete (OPC). Sodium silicate meanwhile was observed to be the largest contributor to CO_2 emissions associated with the hybrid concrete, representing a contribution of 67% of total emissions. The need to validate the use of alternative activators to the industrial ones in the search to further reduce their carbon footprint is highlighted.

Author Contributions: Conceptualization, R.A.R.-S. and R.M.D.G.; data curation, O.R.-D. and L.M.E.; funding acquisition, R.M.D.G.; investigation, O.R.-D. and L.M.E.; methodology, R.A.R.-S. and R.M.D.G.; project administration, R.M.D.G.; supervision, R.M.D.G.; writing—original draft, O.R.-D. and L.M.E.; writing—review and editing, R.A.R.-S. and R.M.D.G. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Colombian Institute for the Development of Science, Technology, and Innovation (Colciencias), grant number 096-2016.

Acknowledgments: The authors want to express their gratitude towards the support from Universidad del Valle, Cali, Colombia.

Conflicts of Interest: The authors declare no conflict of interest.

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