Alkali-activated binary concrete based on natural pozzolan; a real and eco-friendly alternative to the OPC concrete

Rafael Robayo-Salazar *, and Ruby Mejía de Gutiérrez

Composites Materials Group (CENM), School of Materials Engineering, Universidad del Valle, Santiago de Cali, Colombia

Abstract. This research shows the obtaining and characterization of an Alkali Activated Binary Concrete (AABC), based on 70% of a natural volcanic pozzolan (NP) and 30% ground blast furnace slag (GBFS), as a real and environmentally sustainable alternative of replacement to the Portland cement (OPC)-based concrete. As the alkaline activator a mixture of sodium hydroxide and silicate was used. The alkaline binder was characterized prior to the design of the concrete, this included the determination of its compressive strength, setting time and heat of reaction. The mix design of the AABC was performed by adapting the absolute volume methodology used for conventional concretes. AABC was compared equivalently with a concrete based on OPC. The characterization of concretes included the determination of properties such as: slump, compressive strength, density and porosity. In addition, the carbon footprint of the concretes was determined by analysing its life cycle using the LCA methodology. These results are considered as a contribution to the standardization of a real-scale production process of alkaline pre-mixed concretes in countries with deposits of NP such as Colombia.

1 Introduction

Alkali-activated cements are binders that result from the chemical interaction (at relatively low processing temperatures: $25-100^{\circ}$ C) between strongly alkaline solutions (activator) and silicoaluminates (precursor), with low and high calcium contents, which may be of natural origin, such as natural clays or pozzolans, or of artificial origin, such as industrial waste and by-products [1]–[5].

Alkali-activated concretes are considered to be revolutionary materials that in the foreseeable future could replace in some applications to the Portland cement (OPC)-based concrete ; this idea is supported on its lower carbon footprint and, in general, on the excellent mechanical and durable performances that these have demonstrated since its appearance [6]-[8]. However, the commonly precursors (aluminosilicates) used for their production, such as fly ash (FA) and ground blast furnace slag (GBFS) present a great variability in their composition and limited availability (global generation of these by-products in relation to OPC demand) [9]-[12]. In addition to, the lack of standards of alkali-activated materials, makes it difficult to produce these materials on an industrial scale from FA and GBFS [13], [14].

In this sense, local natural volcanic pozzolans (NP) deposits are considered a viable commercial alternative (industrial scale) due to their greater availability and chemical and mineralogical homogeneity [15], [16]. NP deposits account for approximately 0.84% of the soils worldwide (124 million ha), which are distributed

predominantly (60%) in tropical regions [17]. These deposits have an important commercial value for the cement industry, especially in countries with high demographic and economic growth, such as: Iran, Cameroon, Japan, China, Saudi Arabia, Turkey, Jordan, USA, Mexico, Chile, Ecuador and Colombia [18], [19].

The production of alkali-activated binary concretes (AABC) based on a high content of NP (\geq 70%) and a low content of sources of CaO and reactive Al₂O₃ (GBFS) is feasible [20]–[22]. Several authors, including; Allahverdi et al. [23], Lemougna et al. [24], Bondar et al. [25], and Tchakoute et al. [26], report the potential of NP as raw material for obtaining alkali-activated cements. This research shows the design, obtaining and characterization of an AABC, based on 70% of a NP and 30% GBFS, as a real and environmentally sustainable alternative of replacement to the OPC concrete.

2 Materials and methods

The precursor materials used in this study were Colombian NP of volcanic origin and GBFS. The high SiO_2/Al_2O_3 molar ratio (6.79) and the low alkali content (CaO, Na₂O and K₂O) are notable for NP, whereas GBFS has a SiO_2/Al_2O_3 molar ratio of 4.93 and a high CaO content (40.3%) (table 1). The particle size D(4;3), obtained by laser granulometry, was 20.63 and 26.44 µm for NP and GBFS, respectively.

Figure 1 shows the pattern of X-ray diffraction of the precursors. The amorphous phase content of the NP was determined by Rietveld (XRD) refinement and using a corundum (Al₂O₃) standard [27]. The results of the

^{*} Corresponding author: <u>rafael.robayo@correounivalle.edu.co</u>

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quantitative analysis yielded an amorphous phase content of 25.5%. The crystalline fraction of NP is mainly composed of 59.3% by sodium-calcium feldspars or plagioclase (albite-anortite series) in addition to some minerals belonging to the amphibole group (10.4%) and quartz (4.8%). The GBFS XRD reflects its vitreous nature (halo located in the range between 23 and 37° 2 θ). It is also possible to see signals corresponding to crystalline structures associated with gelenite (2·CaO·Al₂O₃·SiO₂) and calcite (CaCO₃).

 Table 1. Chemical composition of the NP and GBFS (% by weight of oxides) (LOI: loss on ignition).

Component	NP	GBFS
SiO ₂	61.9	37.7
Al ₂ O ₃	15.5	15.7
Fe ₂ O ₃	7.3	1.85
CaO	5.2	40.3
Na ₂ O	4.1	0.2
MgO	2.5	1.3
K ₂ O	1.6	0.4
LOI	0.5	



Fig. 1. X-ray diffraction (XRD) of the precursors.

A mixture of industrial grade sodium hydroxide (NaOH) and commercial sodium silicate (SiO₂=32.09%, Na₂O=11.92%, H₂O=55.99%) was used as an alkaline activator. GBFS was incorporated in proportion up to 30% by weight as a replacement for NP in the mixture.

The alkali activated binder (AAB) (70% NP-30% GBFS) obtained was classified and characterized according to ASTM C1157 (American Standard Testing Materials) based on standard physical requirements related to performance, not composition. Mortars based

on AAB were obtained according to the procedure described in ASTM C305. The heat of hydration and the evolution of heat were evaluated by means of an isothermal calorimeter at a test temperature of 25 °C. The setting time was determined by means of the Vicat apparatus according to the procedure described in ASTM C191 (method B).

The mix design of the AABC was performed by adapting the absolute volume methodology used for conventional concretes. The aggregates used in the concretes were crushed gravel, with a maximum size of 12.7 mm and predominantly angular particles, and silica sand obtained from a local river, which presented a fineness modulus of 1.85 and contained mostly round particles. In general, the aggregates used in concrete mixes met the specifications of ASTM standards. The amount of precursor (NP+GBFS) and the liquid/solids (L/S) ratio required to meet the design specifications; fc'≈21 MPa and fluid consistency slump≥150 mm, are 400 kg/m³ and 0.35, respectively. The reference concrete based exclusively on OPC was produced equivalently, following the same design specifications (fc'≈21 MPa and slump ≥ 150 mm).

The characterization of concretes included the determination of properties such as: slump (ASTM C143), compressive strength (ASTM C39), density and porosity (ASTM C642). In addition, the carbon footprint of the concretes was determined by analysing its life cycle using the LCA methodology.

3 Results and discussion

3.1 Characterization of binder

Figure 2 shows the performance of the alkali-activated mortar compared to a standard mortar based on OPC and the minimum compressive strength requirements for mortars produced according to ASTM C305 standards at 3 (8 MPa), 7 (15 MPa) and 28 (24 MPa) days of curing. Recently, ASTM C1157 has classified cements by their performance, not by their composition. The compressive strength is considered the most important variable in the specification of these materials for their possible introduction to the market. The results allow the classification of AAB as a UG-type cement (general purpose) with a strength of 37.24 MPa, a value that exceeds that required by ASTM C1157 (24 MPa) at 28 days by 55%. Although both mortars exceed the minimum values required, the strength development of alkali-activated mortar at early curing ages is lower than that of the mortar OPC; however, it is observed that at longer curing ages (90 days), their performance is superior to that of the reference mortar.

The setting times (initial and final) and heat of reaction (up to 48 hours) of the AAB and OPC listed in table 2. In relation to the total heat of reaction of an OPC paste (190 J/g of cementant), the AAB generates 76% less reaction heat, indicating that according to the ASTM C1157, this alternative binder can be classified as a low-heat of reaction cement (LH type), a characteristic that is

considered of paramount importance in the construction of massive elements.



Fig. 2. Evolution of the compressive strength of the mortar based on AAB (NP+GBFS) compared to a mortar reference based on OPC.

Table 2. Heat of reaction and initial/final setting times of theAAB and OPC (* up to 48 hours).

Blend	Initial setting time (min)	Final setting time (min)	Heat of reaction* (J/g of binder)
AAB	22	30	44
OPC	120	216	190

3.2 Alkali activated concrete properties

The properties of concretes obtained using the methodology proposed above are shown in table 3. In fresh state, the AABC presented a fluid consistency with a slump value (ASTM C143) of 220 mm and a high degree of workability without the presence of exudation and segregation phenomena (figure 3). This consistency allowed the production of optimal surface finishing and a perfect aggregate distribution after molding (figure 4). In a hardened state, the concrete had a density of 2635.7 kg/m^3 and a permeable pore volume of 15.2%. The compressive strength obtained after 28 days of curing was 23.1 MPa, thus meeting the specified design strength (fc'~21 MPa). The increase at 28 days in comparison to the value at 7 days was 46.2% (T≈25°C and Hum. 280%). The strength and its increase with curing time was dependent on the degree of reactivity of the precursor (NP+GBFS); in this case, the addition of GBFS (30%) to the concrete increases the amount of amorphous phases rich in SiO₂ and Al₂O₃ and promotes strength gain over time [20]–[22], [28].

The behaviour of mixtures in fresh and hardened states validates the use of the 70%NP + 30% GBFS mix as precursor for the production of AABC. The GWP per m³ of concrete, based on LCA (Life Cycle Assessment) method, was 207.4 and 344 kg·CO₂·eq for the AABC and OPC concrete, respectively; this represents a 40%

reduction in the GWP, indicating that this material would be more environmentally sustainable.

Fable 3. Properties	of AABC and	OPC concretes.
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Durantin	Concrete type	
Properties	AABC	OPC
Slump (mm)	220	180
Degree of workability	High	Fluid
Density (28 days) (kg/m ³)	2635.7	2632.0
Permeable pore volume (28 days) (%)	15.2	15.8
Compressive strength (7 days) (MPa)	15.8	19.1
Compressive strength (28 days) (MPa)	23.1	23.2
Compressive strength (90 days) (MPa)	29.9	27.2



Fig. 3. Slump and appearance in fresh state of the AABC.



Fig. 4. AABC in hardened state and distribution of aggregates.

4 Conclusions

The results demonstrated the possibility of obtaining an alternative concrete based on a high NP content (\geq 70%) of volcanic origin by applying alkaline activation technology. The AABC obtained presented a performance equivalent to the concrete reference based on OPC, with the advantage of having a carbon footprint 40% lower. Obtaining this alternative concrete is considered a viable and sustainable option from the

technological point of view for the implementation of this new technology on an industrial scale.

The AAB reported a total heat of reaction of up to 48 hours (44.48 J/g), a value that is 76% less than that generated by an OPC (190 J/g). Based on the ASTM C1157 standard, this cement can be classified as a low-heat of reaction cement (LH-type). This behaviour is considered an advantage if the intended use of this material is the construction of massive elements.

AAB exhibits a strength development to early curing ages (≤ 28 days, 25°C) slightly lower than OPC. However, at prolonged ages (90 days), the mechanical performance of this binder exceeds that of the reference material (OPC). The compressive strength results obtained at 28 days allow the classification of the AAB as UG-type cement with a resistance of 37.24 MPa, which exceeds the required by the ASTM C1157 standard (24 MPa) by 55%.

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