

Mechanical properties and absorption of chlorides in alkali activated slag concrete and exposed to carbonation

Propiedades mecánicas y absorción de cloruros en hormigones de escoria activados alcalinamente y expuestos a carbonatación.

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Abstract

This paper presents an experimental study on the durability properties of carbonated alkali-activated slag (AAS) concrete. An ordinary Portland cement (OPC) was also tested for comparative purposes. The durability properties were studied through the measurements of compressive strength, permeable voids, and water absorption and chloride permeation. The results indicated that the AASs showed higher compressive strength at early ages than the OPCs. Contrary, permeable voids and water absorption measurements were lower for AASs than for OPCs.

----- *Keywords:* Granulated blast-furnace slag, alkali-activated slag concrete, Portland concrete, carbonation, compressive strength, permeable voids, absorption, chloride permeability

Resumen

Este trabajo presenta el estudio experimental de las propiedades de durabilidad del hormigón activado alcalinamente (AAS) y expuesto a carbonatación. Las propiedades de durabilidad fueron estudiadas a través de las mediciones de

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resistencia a la compresión, permeabilidad, absorción de agua y la penetración de ion cloruro. Los resultados muestran que los hormigones AAS, generan una mayor resistencia a la compresión a edades tempranas en comparación con los hormigones OPC. En contraste con las medidas de permeabilidad y absorción de agua las cuales fueron más bajas para el hormigón AAS con respecto a los OPC.

-----*Palabras clave:* escoria granulada de alto horno, hormigón activado alcalinamente, hormigón Portland ordinario tipo I, resistencia a la compresión, permeabilidad, absorción de agua, ion cloruro

Introduction

Granulated blast-furnace slag (GBFS) has been used for many years as a supplementary cementitious material (SCM) in ordinary Portland cement (OPC) concrete, either as a mineral admixture or as a component of blended cement [1].

The very high temperatures (1400-1500 °C) required manufacturing OPC, which make it responsible for 40% of all energy consumed, account for the extremely high cost of this process. The environmental impact attributed to OPC manufacturing is largely due to the energy-intensive processes involved. Indeed, the cement industry is regarded to be responsible for 6-7% of all greenhouse gases emitted world-wide [2]. The average intensity of carbon dioxide (CO₂) emission from total global cement production is 222 kg of c/t of cement. In this way the GBFS represents one of the options for emission mitigation.

Alkali-activated cement is a system in which an alkaline activator promotes one or several reactions on an inorganic solid of natural or artificial origin that generates a material with cementitious characteristics. On such material is alkali-activated slag (AAS) cement, which results of mixing granulated blast furnace slag and alkaline substances; its properties and workability, durability and strength are affected by factors such as: type and concentration of the alkaline activator, solution ratio (SiO₂/Na₂O), slag type and fineness, curing conditions, water/cement material ratio, activating solution/slag ratio and the use of admixtures and fibres [3].

The aim of this paper is to study the mechanical, absorption and chloride migration properties of artificially carbonated AAS concrete (3% CO₂). The results were compared with conventional OPC concrete. Specimens were studied using compressive strength measurements, absorption and porosity measurements and chloride permeation at different times of exposure.

Experimental

GBFS from the company “Acerías Paz del Rio”, locate in Boyacá, Colombia, was used with a chemical composition of (% by weight) 33.7 SiO₂, 12.8 Al₂O₃, 3.09 Fe₂O₃, 45.4 CaO, 0.5 TiO₂, 0.64 SO₃, 1.79 MgO, and 2.08 loss ignition, a specific surface area of 398 m² kg⁻¹ and a specific gravity of 2860 kg m⁻³. The basicity (CaO+MgO/SiO₂+Al₂O₃) and quality (CaO+MgO+Al₂O₃/SiO₂+TiO₂) indexes were 1.01 and 1.73, respectively [4]. According to ASTM C 989-99 Standard this material was grade 80 slag [5]. The waterglass used as the activating solution consisted of a mix of commercial sodium silicate (31.7% SiO₂, 12.3% Na₂O, and 56.0% water) with a 50% NaOH solution. The Na₂O concentration in the waterglass activating solution added to the concrete was 5% by weight of slag. The aggregate used was a siliceous gravel with a maximum grain size of 19 mm, specific gravity of 2940 kg m⁻³, and 1.3% absorption, and river sand with a maximum grain size of 19 mm, a specific gravity of 2470 kg m⁻³, and 2.9% absorption. OPC according to ASTM C 150-02 [6] Standard was also tested for comparative purposes, with a specific gravity and specific surface area of 2990 kg m⁻³ and 400 kg m⁻³, respectively. AAS and OPC concretes were prepared with a water/cement ratio of 0.4.

The AAS and OPC specimens were de-moulded after 24 h. In all cases, the AAS and OPC specimens were cured in a climatic cabinet for 28 days at 90% relative humidity (RH) for AAS specimens and at 100% RH for OPC specimens to prevent leaching of the activating solutions and to assure that the hydration reaction and product formation processes were not affected.

Carbonation exposure was simulated by accelerated testing in a cabinet with 3% CO₂, 65% RH, and 25 °C (AASA and OPCA specimens), and exposure in a laboratory environment with 0.03% CO₂, 65% RH, and 25 °C (AASL and OPCL specimens).

Carbonation front progression was determined by sprinkling discs cut from the specimens with an alcoholic solution of 1% phenolphthalein indicator. This indicator reveals changes in pH caused by the reaction between CO₂ and the hydration products in concrete. A violet colour denotes a pH of over 9; i.e. uncarbonated areas. A pH reduction to values near to 9 was observed on AAS concrete exposed to 3% CO₂. The pH values were calculated as the average of seven radial measurements.

Cylindrical specimens (76.2 mm diameter and 152.4 mm length) were used to test the materials for compressive strength according to ASTM C 42-04 Standard [7], absorption and voids in hardened concrete according to ASTM C 642-06 Standard [8], and chloride permeation according to ASTM C 1202-07 Standard [9].

Results and discussion

Carbonation Test

The calculated carbonation rate coefficient (K_c) was 139 mm (year)^{-1/2} for AAS concrete and 25 mm (year)^{-1/2} for OPC concrete. It should be noted that these carbonation rate coefficients were calculated for 45 days of exposure to 3% CO₂ after total carbonation of AASA and partial carbonation of OPCA was observed. For this calculation, the Fick's 1st law was assumed,

which means that the diffusion phenomenon is described by a parabolic law: $X_c = K_c \sqrt{t}$, where X_c is the width of the carbonation front (mm), and t is the exposure time (years) [4].

The high carbonation rate exhibited by AAS concrete may be attributed to the fact that the characteristic activation reactions after slag alkali activation are governed by dissolution and precipitation mechanisms, whose reaction kinetics are faster than the diffusion reactions along water paths or open pores that prevail in OPC hydration [10-11]. When dissolved species such as calcium, silicates and aluminates reach the maximum concentration they can precipitate, prompting the nucleation of the dissolved aluminates and silicates in an alkaline environment. This would favour the formation of calcium-silicate-hydrate (C-S-H) gel characterized by a short range order due to its low Ca/Si ratio and the presence of Q³-type Si units [12]. Moreover, it has been reported that in AAS concrete the carbonation takes place directly on the C-S-H gel [10]. AAS concrete shrinks during the drying process, leading to the formation of microscopic cracks that facilitate the entry of CO₂ inside the concrete. As a consequence, the interaction between CO₂ and this material leads to its decalcification and the loss of cohesion in the matrix [13]. It has been suggested that this unsuitability could be attenuated by grinding the slag much more finely and enhancing the efficiency of curing systems, proposing airtight systems with an average RH of around 90% [4].

The OPC concrete is less vulnerable to carbonation. OPC matrix aluminate contains more than AAS in the residue of calcium silicate (C₃S and C₂S), calcium hydrate (CH) and in hydrated calcium silicate phases (CSH). CSH has a ratio of Ca / Si near 1.7 and is in equilibrium with the pore solution of pH = 12.6-13.5. When the OPC concrete is in contact with CO₂, forming calcium carbonate, which has a low solubility, and when it is precipitated in pores, the diffusivity of the matrix decreases. In the OPC concrete, it generates a surface layer of calcium carbonate due to carbonation. Precipitated calcium carbonate layers

in OPC concrete surface forms a barrier to the diffusion, while the porosity in the interior regions may have increased. This barrier limits the access of CO₂ in the interior. The rate of carbonation reaction declines and thus the extra carbonation of OPC concrete progresses very slowly.

Compressive strength test

Figure 1 shows compressive strength versus age of curing results for AAS and OPC uncarbonated specimens (after 28 days of curing), for AASA and OPCA specimens after exposure to accelerated carbonation (3% CO₂) (45 and 108 days, respectively), and for AASL and OPCL specimens after exposure to a laboratory environment (0.03% CO₂) (45 and 108 days, respectively). The compressive strength results are the average values for three specimens. It can be observed that the highest compressive strength (65.91 MPa) is shown by the AAS specimen after 28 days age of curing in the absence of carbonation. The lowest compressive strength (40.99 MPa) is shown by AASA specimen exposed to accelerated carbonation (3% CO₂), and an intermediate position is occupied by AASL specimen (63.97 MPa) after exposure to the laboratory environment (0.03% CO₂), see figure 1. In contrast, on OPC specimen the highest compressive strength (57.84 MPa) is shown by OPCL specimen after exposure to the laboratory environment. The lowest compressive strength (38.50 MPa) is shown by OPCA specimen after exposure to accelerated carbonation (3% CO₂), and an intermediate position is occupied by the OPC specimen (50.24 MPa) after 28 days age of curing in the absence of carbonation.

The compressive strength index (I_{CS}), in percentage, was calculated according to:

$$I_{CS} = \frac{CS_{AAS} - CS_{OPC}}{CS_{OPC}} \times 100$$

where CS_{AAS} and CS_{OPC} are the compressive strength for AAS and OPC specimen, respectively [4]. The I_{CS} was 31% higher for the early ages of AAS (28 days). This value decreased throughout the curing period to 27% for AASL specimen after 45 days exposure to the laboratory environment.

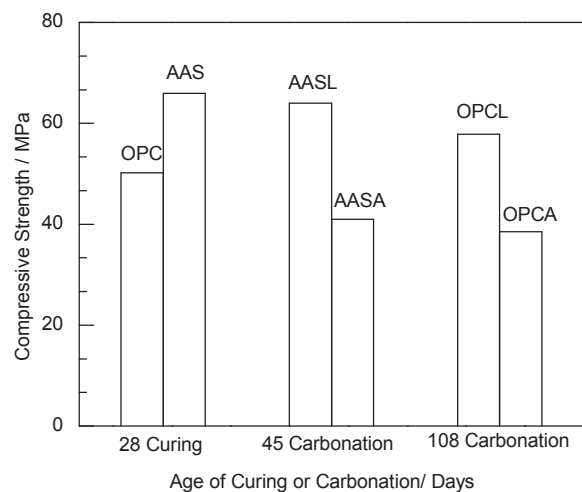


Figure 1 Compressive strength test versus age of curing for the AAS and OPC concretes

By comparing the mechanical strength of the OPC and AAS concrete that is obtained for AAS generated better mechanical properties at early ages due to the trigger that is used in the slag. OPC concrete subjected to accelerated carbonation shows an increase of 14 MPa compared to evaluated at 0 hours, this phenomenon is due to the carbonation of this material was slow and because of this after 1750 hours of exposure you have had a carbonation with exposure of 100% CO₂, which could have caused a blockage of the pores and lead to an increase as high mechanical strength.

Permeable voids and water absorption test

Permeable voids and water absorption measurements in hardened concrete were carried out according to ASTM C 642-06 Standard [8].

Figures 2 and 3 shows permeable voids and water absorption results, respectively, for AAS and OPC concretes. The lowest permeable voids percentage is observed on AAS specimen. The OPC specimen showed a 10% higher value of permeable voids than AAS specimen (see figure 2). These results agree well with results in the literature [13].

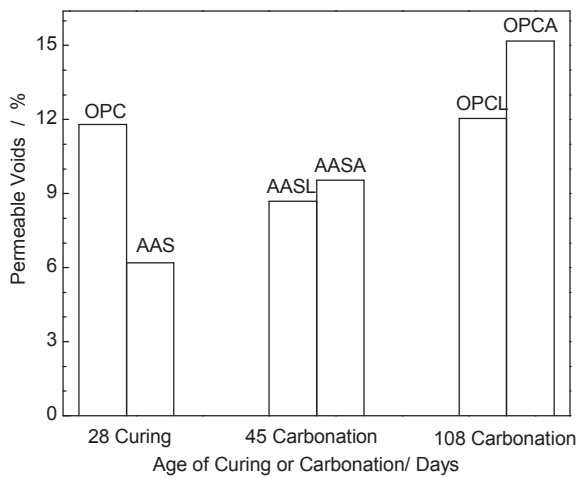


Figure 2 Permeable voids versus age of curing for the AAS and OPC concretes

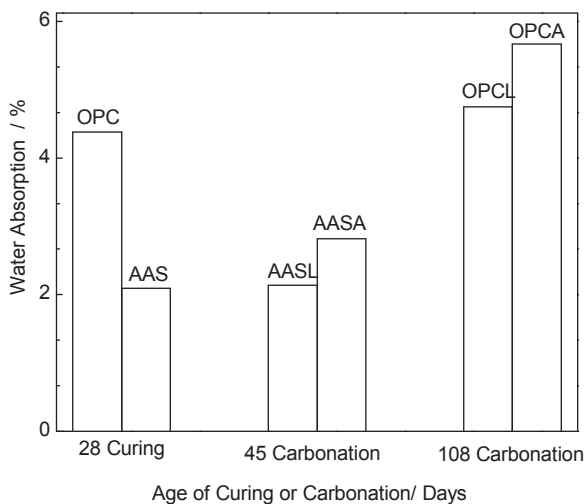


Figure 3 Water absorption versus age of curing for the AAS and OPC concretes

The low capillarity coefficients and high values of resistance to water penetration that had the specific AAS describe the low permeability of this type of material compared to traditional OPC concrete. AAS concretes are those with less permeable pores in all cases, are of good quality concrete. OPC concretes show a higher percentage to 10% in all cases indicating a significant increase in porosity, which is due to the hydration products which are responsible for this property studied.

In the case of concrete obtained with AAS a good property is attributed to the higher density of the paste due to hydration products must be generated at short times generating a lesser percentage of pores. AAS and OPC concretes subjected to accelerated carbonation show an increase in the percentage of permeable pores due to the entry of CO_2 , which generates the pores are interconnected and increasing the % porosity.

Accelerated chloride ion permeability test

Accelerated chloride ion permeability test was performed according to ASTM C 1202-07 Standard [9]. One of the surfaces was in contact with a 3% by weight of sodium chloride (NaCl) solution (anolyte) and the other with a 0.3 N of calcium hydroxide ($\text{Ca}(\text{OH})_2$) solution (catholyte). The total charge passing through in 6 h was measured, indicating the degree of resistance of the specimen to chloride ion permeation. Table 1 includes initial current, resistivity, and total charge passing for the concretes investigated.

Figure 4 shows the total charge passing in 6 hours as a measure of the chloride permeability. The chloride ion penetrability limits suggested by ASTM C 1202-07 Standard [9] were compared with the results. It can be seen that all AAS specimens showed less or equal than 1000 Coulombs total charge passing and these were assessed as very low penetrability. The conventional Portland concrete OPC, OPCL, and OPCA specimens, showed values in the range “very low” to “moderate” according to the assessing criteria, dotted lines in figure 4. Results of figure 4 indicate that AAS concrete performed better with respect to chloride penetrability. The resistivities calculated by considering the initial current also followed a similar trend as the total charge passing, see table 1.

The test performed following ASTM C 1202-07 Standard [9] is mainly a measurement of electrical conductivity which depends on pore structure and chemistry of pore solution. For the experimental conditions tested (specimen size and applied DC

voltage), the initial current can be regarded as a representative of electrical conductivity of the specimen. Table 1 indicates that OPC specimens exhibit higher electrical conductivity than AAS specimens.

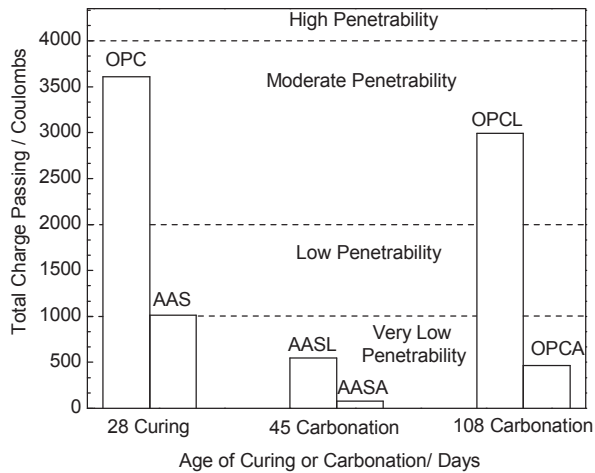


Figure 4 Chloride permeability values for the AAS and OPC concretes

Table 1 Chloride permeability results

Concrete	Initial Current (mA)	Resistivity (ρ) at 60 V ($k\Omega$ cm)	Total Charge Passing (Coulombs)
AAS	27	7.8	1010.5
AASL	18	11.5	549.4
AASA	4	52.3	78.1
OPC	61	3.4	3611.2
OPCL	49	4.3	2991.2
OPCA	9	23.5	464.0

Figure 5 shows the relationship between initial current and resistivity (ρ) with the total charge passing, respectively. It can be seen that as initial current increases the total charge passing increases. There is a good linear correlation between the initial current and the charge passing

(figure 5), this linear relationship agrees with results in the literature [C. Shi, 1789-1799]. The slope of 65.45 on figure 5 is higher than the theoretically expected 21.6 (for a 6-h experiment).

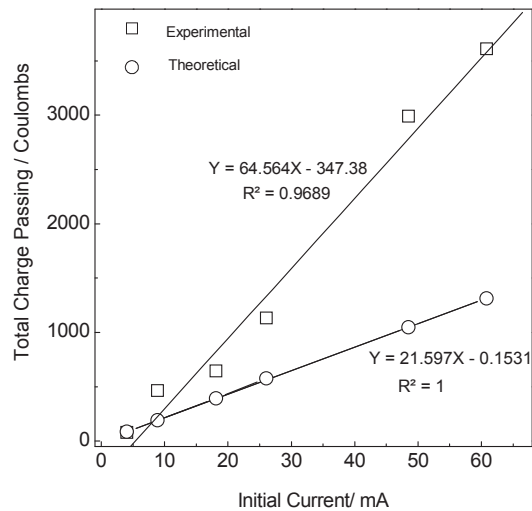


Figure 5 Relationship between total charge passing and initial current

OPC concretes have higher electrical conductivity than AAS concrete. Because the pore solution appears to contribute more to the electrical conductivity or charge passed the pore structure. AAS concretes are those with a higher resistivity value in all cases studied, this is due to the initial current value because in this particular value is always less than the OPC concrete, the tendency of the resistivity both concrete is that as time is evaluated, the value of resistivity increases, and for the case of carbonated concrete is noted that both have a high increase compared to the same hours evaluated but exposed to ambient conditions natural.

Conclusions

Using the Fick's 1st law of diffusion the calculated carbonation rate coefficients (K_c) were 139 mm (year)^{-1/2} for AAS concrete and 25 mm (year)^{-1/2} for OPC concrete, after 45 days of carbonation.

The highest compressive strength (65.91 MPa) is shown by the AAS specimen after 28 days age

of curing and the lowest compressive strength (40.99 MPa) is shown by AASA specimen exposed to accelerated carbonation (3% CO₂). In contrast, on OPC specimen the highest compressive strength (57.84 MPa) is shown by OPCL specimen after exposure to the laboratory environment. The lowest compressive strength (38.50 MPa) is shown by OPCA specimen after exposure to accelerated carbonation (3% CO₂).

Permeable voids and water absorption tests directly representing the permeability, were lower for AASs than for OPCs. The OPC specimen showed a 10% higher value of permeable voids than AAS specimen.

Finally, accelerated chloride ion permeability test showed that for Portland concrete (OPC, OPCL, and OPCA specimens), according to the assessing criteria, the penetrability values were in the range “very low” to “moderate”. Contrary the AAS concrete performed better than OPC concrete with respect to chloride penetrability. There was a good linear correlation between the initial current and the charge passing.

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