Title: Comparison of the durability of alkali-activated cements and ordinary Portland cement using accelerated degradation methods.

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ABSTRACT

This research focuses on the evaluation of the durability of alkali-activated mortars, using accelerated degradation methods, which allow us to analyze their impact on the resistance to chloride attack and corrosion of steel bars. The evaluation of the impact was carried out on mortars elaborated from the use of geopolymers, for which a dosage of zeolite, sand and calcium hydroxide $Ca(OH)_2$ as solid part and an alkaline activator sodium hydroxide Na (OH) in combination with sodium silicate as liquid part were elaborated, additionally a control sample elaborated with Portland cement was prepared. Properties in the fresh state (workability in mortar), in the hardened state (compressive strength) and its impact on corrosion (accelerated corrosion test ASTM C876-91) were evaluated. It was demonstrated that the incorporation of geopolymers can represent an increase in compressive strength of more than 50% compared to samples made with OPC. The workability of mortars made with geopolymers is similar to mortars made with OPC. It is concluded that samples made with geopolymers showed a better resistance against a highly aggressive environment compared to mortars made with OPC, due to their less porous structure.

Keywords: mortars, geopolymers, accelerated corrosión

1. INTRODUCTION.

New green building materials are an area of great interest in the construction field because they can contribute to reducing greenhouse gas emissions. Today, one ton of CO2 for every ton of cement produced is released into the atmosphere and contributes to climate change. In addition, the production of ordinary Portland cement (OPC) emits some 1.35 billion tons of carbon dioxide annually worldwide, accounting for 7% of the world's total. Due to its high consumption, OPC becomes a universal threat to living beings, as it consumes a lot of natural resources and thermal energy, in addition to emitting a huge amount of CO_2 (Aristizabal-Alzate & González-Manosalva, 2021). In this context, new building materials must be designed so that this gas is produced less or eliminated from the manufacturing process. Among other alternatives, alkali activated materials (AAM) can address this concern as a new way to reduce carbon dioxide generation.

The goal of reducing CO_2 has led the entire cement and concrete industry to search for cleaner production technologies and alternative binders over the last decade. Alkaline activators (MAA), also known as geopolymers, are obtained by a chemical reaction between an alkaline activator and a reactive aluminosilicate. The reaction process, the polymerization mechanism and the products of MAAs have been extensively studied. This manufacturing process, which is carried out at room temperature or slightly elevated temperature (60-80°C), is completely different from the traditional OPC calcination and milling process. Since the raw materials are widely available and include industrial wastes such as slag (SG), steel slag, fly ash (FA) and heat-activated clay (e.g. methacholine (MK)), AAM is environmentally friendly, which is much greener than OPC. Although they are more environmentally friendly, AAM have similar mechanical properties to OPCs and, in most cases, higher strength.(Marvila et al., 2021; Wang et al., 2020).

AAM have recently attracted attention as their performance in terms of mechanical properties and durability are like those observed in OPC-based materials, even superior in many cases. In OPC-based concretes, durability is a permanent threat in civil infrastructures due to exposure to aggressive climates (Aguirre & Mejía de Gutiérrez, 2013), corrosion of rebars, (Horsakulthai et al., 2011), chloride ion attack (Bai et al., 2003; Caré, 2003) (Chen et al., 2021; Marvila et al., 2021), carbonation (Chavez-Ulloa et al. 2013; Composites 2012; Frías and Goñi 2013) (Chang & Chen, 2006; Chavez-Ulloa et al., 2013), among others. These problems have led to an increase in the cost of maintenance and rehabilitation.

Durability in OPC is the ability to resist the action of weathering, chemical attack, abrasion or any other deterioration process to maintain its original shape, quality and serviceability when exposed to the intended environment. Knowing the durability of a concrete is a complex process in which different factors are involved, environmental conditions, concrete component materials, the structural design of the work, the quality of execution of the work, the protection systems adopted (Aguirre & Gutiérrez, 2013)(Tang et al., 2015).

Steel corrosion is a problem that occurs in reinforced concrete structures due to the ingress of chloride ions. Although the cement paste creates a passive film around the steel, unfortunately the chloride ion destroys this film and initiates corrosion in the reinforcing steel (Horsakulthai et al., 2011). Corrosion is the reaction of a metal with its environment, leading to the deterioration of its physical and chemical properties. The essential characteristic of this phenomenon is that it only occurs in the presence of an electrolyte, causing perfectly defined regions, known as anode and cathode (Paredes et al., 2001).

Corrosion due to chloride attack is one of the main failure mechanisms affecting the behavior of structures, especially in aggressive environments such as those near the coast. Concrete is responsible for providing physical and chemical protection to the reinforcement, preventing the entry of chlorides that can cause the steel to crumble, which poses a high risk of steel corrosion. The process of transmission of chloride ions into the cement takes place mainly through the connected pores of the cement. This process is not only constrained by changes in the composition, structure and performance of the cement itself, but is also affected by the external service environment of the cement, which makes the transmission mechanism of chloride ions in cement extremely complex (Ding et al., 2021).

A promising alternative that can be used to completely replace cement in concrete is an effective alkaline substance that produces geosynthetic concrete (Amran et al., 2021; Marvila et al., 2021). The name geopolymer was first coined by French researcher Joseph Davidovitz in 1970. The binder composition of geopolymer concrete includes aluminosilicate precursors and alkaline activators. The use of geopolymer concrete as an alternative to conventional OPC concrete has been shown to reduce cumulative carbon by up to 80%, depending on the precursors and activators used. A full life cycle assessment of geopolymers showed that geopolymer concrete is superior to OPC concrete in terms of greenhouse effect and eutrophication capacity. Life cycle assessments of geopolymers have shown that geopolymers are a sustainable alternative and that more significant improvements in durability can be achieved by using locally available alternative precursors and activators (Almutairi et al., 2021).

The objective of this study is to compare the durability of alkali activated mortars and OPC mortars using accelerated degradation methods to increase resistance to aggressive chloride attack and corrosion.

2. DISCUSSION AND DEVELOPMENT.

This research presents the evaluation of the resistance to degradation and corrosion mechanisms of mortars elaborated from the use of geopolymers, for which a dosage of zeolite, sand and calcium hydroxide Ca (OH)2 as solid part and an alkaline activator sodium hydroxide Na (OH) in combination with sodium silicate as liquid part were elaborated, additionally a control sample elaborated with Portland cement was prepared.

2.1. Materials used

Cements used: The cement used for comparison has a chemical composition of 67% CaO, 22% SiO2, 5% $Al2O_3$, 3% $Fe2O_3$ and 3% other components. The OPC used is a pozzolanic cement and is classified according to Ecuadorian standard NTE INEN 2380 as Type GU.

Aggregates: The sand used was extracted from a river and is classified as coarse sand for construction.

The zeolite was characterized by XRD (see Figure 1), where the diffractograms of the raw material in its as-delivered state are compared. The main mineral phases identified by XRD in the zeolite are: Quartz (18.9%), Modernite (28.8 %), Albite (3.5 %) and 48.8 % amorphous material. Zeolite shows a particle size distribution with two dominant fractions between 1 and 1000 μm (see Figure 2).

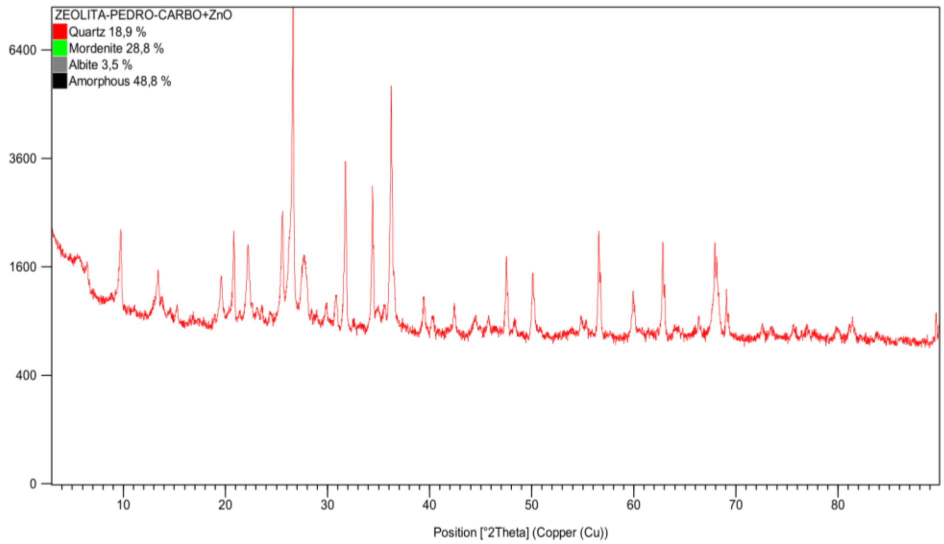


Fig.1. Resultados DRX de la zeolita

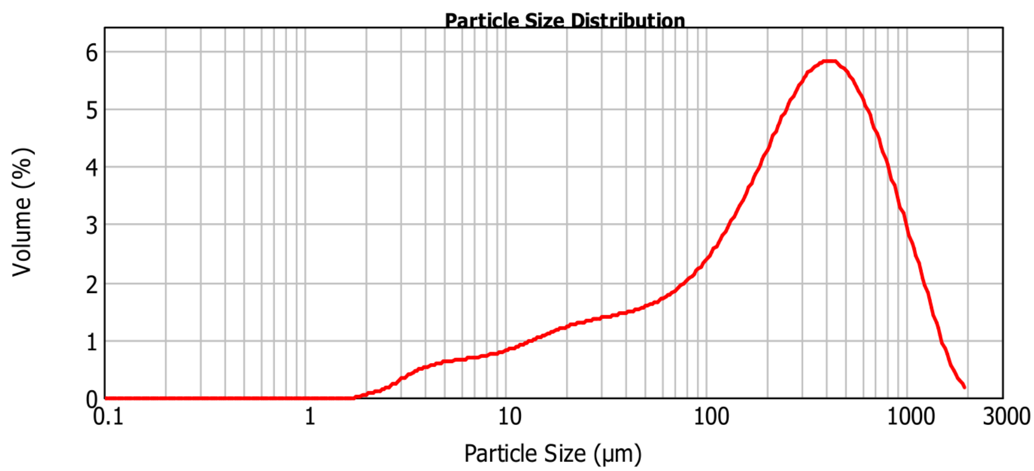


Fig.2. Resultados DTP

Alkaline activation solution: Sodium hydroxide Na (OH) beads with a purity of 99% were used as alkaline activation solution.

Sodium silicate: This was used to aid the workability of the mix (see table 1).

Calcium hydroxide: This was used to increase the strength and hardness of the sample. (see table 1)

Table 1. Chemical composition of raw materials.

Raw Materials	$Ca(OH)_2$	SiO_2	SO_4	Fe	NaO_2	CaC_3	CL	HCL	Density	Relation SiO_2/NaO_2
Calcium hydroxide	74.09	-	0.1	0.05	-	3	0.03	0.1	-	-
Sodium silicate	-	31.85	-	-	13.27	-	-	-	50.3	2.4

2.2. Experimental procedure.

Table 2 presents the proportions used, as well as the liquid/solid ratio, workability and strength values achieved during manufacture.

Table 2. Dosage used in the manufacture of mortars

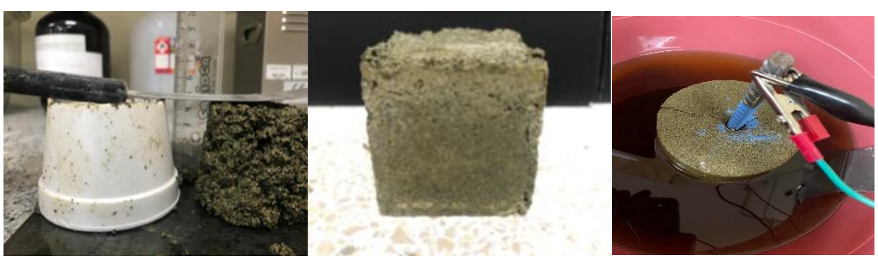
Sample	Experiment design			
	Raw materials		Workability (cm)	Mechanical Strength (MPa)
MC	Sand: Cement	"1:1"	0.3	7.0
	Water/Cement	0.5		
MG1	Ca(OH)2	10	0.3	11.1
	L/S	0.6		
	Zeolite/Sand	0.67		
	SS/NaOH	3		
MG3	Ca(OH)2	11.035	0.5	9.92
	L/S	0.6		
	Zeolite/Sand	0.67		
	SS/NaOH	2		

For the study, a dosage with a zeolite/sand ratio of 0.67 and a liquid/solid ratio of 0.6 was used for the samples made with geopolymers. A ratio of 3 between sodium hydroxide and sodium silicate was adopted. In the control sample data, a sand/cement ratio of 1:1: with a water/cement ratio = 0.5 was used. The specimens used for the evaluation of the tests were cylindrical specimens of dimensions 10 cm in diameter and 20 cm in height.

2.2.1. Ensayos físico mecánicos realizados.

The number of specimens used for each composition was 2 and the curing time was carried out at an oven temperature of 60 °C and analyzed after 28 days by increasing the degree of molecular agitation of the material.

Properties were evaluated in the fresh state (workability in mortar), in the hardened state (compressive strength) and its impact on corrosion (accelerated corrosion test ASTM C876-91 that determines the corrosive activity of the reinforcing steel).



a) Laborability b) Compressive strength c) Accelerated corrosion

Fig.3. Mortar testing protocol

The objectives of the experimental program are:

- Evaluate the impact of on the rheological and physical-mechanical properties of mortars.
- Evaluate geopolymers impact on the durability of mortars.

3. DISCUSSION OF RESULTS

3.1. Properties of mortars when fresh

The workability of the mortars produced reached similar values for both those made with geopolymers and those made with Portland cement type GU, as shown in Figure 4, although the MG3 samples showed a marginally superior performance.

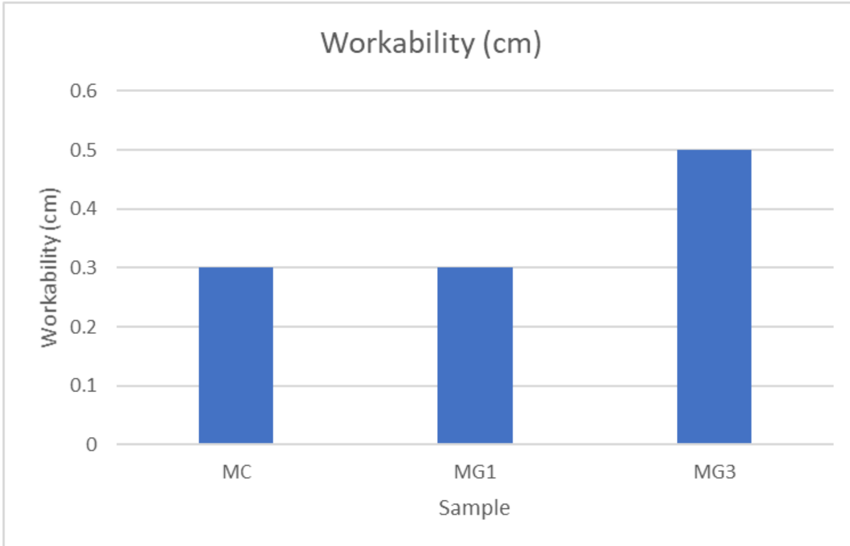


Fig. 4. Workability for mortars

3.2. Mortars properties in hardened state.

According to Figure 5, it is observed that the results obtained for compressive strength at 28 days for each of the samples evaluated. Significant differences are observed between the samples made with GU Portland cements and those made with geopolymers. An increase of approximately 58.5% in strength is observed, especially for the MG1 specimen with respect to the control specimen.

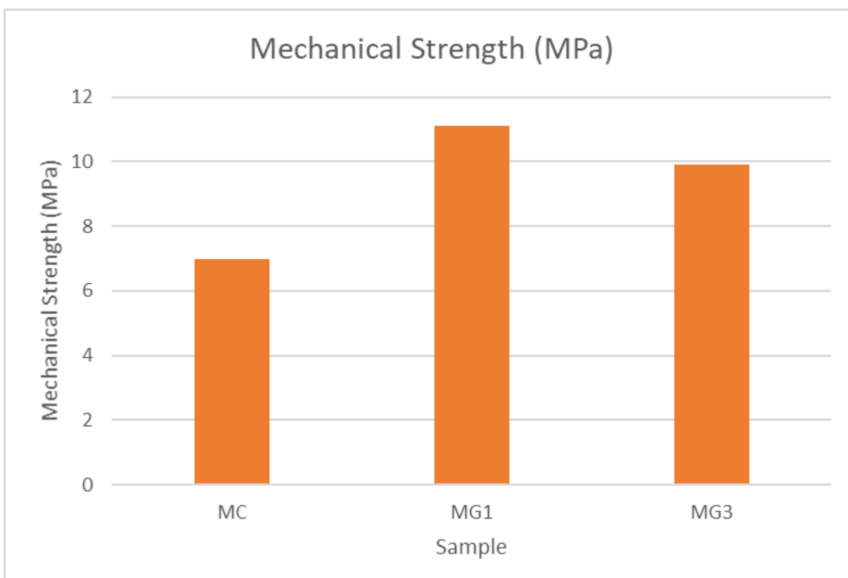


Fig. 5. Compressive strength values of the mortars studied.

his confirms what is stated in the literature that geopolymers can increase compressive strength. (Marvila et al., 2021; Uehara, 2010). These results demonstrate that the use of geopolymers ensures adequate performance of mechanical properties.

3.3. Impact of geopolymers on the durability of mortars.

3.3.1. Chloride ion breakthrough time

Generally speaking, in the accelerated corrosion test (ASTM C876-91, 1999; NT BUILD 356, 1989) the samples made with Portland cement show an unfavorable behavior, evidencing a higher corrosion rate. This is evidenced by a shorter time for the chloride ions to reach the steel bar, evidencing a higher permeability of the cementitious matrix.(Ziegler et al., 2016) (see Fig. 6a).

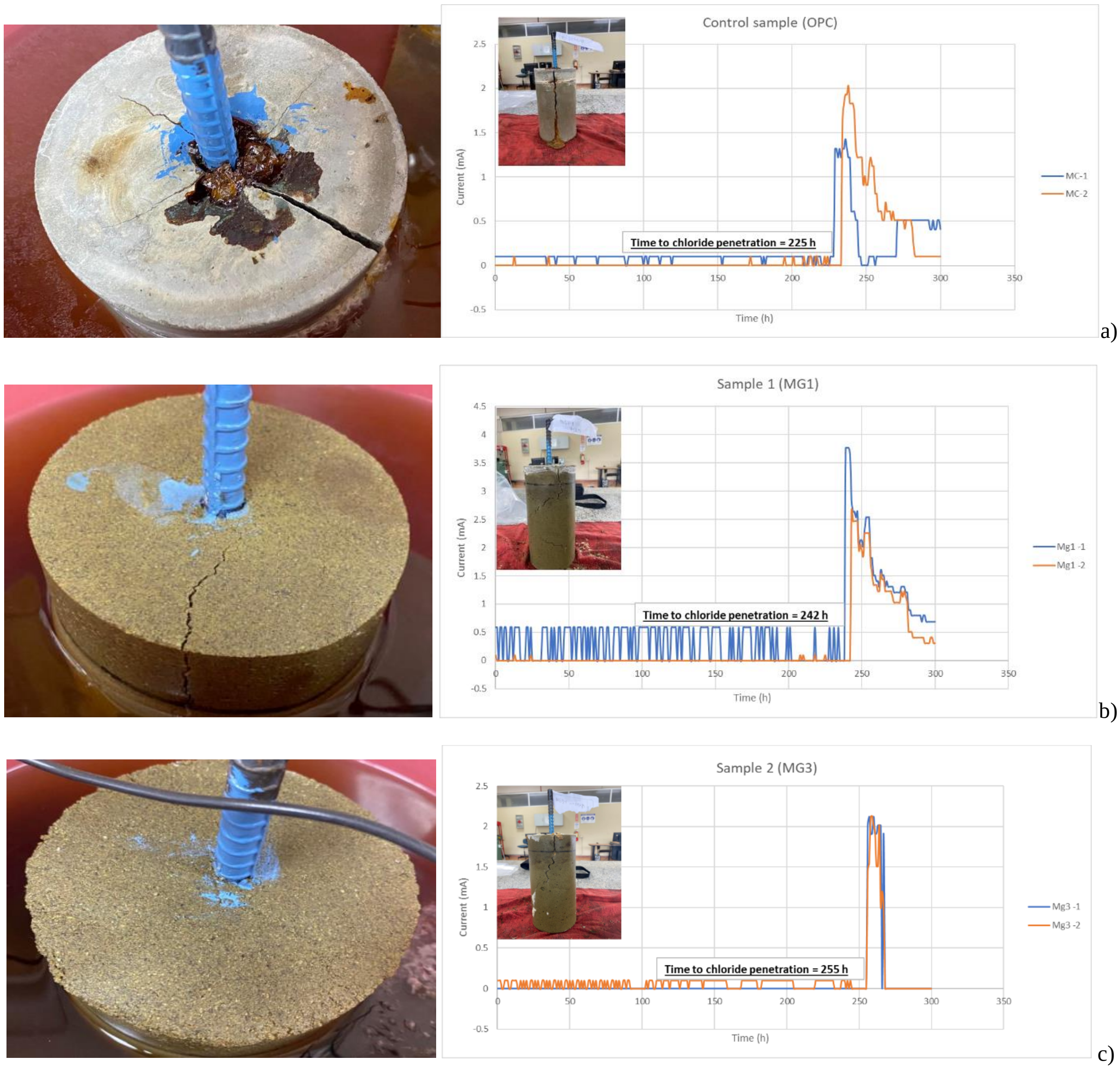


Fig. 6. Time to chloride penetration

On the other hand, the samples made with geopolymers show a favorable result, with an increase in the time in which corrosion begins of more than 13% with respect to the samples made with OPC, in addition to presenting a durability factor (Q) in the range of 1.1 - 1.5 (NT BUILD 356, 1989), which indicates that the samples made with geopolymers have a higher impermeability (see Fig. 6 b and c).

3.3.2. Corrosion of steel bars

As shown in Fig.7 and Table 3, the MC sample, made with Portland cement, shows a significant increase in weight loss than the MG1 and MG3 samples (made with geopolymers), which also corresponds to a higher permeability to chloride ion due to the direct relationship between these two parameters.(Elsener, 2002; Laurens et al., 2016).

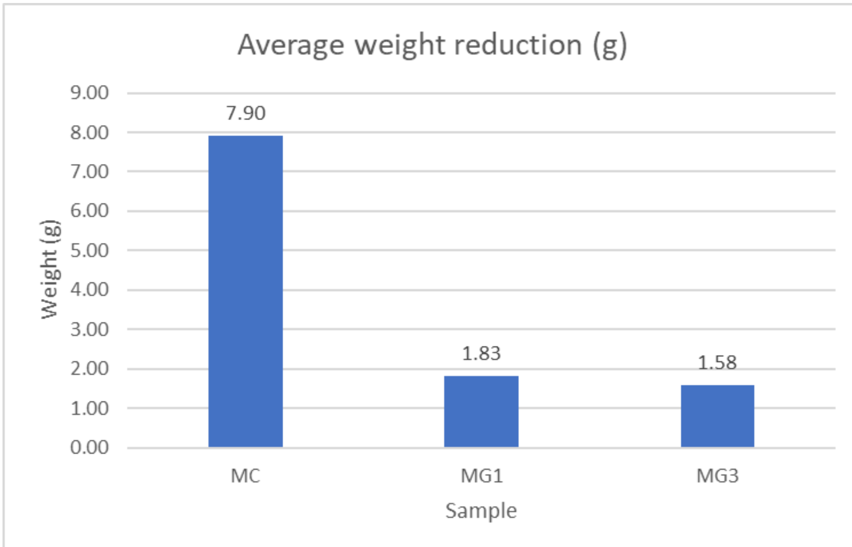


Fig. 7. Weight loss of steel bars

Table 3. Weight reduction of steel bars by corrosion

Sample	Experiment design Raw materials		Steel bars			Initial weight (g)	Final weight (g)	Weight reduction (g)	Average weight reduction (g)
MC	Sand: Cement	"1:1"				154.5	148.7	5.8	7.9
	Water/Cement	0.5				148.5	138.5	10	
MG1	Ca(OH)2	10				143.75	141.6	2.15	1.825
	L/S	0.6							
	Zeolite/Sand	0.67				135.3	133.8	1.5	
	SS/NaOH	3							
MG3	Ca(OH)2	11.035				149.2	148.1	1.1	1.575
	L/S	0.6							
	Zeolite/Sand	0.67				145.75	143.7	2.05	
	SS/NaOH	2							

In Table 4, considering the electrical potential values as corrosion probability indexes, all mortars are classified according to the following standard (ASTM C876-91, 1999) in the ranges of corrosion probability ≥ 95 % respectively.

Table 4. Half-cell test electrical potential results

Accelerated corrosion							
Sample	Experiment design			Half Cell			
	Raw materials		Cross-Section	V. Initial (V)	Average Initial Voltage (V)	V. Final (V)	Average Final Voltage (V)
MC	Sand: Cement	"1:1"		-0.1349	-0.140	-0.7547	-0.806
				-0.138		-0.7048	
	Water/Cement	0.5		-0.1358		-0.7336	
				-0.1352		-0.863	
				-0.1542		-0.881	
				-0.1441		-0.8988	
MG1	Ca(OH)2	10		-0.2962	-0.325	-0.7932	-0.784
				-0.2957		-0.7874	
	L/S	0.6		-0.2963		-0.785	
				-0.3572		-0.7861	
	Zeolite/Sand	0.67		-0.353		-0.7769	
	SS/NaOH	3		-0.3541		-0.7755	
MG3	Ca(OH)2	11.035		-0.2795	-0.384	-0.7707	-0.772
				-0.2799		-0.7664	
	L/S	0.6		-0.2808		-0.7645	
				-0.4876		-0.7801	
	Zeolite/Sand	0.67		-0.4887		-0.7797	
	SS/NaOH	2		-0.4891		-0.7689	

From the point of view of this test, it can be seen that the mortars manufactured with geopolymers in samples MG1and MG3 present a lower permeability than the control sample identified as MC where Portland cement was used. Regardless of the fact that all of them have a corrosion probability higher than 95%, when relating these results with those of weight reduction in Figure 8, it can be seen that indeed samples MG1 and MG3 show a lower weight variation characterized by a lower deterioration of the steel bars than the control sample MC.

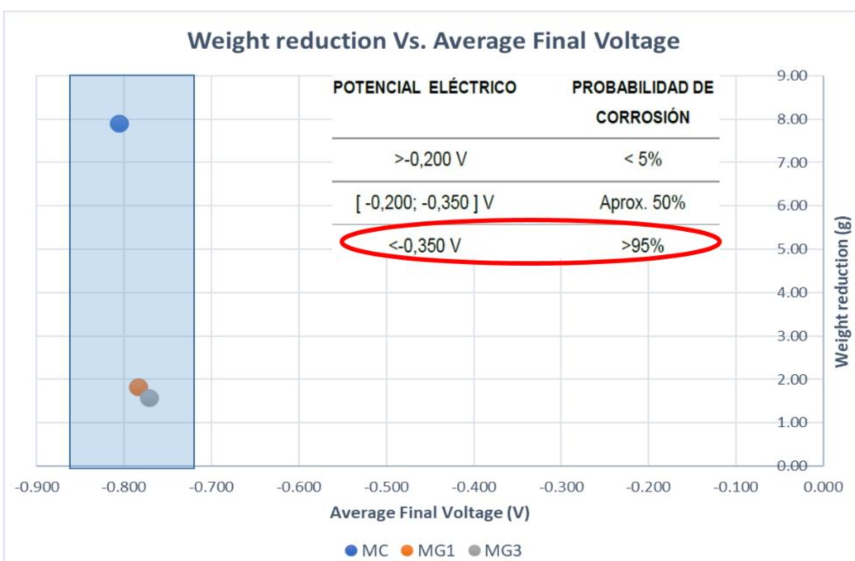


Fig. 8. Weight reduction Vs. Average Final Voltage

It is concluded that samples made with geopolymers showed better resistance against a high aggressive environment compared to mortars made with OPC, due to their less porous structures. In addition, the strength of alkali activated mortars was found to improve in a high aggressive environment, unlike mortars made with Portland cement.

4. CONCLUSIONS

1. The workability of mortars made with geopolymers is similar to mortars made with OPC.
2. It was demonstrated that the incorporation of geopolymers can represent an increase in compressive strength of more than 50% compared to samples made with OPC.
3. It is concluded that the samples made with geopolymers showed a better resistance against a high aggressive environment compared to the mortars made with OPC, due to their less porous structure.
4. Further long-term durability studies are recommended to provide test methods and validation techniques, as most studies focus on the 28-day curing regime.

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