Short and Long-Term Effect of Sodium Chloride on Strength and Durability of Coal Fly Ash Stabilised with Carbide Lime

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<th>Journal:</th>
<th>Canadian Geotechnical Journal</th>
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<tr>
<td>Manuscript ID</td>
<td>cgj-2018-0696.R2</td>
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<tr>
<td>Manuscript Type</td>
<td>Article</td>
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<tr>
<td>Date Submitted by the Author:</td>
<td>08-Feb-2019</td>
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<tr>
<td>Complete List of Authors:</td>
<td>Consoli, Nilo Cesar; Universidade Federal di Rio Grande do Sul, Saldanha, Rodrigo; Universidade Federal di Rio Grande do Sul Scheuermann Filho, Hugo; Universidade Federal di Rio Grande do Sul</td>
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<tr>
<td>Keyword:</td>
<td>environment-friendly product, short and long-term behavior, reuse of industrial wastes, sodium chloride, strength and durability</td>
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<td>Is the invited manuscript for consideration in a Special Issue?</td>
<td>Not applicable (regular submission)</td>
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Short- and Long-Term Effect of Sodium Chloride on Strength and Durability of Coal Fly Ash Stabilised with Carbide Lime

Nilo Cesar Consoli, Ph.D. 1; Rodrigo Beck Saldanha, Ph.D. 2; and Hugo Carlos Scheuermann Filho, M.Sc. 3

ABSTRACT: The present research aims to quantify the influence of the curing period (t), dry unit weight (γ_d), lime amount (L), and the addition of sodium chloride (NaCl) on the short and long-term behaviour of coal fly ash-carbide lime blends. Strength and wet-dry durability tests were carried out for differing values of η (porosity), L, and t (curing time) on mixtures that either contained small amounts of NaCl or contained none. Addition of NaCl to the mixtures resulted in significant increase in early strength gain when compared to specimens without NaCl, which demand longer curing periods to reach similar strength values. The addition of NaCl to coal fly ash-carbide lime blends reduced the accumulated loss of mass (ALM) after 12 wet-dry-brushing cycles for specimens at early stages of curing (about 50% for 7 days). Equivalence in the unconfined compressive strength (q_u) and ALM_{after 12 wet-dry cycles} between the specimens with and without NaCl is achieved in the long term. Finally, a variance analysis performed regarding q_u and ALM results yielded that the order of importance of the controllable factors changed from t, NaCl addition, γ_d and L for strength to γ_d, t, NaCl addition, and L for ALM_{after 12 wet-dry cycles}.

Keywords: short and long-term behavior; coal fly ash; carbide lime; sodium chloride; durability; strength; environment-friendly product.

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1. INTRODUCTION

The construction industry is a significant exploiter of natural resources and contributes notably to environmental impacts (Spence and Mulligan 1995). In addition, those resources are finite and, owing to their unrestricted exploitation, the needs of future generations are being compromised. Hence, there is a prominent necessity to substitute the standard materials and techniques with environment friendly alternatives that present satisfactory mechanical performance.

In this sense, fly ash (FA), originated as a residue of coal combustion at thermal power plants, possesses characteristics (e.g. chemical composition and mineralogical structure) that enables it to be used in the building industry for distinct purposes (Wang and Wu 2006). In the same context, carbide lime (CL), also termed calcium carbide residue, is a by-product of acetylene gas production and due to its composition (mainly calcium hydroxide) can be adequately employed as an alkaline activator in the stabilization of soils and/or pozzolanic materials. Therefore, carbide lime can alkali-activate the coal fly ash and generate cementitious hydration compounds that can be useful for civil engineering like pavement, bricks, soil stabilization and monolithic walls (Beeghly 2003; Consoli et al. 2014a; Saldanha et al. 2017; Jiang et al. 2016; Phummiphan et al. 2017, 2018; Mohammadinia et al. 2017).

The pozzolanic reactions are characterized by the interaction between the calcium hydroxide and the active phase of the pozzolan, which is capable of combining the lime in a hydrated environment and originate binding compounds (Massazza 1998). In the FA-CL system, the hydroxyls (OH\textsuperscript{-}) attack the vitreous phase of the FA (mainly composed of Al\textsubscript{2}O\textsubscript{3} and SiO\textsubscript{2}) through the breakage of the O-Al and O-Si bonds. This implies increased concentration of SiO\textsubscript{3}\textsuperscript{2-} and AlO\textsubscript{2}\textsuperscript{-} ions, which dissolve and react with lime forming poorly crystalline cementitious hydrating products such as calcium silicate hydrate (C-S-H), calcium aluminate silicate hydrate (C-A-S-H), among others (Ingles and Metcalf 1972; Berry et al. 1994; Fu et al. 2002; Malek et al. 2005; Singh and Pani 2014). Nevertheless, the rate of development of pozzolanic reactions in such materials can be considerably slow, which implies the need of long curing periods in order to attain adequate mechanical features. This is one of the main reasons for the underutilization of these kinds of materials in favor of the usage of Portland cement by the standard construction industry, in spite of the environmental issues attached to its
use (Cristelo et al. 2015; Fernández-Jiménez 2017). In order to counteract this tendency, we can attempt to employ stronger alkaline activators (e.g. KOH and NaOH) and/or combine alkaline activators with chemical additives (e.g. NaCl, Na$_2$SO$_4$ and K$_2$CO$_3$) capable of catalyzing the pozzolanic reactions and accelerating strength development in the mixtures. Consequently, the performance requirements would be attained sooner when compared with regular blends (without additives). For the analysis of the mechanical behavior of cemented materials Du et al. (2014) determines some microstructural investigations to characterize the product of cementation, such as: X-ray diffraction (XRD), scanning electron microscopy (SEM), and mercury intrusion porosimetry (MIP). Other tests such as thermogravimetry aid in the identification of hydrated compounds, as well as in the verification of the influence of addition of additives/accelerators on cementation processes (Kishar et al. 2013).

Regarding the usage of chemical additions, Davidson et al. (1960) attested that the addition of small amounts of sodium chloride (NaCl) resulted in strength gain in a soil stabilized with lime and fly ash. In this sense, Mateos (1961) and Narendra et al. (2003) found similar trends, respectively, in soils from Iowa and India, both stabilized with fly ash and lime. Recently, Saldanha et al. (2017) assessed the effect of the addition of NaCl in the durability of a fly ash – carbide lime blends and attested a significant improvement in performance due to this addition for 7 and 28 days. Nevertheless, little is known about the long-term performance concerning fly ash-carbide lime blends with NaCl addition. The great advantage of using sodium chloride instead of sodium silicate or sodium hydroxide is its great availability, reduced market price and reduced amount necessary to accelerate pozzolanic reactions (about 1%) (Saldanha et al. 2017). Otherwise, this accelerator has elements that corrode some metals, so its application should be restricted to structures without steel (e.g. Apostolopoulos et al. 2013).

Regardless of the influence caused by the employment of additions such as NaCl, it is essential to assess other parameters that control the mechanical response of stabilized materials such as lime content (L), porosity ($\eta$) and curing time (t). Hence, it is possible to correlate them with the mechanical response of the material, which can be expressed in terms of unconfined compressive strength (UCS) and durability (Haque et al. 2014; Dash and Hussain 2015; Consoli et al. 2018a). Those tests are commonly engaged in
order to quantify and qualify the influence of the key-parameters that control the response of the stabilized specimens due to its simplicity and effectiveness.

Accordingly, the present research intends to assess the mechanical behavior (unconfined compressive strength and durability) of fly ash stabilized with carbide lime and sodium chloride through wet-dry cycles considering a long curing period range. The evaluated controllable factors are the curing period, the porosity, the amount of carbide lime and the sodium chloride content. Furthermore, the formation of binding compounds and the calcium hydroxide consumption are evaluated along the curing periods.

2. MATERIALS AND METHODS

2.1 Materials

The coal fly ash studied herein comes from southern Brazil, which is the main region of mineral coal exploitation and thermal electricity production in Brazil, generating an amount of 3 to 4 million tons/year of coal ash. The coal encountered in this zone is sub-bituminous with a calorific value between 4200 to 2600 kcal/kg and its ash content ranges between 42% and 59%. Thus, this coal possesses a moderate heating value and generates a large amount of ash as a residue which is classified as type F according to ASTM C618 (ASTM 2017). X-ray fluorescence (XRF) tests revealed that the studied ash is mainly composed of silicon (64.83%), aluminum (20.41%) and iron (4.83%), which are important elements in the development of the pozzolanic reactions. The vitreous fraction of coal fly ash encountered in southern Brazil varies between 50% and 70% (Gobbo et al. 2007) with mineral phases corresponding to hematite, quartz and mullite (Consoli et al. 2017). Table 1 presents more details regarding the physical characteristics of the FA.

The calcium carbide lime \([\text{Ca(OH)}_2]\) is a by-product of the acetylene gas production and is generated nearby the fly ash generation site (~ 30 km). In Brazil, the carbide lime production is about 12 million tons/year. As stated by Saldanha et al. (2018), this residue presents favorable characteristics in order to be used in soil and/or residues stabilization processes, and CL has no environmental impact for heavy metals. The XRF tests attested that this lime is mainly composed by calcium oxide (70.0%) and silicon oxide (3.1%). The CL is generated as aqueous slurry, and was previously dried.
in an oven at 60°C for 48 hours until the moisture content reached 0.50%. This lime was utilized in all of the tests.

The sodium chloride is manufactured by a specialized company, its analytic pureness is of 99% and its specific gravity is 2.17. Distilled water was used in all the steps of the present research.

2.2 Methods

In order to determine the minimum amount of lime, the Initial Consumption of Lime method (ICL), proposed by Rogers et al. (1997), was employed. This one consists in measuring the pH variation of the mixture due to the addition of lime and check the minimum content responsible for the pH stabilization. Through this procedure it was established that a minimum content equal to 5% of carbide lime was needed to create a favorable environment to the occurrence of the alkali-activation processes. Thus, the CL contents used herein were 5%, 8% and 11%.

The dry unit weights ($\gamma_d$) of the coal fly ash-lime blends were defined based on standard energy Proctor tests (ASTM 2012a) and on modified energy Proctor tests (ASTM 2012b) (see Figure 1). Through the results (maximum dry unit weight and optimum moisture content) of three tests the line of optimum (see Figure 1) for distinct energies was defined and three maximum distinct dry unit weights and their respective optimum moisture contents were defined as P1: 11.2 kN/m³ (29.8%), P2: 12.2 kN/m³ (25.7%) and P3: 13.2 kN/m³ (21.6%).

The definition of the amount of NaCl in the mixtures were based on pilot UCS tests with FA-CL blends presenting 12.2 kN/m³ (25.7% of moisture) and 8% of CL which were cured along 28 days at 23°C. The specimens were molded in triplicates and three distinct NaCl contents were tested (0.5, 1.0 and 1.5%). The pilot tests revealed that a content of sodium chloride equal to 1.0% was responsible for the maximum strength gain, which is in accordance to previous researches (Saldanha et al. 2016; Ramesh et al. 1999). Hence, the specimens were tested without NaCl (0%) and with 1.0% of NaCl in respect to the sum of fly ash and carbide lime dry masses.

Intending to assess the mechanical behavior of the studied blend for long curing periods, unconfined compressive strength tests (ASTM 2009) and durability through
wet-dry tests (ASTM 2015) were carried out. This standard (ASTM D559) determines the loss of mass (brushing process), volume and moisture variations of soil cement specimens during 12 cycles of wetting and drying. For the former (UCS), curing periods equal to 7, 14, 28, 84, 168 and 360 days were selected, while for the latter 7, 14, 28, 84 and 168 days were established as curing times.

X-Ray diffraction tests (0.05° step size, 1s for scan step time and 5°<2θ<75° range), thermogravimetry tests (TGA) (10 °C/min from room temperature up to 1000°C) and scanning electron microscopy tests (SEM) (Microscope Model: XL 30 – Philips) were performed in the cured blends aiming to investigate the mineralogical phases created during the cementing reactions for samples with intermediate parameters: 12.2 kN/m³, 8% CL, and with/without NaCl. The samples used for the mineralogy tests were obtained from the UCS test specimens after being taken to failure, considering all the studied curing times.

A complete factorial design was accomplished with the chosen factors (and their levels), which allowed the usage of a statistical analysis of variance (ANOVA). Therefore, it was possible to determine the statistical significance of the main factors (and their interactions) in altering the response concerning the unconfined compressive strength and the durability of the studied blends. The analytical tool used was Minitab® which allowed the analysis independent variables studied to a level of significance of 95%. Table 2 summarizes the investigated treatments performed in each one of the tests.

2.2.1 Unconfined Compressive Strength

For the UCS tests, the procedure followed the recommendations stated by ASTM D5102 (ASTM 2009). The molding processes included (i) the weighting, (ii) the mixture and (iii) the static compaction of each specimen. When NaCl was used, it was previously diluted in the water used for the mixture. The molding was statically done in a cylindrical split mold and, after it was accomplished, each specimen was weighed, measured and sealed in a plastic bag to be stored in a humid room with controlled moisture (95%) and temperature (23°C). After the curing period was achieved, the specimens were immersed underwater for 24 hours in order to minimize suction effects (Consoli et al. 2011). The range of acceptance of the degree of compaction varied between 99% and 101% and triplicates were done for each treatment. The UCS results
were correlated to the adjusted porosity/volumetric lime content index ($\eta/L_v^a$). This correlation enables the strength prediction of soils and residues stabilized with lime and/or cement through a single unique relationship (Consoli et al. 2009).

### 2.2.2 Durability Through Wet-Dry Cycles

The durability tests followed the recommendations described by the standard ASTM D559 (ASTM 2015). Duplicates were molded for each treatment, one to be brushed along the cycles and other in which the volumetric and moisture variations were verified. After the curing period, the specimens were submitted to the cycles that initiated by immersion underwater for 5 h, followed by oven drying at 71°C for 42 h and then brushed with a force equal to 13.3 N (20 brushings along the circumference of the specimen covering it twice and 4 brushings in the top and in the bottom). Those procedures were repeated 12 times. As done for the UCS results, the durability results (presented as accumulated loss of mass for each cycle) were correlated to the $\eta/L_v^a$ index. This allows the loss of mass prediction of the stabilized specimens through a single unique relationship (Consoli et al. 2018b).

### 3. RESULTS AND DISCUSSIONS

#### 3.1 Unconfined Compressive Strength

The unconfined compressive strength results were correlated to the adjusted porosity/volumetric lime content index through a power equation in accordance to the form presented below [Eq. (1)]. An internal exponent equal to 0.11 was employed in order to adjust the $L_v$, which resulted in an external exponent of -3.0.

$$q_u(MPa) = A_s\left[\frac{\eta}{(L_v)^{0.11}}\right]^{-3.0} \quad \text{Eq. (1)}$$

In this equation, $q_u$ corresponds to the unconfined compressive strength of the cemented material (MPa), $A_s$ is the scalar, $L_v$ is the volumetric lime content which is expressed by the ratio between the volume of lime and the total volume of the specimen (%); and $\eta$ is the porosity of the mixture (%).

The internal exponent (0.11) of Eq. (1) was chosen as it provides the best fit (higher coefficient of determination) for the coal fly ash – carbide lime blends, considering its
range varies from 0.01 to 1.0 (Consoli et al. 2014a; Saldanha et al. 2017). The external exponent (3.0) of Eq. (1) has seen to be around 3.0 for all previous studies of distinct soil and/or coal fly ashes stabilized with different limes (Consoli et al. 2014b; Saldanha et al. 2017). In the present study, it also showed excellent responses. However, further studies still have to be carried out to develop a theoretical derivation explaining the internal and external exponents of Eq. (1) for lime treated materials, as the development described by Diambra et al. (2017) for soil-Portland cement blends.

Figure 2 shows the UCS results for distinct curing periods and also for the mixtures with and without the addition of NaCl. Accordingly, within the experimental limits tested herein, it is possible to predict the unconfined compressive strength of the mixtures through the ratio between porosity and volumetric lime content for distinct curing periods and with (or without) the addition of sodium chloride.

Table 3 presents the functions (Eqs. 2 to 13) for the specimens without and with the addition of NaCl for the curing periods (7, 14, 28, 84, 168, and 365 days). For all curing times studied, without NaCl and with 1.0% of NaCl addition, the unconfined compressive strength related to $\eta/\eta_0^{0.11} - 3.0$ with satisfactory coefficients of determination ($R^2 > 0.93$). Thus, it is observable that the strength behavior follows similar trends for the mixtures with and without the addition of NaCl. It allows the establishment of single relationships that correlate porosity and volumetric lime content with the UCS (with 1.0 NaCl and without NaCl) by using distinct scalars depending on the curing periods.

Correlations with time of curing are presented in Figure 3 and evidence the significant early strength gain proportioned by the addition of sodium chloride in comparison with the specimens without NaCl, which demand longer curing periods to reach similar strength values. Moreover, it is possible to add the curing period (t) as a variable through the normalization of the previous equations by dividing $q_u$ per $[\eta/\eta_0^{0.11}]^{-3.0}$. These results are shown in the Eqs. (14) and (15), that can predict the strength of fly ash – carbide lime blends without and with 1.0% NaCl, respectively. The former presents significant strength gains until 84 days of curing, while in the latter strength increase is observed until 168 days. After this period of 168 days the mechanical behavior is similar for the mixtures with and without NaCl. As most chemical additives/accelerators ionize in water by adding them to the cementation system, it is possible to change the
type and concentration of the ionic constituents of the aqueous solution, thus influencing the dissolution of the cementing compounds. In the present case, the addition of Na$^+$ and Cl$^-$ ions (in certain amounts) promotes influence on the solubilization of calcium, silicates and aluminates (Joiel 1973). Consequently, favors the formation of hydrated compounds (binders) at an early stage.

\[ q_u = \left[ -5.2 \times 10^{-4} t^2 + 0.33(t) - 2.7 \right] \times 10^4 \left[ \frac{\eta}{(L_p)^{0.11}} \right]^{-3.0} \quad (R^2=0.97) \quad \text{Eq. (14)} \]

\[ q_u = \left[ 11.21 \times \ln(t_{NaCl}) - 11.33 \right] \times 10^4 \left[ \frac{\eta}{(L_p)^{0.11}} \right]^{-3.0} \quad (R^2=0.93) \quad \text{Eq. (15)} \]

The variance analysis (Table 4) performed in the strength results yielded that the four controllable factors were significant in altering the unconfined compressive strength. Curing period (B), sodium chloride addition (D), dry unit weight (A) and amount of carbide lime (C) were, in this order, the most significant in altering this response (F-Value). Second-order interactions were also statistically significant, especially the interactions between dry unit weight and curing time (AB), dry unit weight and NaCl (AD) and the one between curing time and usage of NaCl (BD).

### 3.2 Mineralogy

The X-Ray patterns for the mixtures with and without NaCl are presented in Figure 4. The main mineral phases identified herein are hematite, mullite and quartz, which are present in the fly ash; portlandite and calcite, arising from the carbide lime; and a mineral form of calcium silicate hydrate that forms due to the pozzolanic reactions in both mixtures (with and without NaCl). In addition, for the mixtures with NaCl, peaks relative to the calcium aluminum chlorohydrate (Ca$_2$Al(OH)$_6$Cl•2H$_2$O) (e.g. \(\sim 11.3^\circ\), 22.5$^\circ$ and 23.5$^\circ$ 2Theta) were observed (Ma et al. 2015; Ogirigbo and Black 2017; Shao et al. 2013). This mineral is formed due to the reaction of alumina (Al$_2$O$_3$ - reactive) in conjunction with calcium and chlorine (Talero et al. 2011). Through the thermogravimetric results (DTG and TGA) of the NaCl containing specimens (Figure 5) it was possible to identify the degradation peak of calcium aluminum chlorohydrate near 290 – 320$^\circ$C and other peaks between 600 – 800$^\circ$C relative to the volatilization of the CO$_2$ that occurs due to the degradation of the carbonates, decomposition of
anhydrous groups and degradation of remaining hydroxyl groups (Shi et al. 2017; Grishchenko et al. 2013; Lannegrand et al. 2001).

Regarding the cementitious compounds, it is observable in the XRD patterns that the peak relative to the calcium silicate hydrate (29.4° 2Theta) grows as the curing period increases for both mixtures (with and without NaCl). This is an indicative of the formation of such compounds along the curing time. The same trend is also observable through the DTG and TGA results for the temperature range between 30°C and 300°C that corresponds to the degradation of aluminates and silicates hydrate binding compounds (Rojas 2002).

For the mixtures containing NaCl, it is possible to attest a more remarkable presence of hydrate cementitious binders at the early stages of curing. Analogously, the consumption of calcium hydroxide, used in the pozzolanic reactions, is more pronounced at this early phase when sodium chloride is added. This can be noticed by the decreasing of the Ca(OH)₂ peak in the DTG curve (between 350°C and 450°C) which is relative to the dehydration of lime (Saldanha et al. 2017). The same Ca(OH)₂ peak decay tendency is observed as the curing period increase, indicating the consumption of lime in the pozzolanic reactions.

For the NaCl containing specimens this decrement stops at 84 days, while this happens after 168 days for the ones without NaCl. This corroborates the stagnation in the strength gains presented in Figure 3. Thus, the sodium chloride performs as a catalyzer of the pozzolanic reactions and enables a faster consumption of carbide lime for the formation of cementitious compounds. The same trend regarding the Ca(OH)₂ consumption is also shown in the XRD patterns through the decay of the portlandite peaks (e.g. ~18°, 29° and 34° 2Theta).

Figures 6(a) and 6(b) present the morphology (obtained through SEM tests) of the mixtures cured along 28 days with and without the addition of NaCl, respectively. In both images it is possible to observe spheres that corresponds to the fly ash. Besides, precipitated binding compounds (C-S-H) are visible and form a net-like structure like characterized in literature by Mehta and Monteiro (2006) and Hilal (2016). In the present SEM test it is possible to attests the net-like structure is more pronounced and denser in the specimen containing NaCl [Fig. 6(b)].
3.3 Durability

As previously showed for the strength tests, the results regarding the accumulated loss of mass (ALM) after 12 wet-dry-brushing cycles were correlated to the porosity/volumetric lime content index. This approach was already done by Consoli et al. (2017 2018b) in the prediction of the ALM per cycle for specimens cured along 7 days. Nevertheless, this method is applied herein for distinct curing period and for mixtures with and without NaCl.

Figure 7 presents the accumulated loss of mass results as a function of the adjusted $\eta/L_{v0.11}$ (best fit) index for the mixtures with and without NaCl and cured along 7, 14, 28, 84 and 168 days. In general, it is observable that the addition of NaCl implied in smaller mass losses, especially for short curing periods. However, both mixtures (with and without NaCl) presented the same trend regarding the mass loss along the cycles, which allowed the same model of equation [Eq. (16)] to represent their behavior along the different curing periods.

$$ALM(\%) = A_s\left[\frac{\eta}{(L_v)^{0.11}}\right]^{7.0}$$  \hspace{1cm} Eq. (16)

The Equation (16) is of the power type and is the general representation of the durability tests results, being obtained as the best fit for those results at each curing period and two sodium chloride contents (zero and 1%). The external exponent was adjusted as 7.0, the internal was maintained equal to 0.11 (equal for the UCS equation) and the scalar ($A_s$) is a function of the curing period and the presence of sodium chloride in the mixes. The coefficients of determination ($R^2$) obtained herein were greater than 0.94, which demonstrates a satisfactory adjustment between this kind of approach and the obtained results.

The equations for all results are shown in Table 5 [Eqs. (17) to (26)], and were obtained for the blends without and with NaCl and cured for 7, 14, 28, 84 and 168 days. For all curing time studied and without NaCl and with 1.0% of NaCl addition, the accumulated loss of mass (ALM) related to $[\eta/L_{v0.11}]^{-3.0}$ with high coefficients of determination ($R^2 > 0.94$).

In order to insert the curing period ($t$) as a variable in the prediction of the durability performance (accumulated loss of mass) of the studied blends, the same normalization
procedure as previously done for the strength tests was performed herein (Figure 8). Thus, Equations (27) and (28) were obtained, respectively, for the mixtures without NaCl and with NaCl. It is noticeable that the addition of sodium chloride improves the performance in the early stages of curing. The equality in the performance between the specimens (with and without sodium chloride) is attained at 84 days of curing. This parity between the mixtures is achieved earlier than the observed for the strength results due to the catalyzer effect generated by the temperature (71°C ± 2°C) at which the specimens are submitted during the drying periods, which accelerates the pozzolanic reactions.

\[
ALM (\%) = [9.22 (t)^{-0.55}]\left[\frac{\eta}{(L)^{0.11}}\right]^{7.0} \times 10^{-11} \quad (R^2=0.99) \quad \text{Eq. (27)}
\]

\[
ALM_{NaCl} (\%) = [2.69 (t_{NaCl})^{-0.27}]\left[\frac{\eta}{(L)^{0.11}}\right]^{7.0} \times 10^{-11} \quad (R^2=0.96) \quad \text{Eq. (28)}
\]

Table 6 shows the results of the statistical analysis (ANOVA) performed for the total loss of mass results for all variables and their levels studied. In this case, all variables are significant in the alteration of the response variable (ALM), being: density, time, addition of NaCl, and carbide lime content the factors (from highest to lowest) (F-Value). In this case, the sequence of the factors with capacity to change the durability diverge from the RCS results and is attributed to the 12 wetting and drying cycles required to simulate an accelerated degradation of the cemented material that influence the pozzolanic reactions (Rao and Asha 2012).

4. CONCLUDING REMARKS

Based on the findings portrayed in this research, the following conclusions can be drawn:

- Significant early strength gain (up to approximately 5 times for specimens in the early stages of curing - 7 days) is proportioned to coal fly ash-carbide lime blends by the addition of sodium chloride (NaCl) in comparison with the specimens without NaCl, which demand longer curing periods to reach similar strength values. The former presents
significant strength gains until 84 days of curing, while in the latter strength increase is observed until 168 days. After this period of 168 days the mechanical behavior is similar for the mixtures with and without NaCl, meaning that NaCl acts uniquely as a catalyzer;

- The addition of NaCl to coal fly ash-carbide lime blends reduces the accumulated loss of mass (ALM) after 12 wet-dry-brushing cycles (about 50% for 7 days of curing) in the early stages of curing. Equality in the performance between the specimens with and without sodium chloride is achieved at 84 days of curing. This parity between the mixtures is reached earlier than the observed for strength results due to the catalyzer effect generated by the temperature (71°C ± 2°C) at which the specimens are submitted during the drying periods, which accelerates the pozzolanic reactions;

- Individual relationships $q_u$, $\eta$ and $L_v$ versus $t$ (see Fig. 2), as well as $ALM_{(after 12 ~wet-dry ~cycles)}$, $\eta$ and $L_v$ versus $t$ (see Fig. 7) were obtained for fly ash-carbide lime and fly ash-carbide lime-NaCl;

- A variance analysis performed in the strength results yielded that the order of importance of the controllable factors was (1) curing period, (2) sodium chloride addition, (3) dry unit weight and (4) amount of carbide lime, while the same analysis regarding loss of mass results yielded distinct results: (1) dry unit weight, (2) curing period, (3) sodium chloride addition, and (4) carbide lime content.

ACKNOWLEDGEMENTS

The authors wish to express their appreciation to Edital 12/2014 FAPERGS/CNPq – PRONEX (project # 16/2551-0000469-2), CNPq (Edital Universal, INCT-REAGEO and Produtividade em Pesquisa) and PROEX-CAPES for funding the research group.
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chloride on the durability of compacted geopolymers monolithic walls.”


Table Captions

Table 1. Physical properties of coal fly ash and carbide lime.

Table 2. Investigated treatments.

Table 3. Equations for UCS without and with NaCl according to the curing period.

Table 4. ANOVA for the unconfined compressive strength.

Table 5. Equations for ALM without and with NaCl according to the curing period.

Table 6. ANOVA for the durability (wet and dry cycles).

Figure Captions

Figure 7. Compaction test results.

Figure 8. Variation of UCS with adjusted porosity/volumetric lime content without NaCl (left) and with 1.0% NaCl (right).

Figure 9. Relationship for the variation of UCS with $\eta$, $L_v$, and time ($t$) without NaCl and with 1.0% NaCl.

Figure 10. X-Ray diffraction: evolution of mineralogy at 7, 28, 84 and 168 days of curing without NaCl (left) and with 1.0% NaCl (right).

Figure 11. Thermogravimetric analysis for different curing times without NaCl (left) and with 1.0% NaCl (right).

Figure 12. Scanning electron microscopy for sample with 28 of curing: (A) without NaCl and (B) 1.0% NaCl.
**Figure 13.** Variation of ALM with adjusted porosity/volumetric lime content without NaCl (left) and with 1.0% NaCl (right).

**Figure 14.** Relationship for the variation of ALM with $\eta$, $L_v$, and time of curing ($t$) without NaCl and with 1.0% NaCl.
### Table 1. Physical properties of coal fly ash and carbide lime.

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<th>Method</th>
<th>Fly Ash</th>
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<td>Specific gravity of grains</td>
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<td>Medium sand (0.2 - 0.6 mm)</td>
<td>ASTM D 422</td>
<td>0.96%</td>
<td>-</td>
</tr>
<tr>
<td>Fine sand (0.06 - 0.2 mm)</td>
<td></td>
<td>20.6%</td>
<td>11%</td>
</tr>
<tr>
<td>Silt (0.002 - 0.06 mm)</td>
<td></td>
<td>76.3%</td>
<td>82.9%</td>
</tr>
<tr>
<td>Clay (&lt;0.002 mm)</td>
<td></td>
<td>2.1%</td>
<td>6.1%</td>
</tr>
<tr>
<td>Mean particle size (D₅₀)</td>
<td></td>
<td>0.024 mm</td>
<td>0.021mm</td>
</tr>
<tr>
<td>Plastic index</td>
<td>ASTM D 4318</td>
<td>Non-plastic</td>
<td>Non-plastic</td>
</tr>
<tr>
<td>Plastic limit</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Liquid limit</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>USCS classification</td>
<td>ASTM D 2488</td>
<td>ML</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 2. Investigated treatments.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>UCS</th>
<th>Durability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Curing period (days)</td>
<td>7, 14, 28, 84, 168 and 360</td>
<td>7, 14, 28, 84 and 168</td>
</tr>
<tr>
<td>Dry unit weight (kN/m³)</td>
<td>11.2, 12.2 and 13.2</td>
<td>11.2, 12.2 and 13.2</td>
</tr>
<tr>
<td>CL content (%)</td>
<td>5%, 8% and 11%</td>
<td>5%, 8% and 11%</td>
</tr>
<tr>
<td>NaCl content (%)</td>
<td>0 and 1</td>
<td>0 and 1</td>
</tr>
</tbody>
</table>
### Table 3. Equations for UCS without and with NaCl according to the curing period.

<table>
<thead>
<tr>
<th>Days</th>
<th>Equations for UCS ($q_u$ - MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0% NaCl</td>
</tr>
<tr>
<td>7</td>
<td>$1.69 \times 10^4 \left{ \frac{\eta}{(L_p)^{0.11}} \right}^{3.0}$ Eq. (2)</td>
</tr>
<tr>
<td>14</td>
<td>$2.51 \times 10^4 \left{ \frac{\eta}{(L_p)^{0.11}} \right}^{3.0}$ Eq. (3)</td>
</tr>
<tr>
<td>28</td>
<td>$6.16 \times 10^4 \left{ \frac{\eta}{(L_p)^{0.11}} \right}^{3.0}$ Eq. (4)</td>
</tr>
<tr>
<td>84</td>
<td>$15.47 \times 10^4 \left{ \frac{\eta}{(L_p)^{0.11}} \right}^{3.0}$ Eq. (5)</td>
</tr>
<tr>
<td>168</td>
<td>$43.04 \times 10^4 \left{ \frac{\eta}{(L_p)^{0.11}} \right}^{3.0}$ Eq. (6)</td>
</tr>
<tr>
<td>365</td>
<td>$49.64 \times 10^4 \left{ \frac{\eta}{(L_p)^{0.11}} \right}^{3.0}$ Eq. (7)</td>
</tr>
</tbody>
</table>
Table 4. ANOVA for the unconfined compressive strength.

<table>
<thead>
<tr>
<th>Source</th>
<th>Degrees of freedom</th>
<th>Sum of squares</th>
<th>Mean square</th>
<th>F-Value</th>
<th>P-Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2</td>
<td>660.14</td>
<td>330.069</td>
<td>2164.91</td>
<td>0.000</td>
</tr>
<tr>
<td>B</td>
<td>5</td>
<td>4275.38</td>
<td>855.076</td>
<td>5608.40</td>
<td>0.000</td>
</tr>
<tr>
<td>C</td>
<td>2</td>
<td>105.46</td>
<td>52.728</td>
<td>345.84</td>
<td>0.000</td>
</tr>
<tr>
<td>D</td>
<td>1</td>
<td>685.34</td>
<td>685.340</td>
<td>4495.12</td>
<td>0.000</td>
</tr>
<tr>
<td>AB</td>
<td>10</td>
<td>252.05</td>
<td>25.205</td>
<td>165.32</td>
<td>0.000</td>
</tr>
<tr>
<td>AC</td>
<td>4</td>
<td>10.31</td>
<td>2.577</td>
<td>16.90</td>
<td>0.000</td>
</tr>
<tr>
<td>AD</td>
<td>2</td>
<td>56.37</td>
<td>28.187</td>
<td>184.88</td>
<td>0.000</td>
</tr>
<tr>
<td>BC</td>
<td>10</td>
<td>45.44</td>
<td>4.544</td>
<td>29.80</td>
<td>0.000</td>
</tr>
<tr>
<td>BD</td>
<td>5</td>
<td>347.69</td>
<td>69.538</td>
<td>456.10</td>
<td>0.000</td>
</tr>
<tr>
<td>CD</td>
<td>2</td>
<td>8.80</td>
<td>4.400</td>
<td>28.86</td>
<td>0.000</td>
</tr>
<tr>
<td>Error</td>
<td>280</td>
<td>42.69</td>
<td>0.152</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>323</td>
<td>6489.66</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

A = Dry unit weight / B = Time / C = Carbide Lime / D = NaCl
Table 5. Equations for ALM without and with NaCl according to the curing period.

<table>
<thead>
<tr>
<th>Days</th>
<th>Equations for ALM (%)</th>
<th>0% NaCl</th>
<th>1% NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>Eq. (17)</td>
<td>$3.14 \times 10^{-11}$</td>
<td>$1.66 \times 10^{-11}$</td>
</tr>
<tr>
<td>14</td>
<td>Eq. (18)</td>
<td>$2.21 \times 10^{-11}$</td>
<td>$1.28 \times 10^{-11}$</td>
</tr>
<tr>
<td>28</td>
<td>Eq. (19)</td>
<td>$1.41 \times 10^{-11}$</td>
<td>$1.01 \times 10^{-11}$</td>
</tr>
<tr>
<td>84</td>
<td>Eq. (20)</td>
<td>$1.41 \times 10^{-11}$</td>
<td>$0.84 \times 10^{-11}$</td>
</tr>
<tr>
<td>168</td>
<td>Eq. (21)</td>
<td>$0.57 \times 10^{-11}$</td>
<td>$0.45 \times 10^{-11}$</td>
</tr>
</tbody>
</table>
**Table 6.** ANOVA for the durability (wet and dry cycles).

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>Adj SS</th>
<th>Adj MS</th>
<th>F-Value</th>
<th>P-Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2</td>
<td>82.220</td>
<td>41.1099</td>
<td>249.80</td>
<td>0.000</td>
</tr>
<tr>
<td>B</td>
<td>4</td>
<td>59.277</td>
<td>14.8192</td>
<td>90.05</td>
<td>0.000</td>
</tr>
<tr>
<td>C</td>
<td>2</td>
<td>13.710</td>
<td>6.8551</td>
<td>41.65</td>
<td>0.000</td>
</tr>
<tr>
<td>D</td>
<td>1</td>
<td>14.777</td>
<td>14.7765</td>
<td>89.79</td>
<td>0.000</td>
</tr>
<tr>
<td>AB</td>
<td>8</td>
<td>20.791</td>
<td>2.5989</td>
<td>15.79</td>
<td>0.000</td>
</tr>
<tr>
<td>AC</td>
<td>4</td>
<td>4.748</td>
<td>1.1869</td>
<td>7.21</td>
<td>0.000</td>
</tr>
<tr>
<td>AD</td>
<td>2</td>
<td>6.940</td>
<td>3.4699</td>
<td>21.08</td>
<td>0.000</td>
</tr>
<tr>
<td>BC</td>
<td>8</td>
<td>3.993</td>
<td>0.4991</td>
<td>3.033</td>
<td>0.000</td>
</tr>
<tr>
<td>BD</td>
<td>4</td>
<td>11.986</td>
<td>2.9965</td>
<td>18.21</td>
<td>0.000</td>
</tr>
<tr>
<td>CD</td>
<td>2</td>
<td>1.290</td>
<td>0.6450</td>
<td>3.92</td>
<td>0.027</td>
</tr>
<tr>
<td>Error</td>
<td>280</td>
<td>42.69</td>
<td>0.152</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>323</td>
<td>6489.66</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

A = Dry unit weight / B = Time / C = Carbide Lime / D = NaCl
Figure 1 - Compaction test results.
Figure 2. Variation of UCS with adjusted porosity/volumetric content of CL without (left) and with 1.0% of NaCl.
Figure 3. Relationship for the variation of UCS with $\eta$, $L_v$, and time ($t$) without and with 1% of NaCl.
Figure 4. X-Ray diffraction: Evolution of mineralogy to 7, 28, 84 and 168 days of curing without (left) and with 1.0% of NaCl.
Figure 5. Thermogravimetric analysis for different curing times with (left) and without NaCl.
Figure 6. Scanning electron microscopy for sample with 28 of curing: (A) 0% NaCl and (B) 1% NaCl.
**Figure 7.** Variation of ALM with adjusted porosity/volumetric content of CL without (left) and with 1% of NaCl.
Figure 8. Relationship for the variation of ALM with $\eta$, $L_v$, and time of curing ($t$) without NaCl and with 1.0% of NaCl.