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# Electrical characterization of Calcium Aluminate (CA) in presence of chloride ions

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***Abstract***
*Chloride ingress is one of the major causes of reinforced concrete degradation. Chlorides accelerate the breaking of the protective layer of rebars favoring pitting corrosion; furthermore, corrosion products generate cracks in concrete, which further accelerate chloride ingress, increase porosity and reduce the strength. From a chemical perspective, the presence of chlorides and its diffusion into the reinforced concrete matrix is highly influenced by the content and distribution of aluminates ($C_3A$), in the same way, in concretes where ultra-rapid strength development and controlled expansion are required the presence of CA determine the chloride diffusion. This can be explained because chlorides react with aluminates to form Friedel's salts and other compounds. Although these reactions have been widely studied, their electrical changes still require further evaluation and analysis.*
*These experimental works use dielectric spectroscopy (DS), a technique that applying an alternating voltage and measuring phase and magnitude of current can determine the dielectric behavior variation. Also, this technique has shown good potential for measuring chlorides in other materials. Within this context, the main objective of this paper is to present the results of a study of the dielectrical behavior of calcium aluminate (in presence of mayenite and other ferrite compountds) when it interacts with solutions of chloride ions ($Cl^-$) at different concentrations (0-1M) using DS. In addition, the paper includes a structural characterization, by SEM, which provides information about changes in the microstructure and the spatial distribution of chemical elements. The results show that changes in dielectric parameters of CA are proportional to chloride content; in addition, chlorides preferentially interact in those zones where Al, Ca, and O are.*

***Originality***
*The Chlorides react with some of the cement's compounds, and its interaction with aluminates ($C_3A$ and CA) reduces the diffusion rate of chloride ions in cements. Although these reactions have been widely studied, their electrical changes still require further consideration. From this perspective, the main contribution of this study is the evaluation and analysis of electrical changes of calcium aluminates in presence of different chloride solutions. These electrical properties can be used with advantage as an alternative to measure chloride content in reinforced concrete.*

***Keywords:*** *Calcium aluminate, dielectric spectroscopy, chlorides, microstructural characterization*

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## 1. Introduction

Chloride ingress is one of the major causes of reinforcement corrosion in concrete structures. Chlorides accelerate the breaking of the protective layer of rebar allowing pitting corrosion. These failures weaken the strength of the material, and corrosion products generate cracks into the structure (Glasser et al. 2008; Andrade et al. 2011).

On the other hand, calcium aluminates (CA, $C_3A$, $C_4AF$, $C_{12}A_7$, cement chemistry notation) are usually used in the steel industry as refractory mixed oxides and in the cement community as hydraulic materials. Nowadays, other applications are developing such as optical devices, oxygen ionic conductors, and catalysts (Chang et al. 2014). Aluminates such as $CaO{\bullet}Al_2O_3$ (CA) and $3CaO{\bullet}Al_2O_3$ ($C_3A$) are essential in cementitious materials, because they are refractory binders (Scian et al. 1987). Thermodynamic studies about calcium aluminates report their formation at temperatures near 1100°C, when Ca ions diffuse into the $Al_2O_3$ (Scian et al. 1987; Mohamed and Sharp 2002).

According to (Yildirim et al. 2011) aluminate content in cements is decisive in the chloride presence and diffusion. This can be explained because chlorides react with calcium aluminates in presence of water to form Friedel's salts. In general, chloride salts (i.e. $CaCl_2$, NaCl or KCl) dissociate in water, and then react with aluminates. Chloride ions go inside hydrated aluminate structure $(Ca_2Al(OH)_6)^+$ replacing $OH^-$ ions, and forming a distorted "Brucite-like" main layers separated by interlayers of $Cl^-$ and $H_2O$ molecules. (Balonis et al. 2010; Lannegrand et al. 2001; Abate and Scheetz 1995; Chang et al. 2014). Although these reactions have been widely studied, their electrical changes still require further evaluation and analysis.

One of these electrical changes is the electric polarization that affects dielectric constant and conductivity (resistivity). Polarization is the alignment of the dipoles in presence of an electric field, and causes stored charge increasing in the material. Four principle types of polarization exist: molecular, electronic, interfacial, and ionic. Molecular polarization is due to the alignment of permanent dipole (e.g. water molecule) with the external electric field, this kind of polarization remains after electric field is removed. When in presence of an external electric field, electrons in the atom of a material shift away from the positively charged nucleus, it is called electronic polarization, and like molecular polarization this one is temporary. Interfacial polarization occurs when charge mobility is accelerated by an electric field, and is stopped by a physical barrier making charge accumulation at that place. This phenomenon is predominant in the low frequency range of $10^{-3}$ to $10^3$ Hz. Finally, ionic polarization happens when anions and cations in crystals are relatively displaced from their normal positions (Pokkuluri 1998; Callister 2008; Ma and Boggs 2014).

Until now, the study of electrical parameters changes on concrete through radio frequencies (3Hz – 300GHz) have been used for detecting chloride (Al-Qadi et al. 1997), and dielectric parameters' variation have been studied for determining changes on the microstructure of cements due to hardening and admixtures presence (Tsonos et al. 2009; Wen and Chung 2001). These experimental works use dielectric spectroscopy (DS), a technique that applying an alternating voltage and measuring phase and magnitude of current can determine the dielectric behavior variation (Tsonos et al. 2009). Also, this technique has shown good potential for measuring chlorides in other materials, such as food (Castro-Giráldez et al. 2010).

For these reasons, the main objective of this research is to study the dielectrical behavior of CA (in presence of other aluminate phases and ferrite compounds in less proportion) when it interacts with chloride ions ($Cl^-$) using dielectric spectroscopy (DS). In addition, structural characterization, by SEM, complements this study, giving information about microstructural changes and spatial distribution of chemical elements.

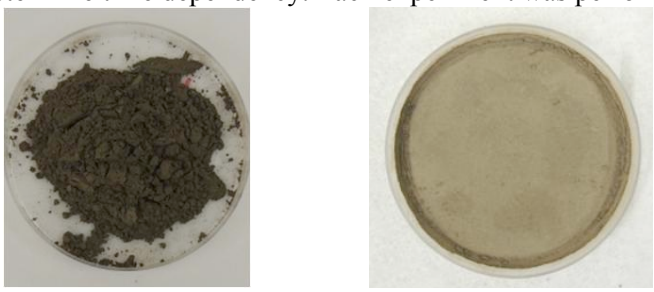
## 2. Experimental details

Commercial monocalcium aluminate was given by Parexlanko, its commercial name is Ternal® RG. To control and to understand the material's properties and behavior, it has been characterized structurally and electrically. Following subsections explain the procedures for both characterizations.

### *2.1. Electrical characterization*

An impedance analyzer Agilent 4294A Dielectric text fixture 16451B was used to characterize the aluminates before, during, and after they react with chlorides. The frequency range was between 100 Hz and 5 MHz and the area (A) of the plates is 1.13 x $10^{-3}$ $m^2$. This device works between 0°C and 55°C, for these experiments the temperature is 19°C±1°C, and it was necessary to do open/short compensation. Calcium aluminate powder (6,6g) is laid and tamped with a rammer during 120sec until it reaches a thickness between 1.84 x $10^{-3}$m and 2.27 x $10^{-3}$m. Figure 1 shows CA sample before and after tamping.

Water deionized (0M) and three NaCl solutions were used to test the dielectrical behavior of CA: 0,5M, 0,7M and 1,0M. Table 1 lists the name and characteristics of each test. In addition, measurements were performed 1 minute after 1mL of NaCl solution is added to CA and every 10 minutes for 1 hour to determine time dependency. Each experiment was performed by triplicate.



(a) (b)

Figure 1 CA samples (a) before and (b) after preparation

Tab. 1 Tests conditions

| Sample name | NaCl Concentration (M - Molar) |
|---|---|
| CA | 0 (Dried) |
| CAH | 0 (Hydrated) |
| CACl0,5 | 0,5 |
| CACl0,7 | 0,7 |
| CACl1 | 1,0 |

### *2.2. Structural characterization*

Before making electrical characterization, calcium aluminate was characterized by X Ray Diffraction (XRD), using Bragg Brentano geometry by powder diffractometry in a Rigaku Ultima III equipment at a speed of 0.6° 2θ/min in the range 5-42°2θ, according to reported researches (Brown and Badger 2000; Sugiyama et al. 2008). Additionally, CA samples were studied by Scanning Electron Microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX), using a microscope JEOL, model JSM 6490-LV at environmental pressure and 2000x, at Universidad de los Andes.

## 3. Results and Discussion

XRD characterization (Figure 2) demonstrated that the aluminate Ternal®RG given by Parexlanko presented small traces of iron oxide, mayenite ($C_{12}A_7$) and other ferrous components ($Ca_2Fe_2O_3$). Also, it showed the presence of monocalcium aluminate, $CaO.Al_2O_3$ (CA) that was the principal compound of the sample.

In general, all of the tests presented the same tendency (Figure 3). It means, in the first 10 minutes of each experiment, they reached a steady value. Figure 3 suggests that relative permittivity does not depend on the time nor the frequency at this range. It is important to take into account that interaction depends on diffusion processes, and it is possible that outliers could be explained because of that. These results state that polarization mechanisms are constant, because of that, dielectric behavior is virtually independent of frequency (Callister 2008; Pokkuluri 1998).

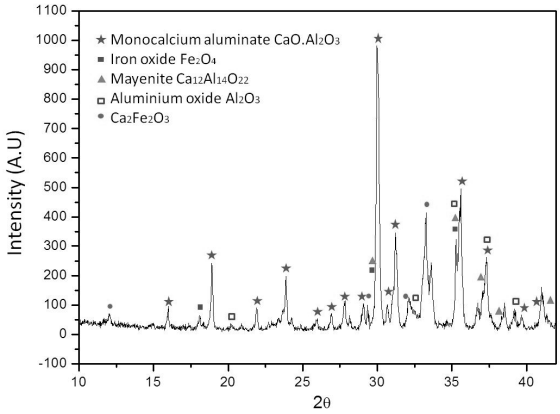



Figure 2 XRD Spectrum of Aluminate Ternal®RG

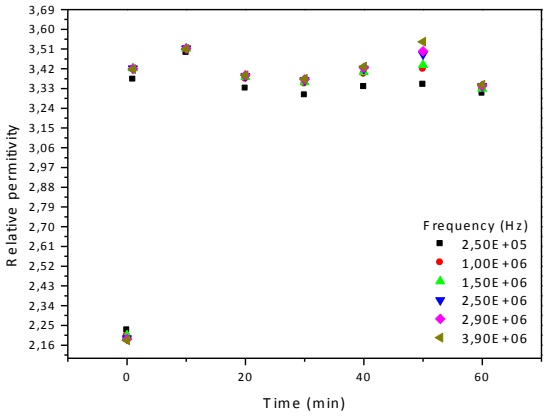



Figure 3 Effect of time on CA's behavior when 0.7 M NaCl solutions are added at specific frequencies. At min 0 the CA was dried.

In contrast, Figure 4 shows the change in relative permittivity as chloride solution concentration was increased. The effect of chloride solutions was to increase the measured relative permittivity. It means that parallel plates capacitance arises due to the ingress of Cl and Na ions that caused an ionic polarization inside the material.

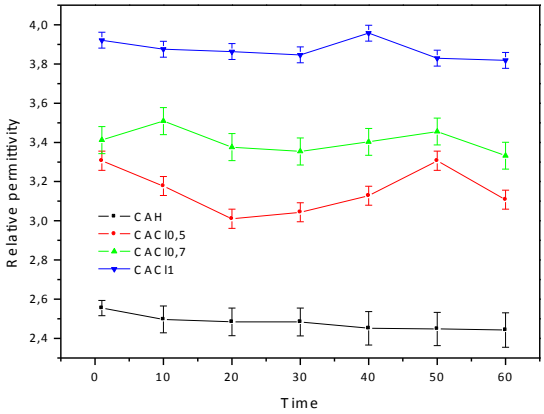


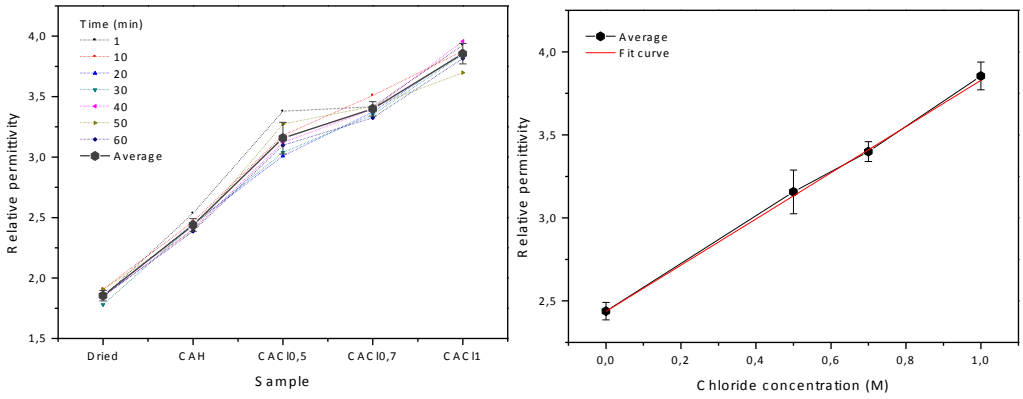

Figure 4 Time effect on CA's electrical behavior when 0M, 0.5M, 0.7M and 1M NaCl solutions are added. Each data set is the mean of three

Figure 5 demonstrates that relative permittivity is proportional to chloride concentration through:

$$\varepsilon_r = 2.438 + 1.391X \quad (1)$$

Where: $\varepsilon_r$ = relative permittivity, and $X$ = chloride concentration [M].

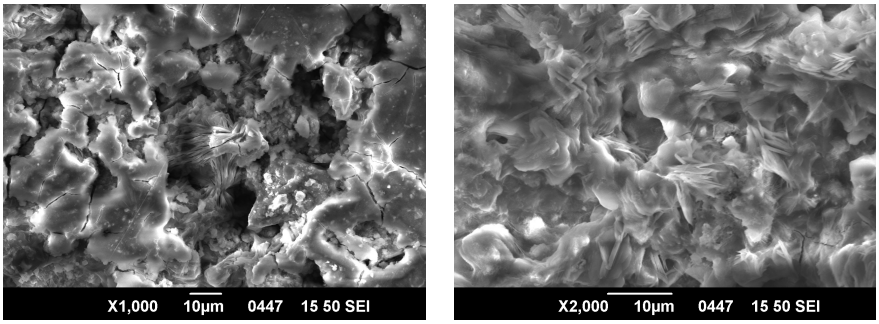
It means that ionic polarization of NaCl and molecular polarization of $H_2O$ lead to higher values of the dielectric constant allowing the increased of stored charge in the CA. Also, ionic penetration into the material causes that electric resistivity decrease, and of course, conductivity increases.




(a) (b)

Figure 5 (a) Effect of chloride content on measured relative permittivity for CA dried and exposed to 0M, 0.5M, 0.7M and 1M NaCl solutions; (b) Correlation between chloride concentration and relative permittivity

Figure 6 shows the impact of NaCl solutions on the CA's microstructure. These images show acicular formation on the samples' surface. This behavior was presented for all interactions solutions-samples. Figure 6a displays the microstructure of the CA after deionized $H_2O$ is added. The micrography shows that the CA was homogeneously hydrated and also, that the structure was not closed by the process, it means that even when the CA was hydrated, it allowed water and ions penetration. Additionally, this image shows the formation of acicular structures. Likewise, Figure 6b also shows acicular structures on the surface. According with (Cornell et al. 1989) acicular growth can be explained by the formation of goethite (α-FeO(OH)) that, as it is shown by Figure 7 is one of the products of hydration of the iron presented in the CA used in this research.




(a) (b)

Figure 6 Micrography of CA when (a) 0M and (b) 0.7 M NaCl solutions are added

Figure 7 states that goethite (13°, 17°, 27°) is present on calcium aluminate surfaces as soon as it comes in contact with water. On the other hand, it is possible to identify the presence of hydrated aluminates ($CAH_{10}$), that is formed by the reaction of water and CA at low temperatures, ~20°C Taylor 1997). This compound is represented by the peaks in 6.8° and 11.8° (Chotard et al. 2011) of the XRD spectra.

Figure 8a displays an image on CACl0,5 samples. And figures 8 b,c,d,e,f and g show the spatial distribution of Al, Ca, Fe, O, Na and Cl, respectively. As they illustrate, $Na^+$ and $Cl^-$ were present on the presence of Al, Ca and O. This fact could be due to the reaction between Al, Ca, O and Cl ions. These maps also show that even when XRD spectrum (Figure 2) illustrated that there are little traces of Fe that, according to these images, was homogeneously distributed in the sample; $Na^+$ and $Cl^-$ did not interact with it. Similarly, Figure 9 shows that CA exposed to 0,7M NaCl solution presented the same behavior as CACl0,5 in other words, those places where Ca, Al and O were present were also the preferential places for $Na^+$ and $Cl^-$.

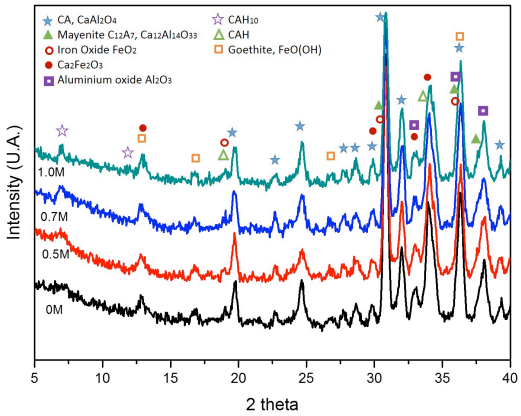



Figure 7 XRD spectrum of dried Aluminate after its interaction with aqueous chloride solutions (0M, 0.5M, 0.7M, 1.0M)

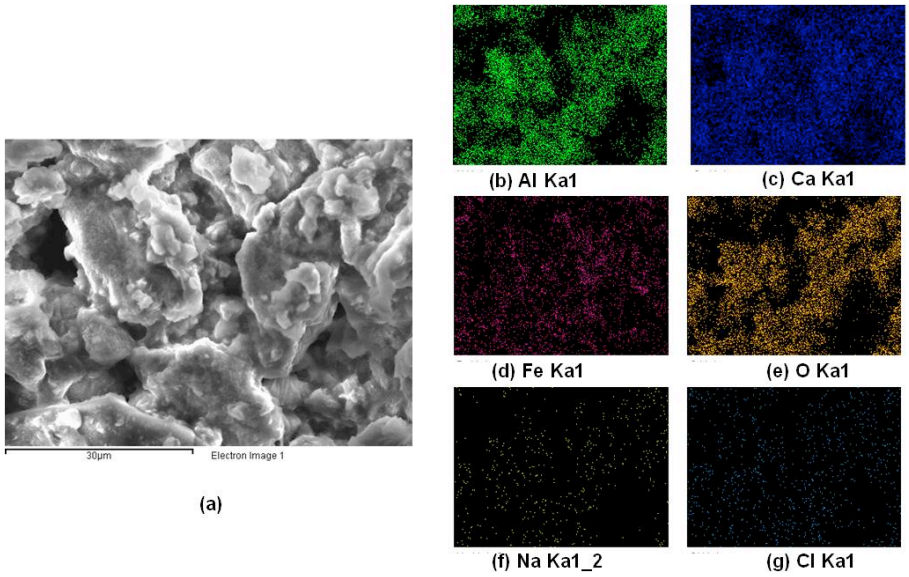



Figure 8 EDX map of CA when 0,5M NaCl solutions are added

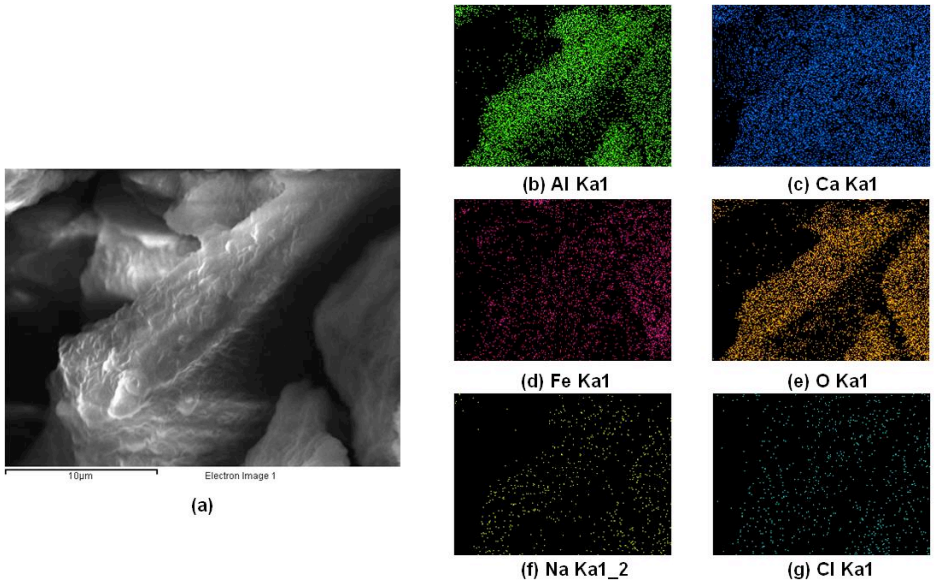



Figure 9 EDX map of CA when 0,7M NaCl solutions are added

## 4. Conclusions

The results of this study can be summarized as follows:

Electric permittivity changes of monocalcium aluminate caused by chloride ions presence and water were observed by DS. Through this technique it has been demonstrated that chloride and water presence have a measurable impact in the dielectric properties of the material

Experiments show that CA's dielectric behavior is independent of frequency and time. It means that i) polarization mechanisms constantly work during and after the contact with chloride solutions, and ii) interaction between CA and $Cl^-$ is fast and reaches a steady state quickly; however, that interaction can be not homogeneous causing shifts in measuring.

SEM micrographies and XRD spectra illustrate that acicular structures are due to interaction between iron presented in CA and deionized water and not because of reactions between CA and $Cl^-$.

EDX maps state that Na and Cl ions have preferential places for interacting. In fact, these ions are fixed where Al, Ca and O exist.

These results suggest that monitoring CA's dielectric behavior can be used for measuring chloride concentration on RC since measurements are steady at the first hour of reaction.

## 5. Acknowledgements

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