Reactivity of calcium dialuminate (CaAl$_2$O$_7$) refractory cement with lithium carbonate (Li$_2$CO$_3$) admixture

Arlin Bruno Tchamba$^{a,b}$, Michel Mbessa$^c$, Tchedele Langollo Yannick$^{a,d}$, Sandra Waida$^b$, Antoine Elimbi$^c$, Uphie Chinje Melo$^{d,e}$ and Thomas A. Bier$^b$

$^a$Research Department, Local Materials Promotion Authority (MIPROMALO), Yaoundé, Cameroon; $^b$Institut für keramik, glas und Baustofftechnik, Technical University of Freiberg (Germany), Freiberg, Germany; $^c$Department of civil Engineering, Civil Engineering Department, National Advanced School of Public Works, Yaoundé, Cameroon; $^d$Department of Mining Engineering, Adamaua, Cameroon, University of Ngaoundere / EGEM Meiganga; $^e$Department of Inorganic Chemistry, Mineral Material Laboratory, Faculty of Science, University of Yaounde I, Yaounde, Cameroon

ABSTRACT

The reactivity of calcium dialuminate CaAl$_2$O$_7$ refractory cement containing little amount of gehlenite Ca$_2$Al$_2$SiO$_6$, belite Ca$_3$SiO$_6$, calcium aluminum iron oxide Ca$_3$(Al,Fe)$_2$O$_9$ and calcium iron aluminum oxide Ca$_3$Fe$_2$SiO$_9$ was studied with and without Li$_2$CO$_3$. The granularity of the cement is $d_{50}$ = 112.58 µm, $d_{10}$ = 9.72 µm and $d_{90}$ = 1.41 µm with water cement ratio W/C = 0.375. Little amount of Li$_2$CO$_3$ from 0.1 wt.% to 0.6 wt.% was added to the cement paste, and the result from calorimetry showed hydration mean peak time reduced from 17 h to 32 min and showed that the hydration heat of CA cement paste with Li$_2$CO$_3$ was 123 J/g lower than the one without Li$_2$CO$_3$ of 168 J/g. XRD of stabilized hydrates show that CaAl$_2$O$_7$, and Ca$_3$(Al,Fe)$_2$O$_9$, participate in the hydration reaction to form Ca$_6$AH$_8$, AH$_3$, and Ca$_3$Al$_{1.5}$Fe$_{0.46}$(OH)$_{12}$. The results from SEM images show nucleation site with plate-like crystal of CAH$_6$ and small particles of AH$_3$ forming a membrane on the cement surface.

1. Introduction

The development of new processes and increased requirements for special mortars has led to constant research on the amelioration of traditional binders. The use of calcium dialuminate refractory cement as binders is not well known [1]. For the long setting time required since the production of building mortars results mainly from a high speed of strength development.

Calcium dialuminate (CA$_2$) is an important constituent of high alumina refractory cements [2], compared to calcium aluminate (CA), the other principal component. CA$_2$ hydrates very slowly at room temperature [3], and the reactivity of CA$_2$ may increase in the presence of CA [3]. Calcium dialuminate exhibits very low thermal expansion and excellent thermal properties and thus considered a desirable phase for refractory applications [4].

Calcium aluminate cement with 70–80 wt.% Al$_2$O$_3$ can be used to produce castables with a temperature resistance ranging from 1800 to 1900°C in order to improve technical performance of Low Cement Castable (LCC) of 5–8 wt.% for high performance refractory material [5]. For a long time, the hydration of CA$_2$ was an open issue [2]; and CA$_2$ was even assumed to be inert. CA$_2$ tends to react very slowly within the first 48 h. For this reason, in many earlier studies, it has been the hydration of CA alone, which has been intensively investigated.

Chudak et al. [6] reported on the hydraulic reactivity of CA$_2$; they investigated on pure CA$_2$ with 70 wt.% Al$_2$O$_3$. Using the DCA technique and describes a slow CA$_2$ cement hydration occurring over several days. Negro et al. [7] concluded that the solubility of CA$_2$ is much lower than that of CA. This could explain the very low hydration reaction activity of CA$_2$ in secar71 (calcium aluminate cement with 71% of alumina), which begins after 23–48 h and finish after several months. And AH$_3$ was observed during hydration of CA$_2$ at ambient temperature [7,8].

Klaus et al. [3] observed that CA$_2$ hydration proceeds together than 22 h, and it is known in the investigations that CA$_2$ was completely dissolved after few days, and they attributed it to the very slow precipitation of C$_2$AH$_7$,$\alpha$ Ca$_6$AH$_8$. These components were occurring not at the particle surfaces on CA$_2$ but from pure solution and therefore hydration can proceed until CA$_2$ is completely dissolved [3].

To accelerate the setting time of alumina cement, Kurdouski et al. [9], Bensted et al. [10], Robson et al. [11], used mixtures of alumina cement and portland cement as binders in type F tile adhesives [PN-EN12004]. The setting time is shorter when the content of one cement in the mixture is between 20 and 80 wt.% [2].

Bensted et al. [10] pointed that the literature concerning possibilities to accelerate the setting and hardening of alumina cement is very extensive. Lithium salts, sodium and potassium hydroxides, portland
cement, calcium oxide, and calcium sulfate hemihydrate are the components that mainly influence the hydration of alumina cement. The presence of alkali metals salts in the alumina cement paste and mortar was subject of the investigations by Matusinovic and vrbos [12,13], Venuat et al. [14], Malgorzata Niziurska [1,15].

It is known that hydration products from pure CA$_2$ forms after 24 h [1–3]. With conventional CA$_2$, the initial CAH$_{10}$ hydration products appear after 3 days followed by the formation of C$_2$AH$_6$ and its conversion to C$_3$AH$_6$ between 3–14 days [7].

The objective of this work was to study the mechanism and conditions that appear when used Li$_2$CO$_3$ as accelerator of setting time of CA$_2$ cement. In this case, Li$_2$CO$_3$ were used from 0.1 to 0.6wt.% in calcium dialuminate refractory cement made. Calorimetry heat flow, XRD, and scanning electron microscope were used to observe the hydration of CA$_2$ with lithium carbonate and the microstructure of cement paste without and with lithium carbonate after 14 days.

2. Materials and methods

2.1. Powder cement preparation

The calcium dialuminate cement was obtained by solid state reaction of a mixture of high quality bauxite (Al$_2$O$_3$ ≥ 80wt.%) with lime (CaO ≥ 95wt.%) (Table 1). The mixture was homogenized in a milling jar for 10 min then dried at 105°C. The agglomerate is treated at 1550°C for 2 h. The clinker obtained was milled in a SiC jar with SiC mill. The medium diameter of the particles was $d_{50} = 9.72$ µm, $d_{10} = 1.41$ µm and $d_{97} = 112$ µm.

2.2. Cement paste preparation

To the prepared powder CA$_2$ cement, varying amount of Li$_2$CO$_3$ 0wt.%, 0.1wt.%, 0.2wt.%, 0.3wt.%, 0.4wt.%, 0.5wt.% and 0.6wt.% is added, respectively. The Li$_2$CO$_3$ is weighed and added to the cement powder and mixed before add the water in the calorimeter for injection method. For external mixing or ready-mixed mixture, Li$_2$CO$_3$ is weighed and added to cement and mixed with water in the rotary mixer before put in the calorimeter and beginning the measurement of heat flow. A paste was prepared with a water cement (W/C) ratio of 0.375. One part of the cement paste was molded in a cylindrical container and vibrated for 10 s and used for XRD and SEM analysis. Another powder was used directly after mixing with water for calorimetry to study the heat flow and hydration heat of cement.

2.3. Analytical techniques

2.3.1. XRF technique

For XRF analysis, a hXRF Niton XL3t980 analyzer (equipped with an Ag-Anode 50 kV X-ray tube and Silicon-Drift-Detector 8 mm spot was used. The raw data were plotted in spectra, where x-axes represent element-specific fluorescence energy (unit keV), and y-axes quantity counts of photons (unit cps) received by the detector. Detection is possible for most of the elements with atomic numbers ranging from 12 magnesium to 92 (uranium). 21 silicon-based standards so-called Certified Reference Material (CRM), filled in cups and covered with 4 µm polypropylene film were measured by a hXRF device specific mode (mining/mineral mode). The measured values were plotted using a trend line equation and the “fitting coefficient” $R^2$ (correlation coefficients) were determined. Afterward, a classification was made according to the quality of the regression line and the distribution of the data.

2.3.2. Calorimetry technique

To illustrate the evolution of heat during the hydration process of the cement paste, an Erlanger calorimeter was used. The measuring principle of the Erlangen calorimeter is based on a temperature difference between the reference sample and the material to be analyzed. This temperature difference is converted into an electrical voltage and measured by a digital multimeter. Data recording of the heat source is carried out via the data transfer program OMI. There are two possible applications for the calorimeter: the injection method and the ready-mixed mixture. In the injection process, the water of about 1.125 g is injected directly into the dry mix about 3 g and the full heat history can be recorded. In the ready – mixed mixture, the quantity of the cement paste is about 8 g with W/C = 0.375 at $20 ± 2°C$. Sample of cement paste were casted into three different plastic crucible, with 20 mm in diameter and 15 mm in height for assessing the measurement of heat flow calorimetry. The $Q_{cement}$ is calculated from $Q_{sample}$ with the formula:

$$Q_{cement} = \frac{\text{mass of sample}}{\text{mass of cement}} \times Q_{sample} \quad (1)$$

2.3.3. XRD technique

XRD measurements were performed using a D8 diffractometer equipped with Lynx-eye position...
sensitive detector (Brucker – AXS), with Cu Kα1 λCu = 1.54056 Å radiation operated at 40 kV and 40 mA, increment 0.013° 2θ, and a measuring time per step of 30 s. The diffraction patterns were collected in the 2 theta range from 7.5 to 90°. Qualitative analysis of the phase composition of the powders was conducted using the PDF-2 2007 release software and X’Pert High Score Plus.

2.3.4. SEM technique
The grain size, surface topology and pore diameter of the hydrated cement was determined using an XL30 series Philips scanning electron microscope XL30 ESEM FEG (Fa, FEE) equipped with an energy dispersive analyzer (EDS), EDAX, Fa Annatet with GENESIS-software, run at 10 kV and at a resolution of 500–7500. The SEM images on cement sample have been done after curing age 14 days.

3. Results and discussion
3.1. XRD results
The results of the XRD analysis of calcium dialuminate refractory cement in powder form is presented in Figure 1 and hydrated form in Figure 2. It is observed from Figure 1 major element attributed to calcium dialuminate CaAl4O7 PDF 23-1037, associated with little amount of gehlenite Ca2Al2SiO7 PDF 20-0199, calcium aluminum iron oxide Ca3(Al,Fe)2O6 PDF 35-0040, calcium iron aluminum oxide Ca3.18Fe15.48Al1.34O28 PDF 52-1258 and calcium silicate Ca2SiO4 PDF 23-1042. When the cement is hydrated and stabilized at 105°C, the XRD pattern reveals the presence of hydrated phases like hydrogamet Ca3AH6 PDF 77-0240, aluminum hydroxide Al(OH)3, calcium aluminum iron hydroxide Ca3Al1.34Fe0.46(OH)12 PDF 45-0570 and non-hydrated ones like calcium dialuminate CaAl4O7, gehlenite Ca2Al2SiO7, calcium aluminum iron oxide Ca3(Al,Fe)2O6, calcium iron aluminum oxide Ca3.18Fe15.48Al1.34O28 and calcium silicate Ca2SiO4. Calcium dialuminate hydrates to hydrogamet and gibbsite following the equation:

$$3(CaAl_4O_7) + 21H_2O \rightarrow Ca_3Al_2O_6(H_2O)_6 + 10Al(OH)_3$$

(2)

And calcium aluminum iron oxide Ca3(Al,Fe)2O6 hydrates to calcium aluminum iron hydroxide Ca3Al1.34Fe0.46(OH)12.

Gehlenite Ca2Al2SiO7 does not hydrates and it is observed on XRD of hydrated cement. Authors Antonovica et al. [5] proposed that gehlenite Ca2AS (considerable amount in cement) does not hydrate [5]. Contrary to this, investigation by Niziurska et al. [1] suggested that gehlenite Ca2AS reacts slowly with formation of stratlingite hydrated calcium aluminosilicate Ca2ASH8 and we know that stratlingite is a stable

![Figure 1. X-ray Diffractogram of powder CA2 cement.](image-url)
hydrate of importance in terms of late strength of alumina cement. Another way, Singh and Majumdar [2] reported that in the presence of granulated blast furnace slag (ggbs) on CA₂ or a mixture of CA₂ + CA will form stratlingite (C₂ASH₈) on hydration at 40°C within 3 days. This formation of stratlingite, which is hydrated calcium aluminosilicate.

The absence of stratlingite on the hydrated cement made (Figure 2) is explained by the low reactive of gehlenite Ca₂Al₂SiO₇ in the cement powder.

3.2. Calorimetry studies of calcium dialuminate cement without lithium carbonate (Li₂CO₃) admixture

The hydration of calcium dialuminate cement paste was studied through the injection method Figure 3(a), presents two hydration peaks, the first one at about 15.22 h and the second one at about 29.42 h; as opposed to the external mixing method where only one stage hydration is observed at 17.05 h after water is added. The first hydration peak time in Figure 3(a) at 15.22 h is attributed to hydration of calcium dialuminate and the second hydration peak time at 29.42 h is attributed to the hydration of calcium aluminum iron oxide Ca₃(Al,Fe)₂O₆ and Ca₃.18Fe₁₅.4₈Al₁.₃₄O₂₈ to calcium aluminum iron hydroxide Ca₃Al₁.₅₄Fe₀.₄₆(OH)₁₂. Authors Antonovic et al. [5], mentioned a difficulties in describing the origin of heat flow between 5 and 12 h when he used a mixture of CA and CA₂. In this context, we supposed that no heat flow have been observed between 0 and 15 h.

In Figure 3(b) the heat flow curve presents one peak at 17.05 h attributed to the hydration of calcium dialuminate in the cement paste.

Figure 2. X-ray Diffractogram of hydrated and stabilised CA₂ cement.

Figure 3. Heat flow of calcium dialuminate cement by injection (a) and external mixing (b).
The calculated value of the enthalpies of reaction for CA$_2$ is $-498$ J/g obtained from corresponding enthalpies of formation by Klaus et al. [3]. But the results of hydration heat obtained by Singh and Majumdar [2] is 192 J/g at 20°C with W/C = 0.4 is higher than the one obtained (Table 2) at 168 J/g at 20 ± 2°C. Contrary, the result obtained in Table 2 for the hydration heat, is higher than the one obtained by Niziurska et al. [1] at 140 J/g with W/C = 0.43 at 23°C. The lower or higher value of hydration heat depends to the particles size distribution, the impurities in the cement like gehlenite and calcium aluminum iron oxide.

### 3.3. Calorimetry studies of calcium dialuminate cement with (Li$_2$Co$_3$) up to 0.6wt.%

#### 3.3.1. Lithium carbonate as the factor for reduction of heat of hydration

The heat flow for calcium dialuminate cement is presented in Table 2 and Figure 4. From Table 2, the hydration heat for cement without Li$_2$CO$_3$ is about 168 J/g and higher than the one with Li$_2$CO$_3$ with an average heat of 123 J/g. Niziurska et al. [1] obtained in the case of hydration of CA$_2$ cement pastes with 0.3wt.% of Li$_2$CO$_3$ the total amount of evolved heat was 80 J/g lower than the one obtained in Table 2. With the addition of lithium carbonate, the total amount of evolved heat is lower than the one without lithium carbonate. The presence of lithium carbonate admixture reduces the hydration heat of cement pastes.

#### 3.3.2. Lithium carbonate as the factor for reduction of hydration time

It’s presented on Table 2 and Figure 4 that the hydration mean peak time of cement with Li$_2$CO$_3$ is about 32 min and without Li$_2$CO$_3$ is about 17.05 h. When a little amount of 0.1wt.% of Li$_2$CO$_3$ is added, the peak time is reduced to 43 min (0.72 h) and this can be further reduced to 24 min (0.40 h) at 0.6wt.% of Li$_2$CO$_3$. We can confirm that Li$_2$CO$_3$ is a good accelerator of calcium dialuminate refractory cement. Lithium carbonate influences the hydration of high alumina cement through its rapid dissolution in solution, and substitution of Ca$^{2+}$ by Li$^+$, lithium ion is a light and less dense element with atomic weight of 6.94 g/mol and density of 0.534 g/cm$^3$, while Ca$^{2+}$ is a heavy element.

| Type            | Name                      | Q sample (J/g) | Q cement (J/g) | Peak time (h) |
|-----------------|---------------------------|---------------|---------------|---------------|
| CA$_2$ cement   | Cement                    | 122.40        | 168.03        | 17.052        |
| Paste E/C = 0.375 | Cement + 0.1wt.% Li$_2$CO$_3$ | 95.13        | 130.85        | 0.72          |
| 20 ± 2°C, up to 24 h | Cement + 0.2wt.% Li$_2$CO$_3$ | 87.75        | 120.62        | 0.67          |
|                 | Cement + 0.3wt.% Li$_2$CO$_3$ | 89.76        | 123.37        | 0.51          |
|                 | Cement + 0.4wt.% Li$_2$CO$_3$ | 88.07        | 121.05        | 0.51          |
|                 | Cement + 0.5wt.% Li$_2$CO$_3$ | 89.55        | 123.08        | 0.49          |
|                 | Cement + 0.6wt.% Li$_2$CO$_3$ | 91.59        | 125.90        | 0.40          |

**Figure 4.** Heat Flow of CA2 cement paste with and without Li2CO3
with atomic weight of 40.08 g/mol and a higher density of 1.54 g/cm³. The substitution of Ca²⁺ by Li⁺ is the first reason for the mobility of lithium ion and rapid setting time of calcium dialuminate cement paste. The influence of lithium ion on the hydration process of calcium dialuminate cement was studied by Dittrich et al. [16]. Introduction of Li⁺ ion leads to precipitation of LA₂H₁₀ in the paste, a phase transition, which prevents the formation of an impermeable coating on CA₂ grains. Substitution of Ca²⁺ ion by Li⁺ ions leads to the crystallization of C₂AH₈, while free Li⁺ cation forms LA₂H₁₀ transition phase again.

Another lithium ion from chloride have been studied by Rodger et al. [17] and Acuna Gutierrez et al. [18]; they reported that LiCl addition form small aggregates of the compound Li₂Al₂O₇(H₂O)₁₁ in the cement that may act as a nucleation site for the hydrated products thus accelerating the conversion process. Friedels salt (JCPDS 089-52-94) Ca₄Al₂O₆Cl₂(H₂O)₁₀ formed by the reaction of CAC with chloride ions from LiCl solution, and through the intermediate stable cubic phase Ca₃Al₂(OH)₁₂ is also present. Nygaard et al. [19] reported from Justnes et al. [20] the effects of the more common alkali carbonates (Li₂CO₃, Na₂CO₃ and K₂CO₃) on setting times and strength of cements. Valenti et al. [21] proposed that Na and K carbonate retarded the setting at lower dosages, but accelerate the setting time at dosages higher than 0.1wt.%; when Li₂CO₃ acted as an accelerator at all concentrations studied. This inhibition of further hydration of grains coated by layer of rapidly growing reaction products and faster conversion of hydrates into hydrogarnets in the case of cement mortars with lithium carbonate leads to strength decrease after 24 hours compared to cement mortars without admixture as observed by Matusinovic [12] and Niziurska et al. [1].

### 3.4. SEM of hydrated calcium dialuminate cement with different amount of Li₂CO₃

Scanning Electron Microscopic analysis of hydrated calcium dialuminate cement with and without lithium carbonate was performed. Figure 5 shows SEM image and corresponding EDS spectra of the hydrated calcium dialuminate cement without lithium carbonate. At this magnification (200 µm scale), two phases are observed: residual cement grain of CA₂ and a hydrated one in the interface of CA₂ cement grain. The surface has a sponge structure with the pores repartition up to 100 µm and open micropores between 10 and 0.1 µm and ultrapores on cement grain between 0.1 µm and 0.01 µm. In Figure 6, the SEM images show the topological repartition of particles in hydrated cement with lithium carbonate. The surface morphology reveals a lot of pores and residual unreacted grains of CA₂ associated with hydrated phase. However, the surface of cement is more compact than the one without lithium carbonate.

Figure 7 presents the surface of cement at high magnification (10 µm and 5 µm scales) on Secondary Electron SE (Figure7(a)) and Back Scattered Electron BSE (Figure 7(b)). The hydrated phase is seen a crosslink and contain many pores are also observed up to 5 µm in diameter. Cracks of length up to 10 µm are also observed. On BSE (Figure 7(b)), the white color and brown color are associated to titanium and iron elements respectively.

![Figure 5](image_url)
Figure 6. SEM images (BSE) of hydrated calcium dialuminate cement with lithium carbonate (ALC1, ALC2, ALC4, ALC5) showing hydrated (b) and non-hydrated phase (a) after 14 days.

(a): CA₂, (b): hydrated phases, (c): pores

Figure 7. SEM images of calcium dialuminate cement with lithium carbonate (a) SE and (b) BSE after 14 days.

(I): crack, (II): pores, (III): Fe and Ti, (IV): pores (V), (VI), (VII) and (VIII): hydrations products
From (Figure 8), short needle-shaped crystal structures of C₃AH₆ are developed on surface of the grain, when AH₃ forms a thin layer deposit mass on the surface. Newman et al. [22], from studying on SEM images of cement paste with W/C ratio of 0.4 observed that the C₃AH₆ is finely dispersed in a matrix of hydrated alumina and presented like a cubic and had a morphology of compact equiaxed faceted crystals, where AH₃ is often poorly crystallized and deposited in formless masses. Niziurska et al. [1] studied the mixture of CA/CA₂ cement paste and observed a significant amount of carboaluminate C₂AH₁₁ and gibbsite AH₃ after 24 h for cement without Li₂CO₃, and when a 0.3wt.% of Li₂CO₃ is added, carboaluminate and crystal of gibbsite are observed after 1 h of mixing with water.

Antonovic et al. [5] reported that irregular cubic crystals are completely or partially observed by a crystalline material. Crystalline gibbsite with diameter between 0.15 and 0.30 µm. When Acuna-Gutiérrez et al. [18] confirmed that water forms hydrated products with cement powder such as CAH₁₀, C₂AH₆, C₃AH₁₀ and AH₃. Although the temperature is higher than 30°C, AH₃ and C₃AH₆ are formed and the possibility to accelerate with LiCl forms small aggregates of Li₂Al₄O₇·(H₂O)₁₁ may act as nucleation site for the hydrated products accelerating the conversion process. In our studies, the hydration process with CA₂ with Li₂CO₃ may be explained as follows.

\[
\begin{align*}
CaAl₂O₆ + Li₂CO₃ \\
+ 11H₂O \rightarrow Li₂Al₄O₇·(H₂O)₁₁ \text{(nucleation site)} + CaCO₃
\end{align*}
\]

\[
(3)
\]

\[
CaAl₂O₇ + 13H₂O \text{ (nucleation site)} \rightarrow CaAl₂O₄·(H₂O)₁₀ + 2Al(OH)₃
\]

\[
(4)
\]

\[
2(CaAl₂O₄·(H₂O)₁₀) \rightarrow Ca₂Al₂O₅·(H₂O)₈ + 2Al(OH)₃ + 9H₂O
\]

\[
(5)
\]

\[
3(Ca₂Al₂O₅·(H₂O)₈) \xrightarrow{T>10°C} 2(Ca₂Al₂O₅·(H₂O)₈) + 2Al(OH)₃ + 9H₂O
\]

\[
(6)
\]

Nucleation site constituting lithium aluminate hydrate Li₂Al₄O₇·(H₂O)₁₁ is formed. This new site is surrounded by crystal of CAH₁₀ and AH₃ as seen from (Figure 9) and corresponding EDS. This new phase assembles into flower like a polymeric structure (Figure 9). Such a small cluster of monomer crystals of CAH₁₀ in the correct arrangement can be transformed in to C₃AH₆ and AH₃, an intermediate stable cubic phase with formation of final stable phase C₃AH₆ and AH₃ hydrated phases.

Niziurska et al. [1] stated that hydration of calcium monoaluminate with lithium carbonate significantly accelerates crystallization of C₃AH₆ defined by a first hydration product of cement phases and rapid conversion into hydrogarnet. Contrary to this statement, the first hydrated phase of CA₂ obtained is CAH₁₀ from the polymeric flower (Figure 9).

Figures 8 and 9 present CAH₁₀ crystal formed on the surface of CA₂, the average diameter of CAH₁₀ prism is 0.3 µm, and C₃AH₆ crystals present the average length reaching 9 µm; prevail irregular cubic crystal completely or partially covered by a crystalline material of about 4 µm (Figure 9). The X-ray microanalysis showed that elemental composition of this sample in molar percentage is Al₂O₃: 48.59%, CaO: 46.94% (H analysis was not performed with the spectrometer). The composition material is similar to CAH₁₀.

Since some literature sources suggests that nitrates may form a complex salt with the aluminate phase in cement, it was initially assumed that the accelerating effect, was dependent on aluminate content of the
cement. However, during the study, it was shown by X-ray diffraction that it was not possible to detect any reflection arising from the calcium-aluminate nitrate compound Ca₃Al₂O₆Ca(NO₃)₂(Η₂O)₁₀.

### 3.5. Discussions

#### 3.5.1. Surface charge on calcium dialuminate cement

The surface charge of cement particles can be obtained for CaAl₄O₇ [4,23,24], by denoting σ⁺ and σ⁻ as the respective surface charges of the positive and negative sites in this compound, according to the relation:

\[
\frac{\sigma^+}{\sigma^-} = \frac{(Ca^{2+})_{\text{surface projection}} + 4(Al^{3+})_{\text{surface projection}}}{7(O^{2-})_{\text{surface projection}}}
\]

Where \((Ca^{2+})_{\text{surface projection}}\), \((Al^{3+})_{\text{surface projection}}\) and \((O^{2-})_{\text{surface projection}}\) are equal to \(n_r\); \(r_{O^{2-}} = 140\) pm, \(r_{Al^{3+}} = 53.5\) pm, \(r_{Fe^{3+}} = 55\) pm, \(r_{Ca^{2+}} = 100\) pm, \(r_{H^{+}} = 10\) pm, \(r_{Li^{+}} = 76\) pm.

The calculated surface charge of calcium dialuminate cement is \(\frac{\sigma^+}{\sigma^-} = 0.16\), for calcium aluminum iron oxide Ca₃(Al,Fe)₂O₆ is \(\frac{\sigma^+}{\sigma^-} = 0.30\) and for gehlenite Ca₂Al₂SiO₇ is \(\frac{\sigma^+}{\sigma^-} = 0.18\). Although the impurities in the cement increase the positive surface charge on the cement, the global surface charge remains negative for the cement and lower than the surface charge of CaAl₂O₄ which is \(\frac{\sigma^+}{\sigma^-} = 0.22\). The strongest negative charge of calcium dialuminate cement improves their resistance to the corrosive effect of certain acids and industrial wastes. The resistance of corrosion down a pH 3.5–5 depends on the type of acid, temperature, length of exposure. It is mentioned that this type of cement can resist to alkali up to a pH of 12 with the exception of alkali hydroxide and give the possibilities to use cement for making concrete resistant to sulfate ground water and seawater.

#### 3.5.2. Influence of additives/admixture on the hydration heat of calcium dialuminate cement

Singh and Majumdar [1] studied different cases of hydration heat of CA₂ cement without and with additives at 20°C and at 40°C (Table 3). They mentioned that the hydration heat of cement during 24 h at 20°C is 192 J/g, and at 40°C, the hydration heat is 359 J/g, and they observed that the evolved heat added to the system increased the speed of hydration of CA₂ products at 40°C than at 20°C. Singh and Majumdar used the granulated blast furnace slag (ggbfs) as the addition to CA₂ cement in proportion 1:1 at 20°C. They obtained the hydration heat of 87 J/g less than half of the pure CA₂ at 20°C and at 40°C, the hydration heat with ggbfs

### Table 3. Hydration heat of CA₂ cement with and without admixture/additives from different works.

| Component | 20°C | 40°C | Niziurska et al. [1] | This work |
|-----------|------|------|----------------------|-----------|
| CA₂       | 192 J/g | 359 J/g | 140 J/g | 168 J/g |
| CA₂ + 0.3wt.% Li₂CO₃ | - | - | - | - |
| 20:80 CA/CA₂ | 118 J/g | 332 J/g | 80 J/g | 123 J/g |
| 50:50 CA₂ + ggbfs | 87 J/g | 210 J/g | - | - |

Figure 9. SEM image of nucleation site surrounding with first hydration products after 14 days.
gives 210 J/g and straitlite \( \text{C}_2\text{ASH}_8 \) was detected in both cases. The studies obtained from the addition of 20wt.\% of CA in CA \(_2\) at 20°C and 40°C with W/C = 0.4 give the total heat after 24 h at 118 J/g at 20°C and 338 J/g at 40°C lower than CA or CA \(_2\) alone. The additives like CA, gbbs can increase the speed of hydration of CA \(_2\) products and reduce the hydration heat of cement.

The work done by Niziurska et al. [2] obtained the amount of evolved heat with lithium carbonate admixture equal to about 80 J/g, while the amount heat during the hydration of cement paste without lithium carbonate was almost 240 J/g. They conclude that, the lower heat of hydration with lithium carbonate was due to the inhibition of further hydration of grains coated by layer of rapidly growing reaction products. It is then observed from Table 3 that the admixture like \( \text{Li}_2\text{CO}_3 \) and additives like gbbs and CA reduce significantly the hydration heat of CA \(_2\) cement. And, it is much more pronounced with \( \text{Li}_2\text{CO}_3 \) than gbbs and CA, respectively.

The rapid setting time of CA \(_2\) with \( \text{Li}_2\text{CO}_3 \) admixture at 0.1wt\% (Table 2) open the way of the research on biomedical applications for his high strength than the minimum required for bone cements according to the ASTM451 standard. The formation of \( \text{AH}_3 \) phase in hydrated CA \(_2\) sample is much more than in CA. This was expected as CA \(_2\) contain more \( \text{Al}_2\text{O}_3 \) the strength of hydrated CA \(_2\) is found to increase than CA.

This result improves the characteristics of cement for construction and biomedical applications.

### 4. Conclusions

A novel approach to understand the reactivity of calcium dialuminate CA \(_2\) cement with lithium carbonate (\( \text{Li}_2\text{CO}_3 \)) admixture have been studied at low temperature 20 ± 3°C. A little amount of 0.1wt\% \( \text{Li}_2\text{CO}_3 \) improve the reactivity of CA \(_2\) by reducing the reaction peak time from 17 h to 43 min. The hydration heat is 168 J/g for the CA \(_2\) cement without lithium carbonate and 123 J/g with 0.3wt\% of lithium carbonate. It was observed from SEM and EDS images that \( \text{Li}_2\text{CO}_3 \) acted as a catalyst; a nucleation site of \( \text{Li}_2\text{Al}_6\text{O}_{15}(\text{H}_2\text{O})_{11} \) for hydrated products accelerating the conversion to \( \text{CAH}_{10} \) and \( \text{AH}_3 \) which assemble to a polymeric « flower » like structure in the correct arrangement. The admixture like \( \text{Li}_2\text{CO}_3 \) reduces significantly the hydration heat of CA \(_2\) cement. While the global surface charge of cement made with lithium carbonate admixture remains negative, thus improving the characteristics of the cement for construction and biomedical applications.

### Nomenclature

| Oxide compounds | \( H \) | \( S \) | \( L \) | \( F \) | \( S \) | \( C \) |
|-----------------|-----|-----|-----|-----|-----|-----|
|                | \( \text{H}_2\text{O} \) | \( \text{SiO}_2 \) | \( \text{Li}_2\text{O} \) | \( \text{Fe}_2\text{O}_3 \) | \( \text{SO}_4^{2-} \) | \( \text{CO}_3^{2-} \) |

### Symbols

- ALC0: 0wt.\% \( \text{Li}_2\text{CO}_3 \)
- ALC1: 0.3wt.\% \( \text{Li}_2\text{CO}_3 \)
- ALC2: 0.6wt.\% \( \text{Li}_2\text{CO}_3 \)
- ALC3: 0.1wt.\% \( \text{Li}_2\text{CO}_3 \)
- ALC4: 0.2wt.\% \( \text{Li}_2\text{CO}_3 \)
- ALC5: 0.4wt.\% \( \text{Li}_2\text{CO}_3 \)
- ALC6: 0.5wt.\% \( \text{Li}_2\text{CO}_3 \)
- PDF: Powder Diffraction File

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### ORCID

Tchedele Langollo Yannick http://orcid.org/0000-0003-4955-1930

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