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Impact of Water Vapour and Carbon Dioxide on Surface Composition of C₃A Polymorphs Studied by X-Ray Photoelectron Spectroscopy

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Number of Figures: 7
Number of Tables: 4

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Abstract

The surface specific analytical method, x-ray photoelectron spectroscopy (XPS), has been used to study the effects of water vapour and CO\textsubscript{2} on the cubic and orthorhombic polymorphs of \( \text{C}_3\text{A} \). Significant differences between the two polymorphs were observed in the XPS spectra. Upon exposure to water vapour, both polymorphs produced \( \text{C}_4\text{AH}_{13} \) on their surfaces. Additionally, the sodium-doped \( \text{o-C}_3\text{A} \) developed NaOH and traces of \( \text{C}_3\text{AH}_6 \) on its surface. Subsequent carbonation yielded mono carboaluminate on both polymorphs. Large amounts of Na\textsubscript{2}CO\textsubscript{3} also formed on the surface of \( \text{o-C}_3\text{A} \) as a result of carbonation of NaOH. Furthermore, the extent of carbonation was much more pronounced for \( \text{o-C}_3\text{A} \) than for \( \text{c-C}_3\text{A} \).

106 Words

Key words: \( \text{C}_3\text{Al}_2\text{O}_6 \) polymorphs (D), prehydration, carbonation (C), X-ray photoelectron spectroscopy
1. Introduction

Tricalcium aluminate (C₃A) constitutes ~ 2 – 12 wt. % of Portland cement clinker. In industrial cement, C₃A usually occurs as one of two polymorphs; cubic or orthorhombic. It is well known that C₃A can incorporate a large number of minor and trace elements into its crystal structure [1 – 4]. The impact of these elements on the crystal structure as well as the hydration behaviour and kinetics has been thoroughly discussed in previous works [5 – 9].

Among those impurities, alkalis (K₂O, Na₂O) appear to be the most important modifying oxides. These oxides are able to change the crystal system of C₃A from cubic to orthorhombic and to monoclinic [8], and sodium oxide plays a significant role in stabilising different modifications of C₃A. The structure of pure, undoped, cubic C₃A has been determined by Mondal and Jeffery. They also discussed the solid solutions of the Na₂O-C₃A series [10]. Isomorphous substitution of calcium by sodium in solid solutions formed at 1250 °C leads to crystallisation into the cubic polymorph at Na₂O contents of 0 - 2.5 % (by mass), the orthorhombic polymorph at 3.5 - 4.2 % Na₂O, and the monoclinic polymorph at > 4.2 % Na₂O [11].

C₃A is the most reactive phase within cement clinker. In the absence of soluble sulphates, it instantaneously forms massive amounts of hydration products, mainly calcium aluminate hydrates (C-A-H phases of different stoichiometric compositions). Owing to this high reactivity, C₃A can react with atmospheric water vapour during storage; a phenomenon known as prehydration of cement [8,12]. It has been demonstrated that, of all the cement constituents, C₃A reacts preferably with water vapour when cement is prehydrated [13], with an impact on the eventual setting behaviour of the cement [14]. However, the cubic and orthorhombic C₃A polymorphs exhibit different behaviours when exposed to water vapour.
For orthorhombic $C_3A$, the onset point at which water sorption starts to occur lies at 55 % relative humidity (RH), compared to 80 % RH for cubic $C_3A$ [15].

Prehydration is predominantly a surface reaction, hence common bulk analysis methods such as x-ray diffraction are of limited value. Instead, surface specific analytical techniques, such as X-ray photoelectron spectroscopy (XPS), may be used to provide information on the composition and speciation of the prehydrated surface, without interference from the unaffected bulk material [16]. In XPS, the sample is irradiated with x-rays in order to provoke the photoelectric effect, with the energy of the emitted photoelectrons being characteristic of the element from which they are emitted and the chemical state of the element. The low energy of the photoelectrons ensures that only those emitted from the surface of the irradiated sample are detected, Consequently, XPS allows the analysis of surface layers typically 1 to 10 nm thick, with all elements bar hydrogen being capable of identification [17].

In the present study, the impact of initial exposure of $C_3A$ to moisture, followed by interaction with atmospheric $CO_2$, has been investigated by XPS. Furthermore, the influence of $Na_2O$, present in the orthorhombic modification of $C_3A$, on these processes was studied.

2. Materials and Methods

2.1 Synthesis of $C_3A$ polymorphs

Pure, undoped cubic $C_3A$ and orthorhombic $C_3A$ doped with 4 wt. % $Na_2O$ were synthesised according to the literature [16], using calcium carbonate and aluminium oxide as starting materials. Sodium nitrate was used as the $Na_2O$ source in the preparation of orthorhombic $C_3A$. The samples, sintered at 1450 °C for 4 hours, were removed from the oven, allowed to cool in air for 3 minutes in covered Pt crucibles and then immediately placed in the cup of a steel ball mill (Planetary Mono Mill PULVERISETTE 6 classic line, Fritsch, Idar-Oberstein,
Germany). Grinding was performed in air at 250 rpm for 10 minutes at a temperature of 21 °C without the addition of a grinding agent. The ground samples were stored in sealed 20 mL glass bottles placed in a vacuum desiccator.

According to quantitative X-Ray diffraction (XRD) analysis of freshly prepared samples, the C₃A phases were 99 ± 0.5 wt. % pure. Their XRD patterns are presented in Figure 1. FTIR-ATR spectra of the synthesised C₃A samples further confirmed their phase purity. Figure 2 shows the characteristic differences between the two polymorphs: with a reduction in the number of IR bands for orthorhombic C₃A, as a result of altered symmetry of the Al₆O₁₈ ring 

(C₃ → C₁). Furthermore, partial substitution of Ca²⁺ by Na⁺ induces disorder in the structure and thus broadening of the bands [2].

Fig. 1. XRD patterns of cubic and orthorhombic C₃A phases as prepared, shown over the range 8 – 40° 2θ
Fig. 2. FTIR-ATR spectra of cubic and orthorhombic C₃A phases as prepared, shown over the range 600 – 1000 cm⁻¹.

The surface of orthorhombic C₃A was investigated by scanning electron microscopy (SEM) using a FEI XL 30 FEG microscope equipped with a large field detector under low vacuum conditions (1 mbar H₂O pressure, corresponding to ~ 4 % RH at room temperature).

2.2 Water and CO₂ exposure of samples

200 mg of powdered C₃A were pressed into pellets (d = 13 mm) at a pressure of 50 N/mm² using a hydraulic press. The pellets of cubic and orthorhombic C₃A were then refired at 1350 °C for 3 h (c-C₃A) or 20 minutes (o-C₃A) to achieve complete dehydration and decarbonation.

However, preliminary XPS analysis of the C₃A pellets still showed evidence of slight carbonation. Thus, to obtain a completely pristine surface, all samples were etched by argon
ion bombardment under vacuum in the spectrometer, prior to any exposure to water vapour
and CO₂.

Each sample was cleaned by ion bombardment in the spectrometer and then subjected to three
different exposure cycles. Pellets were placed in a nitrogen gas filled desiccator which was
placed in a glove box. The relative humidity over the samples was adjusted to 85 % using a
saturated potassium chloride solution within the desiccator [18]. Samples were initially
exposed for 4 hours, and then analysed. Subsequently, the same sample was prehydrated
under the same conditions for a further 8 hours before the second analysis. The third and final
cycle exposed the previously prehydrated sample to atmospheric conditions, i.e. ambient air
containing CO₂, for a further 12 hours. Throughout the rest of the manuscript samples are
identified as; 0h, 4h, 12h and 24c, where h and c indicate exposure to humidity or CO₂
respectively and the number indicates the duration of exposure.

2.3 XPS analysis

Each pellet was stuck onto a double-sided adhesive copper tape and inserted into the vacuum
chamber for analysis. The samples were analysed using a SCIENTA ESCA 300 photoelectron
spectrometer (located at the National Centre for Electron Spectroscopy and Surface Analysis,
NCESS, Daresbury, UK) fitted with a high power rotating anode (8 kW) and a
monochromatic Al Kₐ (hv = 1486.7 eV) X-ray source. The X-ray beam was focused on a
6 mm × 0.5 mm area on the sample via a large, seven crystal double focusing
monochromator. The Al Kₐ line profile had a FWHM (full width at half maximum) energy
width of 0.26 eV. The detection system consisted of a 300 mm radius hemispherical analyser
and a multi-channel detector. The system was operated with 0.8 mm slits and 150 eV pass
energy, giving an overall instrument resolution of 0.30 eV ± 0.05 eV FWHM. Because the
samples were often extremely good electrical insulators, a flood gun was used to compensate for sample charging.

Following an initial survey scan, high resolution spectra were recorded for the elements of interest: Na 1s, Ca 2p, O 1s, C 1s, Al 2p. Derived sensitivity factors were applied to convert signal intensities to atomic compositions [19].

Data were extracted from the spectra via peak fitting using CasaXPS software. A Shirley background was assumed in all cases. Spectra were corrected for charging effects using the adventitious hydrocarbon peak at 284.8 eV binding energy (BE). This peak is ubiquitous due to carbon contamination from the vacuum systems [20]. The presence of inorganic carbon, as carbonate, was always looked for in high-resolution scans.

3. Results and discussion

3.1 XPS analysis of fresh C₃A polymorphs

Figures 3 and 4 show the Al 2p and C 1s XPS spectra obtained from both polymorphs after each exposure. The corresponding binding energies and elemental ratios are tabulated in Tables 1 – 4. Note that, for simplicity, quantification assumed that samples were homogeneous with respect to depth.
**Fig. 3** XPS spectra of non-doped, cubic C₃A sample, fresh and aged, showing the evolution of the Al 2p (left) and C 1s (right) peaks upon exposure to water vapour and subsequent carbonation.

**Fig. 4** XPS spectra of Na-doped orthorhombic C₃A sample, fresh and aged, showing the evolution of the Al 2p (left) and C 1s (right) peaks upon exposure to water vapour and subsequent carbonation.
### Table 1 Binding energies of fresh and aged cubic C\(_3\)A, as obtained by XPS

<table>
<thead>
<tr>
<th>Element</th>
<th>Binding energy (eV)* after exposure period/mode</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 h (fresh)</td>
</tr>
<tr>
<td>Ca 2p(_{3/2})</td>
<td>346.4</td>
</tr>
<tr>
<td>O 1s</td>
<td>529.7</td>
</tr>
<tr>
<td>Al 2p</td>
<td>72.9</td>
</tr>
<tr>
<td>C 1s</td>
<td>289.7</td>
</tr>
</tbody>
</table>

* Shifts relative to C 1s = 284.8 eV

### Table 2 Element ratios and chemical shifts of fresh and aged cubic C\(_3\)A, as obtained from XPS analysis

<table>
<thead>
<tr>
<th>El. ratios</th>
<th>Element ratios and chemical shifts (eV)* after exposure period/mode</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 h (fresh)</td>
</tr>
<tr>
<td>Ca/Al*</td>
<td>1.5</td>
</tr>
<tr>
<td>C/Ca</td>
<td>0.07</td>
</tr>
<tr>
<td>(\Delta)Ca - Al</td>
<td>273.4</td>
</tr>
<tr>
<td>(\Delta)Ca - C</td>
<td>56.8</td>
</tr>
</tbody>
</table>

*: Values represent normalized ratios based on the assumption that etched sample possesses the ideal composition Ca\(_3\)Al\(_2\)O\(_6\).

### Table 3 Binding energies of fresh and aged orthorhombic C\(_3\)A derived from XPS analysis

<table>
<thead>
<tr>
<th>Element</th>
<th>Binding energy (eV)* after exposure period/mode</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 h (fresh)</td>
</tr>
<tr>
<td>Ca 2p(_{3/2})</td>
<td>346.4</td>
</tr>
<tr>
<td>O 1s</td>
<td>529.8</td>
</tr>
<tr>
<td>Al 2p</td>
<td>73.1</td>
</tr>
<tr>
<td>Na 1s</td>
<td>1071.6</td>
</tr>
<tr>
<td>C 1s</td>
<td>289.6</td>
</tr>
</tbody>
</table>

* Shifts relative to C 1s = 284.8 eV

### Table 4 Element ratios and chemical shifts of fresh and aged orthorhombic C\(_3\)A, as obtained from XPS analysis

<table>
<thead>
<tr>
<th>El. ratios</th>
<th>Element ratios and chemical shifts (eV)* after exposure period /mode</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 h (fresh)</td>
</tr>
<tr>
<td>Ca/Al*</td>
<td>1.42</td>
</tr>
<tr>
<td>Na/Ca*</td>
<td>0.12</td>
</tr>
<tr>
<td>C/Ca</td>
<td>0.04</td>
</tr>
<tr>
<td>Na/C</td>
<td>0.47</td>
</tr>
<tr>
<td>(\Delta)Ca - Al</td>
<td>273.3</td>
</tr>
<tr>
<td>(\Delta)Ca - C</td>
<td>56.9</td>
</tr>
<tr>
<td>(\Delta)Na - C</td>
<td>782.2</td>
</tr>
</tbody>
</table>

*: Values represent normalized ratios based on the assumption that etched sample has the ideal composition Ca\(_8\)NaAl\(_2\)O\(_18\).
The Al 2p spectra for the fresh phases were slightly asymmetrical, due to spin orbit coupling of the Al 2p lines, with the undoped, more calcium-rich, cubic C\textsubscript{3}A having a slightly lower binding energy than orthorhombic C\textsubscript{3}A (Figures 3 and 4). The Al 2p spectra for the fresh samples show two contributions, namely at ~ 72.9 and 73.5 eV for the cubic and at ~ 73.1 and 74.0 eV for the orthorhombic C\textsubscript{3}A polymorph (Tables 1 and 3). The spectra reported here for cubic C\textsubscript{3}A are very similar to the binding energy of 73.1 eV reported by Ball et al. [21]. Aluminium binding energies are dependent upon the coordination number [22,23]. In both C\textsubscript{3}A modifications, Al is always tetrahedrally coordinated and occurs as AlO\textsubscript{4}. Six such tetrahedra form an Al\textsubscript{6}O\textsubscript{18} ring in orthorhombic C\textsubscript{3}A which becomes deformed upon replacement of Ca\textsuperscript{2+} by the slightly less electronegative Na\textsuperscript{+} in the centre of the Al\textsubscript{6}O\textsubscript{18} ring [24]. Thus, the slight changes in binding energy from cubic to orthorhombic C\textsubscript{3}A may be due to the symmetry change (C\textsubscript{3} → C\textsubscript{i}) or a change in electronegativity caused by the incorporation of Na\textsubscript{2}O into doped C\textsubscript{3}A.

The Ca 2p binding energies for both fresh polymorphs were the same and in good agreement with the value of 346.3 eV obtained by Ball et al. [21]. Unlike the Al 2p spectra, Ca 2p binding energies are less sensitive to changes in composition, e.g. in both calcium aluminate hydrate [21] and calcium silicate hydrate [21, 22] systems. Consequently, spectra would not be expected to change upon replacement of calcium by sodium.

In addition to the binding energies, changes in the Ca 2p – Al 2p energy separation (Δ\textsubscript{Ca-Al}) were determined (Tables 2 and 4). In previous studies on calcium silicate hydrates, these values have been shown to provide valuable information related to changes in their chemical structure, in particular the degree of silicate polymerisation in calcium silicate hydrates [20,25]. This approach also overcomes problems due to charging when analysing insulating
samples. Here, the incorporation of sodium into the C\textsubscript{3}A lattice, with the conversion from cubic to orthorhombic, did not induce changes in polymerisation, but there was a slight reduction in $\Delta_{\text{Ca-Al}}$ from 273.4 to 273.2 eV, likely as a result of the reduced electronegativity of sodium compared to calcium.

3.2 Exposure to water vapour and CO\textsubscript{2}

In a previous investigation, there was a distinct difference between the XPS spectra of the surfaces of cubic and orthorhombic C\textsubscript{3}A prehydrated in moist air (85 % RH, and including CO\textsubscript{2}) for just 1 h [21]. In this study emphasis has been placed on separation of the effects caused by water vapour and carbon dioxide.

Prehydration under water vapour only (no CO\textsubscript{2} present) was slower than in the previous study where prehydration was performed in moist, CO\textsubscript{2}-containing air. Nonetheless, exposure to water vapour led to spectral changes and shift to higher Al 2p binding energies (Figures 3 and 4). Furthermore, the Al 2p spectra broadened upon prehydration and two peaks were required to fit them, signifying a change in the chemical environment of Al, plausibly due to formation of C-A-H phases. An Al 2p binding energy of 73.8 eV has previously been reported for pure C\textsubscript{4}AH\textsubscript{13} [16]. Here, after exposure of both C\textsubscript{3}A polymorphs to water vapour for 12 h, a peak could be fitted at $\sim$ 73.7 eV, likely indicative of C\textsubscript{4}AH\textsubscript{13} formation. The second peak in the Al 2p spectra was centred at $\sim$ 74.3 eV for the cubic and at $\sim$ 74.5 eV for the orthorhombic modification. These peaks might be attributable to C\textsubscript{3}AH\textsubscript{6} (katoite), as was found by a combination of XRD and XPS in the aforementioned previous study [16].

Upon exposure to air, i.e. upon carbonation, the Al 2p spectra of both polymorphs showed further changes, with formation of carbonate observed in the C 1s spectra, as indicated by a peak at $\sim$ 289 eV (Fig 3 and 4).
For the cubic modification, the relative peak areas of the Ca 2p and C 1s spectra (Ca 2p spectra not shown here) suggest a C/Ca ratio of 0.3 (Table 2), indicating the formation of calcium monocarboaluminate (3 CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 11 H_2O). This is in agreement with the bulk carbonation behaviour of C₃A pastes, as analysed by Raman spectroscopy [26]. The mechanism of the monocarboaluminate formation is based on the reaction of CO₂ with C₄AHₓ phases which possesses a disordered layered structure. In this process, the interlayer OH⁻ is replaced by CO₃²⁻ [27]. The ion exchange stabilises the layered structure and results in shrinkage of the basal spacing from 1.08 nm in C₄AH₁₃ to 0.76 nm for the carbonated species [28].

Carbonation of orthorhombic C₃A was more extensive than for the cubic modification. Sample 24c revealed a C/Ca ratio of 0.8 (Table 4). This ratio was too high to be explained solely by calcium monocarboaluminate formation, and indicated the presence of another carbonate species.

Figure 5 shows the changes in C/Ca and Ca/Al ratios with exposure for both C₃A modifications. While there was no change in the Ca/Al ratio of the cubic C₃A, exposure to water vapour led to an increase in Ca/Al ratio for orthorhombic C₃A. We ascribe this to an increase in the surface pH due to surface enrichment in sodium upon prehydration (see below). Such conditions would accelerate the formation of C₄AHₓ phases, as observed previously [16]. This may also explain the lower relative humidity threshold above which orthorhombic C₃A begins to prehydrate compared to cubic C₃A [8,15,16].
Fig. 5 Normalised ratios of C/Ca (a) and Ca/Al ratios (b) occurring on the surfaces of cubic and orthorhombic C₃A as a function of ageing period and mode, as measured by XPS.
3.3 Impact of Na$_2$O doping

The high resolution Na 1s spectra revealed how the presence of sodium affected the reactivity of orthorhombic C$_3$A, and spectra plus the calculated Na/Ca ratios are shown in Fig. 6. The freshly calcined sample exhibited a Na 1s signal comprising of two signals; the main one centred at ~ 1071.5 eV and a second minor peak at ~ 1072.2 eV. No definitive assignment could be made for the major peak, but we assume it to be due to sodium substituted for calcium within the C$_3$A, while the second peak is of a similar binding energy to the value of 1072.3 eV reported for pure Na$_2$O and NaOH [29,30].

Exposure to water vapour only led to a gradual increase in the intensity of the signal centred at ~ 1072.2 eV; indicating that less and less sodium was bound within the crystal structure of orthorhombic C$_3$A, with the increased intensity due to mobilisation of sodium and its migration to the sample surface. This finding agrees with results from Glasser et al. who observed that Na$^+$ can dissolve into the aqueous phase more rapidly than Ca$^{2+}$ or Al$^{3+}$ [5]. Upon abstraction from the crystal structure, sodium appears to combine with water to form NaOH on the surface, with a binding energy of 1072.2 eV characteristic of NaOH [29].

Exposure to CO$_2$ within ambient air led to further changes in the Na 1s spectra, namely a large growth in intensity and a slight shift back to lower binding energies, with the signal centred at 1071.3 eV. Such binding energy may correspond to either Na$_2$CO$_3$ or NaHCO$_3$, both of which produce a peak at 1071.3 eV [29]. This finding suggests that the initially formed NaOH then carbonated to form Na$_2$CO$_3$ or NaHCO$_3$, which constitutes the main product from the prehydration and carbonation process. The formation of this phase also helps to explain the high C/Ca ratio reported above.
Fig. 6 Na 1s XPS spectra of fresh and aged orthorhombic C₃A samples (a) and Na/Ca ratios after exposure of orthorhombic C₃A sample to moisture and CO₂ in air (b)
The formation of Na$_2$CO$_3$ or NaHCO$_3$ on the surface of o-C$_3$A was confirmed by SEM imaging (Fig. 7). Bright crystalline specks were visible on the surface of sample 24c, which EDX spectroscopy indicated as comprising of sodium, carbon and oxygen, presumably of Na$_2$CO$_3$ or NaHCO$_3$.

Fig. 7 SEM images of the surfaces of a) 0h (fresh) and b) 24c (prehydrated and carbonated) orthorhombic C$_3$A, showing Na$_2$CO$_3$ or NaHCO$_3$ crystals on the prehydrated sample.

4. Conclusions

X-ray photoelectron spectroscopy has been used to follow the interactions of cubic and orthorhombic C$_3$A polymorphs with environmental moisture and CO$_2$ under defined storage conditions.

In the XPS spectra, clear differences were observed for cubic and orthorhombic C$_3$A after prehydration with water vapour and subsequent carbonation in air. During prehydration in the absence of CO$_2$, both C$_3$A polymorphs showed the formation of C$_4$AH$_{13}$ on their surfaces, but the extent was more pronounced for the orthorhombic polymorph. Surface enrichment of sodium, in the form of sodium hydroxide, was observed after prehydration of orthorhombic C$_3$A which was doped with 4 wt. % of Na$_2$O. The increased pH induced by the formation of surface NaOH during prehydration may account for the increased rate of reaction, as has been
reported previously [21]. It may also explain why the effects of prehydration become evident at 55% RH for orthorhombic C₃A, but at 80% RH for cubic C₃A [8,16].

Additionally, the impact of sodium on carbonation of orthorhombic C₃A was studied. Prehydrated cubic C₃A produced monocarboaluminate (3 CaO·Al₂O₃·CaCO₃·11H₂O) on its surface, while carbonation of orthorhombic C₃A resulted in formation of the same phase, together with extensive Na₂CO₃ or NaHCO₃ formation. The reason for the latter is the high amount of NaOH formed after the initial prehydration at the surface of orthorhombic C₃A.

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References


