

Real time study of cement and clinker phases hydration

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Real time studies of hydration of a Portland cement and of calcium silicate extracted clinker were made. X-Ray diffraction measurements were made using either an INEL powder diffractometer (Zr-filtered Mo-K α radiation, CPS120 position sensitive detector) or a MAR diffractometer (synchrotron X-radiation, wavelength 0.90371 Å). The dry samples were mounted in glass capillaries and hydrated *in-situ* by the application of internal nitrogen gas pressure of up to about 150 kPa which pressed the water into contact with the dry sample. This allowed the study of early phase transitions in the reaction mixture. The experiments were conducted over the temperature range 25–100 °C. The laboratory based X-ray experimentation provided similar results to those obtained using the synchrotron radiation, although the counting statistics in the synchrotron data were far superior. The use of constant wavelength synchrotron radiation gave well-resolved lines of powder diffraction data over the angular range investigated. This is in contrast to the less well-resolved reflections previously observed in the energy dispersive diffraction mode. The hydration of the Portland cement showed the immediate formation of ettringite (3CaO·Al₂O₃·3CaSO₄·32H₂O) upon the addition of water. Two silicate extracted clinker residues were considered: one being predominantly cubic C₃A and the other comprising a mixture of orthorhombic C₃A and brownmillerite (Ca₄Al₂Fe₂O₁₀, C₄AF). The reaction paths of these two residues were different. The hydration of cubic C₃A proceeded *via* C₄AH₁₉ to the end product, C₃AH₆, Ca₃Al₂(OH)₁₂. The reaction of orthorhombic C₃A, C₄AF and water proceeded *via* C₂AH₈ to the end product C₃AH₆.

Introduction

Cement clinker compounds are produced from mixtures of minerals in high temperature solid state reactions and contain a variety of phases where the main compounds are calcium silicates, calcium aluminates, and calcium aluminoferrites. The hydration properties of cement have been investigated by several research groups and results of such investigations are plentifully available in the literature on the hydration of Portland cement^{1,2} on the effects of gypsum in cements,³ and on the hydration of calcium aluminate cements.⁴ Investigations of chemical reactions in synthesis and hydration of cements were typically carried out *ex-situ* on reaction products after the reaction has been stopped in some way. There are obvious advantages to making measurements using on-line techniques. An example concerning the production of cements is the development of an X-ray powder diffractometer for on-line diffraction of Portland cement⁵ which combined with a full pattern profile analysis^{6,7} gives a continuous on-line phase analysis of the cement.⁵ Before these types of phase analyses were developed it was more realistic to study pure phases of the cement components rather than the complex heterogeneous mixture of phases of cement. The earliest *in-situ* neutron powder diffraction investigation of the reactions of calcium aluminates with water (D₂O) is an example of this approach.⁸ The powder neutron diffractometer D1B at the Institute Laue–Langevin, Grenoble, was used with 2.517 Å neutrons and the instrument was ideal at that time for these *in-situ* investigations.

Synthetic calcium aluminates were used in the investigation instead of industrially produced cements, as it was estimated that the neutron powder diffraction patterns of samples with several phases present would have too many overlapping reflections to make quantitative phase analysis possible. The rate of reactions between water (D₂O) and the calcium aluminates decreased in the sequence C₃A, C₅A₃, CA to CA₂, where all compounds gave Ca₃Al₂(OD)₁₂ (C₃AD₆) as the final end product at temperatures at and over 30 °C.⁸ (For cement chemical

nomenclature see refs. 1 and 4). The synthetic calcium silicate C₃S reacted faster with D₂O than β-C₂S,⁹ and in these cases the crystalline reaction product was Ca(OD)₂. Brownmillerite reacted with D₂O forming Ca(OD)₂ and C₃AD₆,⁹ and C₄AF reacted faster than CA but slower than C₃A and C₅A₃ at the temperature 63 °C.^{8,9}

The effect of the additive CaSO₄·2D₂O on the hydrolysis of C₃A¹⁰ and C₁₂A₇,^{10,11} with D₂O at 27 °C, and of the addition of CaSO₄·0.5D₂O on the hydrolysis of CA¹⁰ at 80–120 °C was investigated, and in all these cases a precursor phase was formed prior to the formation of ettringite, C₆A₃D₃₂. Ettringite starts to form when the precursor phase is at its maximum in quantity and it is then depleted rapidly in the growth of ettringite. The precursor has a powder pattern which was indexed on a hexagonal unit cell with *a* = 11.19(1) and *c* = 21.42(1) Å, which is comparable to the unit cell of ettringite, *a* = 11.23, *c* = 21.44 Å. It was suggested that the precursor was a metastable form of ettringite and that the differences in the intensities of the Bragg reflections could derive from a less ordered to an ordered arrangement of the deuterium atoms which would be observed in the neutron diffraction case and not in the X-ray diffraction patterns of the precursor and ettringite.

The effect of the additive CaCO₃ on the hydrolysis of CA¹⁰ with D₂O at 80 °C resulted in formation of the compound Ca₄Al₂(OD)₁₂CO₃·5D₂O, and the effect of the additives CaCl₂ and CaBr₂ on the hydrolysis of C₁₂A₇ with D₂O at temperatures up to 108 °C gave the final reaction products α-Ca₂Al(OD)₆Cl·2D₂O and Ca₂Al(OD)₆Br·2D₂O.¹² At temperatures up to 40 °C these two compounds were formed from a precursor phase which had an X-ray (and neutron) powder pattern that suggests the precursor phase to be C₄AD₁₉.

When synchrotron X-ray radiation became readily available in the early 1980s, techniques known from neutron scattering could be applied to X-ray experiments which could be made in energy dispersive as well as in constant wavelength modes. The X-ray synchrotron radiation was orders of magnitude more

Table 1 Composition of the samples in wt%

Sample	C ₃ S	β-C ₂ S	C ₄ AF	C ₃ A _{cubic}	C ₃ A _{orth}	Lime	Ca(OH) ₂	Total
1. Aalborg Portland cement ^a	67.04	3.04	9.43	8.01		1.91		89.43
2. Australian clinker A	63.9	23.3	1.9	9.6	1.0	0.2		99.9
2A. Extracted once	35.3	19.2	1.3	42.7	0.8		0.6	99.9
2B. Extracted twice	19.4	10.6	2.2	67.7	0.1			100.0
3. Australian clinker B	61.9	15.4	14.4	0.0	6.6	1.7		100.0
3A. Extracted once			67.3		32.7			100.0

^a Chemical analysis gave in wt%: Na₂O: 0.16, MgO: 1.33, Al₂O₃: 5.04, SiO₂: 18.70, SO₃: 3.37, K₂O: 1.11, CaO: 63.10, Fe₂O₃: 3.07, free lime: 1.91, total: 95.88%.

intense than the known neutron sources, so experiments could be performed faster and with smaller samples than with neutrons or with X-rays from sealed tubes. An early example of this reduction in time is the measurement of a well resolved powder pattern of barium titanate recorded in 20 s in the energy dispersive diffraction mode.¹³

The energy dispersion diffraction mode was used in a series of *in-situ* studies of the hydration processes of alumina- and Portland-cement components.¹⁴ The sample holder was a cylinder of approximately 10 mm diameter which could be rotated to randomize the particle distribution and in which the solid could be mixed with water during the diffraction experiment.^{15,16} Studies were made on the formation of ettringite^{15–17} where an increase in the unit cell parameter *a* of ettringite was observed during the growth from *a* = 11.14 Å to *a* = 11.22 Å. Ettringite formation starts almost immediately as a carbonate and hydroxy ettringite, and when sulfate ions become available by the dissolution of calcium sulfate then sulfate ettringite is formed which was observed as a peak shift of the 112 reflection during the early part of the hydration process. The hydration reaction of calcium alumina cement at 50 °C shows that CA is converted to CAH₁₀, and C₂AH₈ is then formed as two intermediate phases α-C₂AH₈ and β-C₂AH₈. The final compound C₃AH₆ is starting to appear when α-C₂AH₈ has been converted to β-C₂AH₈, which is then simultaneously depleted during the formation of C₃AH₆.¹⁸ The hydration of C₃A with water was investigated in the temperature range 26–36 °C.¹⁹ C₃A reacts with water to an intermediate phase, and C₃AH₆ does not begin to form until the intermediate phase has reached its maximum level. The intermediate phase had *d*-spacings at 10.7 and 5.36 Å, which fits C₂AH₈ and C₄AH₁₉, but the intensity ratios of the two reflections fits best for C₂AH₈. A small peak at *d* = 3.58 Å supports the conclusion that the intermediate phase was C₂AH₈.^{19,20}

In contrast to the energy dispersive diffraction mode and the use of samples with large volumes as described above, the constant wavelength mode and the use of samples in capillaries is another approach to *in-situ* investigations using X-ray synchrotron radiation. *In-situ* studies of catalysis have been made using this approach,²¹ and *in-situ* studies of phase transitions²² and hydrothermal synthesis²³ have been performed. Counters such as imaging plates,²⁴ INEL position sensitive detectors,²⁵ or MAR area detector diffractometers²⁶ have been used. As well, *in-situ* investigations could be made using sealed X-ray tubes and appropriate position sensitive detectors.

A fair number of investigations have been made on the components of alumina cements and Portland cements, and these components have in most cases been synthesized as pure phases. Limited work has been made on the hydrolysis of industrially produced cements by the *in-situ* methods outlined above. The different phases in industrially produced cement may well take other routes in the hydrolysis process than the pure synthetic phases described above, because the cement phases made from minerals *a priori* not be chemically pure. For this reason, it is important to study the hydrolysis of industrially produced cements, and the results of such investigations are reported below.

Experimental

Three industrially produced products were used in the investigation: a Portland cement and two samples of cement clinker where the silicate phases were removed (or partly removed) from the clinker by extraction with a solution of salicylic acid in methanol.²⁷ The compositions of the samples are listed in Table 1. The composition of the Aalborg Portland cement was derived from chemical analysis and the composition of the clinker samples was obtained from full pattern profile analyses of X-ray powder patterns recorded on a Philips diffractometer using Co-Kα radiation, λ = 1.7889 Å.

Preliminary *ex-situ* batch hydration experiments were made with mixtures of 1 g sample and 2 mL water which were stored in small glass flasks at room temperature. Hydrothermal experiments were made with 1 g sample and 5 mL water in 23 mL volume Teflon-lined autoclaves and heated to 190 °C for 66 h. X-Ray powder patterns of reaction products were measured on a Stoe-Stadi diffractometer using Cu-Kα₁ radiation. Fig. 1 displays powder patterns of (a) the dry Portland cement, (b) the reaction product after contact with water for 97 days, where ettringite reflections are marked with Miller indices, and (c) that following the hydrothermal treatment, for the Portland cement. Fig. 2 shows similar patterns for clinker where the silicates have been partly removed. Positions of C₃A reflections are marked in the upper pattern by Miller indices, and positions of reflections of a hydrolysis product are in the middle course marked with *d*-spacing values.

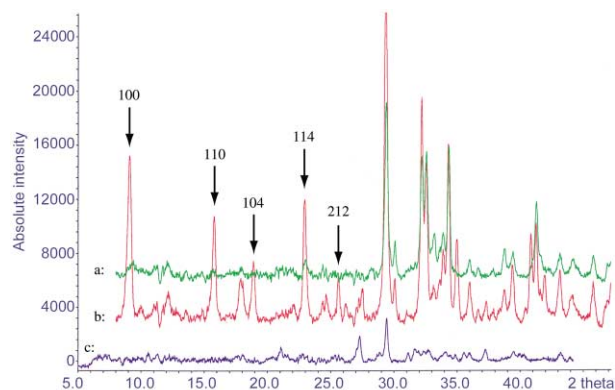


Fig. 1 X-Ray diffraction powder pattern of a Aalborg Portland cement, sample 1, (a) upper pattern, dry sample with reflections of C₃A, C₃S, C₄AF and CaSO₄·0.5H₂O, (b) middle pattern, after reaction with water for 97 days at 25 °C showing reflections of ettringite (#41–1451), calcium hydroxide (#4–733), and C₃S and (c) lower pattern, after hydrothermal treatment at 190 °C for 66 h, where the strongest reflections are from C₃AH₆ (#24–217) and where ettringite is no longer present.

The *in-situ* investigations of the hydrolysis reactions were made using two diffractometers, an INEL CPS-120 based diffractometer at CSIRO Minerals, and a MAR diffractometer at beam line X7B at NSLS, Brookhaven National Laboratory. Zr-filtered Mo-radiation from a sealed X-ray tube, 45 kV and 40 mA, with a horizontal slit of 8.0 mm and a vertical slit of

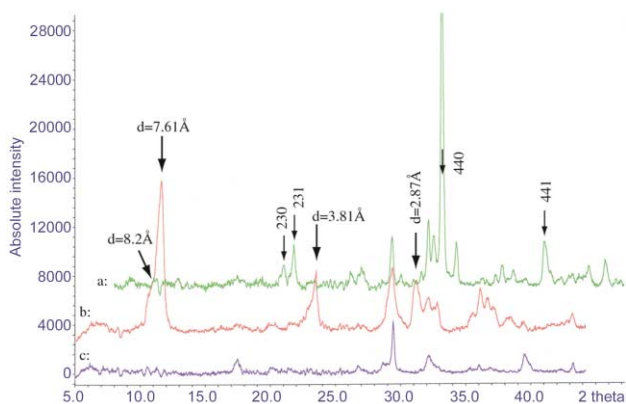


Fig. 2 X-Ray diffraction powder pattern of a calcium silicate extracted clinker, sample 2A, (a) upper pattern, dry sample with reflections of C_3A (#38–1429) and C_3S (#13–272), (b) middle pattern, after reaction with water for 97 days at 25 °C showing reflections of C_3AH_6 (#2–83) and C_3S , and (c) lower pattern, after hydrothermal treatment at 190 °C for 66 h, where the strongest reflections are from C_3AH_6 (#24–217).

0.4 mm was used with the INEL instrument, $\lambda = 0.71093 \text{ \AA}$. This instrument has a 120° curved position sensitive detector. The samples were housed in 1.5 mm diameter glass capillaries. The dry sample was placed in the tip of the capillary and water was then placed in the capillary without contact with the dry sample. After a few diffraction patterns had been recorded, the solid was mixed with water by applying an internal pressure to the capillary of 150 kPa from compressed air. It was not possible to oscillate the sample. However, in order to minimize contributions from single crystal diffractions in the powder patterns, a smoothing function was applied to the powder diffraction data.²⁸ Diffraction patterns were typically recorded for up to 1.5 h at the temperatures 25, 50, 75 and 100 °C. The temperatures chosen to get patterns measured at temperatures comparable to temperatures in the experiments recorded with synchrotron radiation. The recording time for each pattern was 120 s. The samples were heated with a flow of hot air.

The MAR diffractometer has a MAR area detector, and the wavelength used was $\lambda = 0.90371 \text{ \AA}$. The samples were kept in 0.7 mm diameter quartz glass capillaries. The solids were mixed with water as described above by applying a nitrogen gas pressure of 1700 kPa. The capillaries were oscillated 20° to

randomize the crystallites of the samples, and the recording time for a pattern was 120 s. Patterns were recorded at 25 °C, or in a temperature ramp from 25 to 75 °C, where the samples were heated in a flow of hot air.

Results

Sample 1: Aalborg Portland cement

Fig. 3 displays patterns from the hydrolysis of the Portland cement recorded on the INEL instrument, where the sample was kept at 25 °C for 0.75 h, at 50 °C for 1 h, at 75 °C for 1 h, and at 100 °C for 3 h. The main feature is the formation of ettringite which starts at 25 °C and continues during the 5.75 h of the experiment. The quantity of ettringite is increasing during the experiment seen from the increase of the 100 reflection intensity.

Fig. 4 displays patterns from the hydrolysis of the Portland cement recorded on the MAR instrument. The temperature was raised from 25 °C to 75 °C in 2 h, and water was introduced after the second pattern had been recorded. An immediate production of ettringite is observed with the reflections 100, 110 and 104. The two first mentioned reflections are observed before the 104 reflection can be seen in the patterns, indicating different growth rates for the three directions. The change in size of the unit cell parameters reported previously¹⁷ would for the present measurements correspond to a shift of 0.04° in 2θ for the 100 reflection which would be difficult to determine unambiguously. However, in the neutron diffraction investigation, the formation of a precursor phase from which ettringite grows was evident as displayed in Fig. 5(a) in ref. 10. No conversion of ettringite to the monosulfate is observed in the experiment and is not seen in Fig. 3 where the sample has been kept at 100 °C for 3 h. However, in the hydrothermal batch experiment at 190 °C, ettringite is not present as displayed in Fig. 1 (lower pattern). The ettringite to monosulfate reactions has been observed at 150 °C,¹⁴ and at room temperature the reaction takes days.¹ It should be stressed that the hydrolysis reactions in capillaries and in batch experiments at room temperature yields the same reaction product, ettringite.

Sample 2A: residue following calcium silicate extraction from Australian Portland cement clinker

The sample is extracted clinker with a high content of cubic

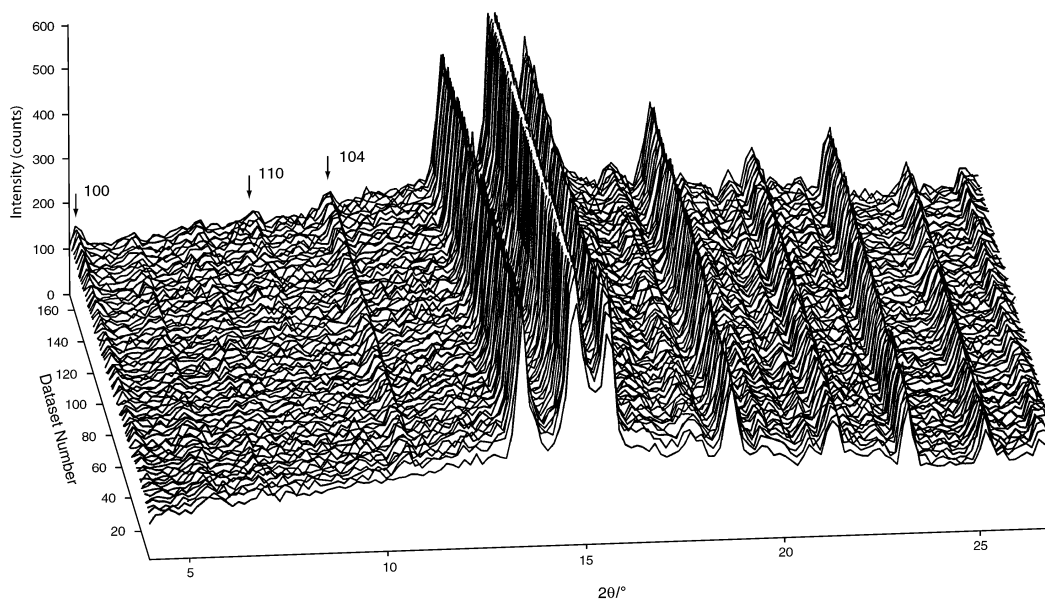


Fig. 3 Stack of powder patterns of Aalborg Portland cement, sample 1, hydrolysed at the temperatures 25, 50, 75 and 100 °C and recorded using Mo-K α radiation. Patterns 1–22 at 25 °C, 23–59 at 50 °C, 60–89 at 75 °C and 90–170 at 100 °C. Positions of ettringite reflections are marked with Miller indices.

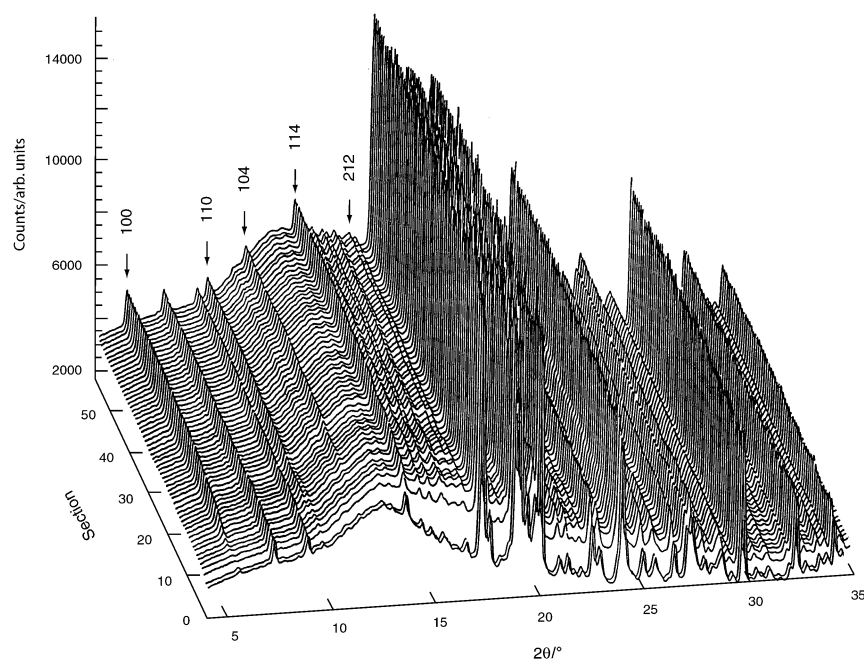


Fig. 4 Stack of powder patterns of Aalborg Portland cement, sample 1, hydrolysed in a temperature ramp from 25 to 75 °C and recorded using synchrotron radiation, $\lambda = 0.90371 \text{ \AA}$. Positions of ettringite reflections are marked with Miller indices.

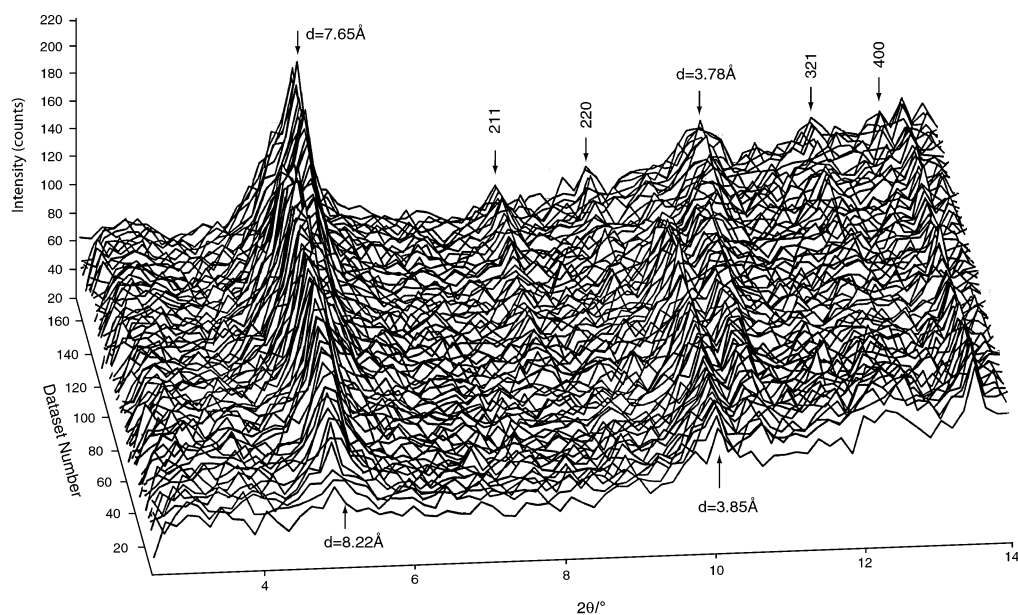


Fig. 5 Stack of powder patterns of calcium silicate extracted clinker, sample 2A, hydrolysed at the temperatures 25, 50, 75 and 100 °C and recorded using Mo-K α radiation. Patterns 1–28 at 25 °C, 29–58 at 50 °C, 59–109 at 75 °C and 110–170 at 100 °C. Positions of C₃AH₆ reflections are marked with Miller indices.

C₃A, but still contains, however, some calcium silicate. The hydrolysis was investigated on the INEL instrument with the sample kept at the temperature 25 °C for 1 h, 50 °C for 1 h, 75 °C for 1.75 h, and at 100 °C for 2.25 h, and Fig. 5 displays the patterns from that experiment. The main results of the experiment are the formation of a phase with a reflection at $2\theta = 4.96^\circ$, $d = 8.22 \text{ \AA}$ at 25 °C, and that this phase is converted at 50 °C to a new phase with a low angle reflection at $2\theta = 5.33^\circ$, $d = 7.65 \text{ \AA}$ before the formation of the hydrate C₃AH₆ starts at 75 °C.

Two *in-situ* experiments using the MAR instrument are reported below, one where the clinker–water mixture is kept at room temperature 25 °C for 2 h, and one where the this mixture is heated in a temperature ramp from 25 to 75 °C over a period of 1 h.

Fig. 6 displays patterns from hydrolysis of the sample at room temperature. The reflections decreasing in intensities during the experiment are the 230, 321, 440, 800, 844 and 880 C₃A reflections, the latter four at 2θ angles higher than 18°. Water is mixed with the dry samples after the third pattern is recorded, indicated by a change in the level of the backgrounds of the patterns, and reduction in intensities of the C₃A reflections starts immediately after water has been added. Reflections with growing intensities are at the 2θ positions 4.80, 6.30, 9.75, 13.40, 18.00, 25.63, 28.68, 31.45°, corresponding to the d -spacings (in Å), 10.8, 8.22, 5.40, 3.87, 2.89, 2.04, 1.824, 1.667 (the latter three are not displayed). The reflections at $d = 10.8 \text{ \AA}$ and $d = 8.22 \text{ \AA}$ increase in intensity with different rates, indicating that they belong to two different reaction products. The reflections at $d = 10.8 \text{ \AA}$ and $d = 5.40 \text{ \AA}$ belong possibly to C₄AH₁₀

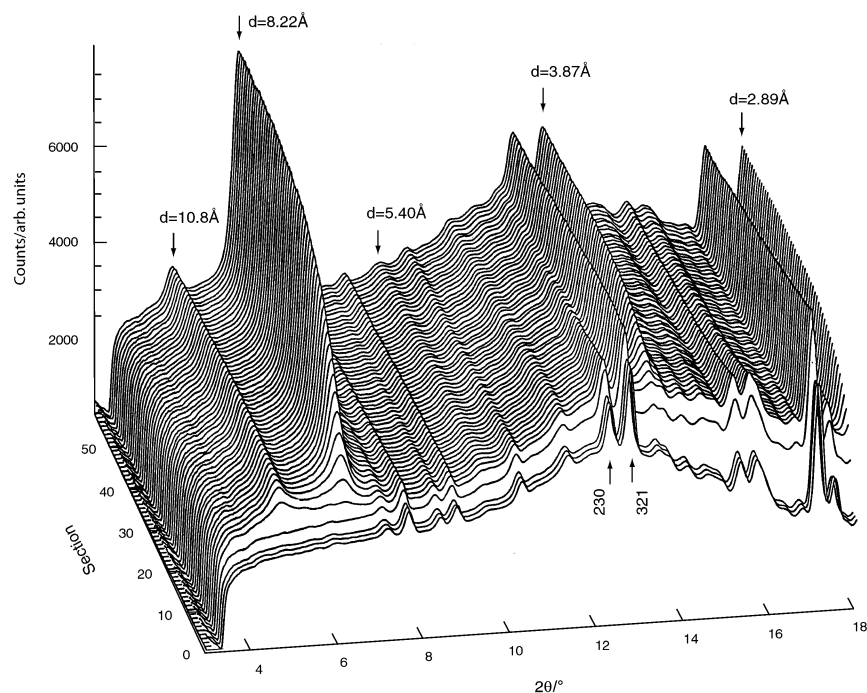


Fig. 6 Stack of powder patterns of sample 2A hydrolysed at 25 °C and recorded using synchrotron radiation, $\lambda = 0.90371 \text{ \AA}$. Positions of C_3A reflections are marked with Miller indices.

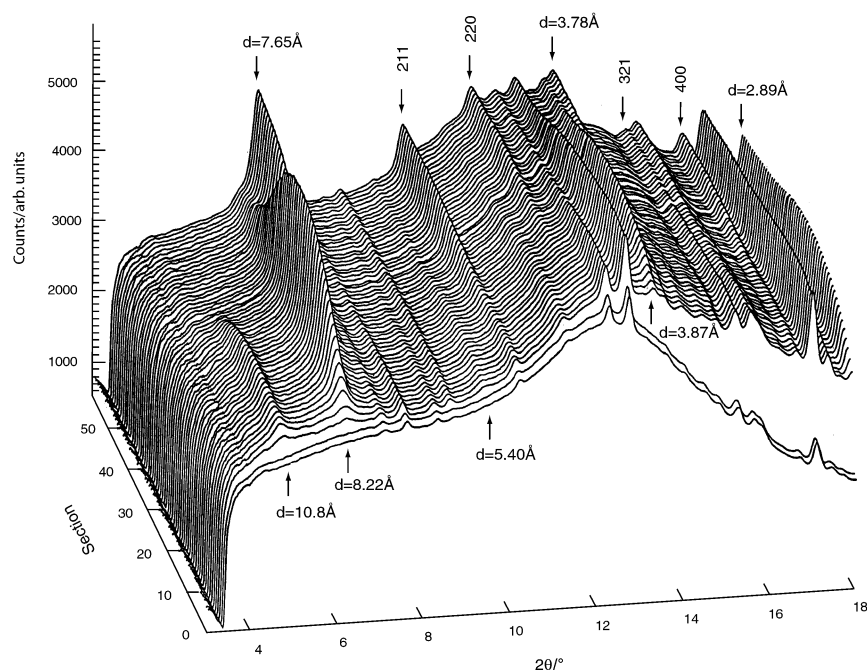


Fig. 7 Stack of powder patterns of sample 2A hydrolysed in a temperature ramp from 25 to 75 °C and recorded using synchrotron radiation, $\lambda = 0.90371 \text{ \AA}$. Positions of C_3AH_6 reflections are marked with Miller indices.

(ICCD data card #42–487). These two reflections could also fit to the pattern of C_2AH_8 (ICCD data card #11–205) but the reflection at $d = 5.40 \text{ \AA}$ has too low an observed intensity. The reflections at $d = 8.22 \text{ \AA}$, $d = 3.87 \text{ \AA}$ and $d = 2.89 \text{ \AA}$ most likely belongs to a C_2AH_{10} phase (ICCD card #16–339). However, the match is not perfect.

Fig. 7 displays patterns from hydrolysis of the sample heated from 25 to 75 °C. The sample is mixed with water after the second scan is recorded. The depletion of C_3A starts immediately, and the formation of the two phases as shown in Fig. 6. They are, however, not stable at elevated temperatures. The reflection at $d = 10.8 \text{ \AA}$ of C_4AH_{19} has its maximum at 40 °C and has disappeared at 53 °C. The reflection at $d = 8.22 \text{ \AA}$ of C_2AH_{10} has its maximum at 48 °C and has disappeared at 70 °C.

Reflections at the 2θ values 10.15, 11.73, 15.56 and 16.62° corresponding to the d -spacings, 5.11, 4.42, 3.33 and 3.12 Å, respectively, start to grow when the C_4AH_{19} phase intensities start to decrease. This represents consumption of C_4AH_{19} as the formation of C_3AH_6 takes place. Two reflections at the 2θ position 6.77 and 13.73° start to grow at approximately 45 °C. These reflections have the d -spacing values $d = 7.65$ and 3.78 \AA and could belong to the calcium aluminium oxide hydrate C_3AH_x (ICCD card #2–83). Fig. 7 clearly shows a shift in d -spacings from 8.22 to 7.65 Å and from 3.87 to 3.78 Å, when the temperature of the sample increases from 25 to 75 °C and when C_3AH_6 is formed. The same observations can be seen in Fig. 5. The phase with $d = 8.22 \text{ \AA}$ could, as mentioned above, be related to C_2AH_{10} , and the phase with $d = 7.65 \text{ \AA}$ could possibly be related

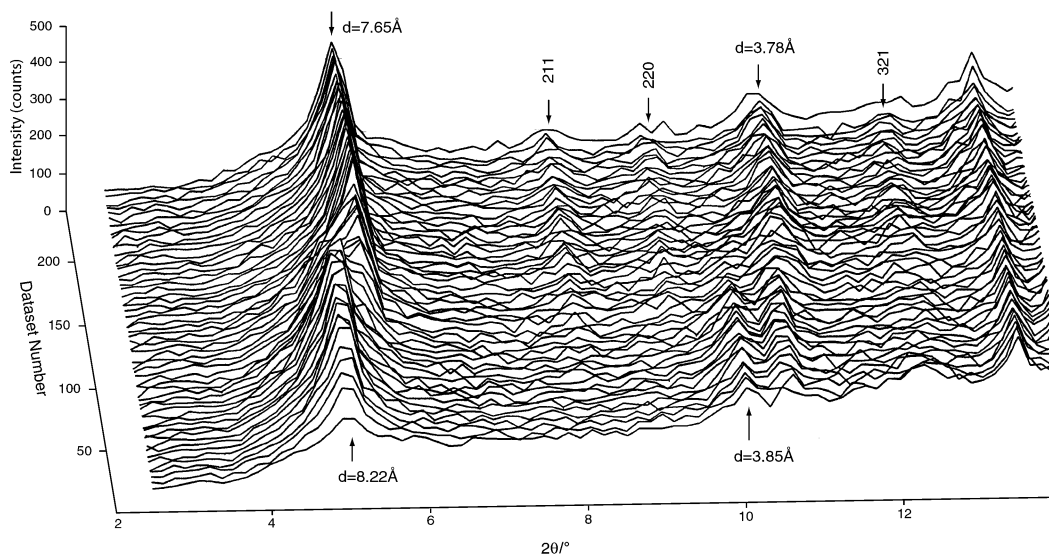


Fig. 8 Stack of powder patterns of sample 2B hydrolysed at the temperatures 25, 50, 75 and 100 °C and recorded using Mo-K α -radiation. Patterns 1–47 at 25 °C, 48–79 at 50 °C, 80–135 at 75 °C and 136–250 at 100 °C. Positions of C₃AH₆ reflections are marked with Miller indices.

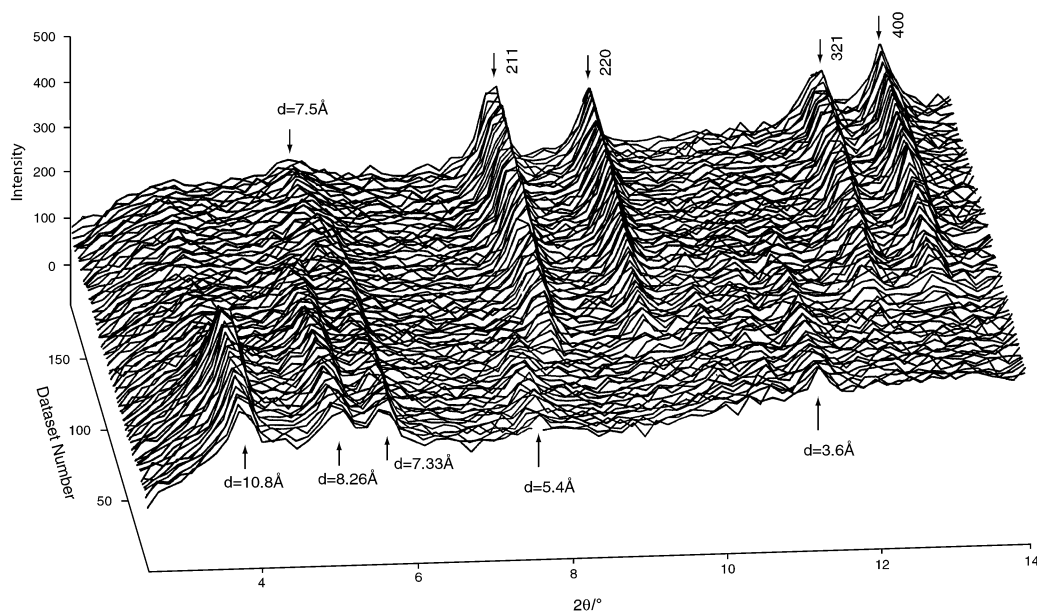


Fig. 9 Stack of powder patterns of calcium silicate extracted clinker, sample 3A, containing orthorhombic C₃A and brownmillerite hydrolysed at the temperatures 25, 50, 75 and 100 °C and recorded using Mo-K α radiation. Patterns 1–30 at 25 °C, 31–60 at 50 °C, 61–90 at 75 °C and 91–200 at 100 °C. Positions of C₃AH₆ reflections are marked with Miller indices.

to Ca₂Al(OH)₇·3H₂O (ICCD data card #33–255) but the match to that pattern is not perfect either. The batch hydrolysis of the sample, Fig. 2 (middle pattern), shows a similar tendency with the strongest lines *d*-spacings of 7.61, 3.81 and 2.87 Å, respectively. This sample had reacted with water at 25 °C for 97 days.

Sample 2B: residue following the second calcium silicate extraction from Australian Portland cement clinker

This sample is the second extract of the clinker used to make sample 2A and contains C₃A in the cubic form and less calcium silicate than sample 2A. The hydrolysis was conducted on the INEL instrument where the sample was kept at 25 °C for 1.5 h, 50 °C for 1 h, 75 °C for 1.75 h, and at 100 °C for 4.25 h. The sample was then kept at 100 °C for an additional 16 h. Fig. 8 displays patterns from the hydrolysis. The main results of the hydrolysis are the same as for sample 2A, a fast formation of a reaction product at 25 °C with a low angle reflection at $2\theta = 4.96^\circ$, *d* = 8.22 Å, conversion to another reaction product

at 50 °C with a low angle reflection at $2\theta = 5.33^\circ$, *d* = 7.65 Å, followed by formation of C₃AH₆. The hydrolysis product after 20 h reaction have reflections of C₃AH₆.

Sample 3A: residue following calcium silicate extraction from Australian Portland cement clinker

This residue contains brownmillerite, C₄AF, and the orthorhombic form of C₃A. Pure C₃A does not exhibit polymorphism, but C₃A can incorporate Na⁺ by substitution of Ca²⁺ plus addition of a second Na⁺ ion on vacant sites in the lattice, thus giving solid solutions of the formula Na_{2x}Ca_{3-x}Al₂O₆. In the composition range *x* = 0.16–0.20 the solid solution is orthorhombic.²⁹ The hydrolysis reactions were made on the INEL instrument with the sample at the temperatures 25 °C for 1 h, 50 °C for 1 h, 75 °C for 1 h and 100 °C for 3.5 h. Fig. 9 displays pattern from the hydrolysis. The main feature is that three low angle reflections are observed at 25 °C at $2\theta = 3.77^\circ$, 4.92° and 5.56° corresponding to the *d*-values 10.8, 8.26 and 7.33 Å. At 50 °C the 7.33° reflection starts to reduce in intensity, and at

75 °C all three low angle reflections disappear and only strong reflections of C_3AH_6 are observed.

Discussion

The investigation shows that it is possible to obtain detailed information from *in-situ* investigations of hydrolysis of industrially produced cements and clinker and using both laboratory and synchrotron sourced X-ray powder diffraction equipment. In this instance the laboratory set-up consisted of an INEL diffractometer fitted with a CPS-120 position sensitive detector and Mo-K α radiation. The synchrotron experiments were conducted at constant wavelength. Both experimental set-ups used small samples housed in capillaries. The information obtained using these techniques is just as detailed as that gained using energy dispersive X-ray powder diffraction and large samples. The counting statistics is as expected much better for patterns measured with synchrotron radiation than in the case of Mo-radiation. It should, however, be possible to improve the quality of the latter and to oscillate the sample during the measurements.

The Portland cement, sample 1, contained calcium sulfate as $CaSO_4 \cdot 0.5H_2O$ which reacts readily with water, possibly through an amorphous intermediate state before $CaSO_4 \cdot 2H_2O$ is formed.³⁰ Sulfate ions are thus readily available for the formation of ettringite, which is observed in the *ex-situ* as well as in the *in-situ* experiments, Figs. 1, 3 and 4. The patterns of the *in-situ* experiments were not sufficiently detailed to demonstrate a precursor phase for sulfate ettringite. However, in the previous neutron diffraction investigation,¹⁰ where the sulfate source was $CaSO_4 \cdot 2H_2O$, a precursor phase was formed which was then consumed in the formation of ettringite.

Many studies have shown that the reaction of C_3A with water at ordinary temperatures gives C_2AH_8 and C_4AH_{19} ,¹ or C_2AH_8 and C_4AH_{13} ,³¹ which are converted to C_3AH_6 at rates that depend on temperature. In dilute suspensions C_4AH_{19} is the first crystalline product formed. C_2AH_8 has a characteristic strong reflection at $d = 10.8$ Å and an additional strong reflection at $d = 5.40$ Å (ICDD card #45–564). α_1 - C_4AH_{29} has a strong d -spacing at $d = 10.8$ Å and a weak d -spacing at $d = 5.35$ Å (ICDD card #14–631), and α_2 - C_4AH_{19} has a strong d -spacing at $d = 10.8$ Å and a weak d -spacing at $d = 5.36$ Å (ICDD card #14–628).

The *ex-situ* and *in-situ* investigations of the hydrolysis of the clinker residue with a high content of cubic C_3A , samples 2A and 2B, gave detailed information on the hydrolysis reactions. The results obtained are interpreted differently from the previously reported hydrolysis reactions of C_3A ,¹⁹ where C_3A reacts with water in the temperature range 26–36 °C via an intermediate phase which was interpreted as C_2AH_8 to the end product C_3AH_6 . As C_2AH_8 and C_4AH_{19} have reflections at $d = 10.8$ Å and $d = 5.4$ Å, the choice between the two compounds must be made on the intensities of the reflections. The reflection at $d = 10.8$ Å in Figs. 6 and 7 does not have a correspondingly strong reflection at $d = 5.40$ Å, and for this reason the presence of C_2AH_8 is ruled out. However, the relative intensities of the intermediate phase obtained in hydrolysis of C_3A ¹⁹ may indicate that the phase is C_2AH_8 . The *ex-situ* (Fig. 2) as well as the *in-situ* experiments (Figs. 5–8) show that two phases are formed, one at the start of the hydrolysis process at room temperature with the characteristic d -spacings 8.22 and 3.87 Å, and one at temperatures above 50 °C with the characteristic d -spacings 7.65 and 3.78 Å, and that the end product C_3AH_6 obtained at temperatures above room temperature grows from the intermediate phase C_4AH_{19} (Fig. 7). These characteristic spacings do not fit too well to the characteristic spacings of C_4AH_{13} and C_4AH_{11} , $d = 8.2$ Å and $d = 7.4$ Å, respectively.³²

The *in-situ* investigation of the clinker residue with the high content of orthorhombic C_3A and brownmillerite, C_4AF , sample 3A, showed reactions different from those of cubic C_3A .

This is to be expected as cubic and orthorhombic C_3A do not have the same chemical composition, the latter being a Na^+ substituted calcium aluminate. At 25 °C the diffraction patterns exhibit three low angle reflections at $2\theta = 3.77$, 4.92 and 5.56°, corresponding to the d -values 10.8, 8.26, and 7.33 Å, and weaker reflections are observed at $d = 5.4$ Å and $d = 3.6$ Å. These three reflections could belong to C_2AH_8 . At 50 °C their intensities are reduced considerably and the patterns show reflections of C_3AH_6 . The reflections at $d = 8.26$ and 7.33 Å disappear at approximately 70 °C and a new reflection at $d = 7.5$ Å appears. These reflections do not fit well to the C_4AH_x phases either.³²

Further work is planned on investigation of the hydrolysis reactions of sample 3A to clarify if the primary hydrolysis product is C_2AH_8 , using synchrotron radiation. Further work is also planned on the formation of ettringite to see if the precursor phase observed in the neutron powder diffraction experiments can be observed in *in-situ* studies using synchrotron radiation.

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