

## Dehydration of Calcium Chloride as Examined by High-temperature X-ray Powder Diffraction

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### Abstract

Although calcium chloride is hygroscopic in nature, the investigation of dehydration in view of structural rearrangement has not been received a substantial attention yet. The structural rearrangement of calcium chloride during dehydration was investigated by high-temperature X-ray powder diffraction technique. The X-ray diffractograms of calcium chloride were recorded at 25, 115, 150 and 200 °C. Results indicate that  $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$  (82%) and  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  (sinjarite, 18%) are the major hydrated forms available at 25 °C. The removal of crystalline water takes place in two consecutive endothermic steps as examined by Thermal Gravimetric Analysis (TGA/DTA) that coincides with the outcome of X-ray diffraction. The removal of crystalline water during the first step of dehydration (from 25 °C to 115 °C) is accounted for obtaining a mixture of monohydrate ( $\text{CaCl}_2 \cdot \text{H}_2\text{O}$ ) and anhydrous ( $\text{CaCl}_2$ ) calcium chloride. The dehydration of monohydrate (second step) is completed at around 150 °C leaving two different phases of anhydrous calcium chloride with the respective unit cell volume of 168 Å<sup>3</sup> (92%) and 324 Å<sup>3</sup> (8%). It is also found that anhydrous calcium chloride with larger unit cell volume is less stable above the temperature of 150 °C that eventually converted to a more stable anhydrous form with smaller unit cell volume (168 Å<sup>3</sup>) at around 200 °C. The structural rearrangements are important to understanding dehydration mechanism that ultimately predicts thermal behavior of calcium chloride.

### Introduction

Calcium chloride is a strong hygroscopic material that has been often used for various domestic and industrial applications. It is also considered an imperative material due to its potential as a thermal energy storage (van Essen et al., 2009, Rammelberg et al., 2012, Quinnell et al., 2011, Wei et al., 2014, Du et al., 2017) and high-temperature molten salt electrolyte (Mohandas and Fray, 2004, Oosthuizen, 2011, Schwandt and Fray, 2005, Chen et al., 2000). Numerous investigations executed to understand the thermal behavior of calcium chloride, however, nor or little attention has been received for accurate determination of hydrated/anhydrous products of calcium chloride during complete dehydration. Despite the hydrated/anhydrous structures of solid calcium chloride upon dehydration, the X-ray scattering was previously employed in determining structures of calcium chloride hydrate melts (in solution) (Yamaguchi et al., 1989). The potential of calcium chloride and its eutectics as a thermal energy storage material eventually accounted for number of investigations to predict the thermal behavior and stability of calcium chloride (van Essen et al., 2009, Rammelberg et al., 2012, Quinnell et al., 2011, Wei et al., 2014, Du et al., 2017), however, the structures of hydrated/anhydrous products have not been greatly discussed. Several attempts were previously reported on structure determination of different hydrated/anhydrous products of calcium chloride by thermal gravimetric analysis/differential thermal analysis (TGA/DTA) and differential scanning calorimetry (DSC); however, the outcomes are less reliable due to limited or inadequate raw data available for accurate estimation of the composition (van Essen et al., 2009, Rammelberg et al., 2012). The main objective of the present investigation is, therefore, to determine the composition of hydrated/anhydrous products of calcium chloride and their relative stability at different temperatures during complete dehydration. Furthermore, the water absorption nature and morphological changes accompanied by particle surface of calcium chloride during hydration are also examined. The high-temperature X-ray powder diffraction and TGA/DTA are employed simultaneously to determine the composition and the thermal behavior of calcium chloride during dehydration. Furthermore, the Fourier-transform infrared attenuated total reflection (FTIR-ATR) is carried out on heated calcium chloride samples to understand the dehydration

process in terms of characteristic IR vibrations of water whereas the surface morphology of the material during hydration is also observed under scanning electron microscope.

### Methods and Materials

Calcium chloride (>99%) was obtained from Avonchem Limited, Oxon, United Kingdom. Rigaku Ultima IV X-ray powder diffractometer equipped with the High-Temperature Attachment (HTA) was employed to investigate the complete dehydration of calcium chloride. The Bruker TENSOR 27 Fourier-transform infrared attenuated total reflection (FTIR-ATR) spectrometer was employed in the qualitative determination of dehydration process. The surface morphology during the progressive hydration process of calcium chloride was observed by ZEISS EVO/LS15 scanning electron microscope.

### The Composition of Calcium Chloride During Dehydration as Examined by High-temperature X-ray Diffraction

The dehydration temperatures related to calcium chloride (during complete dehydration) was initially determined by SDT Q600 V20.9 Build 20 TGA/DTA analyzer. The X-ray diffractograms of calcium chloride during complete dehydration were recorded at around 25, 115, 150 and 200 °C using Rigaku Ultima IV X-ray powder diffractometer (equipped with high-temperature sample attachment) subsequent to ten minutes temperature stabilization period. A moisture free atmosphere inside the sample chamber was achieved by maintaining a vacuum condition throughout the entire period of analysis. The X-ray tube conditions were maintained at around 40 kV (tube voltage), 30 mA (tube current) and 1.2 kW (X-ray power), respectively. The divergence slit, scattering slit and receiving slit were maintained at around 2/3°, 2/3° and 0.45 mm. Both scan rate and sampling width were maintained at around 10.0 degrees per minute (deg min<sup>-1</sup>) and 0.05 degrees, respectively. The composition of hydrated/anhydrous products of calcium chloride during complete dehydration (at 25, 115, 150 and 200 °C) were determined quantitatively using Relative Intensity Ratio (RIR) of each phase and data refinement was carried out by PDXL2 software coupled with ICDD (International Center for Diffraction Data) database. The unit cell volumes of relevant hydrated/anhydrous products of calcium chloride were also extracted by correctly assigned phases.

### Qualitative Determination of Dehydration By FTIR-ATR Spectroscopy and Hydration by SEM

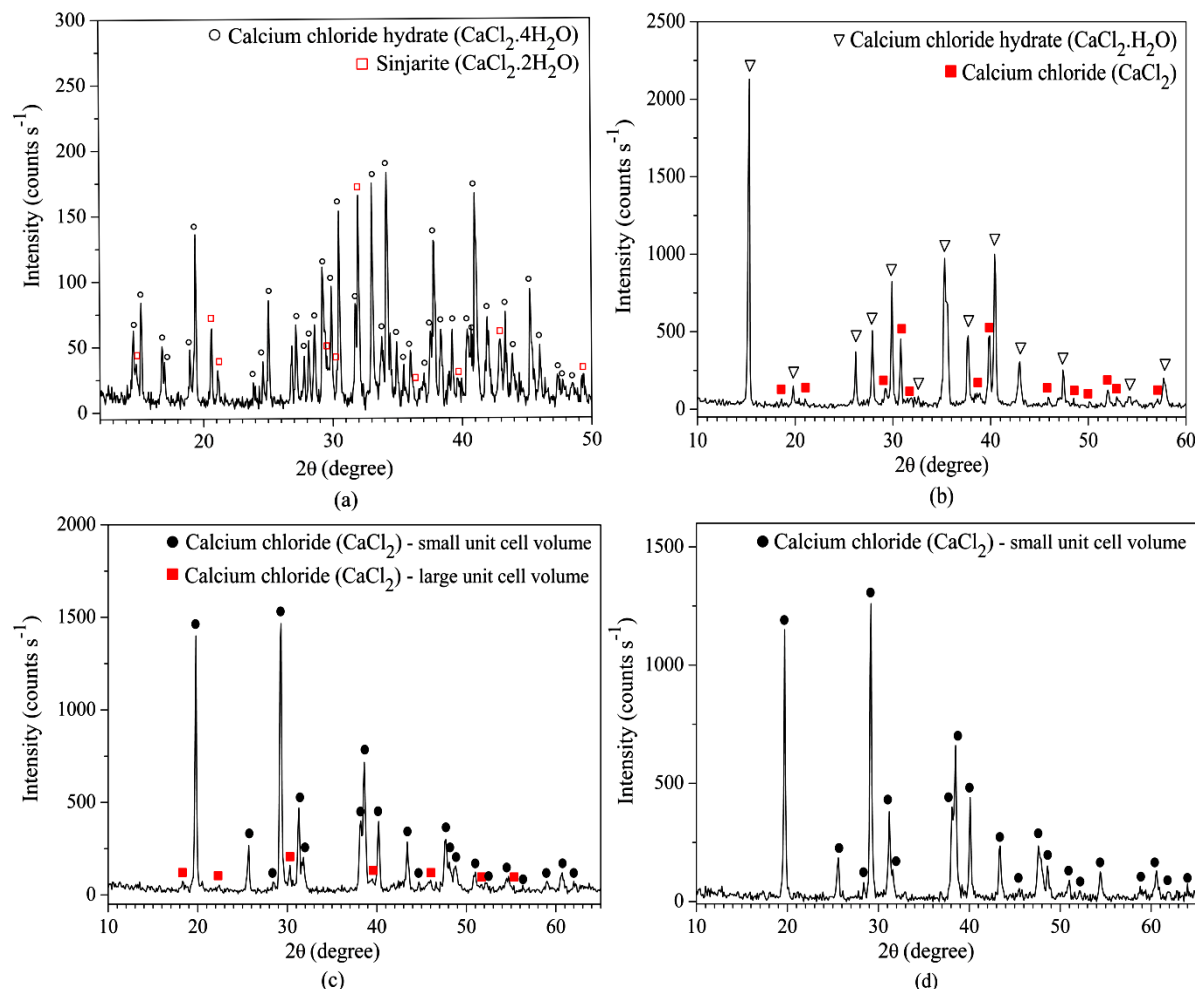
The dehydration process of calcium chloride was qualitatively determined by Fourier-transform infrared attenuated total reflection (FTIR-ATR) spectroscopy. An appropriate amount of calcium chloride was initially heated at around 100, 150 and 200 °C in a vacuum oven (VacuCell). Each heated sample was then carefully transferred by placing inside insulated desiccator (under moisture-free environment) to keep the temperature constant during the measurements. All spectra were collected using Bruker TENSOR 27 Fourier-transform infrared spectrometer by placing a small amount of the heated sample inside the sample holder of attenuated total reflection (ATR) sampling attachment. The transmittance FTIR spectra of calcium chloride at each temperature (at 25, 100, 150 and 200 °C) were recorded between 600 cm<sup>-1</sup> and 4000 cm<sup>-1</sup> (wavenumber) under the resolution of 4 cm<sup>-1</sup> and scan speed of 16 scans.

The morphology changes during the hydration of calcium chloride were observed using ZEISS EVO/LS15 scanning electron microscope. A small amount of calcium chloride initially heated above 125 °C in a vacuum oven (VacuCell) for 1 h was mounted on double-sided carbon tape attached to the surface of SEM sample holder. Calcium chloride sample (gold sputtered) was then observed under different magnifications by maintaining the accelerating voltage at around 10 kV. The SEM micrographs were obtained relevant to the progressive hydration of calcium chloride with time.

### Results and Discussion

The X-ray diffractograms of calcium chloride obtained at specified temperatures (25, 115, 150 and 200 °C) clearly exemplified the composition changes during dehydration. The hydration of calcium chloride readily takes place at room temperature due to hygroscopic nature of the material. The tetrahydrate (CaCl<sub>2</sub>·4H<sub>2</sub>O, unit cell volume: 328 Å<sup>3</sup>) and dihydrate (CaCl<sub>2</sub>·2H<sub>2</sub>O, unit cell volume: 530 Å<sup>3</sup>) are the major hydrated forms of calcium chloride available at around 25 °C (Fig. 1a). The majority of calcium chloride occupied as tetrahydrate rather than dihydrate (Table 1). The X-ray

diffraction analysis further revealed that the crystal system of tetrahydrate is triclinic whereas orthorhombic in dihydrate. The progressive heating is accounted for a sequence of structural rearrangements depends on the amount of crystalline water available and alteration in lattice constants.



**Figure 1:** X-ray diffractograms of calcium chloride during complete dehydration at; (a). 25 °C (room temperature); (b). 115 °C; (c). 150 °C and (d). 200 °C.

The monohydrate ( $\text{CaCl}_2 \cdot \text{H}_2\text{O}$ ) is the dominant calcium chloride over anhydrous product ( $\text{CaCl}_2$ , unit cell volume -  $324 \text{ \AA}^3$ ) available at around 115 °C (Fig. 1b, Table 1). Two different anhydrous calcium chloride phases can clearly observe at 150 °C (Fig. 1c). The relative stability of anhydrous calcium chloride at elevated temperature depends on the magnitude of unit cell volume where the calcium chloride phase with smaller unit cell volume ( $168 \text{ \AA}^3$ ) is quite stable over the phase with larger unit cell volume ( $324 \text{ \AA}^3$ ) (Table 1). The complete conversion of less stable calcium chloride to a more stable form was eventually occurred between the temperatures of 150 °C and 200 °C where the anhydrous calcium chloride was further stabilized by minor rearrangement of the structure (Fig. 1d). It is also found that the crystal system of calcium chloride (including anhydrous and other hydrated forms) except tetrahydrate is orthorhombic.

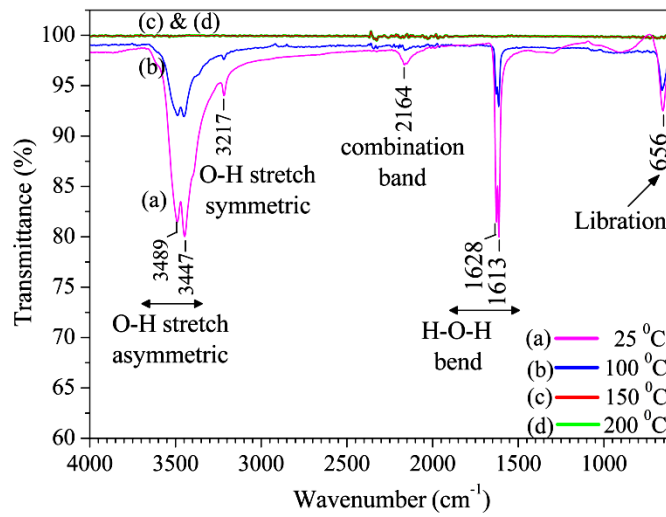
Table 1 Composition of calcium chloride during complete dehydration.

T (°C)	A/H phase	Relative amount (%)
25	CaCl <sub>2</sub> ·4H <sub>2</sub> O	82
	CaCl <sub>2</sub> ·2H <sub>2</sub> O	18
115	CaCl <sub>2</sub> ·H <sub>2</sub> O	87
	CaCl <sub>2</sub> (324 Å <sup>3</sup> )	13
150	CaCl <sub>2</sub> (168 Å <sup>3</sup> )	92
	CaCl <sub>2</sub> (324 Å <sup>3</sup> )	8
200	CaCl <sub>2</sub> (168 Å <sup>3</sup> )	100

The dehydration of calcium chloride as examined by FTIR-ATR (transmittance mode) analysis also coincides with the outcome of X-ray diffraction. The FTIR spectra obtained at around 25 °C, 100 °C, 150 °C and 200 °C clearly exhibited the removal of crystalline water during complete dehydration of calcium chloride (Fig. 2). Typical IR-vibration bands of water can observe in relevant FTIR spectra of calcium chloride at 25 °C and 100 °C, however, the absence of characteristic IR pattern of water at around 150 °C and 200 °C ensured the complete removal of crystalline water during dehydration of calcium chloride. This is a good indication for the existence of hydrated calcium chloride at around 25 °C and 100 °C as previously observed by X-ray diffraction analysis. The magnitude of vibration frequencies with respect to certain vibration modes of water at around 25 °C (see table 2 for typical IR vibrations of water), however, indicated that the crystalline water present in both tetrahydrate and dihydrate experienced different hydrogen bonding (H-bonding) atmosphere. Although the typical IR vibration frequencies of H-bonded O-H groups appeared between 3200 and 3600 cm<sup>-1</sup> (Lappi et al., 2004), three distinct IR vibrations related to O-H stretching of crystalline water can be observed within this range at around 25 °C (Fig. 2). Unlikely broad O-H asymmetric stretching of water (single band), two asymmetric O-H stretching bands (vibration frequencies) can eventually observe at around 3447 cm<sup>-1</sup> and 3489 cm<sup>-1</sup> for crystalline water in all the hydrated forms of calcium chloride. This may be due to O-H stretching under the influence of H-bonding of water molecules as well as chloride ions occupied in the crystal lattice. As a result, two different O-H stretching can take place through O-H···O and O-H···Cl, H-bonding systems that ultimately results in closely separated O-H vibration bands (asymmetric O-H stretch) (Fig. 2). The similar variation can observe for H-O-H bending vibration frequency of crystalline water as well (Fig. 2). The appearance of two distinct bands (1613 cm<sup>-1</sup> and 1628 cm<sup>-1</sup>) instead of a typical single band for H-O-H bending ensured the influence of similar H-bonding environment as previously explained (O-H···O and O-H···Cl). The similar band separation was hardly noticeable for symmetric O-H stretching vibration, a combined band (2164 cm<sup>-1</sup>) and libration band (656 cm<sup>-1</sup>), respectively. However, the magnitudes of vibration frequencies are smaller than the typical values of water (experimental vibration frequencies, see Table 2). This may also due to the H-bonded nature of crystalline water that eventually responsible for shifting of the vibration frequency towards the direction of low energy (wavenumber decreases), hence, account for relatively low vibration frequency bands with respect to typical vibrations of water.

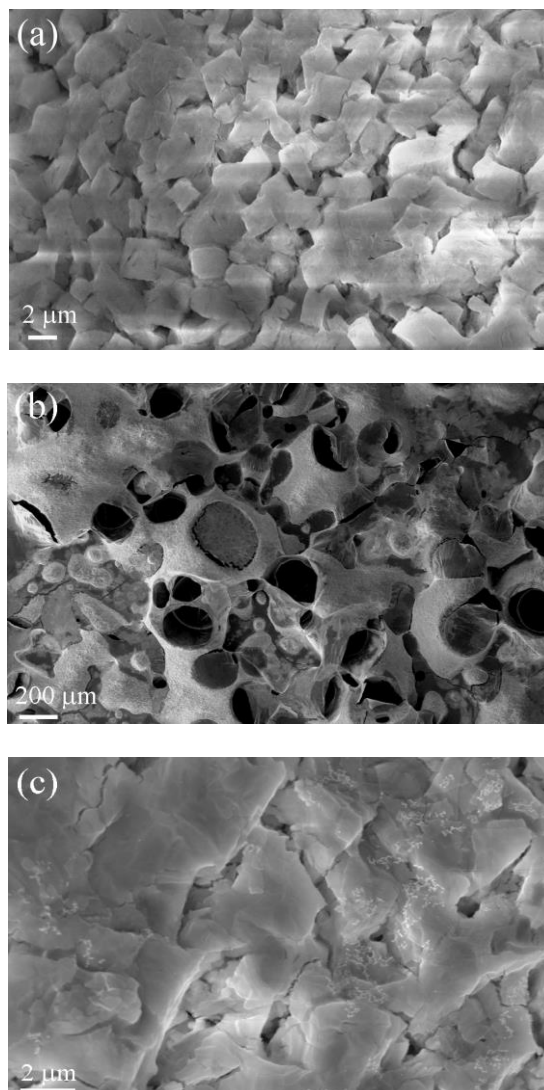
Table 2. Typical IR vibration frequencies for principal experimental bands (wavenumbers) of liquid water (H<sub>2</sub>O) (Lappi et al., 2004).

Normal mode	Assignment	Wavenumber (cm <sup>-1</sup> )
$\nu_2$	H-O-H bending	1639
$\nu_2 + R$	Combination	2134
$\nu_1$	Symmetric stretching	3261
$\nu_3$	Asymmetric stretching	3351



**Figure 2:** FTIR-ATR spectra of calcium chloride during complete dehydration

The scanning electron micrographs revealed the surface morphology changes during hydration of calcium chloride (Fig. 3).



**Figure 3:** SEM micrographs of calcium chloride during dehydration; (a). Anhydrous CaCl<sub>2</sub> containing cubic shape particles; (b). swelling of the material upon moisture absorption; (c). disappearance of the particle boundaries and amalgamation

The anhydrous calcium chloride rather consists of cubic shape particles as observed under SEM (Fig. 3a). The hydration is accounted for the swelling of the material upon moisture absorption (Fig. 3b). The progressive absorption of water further ensured a significant disappearance of particle boundaries and amalgamation is more pronounced (Fig. 3c).

### Conclusion

The dehydration of calcium chloride as examined by high-temperature X-ray diffraction revealed the different hydrated/anhydrous products available at respective temperatures of 25 °C, 115 °C, 150 °C and 200 °C. Both monohydrate and dihydrate are readily available at around 25 °C due to the hygroscopic character of the material. The progressive heating of the material ensured significant water loss via two distinct endothermic dehydration steps that were further accounted for emerging anhydrous calcium chloride beyond the temperature of 100 °C. The relative stability of anhydrous calcium chloride at elevated temperatures mainly depends on the magnitude of unit cell volume. Relatively smaller unit cell volume accounted for more stable anhydrous phase than the phase with larger unit cell volume. It is also evident that at around the temperature of 200 °C anhydrous calcium chloride is stabilized with

smaller unit cell volume upon minor rearrangement of the crystal structure. The crystalline water present in hydrated forms of calcium chloride experienced distinct hydrogen bonding environment under the influence of chloride ions (O-H...Cl) and typical hydrogen bonding by water molecules itself (O-H...O). The major constraint associated with present work is the persisting removal of water at around 115 °C even the X-ray measurements were being progressed. The application of higher scan rates reduced this time frame thus account for reasonable X-ray diffraction outcome on phase identification at a specified temperature. It is believed that the microstructure changes (lattice strain and crystallite size) during dehydration of calcium chloride would provide a better understanding on the relative stability of hydrated/anhydrous products. Therefore, the similar technique (high-temperature X-ray diffraction) can be employed for such estimation and is currently being investigated as an extension to the present work. Furthermore, it is hoped that the thermal behavior of calcium chloride eutectic with other salts can effectively investigate using high-temperature X-ray diffraction. The findings of the present work will positively effect on further advancements in the field wherever the applications involved heating of calcium chloride such as thermal energy storage material and high-temperature molten salt electrolysis.

### Acknowledgement

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