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Cite as: AIP Conference Proceedings **2055**, 050010 (2019); <https://doi.org/10.1063/1.5084829>
Published Online: 22 January 2019

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Temperature Effects on the Dissolution-Precipitation Synthesis of Hydrocalumite

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Abstract. The influence of temperature on the balance of formation between katoite and hydrocalumite (HC) was investigated. The conversion to HC could be increased by providing enough thermal energy to the reaction. Favourable reaction conditions for HC formation were reached at 60 °C. The rate of reaction to HC and katoite could be increased at 80 °C, although the formation of katoite seemingly remained low in comparison to HC formation. At 90 °C an increase in katoite and decrease in HC formation was observed indicating the decomposition point of HC.

INTRODUCTION

Layered double hydroxides (LDHs) are substances with physical and chemical properties similar to clay minerals [1, 1021]. Their general chemical formula is given by



$[M_{1-x}^{II}M_x^{III}(OH)_2]$ describes the composition of the LDH layers consisting of trivalent (M^{III}) and divalent (M^{II}) metal cations, while $[X_{x/q}^{q-} \cdot nH_2O]$ represents the composition of the anionic interlayer [1, 1021].

HC is a hydroxide, carbonate or chloride intercalated Ca-Al LDH. For example, the carbonate intercalated form can be synthesised using dissolution-precipitation of CaO and $Al(OH)_3$ in H_2O with addition of a carbonate source. [2] While investigating the formation of katoite – a HC precursor – with cheaper calcium sources ($Ca(OH)_2$) readily available in South Africa, Wiid [2] observed the formation of small amounts of a HC phase as by-product of the required katoite phase without introduction of a carbonate source and in an inert environment. It is expected that this phase is OH^- intercalated or that CO_2 contamination might have led to the formation of HC as previously observed by Sánchez-Cantú *et al.* [3]. Synthesis of this phase in a one-step fashion from cheaper reactants and without a carbonate source would have large economic benefits and will, therefore, be investigated in this paper.

When forming HC, several different synthesis routes – which include the sol-gel method, urea hydrolysis, coprecipitation, hydrothermal treatment or dissolution-precipitation synthesis [1, 1027-1038] – can be used. The following is known about the formation of HC via a dissolution-precipitation mechanism:

- Wiid [2] investigated the formation of katoite from $Ca(OH)_2$, $Al(OH)_3$ and H_2O in inert conditions and found traces of HC when reacting the mixture below 90 °C using the dissolution-precipitation mechanism. Katoite was found at 120 °C.
- Sánchez-Cantú *et al.* [3] attempted to form a HC-like phase by reacting $Ca(OH)_2$ and $AlOOH$ in water at a Ca:Al molar ratio of [2:1] and following a dissolution-precipitation mechanism; reaction occurred in an inert environment and at 80 °C. HC was formed.
- A HC-like phase has been synthesised by Buttler, Glasser, and Taylor [4] making use of supersaturated solution synthesis – a form of dissolution-precipitation synthesis – in an inert environment.

Formation of HC through dissolution-precipitation requires the desired metal hydroxides (an aluminium and calcium source) to be reacted in water [2] and subjected to conditions in which a dissolution of their ion constituents

is favoured. Dissolution of the metal hydroxides is necessarily a function of the agitation speed due to a maximisation of fluid movement around the solid particles. Precipitation will occur if one or more of the products are insoluble [5, 120-124]. Furthermore, temperature and pH (which is a function of the amount of dissolved metal hydroxides in solution) are believed to play the largest roles during katoite and HC formation as they influence the dissolution behaviour of the metal compounds [2]. The HC phase is stable below temperatures of 85 °C and to break down into katoite and calcite at higher temperatures [6]. LDH decomposition could be ascribed to a decreasing pH with an increase in temperature. The optimum reaction conditions for katoite formation were identified to be 90 °C at a reaction time of 2 h [2].

Literature on HC synthesis from $\text{Ca}(\text{OH})_2$, $\text{Al}(\text{OH})_3$ and H_2O is very limited and no information is available regarding which, and the way in which, reaction parameters influence the reactions in the system. This is especially true with respect to the balance between katoite and HC formation, the extent of reaction, and the product crystallinity. This paper serves to discuss the influence of temperature on the balance between katoite and HC formation.

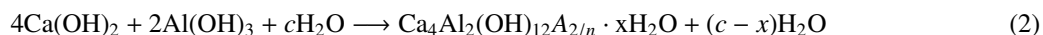
EXPERIMENTAL

Materials

Experiments were conducted using $\text{Ca}(\text{OH})_2$ and $\text{Al}(\text{OH})_3$ from ACE Chemicals (Gold Line) in chemically pure quality. Distilled and dissolved gas free water was used for all reactions.

Method

Experiments were performed in a bench top reactor set up using hotplate stirrers and glass beaker reaction vessels. An inert N_2 environment was maintained in all experiments. 100 ml distilled water was preheated to 80 °C while stirring slowly, allowing dissolved gases to vaporise, and afterwards brought to the desired reaction temperature. 20 g of dry reactant powders in stoichiometric ratio were weighed off according to Equation 2



and incorporated into the preheated water while stirring with a magnetic stirrer. The mixture was kept in suspension by magnetic stirring and reacted for 2 h at the desired temperature. The temperature span was chosen to commence at 30 °C – such that a reaction profile can be obtained – and end at a value at which HC should have exceeded its stability limit (85 °C) as previously found by Wiid [2]. The samples were filtered dry using vacuum filtration and analysed as a wet paste within 15 min.

Characterisation Techniques

X-ray diffraction analysis (XRD) and Fourier transform infrared analysis (FTIR) were used to identify and confirm phases present in the respective samples. XRD measurements were performed on a Panalytical XPert PRO X-ray diffractometer in $\theta - \theta$ configuration, using Fe filtered $\text{Co-K}\alpha$ radiation (1.789 Å), an XCelerator detector and variable divergence- and fixed receiving slits. The data was collected in the angular range of $5^\circ \leq 2\theta \leq 90^\circ$ with a step size and time of $0.008^\circ 2\theta$ and 13 s respectively. Phases were identified using XPert Highscore plus software. Molar fractions of phases present were determined using Rietveld refinement. ATR-FTIR spectra were obtained using a Perkin Elmer 100 Spectrophotometer. Samples were pressed in place with a force arm. Spectra were obtained in the range of $550 - 4000 \text{ cm}^{-1}$ each with 32 scans at a resolution of 2 cm^{-1} . Reactant standard FTIR scans were obtained and overlaid with the experimental data as explained by Galván-Ruiz *et al.* [7] in order to identify absorption peaks.

RESULTS AND DISCUSSION

Five reaction temperatures were tested to find a relationship between temperature and the favoured phase formation, an indication of a reaction profile and to test the influence of temperature on the crystallinity of the product. The conversion of reactants to HC and katoite could be shown through both XRD and FTIR analysis. Figure 1 shows a temperature reaction profile for the reaction obtained from XRD results of each sample.

Three interesting observations could be made from this plot which will be discussed below:

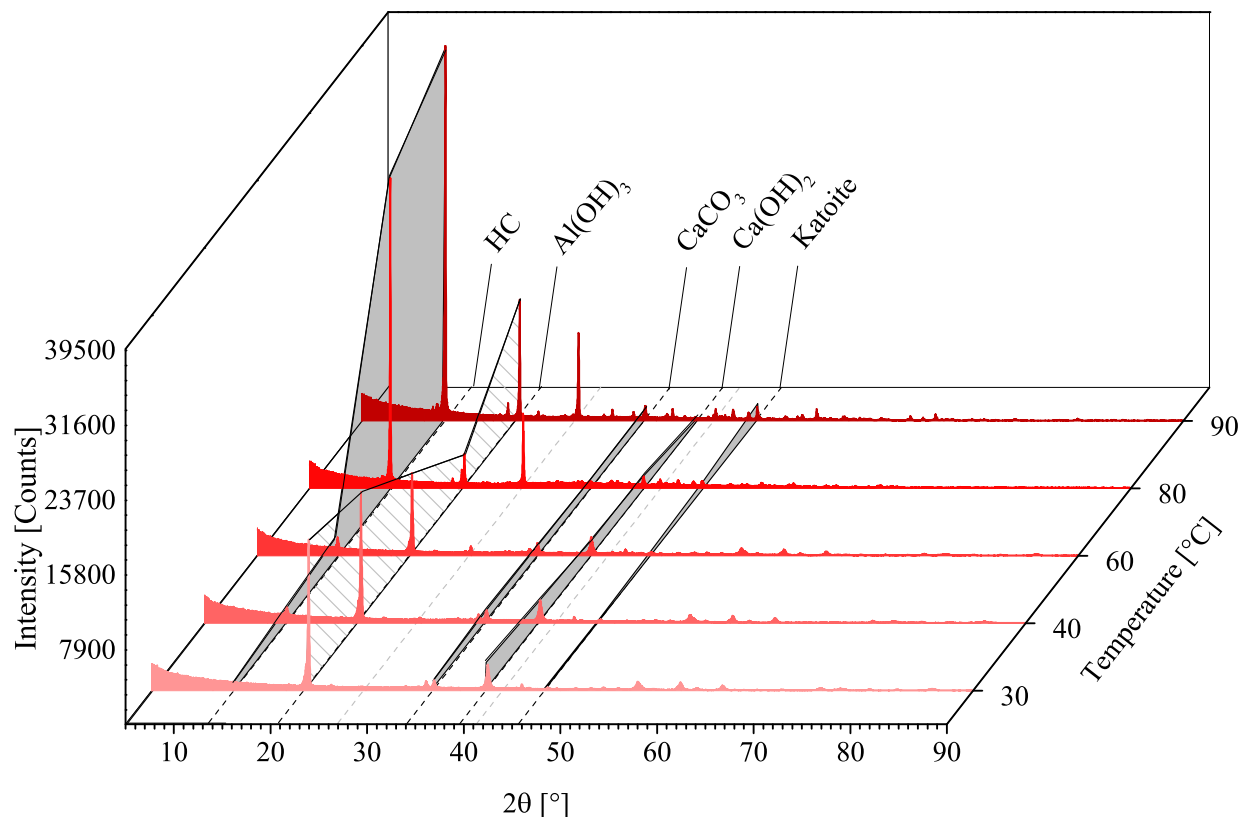


FIGURE 1. Plot of XRD data for the comparison of katoite and HC formation as well as reactant depletion with temperatures ranging from 30 °C to 90 °C. An increase in colour intensity indicates an increase in reaction temperature. Black dotted lines represent the primary peaks of HC, katoite, calcium carbonate and calcium hydroxide. Light grey dotted line represent the secondary and tertiary peaks of HC.

- The relationship between HC and katoite formation and depletion of the reactants with an increase in temperature.
- A sharp increase in the intensity of the aluminium hydroxide peak at 90 °C after following the reactant depletion trend up to 80 °C.
- A drastic increase in HC peak intensity with temperature.

Balance Between Katoite and HC Formation

From Figure 1, it is clearly visible that enough thermal energy must be provided in order to start the reaction to form katoite and HC. With an increase in temperature an increase in HC and katoite and a decrease in Ca(OH)_2 could be observed. It is clear, that favourable reaction conditions for HC formation are reached at 60 °C.

Changes in extent of reaction with temperature could be fully ascribed to the energy required to start the reaction – enough thermal energy must be supplied to favour dissolution of the reactants to form katoite and HC. If not enough energy is supplied, very little conversion of reactants to products will be observed. No increase in katoite formation could be observed until the temperature increased to 90 °C; at this point the rate of HC formation seemingly slowed.

The balance of katoite versus HC was seemingly only influenced when favourable reaction conditions to form katoite exist; at the point where HC decomposition is thought to commence and katoite formation increases. Obser-

variations made by Wiid [2] – a small portion of HC forming at low temperatures – could be validated. It is expected that only katoite exists at 120 °C [2]. An onset of reduction in HC formation was already visible at 90 °C from the obtained results, seemingly confirming previous work in this field.

Aluminium Hydroxide Peak Intensity

It is assumed that the backward reaction from HC to katoite starts influencing the yield of the Ca-Al LDH at temperatures greater than 80 °C. Three explanations for the increase in aluminium hydroxide could be proposed:

1. The solubility of $\text{Al}(\text{OH})_3$ decreases with an increase in temperature and more will therefore remain in the sample at 90 °C compared to 80 °C.
2. With an increase in temperature more energy is available for reaction and it might be possible that the excess in energy shifts the reaction equilibrium from LDH formation to LDH decomposition into katoite and $\text{Ca}(\text{OH})_2$ and finally to a decomposition of katoite into gibbsite or a hydrated alumina phase.
3. The increase in peak intensity is observed through an increase in crystallinity of the remaining phase while the amount of the phase decreased.

Explanation 1 could be confirmed through auxiliary tests. Explanation 2 was also found to be plausible due to the rate of formation of HC seemingly slowing from 80 °C to 90 °C and an increase in katoite peak intensity could be observed. Explanation 3 could also be plausible, seeing that the solubility of aluminium hydroxide decreases and aluminium in solution could re-precipitate in a ore crystalline form.

To test the validity of these explanations, FTIR analysis was performed (Figure 2). Figure 2 shows the reactant

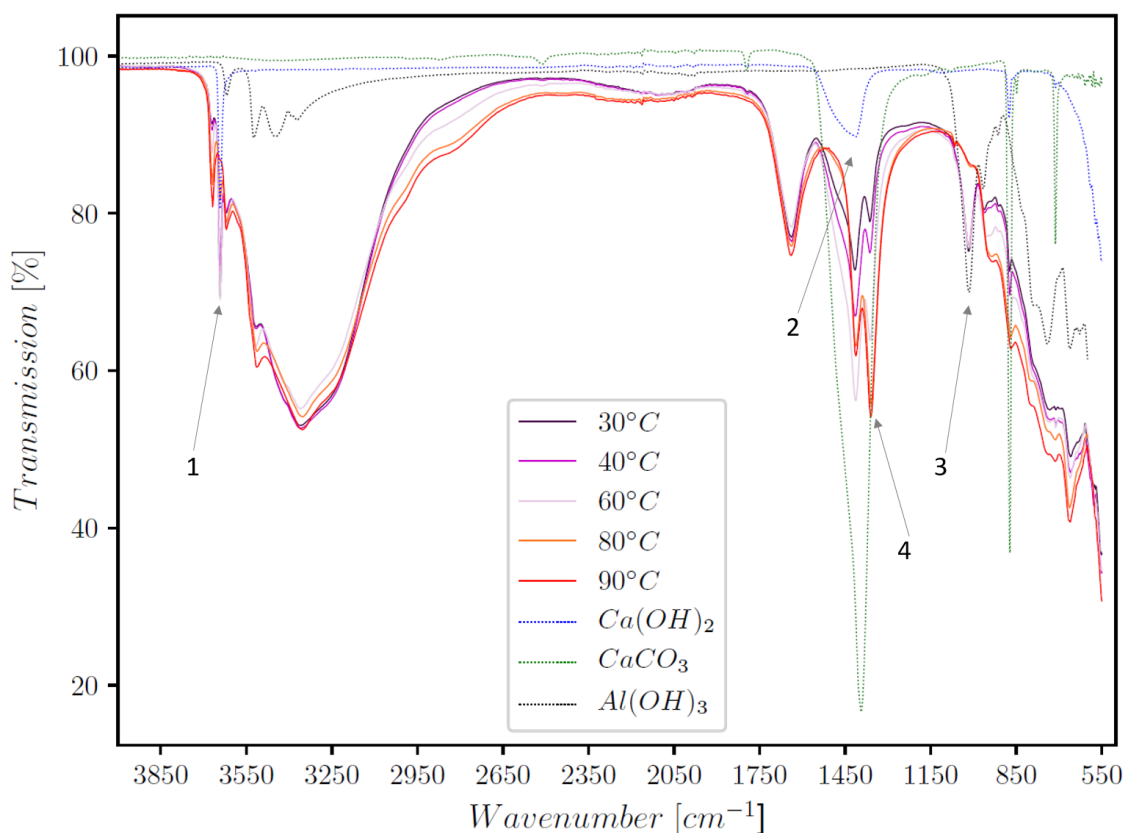


FIGURE 2. Comparative plot of FTIR scans for the temperature test series. Point 1, 2: $\text{Ca}(\text{OH})_2$ depletion, Point 3: $\text{Al}(\text{OH})_3$ depletion, Point 4: HC/ katoite phase.

depletion as already seen in Figure 1 (Point 1-3). However, here, the sharp increase in $\text{Al}(\text{OH})_3$ is not visible. Although

FTIR is not a quantitative analysis technique, a difference was expected in the case of a large amount of $\text{Al}(\text{OH})_3$ being present in the 90 °C sample. Instead, the plots for 80 °C and 90 °C lie almost on top of each other at Point 3. A large difference is however visible at this point between the lower temperature runs and the just-mentioned ones. This could lie in favour with the explanation of the HC phase decomposing and $\text{Ca}(\text{OH})_2$ and $\text{Al}(\text{OH})_3$ being used to form katoite. Decomposition of HC to katoite at this temperature confirms previous observations by Wiid [2]. Further clarification of the exact sample composition could clear this up (e.g. Rietveld refinement). However, techniques such as Rietveld refinement only give reliable information if the peak patterns fit the identified structure exactly and no unidentified peaks remain. With new or undefined structures this is a very difficult task to achieve.

Phase Crystallinity

It remains unclear at this point in time, whether the observed increase in peak intensity results from an increase in the amount of the phase or because of an increase in crystallinity. Other large changes in peak intensity can be observed in the HC peak at 80 °C. This increase in peak intensity can be ascribed to the increase in amount and crystallinity of the phase itself and possibly also to the analysis technique used. It is expected that platelet alignment can influence the intensity of an XRD pattern due to constructive or destructive interference. The higher the constructive interference, the higher the peak count observed in a pattern for the respective crystal structure [8]. This is also observed especially in platelet structures such as clays due to preferred orientation [8]. However, although this might have influenced the measured peak intensities, a relative increase with respect to the other phases is definitely observable, leading to the conclusion that this should only alert to the fact that the samples obtained at high temperatures do not necessarily consist of mainly HC.

CONCLUSIONS AND RECOMMENDATIONS

It was observed that HC formation increased with an increase in temperature. The data obtained also showed that the decomposition of the LDH phase possibly starts occurring between 80 °C and 90 °C. It was reasoned, that this shift in reaction pathway might occur due to a change in favoured katoite decomposition mechanism, due to more energy being available. Further proof needs to be found for this. It is expected that katoite remains as the stable phase at temperatures exceeding the tested temperature span.

Although no quantification of results can be given at this point in time, the correlations between the temperature and an increase in HC formation are quite strong and not unexpected. It would be interesting to further investigate the difference in yield of HC against katoite between 80 °C and 90 °C through quantitative means.

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