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# Preparations for study of a layered synthetic silicate using TGA and DSC

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# Preface

The report is a product of project work performed at Department of Physics at the Norwegian University of Science and Technology (NTNU) during the summer and autumn of 2006. The research group is lead by Professor Jon Otto Fossum, and he is acknowledged for providing main supervision and the opportunity to work on this challenging project. In addition Dr. Ahmed Gmira has been invaluable with technical expertise and his knowledge about former work on this project. A large and active lab group this semester has been available for answering all kind of questions, and especially helpful for my work was Lars Ramstad Alme, which work on x-ray scattering considering similar questions, and Henrik Hemmen, which has developed a LabVIEW program for collecting data from the hygrometer.

Many instrumental difficulties have slowed down the progress this semester, and with this in mind I would like to thank Arnljot Elgseter for loan of peristaltic pumps, necessary for continuing the experiments. Because of several unfortunate incidents with the TGA, main focus of this project is on the DSC and characteristics of the smectic clay sample being used. Hopefully there will be time and opportunity next semester to investigate some of the questions which have arisen during the process of the current work.

As practical use of the DSC, and analysis of heat flow curves, are relatively new topics in the research group, the report is also intended as an introduction of the instrument for future users.

Trondheim, 20 December 2006

Jorunn Hølto



# Abstract

The report presents experimental methods for thermal analysis of the synthetic, layered silicate Na-Fluorohectorite (Na-FH). Main focus is on heat flow curves, which are measured with a Differential Scanning calorimeter (DSC), and necessary adaptations to the instrument, which are necessary for the current use.

Behaviour of Na-FH is observed as a function of temperature under controlled relative humidity, during dynamic dehydration. At heating rate  $2^{\circ}\text{C}/\text{min}$  first-order transitions between the 2-, 1- and 0-water layer hydration states are observed in the temperature ranges  $5\text{-}24^{\circ}\text{C}$  and  $30\text{-}57^{\circ}\text{C}$  respectively. Evaporation of water from mesopores cause a continuous change in the specific heat, however when using different heating rates the dynamic changes.

Because the Thermogravimetal Analyzer (TGA) has been out of order most of the project period only preliminary weight loss curves taken at isothermal conditions are presented. Further combination of techniques is planned during upcoming work.

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# Chapter 1

## Introduction

Smectic clay is a layered mineral, mainly built of  $\text{Si}_8\text{O}_{20}$ -units. In dry state it stacks like a deck of cards, intercalated by cations, to make up a “one-dimensional” crystalline structure. The mineral characteristics are dominated by a charged layer surface causing the ability to swell when in contact with water, while still keeping its structural homogeneity. For these experiments the synthetic, customised smectic clay Na-Fluorohectorite (Na-FH) is used, in which stacks of  $\sim 100$  layers gather somewhat randomly into particles, the latter having a polydisperse distribution when it comes to lateral sizes.

Thermal analysis using thermogravimetry and calorimetric measurements provide direct means of probing macroscopic characteristics in a sample. A Thermogravimetric Analyzer (TGA) measures weight loss as a function of temperature and time, while a Differential Scanning Calorimeter (DSC) observes heat flow in a sample, thus observing changes in the specific heat and location of first-order transitions. These measurements benefit from being combined with other methods, for example x-ray scattering, which is routinely used for mapping of structural properties in these materials. However, each method has its limitations, and when it comes to smectic clay, x-ray experiments can not “see” all levels of water in clay: Micropores between the layers can be observed due to increased layer spacing, but direct means to observe behavior of mesopores inbetween the crystalline stacks are not found yet<sup>1</sup>. To this end thermal analysis can provide helpful information on the behaviour of both intercalated water and diffusion of water in the mesoporous space, at set dynamic or isothermal conditions. The experiments described here thus endeavour to employ both DSC and TGA to gain more information on the detailed dynamic behaviour of clay.

Water content in a clay sample is highly dependent on perturbation of the system, in terms of temperature, pressure and relative humidity. Reproducibility of an experiment is based on all parameters being strictly controlled and monitored. Each of the instruments are built to cater for these needs, but for the current experiments they also set important constraints, which are further investigated in the course of this report.

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<sup>1</sup>Currently experiments are performed to determine what level of relative humidity triggers intercalation of a second water layer.

# Chapter 2

## Theory

### 2.1 Clay

<sup>1</sup> Clay has traditionally been a versatile and common mineral, for example utilised as building material and raw material for pottery. Lately its properties have also been recognized as useful for production of plastic and cosmetics, or as drilling mud. In the development of modern nanotechnology, clay may be exploited to make “nanosandwiches”, and thus its detailed characteristics are important to map.

In the 18th century clay was classified as minerals with size below  $2\ \mu\text{m}$ , as this was the limit for current microscopy technology. A more detailed subdivision of minerals is today made using the Wentworth scale. Several different classes of clay exist, which are distinguished by their properties and composition. Generally clays have a *large surface to volume ratio*, thus their qualities are often based on particular surface properties. It is for example cause for their ability to swell when in contact with water, which is a property no other mineral can claim. The main classes of clays are also distinguished by this: Non-swelling and swelling clay. However, to detail their behaviour an understanding of their basic structure is necessary.

#### Structure

Clays are mainly composed of silicon and oxygen molecules, interconnected in a crystalline structure. A lamellar clay is made up of two basic sheet structures: In a **tetrahedral sheet** tetrahedras of a central silicon atom and four oxygens are coordinated to form an oxygen array. The fourth oxygen points away and is called an apical oxygen, more often than not making up a bond to a neighbouring sheet. Each unit in a **octahedral sheet** consists of six oxygens, forming a central oxygen array coordinated around a cations. At each side of the array apical oxygens again provide bonds, or form hydroxyl units. The two structures interconnects to make up a number of clay structures with very different characteristics.

A **2:1 smectite** consists of two tetrahedral sheets and one octahedral, as illustrated in Figure 2.1(a). Dependent on the number of substitutions, they have a surface charge of  $0.4\text{--}1.2\ \text{e}^-$  per  $\text{Si}_8\text{O}_{20}$  unit [9], which attracts cations and water. Thus these tend to stack like a deck of cards, held together mainly by the intercalated cations. Generally smectites are the only type of clay which are able to swell, while keeping a regular structure.

**Kaolinite**, in Figure 2.1(b), is an example of a 1:1 clay where hydrogen bonds between the tetrahedral oxygen array and hydroxyl units in the octahedral sheet is responsible for making the phyllosilicate stack into a regular structure. This additive effect is strong, making kaolinite a non-swelling clay, with no surface charge.

If a smectite has been crystallized in an environment containing an excess of aluminium, an extra octahedral layer, called Gibbsite, will form and provide a tight binding between the 2:1 layers [1]. This type of clay called **chlorite**, is also non-swelling, and its structure is illustrated in Figure 2.1(c). **chlorite**, is also non-swelling, and its structure is illustrated in Figure 2.1(c).

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<sup>1</sup>Information taken from [8] if nothing else is specified.



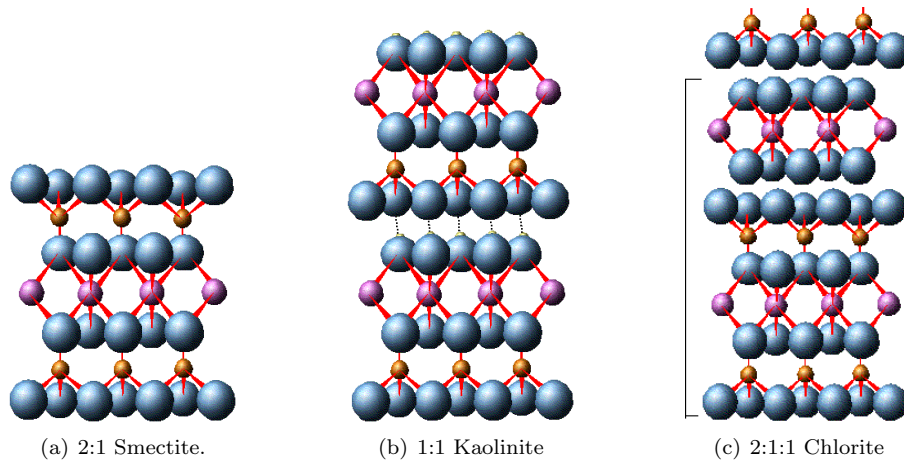


Figure 2.1: Basic structure for three classes of clay minerals. Taken from [1].

### Water intercalation

Intercalation of water in clay take two different forms. Molecules may be *adsorbed* on the layer surface forming a thin film, caused by electrostatic attraction. Generally the water is lost before reaching temperatures  $\sim 120^\circ\text{C}$ , and do not do not produce any other structural alterations than increasing the interlayer distance. In contrast, water may be *absorbed* into the layer structure by forming hydrogen bonds to the oxygen array. Water of this kind is called crystalline, and is lost at higher temperatures,  $\sim 400^\circ\text{C}$  in a dehydroxilation process that causes irreversible structural changes.

### Pores

Clay contains a range of pores that can be filled with water. These may be classified in three different sizes.

- Micro pores are found between the silicate layers, on the scale of 1 nm. Normally the molecules are adsorbed onto the surface and form thermodynamically stable states with a varying number of water layers dependent on humidity, pressure and temperature. Experimental studies of packed powder samples show that the orientation of pores to a certain degree may be controlled [10].
- Mesopores forms between individual stacks of phyllosilicate, at a scale of 2-50 nm. Water movement and swelling is though to be controlled by the diffuse double layer phenomena associated with the osmotic potential [11]
- In addition larger macro pores are found in clay, but these are mainly an effect of packing. If the sample is made more compact the volume of macro pores is the most affected. With size above 50 nm they are filled with “free” water responding to capillary phenomenon (unsaturated case) or pore pressure (saturated case) [11].

*Porosity* is defined as pore volume to total volume in the dried out state [10]

#### 2.1.1 Smectite clay

A smectite clay is characterised by its sheet structure and ability to intercalate water or small organic molecules, causing an increased interlayer distance but no further structural change. Examples of different smectites are vermiculites, montmorillonite, talc, laponite and nontronite. Their quantified behaviour is dependent on different particular properties.

### Surface charge

In a regular smectite unit cell a negative charge imbalance on the surface is conserved. The edge of each particle does however carry a positive charge, which is important for the way the particles agglomerate and behave when in a solution. Substitution of atoms, mainly into the octahedral structure and

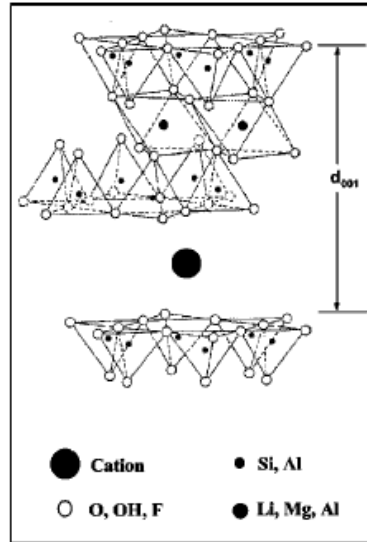


Figure 2.2: Basic structure of a 2:1 smectite clay, with the basal spacing  $d_{001}$  indicated and symbols for typical elements of clay components [2].

its holes, may affect the total surface charge. Either two-thirds of the sites are occupied by trivalent ions, classifying the clay as dioctahedral, or else all the sites are occupied by divalent ions making it a trioctahedral clay.

The total surface charge defines how strong the bonds between layers are, the quantity of cations needed to balance it and how many layers of water it is possible to intercalate while still keeping the structural form.

### Cation

The tetrahedral oxygen array contains asymmetrical holes, approximately 3 nm in diameter. Electrostatic attraction may cause cations to lodge here, and thus contribute to the total surface charge. The size fits perfectly with diameter of  $K^+$ -ions, making these the most common cation for this purpose.

Dependent on the surface charge a number of exchangeable cations is intercalated between layers, contributing to binding them together. The *cation exchange capacity* is defined as a measure of these two fundamental properties of clay, by detailing its capacity for intercalating cations found in a surrounding clay solution.

### Water intercalation and swelling

Water uptake in smectic clay is essentially different from a granular media, because of its multiscale distribution of pores and its evolution when swelling occurs. The multiscale nature of clays can be described using a micro-, meso- and macroscale [11, 12, 13, 14].

The generally low surface charge of smectites makes the quantity of intercalation of water dependent on two sets of variables. First, the thermodynamic parameters as temperature (below  $\sim 120^\circ\text{C}$ ), pressure and humidity. And secondly, the surface charge and position of the cations in respect to the platelets [15]. The water molecules are assumed to be oriented around the intercalated cations, thus increasing the interlayer distance  $d_{001}$ , as indicated in Figure 2.2 of the general smectite structure. Generally the cation may be surrounded by 2 or 4 water molecules, which respectively amounts to a 1 water layer state with interlayer distance  $d_{001} \sim 12.5 \text{ \AA}$  and a 2 water layer state with  $d_{001} \sim 15 \text{ \AA}$ . Some smectites may intercalate even more water molecules while still keeping its structure. Each state with a complete intercalated water layer is more thermodynamically stable than a partial intercalation state, and it takes a varying amount of energy to achieve a transition. But at low temperatures a state

of partial intercalation is often found, as the temperature range for a stable water layer state is narrow.

Structure and physical properties of water near mineral surfaces can be substantially different from those of bulk water. However, the dynamics and physical properties of near-surface water remains incompletely understood [16]. Solid surfaces perturb the the water structure and dynamics by affecting its molecular packing, orientation, rotation and translation. These effects arise due to the “hard wall effect”, the presence of electrostatic fields and local surface specific H-boning donor and acceptor cites. The effect creates a near-surface layering caused by spatial geometric constraints, that no part of an atom or a molecule on the surface can penetrate it. It is an effect that occurs for all confined fluids [16].

Swelling of the  $d_{001}$  interlayer spacings in smectic clay is believed to be controlled by a number of different factors [17].

- Attractive forces
  - Coulombic interaction between the interlayer cations and the sites of negative charge on the crystalline layers.
  - van der Waals attraction between the layers.
- Repulsive forces
  - Between the like-charged tetrahedral silicate surfaces of the 2:1 layers.
- Elastic terms
  - Added terms to free energy of local strain interactions because of expansion and collapse of the interlayer region. This phenomenon is often referred to as ‘resistance’.

Hydration energy [18] can be detailed because of hydrogen bonds between the adsorbed water molecules, surface oxygen atoms in the silicate layers, and interaction of water dipoles with the cations.

The processes of hydration and dehydration often shows signs of **hysteresis** , which is believed to be due to the fact that crystalline swelling is a thermodynamically irreversible process [17].

## Diffusion

Diffusion is associated with the random thermal motion of atoms that produces a change in the macroscopic concentration profile. It is a process which occurs in all types of materials and can provide valuable information about their atomic structure and the defects within them. But more importantly, the diffusion process controls a wide range of kinetic processes associated with synthesis of materials. At a microscopic scale diffusion in materials occure by random motion of discrete entities. Speed and direction depends on the particles mass charge and environment, although both are found to be sporadical and unpredictable variables. A solid can be seen as a dynamic state of matter capable of changing rapidly at sufficiently small lenglht scales, and as such also diffusion is a phenomenon with many different forms and aspects to take into account. [19]

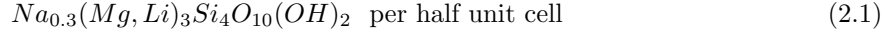
Several mechanisms exists to describe diffusion at an atomic scale in crystalline materials. The choice is dependent on which forces are dominating under the current conditions. Earlier research on smectite clays have demonstrated that movement of water at low temperatures are dominated by diffusion and random nucleation, while at higher temperatures nucleation and growth of reaction fronts may explain the kinetics [20]. But diffusion mechanisms of water in clay include phenomenas that are not fully understood yet.

## First order phase transition

The phase transitions between the 0WL, 1WL and 2WL state are of first order [18]. This involves latent heat in the system, thus a fixed amount of heat is either absorbed or released during the transition, according to the broad classification specified in the Ehrenfest scheme. The energy is not instantly transferred, thus first order transitions are associated with “mixed-phase” regimes where some parts of the system have already reacted and other parts not [21].

### 2.1.2 Hectorite

Hectorite is a smectite clay mineral named after the location where it was first found, south of Hector in California, US. Later it is found also at other locations, such as in Arizona and Nevada, US, France and Turkey[22]. These are minerals altered from volcanic tuff ash with a high silica content related to hot spring activity [23]. The general chemical formula of hectorite before facing any substitu



Categorized according to crystallographic data it is a monoclinic crystal and belongs to point group  $2/m$ , with a molecular weight 383.25 gm [23]. Major uses of hectorite are in production of cosmetics, different chemicals and industrial material production[8].

### 2.1.3 Na-Fluorohectorite

Na-Fluorohectorite (Na-FH) is a syntethic, customised smectic clay with specific weight  $2.8 \text{ g/cm}^3$ . Through substitutions of  $F^-$  into the central octrahedral structure the chemical composition [2]



The proportion  $x$  of  $Li^+$  substituted for  $Mg^{2+}$  is vital for the final surface charge, and in total these atoms occupy all the octahedral sheet sites, classifying Na-FH as a trioctahedral smectite. The surface charge normally is  $1.2 e^-/\text{unit cell}$ , which is rather large compared to other synthetic smectites, as laponite with  $0.4 e^-/\text{unit cell}$  [9]. Each crystalline stack consists of  $\sim 100$  layers, giving a typical height of  $0.1 \mu\text{m}$ . Lateral particle size can reach about  $20\,000 \text{ \AA}$ , but this is a polydisperse distribution, thus the particles have a wide range of sizes [9].

#### Water intercalation

Surface properties of Na-FH make *three stable hydration states* possible. No water molecules surrounds the cations in the 0 water layer state (0WL), making the interlayer distance dependent on the position of each cation relative to the structure. In the 1 water layer state (1WL) a water molecule lies at each side of the cation, as illustrated at the top of Figure 2.3, and in the 2 water layer state (2WL) two water molecules are “standing” at each side of the cation, increasing the interlayer distance further, seen at the bottom of Figure 2.3 [2]. The experimentally determined unit cell basal spacing in each case is given in Table 2.1 [2]. By x-ray scattering the position and proportions of each element in the Na-FH unit cell is determined, illustrated in Figure 2.3.

Table 2.1: Basal spacing for the three different hydration states [2].

| # water layers | Basal spacing $d_{001}$<br>nm |
|----------------|-------------------------------|
| 0              | 1.0                           |
| 1              | 1.2                           |
| 2              | 1.5                           |

#### Specific heat

Since smectites constitutes a heterogeneous system, largely consisting of layered silicate and water, an estimate of the specific heat of the system need to take its nature into account. Earlier research indicates that no structural change of Na-FH occurs [15] in the projected temperature interval, leading to the conclusion that the specific heat of the clay itself stays unchanged throughout the heating period. This is confirmed by obtaining close to identical heat flow curves when the same sample is run twice. If any irreversible structural changes had occurred <sup>2</sup> also the hydration and dehydration characteristics would

<sup>2</sup>Dehydroxilation, meaning loss of structural water, and migration of the intercalated cations are expected at higher temperatures.

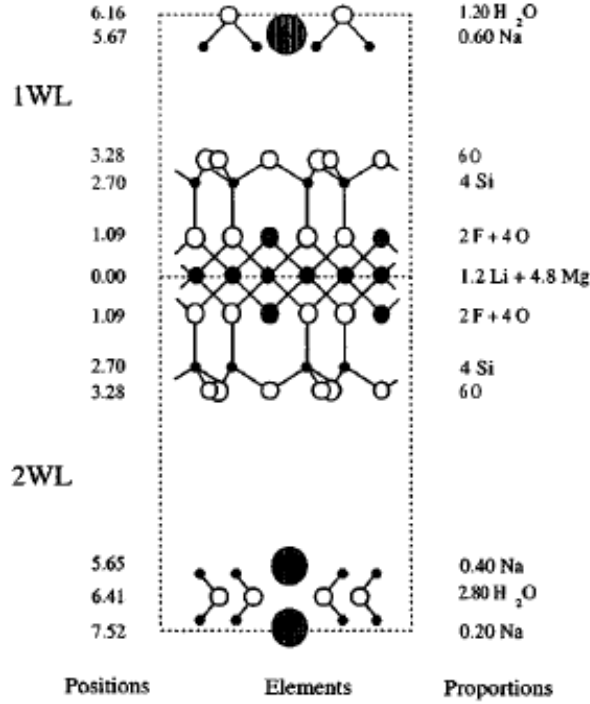


Figure 2.3: Schematic representation of the elements comprising the Na-Fluorohectorite cell. Taken from [2] The origin position (0 Å) is chosen to be the symmetry center of the silicate. The upper region of the figure shows the positions and proportions of the elements for the case of 1 WL; the lower portion is the 2WL case.

be affected.

Thus Na-FH in itself may be considered a stable mineral during the current measurements. Further, intercalated clay can be considered an intimate mixing of two phases, smectite and any intercalated material. Each have a heat capacity, which normally are additive by adhering to the relation [24]

$$C_p(\text{total}) = xC_p(\text{guest}) + (1 - x)C_p(\text{clay}) \quad (2.3)$$

where  $x$  represents the weight percent. In reality however the heat capacity of each component may be changed because of the interaction between the two materials [24].  $C_p$  of a 0WL clay is not the same as a 2WL one, and intercalated water do not have the same  $C_p$  as free water in bulk. In addition to intercalated water an amount of water exists in meso pores and will evaporate at a different rate, as other forces seem to be relevant for their behaviour.

## 2.2 Relative humidity

As a measure for the amount of moisture in the air relative humidity (RH) is used. It is a highly temperature dependent variable calculated by [25]

$$\text{RH} = \frac{\text{Actual Vapour Pressure}}{\text{Saturation Vapour Pressure}} \times 100 \quad (2.4)$$

The saturation vapour pressure is a unique function of temperature, and for example at 24°C it is 29.6 mb [25]. The nature of relative humidity makes it difficult quantity to probe accurately, and it is usually only possible to determine the relative humidity down to a scale of  $\pm 2\%$ .

# Chapter 3

## Experiment

This chapter will provide an introduction to the instruments being used for measurements and the principles they build on. Also included is a description of the set up, and the standard method used to measure the dehydration behaviour of Na-FH.

### 3.1 Experimental setup

#### 3.1.1 TGA

A Thermogravimetric Analyzer (TGA) is a sensitive balance, where the temperature and atmosphere may be controlled. The main components are illustrated in Figure 3.1. A constant stream of nitrogen is used to purge the balance. The local atmosphere of the sample holder is regulated by reactive air being pumped in through a capillary. Normally a shallow aluminium crucible is used as sample holder for temperatures below 650°C. Furnace temperature and time is adjusted by using the software STAR<sup>e</sup>.

There are two main methods when using the TGA: Either the sample is heated at a constant heating rate in a dynamic experiment or the sample may be held at a given temperature for an isothermal measurement.

This semester the TGA has been out of order. For a brief summary of the necessary repairs please see Appendix D.

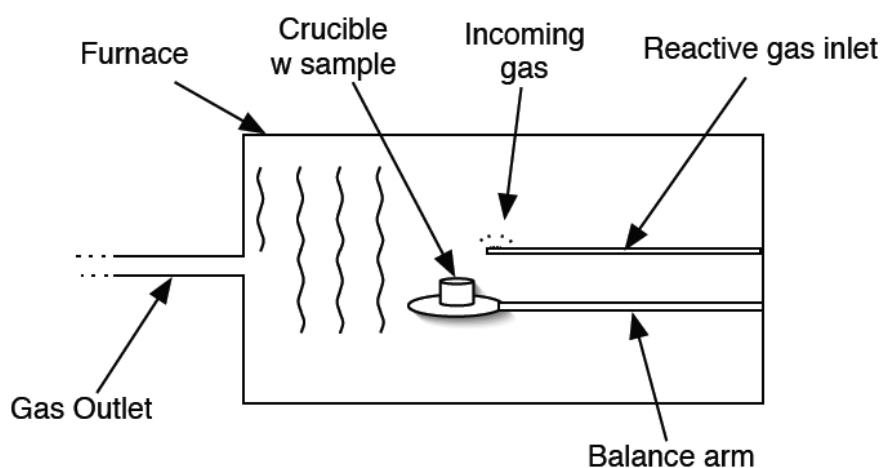


Figure 3.1: Main components of the TGA. Taken from [3].

### 3.1.2 DSC

A Differential Scanning Calorimeter (DSC) employ a thermoanalytical technique for detecting the energy that is consumed or generated by a sample during a temperature dependent process. A heat flux DSC is made to maintain two crucibles at an identical temperature, while implementing a temperature program varying with time, combined with control of the local atmosphere. The lab owns a DSC822<sup>e</sup> from Mettler Toledo, which uses the software STAR<sup>e</sup>. The instrument is depicted in Figure 3.2, where the sample cell is placed in the front, left hand corner.

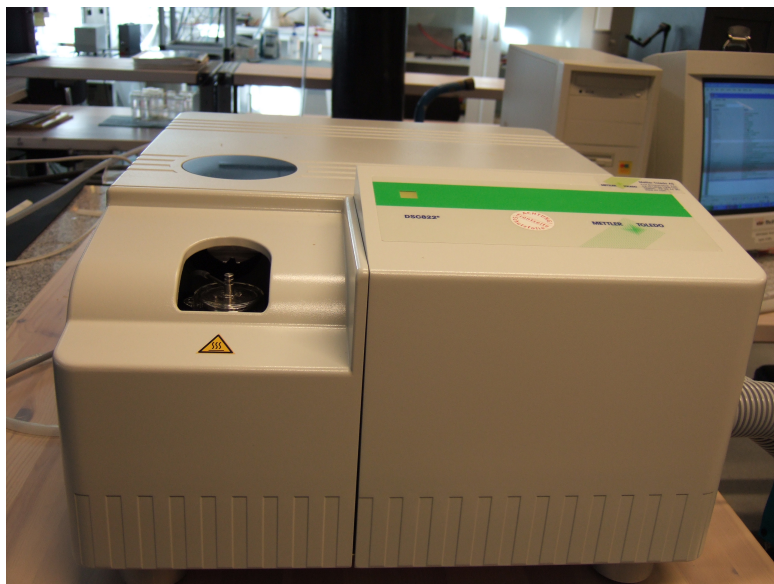
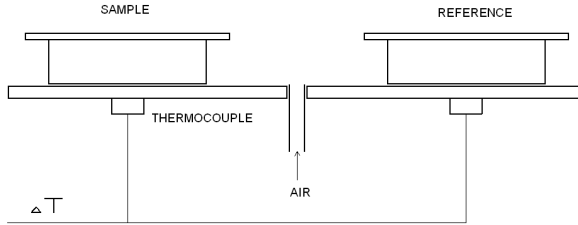


Figure 3.2: DSC822<sup>e</sup> from Mettler Toledo.

The measuring principle is based on monitoring the temperature difference between two crucibles placed on individually controlled heating elements. It is essential that the crucibles are identical, one providing a reference while the other contains a sample of known weight. Both are heated at the same rate, but if the sample consumes or produces energy the heat wave will change the total sample temperature, detected underneath by a thermocouple, and result in a temperature difference  $\Delta T$  between the two crucibles. The signal  $\Delta T$  is used to constantly readjust the furnace temperature underneath the sample to maintain the correct temperature. Output signal represents the heat flow  $\Delta\Phi$  in the sample, which is proportional to  $\Delta T$ . The measuring principle is illustrated in Figure 3.3(a).

Figure 3.3(b) shows the sample chamber with its central heating element holding two crucibles. Else the cell is made up of a metal cylinder, which ideally has a controlled atmosphere inside. Air is heated by a system in the DSC to the current sample target temperature before being let in into the sample chamber through holes placed in between the crucibles. It escapes through a hole in the center of the metal lid. At the same time nitrogen is pumped through the furnace housing and further outside the sample chamber to prevent condensation when measurements below room temperature are made. Both gases are collected under a glass cover on top of the sample chamber and escapes through a central rubber tube. Originally the DSC cell is cooled by a fan, but measurements below room temperature can be achieved by making use of a Refrigerated Circulating Bath. Specifications of the DSC822<sup>e</sup> are listed in Appendix A.

Five quantities are recorded by the software every second during measurements: An index, the time given in seconds, the sample temperature  $T_s$ , the reference temperature  $T_r$  and the current heat flow. Calibration of the instrument is done by using melting point standards and predefined methods. A description of the calibration process, for future users of the instrument, is given in Appendix A, as well as some other information on operation of the DSC.



(a) Measuring principle.

(b) Sample cell on the DSC822<sup>e</sup>.Figure 3.3: The sample cell of a DSC822<sup>e</sup>.

### Heat flow curve

The DSC has got two main modes, isothermal heating or dynamic heating at a given rate. Most experiments on clay are done at a given rate to determine temperature ranges for the peaks. Endothermic peaks, where energy is consumed by the sample, is by the software defined as negative, giving a minimum<sup>1</sup>.

Interpretation of current results is based on general rules: A heat flow curve measured with a DSC can mainly help to identify three types of phenomena, illustrated in Figure 3.4 [4].

- The measured curve shows how the specific heat  $C_p$  changes continuously in the course of a measurement. When a peak occurs an interpolated baseline should be made, in such a way that it connects the curve as if no energy had been exchanged at all. Point 2 and 4 in Figure 3.4.
- A peak indicates that the steady state is disturbed by a temperature-dependent first-order transition producing or consuming energy. The transition starts at a temperature  $T_i$  and ends at  $T_f$ , at the moment where the heat flow curve respectively deviates from and rejoins the baseline. Point 3 in Figure 3.4. Amount of consumed energy, called heat of transition, is found by integrating the peak area.
- A glass transition is found if a change in the heat capacity  $\Delta C_p$  is observed, in the form of a step in the baseline. Point 1 in Figure 3.4.

### Relation between DSC and TGA signals.

2

For macroscopic thermal analysis two different methods are available during the current project work. Using the TGA weight changes can be monitored and the DSC detects heat flow. But the signals are related, and the manufacturer, Mettler Toledo, describes a method for correcting the DSC signal for weight changes by calculating a temperature dependent adjustment factor, originating in a temperature-dependent signal from the TGA.

The TGA has two temperature sensors, one placed at the bottom of the furnace and one sitting directly below the sample crucible. The former is source for a reference temperature calculated using a mathematical model. Thus, output from the TGA also consists of Single Differential Thermal Analysis

<sup>1</sup>This specific definition varies in the literature, and thus whenever examining a heat flow curve the current specifications should be checked.

<sup>2</sup>Based on the two publications [26, 5]



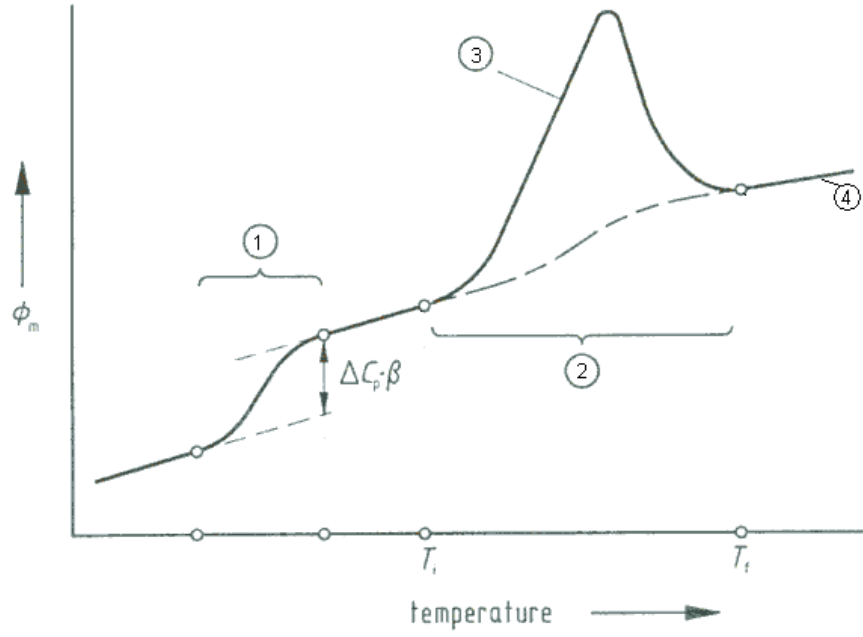


Figure 3.4: The basic parts of a heat flow curve: 1. Step due to  $\Delta C_p$  with  $\beta$  being the heating rate, 2. Interpolated baseline, 3. Peak, 4. Measured curve [4].

(SDTA) stating the difference between these two temperatures at any given time following the relation [27].

$$SDTA = T_s(\text{measured}) - T_r(\text{calculated}) \quad (3.1)$$

During experiments the SDTA signal will indicate whether a weight loss detected by the TGA is endothermic or exothermic. It will also measure heat flow during transitions which do not involve any weight loss. Thus the SDTA signal measure the same phenomena normally detected by the heat flow curve in a DSC, and by determining a conversion factor dependent on calibration of the TGA the SDTA signal may be converted into a heat flow curve. In general this method can be used to correct DSC curves for thermal effects related to mass change or to check if the experimental procedure has been the same for parallel measurements on both instruments.

When using a DSC the measurements are usually normalized to the initial sample mass, thus assuming the sample mass remains constant. But it is not always true, especially for the current research being analysed. At room temperature we expect 1 WL, during cooling in a humid atmosphere additional water is adsorbed in the sample and when heated water is anticipated to evaporate. We assume no chemical alteration of the clay structure itself, thus any weight changes will occur in correlation with natural water content in the given situation. But nevertheless, it could be interesting to see the result of such a signal conversion, to confirm that experiments on the two machines are done under the same conditions.

The method for signal conversion is further detailed in Appendix B.

### 3.1.3 Peristaltic pump

The peristaltic pump which is used to control the local atmosphere during experiments is a Heidolph Pumpdrive 5001, supplied with a pump head and flexible rubber tubes of an inner diameter 7.0 mm and wall thickness 1.5 mm.

The volume of air is decided by adjusting a wheel, which has the scale rounds per minute (rpm). In addition the volume fraction may be regulated by a clamp over the tube. No volume flow is given from the manufacturer, thus it needs to be calibrated for the current conditions. The process and its results are described in Appendix C. For an increase of rpm the volume flow show a linear increase. For the current experiments it is decided to use two different volume flows: With the clamp fully closed 10 rpm give an output of 50 ml/min and 20 rpm produces 87 ml/min. These volumes fit with the capacity of the DSC for heating of reactive air and are easy reproducible for later experiments.

### 3.1.4 Humidity control

As an important part of these experiments the local atmosphere around the sample should be controlled. Both the DSC and the TGA are built to make it possible to pump reactive air into the vicinity of the sample. Air is taken at ambient temperature and pumped through a cylinder with salt, that either absorbs or releases water molecules. The relative humidity (RH) is thus changed according to Eq. 2.4.

#### Salts

Silica gel,  $\text{Co}_2\text{Cl}$ , is used as decessant, and can in a closed system provide relative humidity down to  $\sim 2\%$ . As it absorbs water its colour changes from deep blue to brown, and can subsequently be dried at about  $80^\circ\text{C}$  to regain its original character. Humid air is prepared using a cylinder with a saturated solution of potassium sulphate,  $\text{K}_2\text{SO}_4$ . Air taken at the surface at ambient temperature holds  $\text{RH} \approx 97\%$  [6]. The latter is an example of a salt which provides a constant humidity solution, but generally a closed system where the air is constantly circulated will result in RH closer to the predicted value than if air is only taken at the liquid surface once.

#### Hygrometer

Air temperature and relative humidity is monitored using a HMP37E probe connected to a humidity data processor, hygrometer, of the type HMI38, both produced by Vaisala. For RH below 90% the probe is accurate to  $\pm 2\%$ , and for RH above 90% the accuracy is  $\pm 3\%$ , which gives a rather large total uncertainty. As the nature of humidity makes it a difficult quantity to measure in general it is assumed that the uncertainty of measurement made by the probe is absolute in reference to RH in general. It means that measurement below  $\text{RH} = 90\%$  vary within the uncertainty of the probe but is absolute in reference to the natural uncertainty in the nature of relative humidity.

The lab owns two identical sets of probe and hygrometers. When making a reference measurement in the same atmosphere it was found that their settings had fluctuated, and they did not detect the same relative humidity. Therefore it was found necessary to calibrate both probes, a process which is described in Section 4.1.2. For later use it is recommended that their settings are checked yearly, and further that one probe and one hydrometer are kept as a pair, not being switched back and forth.

The hygrometer has not provided reliable measurements during this semester, because the time consuming calibration process did not finish before the experimental work was concluded. Thus no exact measurements of the relative humidity are available, only estimates based on former use of these constant humidity salts. This will effect the repeatability of the measurements, and makes it necessary to repeat the experiments at a later date.

#### System for humidity control

By use of the internal system for atmosphere control in the DSC (TGA) air is pumped in using a peristaltic pump. No pressure builds at the output because the air diffuses out in the course of passing

through the internal system, but hopeful after passing the sample chamber. Because of the construction of both sample chambers it is not possible to measure the relative humidity close to the sample. However, to improve the total system several initiatives are made.

A rubber **O-ring** , with inner diameter 25.0 mm and thickness 1.7 mm, tolerant of high temperatures is put under the metal lid of the sample chamber to decrease the air flow through this joint. This action should not be cause of any crucial extra temperature gradient in the sample chamber, which could change the general quality of the measurements.

The DSC itself is placed inside a sealed plastic bag, whenever measurements where dry air is needed are performed. A slight overpressure is provided by an extra peristaltic pump. During use it obviously diffuses out since the system seems constant during measurements. In addition supplies of silica gel are placed on top of, and underneath the DSC to exsiccate the atmosphere further. The total system for control is illustrated in Figure 3.5, and depicted in Figure 3.6. The columns with desiccant are here seen behind the DSC.

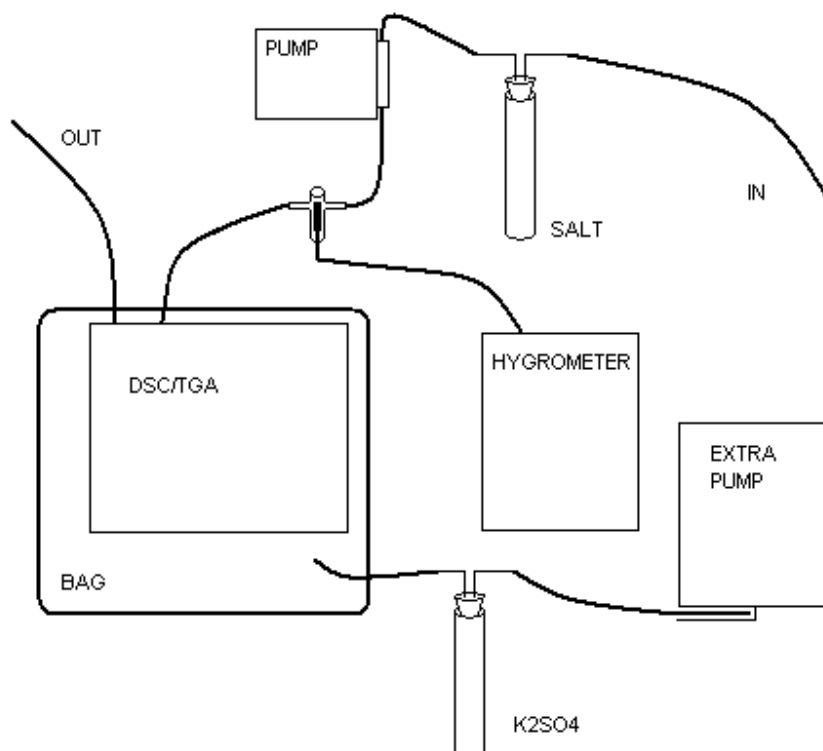


Figure 3.5: System for control of humidity.

### Miscellaneous

Extra supplies of silica gel are placed on and under the DSC during measurements, but the instrument is not that sensitive for movement that it effects the signal. This could however be a problem when similar experiments are implemented on the TGA.

For constant observation of RH a LabVIEW program collecting data from the hygrometer is now available, thanks to work done by Henrik Hemmen. It has also been useful during the calibration process.

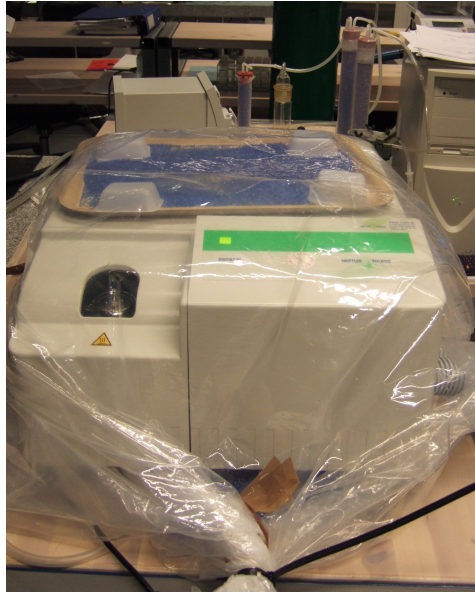


Figure 3.6: Appearance of the DSC during the current experiments.

## 3.2 Experimental method

### 3.2.1 Sample

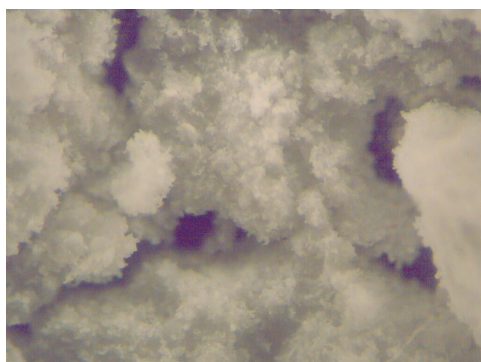
The clay samples consist of synthetic fluorohectorite (Corning Inc., New York), which have been subject to a ion-exchange process to achieve pure sodium fluorohectorite (Na-FH)<sup>3</sup>.

At our research group two different deliveries of Na-FH are currently available. Initially the structural properties were tested using x-ray scattering, by Dr. Ahmed Gmira, indicating slight differences in the water intercalation properties. Heat flow curves were also collected for both samples, and more homogeneous results were achieved for the August batch. Thus this version of Na-FH is chosen for further measurements.

Each sample consists of 2.9 - 3.1 mg Na-FH powder randomly distributed at the bottom of a circular aluminium crucible, which is 1.6 mm an inner diameter 5.5 mm. Such a low weight is chosen to minimize surface effects and because it is convenient when making comparable measurements at other instruments later. The layer of clay is generally thin, just covering the bottom of the crucible, as demonstrated by when comparing the dimensions between clay and crucible in Figure 3.7(b). The random particle structure of Na-FH is shown more clearly in Figure 3.7(a).

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<sup>3</sup>The ion-exchange involves adding NaCl to a sample of Li-FH, this is subsequently mixed for 1 month in a shaker at 300 rpm, and then filled into membranes for cationic exchange. Finally a few weeks of washing with distilled water is necessary to obtain a pure Na-FH sample.



(a) Na-FH, from the August batch.



(b) Na-FH in an Al crucible.

Figure 3.7: Example of a sample used for thermal analysis.

### 3.2.2 Procedure

The measurements are all done according to a fixed procedure, as DSC data are highly sensitive to differences in the conditions. And to ensure the experiment is repeatable all details need to be described.

**Set parameters** Nitrogen gas is used as purge gas, with a constant flow 187 ml/min<sup>4</sup>. This is relatively high, but the possibilities for flow adjustments on the N<sub>2</sub>-bottle are somewhat coarse, reducing our possibilities. Humidity in the system is controlled as described in Section 4.4.2.

The general temperature program is illustrated in Figure 3.8, and its details along with the current humidity are:

1. Cooling from room temperature to 5° at a rate of 10°C/min in ambient humidity.
2. Isotherm at 5° for 2 hours, with a change of humidity from ambient to dry after approximately one hour.
3. Heating until 130° at a rate of 2°C/min.
4. Measurements are terminated after an isotherm at 130°C/min for half an hour.

Any deviations from the described procedure are specified during presentation of the results in Section 4.3.

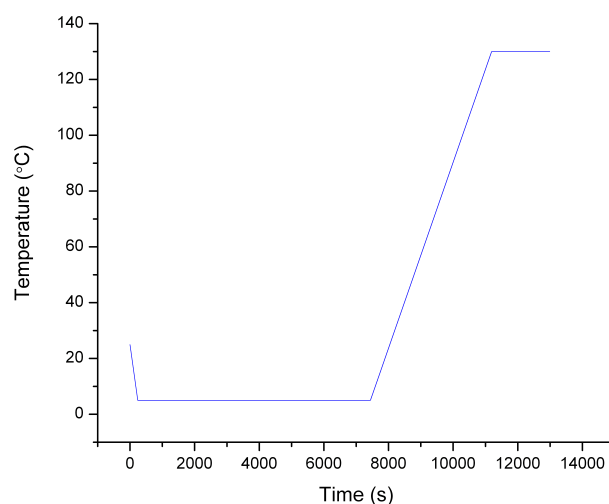


Figure 3.8: Temperature program for a typical measurement of dehydration processes in Na-FH.

<sup>4</sup>Determined by a similar procedure as described in Appendix C

## Chapter 4

# Data analysis and discussion

The experimental results are presented in several sections. First a overview of necessary preliminary experiments, and their implications. Second, general analysis of a heat flow curve for Na-FH collected under normal conditions, to explain the different parts of the curve and its assumed interpretation. Also included is the general method for necessary correction of the heat flow curves. Next, a presentation of results during dehydration of Na-FH using the DSC, and a discussion on different relevant features and implications when comparing the measurements. Finally, a discussion on use of heat flow curves on Na-FH, the experimental conditions of the instrument and their influence on the results.

### 4.1 Preliminary experiments

Several minor experiments are performed during the project period. First, hydration properties of Na-FH at ambient conditions are checked using x-ray scattering. Second, the calibration process for humidity probes is described. Finally, an outline of measurements of isotherms on the TGA, to determine reaction mechanisms on an atomic level, which were started, but unfortunately terminated because the instrument is out of order.

#### 4.1.1 Hydration at ambient humidity

Because of limitations in the air supply system of the DSC it is not possible to pump air in a closed cycle. Even using  $K_2SO_4$  the humidity does not become higher than  $\sim 40\%$  in the current open system. To check if it is possible to reach a 2 WL state at  $5^\circ C$  even at *ambient* conditions, RH  $\sim 25\%$ , an additional measurement using X-ray scattering is made<sup>1</sup>.

The measurements are made by simply cooling the sample down to  $5^\circ C$  while pumping air with ambient humidity through a closed sample cell. Each scan lasts 10 minutes. First, a relatively thin sample of Na-FH is tested, and afterwards a much thicker one.

Scattering profiles for hydration of a thin sample is shown in Figure 4.1, and implies that it takes about 40 minutes before the Na-FH is in a 2WL state. The Bragg peak in the 4. scan is centered at  $2\theta = 5.757$ . Using Bragg's law [28] the layer distance is determined to be  $d_{001} = 15.4 \text{ \AA}$ . This result agrees with the data given in Table 2.1, and confirms that a 2WL state is achieved.

For a thicker sample the hydration process takes longer, but is nonetheless fully achieved in about 150 min, as the scattering profiles in Figure 4.2 show.

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<sup>1</sup>No account for the SAXS instrument or the setup is given, because X-ray experiments on clay are no major part of this project work. For a detailed description see [28].

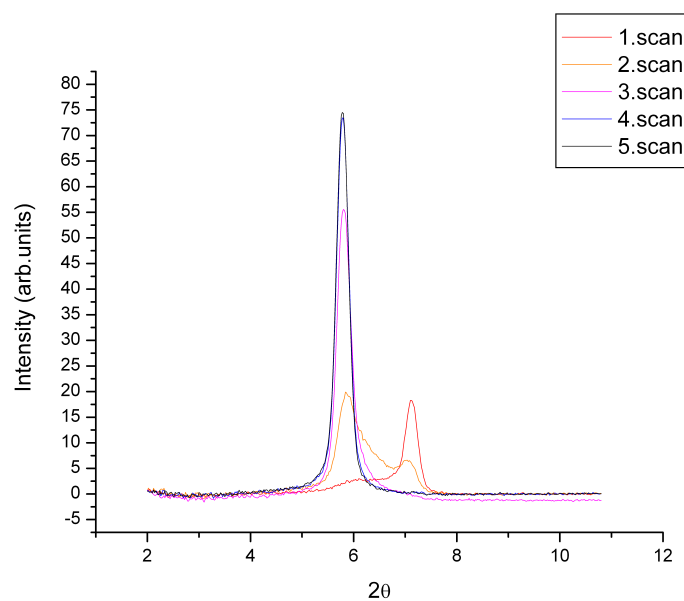


Figure 4.1: Scattering profiles for 10.min scans of a thin powder sample of Na-FH at 5°C and ambient humidity.

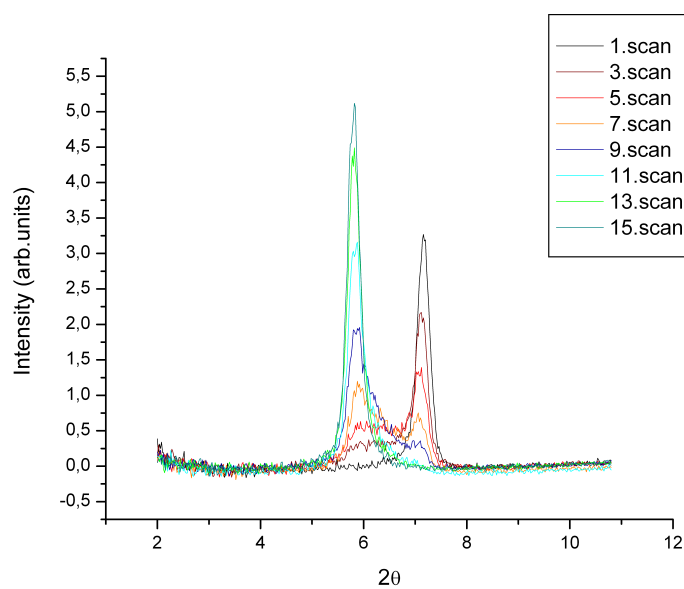


Figure 4.2: Scattering profiles for 10.min scans of a thick powder sample of Na-FH at 5°C and ambient humidity.



### 4.1.2 Calibration of hygrometer probe

Settings of the humidity probe have drifted over time, and they now needed readjustment. The decision is taken based on two different probes showing different humidity when being exposed to the same conditions, thus a time consuming calibration process is started.

For calibration two salts which provide constant humidity solutions are used. If an excess of the water soluble salt is in contact with its saturated solution in an enclosed space, air with constant relative humidity and water vapor pressure will be the result, according to the relation

$$RH = A e^{B/T} \quad (4.1)$$

where  $T$  is the temperature in Kelvin, and  $A$  and  $B$  are constants dependent on the chosen salt. The relative humidity  $RH$  is generally accurate to  $\pm 2\%$ . [6]

According to their properties the two salts NaCl and LiCl were chosen for calibration, one providing humid air and the other dry air. Their specifics are given in Table 4.1.

Table 4.1: Specifics for salts providing constant humidity solutions [6].

| Salt | RH (25°C)<br>% | A     | B   | Solubility<br>g/100 ml |
|------|----------------|-------|-----|------------------------|
| LiCl | 11             | 14.53 | -75 | 63.7 (0°C)             |
| NaCl | 75             | 69.20 | 25  | 35.9 (25°C)            |

When adjusting the relative humidity during experiments practical use has ascertained that a saturated solution is sufficient. However, for calibration, practise showed that even close to the surface the humidity is not stable enough for this purpose.

For a stable relative humidity the solution should be a slush, with an excess of undissolved crystals. With too much water, as in a true solution, even if it is saturated with undissolved crystals at the bottom, the result might be a layer of less-than-saturated solution at the surface. This may produce a lower humidity than anticipated. Conversely, solid crystals above the surface of the liquid might also reduce the humidity. A proper solution may be made by adding water slowly while stirring until about half of the crystals are dissolved [29].

Other points to take into consideration when performing this type of calibration [29].

- Purity of both salt and water. Even a small amount of contamination may effect the result. Some airborne contaminants are also water soluble and may render the sample useless.
- The diffusion rate of moisture from a saturated salt solution is exponential. It involves a quick approach to near equilibrium, but a gradual fine approach to the final end point. The diffusion rate is governed by the difference in water vapor pressure of the solution and that of the vapor, and by the attraction of salt to water. For some salts, the attainment of complete equilibrium requires days, even in stagnant air. For a faster stabilization it is recommended that the surface area of the solution is large as possible, in comparison to the available vapor space. If possible the air should also be circulated inside the closed space.
- Water vapor pressure is a function highly dependent on temperature, making it an important factor in the calibration. However, the salt solutions have different sensitivity for this parameter.

**Setup** The current calibration is accomplished using a salt slush put in small glass containers, pictured in Figure 4.3. Later it was found that the humidity is more stable when the container walls are cleaned for crystals, as these may reduce the humidity, as explained above. For calibration the probe is lowered into the glass container and the system is sealed using parafilm. It is held stable by a metal rack with two clamps, see Figure 4.4(a). Because the probe is slightly light sensitive the setup is covered by a towel and put inside a cardboard box. The final setup is shown in Figure 4.4(b), with the hygrometer

in the lower right hand corner. Beside the hygrometer a handle is taped to the table for stability. This contains two sensitive screws, used to adjust the voltage signal for the hygrometer and thus essential for the calibration process.



Figure 4.3: Salt slushes used for calibration of hygrometer probe.

The calibration is performed in a large lab with much activity, thus the temperature varies during the day. Also, the ventilation system automatically lowers the temperature at night. This throws off the stability of the system, and the collected data reflects this.

The nature of humidity measurements makes it a difficult quantity to measure, as it has a natural uncertainty of  $\text{RH} \pm 2\%$ , as discussed in Section 3.1.4. The probe itself has a certain accuracy against field references, see Section 2.2. Thus it is anticipated that the uncertainty intervals  $\pm 2\%$  and  $\pm 3\%$  for RH below and above 90% respectively, prevails during measurement, and the nature of humidity is taken into account when these are set by the producer. Else the uncertainty interval would be too large to process data in a satisfactory way.

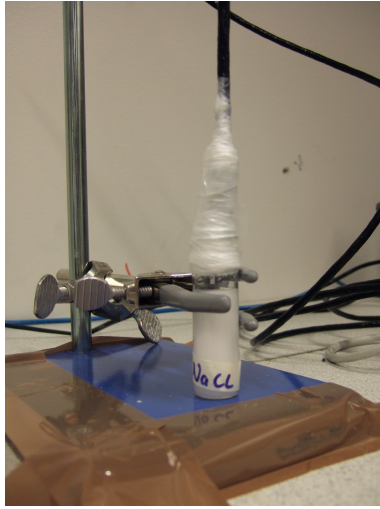
Two salts, which provide significantly different constant humidity are used, as it is necessary to adjust two screws to correct the settings. Thus several measurements are made, alternating the salts, attempting to achieve the correct instrument settings by iteration. And as the solutions take a long time to reach equilibrium the total process is time consuming.

### Temperature sensitivity

If the room temperature changes significantly it takes some time before the system regains equilibrium, because air and water have different specific heat. At typical room conditions air has  $c_p = 1.012 \text{ J/gK}$  and liquid water has  $c_p = 4.1813 \text{ J/gK}$  [21]. This represents a problem when trying to calibrate the sensor, because the system needs to be stable for a period of some hours before one can safely adjust the settings. Normally the sensor will not sit directly above the liquid surface but between 0.5 and 1 cm away, which can cause a temperature gradient. This is another factor that causes the time limits to increase.

As an example for the current salts calculations are made for a temperature difference of  $1^\circ\text{C}$ . If temperature on the liquid surface is  $22^\circ\text{C}$  and  $23^\circ$  is found in the air around the sensor. Assuming the actual vapor pressure,  $AVP$ , is constant throughout the sample container, differences in temperature sensitive saturated vapour pressure,  $SVP$ , will cause significant differences in relative humidity, calculated by Eq. 2.4. The results are presented in Table 4.2, where the saturated vapour pressure at each temperature is  $SVP(23^\circ\text{C}) = 28.04 \text{ mb}$  and  $SVP(22^\circ\text{C}) = 26.39 \text{ mb}$  [30].

When using  $\text{NaCl}$  the difference is 4.70%, calling attention to the significance of waiting long enough to ensure a thermal equilibrium is established in the system. This factor comes on top of actually waiting until the vapor pressure is constant inside the sample container. Both these factors stress the



(a) Glass container with salt and probe sealed with parafilm



(b) Setup covered with a cardboard box, the hygrometer with probe handle is shown in the lower right corner.

Figure 4.4: Setup for calibration of hygrometer probe.

Table 4.2: Effect of temperature differences on the relative humidity during calibration of humidity sensor.

| Salt | assumed RH (23°C)<br>% | AVP<br>mb | calculated RH (22°C)<br>% | $\Delta$ RH<br>% |
|------|------------------------|-----------|---------------------------|------------------|
| LiCl | 11.28                  | 3.16      | 11.98                     | 0.70             |
| NaCl | 75.30                  | 21.11     | 80.00                     | 4.70             |

importance of a stable temperature, a conditions which is not fulfilled with the current set-up.

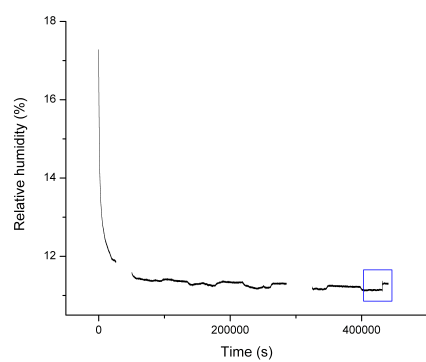
The thermal fluctuations lead to large fluctuations in relative humidity, as illustrated in Figure 4.5. It is remarkable how close the correlation between temperature and relative humidity is when looking at the details in the collected data, and it is thus established as the most dominant error factor in the measurements.

### Calibration data

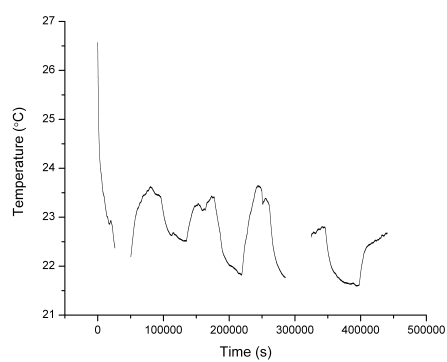
The results presented in Figure 4.5<sup>2</sup> are collected during approximately five days. When looking at the thermal fluctuations in Figure 4.5(b) five temperature maximas are evident (daytime). When comparing these to the fluctuations seen in relative humidity in Figure 4.5(a) a minimum is always found when the temperature increases. The detailed picture in Figure 4.5(c) is a section cut from Figure 4.5(a) (marked with a blue box), and shows how the relative humidity has been stable for the approximately the last 8 hours. The settings are subsequently adjusted, and after another 2 hours the measurements are terminated as the relative humidity still seems stable.

Several measurements are made with each salt, but at the present time the calibration process is not yet finished. Main cause is the large temperature fluctuations, thus for later attempts it would be practical to set up the experiment at a different location.

<sup>2</sup>Blank areas in the curves occur because of flat batteries in the hygrometer.



(a) Relative humidity.



(b) Temperature development.

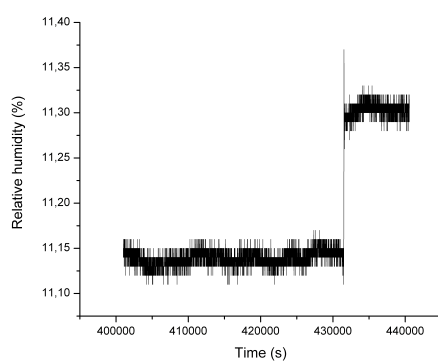
(c) Segment of the relative humidity, when stabilised.  
Cut from Figure 4.5(a).

Figure 4.5: Data collected when using LiCl as calibration salt.

### 4.1.3 Isotherms using the TGA

By measuring the isothermal weight change as a function of time a kinetic analysis of dehydration in Na-FH may be performed, and the mode of diffusion be established (see Section 2.1.1). An equilibrium state will be established in the sample, where both temperature, water content and humidity are taken into account. When finding the fraction transformed  $\alpha$  it is possible to gain insight into the reaction mechanism on an atomic scale, by attempting to fit the data to a series of solid-state equations, and discern the rate controlling mechanism by judging the goodness of fit. employ a general rate equation which expressed by a variable parameter that reflects the rate-controlling mechanism. Or it is possible to employ empirical rate equations that is expressed by a variable parameter that reflects the rate controlling mechanism. Two of those that are most commonly used are developed by Avrami (1939) and Austin-Rickett (1939). This may determine what kind of diffusion mechanism dominates in a given temperature interval, ex. a phase boundary reaction, random nucleation and one-, two-, or three-dimensional diffusion processes. Further calculations makes it possible to determine the activation energy  $E_a$  using the Arrhenius equation. [20]

Though dehydration in clay often is a complex process, these calculations can be implemented on Na-FH. The experiments were started, but temporarily terminated because the TGA has been out of order. The measurements are simple: A sample is shock heated to a given temperature, which is subsequently held constant for an hour, under controlled humidity. An example of weight loss curves converted to percent of weight loss taken at the isotherm 110°C, are presented in Figure 4.6. As seen the weight loss is relatively equal, but disturbances are seen at the very beginning and before the curve levels out. Earlier research using the TGA has shown that the balance is sensitive to abrupt temperature changes, and the response time needs to be corrected for [31]. Because the furnace is purged by nitrogen gas, N<sub>2</sub> a weight loss is seen only by means of this influence, as detected when doing an isothermal measurements at room temperature. A total weight loss of about 4% is seen in Figure 4.7, confirming data presented by Brad and Redfern [20], and will need to be taken into account.

As discussed later as topics for evaluating the performance of the DSC, the system is not air tight and the relative humidity will change as a function of temperature. Also, the sample temperature do not always establish itself at the reference temperature given by the operator of the TGA, as a consequence of the inherent error in the furnace.

These experiments are not brought to a final conclusion, and if time will allow it further research is an highly interesting topic for future work.

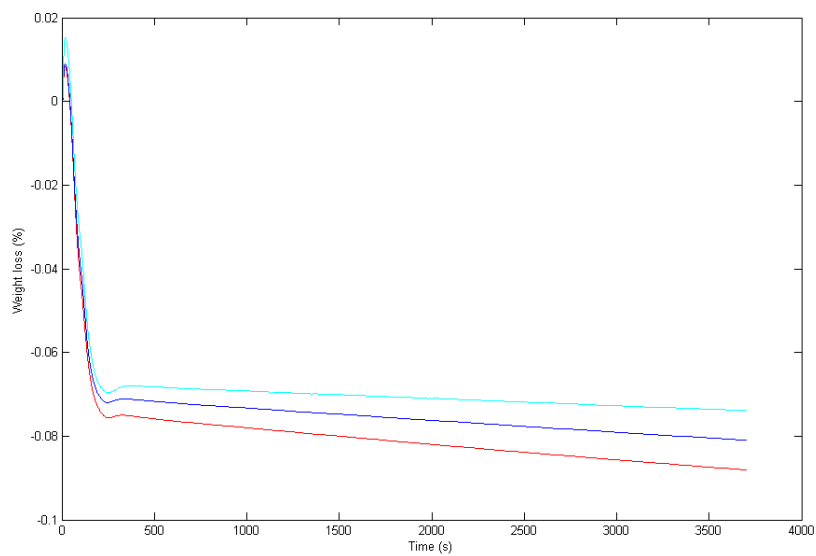


Figure 4.6: Percent weight loss during an isotherm at 110°C.

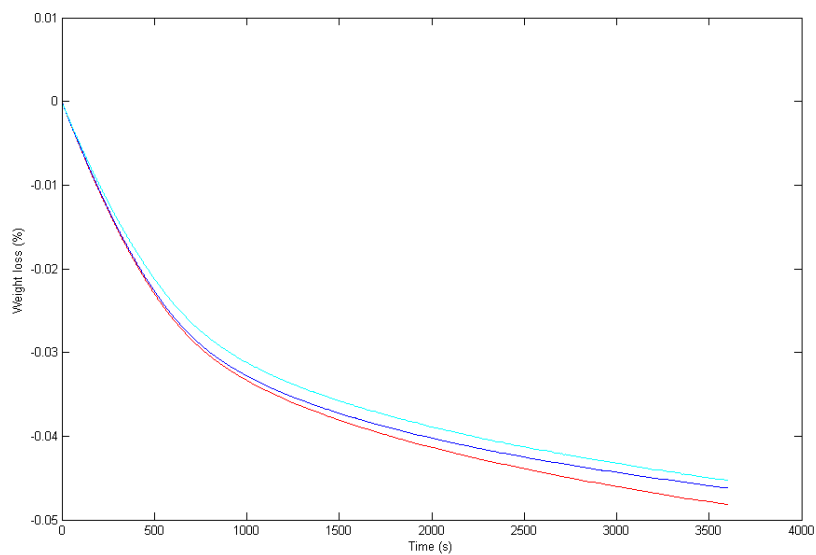


Figure 4.7: Weight loss during an isotherm at room temperature only with the influence of  $N_2$ .

## 4.2 General analysis

A general analysis of a typical heat flow curve for Na-FH is provided to give a basic understanding of the results, before a more detailed analysis in Section 4.3. Also the general method for correction of the current raw data is presented.

Clays are complicated materials and can rarely be seen as homogeneous systems, but at certain conditions they are less heterogeneous than others. Na-FH has three more or less thermally stable and well defined states, 2WL, 1 WL and 0WL. In addition water is absorbed in mesopores, in between semi-crystalline stacks of 2:1 layers. The behaviour of Na-FH is now interpreted with this in mind.

### 4.2.1 Interpretation

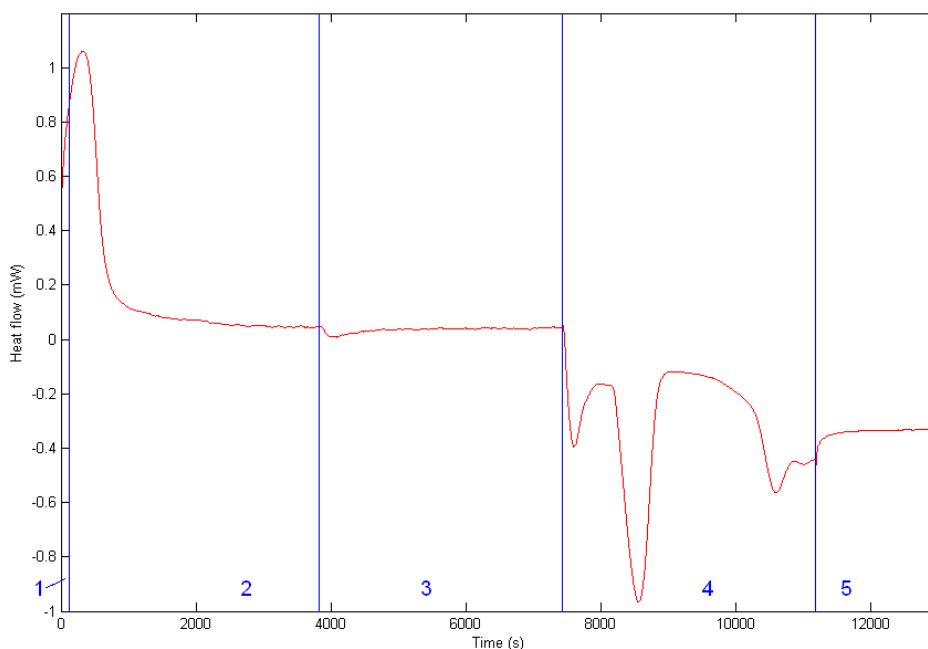


Figure 4.8: A heat flow curve for Na-FH during the entire procedure, divided into relevant illustrative parts.

The heat flow curve for the entire experimental procedure is shown in Figure 4.8, divided into relevant illustrative parts, which are all interpreted in terms of thermal and diffusive behaviour below.

**Part 1: Cooling** The sample is cooled from room temperature to 5°C at a rate of 10°C/min. It represents the start of an exothermic peak, where water is adsorbed in the sample.

**Part 2: Isotherm at 5°C with ambient air** More water is adsorbed in the sample before an equilibrium state is established.

**Part 3: Isotherm at 5°C with dry air** A new equilibrium state is reached when the relative humidity is changed. But the curve stays above zero, thus assuming no large amounts of water is lost.

**Part 4: Dynamic heating** For further analysis this part is isolated and plotted against the reference temperature<sup>3</sup> in Figure 4.9, with a separate section of interpretation.

<sup>3</sup>The reference temperature is chosen because it is convenient. The thermal response of the cell is quite good, as discussed in Section 4.4.1, and the corrections described in Section 4.2.2 are hard to make when the heat flow curves are

**Part 5: Isotherm at 130°C** Still using dry air a new equilibrium is established.

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plotted against slightly different sample temperatures.



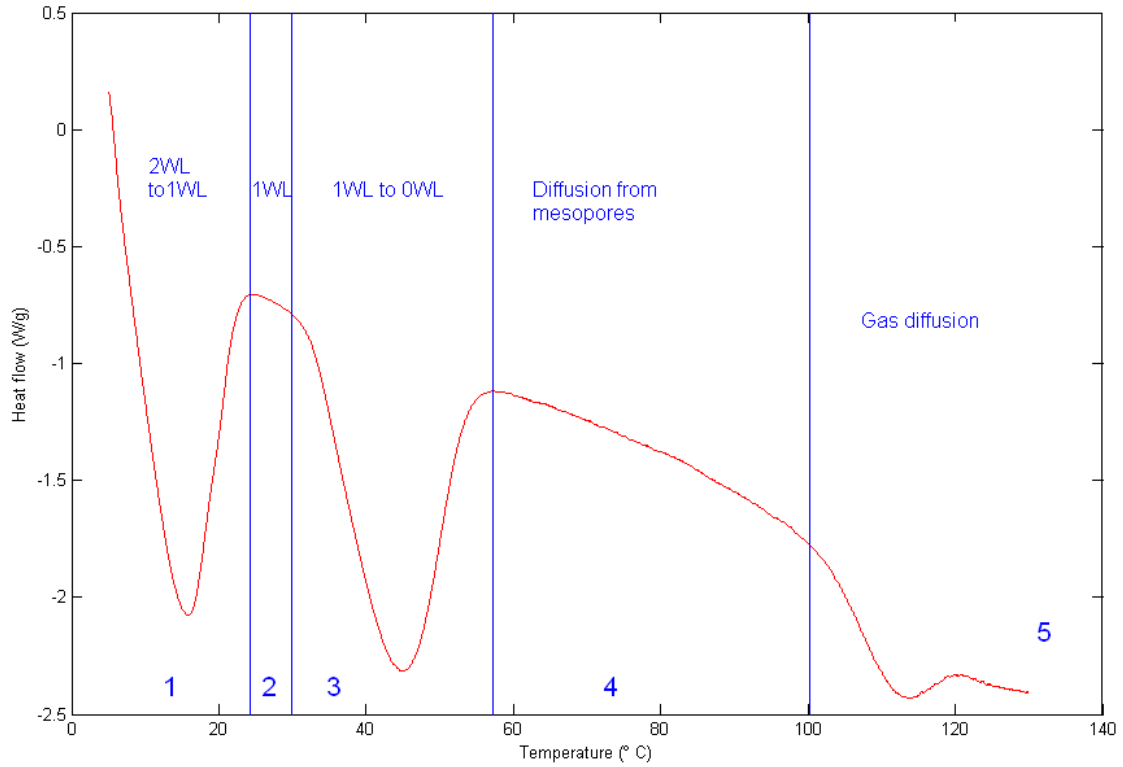


Figure 4.9: A heat flow curve for Na-FH divided into relevant illustrative parts.

The dehydration behaviour of Na-FH in terms of heat flow is shown in Figure 4.9. Based on general knowledge of heat flow curves, as presented in Section 4.2 and known information of Na-FH the results are interpreted in terms of transitions and change of specific heat.

**Part 1: 2WL to 1WL transition** Assuming the sample has achieved a stable 2WL state during the cooling period at 5°C before the heating starts, the first minimum seems to correspond to the heat consuming transition from 2WL to 1WL. Water will gradually evaporate at a rate given by the current curve. The peak position is equal to the maximum transition rate, where most of the sample has achieved a 1WL state. But the first-order transition process involves the entire temperature range of Part 1.

**Part 2: 1WL state** The 1WL state seems more thermally stable than the 2WL state, which could slow the dehydration down [17]. Thus Part 2 is interpreted as a semi stable 1WL state with only small adjustments of the interlayer distance. As a part of the measured curve, the slightly negative slope can also be an effect of changes in the heat capacity  $C_p$  caused by evaporation of water from mesopores (See Part 4).

**Part 3: 1WL state to 0WL state** Second minimum is determined to be the endotherm transition from 1WL to 0WL. A baseline should be interpolated, as demonstrated in Figure 4.17. The baseline is approximated using a spline<sup>4</sup> function, and subsequent integration of the area underneath gives the current heat of transition.

**Part 4: Measured curve and mesopores** Part 4 shows a relatively stable decrease in the baseline, which means the heat capacity  $C_p$  is actually increasing. Thermogravimetric measurements of the same system, at different heating rate and humidity [32], indicates that water from mesopores evaporates at a slow, steady rate and in a large temperature interval compared to loss of intercalated water. It leads to the conclusion that loss of water from mesopores is responsible for the slow changes in the baseline. Not only in Part 4 but for the temperature range of Figure 4.9. But as presented in Section

<sup>4</sup>A function defined piecewise by polynomials and often used for interpolation problems to define smooth curves [21].

2.1.3, changes in  $C_p$  is not only a question of the rate of evaporation but also alteration in interaction between the two components smectite and water.

**Part 5: Gas diffusion** At 100°C the boiling point of water is reached, and different diffusion principles are assumed to dominate than earlier. Thus causing a change in the baseline slope for the remains of the heating process.

### 4.2.2 Correction of curve

All heat flow curves collected by the DSC need to be corrected for two effects before any analysis can take place.

**Zero line** The linearity of the DSC needs to be checked by running test run with two similar, empty crucibles. Thus the thermal behaviour of the instrument is tested, and the results are dependent upon there being small variation in this curve, meaning a good repeatability. It is necessary to determine a individual zero line for every applied heating rate, and any large changes in the supply of reactive air.

The measured zero line needs to be subtracted from the original measured sample signal, as the first part in the correction procedure.

Measured zero lines for the two most frequently used heating rates 2°C and 10°C are presented in the Figures 4.10 and 4.11, respectively.

Three collected zero lines corresponding to the entire experimental procedure are presented as a function of time in Figure 4.10(a) and 4.11(a). In both instances they show a great degree of conformity, verifying that settings of the DSC are stable. The heat flow stabilises at approximately zero during the isotherm at 5°C after starting off being negative<sup>5</sup>. And at both heating rates it takes some time to stabilise when reaching the isotherm period at 130°C, especially when applying 10°C/min.

In Figure 4.10(b) and 4.11(b) the zero lines during the dynamic heating from 5 to 130°C are pictured isolated, with the three parallels averaged. It is interesting to notice the dissimilar form, even though it is important to note the scale of the heat flow. Especially Figure 4.11(b) is deceiving, as compared to the results presented in Section 4.3.2 the zero line is approximately flat.

**Sample size** Initial sample weight vary from 2.9 to 3.1 mg and for comparison the heat flow curve needs to be normalised. Thus all results are given per mg.

**Additional “desmearing”** If an even higher accuracy is needed there are more steps in the correction process, which has the collective name “desmearing” [4].

- Linear transformation of the indicated temperatures at the abscissa, in compliance with temperature calibration of the DSC.
- Transformation of the indicates heat flow rate at the ordinate axes, in compliance with the results of heat flow calibrations.
- Mathematical elimination, deconvolution, of the influence which heat transport phenomena (heat flow rate relaxation) inside the DSC exert on the measured curve.

For the current purpose these steps have been deemed unnecessary, because the accuracy of the DSC should be good enough after extensive calibration.

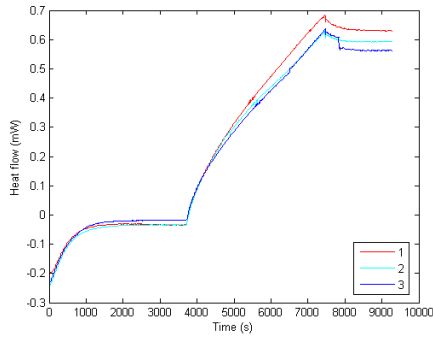
**Conversion of signal** If the need arise the ordinate scale may be converted to give a clear picture of other physical properties: First, specific heat  $C_p$  with measurements from the present DSC is found by the basic relation [4]

$$\Delta\Phi_{SR} = (C_S - C_R) \cdot \beta \quad (4.2)$$

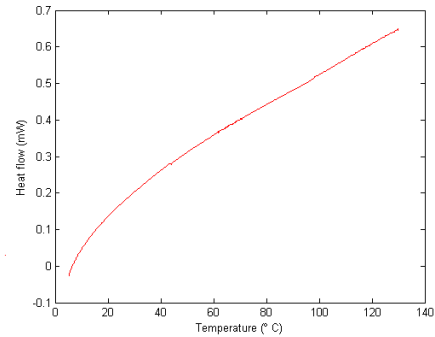
where  $\Delta\Phi_{SR}$  is the heat flow rate and  $\beta$  is the heating rate. Further,  $C_S$  is the specific heat for the sample and  $C_R$  for the reference. The latter is only necessary to provide a correction. For common crucible materials the specific heat is known with necessary accuracy. At the current experiments aluminium crucibles are used, with  $c_R = 0.897$  J/gK.

Second, an integration gives the enthalpy  $\Delta H$  [4].

<sup>5</sup>In comparison to the other curves, parallel 2 in Figure 4.11(a) has a slightly irregular start, of unknown reasons.

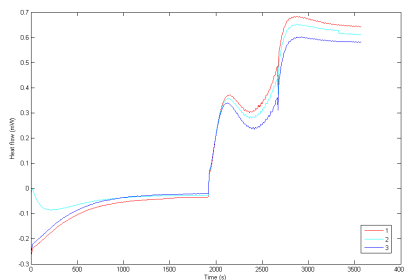


(a) Three parallel zero lines for the entire experiment: Cooling, steady at 5°C, heating and a final isotherm at 130°C.

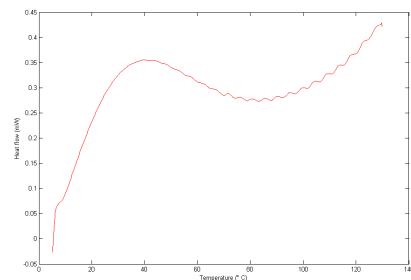


(b) Average zero line in the temperature interval 5 to 130°C.

Figure 4.10: Measured zero line at heat rate 2°C/min with pump speed 87 ml/min.



(a) Three parallel zero lines for the entire experiment: Cooling, steady at 5°C, heating and a final isotherm at 130°C.



(b) Average zero line in the temperature interval 5 to 130°C.

Figure 4.11: Measured zero line at heat rate 10°C/min with pump speed 87 ml/min.

### 4.3 Results and analysis

Main results for an heating rate  $2^{\circ}\text{C}/\text{min}$  are presented and analysed first. Afterwards measurements at other heating rates are presented and compared with expected behaviour.

#### 4.3.1 Normal procedure

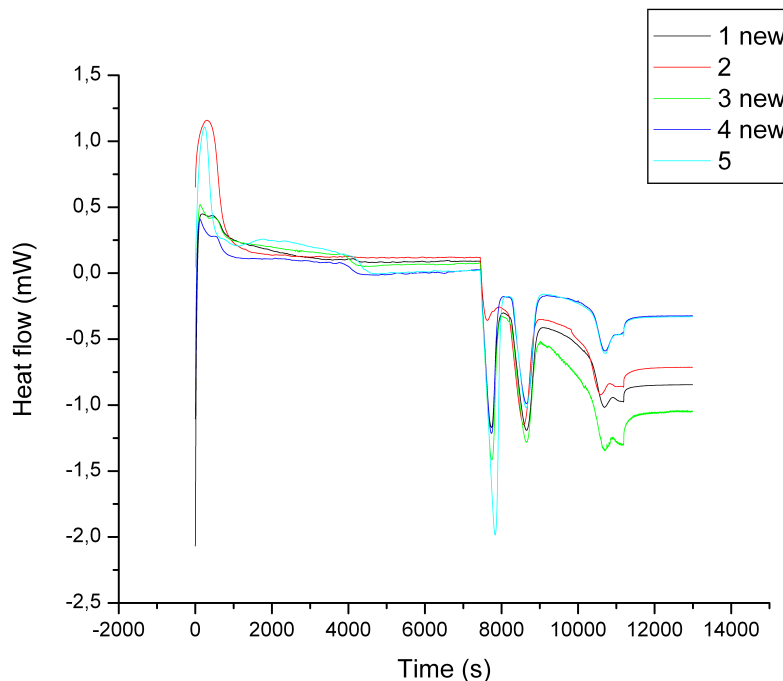


Figure 4.12: Raw data for measurements at heat rate  $2^{\circ}\text{C}/\text{min}$  with pump volume  $50\text{ ml}/\text{min}$  .

The dynamics of Na-FH at heat rate  $2^{\circ}\text{C}/\text{min}$  is examined with two different pump rates. Each are low and chosen for the convenience of easy repeatability, as  $50\text{ ml}/\text{min}$  and  $87\text{ ml}/\text{min}$  corresponds to  $10\text{ rpm}$  and  $20\text{ rpm}$  respectively. For details please see Section C.

Heat flow curves for the entire procedure, presenting five different runs with pump volume  $50\text{ ml}/\text{min}$ , are shown in Figure 4.12. The measurements are taken directly after each other and the legend gives just the number of the run. In addition, if it says “new” it means the sample is exchanged since the last run. A general interpretation of a curve is given in Section 4.2.1. However, further comparison of their form illustrate a number of interesting features. The observations are also valid for the data collected with pump volume  $87\text{ ml}/\text{min}$ , shown in Figure 4.13). A quantifying comparison of the two different dynamics is made on page 35.

First, when water is adsorbed in the sample the curves have different shape. Generally, if the sample is heated for the second time the exotherm peak has the a regular peak shape, and is relatively symmetric. However, in runs where the sample is heated for the first time the peak shape is extraordinary. Two minor peaks can be seen, and it generally takes longer time before the sample reaches an equilibrium state. There is no obvious cause, except that the new samples are taken directly from room temperature conditions, when the reused samples have been cooled in a steady stream of dry air before start of a new run. (Generally the air is not changed to humid until  $25^{\circ}\text{C}$  is attained again.)

Second, when RH changes, a new equilibrium state is generally found fast. The step in the curve is of varying height, but the curve always establishes itself above zero, which means no large amounts of water is lost. One reason for the relatively long time until the heating process starts, is to flush the

system, so in addition to the new clay-water equilibrium, the decrease may be caused by condensed water on the surface or the crucible being flushed away.

Next, the first endotherm, representing the 2WL-1WL transition has large variations in size, with no observed correlation to either the exotherm or the second equilibrium state discussed above. It has been suggested elsewhere [17]<sup>6</sup> that water molecules constituting the second water layer is relatively loosely held. This could be a reason for the varying amount of work it takes to remove it. Other possibilities is that the principles of diffusion which dominates in this situation plays a part. Other possibilities are that the 2WL state is not fully achieved, in despite of the testing described in Section 4.1.1, or part of the endotherm is a result of the system not being sufficiently flushed of unnecessary humidity. As a curiosity it can be mentioned that neither run 5 in Figure 4.12 or run 4 in Figure 4.13 reaches equilibrium before the air supply is changed. And these are the runs with an extraordinary deep first endotherm in comparison with the other runs. Thus of some reason, extra water has been added, and is lost at this stage.

The shoulder between the two endotherms has varying width, and as the second endotherm always starts approximately at the same temperature it is observed that it takes different amounts of time before the first transition is completed.

Size and shape of the second endotherm is relatively homogeneous, confirmed by numbers presented later in Table 4.3. The 1WL state is relatively thermally stable [17], leading to the assumption that the diffusion rate at this stage is uniform, giving a well-defined transition, with a constant consumption of heat.

Finally, when the sample approaches 100°C the baseline slope invariably changes, thus detecting a change in the pattern of diffusion as the state of water is dominated by gas instead of liquid.

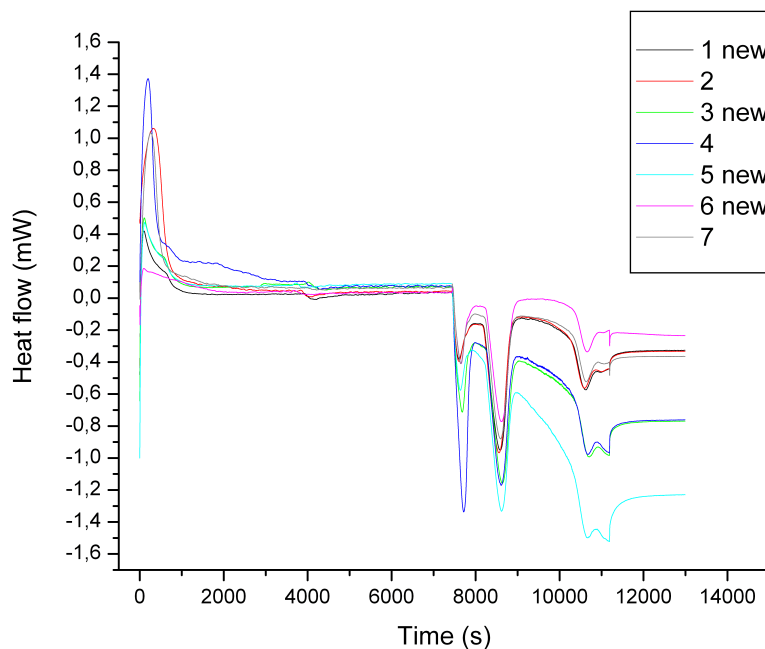


Figure 4.13: Raw data for measurements at heat rate 2°C/min with pump volume 87 ml/min .

The calculations presented in Table 4.3 are made on basis of the corrected heat flow curves presented in Figure 4.14 and 4.15. The overall trend is that the dynamics are faster when the pump volume is 87 ml/min rather than 50 ml/min.

Standard deviation for the quantified dynamics is mainly included for pump volume 87 ml/min because there are more runs to compare. Even in this case the calculations are somewhat tentative, as

<sup>6</sup>Observed for montmorillonite, a similar smectic clay.

Table 4.3: Average peak position, temperature ranges and heat of transition for the dynamics of Na-FH at heat rate 2°C/min.

|                             | Average        | Standard deviation |
|-----------------------------|----------------|--------------------|
| <b>50 ml/min</b>            |                |                    |
| 1. endotherm peak           | 15.87°C        |                    |
| 1.peak range                | 5.00-24.47°C   |                    |
| 2. endotherm peak           | 45.04°C        |                    |
| 2.peak range                | 31.02-57.64 °C |                    |
| Heat of transition, 2. peak | 3.39 W°C/g     | 0.120 W°C/g        |
| <b>87 ml/min</b>            |                |                    |
| 1. endotherm peak           | 12.15°C        |                    |
| 1.peak range                | 5.00-21.19 °C  |                    |
| 2. endotherm peak           | 44.29°C        | 1.304°C            |
| 2.peak range                | 30.11-56.40°C  | 0.88°C             |
| Heat of transition, 2. peak | 3.18 W°C/g     | 0.188 W°C/g        |

it is assumed that two measurements of the sample are independent. However, it does give a useful hint of the conformity between runs. Especially for the heat of transitions since these are so much alike.

**1. endotherm peak** The average peak position is somewhat tentative, if taking into account their variable size and shape <sup>7</sup>. However, the dynamics are still somewhat faster for pump volume 87 ml/min than 50 ml/min. The standard deviations are not included because of the irregular sizes of these peaks.

**2. endotherm peak** The peaks seem homogeneous in size and shape, which is verified by determining the average peak positions. It is roughly 1°C between the two peaks, but the standard deviation with pump volume 87 ml/min is of the same scale, thus a difference in the dynamics can not be confirmed. The *heat of transition* show a large degree of conformity, for both pump volumes, confirmed by relatively small standard deviations.

When comparing the temperature range for each of the transitions for both pump rates, and taking the inherent uncertainty into account, the variations are not large. Thus when presenting the over all results the outer most limits of each range is used.

**Slope of the interpolated baseline and measured curve** When looking at Figure 4.14 and 4.15, which have an absolute scale, it is obvious that the runs on different samples have got different overall slope of the measured curve. This gives information on  $C_P$  changes and is interpreted to give indications on the rate of diffusion from mesopores. Since the slope varies it is assumed that the mesoporosity of the samples vary. Two runs of the same sample more often than not have the same slope, meaning the mesoporosity is defined for each sample. A sample contains Na-FH powder randomly distributed over the entire area of the crucible, and the mesoporosity could be dependent on the total surface area and general distribution of crystalline stacks of nano-layers. It would cause variations in the diffusion and affect the overall energy consumption in the sample. Also, since the measured curve, including the interpolated baseline, changes throughout the whole dehydration process, no distinction for temperatures where only intercalated water evaporate, can be made.

The average dynamics for each pump volume is plotted in Figure 4.16, where the differences in peak position, and general behaviour, are clearly shown. The largest uncertainties are here associated with the overall baseline slope and size of the first endotherm. With basis in the method described in Section 3.1.2, proportions of an appurtenant weight loss curve is shown in Figure 4.17 <sup>8</sup> But to determine the exact weight loss a temperature dependent conversion factor needs to be constructed using the TGA.

<sup>7</sup>Run 2 in Figure 4.14 is omitted because of its extraordinary shape.

<sup>8</sup>Illustrated with run 3 in Figure 4.15.

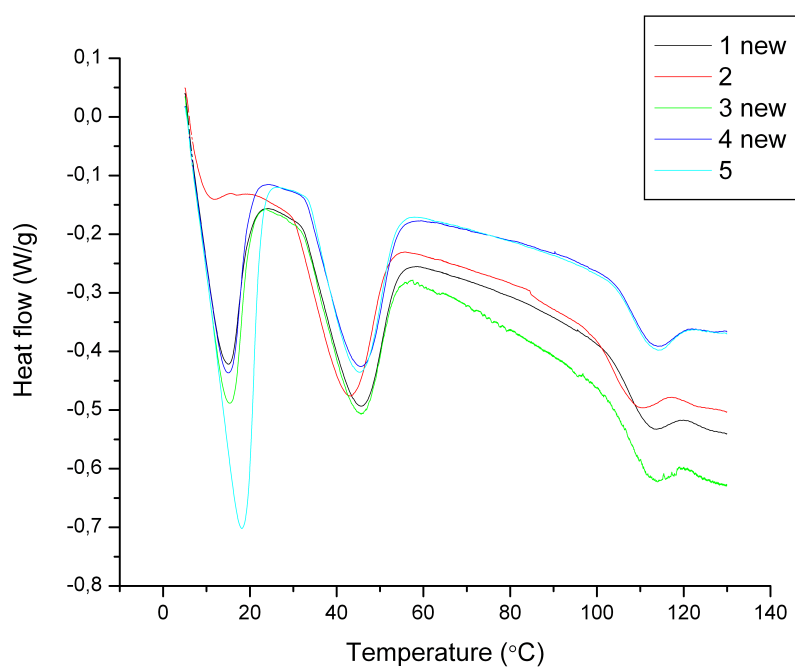


Figure 4.14: Corrected heat flow for dehydration of Na-FH with heating rate 2°C/min and pump volume 87ml/min.

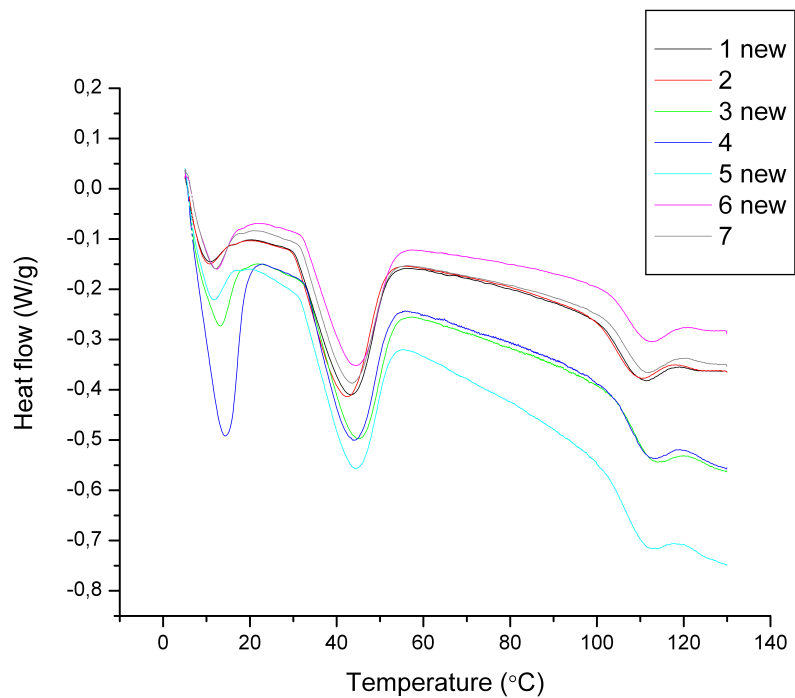


Figure 4.15: Corrected heat flow for dehydration of Na-FH with heating rate 2°C/min and pump volume 87ml/min.



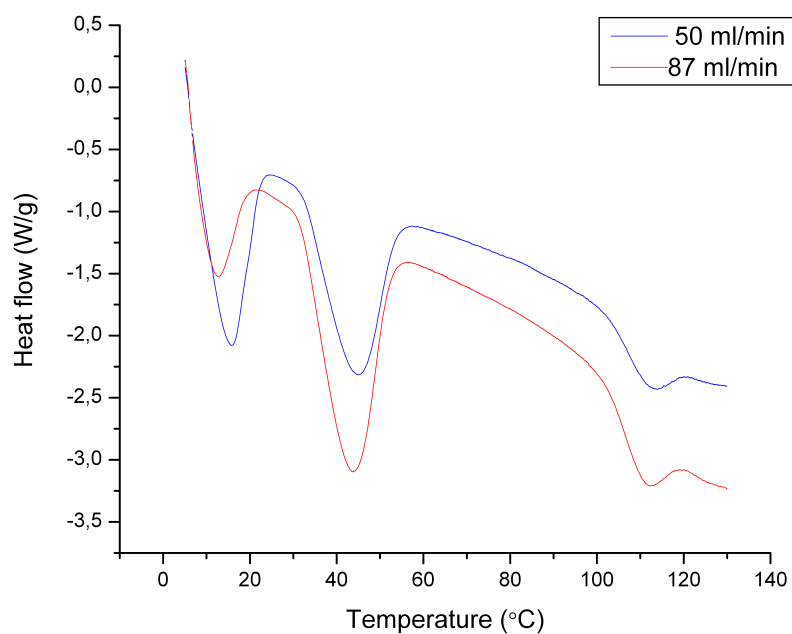


Figure 4.16: Average heat flow for the dynamics of Na-FH at heat rate 2°C/min.

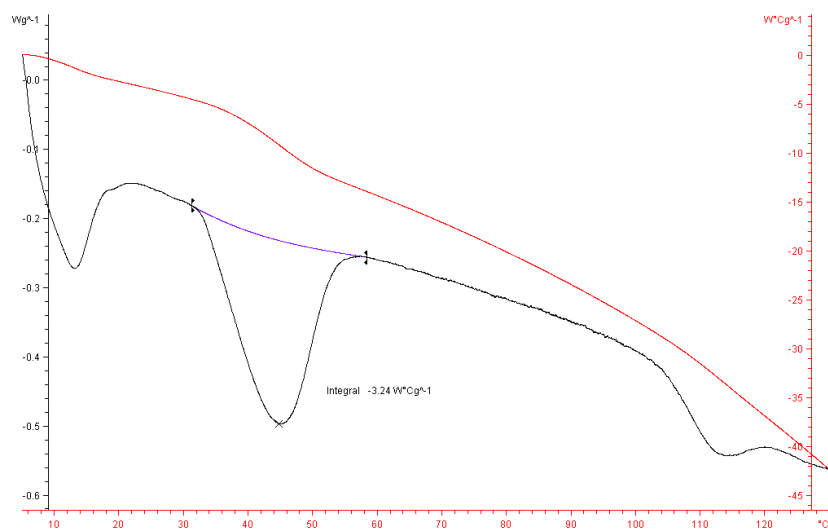


Figure 4.17: Heat flow curve with interpolated baselines, and an appurtenant calculated weight loss curve plotted in red.

### 4.3.2 Other heating rates

For comparison heat flow curves have been measured with heating rates  $0.5^{\circ}\text{C}/\text{min}$  and  $10^{\circ}\text{C}/\text{min}$ . But in these instances not enough parallels have been recorded to draw any final conclusions about the kinetics, and the curves are less homogeneous of some reason. The nitrogen flow is the same and the pump volume is held at  $87\text{ ml}/\text{min}$ . All other steps in the temperature program is the same as for other measurements, except point 2 (see Section 3.2.2).

Generally one expects a temperature shift of the peak placement, as by shifting the heating rate from 10 to  $0.5^{\circ}\text{C}/\text{min}$  a shift of up to  $100^{\circ}\text{C}$  is observed for other clay minerals [33]<sup>9</sup>. However, each clay has a characteristic shaped heat flow curve that can be used for identification. But the obtained curves differ significantly from the relatively homogeneous heat flow curves at heating rate  $2^{\circ}\text{C}/\text{min}$ , thus possible causes and an interpretation is stated. But generally these qualitative results can be emphasized as cause for further investigations during my continued work next semester.

#### Heating rate $0.5^{\circ}\text{C}/\text{min}$

Two parallels with different samples are shown in Figure 4.18, where the signal is significantly smeared in the peak areas<sup>10</sup>. Three apparent causes can be stated.

- Sensitivity of the DSC is low on the expense of increased resolution, making high levels of noise evident in the signal. But why then is the signal outside the peak areas not smeared?
- Low sample size give a limited signal to the DSC, as the total reaction time is significantly increased and increasing the mass may give better measurements.
- The smearing is caused by real nuances in the dehydration reaction not seen when the heating rate is higher.

The heat flow curves now have three main minima. During the first of them the curve is smooth, but the two others are rough. As the last extensive shoulder is assumed to be caused by evaporation from mesopores, it could be that heat flow from larger pores give a smoother signal, than the transitions between hydration states. But the first smooth peak shows evidence of being a perfect first-order transition, and should therefore represent a transition between water layer states. If it represents the 2WL-1WL transition, the two rough peaks must be caused by the 1WL-0WL transition. But as this was the most stable part of the heat flow curve during heating at  $2^{\circ}\text{C}/\text{min}$  it seems unlikely that the behaviour should change this drastically when lowering the heating rate. Thus it seems probable that the rough curve is caused by limited sensitivity, but for any final conclusions to be drawn further parallel measurements need to be made.

#### Heating rate $10^{\circ}\text{C}/\text{min}$

When heating the Na-FH sample at a rate of  $10^{\circ}\text{C}/\text{min}$  the heat flow curves, presented in Figure 4.19, do not show a great level of conformity. Run 2,3 and 4 can be related to the results found at heating rate  $2^{\circ}\text{C}/\text{min}$ . The second peak then representing the transition from the 1WL state to 0WL, centered at about  $57^{\circ}\text{C}$ . The shoulder between the first and second peak is non-existent, likely because the system do not have time to establish an equilibrium state. The first peak has varying size, as it does in the earlier data. And the last shoulder is caused by evaporation from mesopores. But these assumptions are contradicted by the three other runs made under the same conditions. Here the two first peaks are combined to one, and the second half of the curves are dominated by a number of irregular peaks. It can be assumed that the latter results are caused by unfortunate variations in the given parameters, as humidity or pump volume. Thus, also in this instance the only conclusion to be drawn is that more parallels of the outlined experiment need to be run to confirm the heat flow curve at heating rate  $10^{\circ}\text{C}/\text{min}$ .

<sup>9</sup>For measurements made on a larger temperature interval than currently.

<sup>10</sup>The curves are not corrected for baseline, due to lack of time

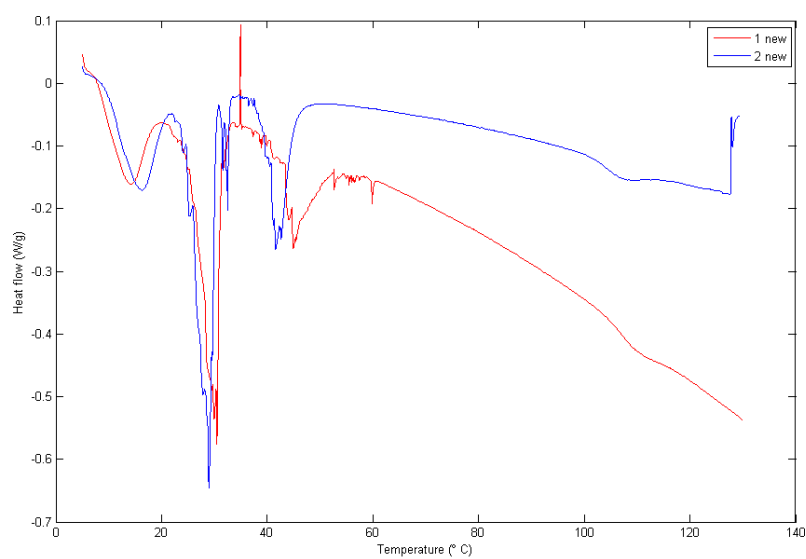


Figure 4.18: Heat flow curve at heating rate 0.5°C/min and pump volume 87 ml/min.

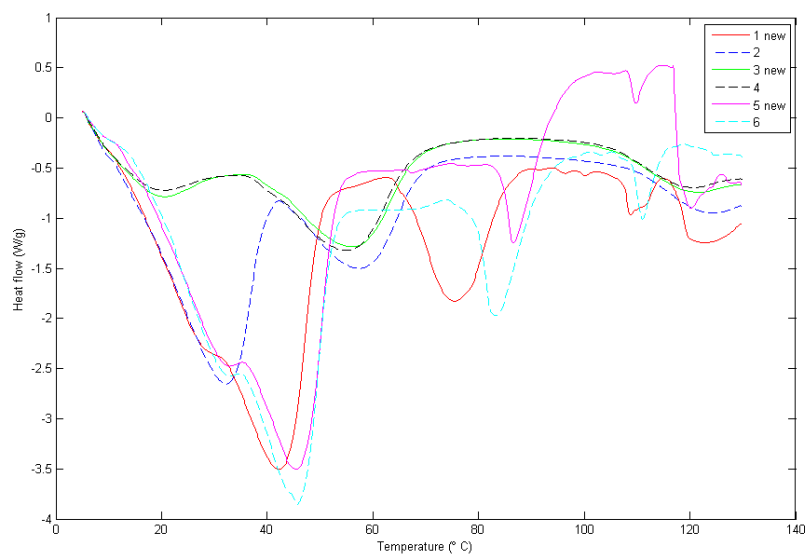


Figure 4.19: Heat flow curve at heating rate 0.5°C/min and pump volume 87 ml/min.

## 4.4 Discussion

To perform thermal analysis on a clay samples involves many inherent problems. Mainly, there is no simple way to ensure the rapid and complete removal of of vapor during the dehydration process. To exploit the DSC for the purpose of investigating clay it is best to use the results in a comparative manner, rather than in an absolute sense [24]. Thus, previous research done on minerals similar to Na-FH mostly use heat flow curves from a DSC for comparison and enhancement of TGA weight loss curves. The heat flow curves may determine temperature intervals where transitions take place, and to help calculate percent of total weight loss during the different transition peaks [18, 20, 34, 35, 36, 37]<sup>11</sup>. But use of heat flow curves when characterising clay is a useful and often used method for this specific purpose, though often for a larger temperature interval than used for these measurements. Determination of the correct rate law or the activation energy is described by R.F. Giese [24], but the more quantitatively correct weight loss curves from the TGA seems better for the purpose of quantifying the kinetics of a clay sample [20], as outlined in Section 4.1.3. Thus the achieved results from the experiments this semester are mostly used for qualitative and comparative analysis. The final objective for the project is to compare results from parallel measurements made with three different techniques: DSC, TGA and X-ray scattering, to look at different aspects of the dynamics of water in Na-FH. Because of instrumental problems no measurements are made on the TGA, but are planned along with X-ray scattering experiments during spring 2007. The planned measurements are necessary to ensure that all parameters and conditions are identical, and then reduce the presence of error sources when comparing the results.

### Method

Details of the sample and method may effect the achieved quality of measurements.

When comparing TGA and DSC curves of clay it is desirable that the samples are close to identical. However, for good measurements on a TGA it is best if the sample is distributed over the whole area of the crucible. But heat flow is detected best if the sample is gathered in a pile directly above the position of the temperature sensor. At all the current experiments the Na-FH sample is equally distributed in the crucible, which **could** have affected the time response of the sample in the DSC[33].

Kinetics of clay is slow, making it desirable to examine it during slow heating. However, the sensitivity of a DSC is generally inversely related to the resolution. Therefore it could be that the best overall results are not achieved at the slowest possible heating rate [33]. The samples used here have a low initial weight which means that the heat flow signal is small during such a temperature program. Thus, maybe the overall results at slow heating rates would improve if the sample weight was increased. This may give increased surface effects, and variations in packing but could be attempted. DSC (or DTA) is during dynamic experiments on clay samples mostly used at higher heating rates, 10 or 20°C/min [20, 34, 35, 37]. There are also examples on research done with low heating rates [36], but nothing on heating rates below 2°C/min. Another example is made by [18, 38], which have both done experiments using heating rate 2°C/min, but the sample size is then about 40 mg.

Thus, further checks of the expected sensitivity of the DSC822<sup>e</sup> at low heating rates may be necessary as part of later research, based on litterature and the smeared signal found when attempting to use the heating rate 0.5°C.

### Interpretation

A DSC is generally able to detect two kind of reactions in a sample, changes in the specific heat  $C_p$  and first-order transitions (see Section 3.1.2). In this respect a DSC suitable for this kind of sample as transitions between 0WL, 1WL and 2WL hydration states are of first-order [18]. Thus interpretation of the peaks is relatively unambiguous. Continuous changes of  $C_p$  as a consequence of changing slope of the measured curve interpreted as diffusion and evaporation from mesopores, can be expected, as the interacting forces are changing throughout this process.

<sup>11</sup>For thermal analysis, heat flow curves are often detected using other techniques than DSC, ex. DTA, a similar technique, where the sample temperature is not readjusted when transitional peaks occur [8], or simply SDTA signals.

The 1. endotherm peak has varying area and peak placement, which may mainly indicate two phenomena: Either water molecules constituting the second water layer are held relatively loosely within the interlayer [17]. Or the 2WL state is not complete by the start of measurements, despite checking the ability of clay to reach the 2WL state in ambient humidity, see Section 4.1.1. The difference seen in the established equilibrium state while at 5° can be caused by an incomplete 2WL state, or different mesoporosity and surface effects, as is assumed to cause the varying slope of the measured curve. Stable area of the 2. endotherm peak indicates a well defined heat of transition, thus the adsorbed water molecules constituting the 1WL state give a thermally stable state.

Because of the irregular results when detecting the heat flow curve below 20°C it is necessary with further measurements in this temperature interval.

### Accordance with other experiments

Currently only a comparison with earlier experiments, that are similar but not identical, is possible. It is included to show the possibilities when combining techniques.

Slow dehydration of Na-FH powder, as a function of temperature, on the TGA [32] show a weight loss of ~ 7 % that occurs mainly in the temperature range 25-60°C<sup>12</sup>. My achieved results indicate that the first-order transition 1WL-0WL occur in the temperature interval 30-57°C, which shows a good accordance with previous work.

Figure 4.17 presents the proportions of a weight loss curve, generated by an integral of a heat flow curve. compared to previous results on the TGA [32, 31] the curve seems too steep. In the upper temperature range, where water is lost only by mesopores, TGA curves are relatively flat in comparison. But this is maybe corrected when using the necessary conversion factor, as described in Section 3.1.2.

Hydration transitions observed with x-ray scattering in a dried and pressed sample of Na-FH [15] find that to some degree the 1WL state is observed for the entire temperature range, but a significant volume of the sample is in this state only between 25 and 40°C. I observe a peak in the 1WL-0WL transition at ~45°, which means that most of the sample has by then transferred to the 0WL state, but still a degree of mixed intercalation is expected at least until the base of the peak, at about 57°C. Taking into account that the samples are prepared differently, these experiments also show a degree of conformity.

### Instrumental challenges

Both the DSC and TGA are routinely used for thermal analysis, but their internal properties offer problems, and adaptations to the current use raise some challenges of its own. The discussion is focused on use of the DSC, because main the main work load during this project has been on use this instrument. Also included are some challenges which might arise when the current method needs to be implemented on the TGA.

- Neither the DSC or the TGA are air tight. No pressure builds at the gas outlet, even if nitrogen and air escapes together, at both instruments. Hopefully the path leading to the sample is tight, and the gas diffuses afterwards making the experimental conditions best possible. Due to special construction of the sample chamber it is not possible to probe the conditions with any available equipment at either machines. Which means that any reference measurements made before air enters the system will represent the ideal case and if measured afterwards will give an indication of how much water is lost by the sample, and elsewhere in the system.
- The relative humidity of air at room temperature is different than at high, or low, temperatures. Air pumped through the system is heated to the current sample temperature before entering the sample chamber, and again, because it is not possible to probe the current conditions, it is not possible to detail the absolute conditions at a given time, and impossible to assume constant humidity. A presentation of the theoretical development of this problem is given in Section 4.4.3

<sup>12</sup>The measurements start at 25°C, and therefore do not include the 2WL-1WL transition.

- The gas paths are different in the two instruments, giving unequal conditions. In the TGA nitrogen passes through the sample chamber, affecting the weight loss, as shown in Figure 4.7. But in the DSC, nitrogen passes outside the sample chamber, for the purpose of preventing condensation. The gases join first after the air has passed through the sample chamber.
- During dynamical experiments the air temperature needs to keep up with temperature changes in the sample. As the heating rate increases this can present a source for error, as one wants to keep the surface temperature equal to the sample temperature being measured underneath the crucible.
- Temperature response of the sample when abruptly changing the temperature is good, for measurements with the DSC, see Section 4.4.1. However, earlier experiments on the TGA show that the balance is affected by abrupt temperature changes, thus making corrections necessary [32, 31].

Constant, controlled humidity is assumed during these measurements, but details on how the system for humidity control can cause instability in RH is discussed in Section 4.4.2. How influx air can cause a temperature gradient in the surrounding air during dynamic experiments, is discussed in Section 4.4.1. As the object is to investigate the kinetics at given conditions, these concerns make it difficult detail the actual conditions used, and further the effect it may have on the sample. But when using identical conditions for each run, the measurements are at least comparable.

#### 4.4.1 Thermal properties

As the main object of a DSC is to keep two crucibles at the same temperature, it is important to minimize any form for heat loss during measurements.

**Sample chamber** To optimize conditions the sample chamber should be air tight and loose an minimal amount of heat. The latter feature is hopefully improved by inserting a thin rubber O-ring, which in itself should not contribute to much extra heat loss as the is not sensitive to temperatures in the low interval being used presently. The samples are heated from underneath and looking at the temperature difference at all times seems small. An average temperature difference  $\Delta T_{rs}$  between the sample and reference is found when taking an average during an entire run. An average  $\Delta T_{rs}$  for each of the two series are shown in Table 4.4.

Table 4.4: Average offset temperature for each series.

| Pump volume | Offset temperature $\Delta T$<br>°C |
|-------------|-------------------------------------|
| 50 ml/min   | $0.0136 \pm 0.0029$                 |
| 87 ml/min   | $0.0091 \pm 0.0049$                 |

For each run the differences are relatively small, and even though the offset is somewhat higher for the runs with pump volume 50 ml/min this could be entirely random. More important is the response time of the sample to sudden changes in the temperature, for example when it changes from isotherm to a dynamical heat rate. Examination of the temperatures show an almost perfect fit, as plotted in Figure 4.20. Data are collected each second, and the result are two linear temperature developments with a transition from isothermal conditions at 5°C to a heat rate 2°C/min.

Air is supplied to the system at a steady rate. But when the sample temperature is changing fast it may be hard for the DSC to heat air at the same rate. It may result in a temperature gradient in the surrounding atmosphere, therefore affecting the sample. Also, limit the air volume to below 100 ml/min, as the DSC has a limited capacity for heating the reactive gas.

**Crucible** Standard aluminium crucibles from Mettler Toledo are used, which are prepared by machine and thus all identical. The base is strong and flat providing an excellent thermal contact between crucible and sensor, with low temperature gradients [39]. These should not give any large added deviations for the measurements, and powder is relatively easy form of solid material to use as samples as it usually

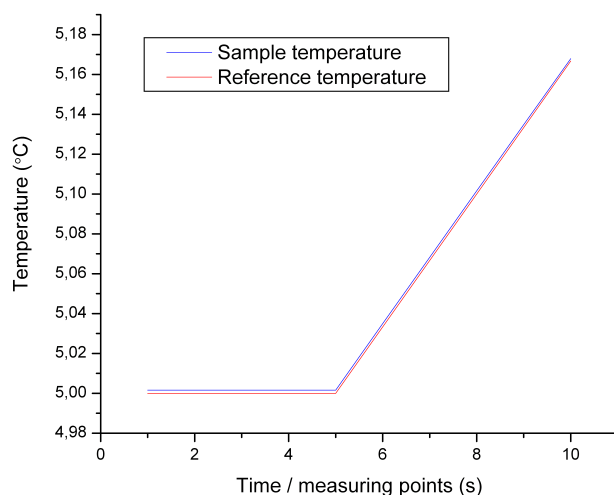


Figure 4.20: Both reference and sample temperature plotted for the transition from isotherm to heat rate 2°C.

have good thermal contact with the crucibles. But they do have a wide rim, which hopefully do not provide room for too much condensated water. From this supplier no better alternative was found.

#### 4.4.2 Humidity control

To improve the air tightness of the system two main initiatives are made. When first implemented, measurements were done and the system seemed satisfactory. However, in time it was discovered that the humidity sensor needed a calibration, thus the collected data are not reliable, and thus not included as a part of the presented results. Because of the time consuming calibration process only reference measurements are made at the end of the project period. For further measurements, a LabVIEW program for monitoring measurements is available, thanks to Henrik Hemmen. Thus one focus for further work is to map the humidity during the dehydration process. Because of the lack of data a discussion on the benefit of the improved system is somewhat hard to undertake but some points are worth mentioning.

When performing the current measurements a main point has been to keep the conditions equal for each run, thus at this point at least the data are comparable.

It is specified that the system for purging the DSC is not air tight. However, it does not say if the air leaks before or after passing through the sample cell. Construction of the sample cell makes it difficult to measure the current relative humidity with the available equipment. A task for further work could be to find a solution to this problem.

In comparison to the original DSC an O-ring has been put between the main sample cell and its lid, to minimize air lost at this junction. In addition the instrument is now placed in a sealable plastic bag with silica gel and a slight overpressure, thanks to a peristaltic pump. This should improve the overall performance, but unfortunately no reliable data can back this up yet, and may be object to further improvements as further work is done.

#### 4.4.3 Relative humidity versus temperature

The relative humidity  $RH$  is given by Eq. 2.4 and thus dependent upon how two parameters varies with temperature.

**Actual vapor pressure** The variable is simply a measurement of the present water vapor pressure.

But if the temperature increases and the available volume  $V$  is constant for a fixed number  $N$  of water molecules, their kinetic energy will increase and give an increased pressure  $P$ , following the ideal gas law.

$$P \cdot V = NkT \quad (4.3)$$

where  $k$  is the Boltzman constant. The relation assumes that all molecules are point particles which interacts through elastic collisions. This is of course an simplification, but for dilute gases used for experimental purposes it is often a good enough approach [40]<sup>13</sup>. For a mixed gas, as air, one must further presume that at all temperatures the partial pressures may be added.

**Saturated vapor pressure** Air at thermal equilibrium can amount to a certain total pressure. There are several approaches to determine the saturated vapor pressure, but all equations give only approximated values. One, which is accepted as a good estimate for low-pressure conditions is the Goff-Gratch equation<sup>14</sup> [21]. In addition the pressure will vary with your current altitude above sea level. Calculations show that the temperature dependent development of the saturated vapor pressure is close to exponential for temperatures below 130°C.

#### Temperature dependent variation of $RH$

If the air is heated after the relative humidity is measured,  $RH$  will change during the experiment. The development may be estimated by assuming a constant volume  $V$  and number of particles  $N$ . The initial temperature  $T_i$  and pressure<sup>15</sup>  $P_i$  are used to determine the volume fraction by Eq. 4.3

$$\frac{V}{Nk} = \frac{T_i}{P_i} \quad (4.4)$$

When the gas properties change to  $T_f$  and  $P_f$  the current relative humidity is then estimated by using

$$RH = \frac{P_f}{SVP_f} = \frac{Nk/V \cdot T_f}{SVP_f} = \frac{P_i \cdot T_f}{SVP_f \cdot T_i} \quad (4.5)$$

where  $SVP_f$  is the saturated vapor pressure at the final temperature, which may be found in a suitable table.

As an example the development of  $RH$  is plotted in Figure 4.21 with the initial conditions  $T_i = 21^\circ\text{C}$  and  $RH = 5\%$ . A table of values for the estimated saturated vapor pressure is found by using an online calculator [30]. The curve has a maximum at  $T=16^\circ\text{C}$ , which turns out to be valid for all initial relative humidities. And for high temperatures  $RH$  approaches zero.

#### Validity for the current experiment

When trying to achieve dry air for the dehydration process silica gel is used, and the relative humidity is measured before the air enters the machine, or alternatively when it exits but then mixed with nitrogen. Before air enters the sample chamber it is heated, or cooled, approximately to the current sample temperature. This could lead to a change in the relative humidity on the form depicted in Figure 4.21. But the calculations assume a constant volume, which is not true for air that enters the sample chamber. By looking at Eq. 4.3 it is evident that an increased volume will lift the estimate to higher  $RH$ . With the current available equipment it is not possible to measure  $RH$  inside the DSC sample cell, but at least it is possible to say that the relatively constant  $RH$  measured before heating is not conserved throughout the experiment. It gives an added element of uncertainty, because the equilibrium of the Na-FH sample at any temperature is dependent on the current relative humidity, and thus the clay dynamics may be affected.

<sup>13</sup>If the properties of an atom can not be neglected one may use *van der Waals equation of state* which is a modification of Eq. 4.3 [40].

<sup>14</sup>Several approximation methods exist, dependent on the necessary temperature interval.

<sup>15</sup> $P_i$  is found by using Eq. 2.4 and the initial saturated vapor pressure.



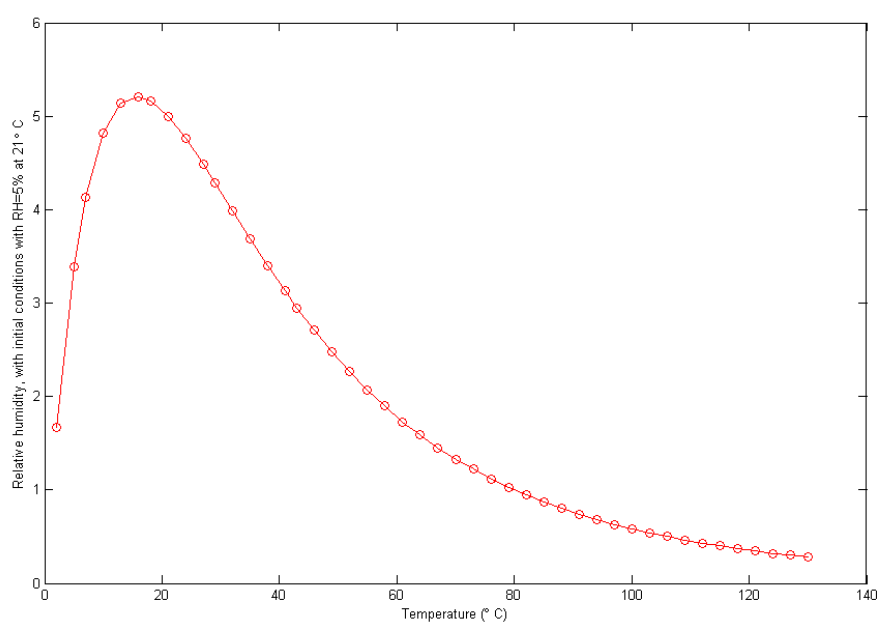


Figure 4.21: Theoretical temperature-dependent development of the relative humidity, with initial conditions  $RH = 5\%$  at  $T_i = 21^\circ\text{C}$  .

## Chapter 5

# Concluding remarks

Macroscopic properties of clay samples are here investigated by means of thermal analysis using TGA and DSC. For an even more complete picture of its behaviour these techniques may with advantage be combined with structural observations, made by x-ray scattering. The over all goal is to make parallel measurements using all the three experimental methods, but this report focuses on heat flow curves detected by a DSC, and instrumental challenges arising when trying to adapt the instrument to our current needs.

Heat flow curves are routinely used to characterise the dynamic behaviour of clay as a function of temperature, and under controlled humidity, by determining the temperature ranges for first order transitions and observing changes in the specific heat. Dehydration of the synthetic, layered silicate Na-FH at a rate  $2^{\circ}\text{C}/\text{min}$  reveal two distinct transitions between the 2-, 1- and 0- water layer hydration states, in the intervals  $5\text{-}24^{\circ}\text{C}$  and  $30\text{-}57^{\circ}$  respectively. The first transition has a variable heat of transition, making further investigations into the lowest temperature range necessary. But the second peak is stable, indicating a well defined transition and diffusion rate. Multi scale distribution of pores in smectites, is detected by a constant increase in the specific heat, indicating evaporation from mesopores. But the dynamics are also dependent on volume of the air purge and heating rate, which are both further investigated.

Heating rate  $0.5^{\circ}\text{C}/\text{min}$  yields a smeared curve, but further measurements are needed to confirm the cause, which could be limited sensitivity of the DSC or inherent properties of the sample. Also measurements at  $10^{\circ}\text{C}/\text{min}$  give data which are hard to explain at the present time, and more runs should be made at the same conditions to confirm the shape of the heat flow curve.

It was discovered that the humidity probes were decalibrated, and thus a time-consuming calibration process using constant humidity solutions was deemed necessary. Therefore, no reliable measurements of the relative humidity during measurements are available. Comparability between individual runs are ensured by always implementing the same conditions. But nevertheless, if these data had been collected too it would be easier to determine if the assumptions are correct.

All the experiments assume constant, controlled relative humidity (RH). But the system is not air tight and the nature of humidity makes RH temperature dependent. Discussions on these features are included, along with other properties of the DSC.

The TGA has been out of order most of the project period. Consequences of the unfortunate series of incidents, the necessary repairs and adjustments are described in Appendix D. Outline of a planned project to investigate the reaction mechanisms during dehydration on an atomic level is included in Section 4.1.3. And an essential part of upcoming work on the TGA is to perform parallel experiments to those implemented on the DSC.

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# Appendix A

## DSC822<sup>e</sup> specifications

Specifications for DSC822<sup>e</sup> from Mettler Toledo [7].

- Heat flux Differential Scanning Calorimeter.
- 200 W furnace with a temperature range from RT to 500°C.
- Measuring cell with ceramic sensor, time constant  $\tau = 3$  s.
- Gold/paladium thermocouples, resolution  $\prec 4 \mu\text{W}$ .
- A built-in fan cools the instrument as far as room temperature (RT).
- Additional cooling by a Haake DC10-K10 Refridgerated Circulator Bath, with a range down to -10°C.
- Leaves a possibility to regulate the influx of air into the sample chamber, but system is not air tight.
- Use of protective gas N<sub>2</sub> is recommended for measurements below room temperature.

### A.1 Calibration

For calibration, a range of pure materials with known heat of melting is used. By a method called peak area calibration the consumed heat  $Q$  is measured and compared to the known heat requirement for this specific material. For the DSC822<sup>e</sup> automatic evaluation programs are made for indium and zinc. These materials are chosen to be able to cover a large temperature range, and thus check the linearity of the instrument. Defined tolerance limits for both materials are given in table A.1.

Predefined calibration is done on three different levels. First, check the current parameters. Second, if they need to be adjusted a total calibration may be accomplished using both materials. But generally it is more successful and less time consuming to implement individual indium and zinc checks. Finally, please check the parameters again. If they are not within the tolerance limits then please repeat the calibration until successful.

Details on the procedure, for future users of the instruments, are explained below.

Table A.1: Tolerance limits for calibration of the DSC822<sup>e</sup>, defined by Mettler Toledo [7].

| Material | Onset temperature<br>$^{\circ}\text{C}$ | Heat flow<br>$\text{J/g}$ |
|----------|-----------------------------------------|---------------------------|
| Indium   | $156.6 \pm 0.3$                         | $28.45 \pm 0.6$           |
| Zinc     | $419.6 \pm 0.7$                         | $107.5 \pm 3.2$           |

## Check

First, a routine check of the current parameters is necessary. It is done individually for the two materials, to check if the parameters fit for both temperature intervals. Normally melting is an exotherm reaction, but four different methods are given, 'Check DSC<sup>endo</sup> In' and 'Check DSC<sup>endo</sup> Zn' should be used when the curve has a maximum upon melting. Differently, 'Check DSC<sup>exo</sup> In' and 'Check DSC<sup>exo</sup> Zn' are used when observing a minimum. The check is automatically evaluated when finished, giving the two options 'The DSC module is within specifications!' or 'Please calibrate the DSC module to get it within specifications.' To have the check approved both the  $\Delta H$  ('normalized') and the temperature must be within specifications. Please continue your work according to the evaluation.

## Total calibration

As a first attempt at calibration this method will try to calibrate all the necessary parameters, temperature, tau lag and heat flow at the same time, based on melting of both indium and zinc. The crucible should be prepared with a piece of indium, and a piece of zinc wrapped in aluminium - use a lid. But the results are often achieved faster and are more accurate just using a manual calibration.

## Manual calibration

When a check is not within specifications, either  $\Delta H$ , the temperature or both can be in need of calibration. To calibrate the heat flow individually use 'Calib DSC Heat Flow Single...In' and 'Calib DSC Heat Flow Single...Zn'. Make a measurement or two with both materials. Then access the menu 'Calib/Adjust' and choose 'Single Heatflow'. Your results should then be automatically stated for each of the measurements, if you change the label 'Position'. If the results are accepted a new value for 'E Indium' will be calculated, and implemented if you deem the result good and save it. Run a new check for both materials and see if you are now within specifications. The same may be done to change the temperature parameters, but then access the menu 'Calib/Adjust' and choose 'Single Temp...'. Here it is also mandatory to specify type of crucible and influx air.

## A.2 Miscellaneous

- $\Delta H$  is supposed to be stated with a minus when using the methods 'Check DSC<sup>endo</sup> In(Zn)'
- A properly prepared calibration crucible and the reference crucibles may with advantage be used for multiple measurements, as the temperature gradient in the metals is more even after initial use.
- If the pan includes more than one material make sure they do not touch. If they do a low melting eutectic will form at the wrong temperature, and give false results.
- A self-defined method can only consist of 10 parts, isothermal or dynamic. If more are necessary it is possible to start the next method automatically without disturbance of the sample defining the end behaviour to 'Standby temperature'. It is done while the experiment is still pending, by accessing the 'Edit experiment' menu.
- Material for calibration may be bought via Mettler Toledo, from Impag in Switzerland. Please contact one of their salespersons, ex

Stein Erik Rognan  
steinerik.rognan@mt.com  
via switchboard ph. 223 04 490

- For questions concerning the calibration or operation of the instrument itself please contact:

Service engineer  
Kai Rune Ringen  
kai.ringen@mt.com  
ph. 922 35 607

## Appendix B

# Method for signal conversion: TGA to DSC

Via the SDTA signal found using the TGA a heat flow curve comparable to the measurements made with a DSC is found, as discussed in Section 3.1.2. The method for signal conversion is presented below, based on [26, 5], and further examples of application are found within these articles.

To determine the calibration curve melting point standards were used. To cover the entire temperature range up to 1600°C for example high purity samples of the metals presented in Table B.1 can be used. For low temperature samples aluminium crucibles are suitable but at higher temperatures platinum crucibles should be utilised. In the latter case it is also useful to spread alumina powder uniformly in the bottom of the crucible to avoid reactions between the melting point standard and the crucible.

Table B.1: Characteristics for materials used as melting point standards.

| Substance | Melting point<br>°C | Heat of fusion<br>$\Delta H_{lit}/\text{J g}^{-1}$ |
|-----------|---------------------|----------------------------------------------------|
| Indium    | 156.6               | 28.5                                               |
| Zinc      | 419.5               | 107.5                                              |
| Aluminium | 660.3               | 397.0                                              |
| Gold      | 1064.2              | 63.7                                               |

After collecting a SDTA curve for the melting point standards the calorimetric sensitivity is determined by comparing the the measured SDTA peak area,  $F_{peak}$ , with the theoretical heat of fusion,  $\Delta H_{Lit}$ , here presented in Table B.1. The corresponding calibration factor is calculated using the following equation.

$$K = \frac{m_0 \cdot \Delta H_{Lit}}{F_{peak}} \quad (\text{B.1})$$

Results for calculation of a calibration factor  $K$  are shown in Figure B.1. The upper curve consists of melting curves for four different melting point standards, Indium, Zinc, Aluminium and Gold, taken at a rate of 15 K/min. Several measurements were made for each material, and used for calculation of the calibration curve shown as the lower curve in Figure B.1, with the unit mW/°C. It is fitted using a quadratic polynomial, and a direct conversion from the SDTA signal into a heat flow curve is achieved by multiplication.

In the work done by Riesen et al. a variety of measurements are made to determine if parameters other than temperature influence the calibration factor  $K$ , and their conclusions are presented below.

- Changing the furnace atmosphere from air or nitrogen to helium resulted in decrease in the calorimetric sensitivity by a factor of 3, caused by helium having a better thermal conductivity. (Measured at 156°C.)

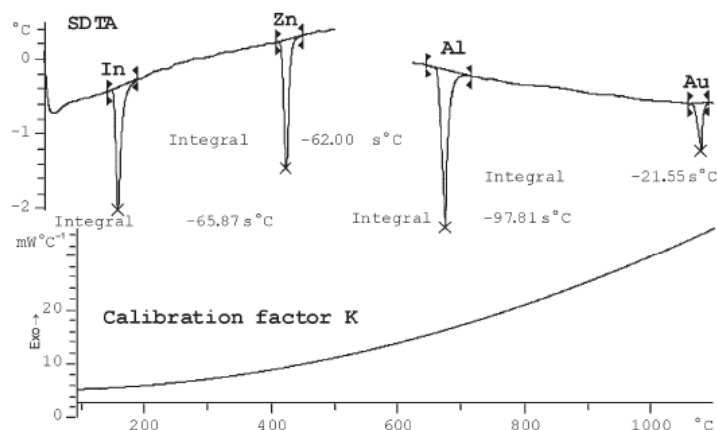


Figure B.1: SDTA melting curves for four melting point standards. The lower curve shows the calculated calibration factor  $K$ . [5]

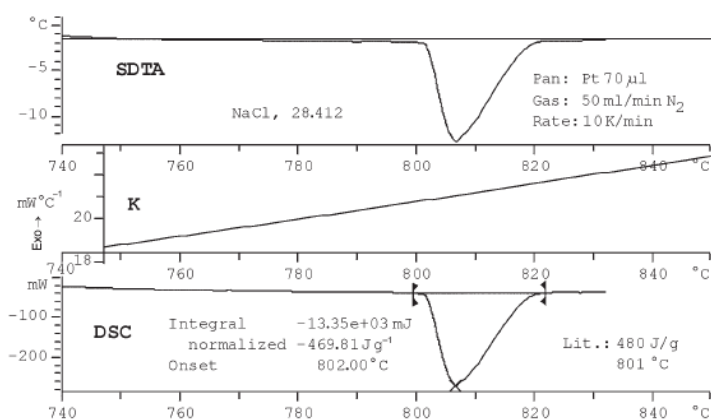


Figure B.2: Illustration of conversion of SDTA signal to DSC heat flow curve via a calibration factor  $K$ , for measurements of sodium chloride. [5]

- The type of crucible had only a minor effect on  $K$ .
- Results for different initial sample mass, from 1 to 30 g Indium, were found to be within the accuracy of the evaluation (position of the baseline for integration).
- Changing the heating rate from 5 to 20 K/min had no influence on  $K$ , as well as changing the nitrogen purge flow rate from 10 to 30 ml/min.



## Appendix C

# Calibration of peristaltic pump



Figure C.1: Setup for calibration of the peristaltic pump.

To determine the air flow through the peristaltic pump a simple setup is used, depicted in Figure C.1, consisting of a plastic container and a ml-measuring cylinder, in addition to flexible tubes and a stopwatch. The measuring cylinder is filled with water and placed upside down in the partly filled container. The end of the tube is placed inside the cylinder and the time necessary to fill a given volume with air is measured, at different rpm. At each rpm three measurements are made, to calculate an average time. Two series are made, one with the clamp over the tube fully closed, and the other with a partly closed clamp. The airflow given in ml/min is calculated by  $V = \frac{V \cdot 60}{t}$  with the results illustrated in Figure C.2.

The measurements show a strictly linear result, with the airflow slightly lower when the clamp fully closed, because the tube is then pressed flat and there is simply less room for air.

The measurements are very simple, but some elements of uncertainty is worth mentioning:

- Human error when using a stopwatch.
- More bubbles the higher airflow, making it difficult to determine the water level.

More small errors could be mentioned, but the results prove to be fairly accurate, with a calculated degree of fit  $R^2 = 0.99$  for a fully clamped tube and  $R^2 = 0.98$  for a partly clamped one.

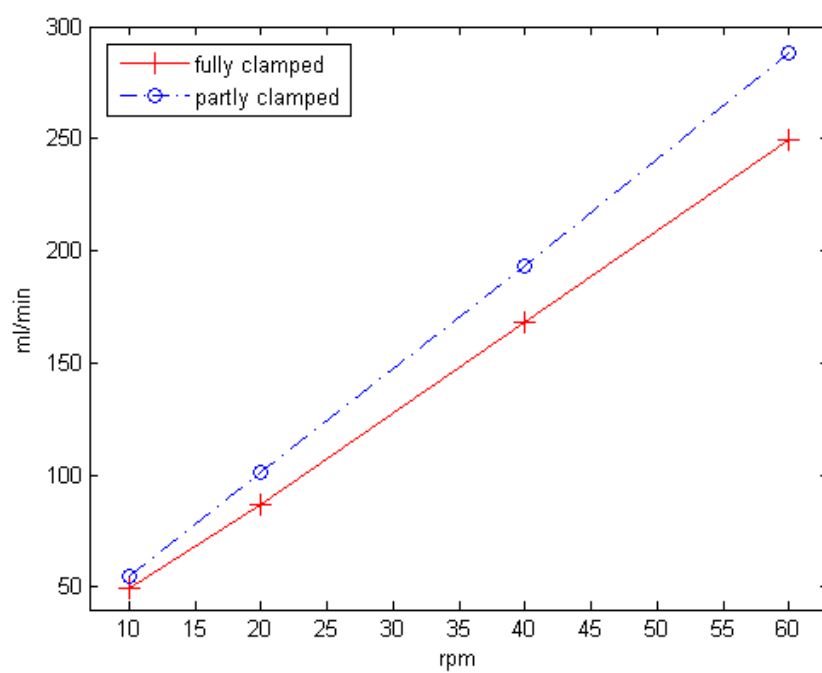


Figure C.2: Airflow through the peristaltic pump.

# Appendix D

## State of the TGA

A number of circumstances have caused the TGA to be out of order for the whole duration of this semester. This section provides a brief overview of the problems, and how a solution was found. Initially, the outward appearance of the dissembled TGA consists of a furnace and a cell, respectively Point 2 and 3 in Figure D.1(a). In addition the figure shows an additional room behind the furnace, where an extra computer terminal and a software cartridge are found.

In July the gas capillary sitting above the balance broke during a manual cleaning of the machine. As I still was not sufficiently familiar with the instrument to recognise the problem immediately, it took some time before a new part was ordered and received. But after installation an unfortunate accident led to an even worse problem, as an aluminium crucible was heated to above 700°C, when its melting point is 660.7°C. The sample holder was thus destroyed, and the actual balance arm needed to be replaced. It was ordered, but as the mounting process involves a risk of perturbing the balance mechanics the supplier Mettler Toledo suggested to fly in service engineer Kai Rune Ringen from Oslo to perform the exchange. However, current financial restrictions prevented his direct participation, but he was helpful when faced with our questions.

After looking at the attachment of the balance arm and any electronics Dr. Ahmed Gmira decided to make the exchange himself. The arm fits into a sensitive holder, closed with a cone, as highlighted as Point 1 in Figure D.1(c), and two wires providing feedback signals from the sample temperature sensor located underneath the sample holder. The wires are connected to the instrument electronics at Point 2 in Figure D.1(b), pressed between two plates by a screw. When replacing the sample arm, these were the two relevant points. At restart of the TGA, the weight itself seemed to be correct, as it gave the correct mass for a reference weight. But an error message reported a lack temperature data from the sample sensor. Thus the TGA cell was opened again to check these connections. But afterwards the instrument refused to restart, as the self-calibration which always takes place at start-up, never finished. (Error message 40) Telephonic contact with service engineer Kai Rune Ringen provided some new input, for example that some additional weights should be suspended on the sample temperature sensor wires to provide a dead weight. But these were never found at replacement of the old arm, and seemed unimportant as the balance was working correctly when first starting the machine.

Technician Ole Tore Buset started looking at the TGA when starting in his position the 1 December, and contact with a local service engineer from Mettler Toledo gave additional expertise. He found that one of the two calibration weights, Point 1 in Figure D.1(b), gave an overload of the system<sup>1</sup>. It took some considerable effort to establish communication with the instrument<sup>2</sup>, enough to make it understand that this weight should be lifted, thus making the TGA able to find its zero weight. This achieved, the TGA still did not work. Disassembling of the furnace revealed that the balance arm was positioned too low. Movement is constricted by a hole between the cell and the furnace, as seen in

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<sup>1</sup>The automatic calibration process at each start-up of the TGA involves lowering these two weights in a series of combinations to check the linearity of the system.

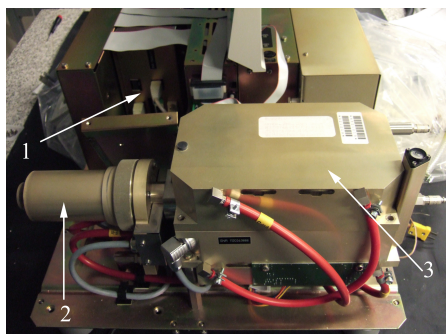
<sup>2</sup>Communication was established after attempting to use an extra service panel plugged in at the backside of the instrument, Point 2 and 4 in Figure D.1(d) respectively, a service software cartridge plugged in at Point 1 in Figure D.1(a) and an old fashioned printer that dated from a time before computers.

Figure D.1(e). Position of the arm may be adjusted by unfastening the two grub screws located below the balance fastening inside the TGA cell, Point 2 in Figure D.1(c). This done, followed by resetting the communication parameters and rebooting the machine, made the TGA able to self-calibrate once more.

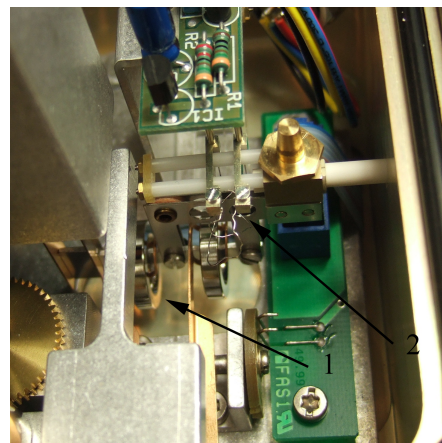
What caused the instrument to malfunction in this last instance is probably a perturbation of the new balance arm when opening the cell. When downwards movement of the arm was constricted by the hole, the self-calibration process was not able to go to completion. And the output error message ended up being “Remove sample pan” as the system perceived an overload on the system, that in reality was caused by the calibration weight. At resolving this problem the original error message when heating the system resurfaced: “Sample temperature is off specified value” (Nr. 40). A check of the recorded data during a test run revealed that the sample temperature  $T_s$  decreased as the furnace temperature increased. After changing the polarity of the two wires from the sample temperature sensor,  $T_s$  is now too high in comparison to the reference temperature. By the present time, this problem still needs to be solved, and in addition the gas capillary is broken again and needs to be replaced.

Other points to take into consideration when performing service on the TGA.

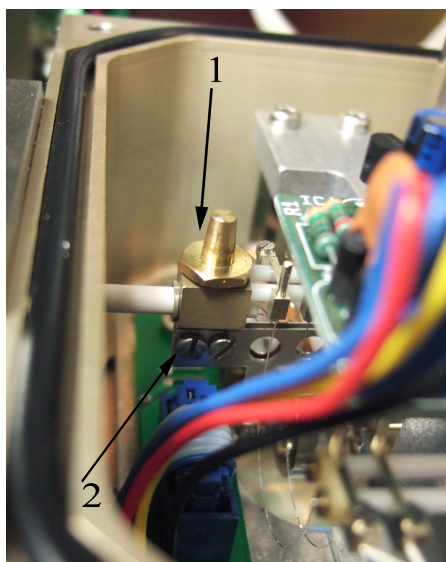
- The service panel can not be plugged in when operating the TGA, as the machine then receives two control signals.
- Of the two wires from the sample temperature sensor, the longest should be attached to the connection to the right, Point 2 in Figure D.1(b), to achieve the correct polarity.



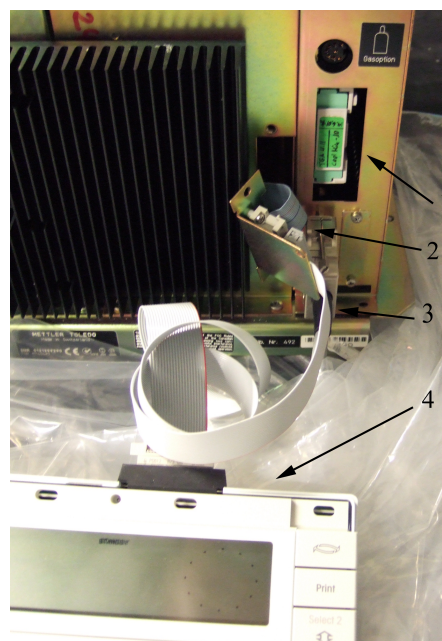
(a) Front view of the disassembled TGA: 1. Room containing an extra computer terminal and software cartridge 2. Furnace containing the balance, 3. Cell, containing electronics and the balance mechanics.



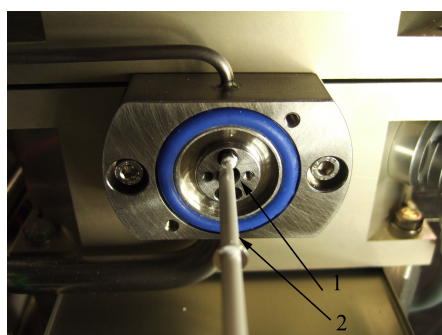
(b) Cell seen from left: 1. Calibration weight, 2. Contact point for wires from sample temperature sensor.



(c) Cell seen from right: 1. Cone for the sample arm holder, 2. Grub screws for adjusting position.



(d) Backview of TGA: 1. Software cartridge 2. Output for service panel, 3. Computer terminal, 4. Service panel.



(e) Base of balance: 1. Restriction of the balance arm as it passes from the furnace into the TGA cell, 2. Balance arm.

Figure D.1: Details of the TGA, with highlighted parts.