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STUD. TECHN. JORUNN HØLTO

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Norsk tittel: *“Eksperimentelle studier av en lagdelt, syntetisk silikat:
TGA, DSC og røntgenspredning”*

English title: *“Experimental Studies of a Layered, Synthetic Silicate:
TGA, DSC and X-ray Scattering”*

This work has been carried out in the Laboratory for
Soft and Complex Matter Studies at Department of Physics, NTNU,
under the supervision of Professor Jon Otto Fossum

Trondheim, 2 July 2007

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Abstract

The unique properties of clay are strongly dependent on interaction with water and air. For future use of these silicates in nanotechnology the detailed characteristics as a function of temperature and humidity are thus important to map. Three different experimental methods are here implemented to improve our understanding of the synthetic, layered silicate Na-Fluorohectorite (Na-FH).

Behaviour of Na-FH was observed during dynamic heating in the temperature interval 5 - 130°C by use of a Thermogravimetric Analyzer (TGA) and a Differential Scanning Calorimeter (DSC), which registered weight loss and heat flow curves respectively. Two main transitions, between the three stable hydration states in Na-FH was observed. For heating at rate 2°C/min the 2- to 1- water layer transition took place at 5 - 20°C. Transfer from 1- to 0- water layers occurred in the main temperature interval 22 - 56°C. It corresponded to a 4.8% weight loss consuming 3.39 W °C/g. Evaporation of water from mesopores caused a slow, steady weight loss, which continuously changed the specific heat of Na-FH. Step heating gave faster dynamics, while implementation of the heating rate 10°C/min shifted the characteristic curve to higher temperatures, but the total weight loss was identical.

A method for kinetic analysis of isothermal weight loss data was developed and tested, while taking limitations of the TGA into account. Empirical rate equations were used to estimate the rate controlling mechanism in Na-FH at different temperatures. However, the current numerical results were insufficient to make a final conclusion concerning the diffusion pattern at this point.

To investigate the interlayer distance in a small number of Na-FH crystallites a focused X-ray beam was used. When a humidity gradient was enforced on a powder sample, both 1- and 2- water layer hydration states were observed, in addition to the transitional state described as Henricks-Teller (HT) random intercalation. Characterisation of the HT scattering pattern was attempted, in terms of asymmetry and fit to a Gaussian distribution, but the collected data did not provide enough details to make any final conclusions at the present state. However, the technique proved that it was possible to isolate the HT-scattering pattern, which provides great possibilities for further investigation.

Preface

The work presented is my master's thesis performed in the tenth semester of a five year master degree program (norwegian "sivilingeniør") at Norwegian University of Science and Technology (NTNU) in Trondheim, in Laboratory for Soft and Complex Matter Studies. The extensive introduction to experimental physics has made me learn to work more independently and solve practical problems. In addition it has made it obvious how much time is necessary to use on both planning and data analysis. It has been a valuable preparation for future work as a researcher, and a good conclusion to my studies at NTNU.

Research on the dynamics of Na-FH during heating is built on work presented during my project work, autumn 2007: *Preparation for study of a layered synthetic silicate using TGA and DSC* [1]. But two additional experiments are also introduced. First a method and possible interpretation of isothermal measurements at the TGA. Second, the use of a focused X-ray beam to observe details of the hydration state in Na-FH when enforcing a humidity gradient on the sample. The latter experiment was performed at the synchrotron facility Pohang Light Source (PLS) in Pohang, South-Korea. Both are sources for future work in the research group.

Acknowledgments

Professor Jon Otto Fossum provided the opportunity to work on this project and his help and contacts made a visit to South-Korea for field work possible. Also thanks to Dr. Ahmed Gmira for help on using the TGA and DSC. The TGA would not be up and running again but for the patience of technician Ole Tore Buset. The X-ray scattering experiments are to a large degree built on previous work by Lars Ramstad Alme. And companionship provided by the large and active lab group this semester has made work easier.

The experiments in South-Korea were made possible by Professor Do Young Noh and support from his research group. A small beam size was provided through excessive work by Dr. Jinwoo Kim and PhD student Yong Sam Kim. And for our entire visit PhD student Yavus Öztürk worked tirelessly to achieve good results, both at my experiment and those of my fellow student Nils Ivar Ringdal. Thank you for making our visit to South-Korea worthwhile.

Trondheim, 2 July 2007

Jorunn Hølto

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Chapter 1

Introduction

“To extract physical knowledge from a system one must focus on the right level of description.”

(Goldenfeld and Kadanoff [2])

There are a number of techniques which are useful when trying to characterise the properties of a layered clay, because these minerals have got a very complex reaction pattern for interactions with water and air. This work focuses on different descriptive methods which can give complementary information, and result in a more complete picture of the dynamic behaviour of the smectite clay Na-Fluorohectorite (Na-FH).

It is believed today, that clay may be used in the development of modern nanotechnology, because of its unique properties. As a powder sample of layered silicate, it has the ability to intercalate guest ions, a fundamental characteristic of *nanosandwiches*. Surface properties of these layers allow three stable hydration states in Na-FH, which are described as 0-, 1- and 2- water layers. Transitions occur in a stepwise fashion, and will subsequently change its structural configuration. Water is also located around the layered crystallites in mesopores, and the total water content is highly dependent on thermodynamical parameters such as temperature, humidity and pressure. For the purpose of looking closer at this dependency for a powder sample three different experiments are implemented, using a range of different techniques, which are now presented.

To observe changes in the water content as a function of temperature three different experimental techniques are employed. The Thermogravimetric Analyzer (TGA) measures weight changes, while the Differential Scanning Calorimeter (DSC) monitors heat flow in the sample. In addition Wide Angle X-ray Scattering (WAXS) is used to probe structural changes. By implementing identical heating rates in an atmosphere of low humidity with all three instruments, the object is to characterise the dehydration pattern of Na-FH at different levels and to obtain detailed information on the conduct of Na-FH.

Water evaporates from a powder sample through a diffusion process which is dependent on temperature, thus an attempt is made to perform kinetic analysis of Na-FH. By employing empirical rate equations, as in a method suggested by Hancock & Sharp [3] it should be possible to estimate both the rate controlling mechanism of diffusion and the activation energy for this reaction in a porous material like Na-FH. Data analysis is based on isothermal weight loss data collected by use of the TGA, which made the object of this experiment to develop a suitable method and subsequently perform a numerical analysis.

There still remains questions concerning details in the stepwise transition between hydration states in Na-FH, and these are here addressed through observation of a limited number of crystallites by a focused X-ray beam, provided at the synchrotron facility Pohang Light Source (PLS)

in South-Korea. The object is to test this technique for its suitability to characterise the transitional states with a better spatial resolution than before, and to analyse the resulting diffraction pattern. For this purpose a powder sample is placed in a glass capillary, where an humidity gradient is enforced to produce an intercalation front. The gradual structural changes in Na-FH are then observed throughout the capillary.

Chapter 2

Theory

2.1 Clay

¹ Clay has traditionally been regarded as a versatile and common material, for example utilised in buildings and raw material for pottery. Lately its properties have also been recognized as useful for changing the viscosity of liquids, now used in the production of plastics and cosmetics, and in drilling mud for the oil industry. Also 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 μm , as this was the limit for current microscopy technology. A more general subdivisioning is today made using the Wentworth-Udden scale [5], presented in Fig 2.1.

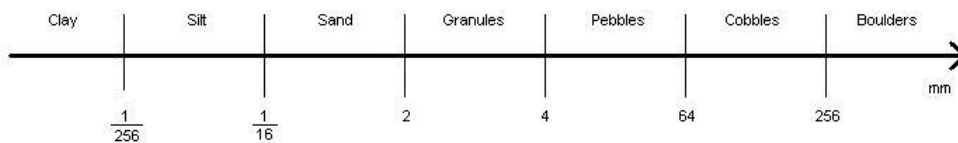


Figure 2.1: Wentworth-Udden size scale for sedimentary mineral structures. Based on [5].

A collective characteristic for clays is given by inclusion in a group called *phyllosilicates* due to their intrinsic layer structure. A typical feature is their *large surface to volume ratio* which is crucial for their performing abilities. Clay is a mineral found as a part of the ground but most of their properties is due to the interaction with water and air. Thus there are many nuances to the behaviour of clay in different situations, and it can on one hand be regarded as an *aqueous suspension of physical colloids*, where the interaction between the plate-like particles may be tuned by varying the salt concentration. Hence a range of various gel and sol structures are possible, with different rheological and optical properties. On the other hand, dehydrated clays are described as *intercalation compounds*, also generating new possibilities for nanotechnology. However, most clays are a very heterogeneous mix of minerals, which may cause both theoretical and experimental difficulties. But today it is possible to prepare pure clays synthetically, which are better suited for detailed experimental investigation [6]. Complementary information can

¹Information taken from [4] if nothing else is specified.

also be found by theoretical simulations, a method constantly improving as faster computers and more efficient algorithms are presented.

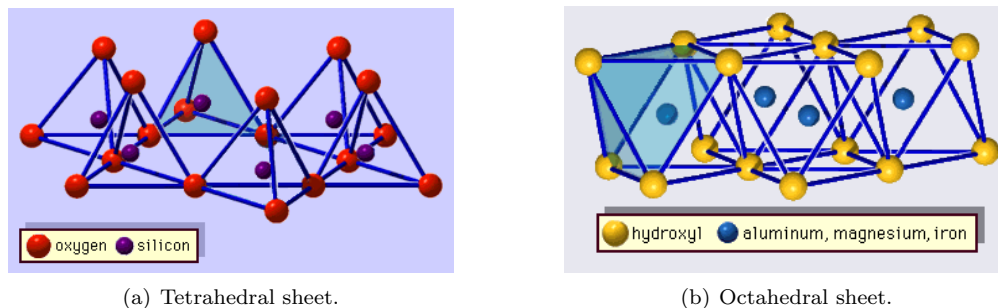


Figure 2.2: The two main sheet structures building clay minerals. Taken from [7].

Structure and Charge Characteristics

A lamellar clay is mainly composed of silicon and oxygen atoms, interconnected in a crystalline pattern, made up of two main structures shown in Fig 2.2. In the *tetrahedral sheet* structure a central silicon atom and four oxygen atoms are coordinated in tetrahedrons, forming an oxygen array. At the opposite end of each tetrahedron one finds the apical oxygen, often providing a proper location for bonds to neighbouring structures. Each unit in an *octahedral sheet* consists of six oxygens, forming a central oxygen array coordinated around a cation, with an apical oxygen at each side. The two sheet structures interconnect to make up a number of clay minerals with very different characteristics, where the individual types are differentiated due to the amount of ion substitution in the structure. Each have a general name reflecting the number of each sheets making up the basic structure, first tetrahedral and second octahedral sheets.

The fashion layers are bonded together depends on the layer configuration, as well as the amount of substitutions in the structure. Generally electrostatic forces and hydrogen bonds play an important role. But the introduction of water tend to make the interaction dynamics more complex, see Sec. 2.1.1.

A *2:1 smectite* consists of two tetrahedral sheets, with one octahedral sheet inbetween, as illustrated in Figure 2.3(a). The configuration causes a surface charge of $0.4\text{--}1.2\text{ e}^-$ per Si_8O_{20} unit [8], dependent on the number of substitutions in the structure. Smectites thus tend to stack like deck of cards, held together mainly by cations intercalated between each layer. Generally smectites are the only class of clay which is able to swell, while keeping its regular structure, thus giving the name *swelling clays*.

Kaolinite, shown in Figure 2.3(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 this phyllosilicate stack into a regular structure. The additive effect is strong, making kaolinite a non-swelling clay, with no surface charge.

If a smectite has been crystallised in an environment containing an excess of aluminium, an extra octahedral layer, called *Gibbsite*, will form and provide a tight bond inbetween the main layers, giving the structure 2:1:1. Such a clay is for example *chlorite*, with structure as shown in Figure 2.3(c) and is also non-swelling.

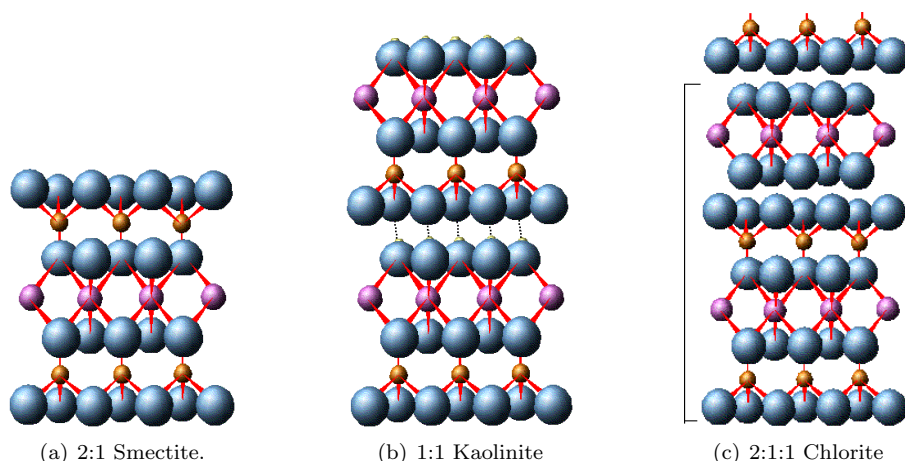


Figure 2.3: Basic structure for three classes of clay minerals, individual kinds differentiated by the amount of substitution. Oxygen atoms are blue, silicon are yellow and cations are mauve, while hydrogen atoms are small, white orbs. Taken from [9].

Intercalation and Swelling

As typical for layered materials, clays easily form intercalation compounds, where guest species may be included and in turn change the interlayers distances. Simultaneously the host structure itself will stay relatively unchanged. But clay is particularly versatile because of its surface properties, and may intercalate a range of species and quantities.

Two main types of intercalation processes should be accounted for. In the process of *absorption* ions are admitted into the clay structure either by substitution or occupying accessible cavities, hence changing the materials properties, for example the surface charge. In contrast, during *adsorption* molecules or liquids are accumulated on the surface, interacting with both exchangeable cations and the clay structure itself.

Clays are not necessarily able to absorb foreign material, but all clays can adsorb guest species, and in turn change its interlayer distance (parameter c in Fig 2.4). To which degree is dependent on the layer charge and the interacting forces between components, see Sec. 2.1.1. The amount of intercalation is also strongly dependent on thermodynamic conditions, as humidity, temperature and pressure.

2.1.1 Smectite Clay

Smectite clay is a phyllosilicate mineral species found in many forms, differentiated by variations in its chemical composition involving substitutions of embedded ions. These minerals have got unique properties, such as a large chemically active surface area and interlamellar surfaces with unusual hydration characteristics.

Negative Layer Charge

Any charged ions found embedded in the structure will contribute to a total negative layer charge at the surface of each clay sheet structure. Its size is decisive for the characteristics of a clay material.

Tetrahedral Charge Site Cations found in the tetrahedral sheets are principally Si, and by convention it is assumed that all sites are occupied stoichiometrically. All anions found in this sheet structure are oxygen.

Octahedral Charge Site The species found embedded in the octahedral sheet structure is more varied in species, for example Al, Mg or Fe^{2+} . The total number of ions present in octahedral charge sites may vary from species to species. Generally, either all sites are occupied, making it a *tri-octahedral* clay or only an average of two out of three sites are filled, giving it a *di-octahedral* nature.

In addition the hydroxyl anion structures can to some extent be substituted with F or Cl in some clay structures.

Interlayer Ions

To compensate for the negative layer charge cations are found inbetween each layer, being conducive to holding them together. There are mainly two types, either tightly fixed positive charged ions which are almost exclusively potassium. Or there are exchangeable cations, which can be either monovalent or divalent. Virtually any hydrated cation can be found, but in smectite clays calcium is predominant, while sodium and magnesium are common [4]. The species of interlayer cations are vital for the characteristics of a smectite clay as generally, it is the capacity of such counterions to solvate in the presence of water molecules and other polar solvents which causes clay to swell, and thus control its interlayer spacing [10].

Structure at Different Scales

The structure of a smectite clay can be described at many levels, when trying to explain some of the complexities that define their behaviour. As seen in Fig. 2.4 (a) the basic structure of a 2:1 smectite clay in terms of its swelling properties can be described by the layer thickness c . (b) shows that on a micron-scale they form a stacked lamellae, where the internal negative layer charge is compensated by interlayer cations. However at the particle edges the structure induced charge will be only partly compensated for, hence it is surmised that a (c) face-to-edge and edge-to-edge aggregation of clay particles is found. It is an isotropic structure, called “house of cards” and is an area of interest for many theoretical investigations [11].

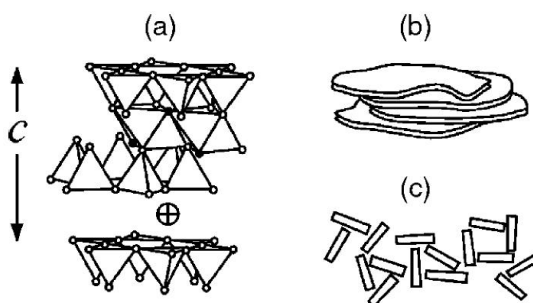


Figure 2.4: Structure of 2:1 smectite clay at different levels with c being the layer thickness, (a) Generic structure of 2:1 smectite clay, (b) micron-scale clay particle formed from stack lamellae, (c) face-to-edge and edge-to-edge aggregation of clay particles. Taken from [11].

Pores

Clay is a complex porous material with pores in a range of sizes, which interact and may in turn be filled with water. These may be classified into three different sizes.

- Micropores are defined as the pore volume found between the individual mineral layers, at a scale of 1-5 Å. Often the water will be oriented in respect to the layer surfaces and the interlayer cations, forming a varying amount of thermodynamical stable hydration states 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 [12].
- Mesopores are formed between individual stacks of phyllosilicate, at a scale of 2-50 nm. These will provide the water supply necessary for interlayer swelling of micropores and be a determining factor as to the tempo.
- Additional macropores are also found in clay, but these are mainly an effect of packing. If the sample is made more compact the volume of macropores is the most affected.

To characterize a clay material in terms of its water content *porosity* is defined as pore volume to total volume in the dried out state [12].

Crystalline Swelling

Water is attracted to the charged mineral surfaces, creating a reservoir of water in mesopores, available for its surrounding particles. By diffusion and capillary forces water can be further drawn into the interlamellar voids. For smectites, only a limited number of different water configurations are energetically favourable, thus expansion of a clay mineral generally takes the form of a series of discrete steps. Each correspond to a transition between hydration states, generally known by the term crystalline swelling. In simple terms it is associated with the formation of molecular layers of interlayer solvent, but is in fact closely related to the solvation by stages of the counterions themselves. (See page 8) But the hydration state is not only dependent on structure and thermodynamical parameters, in addition history of the water-clay system and its initial state may be a deciding factor [13].

Generally smectites swell at low temperatures, below 200 - 300°C. If heated to higher temperatures it will undergo *dehydroxilation* losing water molecules that are embedded in the structure. It corresponds to some degree of irreversible structural modifications, changing its properties [14].

Structure and Dynamics of Water in Smectites

The macroscopic volume changes observed in clay are found to depend upon both the relative volume of interlayer and interparticle voids, the size and structure of the smectite crystallites, and the size distribution and connectivity of the interparticle voids [15]. Smectites are complex materials, with a complex hydration pattern which is very sensitive to any change in the surroundings.

Details on the how smectites are dependent upon for example relative humidity can be quantified in terms of gravimetric water content. At a maximum RH of 85% a Na⁺ and Ca²⁺ smectite is found to contain 15.5% and 18.0% water respectively² [15]. And at a microscopic scale the Bragg peak displacement as a function of RH can be observed, using X-ray scattering³.

²Measured by sorption isotherms on an initially dehydrated sample

³A mapping of these properties for Na-FH has currently been undertaken by Lars Ramstad Alme [16, 17].

Static Forces To quantify some of the details for crystalline swelling it is useful to look at the participating components. Through research it is found that the nature of clay-fluid interactions are mainly determined by [10]

- Valence, radius and number density of the interlayer counterions.
- Number density and origin (tetrahedral or octahedral substitution) of the clay layer charges.

And looking at the pattern for crystalline swelling the phenomenon is believed to be controlled by several competing factors [18].

- Attractive forces.
 - Coulombic interactions⁴ between the interlayer cations and the sites of negative charge on the crystalline layers.
 - van der Waals⁵ attraction between layers.
- Repulsive forces
 - Between the like charged tetrahedral silicate surfaces.
- An elastic term is added by expansion and collapse of the interlayer region.

Hysteresis A phenomena often seen during heating and subsequent cooling, as crystalline swelling is believed to be a thermodynamically irreversible process [18].

Ion Hydration Crystalline swelling is believed to be closely related to the hydration of the exchangeable cations inbetween layers. Thus a closer look at the latter's characteristics may give new information. A charged ion is able to attach itself to water molecules, and thus change its state and location. Fig. 2.5 illustrates how an ion can graduate from an inner-sphere complex, embedded in the structure, to an outer-sphere complex, hydrated but in contact with the structure, and further to a diffuse complex, which is more independent [10]. The phenomena has been identified as a key element in the mobility of ions and for the ability of clays to swell.

Sodium typically forms a hydration shell⁶ of ~ 6 water molecules at a typical Na^+ -O distance of 2.40 Å [22] and has a solvation enthalpy of the order -390 kJ/mol [10].

A fundamental difference is expected between tetrahedral and octahedral clay charge sites. Simulations suggest that sodium suffer indecision faced with the competitive attractions of the charged clay sheet and interlayer water molecules. It seems sodium prefers to form inner-sphere complexes adjacent to tetrahedral charge sites, and outer sphere to the more shielded octahedral sites [10]. Simulation on the behaviour of sodium montmorillonite⁷ with only octahedral substitutions [24] show that a one-layer hydrate consists of counterions bound to the mineral surface in inner-sphere complexes, and water molecules located in the centre of the layer oriented by hydrogen bonds to the clay surface oxygen atoms. Swelling proceeds at higher water pressure

⁴Basic electromagnetic theory tell us that like charges will repel eachother and different charges will attract eachother, quantified for a pair of charges by Coulombs law [19].

⁵van der Waals forces are a class of intermolecular forces which arise from the polarization of molecules into dipoles (or multipoles). Such forces work on both a short range- and time scale, but will occur between most neutral atoms or molecules [20].

⁶The group of water molecules oriented around an ion dependent on its charge distribution, which can be further classified into the first and second shell. It results in weakening the structure of the hydrogen bond network [21].

⁷Montmorillonite is a 2:1 smectite clay mineral with the chemical formula $(\text{Na,Ca})_{0.33}(\text{Al,Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ [23]. Its behaviour is typically comparable to other smectite minerals.

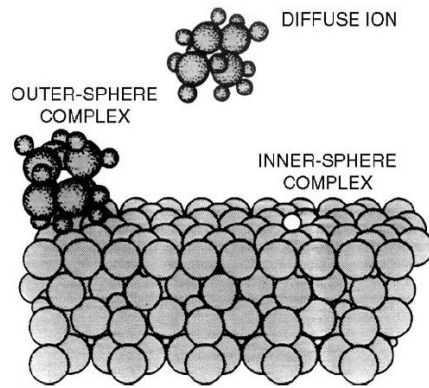


Figure 2.5: Ion speciation at clay surfaces, the different ion complexes are illustrated in a schematic fashion. Taken from [10]

by forcing the water molecules to form two layers. Less confinement of the water molecules allows them to orient themselves to the counterions, weakening the system of hydrogen bonds and making the counterions form outer-sphere complexes by becoming fully hydrated. Driving force of the counterion flux is the energy associated with full hydration of these ions. As the extent of swelling strongly depends on the charge locus, and is assumed to change if a larger share of tetrahedral substitutions are in place, as the latter are located closer to the the interlayer and will give more closely bound inner-sphere complexes [24].

Studies of water confined in sodium vermiculite⁸ show that the dynamics of interlayer water is almost entirely two-dimensional (2D), parallel to the platelets⁹ [26]. In addition, translational motion in the 2WL state is rather similar to that in bulk water, suggesting that the short range hydrogen bonds are mainly determining the water dynamics [26]. The dynamics of interlayer water is restricted by hydrogen bonds between the water molecules and oxygen at the clay surface, and thus plays an important role when determining the diffusivity of the system [27], depending on the interlayer spacing.

Heat Capacity

An intercalated material can be considered as two phases that are intimately mixed, a state which is quite different than a pure bulk state. Each participant has an individual heat capacity, first the host material, clay, and second the intercalated material, the guest, in most cases water. The relationship can be described as

$$C_p(\text{total}) = x C_p(\text{guest}) + (1 - x) C_p(\text{clay}) \quad (2.1)$$

where x details the fraction of each material. Experimentally, $C_p(\text{clay})$ and $C_p(\text{total})$ are measured, and $C_p(\text{guest})$ is computed. The technique has been used successfully to examine both water and host materials, even if the relationship really is somewhat more complicated. The quantity $C_p(\text{clay})$ can not be measured directly as the heat capacity of dried-out clay material

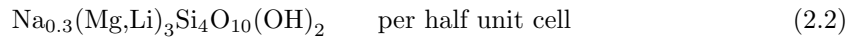
⁸Vermiculite is a 2:1 smectite clay mineral with chemical formula $(\text{Mg,Fe,Al})_3(\text{Al,Si})_4\text{O}_{10}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ [23]. In a natural state vermiculite and hectorite are often considered more homogeneous than montmorillonite in respect to different ions and hydration states [25].

⁹Valid on the experimental time scale used, and there were weak indications of fast rotational motion of single water molecules perpendicular to the plane.

is not the same as if the layers are separated by guest molecules, which needs to be taken into account during measurements [28].

2.1.2 Hectorite

Hectorite is a smectite clay named after the location where it was first found, south of Hector in California, US. Later it is also found at other spots, such as in Arizona and Nevada, US, France and Turkey [29]. These are minerals altered from volcanic tuff ash with a high silica content related to hot spring activity [30]. The general chemical formula of hectorite before facing any substitutions is



Categorized according to crystallographic data hectorite is a monoclinic crystal and belongs to point group¹⁰ 2/m, having a molecular weight 383.25 gm [30]. Major used of hectorite are for production of cosmetics, various chemicals and industrial materials [4].

2.1.3 Na-Fluorohectorite

Na-Fluorohectorite used for research is a synthetic, customised smectite clay with specific weight 2.8 g/cm³. Through substitutions of F⁻ into the octahedral structure the chemical structure differs from what expected in a normal hectorite clay, see Eq. 2.2



The proportion x of Li⁺ substituted for Mg²⁺ is vital for the final layer surface charge, as a change could affect its characteristics. In total these ions occupy all the octahedral sheet sites, classifying Na-FH as a trioctahedral smectite. The surface charge is normally 1.2 e⁻/unit cell, which is rather large compared to other synthetic smectites, for example laponite, with 0.4e⁻/unit cell [8]. Each crystalline stack consists of about 100 layers, each 10 Å thick. Typical particle height will then be 0.1 μm. The lateral particle diameter can reach about 20 000 Å, but as it is a polydisperse distribution the particles have a wide range of sizes [8].

Crystalline Swelling

Na-FH generally experience dehydration at low temperatures, below 130°C. At higher temperatures structural changes are observed. Surface properties of Na-FH make *three stable hydration states* possible, under the correct thermodynamical conditions. These structures are described, and referred to as *0 water layer* (0WL), *1 water layer* (1WL) and *2 water layers* (2WL). Each are found to be quite well ordered in the stacking direction. The basal layer spacing has been determined experimentally, as given in Table 2.1, but the dimensions have been found to vary slightly dependent on the mode of scattering and the current sample. The spatial configuration of water in respect to the sheet structure is not yet fully known, but their model structure is shown in Fig. 2.6 along with position and proportions of the constituent atoms in the sheet structure [6].

¹⁰Method for categorising crystal in terms of their symmetry properties.

Table 2.1: Observed basal spacing for the three different hydration states in Na-FH [6].

# water layers	Basal spacing d_{001} Å
0	9.6
1	12.2
2	15.1

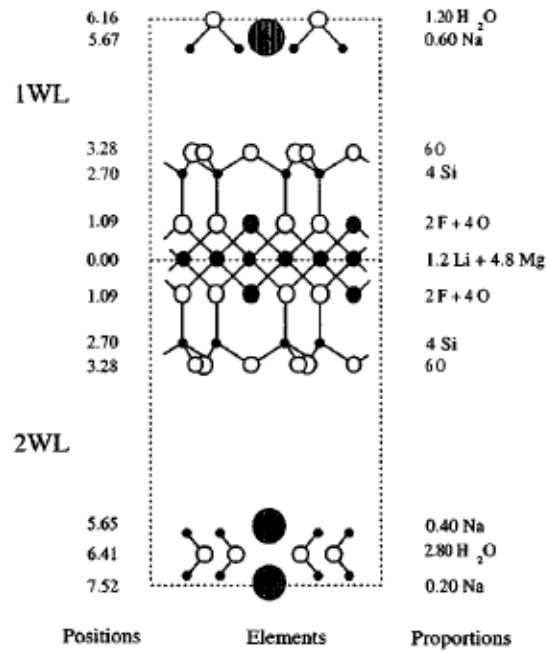


Figure 2.6: Schematic representation of the Na-FH structure, and model structures for the 1WL and 2WL hydration states. The position of silica in the octahedral sheet is chosen as origin position, 0 Å. Position of other constituents are given on left hand side, and its proportions on the right hand side of the picture. In the upper part the 1WL case is shown, 2WL at the bottom. Taken from [31].

2.2 Diffusion

Diffusion can be described as the random, thermal motion of atoms. It produces a change in the macroscopic concentration profile, aiming to reduce concentration gradients [32]. It takes place in all kind of materials, and when investigated it can provide valuable information on both the atomic structure of the material and the dynamics in a range of processes, as diffusion is often a controlling factor.

At a microscopic scale diffusion in materials often occur by random motion of discrete entities. Speed and direction depends on the particles mass and environment, although both are found to be sporadic and unpredictable variables. It is a spontaneous process, aiming to minimize the thermodynamical variable Gibbs free energy ¹¹. The nature of diffusion can be described mathematically by a relation between the atomic current and the concentration gradients. It is a direct analogy to the similar equations describing electrical or thermal conductivity as all actually attempt to achieve homogenisation of the respective concentration within the system [32].

2.3 Kinetic Analysis

¹² To determine the rate controlling mechanism of diffusion in a condensed matter sample, a number of equations can be used. Ideally one wants to identify an isokinetic reaction, meaning a reaction which is dominated by a single mechanism at all temperatures. But for a complex material this is not always the case.

The theory below is used when analysing weight loss data from isothermal measurements. A sample is shock-heated to a set temperature, which is then held constant for a set time. Information on the rate controlling mechanism and the kinetics is contained in the shape of the plotted data and the relative weight loss detected at the end-point of measurements.

2.3.1 Solid State Rate Equations

To analyse kinetic data for condensed matter it is customary to use a general rate equation, which is a product of the fraction transformed¹³ α and a rate constant, k .

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (2.4)$$

which further can be expressed in integrated form as

$$g(\alpha) = kt \quad (2.5)$$

To infer an atomic reaction mechanism the dependence of the function $g(\alpha)$ on the reaction mechanism is found. When presenting experimental measurements in reduced time scale plots¹⁴,

¹¹The thermodynamical potential of an isothermal, isobaric system [32].

¹²Based on article by Bray & Redfern [33], if nothing else is specified.

¹³The fraction transformed α , is a parameter used as the reaction coordinate. For isotherms α is defined as the end-point of the reaction which has the largest relative weight loss, and the final state is thus defined as $\alpha = 1.0$. The state of other measurements are then expressed as a fraction of α .

¹⁴A reduced time scale plot is based on normalization of a time-dependent function, which facilitate the comparison of experimental data [34]. It is found if dividing by for example $t_{0.3}$, meaning the time elapsed until 30% of the reaction is reached.

the data can be compared to the expected behaviour, described by a number of different theoretical rate equations. Thus the rate controlling process can be discerned by judging the goodness of fit. The rate controlling equations are presented in Table 2.2, divided into three general categories of reaction mechanisms, each marked by an abbreviation consisting of a capital letter and an integer n .

- Phase-boundary and first order reactions - Rn and Fn .
- Diffusion controlled reactions - Dn .
- Reactions described by the Avrami equation - An

2.3.2 Empirical Rate Equations

A different technique for determining the reaction mechanism is based on employing empirical rate equations, where the function $f(\alpha)$ from Eq. 2.4 is expressed in a general manner, but always dependent on the two parameters m , related to the rate controlling mechanism and the geometry of the system [28], and the rate constant k . Two equations are developed, and commonly used for this purpose.

Instead of judging goodness of fit by using numerical tables, the data is now presented in a $\ln\ln$ -plot and should ideally be linear. By determining the slope a comparison to calculated values can be made, and thus a match to the theoretical equations may be found more easily [3].

The Avrami Equation

One equation was presented by Avrami in 1939 [35], designed to present isokinetic reactions as parallel lines.

$$\frac{d\alpha}{dt} = k^m \cdot t^{m-1}(1 - \alpha) \quad (2.6)$$

A linearised form of the equation may be found after performing an integration.

$$\ln(-\ln(1 - \alpha)) = m \ln k + m \ln t \quad (2.7)$$

When making a $\ln\ln$ -plot of the data, the values of k and m can be determined by the intercept and gradient of the resulting curve. Calculated values of the slope parameter m in Eq. 2.7 was first presented by Hancock and Sharp [3], dependent on different boundary conditions. Values calculated by Bray & Redfern [33] for $0.15 < \alpha < 0.5$ are presented in Table 2.2.

The short range in which α is expected to be approximately linear, is caused by the limitations set by uncertainty. In the start of measurements by the initial conditions of the sample and later the data may be affected by the particle size distribution and other geometrical factors [3].

The Austin-Rickett equation

If the term $(1-\alpha)$ in Eq. 2.6 is replaced by $(1-\alpha)^2$ the empirical rate equation becomes equivalent to the equation found by Austin and Rickett in 1939 [36]. This transformation is often useful if the Avrami $\ln\ln$ -plots show a slight negative curvature, thus making direct analyses difficult [3].

$$\frac{d\alpha}{dt} = k^{m_A} \cdot t^{m_A-1}(1 - \alpha)^2 \quad (2.8)$$

Further, the equation may be rewritten on a linearised and integrated form.

$$\ln \frac{\alpha}{1-\alpha} = m_A \ln k_A + m_A \ln t \quad (2.9)$$

Thus, a new exponent m_A and a rate constant k_A are defined, which differ from m and k in the Avrami equation, Eq. 2.7. A set of values for m_A is also presented in Table 2.2.

2.3.3 Determination of the Activation Energy

The activation energy E_a is defined as the threshold energy which must be overcome for a chemical reaction to occur [32], and can be estimated based on the use of rate equations.

The Arrhenius Equation

The Arrhenius equation provides a direct dependence between the activation energy E_a , the temperature T and the rate constant k for a chemical reaction, which can be determined using Eqs. 2.7 or 2.9.

$$k = A \cdot e^{-E_a/RT} \quad (2.10)$$

R is the gas constant ¹⁵ and A is simply a prefactor. Derivation of the Arrhenius equation for application in solid-state kinetics, is based on theoretical principles known from kinetic theory for gases [37].

¹⁵The gas constant R is a physical constant used in equations of state to relate various groups of state functions to each other, for example in the ideal gas law. $R = 8.314472 \text{ J/K}\cdot\text{mol}$. [32]

Table 2.2: Rate equations and their characteristics for application to solid state materials [33].

Reaction mechanism	Function $g(\alpha)$	Slope (m)	Slope (m_A)
R2 - Phase boundary reaction, cylindrical	$1-(1-\alpha)^{1/2}$	1.10	1.31
R3 - Phase boundary reaction, spherical	$1-(1-\alpha)^{1/3}$	1.06	1.27
F1 - First order. Random nucleation, one nucleus/particle	$-\ln(1-\alpha)$	1.00	1.19
A2 - Random nucleation, Avrami equation	$[-\ln(1-\alpha)]^{1/2}$	2.00	2.39
A3 - Random nucleation, Avrami equation	$[-\ln(1-\alpha)]^{1/3}$	3.00	3.58
D1 - One-dimensional diffusion	α^2	0.60	0.72
D2 - Two-dimensional diffusion, cylindrical	$(1-\alpha)\ln(1-\alpha) + \alpha$	0.57	0.67
D3 - Three-dimensional diffusion, spherical	$[1-(1-\alpha)^{1/3}]^2$	0.53	0.63
D4 - Three-dimensional diffusion, spherical, Ginstling/ Broughtein	$(1-\frac{2}{3}\alpha) - (1-\alpha)^{2/3}$	0.55	0.66

2.4 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 [38]

$$RH = \frac{\text{Actual Vapour Pressure}}{\text{Saturation Vapour Pressure}} \times 100 \quad (2.11)$$

Actual Vapor Pressure, AVP It is simply a measure of the amount of water found in a constant volume, and will not change significantly during temperature variations.

Saturated Vapor Pressure, SVP Air at thermal equilibrium can hold a limited amount of water before it condenses at the surface, which is quantified through SVP . It is also a unique function of temperature, which makes it essential to also monitor the temperature if RH is observed. To estimate the theoretical development several equations exist, but usually the Goff-Gratch equation is made use of [39], which shows that SVP is close to exponential for temperatures below 100°C.

2.5 X-ray Scattering

X-rays are a form of electromagnetic radiation with wavelength in the range of 0.01 to 10 nm. The phenomenon was first observed by W.C. Röntgen in 1895, and has since been developed for use in diagnostic radiography and scientific structural investigations. It is a useful probe as generally scattering experiments are limited by the wave length, which needs to be in the same order of size as the structure in the current sample, a restriction which X-rays in most cases can meet. But X-rays are also ionizing, and can thus be dangerous for living organisms.

As X-rays are a part of the electromagnetic spectrum it is naturally a part of radiation from the sun for example. Sources for man-made X-ray radiation can be a X-ray tube¹⁶ with a rotating anode generating electrons or a synchrotron facility (please see Sec. 2.7).

Scattering occurs as a result of an interaction between incoming radiation and the sample material. X-rays are sensitive to the electrons present, its scattering power is proportional to the electron density of the sample. It means that a heavy atom will usually be more visible than a light one, like hydrogen.

Thomson Scattering During an elastic¹⁷ collision between incident electromagnetic (EM) radiation and an electron, the latter will start to oscillate with a frequency equal to that of the incoming wave, as it is accelerated. Thus it will emit radiation in all directions with this specific frequency, causing Thomson scattering to consist of radiation of the same frequency as the incident radiation. This phenomenon is what is of main concern during low energy X-ray experiments.

Compton Scattering Inelastic scattering will result in a longer wavelength of the scattered radiation compared to the incident one, as some energy is consumed during the interaction with the sample.

Crystal Structure In contrast to a random collection of atoms, a crystal structure is identified by its well-defined structure. It is composed by unit cells, a unique arrangement of atoms,

¹⁶A vacuum tube with an emitter of electrons, being a filament or a cathode, and an anode to collect the electrons, thus establishing a flow of electrical current through the tube - the beam.

¹⁷All energy is conserved during the interaction.

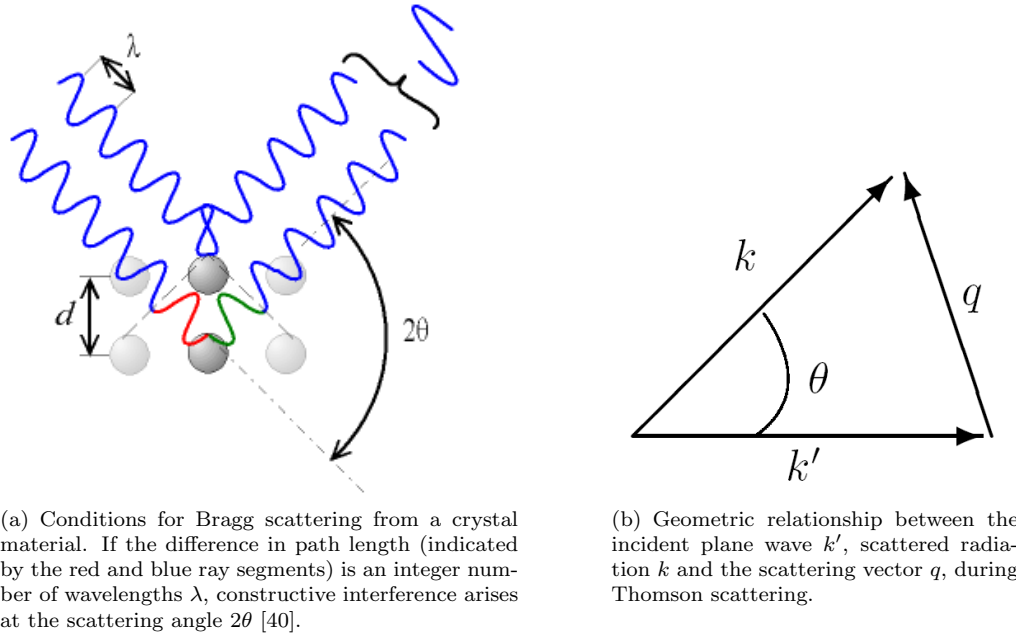


Figure 2.7: Illustration on scattering principles.

where the placement of each is defined by vectors called lattice parameters $\mathbf{r}$, in reference to the one atom defined as origin. Inherent symmetry properties of the unit cell is vital for the material characteristics and is used to classify the crystal¹⁸. Because of their regular structure Braggs law (Eq 2.12) often applies, and scattering is a customary method for investigation of the crystal structure, then termed *crystallography* [20].

2.5.1 General Properties

Braggs Law When using a monochromatic X-ray beam, it is diffracted on all atoms in a crystal and proceed to interfere constructively, causing observable diffraction peaks in certain directions. The phenomenon is explained by Braggs law, where all atomic planes are regarded as semi-transparent mirrors for the incoming beam. The condition for constructive interference is given by

$$2d \sin \theta = n \lambda \quad (2.12)$$

Each parameter is illustrated in Fig 2.7(a) and are defined as the distance between crystal planes d , the wave length λ and the scattering angle 2θ . n is an integer detailing the number of wave lengths constituting the vital difference in path length for two rays.

Scattering Vector To quantify the scattering direction one may also utilize the scattering vector $\mathbf{q}$, defined by the incident wave vector $\mathbf{k}'$ and direction of the scattered radiation, given by $\mathbf{k}$. As seen in Fig. 2.7(b) these three will form an triangle, with a top angle θ during Thomson scattering. Looking at the geometry the scattering vector $\mathbf{q}$ can be defined mathematically as

$$|\mathbf{q}| = \left(\frac{4\pi}{\lambda} \right) \sin \theta \quad (2.13)$$

¹⁸A crystal unit cell can hold either translational, rotational or mirror symmetries, or any combination of these factors.

2.5.2 Kinematical Diffraction

For scattering that can be considered weak, a simplified theoretical approach can be implemented, as it allows several multiple scattering effects to be neglected. The weak scattering limit is also known as the kinematical approximation, and is suitable for the current experiments.

For a thorough treatment of diffraction theory and further derivation of formulas please see for example Hecht [41] or Als-Nielsen & McMorrow [42]. This section presents the relevant specifics for scattering from a layered material using a X-ray source only. It is based on an expression for the scattered intensity I_{sc} from a crystallite [42]

$$I_{sc} \left(\frac{\text{photons}}{\text{s}} \right) = \Phi_0 \left(\frac{\text{photons}}{\text{unit area} \times \text{s}} \right) r_0^2 |F(\mathbf{q})|^2 N \frac{\lambda^3}{v_c} \frac{P}{\sin 2\theta} \quad (2.14)$$

with a brief explanation of the different terms.

First, the incoming flux Φ_0 of photons is limited by its beam area and normalised in time.

Second, as electrons are the basic scattering unit for X-rays, the amount of scattering is dependent on the electron density in the sample. For a single electron its scattering strength is defined in terms of the *Thomson scattering length* r_0 .

Next, any X-ray source will have an inherent *polarization factor* P which is dependent on its design. Both main setups are described later, please see Sec. 3.2.4 and Sec. 2.7 for rotating anode and synchrotron radiation respectively.

$$P(\theta) = \begin{cases} 1 & \text{Vertical scattering plane synchrotron} \\ \cos^2 2\theta & \text{Horizontal scattering plane synchrotron} \\ \frac{1}{2}(1 + \cos^2 2\theta) & \text{Unpolarized source (anode)} \end{cases} \quad (2.15)$$

And as atoms are not point-like particles, but is described in terms of its electron density, a phase delay $e^{i\mathbf{q} \cdot \mathbf{r}}$ is expected, for X-rays scattered at different locations inside an atom. The summarized effect for a three-dimensional crystal unit cell is contained in the *unit cell structure factor*

$$F(\mathbf{q}) = \sum_{\mathbf{r}_j} n_j f_j(\mathbf{q}) e^{i\mathbf{q} \cdot \mathbf{r}_j} \quad (2.16)$$

where the position of each electron inside the unit cell is given by the vector $\mathbf{r}_j$ the number of atoms of each type is given by n_j and f_j is the structure factor for each atom contained in the structure.

The parameters N and v_c is the number of unit cells and the volume of each unit cell, respectively. They are both introduced because of the necessary summation over a three-dimensional lattice.

Finally, λ is the X-ray wavelength, while the entire last fraction of Eq. 2.14 equals the *Lorentz polarisation factor* L_p for a three dimensional lattice. It is calculated through integration over both k' and θ , necessary to observe all facets of a Bragg peak. It is a measure for how much of the scattering is seen by a detector, and is highly dependent on the experimental method, thus it will often take a different form.

2.5.3 X-ray Powder Scattering from a Layered Material

There are practical differences in the intensity patterns collected from a large crystal with overall symmetry, in contrast to a powder sample with randomly oriented small crystallites. Thus the expression for observed scattering, Eq. 2.14 needs to be modified to include sample specific considerations.

Layered material

If the sample consists of small, thin crystallites as opposed to one large crystal, it is necessary to redefine the structure factor $F(\mathbf{q})$ because not all observed scattering is concentrated at the Bragg angles of diffraction. There can be additional scattering adjacent to these peak positions important to describe the nature of crystalline aggregates. The effect is separated out by defining the *interference function* $\Phi(\theta)$ for a layered material, based on the approximation to a two-dimensional lattice. The conditions for such Bragg scattering are illustrated in Fig. 2.8, while the interference function itself is also dependent on the number of stacked unit cells N [43]

$$\Phi(\theta) = \frac{\sin^2 \left(\frac{2\pi N d \sin \theta}{\lambda} \right)}{\sin^2 \left(\frac{2\pi d \sin \theta}{\lambda} \right)} \quad (2.17)$$

But in addition it is necessary to find a structure factor that is not dependent on a Bragg peak position, but rather a continuous function of θ . Thus the *layer structure factor* $G(\theta)$ is found by using a one-dimensional analysis of Bragg's law, defining the parameter z_j for the displacement of the atomic layer [43]

$$G(\theta) = \sum_{\mathbf{r}_j} n_j f_j \cos \frac{4\pi z_j \sin \theta}{\lambda} = \sum_{\mathbf{r}_j} F_j^{\text{mol}} \cos q z_j \quad (2.18)$$

Powder Diffraction

A good powder sample consists per definition of a large number of crystallites with a random orientational distribution. Each will be source for Bragg scattering, but because of geometric concerns, illustrated in Fig. 2.9 the peak will be dispersed into a ring, called the Debye-Scherrer cone. If the beam sees enough crystallites simultaneously the ring will be both continuous and symmetric. Geometric considerations of Fig. 2.9 give the Lorentz factor for a powder sample

$$L_{\text{powder}} = \frac{m_{hkl} P}{2 \sin \theta \sin 2\theta} \quad (2.19)$$

When comparing the two Lorentz polarisation factors, from Eqs. 2.14 and 2.19, it is apparent that their behaviour is very different at low values of 2θ , as shown in Fig. 2.10. And as most samples are neither perfect crystals nor perfect powders an sample dependent version is developed

$$L_p = \frac{2P}{\sin 2\theta \sin^\nu \theta} \quad (2.20)$$

where the parameter ν is equal to 1 for a perfect powder and $\nu = 0$ for a perfect crystal.

General Expression for Intensity

Taking the presented sample dependent factors, Eqs. 2.17, 2.18 and 2.20, into account the relation for scattered intensity, Eq. 2.14 is for a layered powder sample redefined into

$$I(\theta) \propto |G(\theta)|^2 \Phi(\theta) L_p \quad (2.21)$$

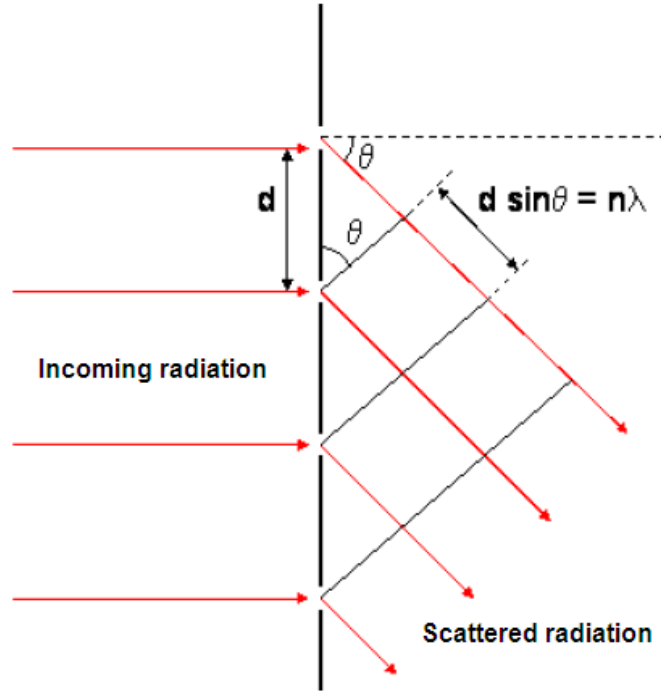


Figure 2.8: A layered material approximated by a two-dimensional lattice. The condition for multiple Bragg peaks is given by $d \sin \theta = n \lambda$, where d now indicates the layer distance.

Experimental Correction Factors

When extracting intensities from a crystal or powder diffraction pattern several sources for systematic errors need to be taken into account, and corrected for.

Lattice Vibrations A real crystal lattice is not perfectly rigid, rather atoms will vibrate of two different reasons. The first is of quantum mechanical in origin, and arises from the uncertainty principle. These vibrations are independent of temperature, and will even occur at the absolute zero of temperature and are thus named *zero-point fluctuations*. Thermal energy will at any finite temperature increase the amplitude of lattice vibrations, by thermally excitable *phonons*. The effect of lattice vibrations is an instantaneous position displacement $\mathbf{u}_{qj}$ parallel to $\mathbf{q}$ for the j 'th atom. The effect is accounted for by including a *Debye-Waller factor* $e^{\frac{1}{2}q^2 \langle u_{qj}^2 \rangle} = e^{B_T^j (\frac{\sin \theta}{\lambda})^2}$ when calculating the form factor. B_T includes the temperature-dependence, and its amplitude will increase with temperature [42]. Thus Eq. 2.18 is changed into

$$G(\theta) = 2 \sum_j n_j f_j e^{B_T^j (\frac{\sin \theta}{\lambda})^2} \cos qz_j \quad (2.22)$$

Source Dependent Polarization Electrons can only oscillate in a direction perpendicular to the beam direction. Therefore the amplitude of the oscillation vector is decreasing with increasing scattering angle 2θ , and a correction is necessary, dependent on Eq. 2.15.

Background Scattering Some noise in the scattering pattern can be expected in most experiments, as a contribution of small angle scattering from for example impurities in the sample or the sample holder. Generally the intensities will decrease with increasing scattering angle 2θ , and the effect can thus be corrected for during analysis.

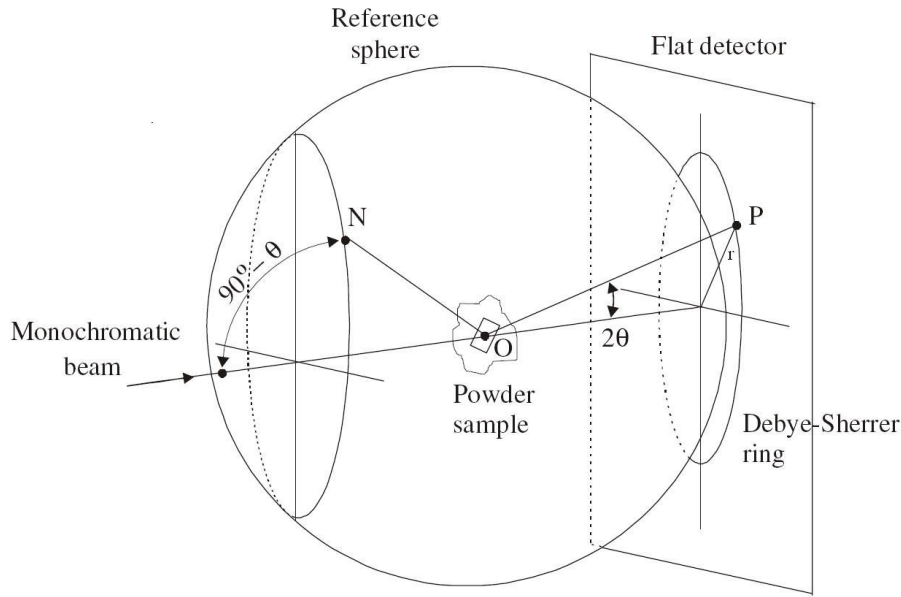


Figure 2.9: Illustration of powder scattering and its resulting Debye-Scherrer cone. In a powder sample with a random orientational distribution of crystallites each single crystallite will be a source for Bragg scattering to one point on the ring. If enough crystallites are present the ring will be continuous and symmetric. Taken from [44].

Experimental Width of a Bragg Peak Generally a powder diffraction peak consists of three parts. First the background B , or small angle scattering. Second the integrated intensity of the reflection and its profile I , which can be regarded as a convolution of the spectral distribution of the X-ray radiation W and the instrument G (instrumental broadening). Finally, the real structure of the sample represented by its grain size and lattice structure [45].

$$F(2\theta) = I \cdot [(W * G) * S] + B \quad (2.23)$$

Determination of the pure sample profile should be possible by use of a Fourier transform, but it is a time consuming process and requires prior knowledge of either of the terms in Eq. 2.23, which is seldom available [46].

2.5.4 Peak Fitting

For approximation of diffraction peaks two basic distributions are of interest, the Gaussian distribution and the Lorentz distribution, both described in App.F. A convolution of these has the potential to separate both the instrumental and specimen contribution, and the size and strain contribution in the profile [46]. But still an advanced numerical analysis is needed. Thus a pseudo-Voigt function is often used to approximate this convolution, as it involves a simple addition of the two functions instead. Linewidth of the Gaussian component is generally attributed to the instrumental resolution [6], while the Lorentzian lineshape is dependent on the thickness of the crystallite particles and their strain or lattice disorder [46].

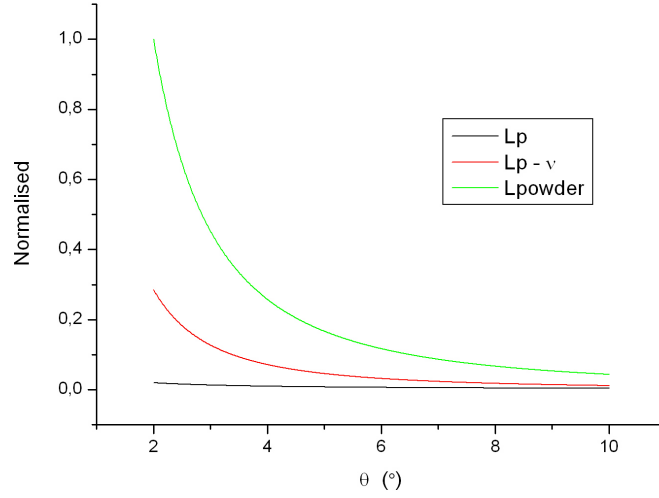


Figure 2.10: The three different versions of the Lorentz polarisation factor L_p . For a crystallite, L_p given by Eq. 2.14, for a powder Eq. 2.19 and for a sample dependent version Eq. 2.20 with $\nu = 0.94$.

$$\Phi(q) = \underbrace{\eta \frac{2}{\pi \Gamma (1 + 4 \left(\frac{q - q_c}{\Gamma} \right)^2)}}_{\text{Lorentzian distribution}} + \underbrace{(1 - \eta) \frac{2}{\Gamma} \left(\frac{\ln 2}{\pi} \right)^{1/2} e^{-4 \ln 2 (q - q_c)^2 / \Gamma^2}}_{\text{Gaussian distribution}} \quad (2.24)$$

Here Γ is the experimental width at half maximum of the measured curves, q_c is the peak center and η is a mixing constant which ranges from zero to one. It is thus responsible for changing the resulting line shape from Gaussian to Lorentzian. The difference it makes for the final shape is illustrated in Fig. 2.11. The individual linewidths Ω_G and Ω_L for the Gaussian and Lorentzian contributions respectively (Eqs. F.3 and F.4), are related to the total linewidth at half maximum Γ and the fraction η by [6]

$$\Gamma = (\Omega_G^5 + 2.6927 \Omega_G^4 \Omega_L^4 + 2.4284 \Omega_G^3 \Omega_L^2 + 4.471 \Omega_G^2 \Omega_L^3 + 0.0784 \Omega_G \Omega_L^4 + \Omega_L^5) \quad (2.25)$$

$$\eta = 1.36603 \frac{\Omega_L}{\Gamma} - 0.47719 \frac{\Omega_L^2}{\Gamma^2} + 0.1116 \frac{\Omega_L^3}{\Gamma^3} \quad (2.26)$$

For scattering experiments the pseudo-Voigtan distribution Φ is related to the measured intensity by

$$I(q) = C(q) \Phi(q) \quad (2.27)$$

where C is a parameter related to the scattering structure and polarisation factors, giving for practical purposes

$$C(q) = |G(q)|^2 L_p(q) \quad (2.28)$$

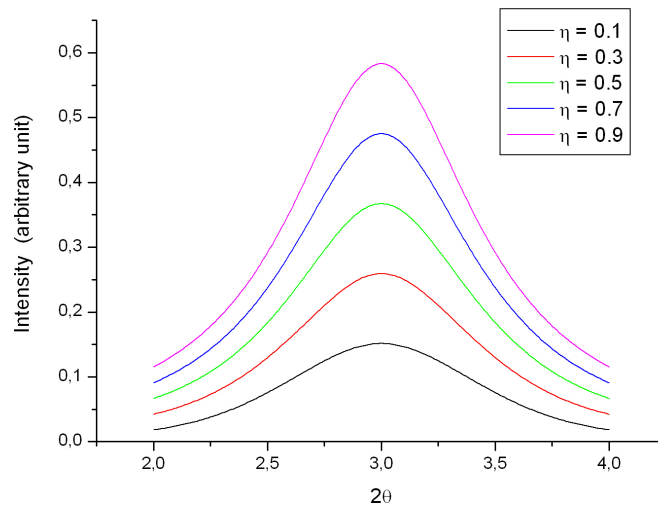


Figure 2.11: The Pseudo-Voigt function, Eq. 2.24, plotted for different values of the fraction η , to illustrate the difference in line shape of the Lorentzian and Gaussian distribution, dominating at low η and high η respectively.

2.6 Hendricks-Teller Random Intercalation

Line broadening in the scattering pattern from a layered material can suggest slightly different d - parameters. Hence one type of disorder in a perfect layered crystal can be defined as an irregular sequence of layers of different kinds. The theory describing this phenomenon was developed by S. Hendricks and E. Teller in 1942 [47], and the diffraction effects expected upon random interstratification were calculated and published by MacEwan in 1949 [48] and Brown & MacEwan in 1950 [49]. The predicted effect was seen during X-ray scattering on samples of the smectite clay montmorillonite in 1954 by Brown & Green-Kelly [50]. Further observations are made of for example Løvøll et al [51], but there are many details concerning Hendricks-Teller theory that still need to be investigated.

In cases where the material can be described as an irregular sequence of layers of different kinds Hendricks-Teller theory can be used to account for it, dependent on the following conditions [52]

1. Only two types of layers are present, represented by the interlayer distances d_1 and d_2 .
2. Both layers have the same structure factor.
3. Fractions f_1 and f_2 of the interlayer distances corresponds to the parameters d_1 and d_2 respectively.
4. Dimensions of the crystal are macroscopic.
5. Geometric factors in the X-ray experiment are not considered.
6. Thermal factors are neglected.

Under these assumptions, a phase shift ϕ_i will occur between successive layers for incoming X-rays, given by

$$\phi_i = \frac{4\pi d_i}{\lambda} \sin \theta \quad (2.29)$$

If there are indeed two different layer distances present, d_1 and d_2 , then two phase shifts, ϕ_1 and ϕ_2 respectively, will occur.

For N layers, each having an identical structure factor, the normalized scattering intensity is given by [53]

$$I(q) = \frac{1}{N} \sum_i \sum_j e^{iq(x_i - x_j)} \quad (2.30)$$

where x_i and x_j are the position of planes. These may be replaced by the characteristic distance Δd_i which in turn can be substituted by either d_1 or d_2 . In the limit $N \rightarrow \infty$ the average scattered intensity per layer can after further deliberation be expressed as [52]

$$I_{av} = |V_L|^2 \frac{1 - C^2}{1 - 2C \cos \bar{\phi} + C^2} \quad (2.31)$$

Here V_L is the layer form factor and C is a parameter, expressed in detail as

$$C = f_1 \cos(\phi_1 - \bar{\phi}) + f_2 \cos(\phi_2 - \bar{\phi}) \quad (2.32)$$

C is then further dependent on the average phase shift

$$\bar{\phi} = \arctan \frac{f_1 \sin \phi_1 + f_2 \sin \phi_2}{f_1 \cos \phi_1 + f_2 \cos \phi_2} \quad (2.33)$$

The main expression determining the positions, line shapes and widths is $I_{av}/|V_L|^2$ from Eq. 2.31, where the three independent variables d_1 , d_2 and f_1 are contained, plus the dependent variable θ . The computed linewidths correspond to disorder of layers only, while measured linewidths are also influenced by for example instrumental linewidth [52].

Remarks When discussing the conditions for Hendricks-Teller theory in terms of a real layered material, a number of concerns should be taken into consideration [50]. To assume that all layers have the same structure factor is equivalent to saying identical layers are separated by different distances, but with no interlayer material to support it. However, if the layers consist of heavy atoms with high scattering power compared to the interlayer material the theory should still be valid. Likewise, crystallites with infinite extent would imply a δ -function diffraction maxima. From finite crystallites the diffraction maxima is broader the smaller number of layers in each crystallite, and this is the expected result during an experiment.

2.7 Synchrotron Radiation

¹⁹ Synchrotron radiation is a general term used to describe radiation from charged particles travelling at relativistic speed, and forced by an magnetic field to travel along a curved trajectory. The phenomenon can be observed naturally, produced by astrophysical sources. During the development of particle accelerators, in the early 1920s, synchrotron radiation was considered a nuisance, as it was caused by an energy loss in the particles. This type of facility is now called a first generation source of synchrotron radiation, as it is considered a by-product. Second-generation sources are built for the single purpose of production and use of synchrotron radiation, and are also defined as storage rings. Here electrons or positrons are stored in a closed circuit at a fixed energy. The lost energy is replenished by appropriately placed radio-cavities along the ring. In addition a linear accelerator re-introducing particles is essential.

The primary source for synchrotron radiation in such storage rings is bending magnets. As electrons passes thorough the applied magnetic field, a Lorentz force²⁰ will work to alter their trajectory, thus they will loose energy, in the form of photons, which are defined as synchrotron radiation. The ray will be tangential to the trajectory, and take the form of a cone. Its extension is decided by the angle $1/\gamma$, defined by the particles relativistic energy: $E = \gamma mc^2$, m is its mass and c is the velocity of light. $1/\gamma$ is typically 10^{-9} radian. The emitted spectrum is very broad, ranging from the far infrared to to the hard X-ray region. The third generation of sources include the use of insertion devices in the straight sections of a storage ring. The two main types are known as wigglers and undulators, but both will produce synchrotron radiation by the passage of relativistic electrons through periodic magnetic structures.

The quality of a X-ray beam may be characterised by its brilliance, given by

$$\text{Brilliance} = \frac{\text{Photons/second}}{(\text{mrad})^2(\text{mm}^2\text{source area})(0.1\%\text{bandwidth})} \quad (2.34)$$

where bandwidth is a measure of the expected frequency range.

Typically a wiggler will provide X-ray radiation with a brightness one to two orders greater than what obtained with a bending magnet, while from undulators it is four to five times greater. And the brilliance from an undulator is about 10 orders of magnitude larger than what produced by a rotating anode [42]. Higher intensity is the greatest advantage by utilising synchrotron radiation, as samples that have a limited ability to scatter, can still be observed.

Polarisation Light from a synchrotron source will be polarised, because the electrons orbit is in the horisontal plane, thus also their acceleration is in this plane. Hence the emitted X-rays are horisontally polarised. A scattering experiment performed in the horisontal plane will therefore correspond to the polarization factor $P = \cos^2\theta$, θ being the scattering angle. For a verticle scattering geometry the full acceleration is observed at all scattering angles, thus $P = 1$. The relations are also given by Eq. 2.15.

¹⁹Based on [42, 40] if nothing else is specified.

²⁰The force exerted on a charged particle in an electromagnetic field [19].

Chapter 3

Experiment

3.1 Sample

The clay samples consist of synthetic Fluorohectorite (Corning Inc., New York), which have been subjected to an ion-exchange process¹ to achieve pure Na-Fluorohectorite (Na-FH).

For macroscopic investigations using TGA or DSC each sample was randomly distributed in a circular aluminium crucible. A low weight is chosen to minimize packing effects and because the overall reaction in a small sample should be faster, which is convenient for later comparison of results. The crucibles have an inner diameter of 16 mm and are 5.5 mm high. These are chosen because they are produced to be identical and for maximum heat transfer. A section of a prepared crucible is shown in Fig. 3.2(a), with a more detailed view of the random powder structure pictured in Fig. 3.2(b).

Prior to experiments the samples are kept in a closed glass container in room temperature, about 22°C, and at ambient humidity which may vary somewhat during the year. As the water content is humidity-dependent the initial conditions and the samples thermodynamical history can be a source of error for the experiments. But as the initial state of each sample is normally adjusted before starting the relevant measurements, as described in Sec. 3.3, it should not be an important factor.

For X-ray scattering experiments the sample geometry is important, and the fraction which is actually visible to the beam. Decisive for these experiments are that the sample was not pressed, thus no orientational order of the individual crystallites was expected. The opposite case is pictured in Fig. 3.1. Hence a continuous Debye-Scherrer ring is expected and the beam direction in reference to the sample is not important, as the same amount of nano porosity is visible at all times.

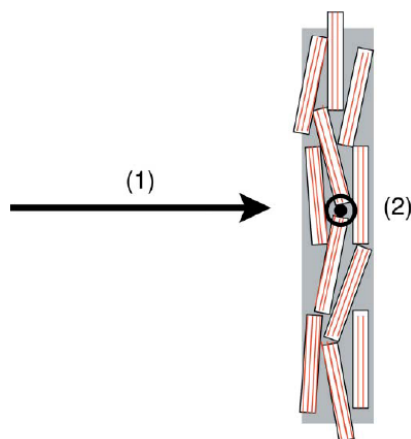


Figure 3.1: Vertical cut of a dry-pressed powder sample of Na-FH. Grey shadings denote mesopores in the sample while red lines represent the nano porosity inside each stack of crystallites. In a pressed sample the particles will have a defined orientation (2) in respect to the beam direction (1). While in a powder sample each particle will be randomly oriented. Taken from [54].

¹The ion-exchange involves adding NaCl to a sample of Li-FH, which 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 sample of Na-FH.

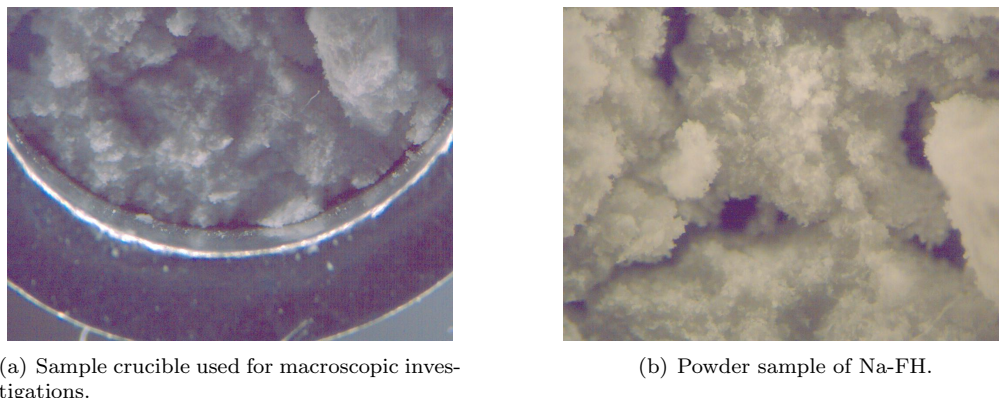


Figure 3.2: Na-FH sample used for experiments.

3.2 Experimental Setup

Four main setups were used to implement the three experimental methods described in Sec. 3.3. Each are described below, plus an introduction on humidity control during the procedures.

3.2.1 Humidity Control

An important part of these experiments are to control the local atmosphere properly. All the three setups for heating of the sample are built to allow a flow of reactive air, at the current sample temperature, close to the powder sample. Air is taken at ambient temperature and pumped through a cylinder with salt, which either absorbs or releases water molecules. The relative humidity is thus changed according to Eq. 2.11, by using the components pictured in Fig. 3.3.

Salts

Silica gel, Co_2Cl was used as a decissiant, and can in a closed system provide relative humidity down to $\sim 2\%\text{RH}$. As it absorbs water its color changes from deep blue to brown, and may subsequently be dried at about 80°C to regain its original character.

Humid air was prepared using a cylinder with a saturated solution of potassium sulphate, K_2SO_4 . The solubility at 20°C is $11.1\text{ g}/100\text{ ml}$ [55]. Air close to the surface at ambient temperature holds about $97\%\text{RH}$ [55]. It is an example of a salt which will provide a constant humidity solution, but generally a closed system where air is constantly circulated will result in RH closer to the predicted value than if air is only taken at the liquid surface once.

As relative humidity is extremely temperature dependent it is important to register both variables and take temperature changes near the sample into account during measurements. In relation to the TGA and DSC the effect is discussed in Sec. 4.2.5, see also below about improvements to the systems.

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 $\pm 2\%\text{RH}$, while above $90\%\text{RH}$ the accuracy is $\pm 3\%\text{RH}$.

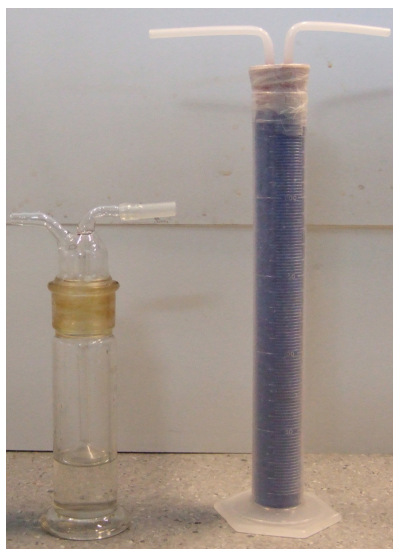


Figure 3.3: Cylinders with silica desiccant (right) and solution of K_2SO_4 for humidity control.



Figure 3.4: Setup of the TGA during measurements below room temperature, placed inside a plastic bag with supplies of silica gel.

The lab owns two identical sets of probe and hygrometer. Comparing their output it was found that their settings had fluctuated, and during autumn 2006 calibration using different constant humidity solutions provided by salts [1, 17] was attempted. Current tests of the two probes show no significant difference and thus the calibration process seems successful.

For constant observation of temperature and relative humidity using a hygrometer and two probes a LabVIEW program has been developed by Henrik Hemmen, which has proved useful for experiments.

Peristaltic Pump

The peristaltic pump 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 air flow is adjusted by changing its velocity, given in rounds per minute (rpm), or it may be regulated by a clamp covering the tube. No volume flow is given by the manufacturer, thus it needs to be calibrated for the current conditions. The process and its result are given in App. D. With the clamp fully closed 10 rpm gives an output of 50 ml/min. This volume fits with the capacity of both the TGA and DSC for heating of reactive air, and is easily reproducible for later experiments.

3.2.2 TGA

The Thermogravimetal Analyzer (TGA) is a sensitive balance, where the temperature and atmosphere may be controlled. Its main components are illustrated in Figure 3.5. A constant volume flow of nitrogen is used to purge the balance, while the local atmosphere of the sample is regulated by reactive air being pumped in through the capillary. Normally a shallow aluminium crucible is used as sample holder for temperatures below 650°C. Temperature- and time programmes for the furnace are preset using the software STAR^e.

Detailed specifications for the TGA/SDTA851^e are given in App. A. The furnace has temperature range 25° to 1100°C. There are two main cooling systems, one for the furnace and one for the balance cell. It is mandatory to use a thermostat for the furnace, but the cell should also be cooled if measurements below room temperature are attempted. The balance cell should be held at 22°C at all times, and is shut down at 15°C. For this purpose two thermostats are currently used. Below room temperature condensation can be a problem, but an improvement to the system is suggested below.

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

Fall 2006, and until February 2007 the TGA was out of order, thus a brief summary of the necessary repairs is given in App. B.

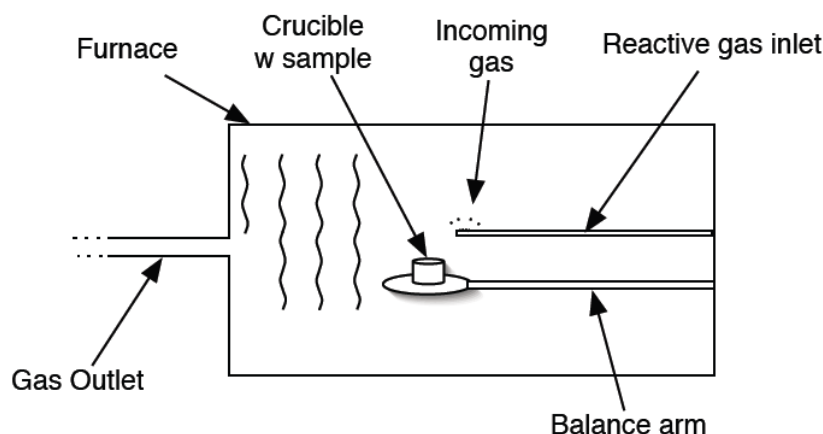


Figure 3.5: Main components of the TGA. Taken from [56].

Improvements to the TGA Setup

The TGA furnace is designed to provide an airtight sample chamber to make control of the local atmosphere possible. Both reactive gas and purge gas escapes through a hole at the far end of the furnace and subsequently through an attached rubber tube. This connection was originally improved by use of a spring [57], which apparently now had gone missing. It was replaced, and when measuring the outlet pressure in reference to the inlet gas flow a 3% difference was found. The same method was employed as described in App. D, and as such the difference is also dependent on the primitive equipment. Thus the furnace is found to be sufficiently air tight.

At measurements below room temperature condensation can be a problem. A solution is to exsiccate the surrounding air using large amounts of silica gel. During previous work [58, 59, 56] the TGA was put inside a wooden box with a lid of plexiglass closed by a rubber seal. But as wood absorbs humidity the system did not achieve a sufficiently low humidity. Currently a large plastic bag closed with plastic strips is used, and during experiments the TGA now has the appearance shown in Fig. 3.4.

The TGA is sensitive to any changes in the system setup, thus when attempting measurements below room temperature where the furnace is cooled to 2°C it is necessary to let the instrument stabilise over night [57] before starting the measurements. This is also an argument against changing the settings of the thermostat during long lasting measurements, to ensure a stable temperature and not to change the conditions for relative humidity. But then a difference between reference and sample temperature must be expected, because of the instruments design. In addition nitrogen should be allowed to purge the balance constantly previous to experiments to ensure a stable system [57].

3.2.3 DSC

The 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. The lab owns a DSC822^e from Mettler Toledo, which uses the software STAR^e. The instrument is depicted in Figure 3.6.

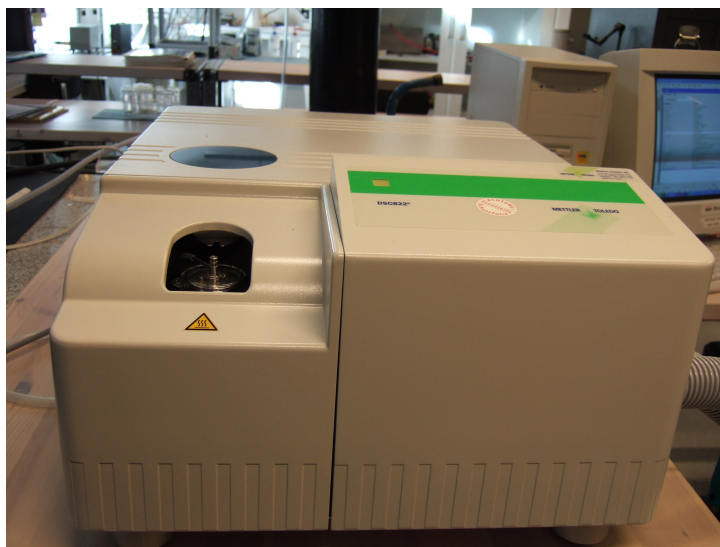
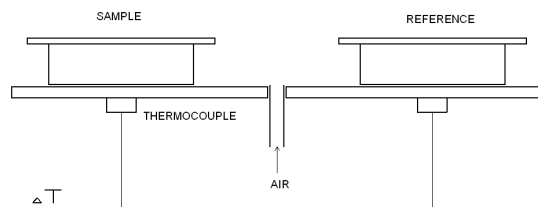


Figure 3.6: DSC822^e from Mettler Toledo, where the sample cell is located in the front, left hand corner.

The measuring principle is illustrated in Fig. 3.7(a). It 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 any energy the heat wave will change the total sample temperature, detected underneath by a thermocouple, and result in a temperature difference ΔT between the two crucibles. The signal ΔT is used to constantly readjust the furnace temperature underneath the sample to maintain the correct temperature, and the output signal represents the heat flow $\Delta \Phi$ in the sample, which is proportional to ΔT .



(a) Measuring principle.

(b) Sample cell on the DSC822^e.**Figure 3.7:** Sample cell of the DSC822^e.

Figure 3.7(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 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 thermostat. Specifications of the DSC822^e are listed in App. 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. For future users of the instrument a description of the calibration process and other information is given in [1, 60].

Improvements to the DSC Setup

The DSC is designed to provide opportunity for control of the reactive air inlet, but no pressure builds at the outlet, because air diffuses out through the many joins in the internal rubber tube system. If one wants to check the humidity an peristaltic pump must be used, and as both purge and reactive gas escapes together a different volume flow must be expected.

A check of the system using two humidity probes, two peristaltic pumps and no sample showed that when using one column of silica gel the inlet air flow was about 9%RH and an outlet flow of $\sim 4.5\%$ RH was observed, giving a difference of 4.5%RH. The stabilisation time for RH was about one hour, reinforcing why it is important to allow time for a new equilibrium to establish in the sample during isotherms at 5°C, simply because it takes some time to flush humidity out of the system.

Two main initiatives are made to improve the performance of the DSC. First the DSC is placed inside a plastic bag with silica gel, both to avoid condensation and to provide a dry atmosphere

if air should diffuse into the DSC system. The setup is illustrated in Fig. 3.8 and generally it will have the same appearance during measurements below room temperature as the TGA in Fig. 3.4.

Second, the sample chamber is made up of a steel cylinder with steel lid. To ensure minimum air diffusion through this joint a rubber *O-ring* with inner diameter 25.0 mm, thickness 1.7 mm and tolerant for high temperatures is added.

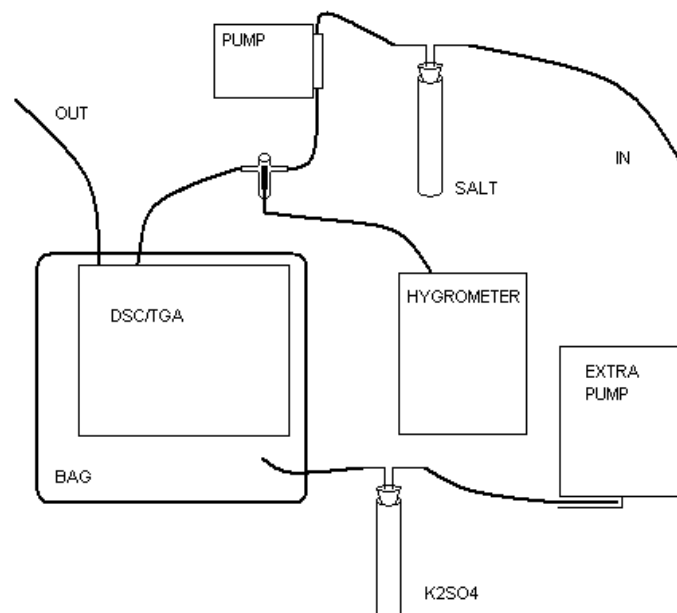


Figure 3.8: System for humidity control for use of the DSC. Placed inside a plastic bag for controlled atmosphere, and use of an extra pump for overpressure. A column with salt to regulate the reactive air inlet, controlled by a humidity probe at room temperature.

Heat Flow Curve

The DSC has got two main modes, isothermal heating or dynamic heating at a given rate. Most experiments on clay are made at a given heating rate to determine temperature ranges for the transitional peaks. Endothermic peaks, where energy is consumed by the sample, is by the software defined as negative, giving a minimum².

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 3.9 [61].

- 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, see Point 3 in Fig. 3.9. The amount of consumed energy, called heat of transition, is found by integrating the peak area.

²This specific definition varies in the literature, and thus whenever examining a heat flow curve the current specifications should be checked.

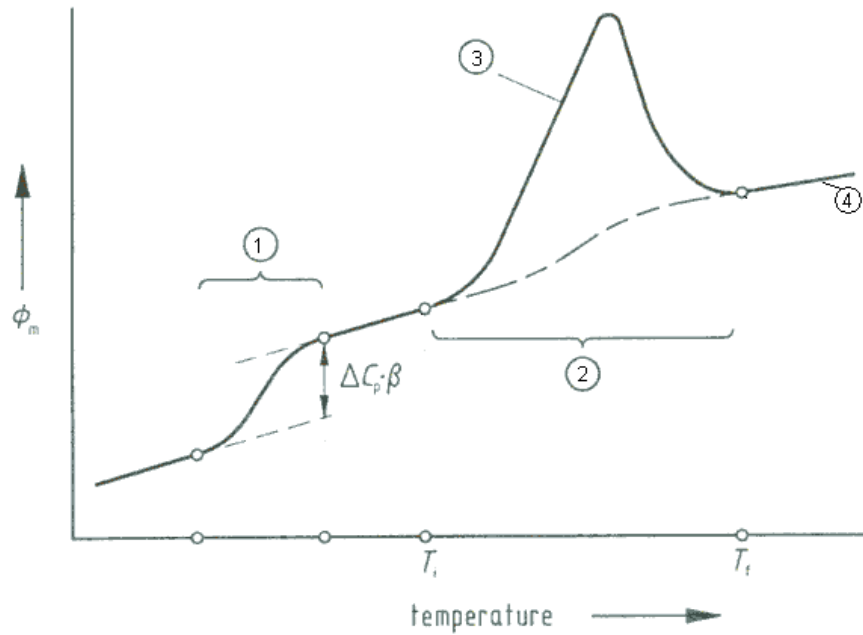


Figure 3.9: The basic parts of a heat flow curve: 1. Step due to ΔC_p with β being the heating rate, 2. Interpolated baseline, 3. Peak, 4. Measured curve. Based on [61].

- 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, illustrated by Point 2 and 4 in Fig. 3.9.
- A glass transition is found if a rapid change in the heat capacity ΔC_p is observed, in the form of a step in the measured curve, shown as point 1 in Fig. 3.9.

Relation Between DSC and TGA Signals.

³ 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 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 (SDTA) stating the difference between these two temperatures at any given time following the relation [64]

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

³Based on the two publications [62, 63].

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 and to check if the experimental procedure has been the same for parallel measurements on both instruments.

The method for signal conversion is further detailed in App. C.

3.2.4 WAXS



Figure 3.10: Components of the NanoSTAR system, 1. Rotating anode source, 2. Pinhole collimating system, 3. Sample chamber, 4. Detector.

Wide angle X-ray scattering (WAXS) experiments on a Na-FH powder sample as a function of temperature at low humidity was performed at NTNU. The NanoSTAR system was used, supplied by Bruker AXS, with a range of possible sample-detector distances. Its main components are pictured in Fig. 3.10 and a brief description is given below.

Rotating Anode Source The generating source is water cooled copper anode. A characteristic wave length K_α is chosen from the continuous white spectrum by use of *Göbel mirrors*⁴ as monochromators. Simultaneously the beam is focused from a 2-dimensional divergent beam to a two-dimensional parallel beam. For practical purposes the wavelength is defined as $\lambda = 1.541838 \text{ \AA}$.

Pinhole Collimating System To ensure a perfectly parallel beam and limit the beam size to a defined cross section, a system of three pinholes limit the beam size. It results in a point focus of $0.4 \text{ mm} \times 0.8 \text{ mm}$ (width $\times$ height) [66].

Sample Chamber A closed sample chamber is provided to reduce the amount of radiation exposed to users. It contains a software operated goniometer which allows positioning of the

⁴A pair of multilayer parabolic mirrors are set at vertical and horizontal grazing incidence for the beam to reflect a characteristic wavelength and achieve parallelisation. The geometrical properties are influenced of the material layer thickness and curvature in the mirrors [65].

sample in the xy-plane perpendicular to the incoming beam, with xy-range $80\text{mm} \times 100\text{mm}$ and accuracy $10\mu\text{m}$ [66].

Detector A 2-dimensional HiStar detector is used, composed of a multiwire grid and pressurised xenon gas. When the noble gas is ionised during impact with X-rays, these charged particles interact with the grid of electrodes producing an electrical signal which is indicative of the position on the detector area, and finally mapped as belong to one of the pixels. Diameter of the active detector area is 10.5mm , and it has a resolution 1024×1024 pixels [66]. For WAXS experiments the sample-detector distance is set to 26cm .

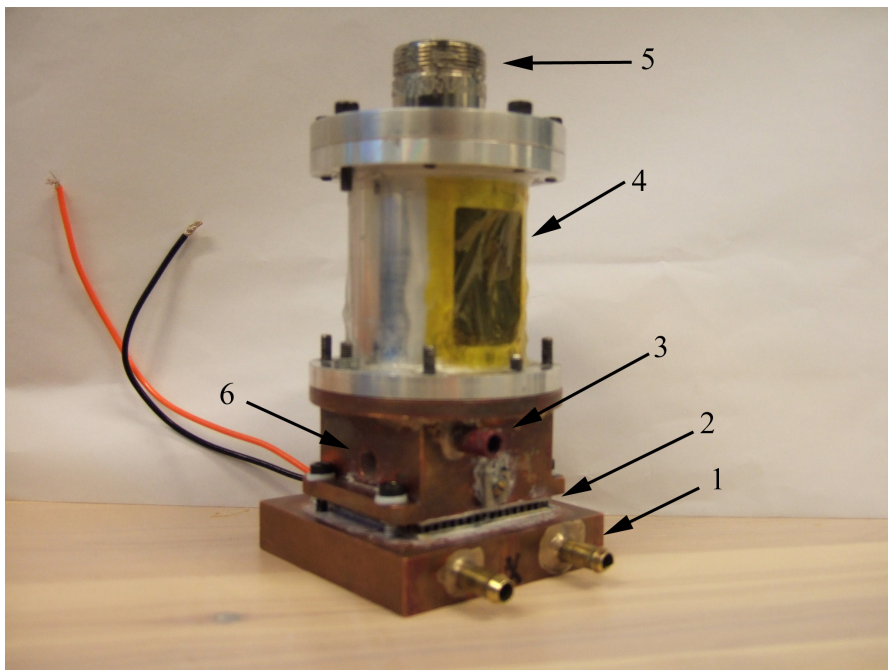
Sample Cell and Equipment

The sample cell is built for control of the thermodynamical parameters humidity and temperature. The first is provided through a closed atmosphere and a steady, controlled air flow, and the second by a temperature adjustable sample holder. The equipment has recently been used for investigations of layer spacing as a function of humidity at 15°C [17]. But by a few simple adjustments it should also be possible to examine d as a function of temperature at low humidity.

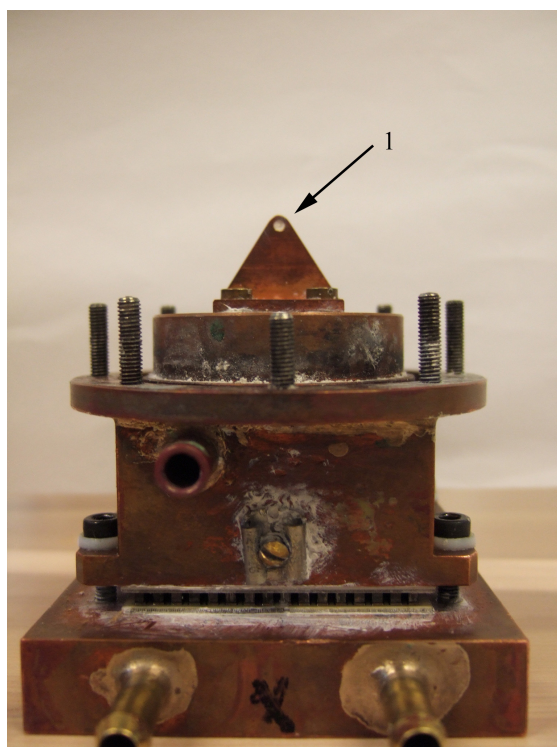
The outline of the sample holder is shown in Fig. 3.11(a), while the actual sample holder is depicted in Fig. 3.11(b). For maximum heat conductivity the sample holder is built of copper, and formed as triangle. This particular shape is chosen to make the area available for water to condensate on as small as possible, as liquid water will change a powder sample to “paste” and thus ruin the measurement. The sample itself is placed in a circular hole with diameter 1mm (see Point 1 in Fig. 3.11(b)), considered small enough to assume a minimal temperature gradient in the sample, and for further purposes the sample temperature is considered to be equal to the temperature in the copper holder. The sample holder is mounted on a square copper base with an integrated system for air supply, the inlet is Point 3 in Fig. 3.11(a). Using peristaltic pumps air is pumped into the sample cell, passing through the copper base before entering, to adjust the air temperature to the current sample temperature.

Temperature control is achieved using three separate systems seen in Fig. 3.11(a). First, the base of the holder is made up of a copper block with possibility to circulate liquid, thus providing a source of heat or means for cooling the cell, see Point 1. Secondly, a Peltier element is set on top to cool or heat the cell, Point 2. Its effect is controlled using a manual voltage source, and as sum these two elements provide the opportunity to coarse temperature adjustment. At last a heater is mounted in a circular hole in the upper copper block, see Point 6, thus fine-tuning the temperature by means of a PID controller.

The sample chamber is shut by use of a circular steel cylinder, with windows closed with kapton film which is invisible to X-rays, see Point 4 Fig. 3.11(a). At the top room is made to include a humidity- and temperature sensor directly above the sample, collecting data continuously, see Point 5.



(a) Main sample holder, originally mounted on the goniometer. 1. Bottom copper block with inlets to circulate fluids, 2. Peltier element, 3. Inlet for circulating air in the sample chamber, adjusted to the current sample temperature, 4. Air tight sample chamber, closed with kapton film which is invisible to X-rays, 5. Opening for the humidity sensor, 6. Room for the PID-controller fine-tuning the sample temperature.



(b) Inside the sample chamber. 1. Powder sample mounted in a 1 mm circular hole in the uppermost copper block.

Figure 3.11: Sample holder for X-ray scattering at the NanoSTAR system at NTNU, investigating layer distances in Na-FH as a function of temperature, at low humidity.

3.2.5 PLS



Figure 3.12: The *KJIST X-ray Scattering* beamline at Pohang Light Source, Pohang, South-Korea. Featuring two different beam outlets, *5C1* being the hindmost box seen here.

Pohang Acceleratory Laboratory (PAL) in South-Korea hosts a X-ray synchrotron facility, which was completed in 1994 as a project financed by the Korean government and POSCO, the national steel producer. Today it is operated by PAL and POSTECH, Pohang University of Science and Technology, serving both domestic and international users.

The Pohang Light Source (PLS) consists of a 150 m long, 2.5 GeV Electron Linear Accelerator which acts as an injector for a storage ring where electrons are circulated. The storage ring itself has an outside diameter of 141 m⁵ and 32 beam ports. Its performance has continuously been improved, but has since early 2000 been running at 2.5 GeV with 180 mA [67].

The nature of synchrotron radiation is described in Sec. 2.7, thus this segment will relate the specifics of components in the setup. The beamline used was *5C1 KJIST X-ray Scattering*, belonging to Gwangju Institute of Science and Technology (GIST) by Professor Do Young Noh [68]. An overview of the system, consisting of two beamlines, is pictured in Fig. 3.12.

A monochromator is used to limit the frequency range of the white spectrum originating from the bending magnet. The utilised wavelength is 1.30 Å with an estimated error ± 0.05 Å.

KB-mirrors To focus the X-ray beam a system of mirrors called KB, devised by Kirkpatrick and Baez in 1948, is used. The layout is shown in Fig. 3.13, which builds upon the principle

⁵This is the diameter of the building housing the storage ring and all its beamlines.

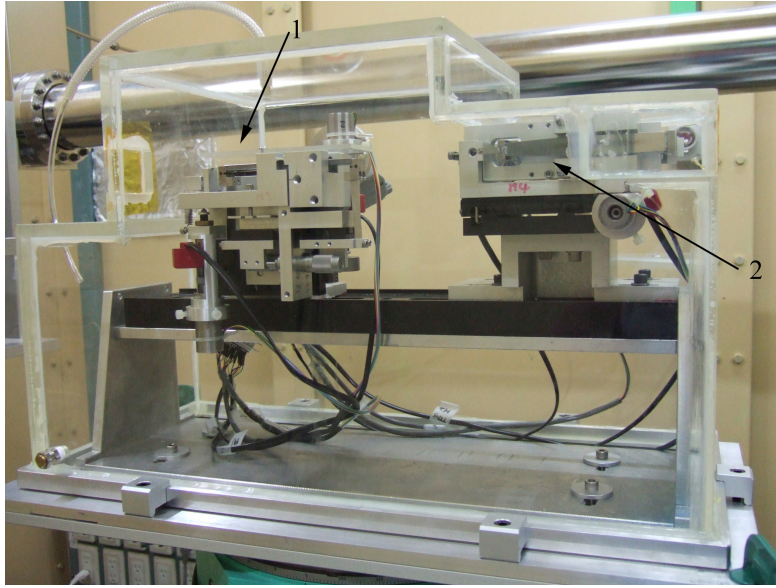


Figure 3.13: KB-mirrors used to focus the X-ray beam. 1. First mirror, 2. Second mirror, placed perpendicular to the first one.

that X-rays can be reflected at glancing incidence from a polished surface. The system consists of two spherical mirrors placed normal to each other, to prevent defects in the image caused by astigmatism⁶, through having a much larger sagittal⁷ radius of curvature than tangential. Their placement relative to each other makes the sagittal rays from the first mirror become the tangential rays of the second mirror, and simultaneously the ray is strongly focused [70]. In this setup sensitive micrometre screws are used to change the mirror curvature until the beam size is as demanded.

One-dimensional Detector To measure the scattering pattern a point-detector scanning 2θ horizontally is used. It is a NaI-scintillator produced by Saint-Gobain Crystals, suitable for low-energy gamma and X-ray detection, and is sensitive for photon energy down to 3 keV [71]. The detector exploits the fact that a transparent crystal, here NaI, will fluoresce when struck by ionising radiation. The crystal is thus called a scintillator, and a sensitive photomultiplier tube will subsequently measure the light from the crystal and quantify the count into an electric signal.

Using the one-dimensional detector, shown as item 3 in Fig. 3.14(a), three variables may be adjusted: The interval of 2θ which should be considered, the amount of point measurements made in this interval and exposure time at each point.

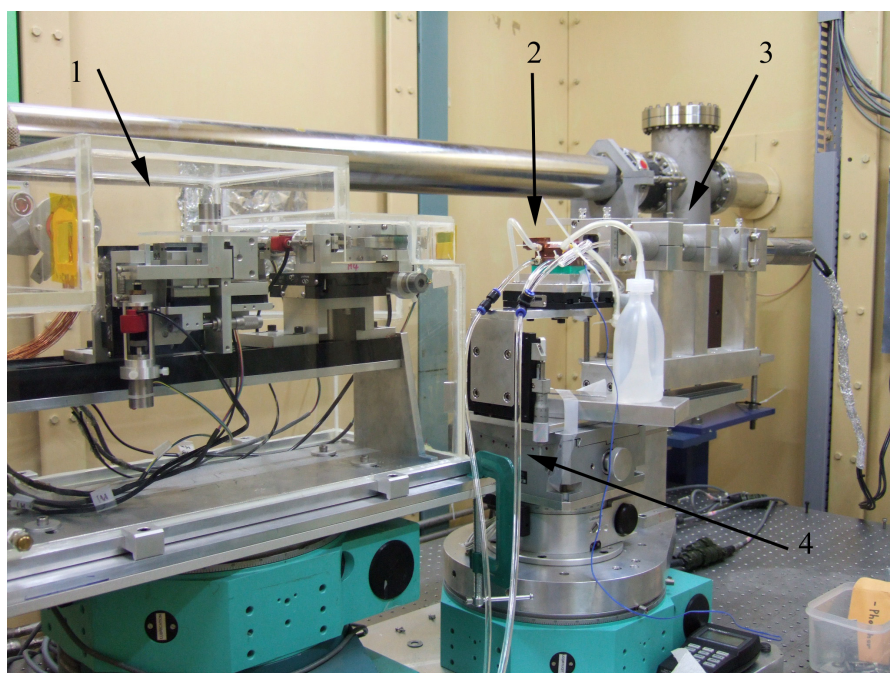
⁶Astigmatism is an optical phenomenon which occurs when an optical system has different focus point for rays which propagate in two perpendicular planes. Thus normal and tangential components of the ray, relative to the mirror plane, can be focused in different points. At extreme glancing incident these two images are separated by a large distance [41].

⁷The sagittal plane divides an object into a left and a right portion [69].

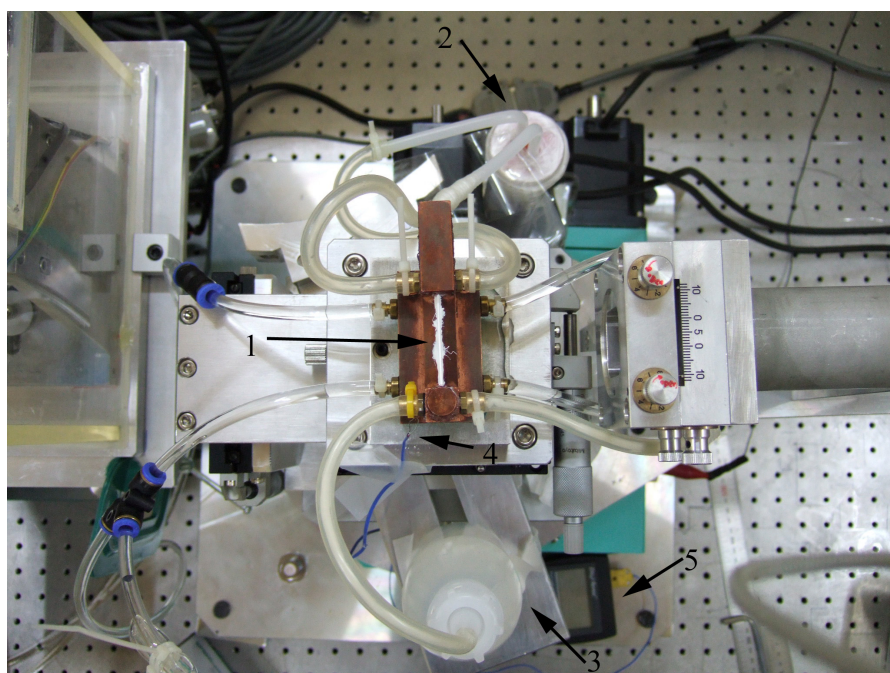
Sample Holder The sample holder is shown as item 2 in Fig. 3.14(a), and its details can be seen in Fig. 3.14(b).

To observe the effect of an humidity gradient on a Na-FH powder sample, a glass capillary of diameter 1 mm and wall thickness 0.1 mm is used. As seen in Fig. 3.14(b) the capillary is laying on a triangle shaped copper block, attached with thermal paste, for maximum heat transfer. Each end is terminated inside a closed space, both shut with copper lids and glued airtight using silicon paste. This closed space is further open for a connection out using plastic tubes. Thus one end is supplied with humid air using a string of blotting paper and water in a closed container. At the other end a supply of silica gel keeps the air dry. In addition the copper lid is at this end enlarged to make room for a small volume of silica gel close to the sample, to improve the conditions further. Temperature adjustment of the sample is achieved by two holes at the bottom of the main copper block, in which water is circulated by a water bath. Hence the sample is cooled to 15°C, a temperature which is chosen because it by experience provide a quite slow interlayer water dynamics, suitable for this type of observation [16, 17].

The main sample holder is thermally insulated from the rest of the system using a plastic disc, before being mounted on a steel plate fixed to a goniometer. Thus the sample can be translated both vertical and horizontal using micrometre screws.



(a) Overview of the setup, consisting of 1. KB-Mirrors, 2. Sample holder, 3. One-dimensional detector, 4. Circulated cooling liquid.



(b) Sample holder. 1. Glass capillary containing crushed Na-FH, 2. Column containing silica gel supplying dry air, 3. Bottle containing water supplying humid air by means of blotting paper drawn through the adjoining plastic tube, 4. Thermocouple, 5. Multimeter giving the temperature of the sample holder (and sample).

Figure 3.14: Experimental setup for X-ray scattering at beamline 5C1, PLS, South-Korea.

3.3 Experimental Method

Three separate experimental methods are implemented. Each investigate a different aspect of Na-FH, but can also provide supplementary information on its behaviour.

3.3.1 Heating

For powder samples of Na-FH it is interesting to investigate the response to heating in the temperature interval 5 to 130°C, at low humidity. Different aspects of the sample was observed by implementing three different techniques, for complementary information. Using TGA and DSC the macroscopic characteristics weight and heat flow were observed, while WAXS was utilised to map its microscopic properties, in terms of its current layer distance. Two main temperature programs were used, continuous heating at different rates, and step heating.

It was essential to provide a similar initial state for all samples. At room temperature Na-FH has approximately 1WL. Thus first, the sample was cooled to 5°C in an atmosphere of humid air. An isotherm was run for two hours, to reach an equilibrium with a 2WL hydration state for all Na-FH samples. A check made with x-ray scattering confirmed that this time interval was long enough even for a quite large sample volume [1]. The air supply was subsequently changed to dry air, to establish a new humidity dependent equilibrium and flush the instrument for humidity before the heating process was started.

Now different heating programmes were started, and on reaching 130°C an 1/2 hour isotherm was run to confirm that a new equilibrium was established.

The two instruments for thermal analysis have different tolerance for volume flow of reactive air, thus at the TGA 50 ml/min was used, whereas at the DSC both 50 ml/min and 87 ml/min was used, to investigate if an effect on the dynamics was seen. A low initial sample weight was preferred to minimize packing effects, thus set to 2.9 - 4.0 mg.

Continuous Heating Both the TGA and DSC made it possible to heat the sample at a constant rate. As the clay powder was suspected to be sensitive to the method used, two different heating rates are used in the interval 5 - 130°C: 2°C/min and 10°C/min.

Step Heating As the heating method is of importance, also step heating of the sample was implemented. At the DSC and TGA each step was a 1 or 2 hour isotherm, dependent on how stable the sample had proved to be at this specific temperature (a test run was made with the TGA). Thus after cooling the sample to 5°C to absorb water, the sample was heated on a rate 2°C/min in steps of 3°C until 20°C and in steps of 5° afterwards, until 130°C. Smaller steps at low temperatures was deemed necessary because earlier experiments on the DSC showed that it was a very active interval where much happened [1] and not much focus has been on this temperature interval in earlier work [31, 56, 59, 58].

To compare data a similar step heating procedure was implemented using WAXS. Continuous heating was not an alternative as the current layer distance had to be observed by a number of 15 min scans. Such a time interval is by experience necessary to gather enough information, caused by a combination of the nature of scattering from the sample and the beam intensity [17]. The system for heating the sample was intricate, but by combining the three heating sources it was made possible to reach 105°C.

The system of plastic tubes leading air with controlled humidity into the sample chamber was long, and it was necessary with a quite high pump volume to achieve a good level of control, at least 20 rpm (87 ml/min). As the setup included an humidity sensor close to the sample, an immediate *RH* change was observed whenever the volume flow was adjusted. Because of a

substantial number of joints in the system of rubber tubes some loss of pressure was registered, and no air flow was detected at the outlet.

The powder sample was only lightly pressed, as it was formed to fit the cylindrical sample holder, with diameter 1 mm.

3.3.2 Isotherms

By monitoring the sample weight at varying isothermal conditions, it is possible to determine the prevailing reaction mechanism, as water evaporates from the sample and an equilibrium state is established. Making use of the equations described in Section 2.3 to define a slope, these data are compared to the theoretical values in Tab. 2.2.

At room temperature a Na-FH sample has approximately 1WL, plus additional bulk water found in mesopores [31]. When heated, a fraction of the water will be lost in a temperature-dependent reaction. Also the relative humidity may influence the equilibrium state, thus a steady flow of nitrogen gas, giving an inert atmosphere with no humidity content [72], is used to purge the sample during the current experiments, calibrated to ~ 50 ml/min.

A preheated furnace was used for isothermal measurements of a 5.0-5.6 mg Na-FH powder sample. To start data collection immediately the TGA had to be force-started by pressing 'OK'. Each isotherm lasted one hour, and at least three parallel measurements were made. The procedure was repeated with an empty crucible, to collect zerolines for the essential correction process, described in Sec. 4.1.1.

Because of time constraints isothermal measurements were only accomplished at three different temperatures, 50°C, 90°C and 130°C. These three were chosen to represent the entire relevant temperature interval for dehydration of Na-FH.

3.3.3 Humidity Gradient

The main objective by x-ray scattering experiments performed at PLS was to achieve a better spatial resolution of the water intercalation front in a Na-FH powder sample, than during previous experiments [16, 17, 51]. By enforcing an humidity gradient on a powder placed in a glass capillary a diffusion front moved through the sample volume, which further resulted in an observable intercalation front as the structural properties of the Na-FH changed [51].

To map the water layer hydration state throughout the capillary an appropriate height was found, 0.3 mm below the upper edge. Further, horizontal translation was achieved manually, by use of the micrometer screw. Thus a systematic mapping was made, where the measurements started at the dry end of the capillary approaching the water front.

Using a one-dimensional detector it was only possible to observe the horizontal, radial intensity, not the entire Debye-Scherrer ring. To better confirm if the reduction of observed sample volume resulted in an asymmetric ring, scans were made horizontally for both positive and negative 2θ values.

At each scan the detector measured the intensity between $2\theta = -8.5^\circ$ to -2° and $2\theta = 2^\circ$ to 8.5° . Each interval contained 65 point measurements, that all lasted for 30 s.

Step Size Using a highly focused beam two main advantages must be emphasized: First, the possibility of observing a small amount of crystallites at the time. Second, a small beam size makes it feasible to move with smaller steps along the glass capillary. Because of time constraints⁸ it was not possible to move along the capillary with as small steps as one could have wished.

⁸Approximately 48 hours of beam time remained when the data collection was started.

Instead the current water layer state was mapped in steps of (mostly) 2 mm, starting at the end where dry air was supplied. Later the main areas of the transition between 1WL and 2WL was focused on more thoroughly, by smaller detector steps, more point measurements and also by moving the beam vertically across the capillary.

Chapter 4

Data Analysis, Results and Discussion

There are four main parts contained in this chapter. First, the method for data acquisition and correction of data from each of the four instrumental setups used. Second, the subsequent data analysis and discussion of the three main experiments are included separately.

4.1 Data Acquisition and Corrections

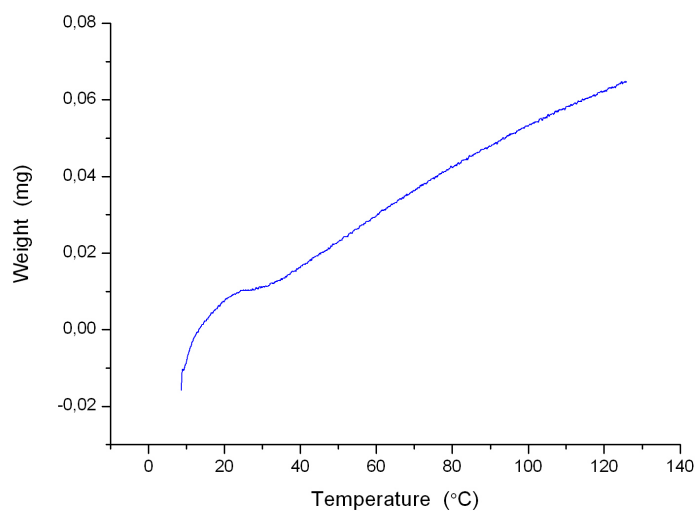
Data collected with each of the four instruments used for experiments have a need to be corrected, either for instrument dependent causes or sample dependent effects. The necessary procedures for each are described below.

4.1.1 TGA

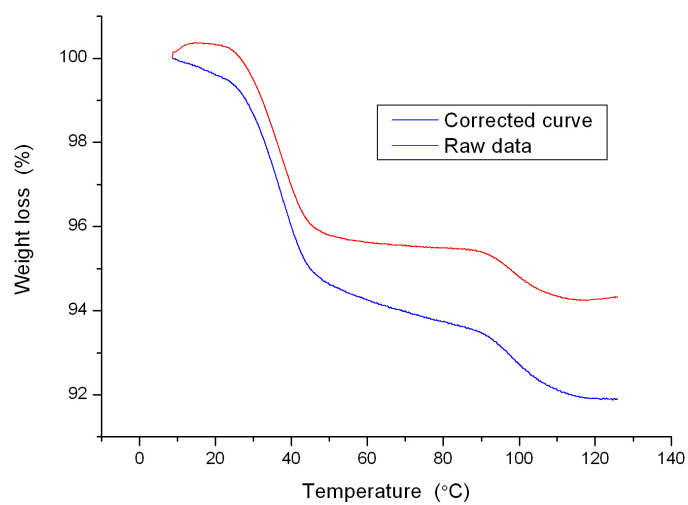
The TGA balance is very sensitive, but is unfortunately also sensitive to sudden temperature changes [58, 59]. Thus an over- or undershoot was observed in transitions between isothermal and dynamic measurements. It turned out to be of vital importance to measure the zeroline of every temperature programme by running a measurement with only an empty crucible. Once the zeroline was determined it was used as a reference and subtracted from the final measurement to establish weight change in the sample.

The difference this made to the current measurements is demonstrated in Fig. 4.1. For continuous heating at a rate of $2^{\circ}\text{C}/\text{min}$ the TGA zeroline is plotted in Fig. 4.1(a). In Fig. 4.1(b) both the raw data and the corrected data for heating of Na-FH are displayed. It is obvious that application of the zeroline makes a vital difference to the registered sample dynamics, and is thus a necessary step to data analysis of any TGA experiment. As the zeroline changed when modifications were made to the temperature programme a reference measurement for each programme was of vital importance.

During heating experiments the start of a dynamic segment was well-defined, but for isothermal measurements in a preheated furnace the data-collection was force-started. Therefore data collection may start some seconds apart. Each parallel measurement was therefore tared to the over-shoot which happened first, to obtain overlapping dynamic patterns. In addition use of zerolines were necessary.



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



(b) Both the raw data and corrected data plotted to illustrate the vital difference.

Figure 4.1: Measured zero line at the TGA during heating at the rate 2°C/min, and the difference the correction procedure made to a measurement.

4.1.2 DSC

All heat flow curves collected by the DSC need to be corrected for two main effects before any attempt at analysis is made, and there are three main possible initiatives which could be made.

Zeroline The linearity of the DSC needs to be checked, by running a test with two similar, empty crucibles to test the thermal behaviour of the instrument. The results are also dependent upon there being small variations between parallel measurements, termed a good repeatability. It is necessary to determine individual zerolines for every applied heating rate, and any large changes in the reactive air supply, as it may effect its thermal capabilities.

As the first part of the correction procedure before analysis the zerolines must be subtracted from the total measured signal from the sample.

Measured zerolines for the most frequent heating rate, 2°C/min are presented in Fig. 4.2. First, three parallel zerolines for the entire temperature procedure are plotted in Fig. 4.2(a). They are close to overlapping, which suggests a good repeatability. Second, an average zeroline for the heating procedure only as a function of temperature is presented in Fig. 4.2(b). As the temperature increases, so also does the heat requirement of the system, gradually levelling out to a linear development.

Sample Size Initial sample size may vary, and should be determined using an external weight. For further comparison all heat flow curves were normalized, and all results are thus given per mg.

Additional “Desmearing” If an even higher accuracy is needed there are more possible steps to the correction process, which are collectively named “desmearing” [61].

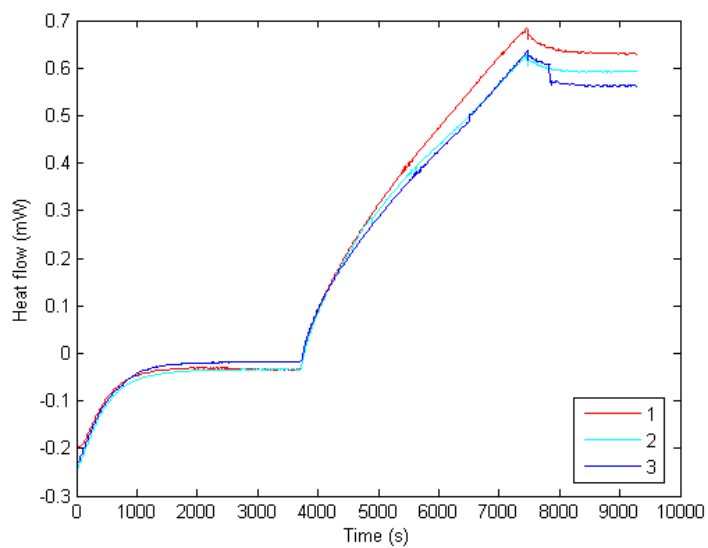
- Linear transformation of the indicated heat flow rates at the abscissa and at the ordinate axis, in compliance with the temperature calibration of the DSC.
- Mathematical elimination, deconvolution, of the influence which heat transport phenomena (heat flow rate relaxation) inside the DSC exert on the measured curve.

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

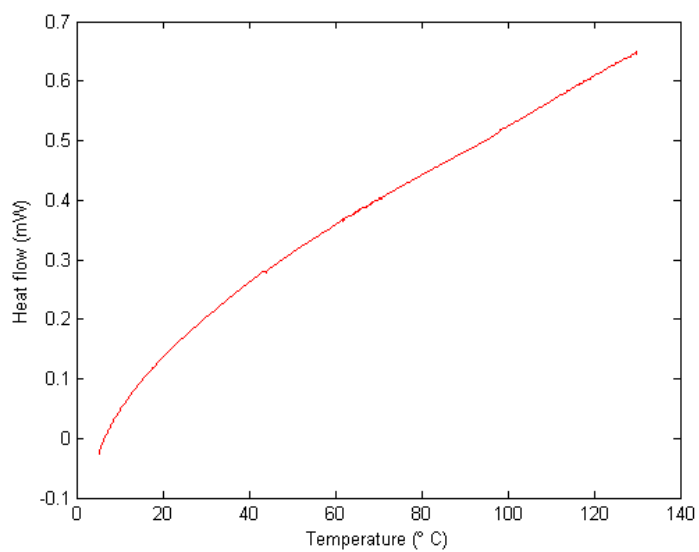
Conversion of Signal If the need arises the ordinate scale may be converted to give a clear picture of other physical properties. First, the specific heat C_p is found by the relation

$$\Delta\Phi_{SR} = (C_S - C_R) \cdot \beta \quad (4.1)$$

Φ_{SR} is the heat flow rate, while β is the heating rate. Further, C_S is specific heat for the sample and C_R is for the reference. The latter is only necessary to provide a correction factor. For common crucible materials the specific heat is known with necessary accuracy. During the current experiments aluminium crucibles were used, with $c_R = 0.897$ J/gK. Also the enthalphy can be found by similar simple calculations [61].



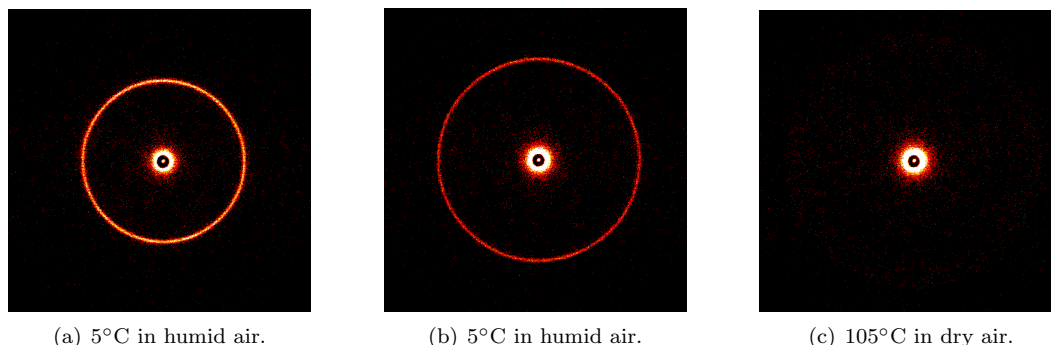
(a) Three parallel measurement of zeroline for the entire temperature procedure.



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

Figure 4.2: Measured zeroline at the DSC during heating at the rate 2°C/min.

4.1.3 WAXS



(a) 5°C in humid air. (b) 5°C in humid air. (c) 105°C in dry air.

Figure 4.3: Examples of scattering pattern during a 15 min WAXS scan of Na-FH at different temperatures.

For scattering patterns from the WAXS setup the different stages of data collection is described briefly below, plus the procedure for correction of the experimental data, dependent on both limits set by setup and sample.

Nanography A fast scan to locate the sample and determine the position for collecting data.

Scans To detect enough information for analysis each position is held for 15 min, giving a gfrm-file as output. Examples are plotted in Fig. 4.3 for different temperatures.

Data Frame All collected data are stored as pixel frames, identified by its scan number. The current temperature was monitored manually on the PID-controller and written in the lab journal.

Automatic Corrections The SAXS software contains an integrated function called *unwarp*, for necessary corrections of the detected raw data, caused by properties of the system. It rectifies for the lack of curvature in the detector, and different pixel sensitivity [66].

Integration All data were radially integrated with respect to conic line segments, using a function in the SAXS software called *bin normalisation*, which includes simultaneous *radial normalisation*. As the circular scattering pattern is detected the intensity at a scattering angle 2θ is necessarily proportional to the circumference of the conic segment. Thus each conic segment is basically divided by $\sin 2\theta$.

Data Corrections and Peak Fitting

A specific Matlab program for data corrections and peak fitting of integrated x-ray scattering data, detecting Bragg peaks from Na-FH was developed by Lars Ramstad Alme. For the current experiments these files were essentially used in their initial form, as seen in [16, 17]. The following section briefly describes the essential elements during the data correction.

Background Subtraction A contribution of small angle scattering is expected, caused by air in the capillary tube, the varying amount of water found in mesopores throughout the sample, the capillary glass or even the sample holder. Normally the intensity of this background scattering will decrease with an increase in the scattering angle 2θ , and can be successfully fitted with a power law. Thus, for each frame the background is fitted by a power law and subtracted, removing unwanted noise.

Layer Structure Factor and Polarisation Factor Corrections The scattered intensity has several contributions, consisting of the layer structure factor, the Lorents polarisation factor and

the interference function. The dynamics of water in the sample is reflected in the dynamics of the interference function, as it is directly associated with the layer spacing through Eq. 2.17. To extract the interference function the integrated, normalized and background subtracted data are divided by the the product of the layer structure factor $G(\theta)$ and the Lorentz polarisation factor L_p , as all expressed as a function of the scattering angle 2θ in Eq. 2.21

The exponent ν in Eq. 2.20 is related to the number of crystallites favourably oriented for diffraction and accepted into the detector at a given Bragg angle. For natural clays and for finite resolution measurements the correct value of ν is unknown. At most one can say ν is between 0 and 1, the two perfect situations [43]. Previously ν is estimated for the Na-FH 0WL and 1WL hydration state to $\nu = 0.94$ and $\nu = 0.98$, respectively [6]. Hence an average value of $\nu = 0.96$ is chosen for corrections of the current data [16].

Peak Fitting To further evaluate the scattering pattern, consisting of the purified, extracted interference function, it is necessary to fit the observed Bragg peaks to achieve a quantification of the data. As mentioned the interference function is directly related to the layer spacing, and as a greater number of water molecules are intercalated in the dynamic transition from 1WL to 2WL state the layer spacing will increase and by Braggs law move the Debye-Scherrer cone to lower scattering angles. During the transition scattering appear between the expected Bragg peak positions, which is a well known characteristic of mixed intercalation, or random layer spacing, known by the term Hendricks-Teller scattering, further discussed in Sec. 2.6.

To determine the area of the main Bragg peaks they are fitted using a pseudo-Voigt peak function, with main parameters being the shape factor η , peak position q_c and peak width Γ as described by Eq. 2.24. The goodness of fit largely depends on the angular interval chosen for the fitting. For a symmetric, well defined peak it would be preferred to fit across the entire peak interval. However, at different stages of a transition from one water layer state to another the pure Bragg peaks are developing a asymmetrical peak shoulder on the same side as the mixed intercalation region. For a slight peak displacement caused by some degree of dynamic transition to another water layer state it seems better to fit the peak from the side which is less affected. Hence for a 1WL peak moving towards a 2WL state the fitting is started from the right side, and for the reverse situation the fitting is started from left.

Evaluation To extract information from the scattering data it is normal to plot the extracted interference function as a function of the scattering angle 2θ at different temperatures to observe the overall trend. But by fitting Bragg peaks with a pseudo-Voigt function it is possible to estimate the fraction of the sample currently being in any hydration state. It is done by normalising the fitted area of an experimental Bragg peak to the area of a perfectly symmetrical Bragg peak of the hydration state under investigation.

4.1.4 PLS

Output from the one-dimensional detector was a text-file detailing the intensity as a function of the scattering vector q , plus the calculated statistical counting error inherent to the detector. Background subtraction and data corrections was made by utilizing the Matlab program made for WAXS data, only changing the Lorentz polarisation factor according to Eq. 2.15. But the datasets did not contain enough point measurments to attempt a fit with the pseudo-Voigtan distribution. Thus approximations and further data analysis was achieved using the software *Origin*.

4.2 Heating

This section provides results and discussion on heating of Na-FH using both TGA, DSC¹ and WAXS. First, a general analysis is made to introduce the data and the terms used to describe them. Second, curves collected with the different techniques are presented and discussed in terms of each instruments performance. Next, the WAXS experiment is evaluated separately, as it was of limited success. The extracted numerical information are then presented, compared and discussed, and finally summarised.

The main objective for investigating the dynamics of Na-FH was to see the effect of different heating procedures and gather complementary information to create a more complete picture of its behaviour. In addition a thorough discussion on the different instruments properties seemed necessary.

4.2.1 General Analysis

To define the terms used during further presentation and analysis of data from the heating procedures Fig. 4.4 is included. Based on common knowledge about heat flow and weight loss curves a general analysis is made [28, 33, 61, 73].

As an endotherm peak is generally attributed to a first-order transition consuming energy, the 1st and 2nd endotherm peak was assumed to represent the 2WL to 1WL transition and the 1WL to 0WL transition respectively, as both were expected to occur in the temperature interval 5 to 130°C, and these are the two main endotherms registered. The weight loss curve showed a fast loss during the 1st step² almost overlapping with the 2nd endotherm, leading to believe evaporation from micropores happens has a rather small time constant.

The 3rd endotherm started approximately at 100°C simultaneously with the 2nd weight loss step, giving the assumption that different diffusion principles dominated when the sample reached the boiling point of water.

The intervening baseline between endotherms show a close to linearly increasing heat demand. Simultaneously a slow, steady weight loss was observed, which has been generally attributed to evaporation of water from mesopores [59, 58] which has a larger time constant than what was observed for micropores.

4.2.2 Results Using the TGA

Three different heating rates were implemented at the TGA, giving weight loss curves as a function of sample temperature T_s . Most extracted numerical information is presented in Tabs. 4.2 and 4.3 in Sec. 4.2.5.

Two main points are focused on during the presentation. Quality of the data and development of the sample temperature T_s compared to the reference temperature T_r set by the software.

Continuous Heating at Rate 2°C/min

Heating at a continuous rate of 2°C/min gave the weight loss curves presented in Fig. 4.5. Four parallel measurements were run, which all showed similar characteristics. The total weight loss was found to differ about 0.25%, a quite good repeatability for weight loss curves. Any deviations

¹Most of these results are presented earlier in [1], but repeated for comparison and discussion.

²The weight loss steps are named differently than the heat flow endotherms because of earlier work on the TGA, where the dynamics below room temperature was not investigated [56, 59, 58].

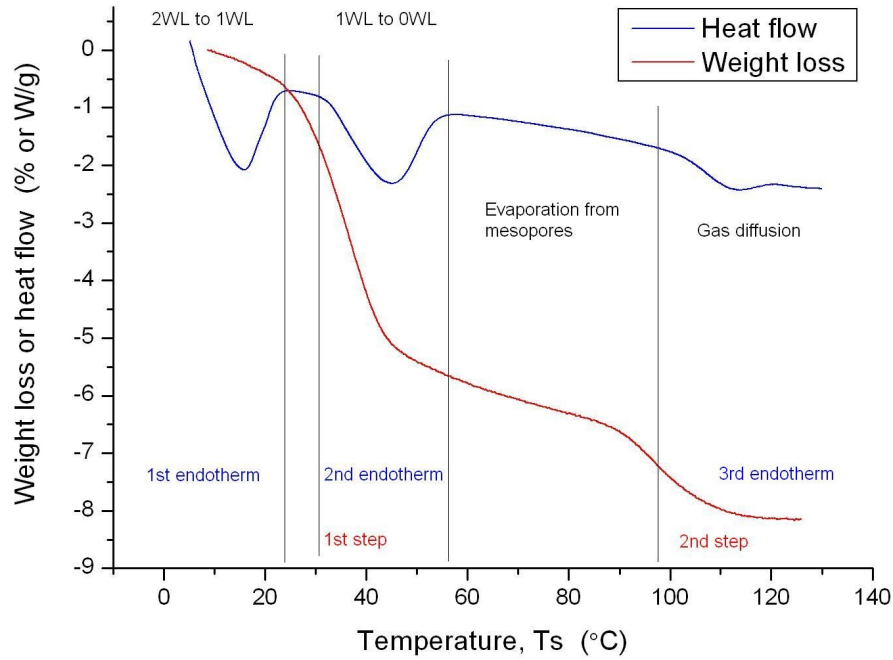


Figure 4.4: General comparison of heat flow and weight loss curves collected at the rate $2^{\circ}\text{C}/\text{min}$. The heat flow curve was here divided into parts to mark the dominant event in the relevant temperature interval, and as a heat flow curve should correspond to the differentiated weight loss curves it also reveals that the dynamics contained in the weight loss curve was not completely overlapping. At the bottom terms used to describe each curve was defined, 1st & 2nd endotherm was relevant for the heat flow curve and 1st & 2nd step for the weight loss curve.

could have three main potential causes. First, the local atmosphere may have varied, despite attempts to control the reactive air inlet. Second, when using powder samples packing effects are found to influence the measurements [33]. Finally, the TGA and its setup could have caused deviations.

Time-dependent development of T_s in comparison to the T_r during the entire temperature programme is presented in Fig. 4.6, and seems reasonable taking Newton's law of heat conduction into account³. But the thermostat settings seemed to affect the furnace performance, as the difference $T_r - T_s = \Delta T_{rs}$ when starting the heating procedure was -3.7°C , while at the end $\Delta T_{rs} = 4.0^{\circ}\text{C}$.

As proposed in Sec. 3.2.3 a differentiated weight loss curve should essentially give the same qualitative information as a heat flow curve collected at the DSC. Thus the derivative of data in Fig. 4.5 is presented in Fig. 4.7 for comparison with DSC data collected at the same rate.

³The rate of heat transfer is proportional to the difference in temperature between the body and its surroundings, and will in most cases have the general shape $f(x) = 1 - e^{-x}$ [32].

Continuous Heating at Rate 10°C/min

Also heating of Na-FH at rate 10°C/min showed good repeatability between samples, as presented in Fig. 4.8. Deviations from expected temperatures were also observed now, with $\Delta T_{rs} = -4.3^\circ\text{C}$ and 0.8°C at the start and end, respectively.

Step Heating

Fig. 4.9 shows the absolute weight loss during step heating of Na-FH powder, including standard deviations, estimated for the last 10 min of each isotherm. These were used as a measure of how stable the sample weight had become. All seemed insignificant, except at 45°C and 100°C , where the temperature should have been held stable for a longer time to reach equilibrium.

The experiment was implemented once, but in addition one test run was made. It was established that some isotherms needed to be longer than one hour, to reach a more stable condition, namely at 17°C , 20°C , 25°C , 90°C and 95°C . The test was also used to check the temperature capability of the TGA. As seen in Fig. 4.10 the desired reference temperature was usually not achieved. Here $\Delta T_{rs} = -2.5^\circ\text{C}$ in the beginning and $\Delta T_{rs} = 5.4^\circ\text{C}$ at the end of the heating procedure. It was discovered that main cause for this deviation was the current temperature setting of the circulating water baths. For experiments below room temperature there were always two in use. The one cooling the furnace was set at 2°C . It turned out that if the setting was changed it effected the entire measurement, as the furnace heating system was not sensitive enough to tolerate such external disturbance.

The TGA was originally not designed for measurements below room temperature, but because of the need to investigate the dynamics of Na-FH down to 5°C new software was made especially for our research group [59]. As the TGA balance cell functions optimally if held at 22°C [74] the second water bath was held at 22°C . But as the units are not thermally isolated, the balance system could also be affected by temperature changes.

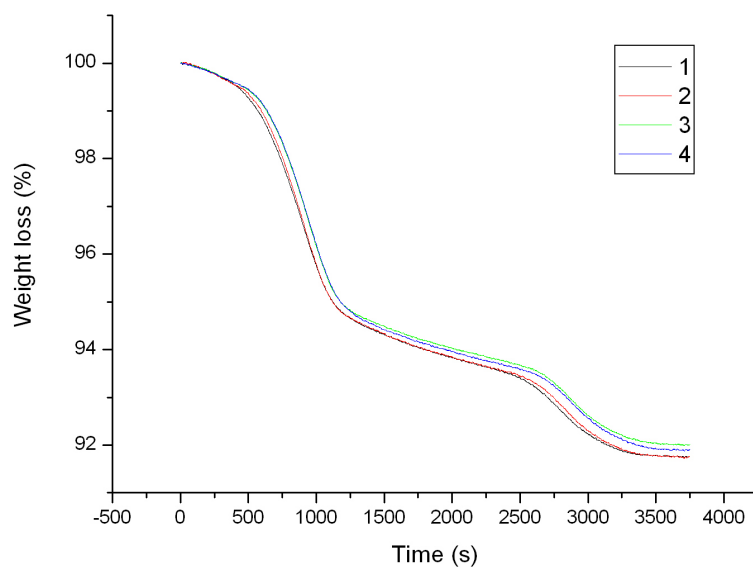


Figure 4.5: Weight loss curves taken at heat rate $2^{\circ}\text{C}/\text{min}$, corrected using zero lines.

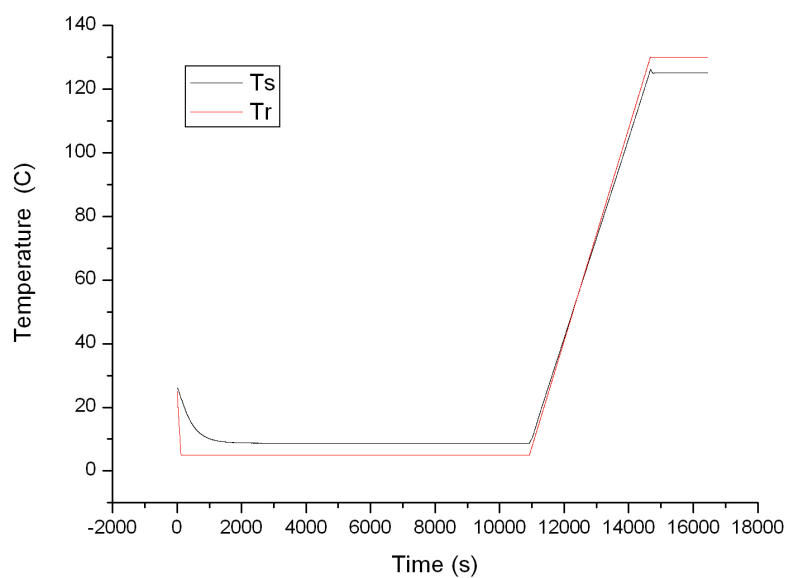


Figure 4.6: Sample temperature development as a function of time during continuous heating at the rate $2^{\circ}\text{C}/\text{min}$.

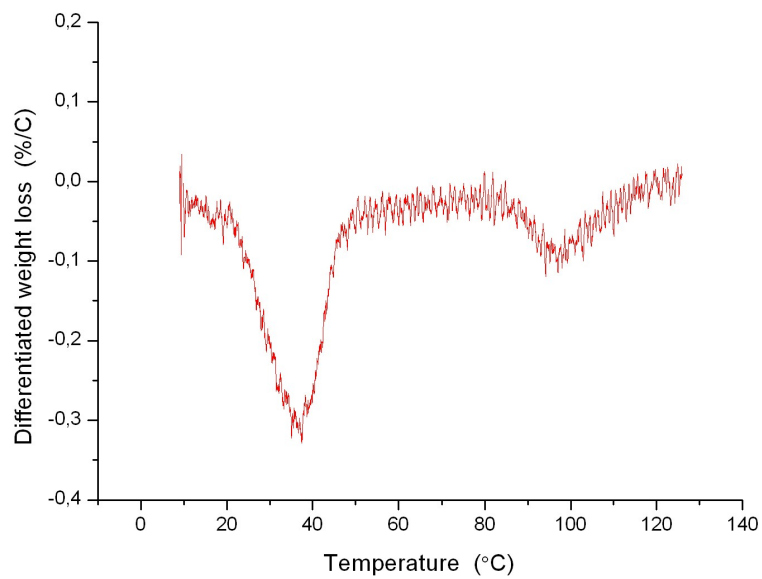


Figure 4.7: Differentiated weight loss curve, based on Fig. 4.5.

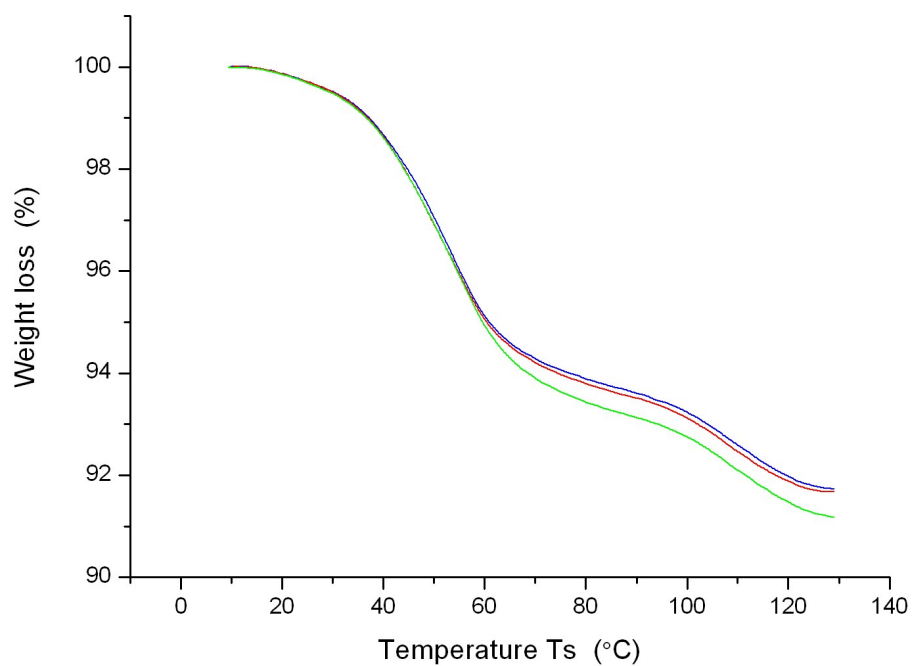


Figure 4.8: Weight loss during continuous heating at rate 10°C/min, where three parallel measurements all show similar characteristics.

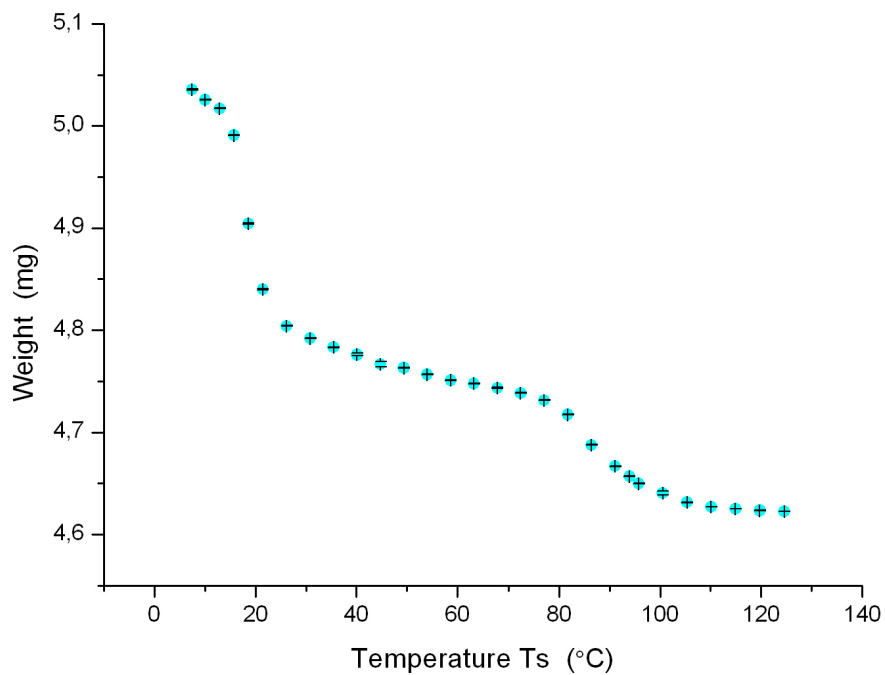


Figure 4.9: Weight loss for Na-FH during step heating, with standard deviations to quantify how stable the sample weight was at the end of each step.

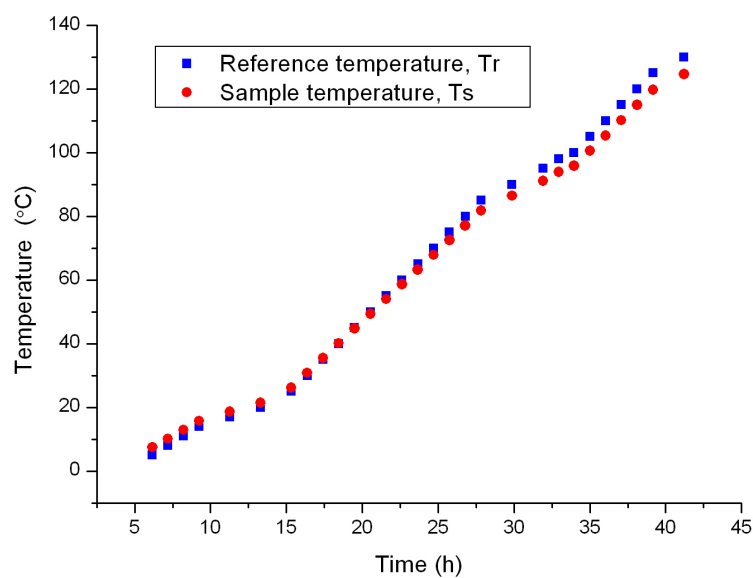


Figure 4.10: Sample- and reference temperature development during step heating of Na-FH at the TGA.

4.2.3 Results Using the DSC

Also at the DSC three different heating rates were implemented, which gave heat flow curves as a function of sample temperature T_s . All numerical information mentioned in the text is also given in Tab. 4.3 at p. 70.

Continuous Heating at Rate 2°C/min

The dynamics of Na-FH was investigated in terms of heat flow at heating rate 2°C/min, implemented with two different reactive air volumes to see if it affected the pace of the dynamics. This was only done with the DSC, as it has a higher tolerance than the TGA, which is 80 ml/min as opposed to 50 ml/min [60, 57]. All parallel measurements are plotted in Figs. 4.11 and 4.12 for 50 ml/min and 87 ml/min respectively, normalised for weight. They were collected successively, and for all parallels labelled *new*, a new sample volume was introduced.

First, 1st endotherm varies greatly in both area and temperature interval. As it was assumed to represent the 2WL to 1WL transition, it seems that the preceding procedure to ensure a 2WL hydration state at 5°C was of limited success. But it has also been suggested that water molecules constituting the 2WL state are relatively loosely held [18], which could be a reason for the differing amount of work it took to remove them.

Second, the shoulder inbetween the two main endotherms was of varying width. As the 2nd endotherm always started at approximately the same temperature, it was assumed to mean that it took different amount of time before the first transition was completed. It is suggested that the shoulder signifies a quite stable temporary 1WL hydration state.

Next, area and shape of the 2nd endotherm were approximately homogeneous, confirmed by the calculated heat of transition which had a small standard deviation, see Tab. 4.3. As the 1WL hydration state is considered relatively thermally stable [18] it seems the diffusion pattern at this stage was well-defined, which gave an identical transition with a constant consumption of energy.

A stabile, increasing heat demand was observed by means of the baseline, in a wide shoulder above 100°C, where evaporation of water from mesopores was expected [58, 59]. The slope however varies, but it was interesting that two successive measurements of the same sample held about the same baseline slope. Thus, any difference in the slope between the samples could be caused by surface and packing effects, giving different mesoporosity for each sample and hence a varying energy demand.

Finally, when the sample approached 100°C the baseline slope invariably changed to reveal an asymmetric 3rd endotherm. The cause was assumed to be a change in the diffusion pattern occuring as the state of water is dominated by gas instead of liquid.

Pace of Dynamics Position of the 1st endotherm peak was somewhat tentative, as both area and shape varies, but the transition was generally accomplished before 24°C and 21°C for 50 ml/min and 87 ml/min respectively. A look at the 2nd endotherm peak revealed more distinct pattern. At 50 ml/min the peak occurred between 31 and 58°C, with peak position at 45°C. While with volume flow 87 ml/min it was located at 30 - 56°C with its bottom at 44°C. Thus it seems the dynamics were somewhat faster when implementing a larger air volume. But the heat flow curve showed the same characteristic pattern, giving the impression that what occurred was only more effective transportation out of humidity.

Fig. 4.13 presents the average dynamics for both pump volumes. When comparing the relevant temperature intervals for each of the transitions the variations are not large, if taking inherent uncertainty for both sample dynamics and relative humidity into account. Thus during presentation of the overall results the outer most limits of each range were used.

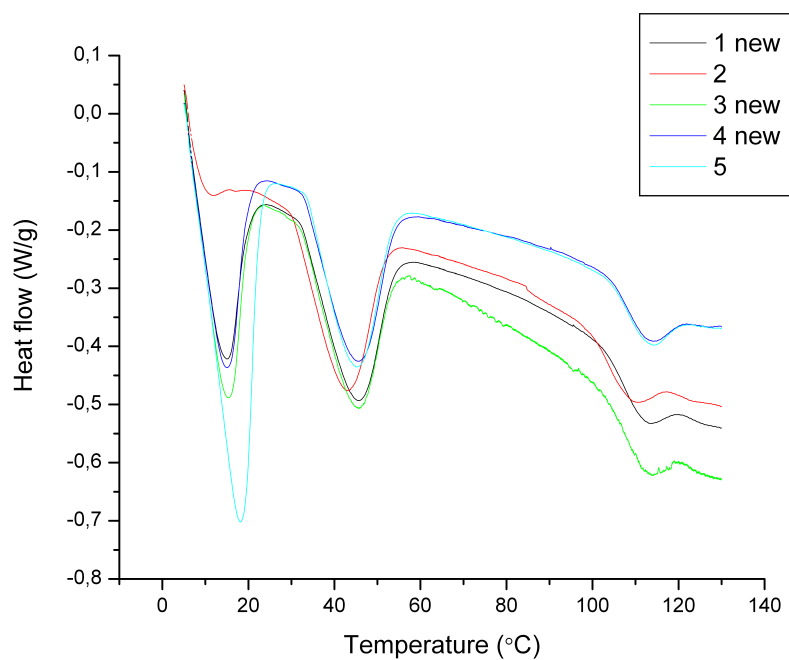


Figure 4.11: Corrected heat flow curves for dehydration of Na-FH at rate 2°C/min and pump volume 50 ml/min.

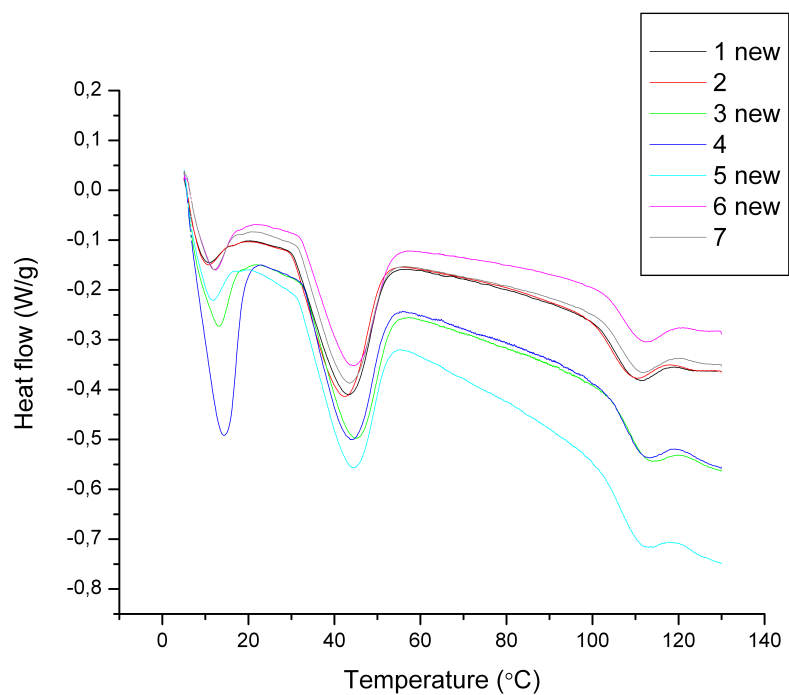


Figure 4.12: Corrected heat flow curves for dehydration of Na-FH at rate 2°C/min and pump volume 87 ml/min.

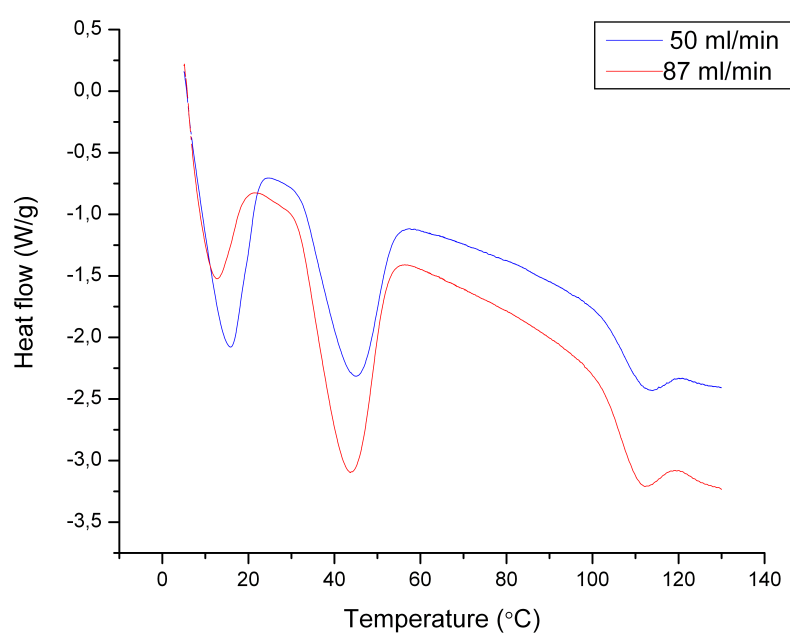


Figure 4.13: Average heat flow for the dynamics of Na-FH powder at heat rate 2°C/min, collected at the DSC with two different volume flows of reactive air.

Continuous Heating at Rate 10°C/min

Also heating at a rate of 10°C/min was attempted, where the resulting heat flow curves are presented in Fig. 4.14. But these curves do not show a great degree of conformity. A comparison with data taken at 2°C/min show that run 3 and 4 showed most correspondance to the characteristic curve for Na-FH. These have three main endotherms. The second peak was centered at about 57°C, which was about 12°C higher than previously observed. It seemed correct, as also weight loss data collected at the same heating rate cause slower dynamics than at 2°C/min.

But the four other parallel measurements have a number of irregular peaks, raising the question why the repeatability for Na-FH powder samples at the DSC was now poor. All parallels of weight loss data presented in Fig. 4.8 showed similar characteristic shape, thus the DSC itself seemed responsible for the deviations, not the sample dynamics. The DSC is designed to handle far greater heating rates [60], hence the cause was assumed to be collection of these particular data. It is suggested that the sample size was too small, or that the DSC was unable to keep the same heating rate for the influx air temperature as for the main sample, thus affecting the sample surface.

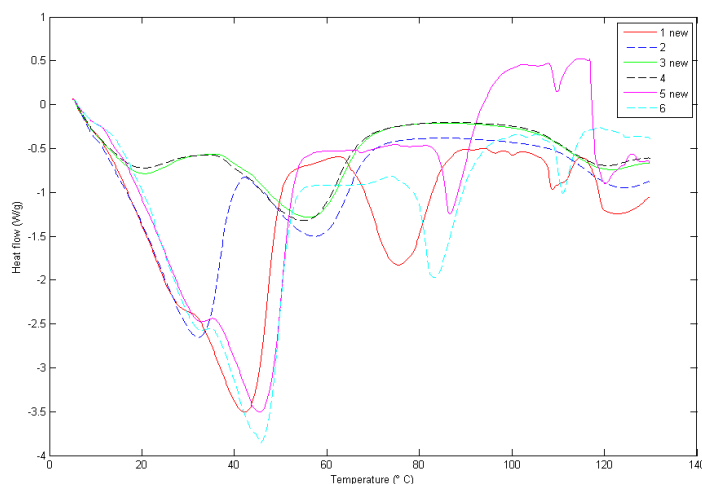


Figure 4.14: Heat flow curve during heating at rate 10°C/min, with pump volume 87 ml/min.

Step Heating

An attempt at step heating of Na-FH at the DSC was made, but it was concluded that the method not was suitable for observing the dynamic transitions between hydration states. The results are presented in Fig. 4.15, and it basically plots the interpolated baseline for a dynamic experiment. Any deviations from the outlined curvature, was assumed to be caused by the sample not being in equilibrium at the end of the specific isotherm. A trend which was confirmed by the fact that most of these point measurements had larger standard deviations.

A look at the heat flow pattern during an isothermal measurement revealed that at a temperature step the necessary energy was supplied both to heat the sample and for any part of a first-order transition taking place. As the temperature was held stable, the transition would come to an equilibrium, as the heat flow evened out to a level corresponding to the current specific heat. The latter is detected by a change in the baseline, as was confirmed by measurements.

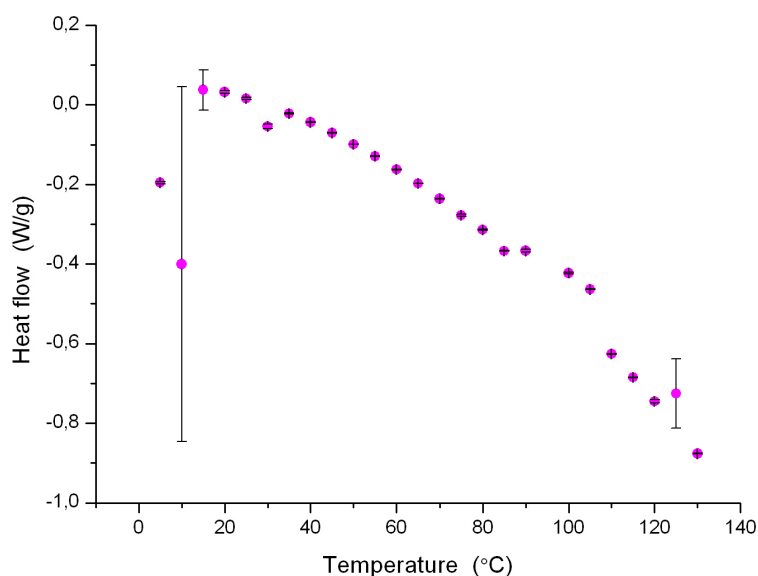


Figure 4.15: Heat flow during step heating of Na-FH. The data are not corrected for zero line.

4.2.4 Result and Discussion of WAXS Data

In comparison to similar experiments performed earlier⁴ [31] on Na-FH powder, the main goal was to investigate the water content in micropores at temperatures below 25°C, and confirm the acknowledged results at higher temperatures also for this particular delivery of Na-FH.

The collected data are presented in two different fashions. First, in Fig. 4.16 in terms of the fraction of sample observed in each of the three different hydration states, as a function of temperature. Second, in Fig. 4.17 as a selection of the corrected diffraction patterns at different temperatures are plotted as a function of the scattering angle 2θ . The results are summarized in Tab. 4.1, which gives the main temperature interval where a significant fraction of the sample was observed in each hydration state.

Upper part of Fig. 4.16 indicates the interlayer hydration state at different temperatures. Several 15 min scans were taken during each isotherm, thus the level of structural equilibrium can be approximated by looking at the degree of overlap between measurements. At each temperature the conditions were held stable for 1-2 hours. In most cases it seemed long enough, except below 25°C, where there the structure seemed to change greatly.

A 2WL hydration state was only found in a short interval, below 11°C. It was peculiar that the 1WL state was only observed in a significant fraction of the sample below 25°C, as earlier [31] the similar interval was between 25°C and 40°C. In the large temperature interval 25 - 100°C a right-shifted low intensity peak was seen, signaling a slightly lower layer spacing than what was expected of a 1WL state. The diffraction pattern did not change considerably until 100°C was reached, when an indication of a 2WL peak appeared. The latter is not visible in Fig. 4.17 because of its low intensity compared to other data, but an individual plot is included as Fig. 4.18. It verifies that a transitional peak with a left hand shoulder was seen, rather than a symmetrical 2WL Bragg peak. Thus the Pseudo-Voigtan fit was of limited success, as also illustrated in Fig. 4.18. The situation was similar for the indication of a 2WL peak observed at low temperatures, but with a right hand shoulder instead. Thus no numerical value for the interlayer distance d was calculated for neither 0WL or 2WL hydration states, as both seemed to be representing a dynamical state rather than a stable condition.

A humidity probe was placed directly above the sample, continuously collecting temperature and humidity data by use of a LabVIEW program. These are plotted for the entire experiment in the lower part of Fig. 4.16. The humidity was low at all times, as the air dried out because of the high temperatures, discussed at p. 71. Manual comparison confirmed a good correspondance between air temperature and the current sample temperature, defined by the copper holder.

As the current results did not corroborate earlier observations on layer distance as a function of temperature [31] and do not back up the macroscopical data on heating of Na-FH (see further discussion on p. 66) it indicates that the implementation of the experiment was not successful. The identical setup has been used for extensive mapping of layer spacing as a function of relative humidity at 15°C [17], and no major changes were made. There were no obvious reasons for this deviation. It seems as though the air flow was too high, flushing water out of the sample, or in spite of the simple setup change, it was not suited for this application.

⁴Experimental setup was similar, although it is not specified if air was run in a closed loop, as opposed the current open one. It could cause differences in the achieved relative humidity. And the samples used were pressed and dried-out, in distinction to the current powder sample.

Table 4.1: Temperature intervals where a significant part of the sample was observed in a given hydration state during WAXS experiments.

Hydration state	Main temperature interval °C	2θ °	d Å
2WL	5-8	No symmetric peak	
1WL	11-20 (100)	7.1	12.4
0WL	100-105	No symmetric peak	

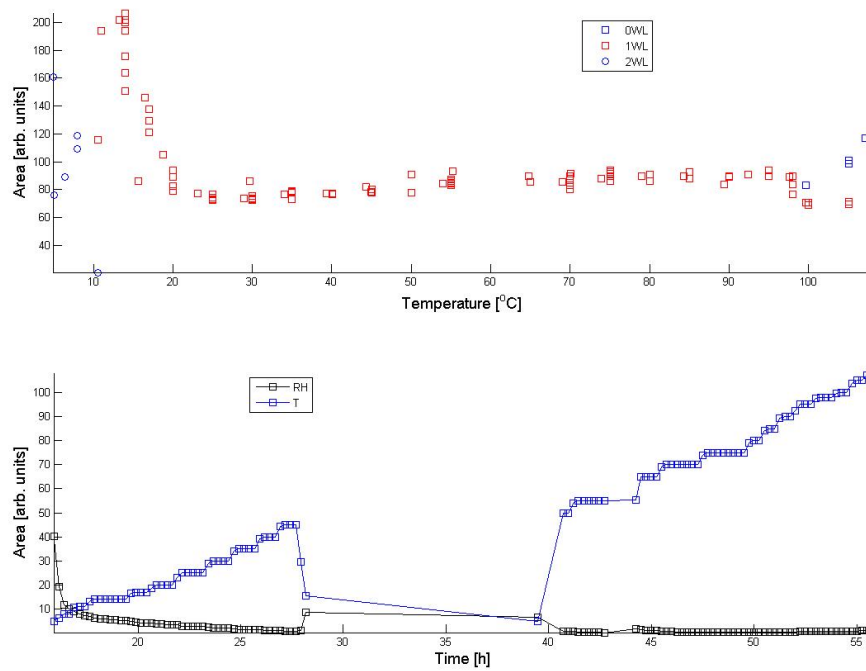


Figure 4.16: Main result from the WAXS experiment on heating of Na-FH powder. Upper plot: Fraction of the sample being in the three different hydration states are marked. Lower plot: Temperature and humidity registered directly above the sample. The experiment was interrupted at 50°C but restarted after some hours.

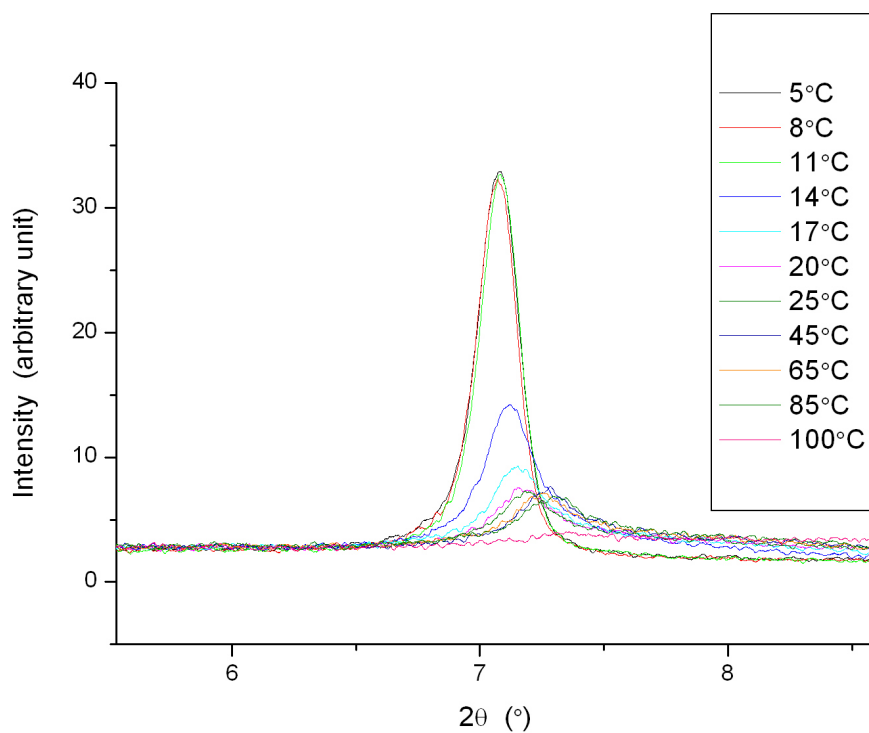


Figure 4.17: Intensity as a function of scattering angle 2θ for scans at different temperatures. A 1WL Bragg peak was seen at 5°C gradually disappearing as the temperature increases, simultaneously a right shoulder was growing, indicating random intercalation. But no definite transition to a 2WL state was observed when the measurements are terminated at 100°C.

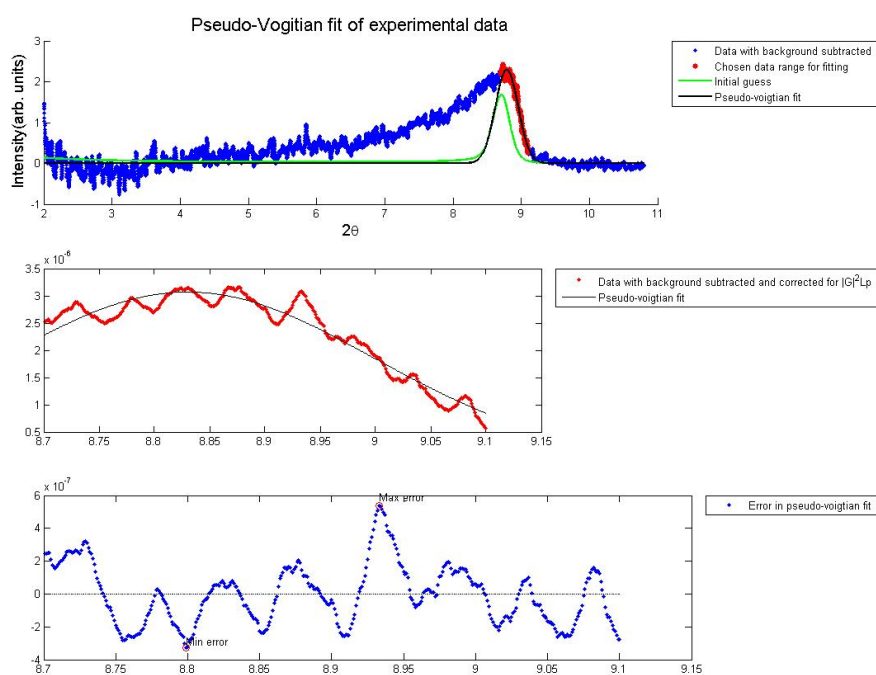


Figure 4.18: Graphic output from the Matlab correction program for a scan at 105°C during WAXS scattering. First the Pseudo-Voigtian fit to indication of a 2WL Bragg peak. Second, details of the fit, and finally an illustration of the degree of fit.

4.2.5 Data Analysis and Discussion

Assembling data collected during both continuous- and step heating of Na-FH presented in Figs. 4.5, 4.7 and 4.9 results in Tabs. 4.2 and 4.3. These give numerical information on the weight loss steps and endotherms in the heat flow curves respectively. In addition Fig. 4.19 plots the relative weight loss during both continuous- and step heating for a graphic presentation. Three of the included experiments were deemed unsuccessful or unsuited for their intended purpose, and are not included in the discussion. For details please see p. 60, p. 61 and p. 62 for heating rate 10°C/min at the DSC, step heating using the DSC and WAXS experiments respectively.

Table 4.2: Relative weight loss detected for Na-FH powder at the TGA.

<i>Method</i>	1st step		2nd step		Total loss
	Weight loss %	Temp. interval °C	Weight loss %	Temp. interval °C	%
Step heating	4.5	13-40	2.0	77-105	8.2
Heating 2°C/min	4.8	21-46	1.5	86-110	8.2
Heating 10°C/min	5.0	34-65	1.8	95-125	8.3

When looking at heat flow curves versus weight loss curves an endotherm represents a dynamic transition in the sample, synchronously with a weight loss registered by the TGA, as demonstrated in Fig. 4.4 for the collected data. At the endotherm peak a main fraction of the sample should have undergone the transition under investigation.

1st Endotherm The heat flow curves in Figs. 4.11 and 4.12 showed both varying temperature interval and area for the 1st endotherm peak. If the peak does signify the transition from 2WL to 1WL hydration states, it suggests that the area is dependent on how large fraction of the sample has achieved the initial transition to 2WL during the 5° isotherm in humid air.

The 1st endotherm is not distinct when differentiating the weight loss curve collected at 2°C/min. During measurements at the TGA 5°C was never achieved, because of limits set by the cooling system. Rather the sample was kept stable at $\sim 8.5^\circ\text{C}$. Thus a clean 2WL state could not be expected, and this was supposedly the reason for no visible endotherm. Below 20°C a slow stable weight loss was instead observed, which could be a remnant of the transition or evaporation of water from mesopores.

2nd Endotherm / 1st Step By comparison of temperature intervals for the 2nd endotherm given in Tab. 4.3 with the 1st weight loss step in Tab. 4.2 it seems the weight loss was registered at slightly lower temperatures than the endotherm. But taking expected experimental deviations in the implementation procedures into account it seemed the phenomena were matching.

Analysis of heat flow curves showed that the heat of transition was remarkably stable, indicating that the 1WL to 0WL transition occurs in a similar fashion for all Na-FH samples.

The current WAXS experiments were deemed unsuccessful, but comparison with a similar step heating procedure by daSilva et al. [31] reveals that a 1WL hydration state was observed in a significant fraction of the sample in the narrow temperature interval 25 to 40°C. Though intensity at the 1WL peak position was detected in the entire temperature interval 5 to 125°C. Step heating at the TGA placed the 1WL to 0WL transition at 13 to 40°C, which indicates a good corroboration. Useful data from step heating at the DSC could not be extracted, but continuous heating at 2°C/min show that a main fraction of the sample has achieved the transition by 45°C.

At a slower heating rate the peak position should have been shifted further downwards, in good agreement with the other data.

The Na-FH sample investigated in [31] was dried-out and pressed, in contrast to the powder samples investigated currently. But looking at the dehydration pattern of powder versus pressed sediment samples using TGA [58, 59] the same amount of weight loss was registered, although the dynamics are somewhat slower using sedimented samples over Na-FH powder. The most significant weight loss, 7.5%, was observed from 25 - 50°C (until 65°C for sedimented samples) thus a general parallel to [31] should still give correct conclusions.

In total it seems both macroscopic and microscopic data verify that the dynamic transition from 1WL to 0WL hydration state was recognised by all the three techniques, which does give complementing information. Thus continuous heating at rate of 2°C/min indicated the 1WL to 0WL transition occurred in the main temperature interval 22 - 56°C, when 4.8% of the weight was lost, consuming about 3.39 W °C/g.

3rd Endotherm / 2nd Step Both are found to start at about 100°C, implying that water was evaporating by an energy consuming process as the diffusion pattern changes as one reaches the boiling point of liquid water. This assumed change could be confirmed by use of kinetic analysis, as described in Sec. 4.3.

Evaporation from Mesopores / Change of Specific Heat The slow weight change seen from 40°C to 90°C was earlier found to be caused by evaporation from mesopores [58]. In the current DSC curves, Fig. 4.13 it was registered as a linearly increasing energy demand, signifying a change in specific heat. But probably the reaction was more complex than that, because as seen by X-ray scattering [31] intensity on the 1WL peak position was observed also in this temperature interval. From 70°C the 0WL state dominated, but the 1WL peak position gradually shifted left signifying a gradually decreasing basal spacing. It means that the transition was never complete, and 1WL will to some degree coexist with the 0WL hydration state also at higher temperatures. Thus the hydration state of the sample changes, simultaneously with evaporation of water from mesopores.

The phenomenon Hendricks-Teller random intercalation can account for two hydration states being present at the same temperature, although many details concerning the theory are still not adequately understood. It is further discussed, for observation of a humidity gradient in Na-FH in Sec. 4.4.

Effect of Heating Rate The other matter investigated was the effect of different heating rates on the sample dynamics. Step heating yielded a more rapid dynamics, but with the same characteristic pattern and an identical total weight loss, as shown in Fig. 4.19 and quantized in Tab. 4.2. As the sample has time to reach equilibrium at each step, it is suggested that all available water in mesopores was lost at each step, instead of continuously.

Likewise, the heating rate 10°C/min slowed the dynamics down, postponing the 1st step to the range 34 - 65°C. Thus it was obvious that the heating rate was of great importance for the dynamics of Na-FH, as the temperature ranges shift for each weight step. Similar phenomena should have been recognised by heat flow curves, but no successful measurements at other rates than 2°C/min were accomplished during this work. However, each clay has a characteristic heat flow curve, which can be used for identification [75]. But when changing the heating rate one generally expects a temperature shift of the peak placement. For other clay minerals a shift of up to 100°C is observed when implementing both 0.5°C/min and 10°C/min⁵ [75].

It seemed interaction between mesopores and micropores were a deciding factor during the dehy-

⁵For measurements made on a larger temperature interval than currently.

dration process. For step heating the mesoporosity had time to reach equilibrium, thus making the pattern more precise. At a faster rate the reaction in micropores needed time before being observable. For crystalline swelling it has been observed that it seems a the surrounding vapor concentration must reach a critical value before a structural change happens [51]. It seems a corresponding phenomena takes place during the dehydration process, as some water must evaporate from mesopores before the interlayer transition starts. A number of interlayer forces controls the structural dynamics, as described in Sec. 2.1.1, but the mesopores may help to control the pace.

An identical total amount of water was lost during the three procedures, thus the heating rate did not effect the final result and the recent thermal history did not seem important. During similar heating procedures starting at 25°C a total weight loss of about 7% was registered [59], thus some water was gained by the sample during the 5°C isotherm, even if the 2WL to 1WL transition was not distinct in the differentiated signal.

As heating rate does indeed effect the dynamic pattern during diffusion, a cause for deviations arises from use of the thermostat at the TGA. As seen in Figs. 4.6 and 4.10 the sample temperature can not be counted on to always agree with the given reference temperature. A linear fit to T_s show that the samples were actually heated at the rates 1.88°C/min and 9.68°C/min, instead of 2°C/min and 10°C/min, respectively. In comparison the DSC, which achieves a perfect fit, it could cause a small difference, and be one of the reasons for not seeing a perfect correspondance between endotherms and weight loss steps.

Effect of Volume Flow For DSC curves the effect of higher reactive air flow was a slight shift in dynamics to lower temperatures. This effect was not tested on the TGA, as the balance is sensitive to air flow and maximum volume is set by the producer to ~50 ml/min, versus a limit of about 80 ml/min when using the DSC.

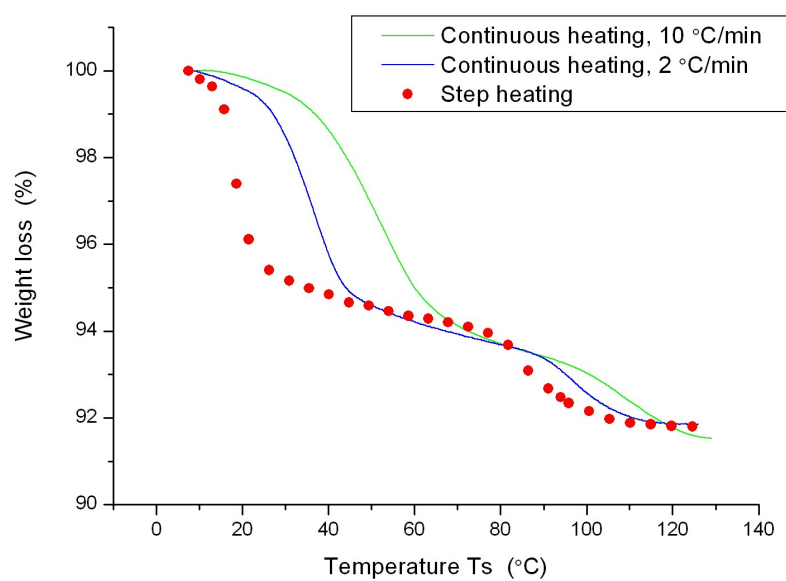


Figure 4.19: Comparing weight loss curves for step heating and continuous heating at rate 2°C/min and 10°C/min. Pace of the dynamics was faster for slower heating rates, but the total weight loss was similar.

Table 4.3: Peak temperature and temperature interval for the different observed endotherms in heat flow curves.

<i>Method</i>	1st endotherm		2nd endotherm		Heat of transition W °C/g
	Peak temp. °C	Temp. interval °C	Peak temp. °C	Temp. interval °C	
<i>DSC</i>					
	Heating 2°C/min, 50 ml/min	15.9	5.0-24.5	45.0	3.39 ± 0.12
	Heating 2°C/min, 87 ml/min	12.2	5.0-21.2	44.3	3.18 ± 0.19
<i>TGA</i>					
Differentiated signal, 2°C/min		Not distinct	38	20-52	

Remarks Thermal analysis of clay involves some inherent problems. Mainly there was no simple way to ensure the rapid and complete removal of vapor during the dehydration process. As the current temperature program also involves a change of the local atmosphere, from humid to dry, it was also dependent on sufficiently flushing the system for humidity. And as the design of both the TGA and DSC prevent use of a humidity sensor close to the sample, it was dependent upon experience to adjust the conditions appropriately.

As regards the DSC is it often best to use the results in a comparative manner, rather than in an absolute sense [28]. Thus, previous research on minerals similar to Na-FH mostly use heat flow curves for comparison and enhancement of weight loss curves, as it may determine temperature intervals for first-order transitions and be used for calculation of the percentage of total weight loss during the different transitional peaks [18, 76, 77, 73, 78, 79] ⁶.

A different approach to observation of steps in the weight loss curve has been tested by Ding & Frost [72]. By combining high-resolution thermogravimetric analysis (TA) with mass spectrometry (MS) of the evolved water vapour, the sample is heated at a preset constant decomposition rate of 0.15 mg/min, instead of a constant heating rate. A better resolution of the thermal decomposition steps is obtained, where the weight changing steps are more easily separated, but shifted to a higher temperature.

Relative Humidity versus Temperature

Air with initial relative humidity RH_i at roomtemperature, 25°C will experience a change if the temperature changes, and achieve a final relative humidity RH_f . The development may be calculated using Eq. 2.11 and by assuming AVP was constant during the experiment, giving the relation

$$RH_i \cdot SVP_i = RH_f \cdot SVP_f \quad (4.2)$$

The development is found to be exponential, as illustrated in Fig. 4.20 for two different initial conditions at $T_i = 25^\circ\text{C}$: $RH_i = 25\%$ and $RH_i = 5\%$. Observations during the WAXS experiments support these calculations, where humidity and temperature were monitored close to the sample.

Validity for the Current Experiments The construction of both the TGA and DSC makes it impossible to measure the relative humidity inside the respective sample cells. When performing experiments during a range of temperatures the relative humidity will change in accordance to Fig. 4.20, but it can not be monitored directly, only estimated based on measurements in room temperature.

This shows that a sample temperature of 5°C , will give RH_f significantly higher than outside the instrument. $RH_f = 100\%$ would be obtained when $RH_i \approx 28\%$, thus it was not deemed necessary to provide more humid air than in a normal room to wet the sample during experiments. More importantly, if a solution of K_2SO_4 is used to obtain humid air 100%RH is always achieved at 5°C . Hence water may condensate and either ruin the sample or clog the system. It did happen once during the WAXS experiment, but was detected and rectified immediately as at this instance the relative humidity was monitored close to the sample.

And correspondingly, at higher temperatures RH_f can be assumed to be below $\sim 1\%\text{RH}$ almost independently of the initial relative humidity outside the instrument.

Even if the RH development to some degree can be predicted the nature of RH will constitute a major source of error in these experiments. What is relied on is a good repeatability, thus at least all measurements are taken under equal conditions.

⁶For thermal analysis, heat flow curves are often collected using other techniques than the DSC, for example DTA which is a similar instrument where the sample temperature is not adjusted when transitional peaks occur [4], or SDTA signals.

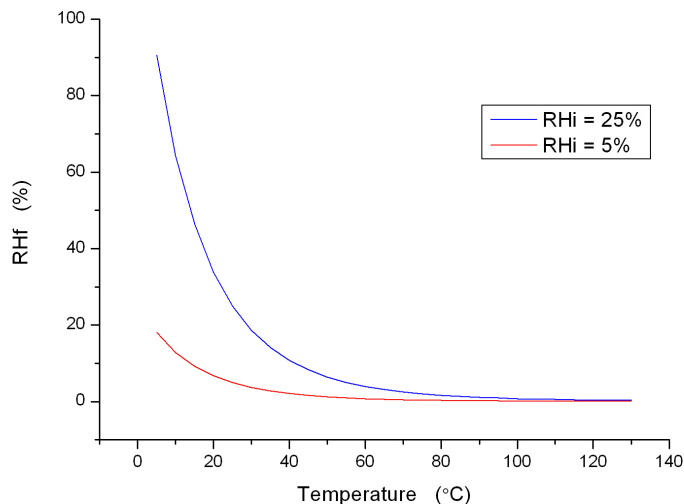


Figure 4.20: Temperature dependent development of the relative humidity. The initial conditions at 25°C are $RH_i = 25\%$ and $RH_i = 5\%$.

Thermal Properties of the TGA and DSC

Both of the instruments for macroscopic investigations have good temperature specifications, as presented in App. A. But the actual response during experiments was found to differ.

For a transition between isothermal and dynamic measurement segments the DSC temperature response is plotted in Fig. 4.21, where T_s followed T_r in a 1:1 relation. The low ΔT_{rs} error was also confirmed through estimation of average error for a measurement at 2°C/min, which gave $\Delta T_{rs} = 0.014 \pm 0.003$ °C.

But as demonstrated during heating experiments in Sec. 4.2 the TGA was quite sensitive towards the thermostat temperature. And as the principle behind the current experiments is to implement an identical heating pattern and compare the different data deviations may arise from this source.

During use of the TGA and its thermostat, it is recommended from the producer to let it stabilise for some hours whenever the thermostat temperature is changed [57]. Thus it was no alternative to change the settings during a long lasting experiment, for example step heating.

If a better temperature correspondance between the TGA and the DSC is wanted, both regarding start and end temperature and heating rate, a number of initiatives could be made to improve it. To reach 5°C the thermostat has currently been set at 2°C. For future experiments the system could be tested for settings closer to, or below, 0°C. The end point of the temperature programme must also be changed to actually reach 130°C. A greater deviation from planned heating rate would thus be expected. But it can be compensated for by increasing the theoretical heating rate until the actual heating rate is correct.

Crucible Standard aluminium crucibles from Mettler Toledo are used for the macroscopic investigations. These are prepared by machine, with a strong and flat base providing good thermal contact down to the temperature sensors placed below [80]. Two zerolines for the TGA collected at rate 10°C/min are presented in Fig. 4.22, confirming that the temperature response corrected for during measurements was caused by the TGA balance arm not the crucible. The sample itself should not cause any problems as powder generally has good thermal contact with crucibles. The appearance of these curves can be affected by packing density [37], and it was assumed to affect

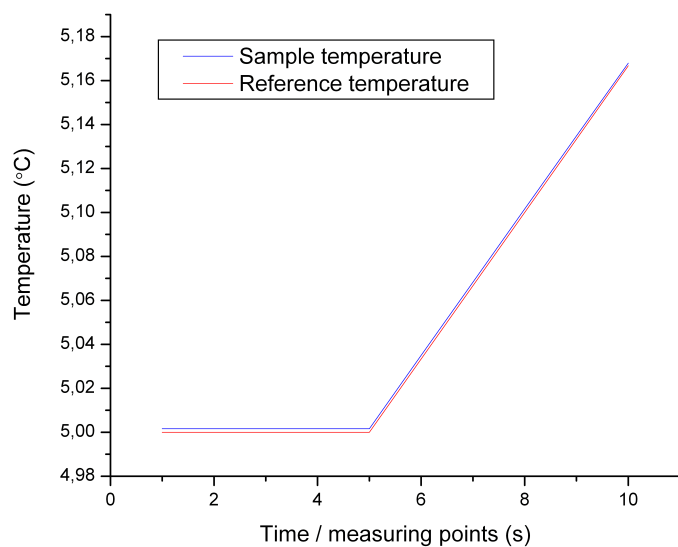


Figure 4.21: DSC temperature response in the transition from isotherm to heat rate 2°C/min, with a very good precision.

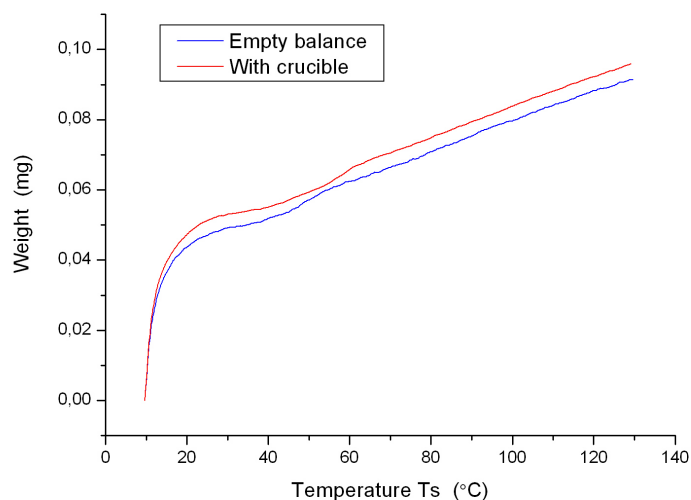


Figure 4.22: Zeroline for the TGA collected both with and without a crucible at heating rate 10°C/min. Most of the interfering temperature response during measurements are thus caused by the TGA balance arm.

the baseline slope of DSC data. However, by taking an average of several parallel measurement this source of error should have been minimized.

The crucibles do have a wide rim, which hopefully did not leave room for condensated water. From this supplier no better alternative was found, which could have eliminated the possibility.

4.2.6 Summary on Heating of Na-FH

Heating of Na-FH at different known rates and by use of three different techniques was meant to help create a better understanding of Na-FH and its behaviour, as well as an improved understanding on the use of these three different instruments. For a better overview the main observations are summarised below.

- Weight loss curves collected at the TGA and heat flow curves observed by use of the DSC provided complementary information, with a good of overlap between the relevant temperature intervals.
- The WAXS experiment was deemed unsuccessful, as the observed interlayer dynamics did neither corroborate with earlier data [31] nor the knowledge about macroscopic behaviour accumulated by use of TGA and DSC. For further reference on structural properties as a function of temperature work by da Silva *et al.* [31] was used.
- The 2WL to 1WL transition occurred below 20°C, but a strongly varying area of the endotherm peak was observed, and this transition was not recognised in the weight loss curves. Thus it seemed that despite attempts to attain an initial 2WL hydration state in all samples through an isotherm at 5°C in humid air, the technique was not entirely successful.
- The 1WL to 0WL transition at heating rate 2°C/min was uniform, indicating 4.8% weight loss consuming 3.39 W °C/g in the temperature interval 22 - 56°C.
- Above approximately 100°C an asymmetrical endotherm and about 1.8% weight loss was observed, assumed to be caused by a change in the diffusion pattern as the boiling point of water was reached. Kinetic analysis, as described in Sec. 4.3 may at a later date confirm this indication.
- The baseline slope between endotherm peaks, was found to vary dependent on sample volume, indicating surface effects.
- In between the main weight loss steps a slow weight loss was observed, simultaneously with a steadily, increasing heat demand. It is assumed to mainly be caused by evaporation of water from mesopores. But coexistence of structural hydration states and a subsequent gradual change may simultaneously occur.
- Step heating led to a faster and more precise dehydration pattern, as all available water in mesopores is assumed to evaporate at each step.
- Heating rate 10°C/min shifted the weight loss pattern to higher temperatures, by 10 - 20° C. The temperature shift is assumed to be controlled by the pace of water evaporation from mesopores.
- Total weight loss was identical independent of heating rate, observed to be 8.2%.
- The thermostat which cooled the TGA furnace was set to 2°C. But sample temperature 5°C was not reached, and it caused further deviations from the intended experimental procedure as the sample was heated at a slightly different rate than theoretically given.
- Rapid temperature changes caused a response in the TGA balance, which was corrected for by use of zerolines.
- The DSC provided a very good thermal response, with use of the same thermostat settings.
- Step heating and heating at rate 10°C/min was not successful when performed on the DSC.

- An increased volume flow was found to shift the heat flow curves to slightly lower temperatures, generally 1 - 2°C.
- Design of the TGA and DSC prevent measurement of relative humidity close to the sample. Thus the temperature dependent development of RH was estimated based on theory, and is further assumed to be a main error source.

Details on the temperature intervals may be found in Tabs. 4.2 and 4.3.

4.3 Isotherms

To investigate the kinetics of Na-FH it was attempted to collect data isothermal weight loss data by use of the TGA, inspired by previous work published by Bray & Redfern [33] and Girgis & Felix [81, 82]. But to find a method suited for the intended experiment, and simultaneously possible to implement on the TGA was more of a challenge than anticipated.

4.3.1 About Method for Isothermal Measurements, and Preliminary Results

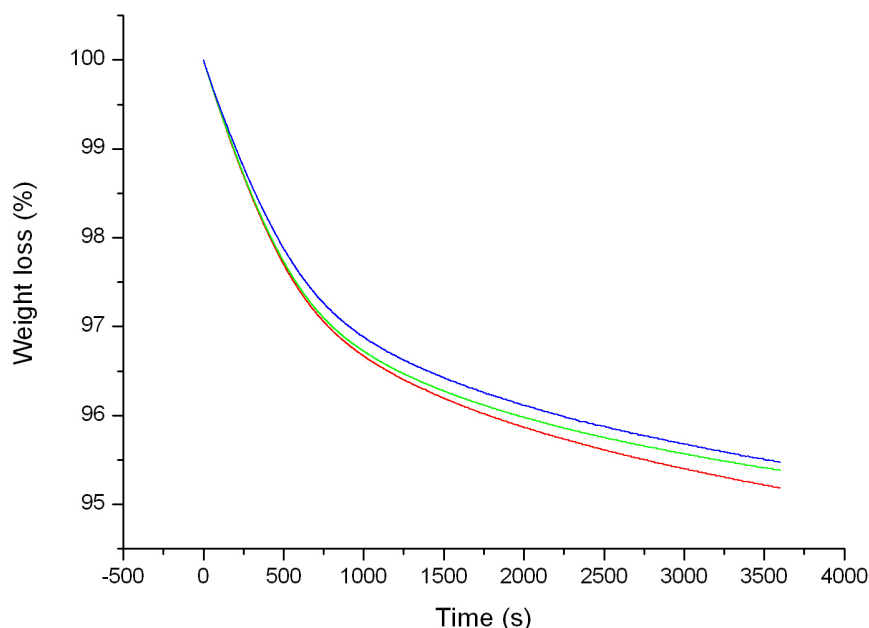


Figure 4.23: Weight loss caused by humidity-dependent dehydration when purging the TGA furnace with nitrogen at room temperature, with three parallel measurements.

During the experiments a steady flow of nitrogen, 50 ml/min⁷ was used as a purge gas, as it contains no humidity. To confirm how the gas flow influenced the experiment, data was collected at room temperature for one hour, in three parallel measurements. As confirmed by Fig. 4.23 the sample lost approximately 4% weight in the enforced dry atmosphere, due to humidity-dependent dehydration, an effect also observed by Bray & Redfern [33].

For collection of isothermal mass loss data at different temperatures, it was necessary to shock heat the sample in some way. Using the STAR^e software it was attempted to heat the sample at a known rate 50°C/min, with a subsequent one hour isotherm. But as shown in Fig 4.24 the time constant of the TGA temperature regulator system caused a large overshoot, and thus it took up to 500 s until the sample temperature was stabile. Hence weight loss data collected in

⁷The gas flow was calibrated simply using a cup of water and a stop watch, as described in App. D.

this interval was worthless in the context of isotherms, as the weight development is important, not only the end result. When compared to the relative weight loss data presented in Fig. 4.25 this method was discarded, as the weight loss mainly occurred before 500 s has passed.

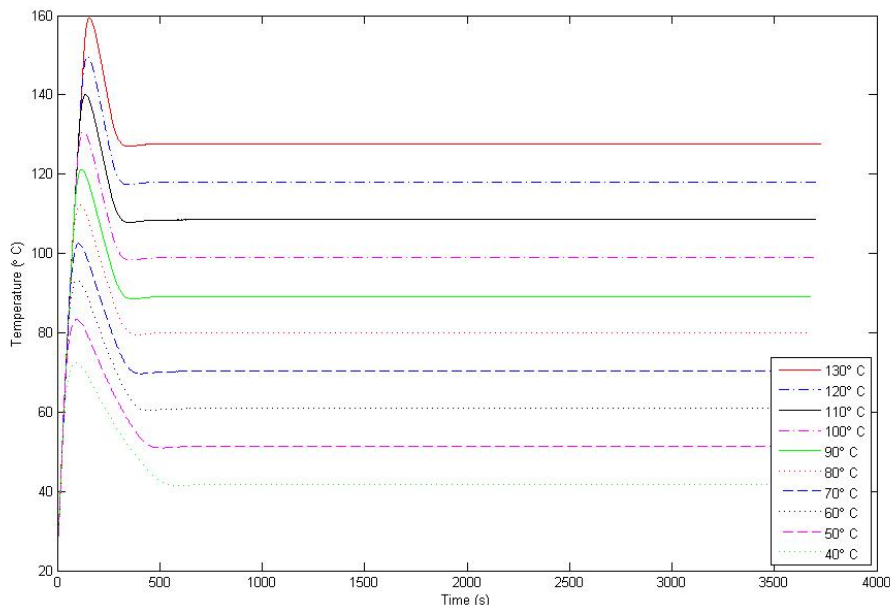


Figure 4.24: Sample temperature during isothermal measurements at the TGA, with a known shock heat rate 50°C/min. A large overshoot is observed, caused by an inherent time constant of the TGA temperature regulator system. Dependent on temperature it takes up to 500 s until the T_s stabilises.

But Fig. 4.25 was interesting in its own terms, as a distinct negative slope is observed at 70°C, 80°C and 90°C. It means that the weight did not stabilise inside the time frame of one hour.

Attempts to run an isotherm for longer time showed that the weight loss at 90°C needed a time frame of about 50 hours to reach stabilisation, presented in Fig. 4.26. Other similar test confirm that when using the TGA Na-FH need long time reach a stabile weight at some temperatures. It seems as it was the water content in mesopores which was the deciding factor when trying to obtain a macroscopic equilibrium, as observations using X-ray scattering show that only a short time is needed to reach a structural equilibrium, in terms of interlayer spacing [16, 17, 31]⁸. This was also confirmed during the WAXS experiments presented in Sec. 3.2.4.

Alternative Methods As opposed to shock heating at a known rate it would be possible to heat the sample more slowly to reduce the temperature overshoot. However, this had a character of dynamic heating than isothermal measurements.

Investigating the TGA it seemed possible to heat the TGA to a given temperature, open the furnace and insert a crucible without lowering the furnace temperature more than $\sim 0.5^\circ\text{C}$, thus isothermal conditions were achieved in terms of the TGA temperature system. To tare the balance, an empty crucible was inserted, and tests were run to check if the data were influenced by the crucible still being warm as opposed to cooled until room temperature. No major difference

⁸The conditions differ somewhat in [16, 17] as the layer spacing is studied as a function of humidity, but [31] work on similar problems.

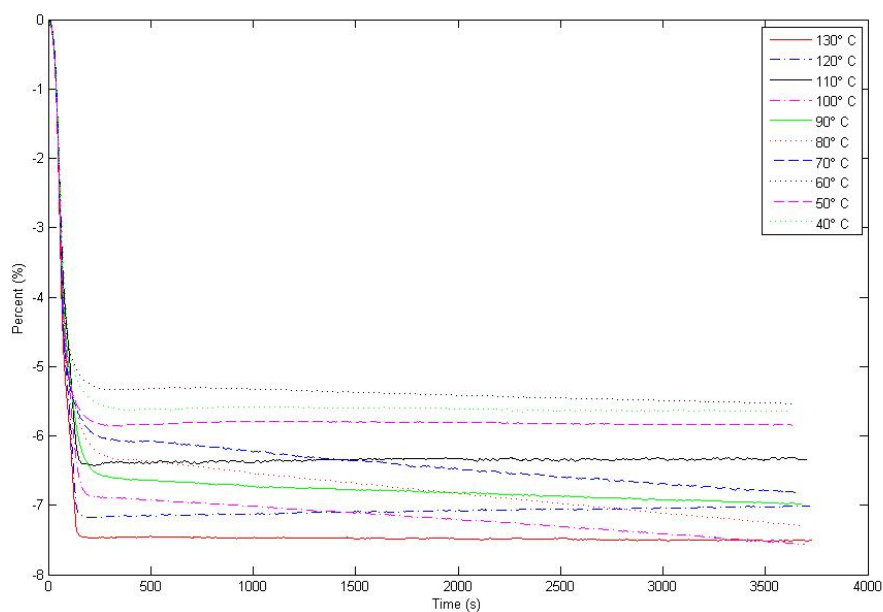


Figure 4.25: Relative weight loss during isothermal measurements at the TGA, with a known shock heat rate $50^{\circ}\text{C}/\text{min}$. The curves are characterised by a large initial weight loss, but the weight is not stabilised at all three temperatures. At 70°C , 80°C and 90°C a stable negative slope is observed.

was found, so for subsequent measurements the crucible was cooled to room temperature before distributing the powder sample and inserting it into the furnace, as these terms ensure more similar conditions for all parallel measurements.

Inherent to the TGA is that data collection will not start until the sample has reached the target temperature and it has been stable $\pm 0.3^{\circ}\text{C}$ for at least 20 s [57]. When implementing isothermal measurements this would compromise the results, as again a significant part of the weight was lost before the data collection had started. But the TGA can be force-started by pressing 'OK' twice. Each measurement was therefore started at slightly different times, but it was compensated for during analysis of the data, simultaneously with corrections using zerolines.

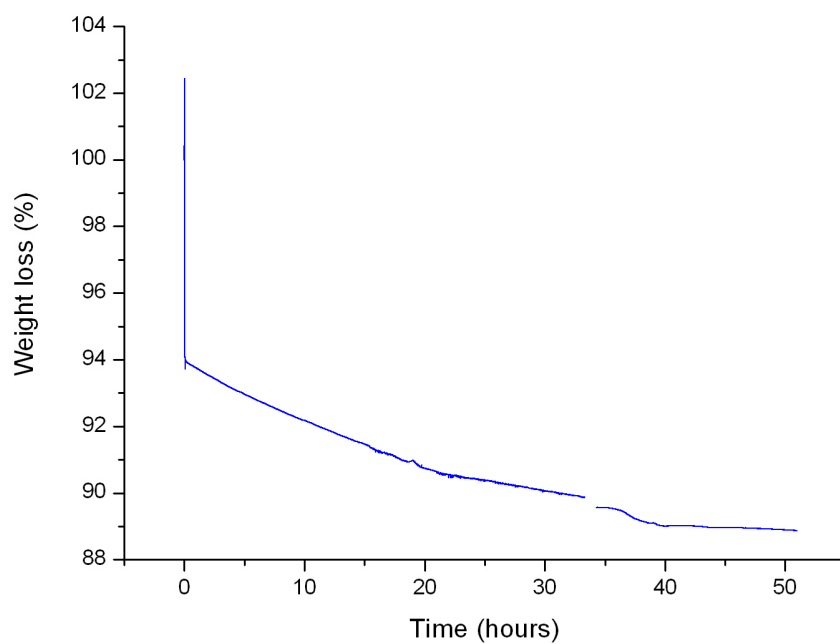


Figure 4.26: Weight loss during a long isotherm at 90°C. Na-FH used about 50 hours to lose approximately 11% of its initial weight. The conditions were retained, but the data collection was interrupted after 32 hours, and the curve is not corrected for its zero line. Thus these data are only indicative of the actual weight loss.

4.3.2 Results and Kinetic Analysis

Because of time constraints isothermal measurements in a preheated furnace was only performed at three different temperatures, 50°C, 90°C and 130°C, to obtain some information on use of the method and its suitability for kinetic analysis of Na-FH.

Relative weight loss curves are shown in Fig. 4.27, which all are an average of at least three parallel measurements. It was not expected that more water evaporates at 90°C than at 130°C, as the kinetic energy increases with temperature and should be indicative of the total weight loss. A significant difference in the shape of the weight loss curves was observed, and maximum weight loss is about 7%, a quantity comparable to what is observed for powder samples during different heating procedures before [58, 59].

The sample temperature during measurements is presented in Fig. 4.28. Also in this instance T_s use some time to reach the target temperature, but this response seems the natural one in a sample which has experienced a quick temperature change. The sample does not stabilise at the exact reference temperature, but this is inside the expected uncertainty in the TGA furnace, by previous experience during heating experiments, see Sec. 4.2.

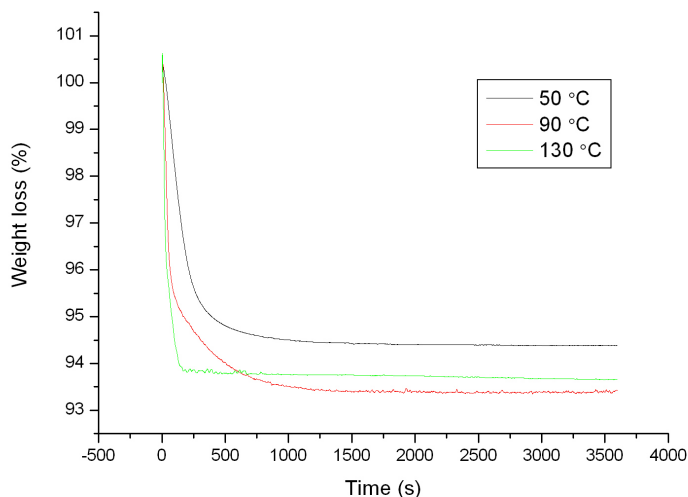


Figure 4.27: Relative weight loss during one hour isothermal measurements at the TGA, for three different temperatures.

The isothermal data were further interpreted employing the method suggested by Hancock and Sharp [3], by use of the empirical rate equations described in Sec. 2.3.

First the reaction coordinate, defined as the end-point of the reaction α_f , where $\alpha = 1$, was established. The correct interpretation when the sample lost more weight at 90°C than at 130°C was not certain, thus two sets of final calculations are made. One with α_f defined as the percentage of weight loss after one hour at 130°C, and an alternative α_f set to the end-point of the isotherm at 90°C. Each weight loss curve could have been fitted with an exponential function, but this step was not implemented. Rather the raw data are used also for calculations as no good fit could be found, and the calculated curves were still smooth, not jagged.

To investigate the kinetics of the reaction, α was plotted using the Avrami equation, Eq. 2.7 and the Austin-Rickett equation, Eq. 2.9. There are two sets of calculated plots, for α_f set at 130°C please see Fig 4.30. Alternatively, with α_f defined as the endpoint of the isotherm at 90°C, see

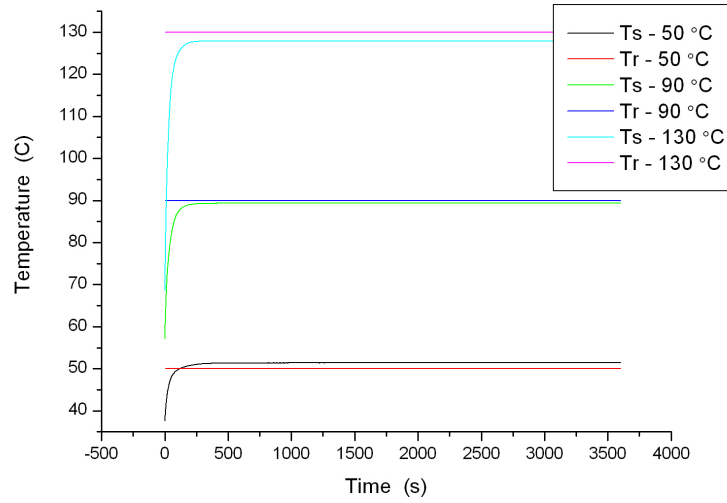


Figure 4.28: Sample temperature as a function of time during isotherms in a preheated furnace.

Fig. E.1. The plots are made for $0.15 < \alpha < 0.85$, but the theoretical values were estimated for $0.15 < \alpha < 0.50$ because of limits set by uncertainty [33].

At low $\ln(t)$ the plots are generally linear, while later it deviates, and a negative curvature was seen. A linear fit at low $\ln(t)$ provides a measure for the exponents m and m_A in Eq. 2.7 and 2.9 respectively, presented in Tab. 4.4. After limiting the curve interval all coefficients of determination r^2 were larger than 0.988, indicating a good linear fit.

Table 4.4: Calculated exponents for the Avrami- and Austin-Rickett equation for isothermal measurements.

	Avrami, m	Austin-Rickett, m_A
α_f at 130°C		
50°C	1.53	1.94
90°C	1.91	2.27
130°C	2.11	2.41
α_f at 90°C		
50°C	1.54	1.90
90°C	2.00	2.28
130°C	2.14	2.36

Comparison with the theoretically estimated exponents for these empirical rate equations, given in Tab. 2.2, suggested that the currently calculated m and m_A were of the correct order of magnitude. Whether defining α_f at 130°C or at 90°C did not make a large difference. For the Avrami equation the exponent m changes from 1.54 at 50°C to ~ 2.1 at 130°C . None of the suggested diffusion patterns matches perfectly, but it indicates a change from a cylindrical phase boundary reaction to an A2 random nucleation process. Use of the Austin-Rickett equation, Eq. 2.9 proposed the same pattern, because also the exponents m_A are large, compared to the scale given by the different diffusion processes in Tab. 2.2.

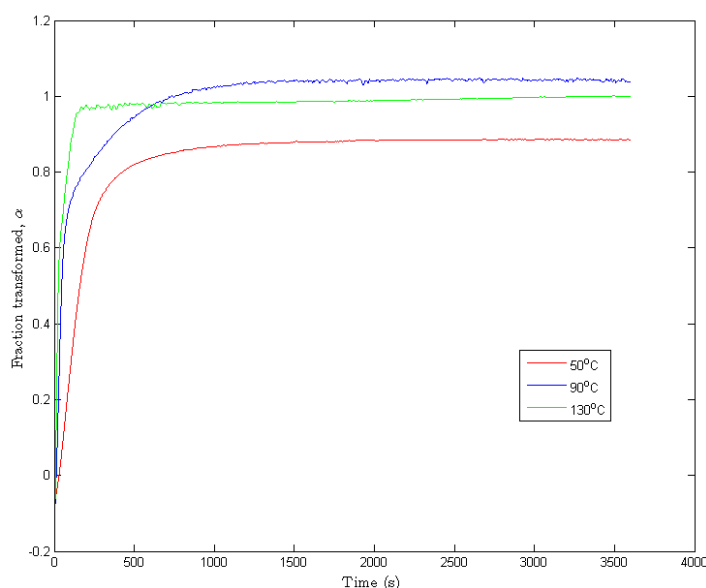


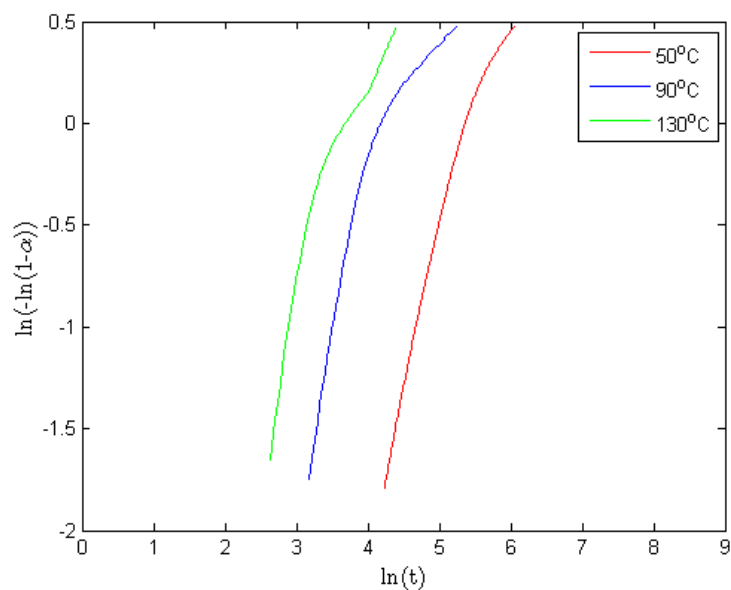
Figure 4.29: Fraction transformed α , calculated from the relative mass change as a function of time.

This method for kinetic analysis of clay was also successfully tested in [37, 83]. For kaolinite [84] it is indicated that the rate controlling process changes with temperature and with α . For Ca-montmorillonite the dehydration kinetics [33] is found to have two main stages. Below 90°C a nucleation and growth process is observed, changing to a reaction controlled by diffusion above 90°C. These two stages are associated with the primary collapse of the interlayer and movement of water hydrated to cations in the interlayer, respectively. Further analysis to determine the activation energy E_a by use of the Arrhenius equation, Eq. 2.10, showed that the two stages also have different activation energies.

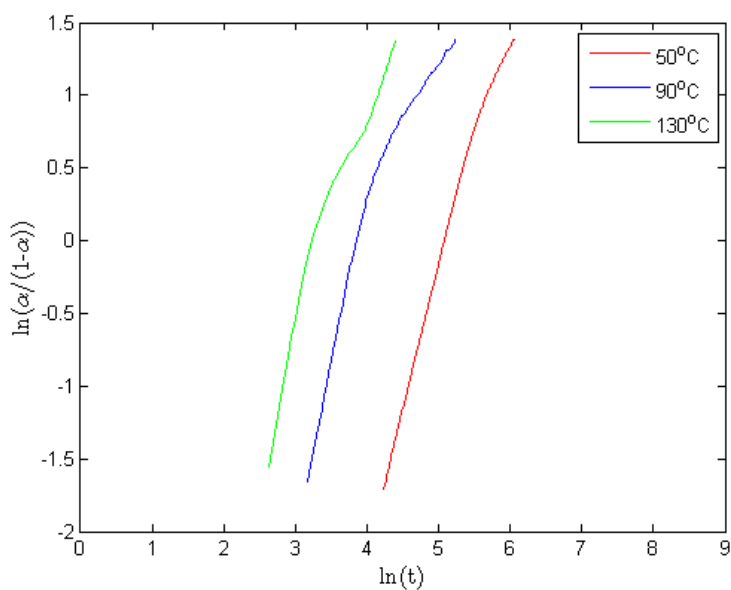
These equations may also be utilised for isothermal data collected by use of x-ray scattering, as demonstrated by Bray *et al.* [18], for Ca-Montmorillonite. The sample is found to be controlled by the same two mechanisms as presented above. Upon shock heating, the rapid dehydration results in a heterogeneous system far from equilibrium, where the removal of water appears controlled by strain effects and collapse of the interlayer. As it approaches a more homogeneous state it relaxes toward equilibrium, and is again controlled by a diffusion process.

As Ca-montmorillonite is a smectite clay similar to Na-FH the potential for kinetic analysis of Na-FH should be good. But the current experimental data indicate that the diffusion process in Na-FH is different to what is earlier found for similar clays. Thus further work is needed to collect a sufficient amount of data for a thorough kinetic analysis, and estimation of the activation energy. Because either the diffusion the process must be proved to be different in Na-FH, or the method will turn out not to be well adapted for the TGA afterall.

Also interesting was the pattern formed by isotherms, which suggested that Na-FH lose more weight at 90°C than at 130°C, as the latter temperature is normally used as a condition for drying samples [59]. If the deviation was not brought about by varying conditions caused by the TGA, or different initial conditions for the sample, it warrants further investigation.



(a) Avrami lnln-plot.



(b) Austin-Rickett plot.

Figure 4.30: Isothermal measurements plotted using empirical rate equations, both with $0.15 < \alpha < 0.85$, and reference α set at 130°C. The two plots were quite similar and indicated similar rate controlling mechanisms for Na-FH.

4.4 Humidity Gradient

Use of X-rays to describe time-evolution of the intercalation front in a Na-FH sample has showed evidence of an transient Hendricks-Teller mixed-intercalation state[51]. Its observed when a Bragg peak for one of the water layer hydration states grows asymmetric, with a shoulder indicating a dynamic state where the interlayer distance shifts some. This broad HT-peak inbetween the Bragg peaks in the diffraction spectrum, is also interpreted as a sign of increasing humidity, as the diffusion front enters the mesoporosity around the layered crystallites. But until now it has not been possible to isolate the HT-scattering pattern, because in the sample volume visible to the X-ray a range of different hydration states coexist, as the beam cross-section was relatively large. The intercalation front has previously been observed to be 2 mm wide [51], which did not leave a possibility to single out the area of mixed intercalation.

During scattering experiments at PLS in South-Korea a focused X-ray was used to achieve a better spatial resolution than during previous similar experiments [31, 51, 16]. A small beam size did prove useful to isolate details in the scattering pattern from a powder sample placed in a glass capillary with an imposed humidity gradient. A state of Hendricks-Teller random intercalation was found to be present, and possible to isolate. Data analysis is performed concerning four main phenomena, and mainly discussed separately.

An estimate of the amount of visible crystallites for use of two different beam sizes was made, built on a number of assumptions. First, during WAXS scattering at NTNU the beam size was $0.4 \text{ mm} \times 0.8 \text{ mm}$ [66] (used for similar investigations [16, 17]), while the achieved beam cross-section at PLS was $15 \text{ }\mu\text{m} \times 90 \text{ }\mu\text{m}$. Second, each crystallite has 100 platelets, each 1 nm thick and with diameter $2 \text{ }\mu\text{m}$ [8]⁹. Next, a sample pressed with a light load of 50 kg has been found found to hold about 50% porosity [85]. Since the current sample was neither dried out nor pressed it is reasonable to assume at least the same level of porosity. Next, the sample holder is a glass capillary with diameter 1 mm, which represents the maximum thickness of the sample. Finally, it is assumed that the total number of particles eligible for Bragg scattering is distributed on all 360° of a full circle. In addition, but not considered during the calculations, the current sample is not pressed, thus the particles have different orientation in respect to the beam direction, which would lower the number of eligible particles further (see Fig 3.1). This is also a result of the isotropy causing the Debye-Scherrer cone, but to observe every particle the capillary also needs to be rotated around its axis.

Calculations then show that during WAXS experiments approximately 3.5×10^5 particles are available for scattering while at PAL only about 1500 particles are scattered to each degree of the Debye-Scherrer cone.

Hydration State throughout the Capillary

The sample set-up was prepared about 16 hours before the X-ray scattering experiments were started. The first scans were made to map the structural changes caused by the water intercalation process, throughout the capillary. Point measurements were mostly made for both positive and negative q -values to look for asymmetry in the pattern. Selected scans collected at negative q -values are presented in Fig. 4.31, where the distance refers to scan placement relative to the humid end of the capillary. At 0 mm at 2WL Bragg peak with a small right hand shoulder was seen, with peak maximum at $q = 0.34 \text{ 1/\AA}$. The shoulder indicated a dynamic state which lowered the interlayer distance slightly. The scans revealed a gradual change until a quite symmetric 1WL Bragg peak was observed at 17.5 mm, centered at $q = 0.45 \text{ 1/\AA}$. A gradual change was seen in the intervening distance, when a broad peak was exposed. This phenomenon was assumed

⁹The size of fluorohectorite particles is usually polydisperse and dependent on how the sample is prepared.

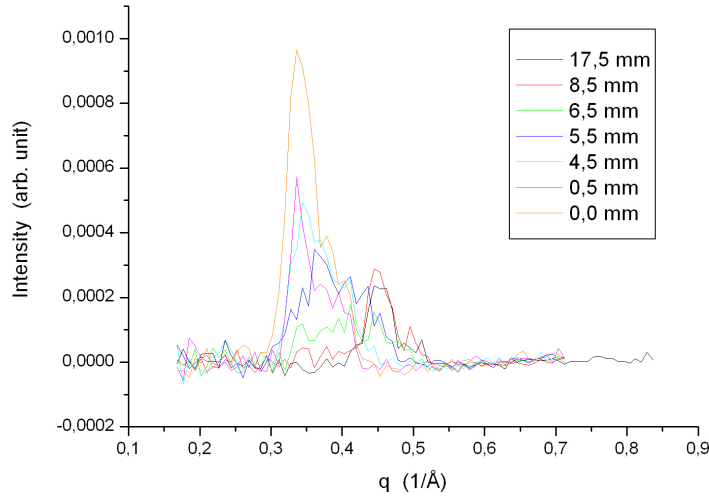


Figure 4.31: Development of the hydration state in a glass capillary with an enforced humidity gradient. The plotted data were originally collected at negative q -values.

Table 4.5: Observed layer distance for Na-FH at PLS, with an error estimate.

#	q 1/Å	2θ °	d Å	$\pm\Delta d$ Å
1WL	0.45	5.39	13.9	1.5
2WL	0.34	3.93	18.7	2.7

to be caused by a state of Hendricks-Teller random intercalation [47, 31]. Eq. 2.12, Bragg's law was used to calculate the interlayer distance d , presented in Tab. 4.5.

A relation between q and d was found by combination of Eqs. 2.12 and 2.13, hence $d = \frac{2\pi}{q}$. Application of Gauss law for propagation of error, given by Eq. F.1, made the error during measurements be estimated by $\Delta d = \frac{2\pi}{q^2} \times \Delta q$. As the one-dimensional detector mostly¹⁰ had step size $q = 0.1$ 1/Å it gave an individual error $\Delta q = \pm 0.05$ 1/Å. The numerical estimates are ± 1.5 Å and ± 2.7 Å for the 1WL and 2WL state respectively, also given in Tab. 4.5. These were found to be large compared to the observed d -values, about 10% and 15% for 1WL and 2WL, respectively.

The observed interlayer distances were larger than what is expected for Na-FH. Earlier experimental data are given in Tab. 2.1. For comparison, during WAXS experiments presented in Sec. 3.2.4 d was then found to be 12.4 Å for a 1WL Bragg peak, while during scattering at PLS d was 13.9 Å.

The calculated error estimates were unfortunately not quite large enough to explain the difference. Measurements without the KB-mirrors in place, has confirmed the wavelength to be 1.30 ± 0.05 Å. As mirrors should not effect the beam energy significantly, it was not deemed important. The collected data were symmetric relative to origin, thus it was acknowledged that

¹⁰More detailed scans with step size $q = 0.05$ 1/Å were made at the distance 7 mm.

the beam was indeed centered at $q = 0 \text{ 1/\AA}$. But still there could be an element of uncertainty concerning movement of the detector, as it need not have been perfect relative to the software commands. A Na-FH sample is generally sensitive to its sample preparation method. It was, as normal, crushed by use of the labs grinding mill. As this particular delivery has been used successfully for multiple X-ray experiments at NTNU without observing interlayer distances of such extent [16, 17] the source of error was not evident.

During the approximately 48 hours of scan time no large movement of the intercalation front was seen. Similar experiments have shown that the intercalation front can typically be described well by a stretched exponential [16]

$$x = x_0 \left[1 - e^{-(t/\tau)^\beta} \right] \quad (4.3)$$

where the constants for dynamics in a normal glass capillary were $x_0 = 15 \text{ mm}$, $\tau = 70 \text{ h}$ and $\beta = 0.8$. According to these data the intercalation front should after 48 hours have moved 7.8 mm into the capillary and move 0.8 mm the next 12 hours. As the detector step size was 0.5 to 1 mm in the main focus area these nuances may not have been detected.

It is therefore suggested to use a smaller detector step size or a two-dimensional detector for further experiments. But as neither a perfectly symmetric 1WL nor 2WL Bragg peak was observed, the case may also be that the sample was not prepared correctly. The end piece might not have been perfectly airtight, or a drop of water had damaged the humid end of the capillary, obstructing the expected water diffusion. However, as the main objective of this experiment was to observe the random intercalation states inbetween the symmetric 1WL and 2WL Bragg peaks the questions concerning the dynamics were not crucial.

The one-dimensional detector had an inherent statistical counting error calculated by the software. Its order of magnitude is illustrated in Figs. 4.32(b) and 4.32(a) for negative and positive q -values respectively. The plots show that because of the low detected intensities this error amounted to a significant part of the absolute intensity. Hence it is reinforced that these data can not be used for precise assertions about the Na-FH powder sample.

Asymmetry

As only a limited number of Na-FH particles were visible to the focused beam at any given time, a certain level of asymmetry was expected, not visible in WAXS data. Fig. 4.33 feature plots with data both for positive and negative q -values taken at the same point in the sample. Figs. 4.33(a) and 4.33(b) are taken at 7 mm and 8.5 mm respectively and both show an indication of asymmetry.

To quantify the difference between datasets the correlation coefficient $\rho_{X,Y}$ was calculated (defined by Eq. F.2), based on the q -range where the broad peak is observed, disregarding the area with background scattering.

For Figs. 4.33(a) and 4.33(b) $\rho_{X,Y}$ is 0.84 and 0.78 respectively. More datasets were analysed to estimate the level of asymmetry, of which some are plotted in Figs. G.1, G.2, G.3 and G.4. The correlation ranges from 0.76 to 0.90.

Evaluation of the correlation coefficients thus confirm that the Bragg scattering at opposite sides of the Debye-Scherrer cone were somewhat asymmetric, as for a perfectly symmetric pattern $\rho_{X,Y}$ should be 1.

The width of peaks can also be an indication of asymmetry, and to compare scattering patterns it is usual to use the parameter Full Width at Half Maximum, *FWHM* [42]. For the observed peaks, both Bragg and those of HT-origin, this was however difficult to measure because of the

limited amount of point measurements. Approximations by use of a Gauss distribution were only of limited success, as discussed below. Thus it leaves the option to observe that the width in most cases seemed quite similar for overlapping plots including both positive and negative q -values. A question for further consideration is if this inclination for asymmetry is large enough to exclude the effect of random differences in the pattern.

Vertical Scan

Most scans were made at a distance 0.3 mm below the top of the capillary, to further reduce the amount of sample which was observed. A vertical scan of the capillary was made at 8 mm, plotted in Fig. 4.34, an area in the capillary which was characterised by a state of random intercalation. These indicate that the total intensity increased as the distance from the top increased, as expected when the number of visible crystalites also increases. A more pronounced 2WL Bragg peak was seen at a distance 0.5 mm below the top. Thus it seemed that the intercalation state changed when moving downwards. It could be a consequence of details in the profile of the intercalation front, or simply that the sample geometry changed to include more scatterers. As the source of change was not evident, such vertical scans should be a source of interest for further experiments.

Gaussian Approximation

To describe the transitional state observed between the two Bragg peak position Hendricks-Teller theory was used, as described in Sec. 2.6. The equations give a theoretical explanation, but no good account for the observable effect in a real layered material.

To describe the collected data in terms of a peak function, it was attempted to fit the data with a Gaussian distribution, Eq. F.3. Two different approaches were tested, both fit to the raw, corrected data, and in addition some datasets were smoothed by adjacent averaging over 5 or 10 point measurements, dependent on detector step size, to even out some of the sharp spikes in the pattern.

Two examples are plotted in Figs. 4.35(a) and 4.35(b), and their estimated parameters for the Gauss distribution are given in Tab. 4.6. Two additional sets of plots are included in Figs. 4.3(c) and 4.3(c) with their parameters, where both approaches are tested on the same data. The coefficient of determination for raw data ranges from 0.7 to 0.8, while for smoothed data r^2 is between 0.91 and 0.97 in the peak area. Thus approximation by a Gaussian distribution seems to give an acceptable fit, even if it is somewhat dependent on the manual choice made as to which points were included in the fitting procedure.

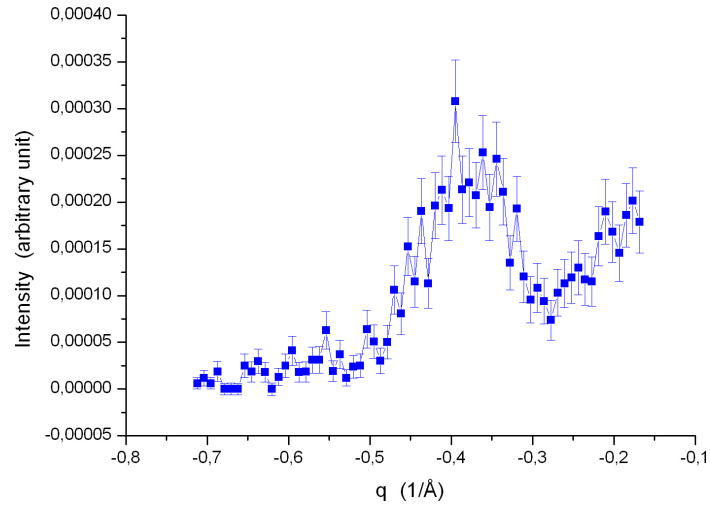
If the data collected between 6.5 and 8.5 mm (referring to the collection of plots used for analysis) are compared in terms of visual shape of the curves, all do display a broad peak that can not be identified by Bragg scattering. All fit approximately with a Gauss distribution, but nonetheless their shape is slightly varying. It seems the intensity distribution is strongly dependent on finding the best possible location relative to the intercalation front. Hence an even more symmetric peak might have been observed by moving only 0.01 mm to either side.

Thus, from the available data it was not possible to confirm if the scattering originating from the randomly intercalated sample answers to a Gauss distribution, because of the level of noise, coarse scanning and too few point measurements. But as it can not be excluded as a possibility it is a very interesting topic for further investigation.

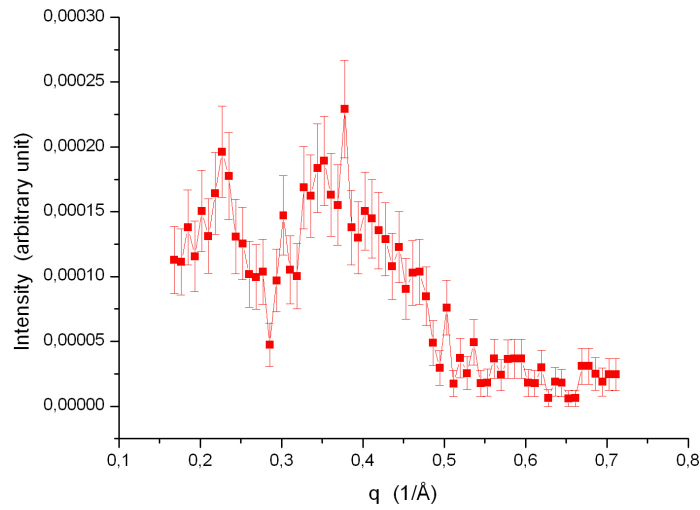
It is suggested to employ a two-dimensional detector, or smaller step size and longer scans time to improve the basis for data analysis. However, use of a one-dimensional detector is limited by the available beam time, and the dynamics in the intercalation front. If the hydration state should change significantly during a scan the data will be of less value.

Table 4.6: Parameters for the Gauss curves used to approximate the intensity patterns in Figs. 4.35(a) and 4.35(b).

Distance	y_0	μ	σ	A	r^2
7 mm	-0.00001	-0.392	0.099	0.00002	0.95275
8.5 mm	-0.00002	0.386	0.103	0.00002	0.97695

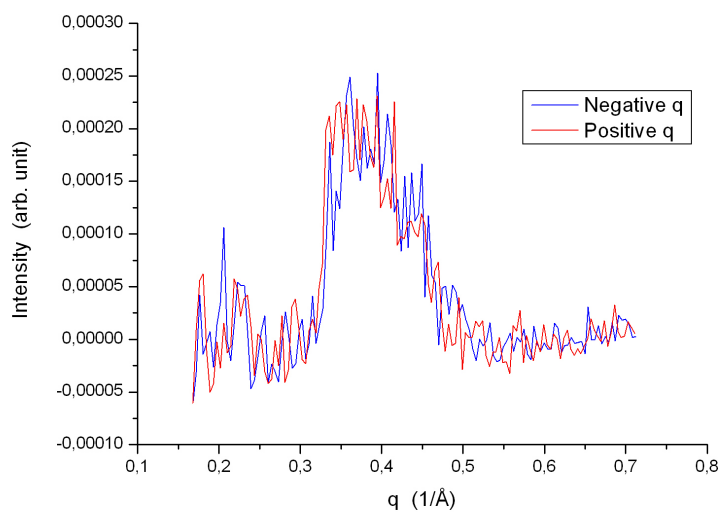


(a) Positive q -values.

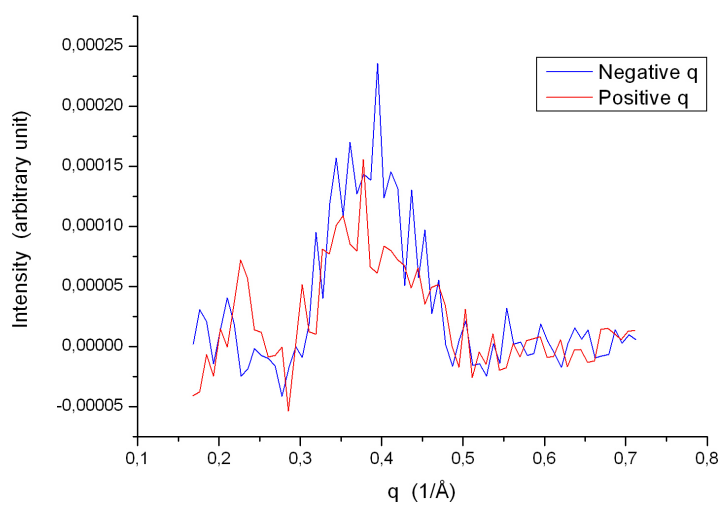


(b) Negative q -values

Figure 4.32: Scans taken 8.5 mm into the capillary, plotted with error bars indicating the statistical counting error automatically estimated based on the characteristics of the one-dimensional detector.



(a) Taken 7 mm into the capillary.



(b) Taken 8.5 mm into the capillary.

Figure 4.33: Data collected for both positive and negative q -values, as a demonstration of the level of symmetry for these type of measurement.

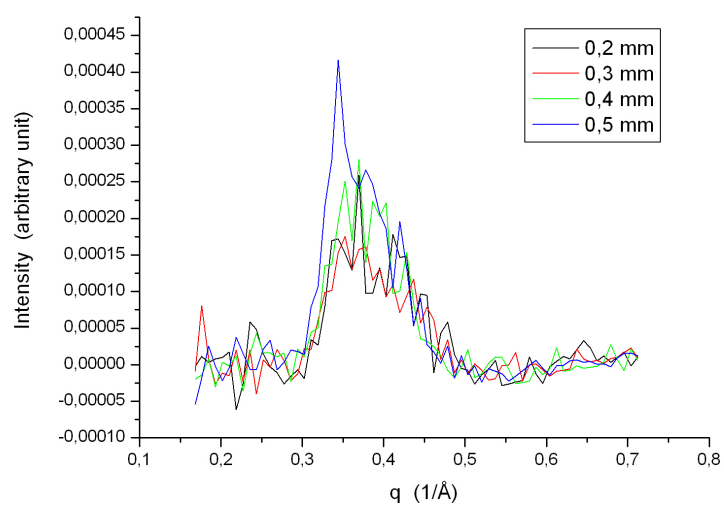
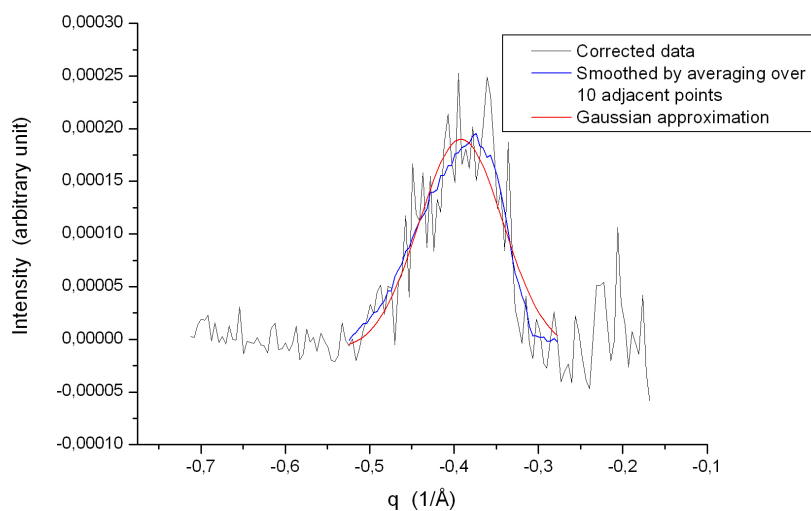
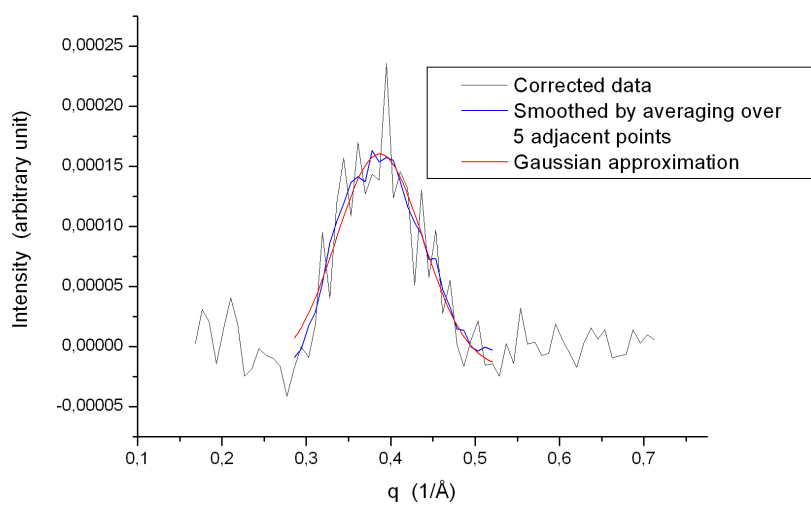


Figure 4.34: A vertical scan of the glass capillary, which demonstrate slight changes in the diffraction pattern as more particles become visible to the beam.



(a) Taken 7 mm into the capillary.



(b) Taken 8.5 mm into the capillary.

Figure 4.35: Two datasets are smoothed by averaging over 5 (10) adjacent points, and then fitted by a Gaussian approximation.

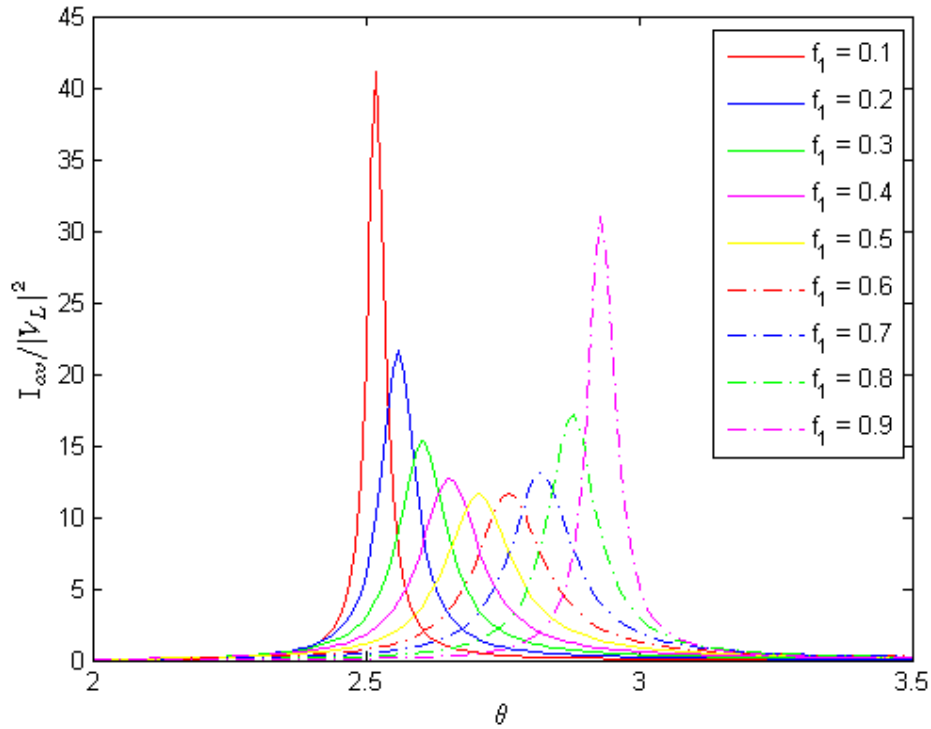


Figure 4.36: Theoretical intensity patterns for different fractions f_1 , based on Eq. 2.31

Remarks Theory on Hendricks-Teller predict the position, line shape and width of the scattered intensity from a randomly intercalated sample. Eq. 2.29 contains the dependency on θ , while the main expression is Eq. 2.31. For different fractions f_1 the intensity pattern for a randomly intercalated sample of Na-FH with layer distances $d_1 = 12.5 \text{ \AA}$ and $d_2 = 15.0 \text{ \AA}$ for the 1WL and 2WL hydration state, respectively would take form as shown in Fig. 4.36.

If these curves are approximated with a Gaussian distribution the coefficient of determination is an average of $r^2 = 0.9768$, which means the fit is good but not perfect. When fitted with a Lorentzian distribution $r^2 = 0.9989$ on average. Hence, the predicted intensity patterns are close to perfectly fitted by a Lorentzian peak function.

During X-ray scattering experiments of clay a pseudo-Voigt function is used to quantize the pattern. The Lorentzian contribution is generally attributed to size and thickness of the crystallized domains, or any strain and disorder in the lattice spacing [6], while the the Gaussian contribution is considered an effect of instrumental broadening.

The main difference between a Lorentz and a Gauss plot is mainly in its tails and overall curvature compared to width [86]. The general difference is illustrated by Fig. 2.11. Thus if the experimental data were fitted with a Lorentzian distribution, about the same level of goodness of fit was observed, as only the peak area was fitted, excluding the background scattering. But considering the overall shape of the theoretical curves a Lorentz distribution also seems a good option for fitting procedures, especially as HT-scattering is considered an effect of disorder in the sample.

Chapter 5

Concluding Remarks and Future Work

Three different experiments were implemented to observe different features of the dynamics of water in the layered, synthetic silicate Na-FH, dependent on temperature and humidity.

Dynamics during Heating

Dynamics during dehydration of Na-FH powder samples was observed by use of three different instruments, to gather complementing information in the temperature interval 5 - 130°C. Macroscopic properties as weight loss and heat flow were collected using TGA and DSC, respectively. An attempt was also made to observe the interlayer distance as a function of temperature using WAXS, with focus at low temperatures. However, the experiment was unsuccessful, and earlier work by daSilva *et al.* [31] was used for further reference.

Three main endotherms were recognised in the heat flow pattern, with corresponding weight loss steps. The first transition corresponded to a change from 2WL to 1WL, mainly occurring below 20°C, but it was not quantitatively stable. Continuous heating rate 2°C/min indicated that the 1WL to 0WL transition regularly occurred in the main temperature interval 22 - 56°C, where 4.8% of the initial weight was lost while it consumed about 3.39 W °C/g. The third transition was caused by a change in the diffusion pattern as the boiling point of water was reached. Step heating gave faster and more precise dynamics, as the sample reached equilibrium at each temperature, while the rate 10°C/min shifted the characteristic heating pattern to higher temperatures. But independent of temperature programme, the total weight loss was identical, set to 8.2%.

During these experiments the TGA has proved very sensitive to the current thermostat settings and sudden temperature changes, which both caused deviations, while the DSC exhibited a very good thermal response.

The main focus has been dehydration of Na-FH. It is suggested that the same level of detailed analysis should be made for rehydration patterns as some level of hysteresis is expected. This is because crystalline swelling is assumed to be a thermodynamical irreversible process.

Kinetic Analysis

A method for kinetic analysis of Na-FH using isothermal data collected at the TGA was developed and tested. Operational limitations of the instrument had to be taken into account, causing challenges as the sample dynamics initially was very fast. By use of empirical rate equations it

was attempted to determine the dominating rate controlling mechanism in Na-FH, by a method demonstrated by Bray & Redfern [33]. However, the current experimental data were insufficient to make a final conclusion at this point.

During future work more data should be collected to make a more thorough numerical analysis possible.

Interlayer Dynamics

By enforcing a humidity gradient on a glass capillary containing Na-FH powder the possibility of observing details in the dynamic water intercalation front was explored. A better spatial resolution than during previous experiments was provided by use of a focused X-ray beam with cross-section $15 \times 90 \mu\text{m}$ at the synchrotron facility PLS in South-Korea. The basal spacing for 1WL and 2WL hydraton states were higher than normal, for unknown reasons.

More importantly, the transitional state described as Hendricks-Teller random intercalation could be observed independently. A vertical scan across the capillary provided a changing intensity pattern, possibly observing details in the intercalation front. Some degree of asymmetry in the Debye-Scherrer scattering pattern was observed caused by the limited number of available scatterers. In addition attempts were made to characterise the HT-scattering pattern by fit with a peak distribution. But the data did not include enough point measurements, and the step size was too large for any conclusions to be made at this time. However, the technique did provide new details HT-scattering pattern in the intercalation front, not observed before.

To provide more thorough data during future experiments a two-dimensional detector should be used. If a one-dimensional detector is employed a smaller step size could help to observe detailed changes in the pattern. More point measurements are also necessary, but because a focused beam typically has low intensity each scan takes time. Thus the level of detail will be dependent on available beam time and the pace of interlayer dynamics.

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Appendix A

TGA/SDTA851^e and DSC822^e Specifications

Detailed specifications on the two thermoanalytical instruments are given below.

TGA/SDTA851^e from Mettler Toledo [57].

- Thermoanalytical Analyzer, with a large furnace (LF1100) giving the temperature range RT to 1100°C, temperature accuracy $\pm 0.3^\circ\text{C}$ and temperature reproducibility $\pm 0.2^\circ\text{C}$.
- Weight measurement range 5 g or a 12 mm crucible with volume 900 μl , with resolution 1.0 μg and noise (RMS) $< 1.5 \mu\text{g}$.
- For SDTA data the resolution is 0.005°C with noise level (RMS) 0.01°C.
- Two integrated system for individual cooling of the furnace and the balance cell using thermostats.
- Possible to regulate the local sample atmosphere with a maximum air flow 50 ml/min, as the system is approximately airtight.
- Use of purge gas N₂ is recommended at all times.

DSC822^e from Mettler Toledo [60].

- Heat flux Differential Scanning Calorimeter.
- 200 W furnace with temperature range from room temperature (RT) to 500°C.
- Measuring cell ceramic sensor, time constant $\tau = 3$ s.
- Gold/palladium thermocouples, resolution $< 4 \mu\text{W}$.
- A built-in air fan cools the instrument as far as RT.
- Integrated system for extra cooling using a thermostat.
- Leaves a possibility to regulate the influx air of reactive gas into the sample chamber with maximum air flow 80 ml/min, but the system is not air tight.
- Use of protective gas N₂ is recommended for measurements below RT.

Additional cooling is achieved using two Haake DC10-K10 Refrigerated Circulator Baths, with range down to -10°C.

Appendix B

State of the TGA

By January 2007 two main problems was in need of a solution concerning the TGA

- The sample temperature differed 200-400°C from the reference temperature during measurements.
- The gas capillary was broken, and thus had to be replaced.

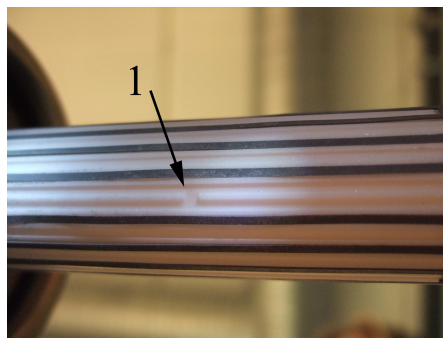
The second problem was easily remedied by ordering a new gas capillary from Mettler Toledo, and it was replaced in a simple procedure. However, to correct the temperature offset different software solutions were tested first: Calibration, importing calibration data from a floppy disk belonging to the instrument and installing a new module. Neither made any difference, thus the hardware had to be examined. At the base of the dissembled furnace a temperature sensor was located, pictured in Fig. B.1(a), at the end of a coil of wires. We were concerned these had been touching each other and thus measuring the furnace temperature in the wrong place. This did not seem to be the case. But the sensor was not attached to any firm surface, and the TGA operating instructions [57] actually showed that the sensor should be set directly below the position of the sample crucible during measurements. The furnace itself has a number of grooves on the outside, for better fitting of the heating elements, and underneath room is made for the temperature sensor also, see Fig. B.1(b). To attach it in this position the wires were staighened and the ceramic sleeves belonging to the furnace, are now holding the sensor in place. The final setup is pictured in Fig. B.1(c). Further checks and calibration of the TGA showed that the sample temperature was now correct, as the furnace was no longer overheated, to compensate for the heat having to reach the misplaced furnace temperature sensor. Sadly it looks like the furnace temperature sensor has been set in the wrong place from the time the instument was first used. Then something made the situation worse during repairs performed fall 2007. But onwards the temperature precision should hopefully be improved.

Other useful accumulated knowledge about the TGA:

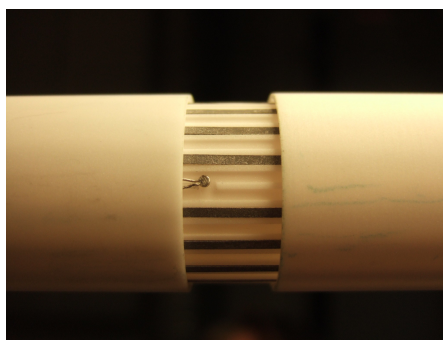
- Mettler Toledo has set limitations for cooling of the TGA, however new software was written to allow cooling down $\sim 0^\circ\text{C}$, barring the condition that two circulating water baths should be used. But what has not been written down is that the the software will only allow cooling of the furnace. Ideal temperature for the cell is 22°C , and the temperature of the water bath should reflect this. If the cell temperature approaches 15°C the TGA will shut down.
- When starting a new experiment the TGA will take some time to stabilise on the insert temperature, as it is stipulated that the sample must be stable $\pm 0.3^\circ\text{C}$ for 20 s. But



(a) Base: 1. Temperature sensor, at the end of a coil of wires.



(b) Grooves are made in the ceramic, 1. Room is made for the sensor.



(c) The sensor is relocated, and held in place by the ceramic sleeves fitted outside the heating elements.

Figure B.1: Details of the TGA: Outside of the disassembled furnace, underneath.

if the importance of starting the measurement immediately overrides the importance of stabilising the temperature perfectly, the data collection can be force started by pressing 'OK' two extra times.

Appendix C

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 Sec. 3.2.3. The method for signal conversion is presented below, based on [62, 63], 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 1100°C for example high purity samples of the metals presented in Tab. C.1 can be used. For temperatures below 650°C 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 C.1: Characteristics for materials used as melting point standards.

Substance	Melting point °C	Heat of fusion $\Delta H_{lit}/\text{J g}^{-1}$
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, ΔH_{Lit} , here presented in Tab. C.1. The corresponding calibration factor is calculated using the equation

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

Results for calculation of a calibration factor K are shown in Fig. C.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 Fig. C.1, with the unit mW/°C.

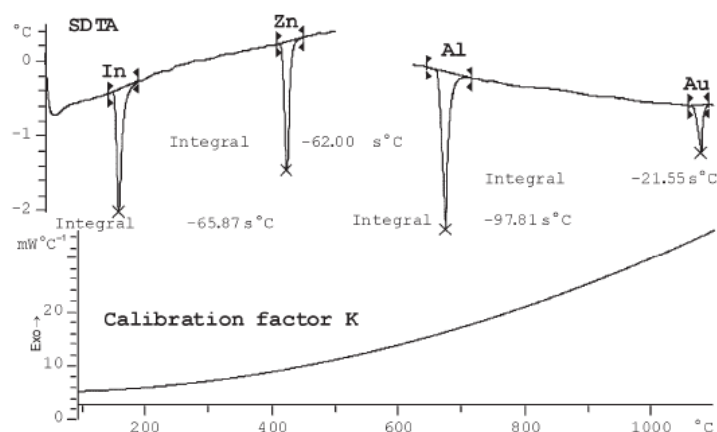


Figure C.1: SDTA melting curves for four melting point standards. The lower curve shows the calculated calibration factor K . [63]

It is fitted using a quadratic polynomial, and a direct conversion from the SDTA signal into a heat flow curve is achieved by multiplication.

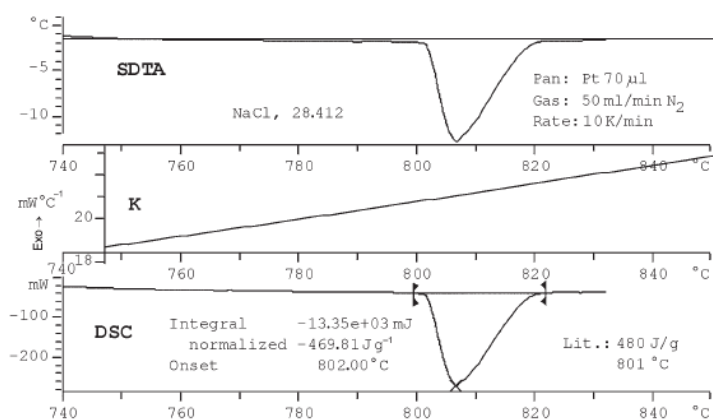


Figure C.2: Illustration of conversion of SDTA signal to DSC heat flow curve via a calibration factor K , for measurements of sodium chloride. [63]

In the work done by Riesen *et al.* [63] 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).
- 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 D

Calibration of peristaltic pump



Figure D.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 D.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 D.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.

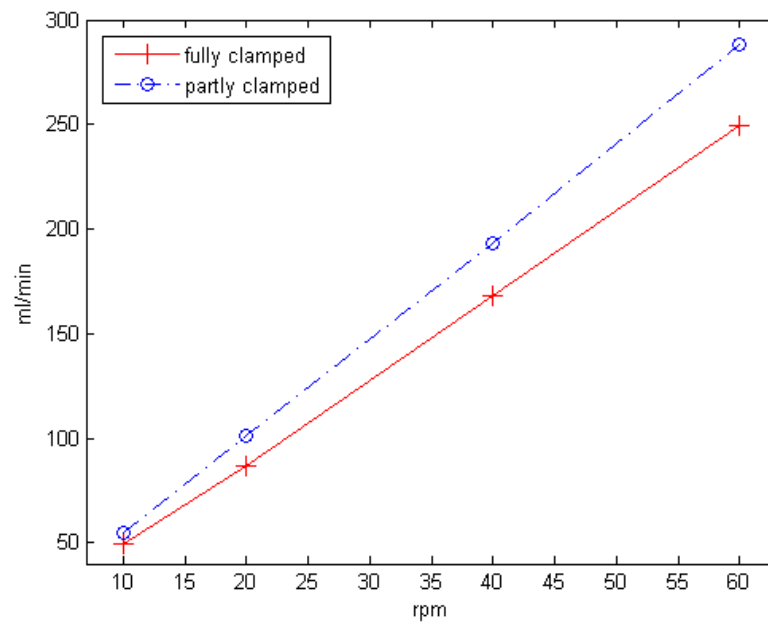


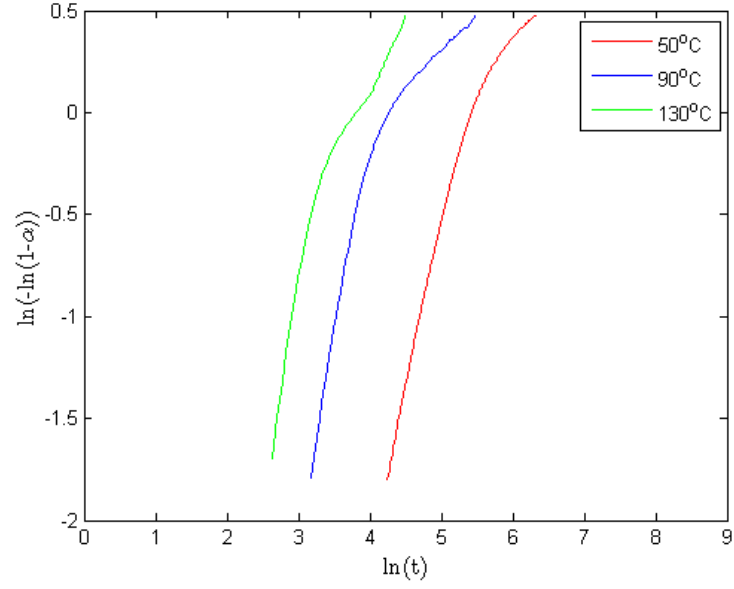
Figure D.2: Airflow through the peristaltic pump.

More small error sources 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.

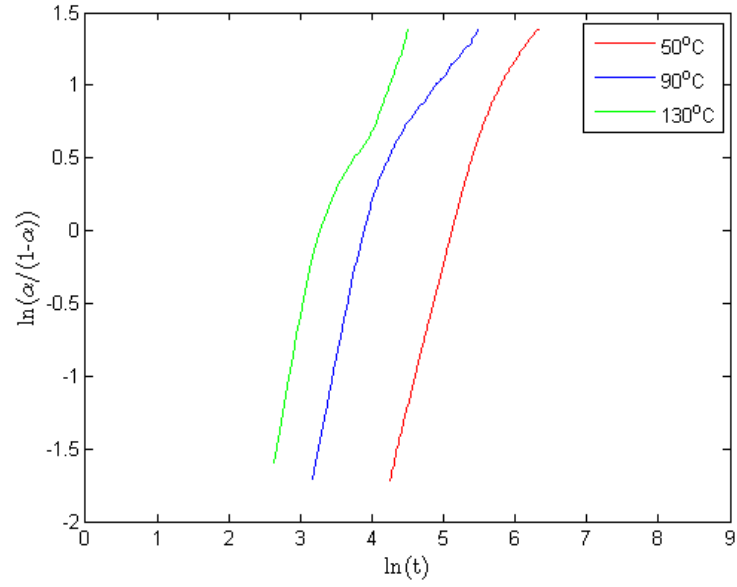
Appendix E

Additional Data for Isothermal Measurements

For α_f set at the end point of the isotherm at 90°C kinetic analysis by use of the Avrami and Austin-Rickett equations, 2.7 and 2.9 respectively, gave the plots shown in Fig. E.1.



(a) Avrami lnln-plot.



(b) Austin-Rickett plot.

Figure E.1: Isothermal measurements plotted using empirical rate equations, both with $0.15 < \alpha < 0.80$, and reference α_f set at 90°C.

Appendix F

Tools for Statistical Analysis

Gauss Law for Propagation of Error

To see how different elements in an equation effect the final error estimate, Gauss law for propagation of error is useful, given on the form [87]

$$f(x, y, ..) = \sqrt{\left(\frac{\partial f}{\partial x} \Delta x\right)^2 + \left(\frac{\partial f}{\partial y} \Delta y\right)^2 + (..) ^2} \quad (F.1)$$

Correlation Coefficient

The correlation coefficient $\rho_{X,Y}$ for two random arrays X and Y is dependent on the expected values μ_X and μ_Y plus the standard deviations σ_X and σ_Y , and hence defined as

$$\rho_{X,Y} = \frac{\frac{1}{n} \sum_{i=1}^n (x_i - \mu_X)(y_i - \mu_Y)}{\sigma_X \cdot \sigma_Y} \quad (F.2)$$

where $-1 \leq \rho_{X,Y} \leq 1$. The correlation coefficient indicates the degree of linear dependence between variables, 1 suggesting an increasing linear relationship while -1 shows a decreasing linear connexion [86].

Gaussian Distribution

The Gaussian distribution is a mathematical expression for the central limit theorem: If the sum of independent variables has a finite variance then it is approximated by the Gaussian distribution. An area Gaussian distribution is given on the form below [86]

$$y(x; \mu, \sigma) = y_0 + \frac{A}{\sigma\sqrt{2\pi}} e^{\frac{1}{2}\left(\frac{x-\mu}{\sigma}\right)^2} \quad (F.3)$$

where μ is defined as the mean value and σ as the standard deviation, plus y_0 as the start value on the vertical axis and A being a parameter for the area of the curve.

Lorentzian Distribution

The Lorentzian distribution has no defined mean, and is found important in physics because of its ability to describe line shapes which are broadened by many different mechanisms. It is expressed as [86]

$$f(x; x_0, \gamma) = \frac{1}{\pi\gamma \left[1 + \left(\frac{x-x_0}{\gamma} \right)^2 \right]} \quad (\text{F.4})$$

where x_0 is its peak center and γ is its width parameter.

Coefficient of Determination

A measure of how well any fitted curve approximates any experimentally collected data is given by the coefficient of determination, defined as $r^2 = \rho_{X,Y}^2$. The latter is given by Eq. F.2, where $r^2 = 1$ indicates a perfect fit [86].

Appendix G

Plot of Data from PLS

Additional plots of data collected during scattering experiments performed at PLS, South-Korea are here included. For data analysis and discussion please see Sec. 4.4.

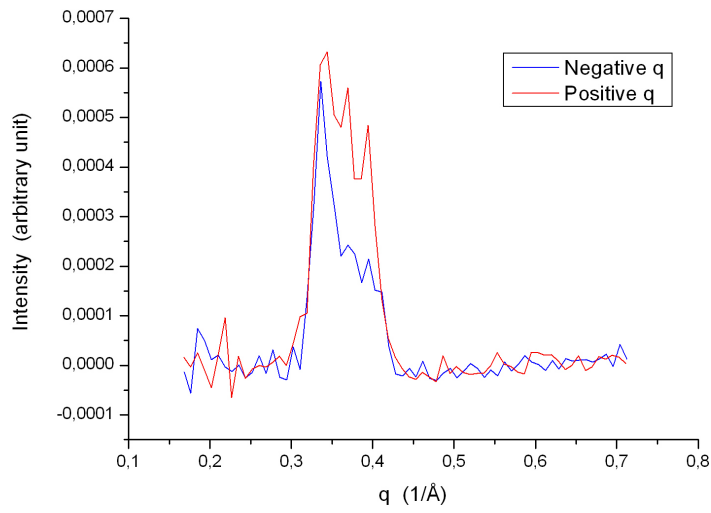


Figure G.1: PLS data collected at 0.5 mm, where a 2WL Bragg peak with a right hand shoulder is visible, indicating a dynamic state interpreted as a HT-contribution. $\rho_{X,Y} = 0.9008$.

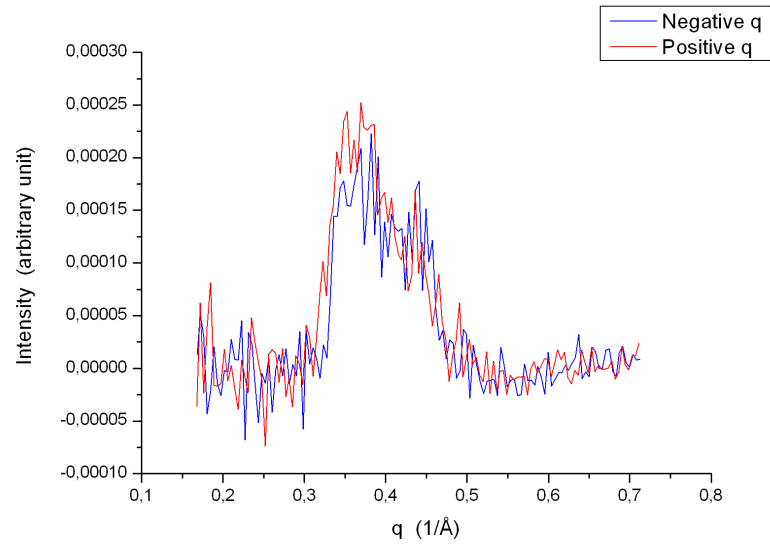


Figure G.2: PLS data collected at 7 mm, with $\rho_{X,Y} = 0.8390$.

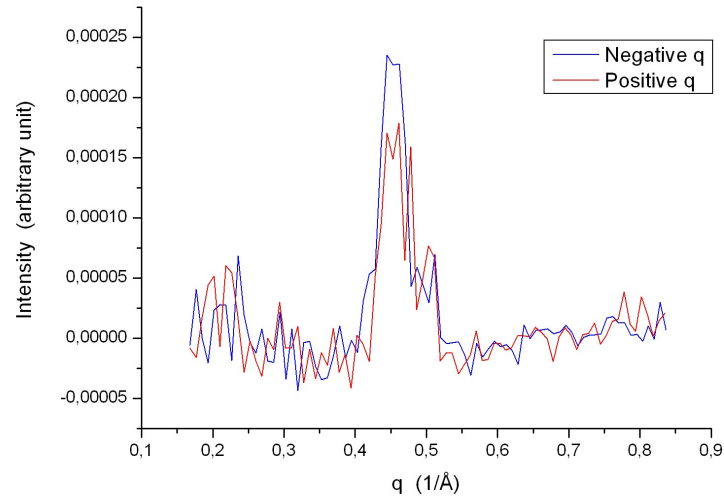


Figure G.3: PLS data collected at 17.5 mm, with a visible 1WL Bragg peak. $\rho_{X,Y} = 0.8299$.

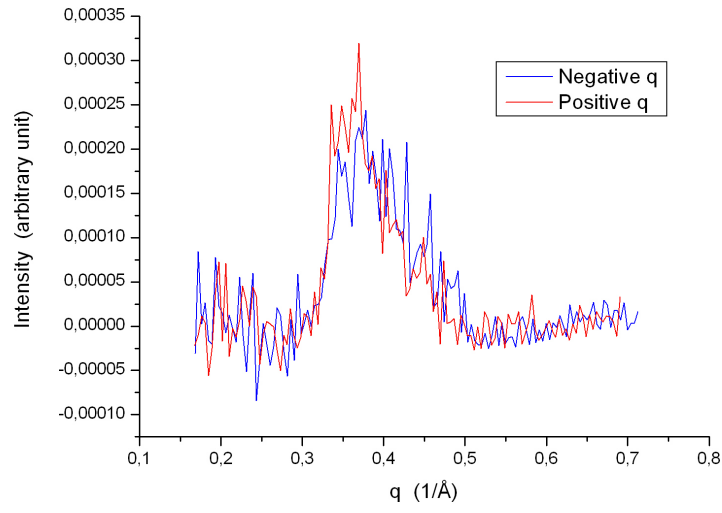
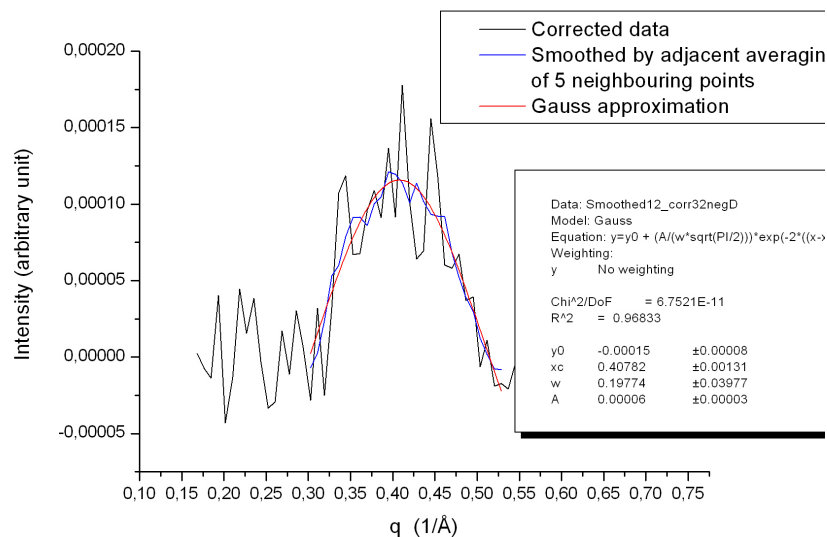
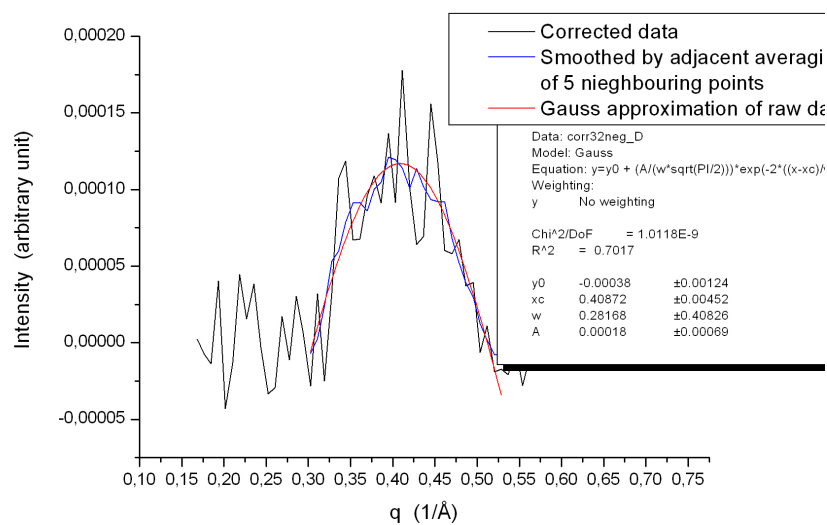


Figure G.4: PLS data collected at 7 mm, with $\rho_{X,Y} = 0.7595$.

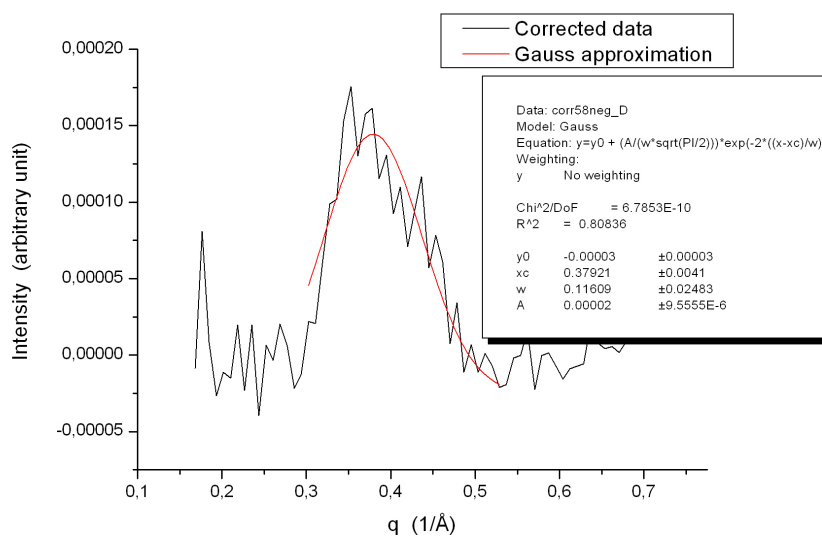


(a) Gauss fit of smoothed data.

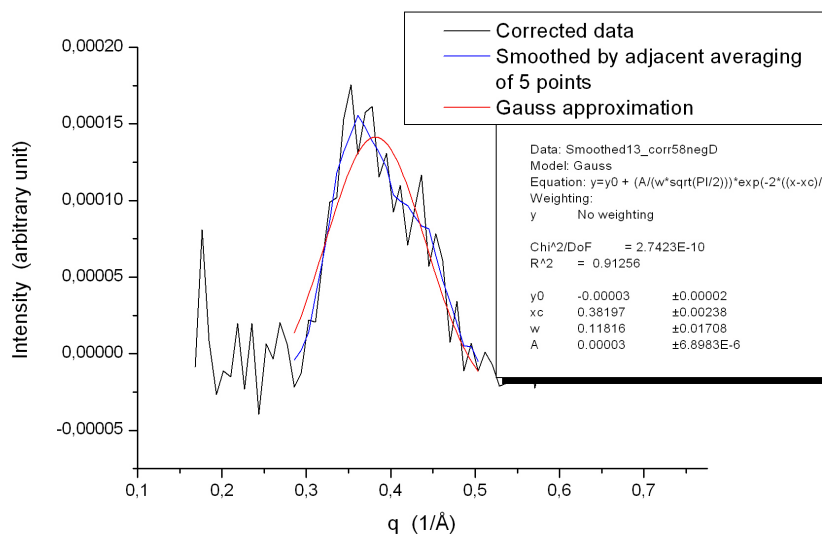


(b) Gauss fit of corrected, raw data.

Figure G.5: PLS data collected at 6.5 mm, fitted with a Gauss distribution.



(a) Gauss fit of corrected, rawdata.



(b) Gauss fit of smoothed data.

Figure G.6: PLS data collected at 8 mm, fitted with a Gauss distribution.

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