



**Study carried out by Julie FERRIGNO
from 05.24.04 to 09.13.04**

Synthetic Smectite Clay studies using Thermogravimetric Analysis

**Supervisor: Jon Otto FOSSUM, Professor at Department
of Physics.**

Co-supervisor: Ahmed GMIRA, Post Doctoral fellow.

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Last, but not least, I would like to forward my most sincere gratitude to all the staff at the division of complex materials.

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INTRODUCTION

I did my training period at NTNU, Norwegian University of Science and Technology, Department of physics. The project was in the division of complex materials, department of experimental investigations of soft materials and complex systems. I worked under the supervision of Professor Jon Otto Fossum, section leader for complex materials, and Ahmed Gmira, Post Doc.

During four months, my project consisted of clay studies using the thermogravimetric analysis. Clay represents one of the traditional materials which has been widely studied and discussed by geologists, geo-chemists, geophysicists, and modern industrial uses of clays are based on this history and knowledge.

In a first part, the report will deal with a presentation of the laboratory. In a second part, I will introduce the general characteristics of clay. In the third part, the experiment setup and the devices will be presented. And finally, the results obtained with the TGA and the discussion about them will be presented.

I - PRESENTATION OF THE LABORATORY

1) Division of complex materials

Staff :

Professor Arnljot Elgsæter

Professor Jon Otto Fossum

Professor Alex Hansen

Professor Arne Mikkelsen

Professor Frode Mo

Professor Steinar Raaen

The division was established July 1st 2003.

The research is focused on the Physics of Soft and Complex Materials including Biological Physics. The studied phenomena include : the structure and dynamics of nanostructured surface alloys, structural phase transitions in ferroic compounds, clay containing systems and polymers, electro-rheological properties and diffusion properties of natural and synthetic clay particles , folding and conformational dynamics of proteins and other biopolymers, anomalous diffusion processes, mechanical properties of rough surfaces, brittle fracture, mechanical properties of granular media, multiphase flow in porous media.

The research comprises the use of experimental methods, computer simulations and theoretical methods.

The home laboratories of the division contain facilities for : solid state surfaces in ultrahigh vacuum, wide-angle x-ray scattering, static and dynamic light scattering, light microscopy, atomic force microscopy, preparation of soft aqueous samples for transmission electron microscopy , measurements of static and dynamic viscoelastic properties of soft materials (rheology), micro- and nano-calorimetry, thermo-gravimetry, studies of dynamic electro-optic properties of soft materials, isolation and purification of nanoparticles including

biopolymers. Some members of the section are also regular users of the synchrotron facilities in Grenoble, France and at Sao Paulo, Brazil.

The computer simulation methods include Brownian dynamics, Monte Carlo and deterministic particle dynamics methods.

The theoretical studies are mainly on condensed matter physics theory and statistical physics.

2) Synthetic clays, Experimental investigations of soft materials and complex systems

Professor Jon Otto Fossum

Yves Méheust Post Doc

Ahmed Gmira Post Doc

Davi de Miranda Fonseca PhD student

Kanak Parmar PhD student

The research group has during several years focused on basic understanding of problems within soft materials and complex systems, in particular physical phenomena in soft matter using synthetic silicates (clay) as the physical complex model system. Important experimental methods being used include rheology and light scattering, synchrotron x-ray scattering (at ESRF and other sources) and neutron scattering (mostly at IFE, Kjeller), atomic force microscopy, electrorheology, differential scanning calorimetry, analysis thermogravimetric. A significant part of the activity also involves upgrading of instrumentation and experimental methods for soft condensed materials studies and phenomena on the nanoscale.

AFM techniques are increasingly used for studies of materials surfaces on micro- and nano-scales. AFM readily provides high-resolution digitized images of surface features. In situ surface characterization helps to develop a better understanding of microstructure evolution of materials such as clay (Figure 1).

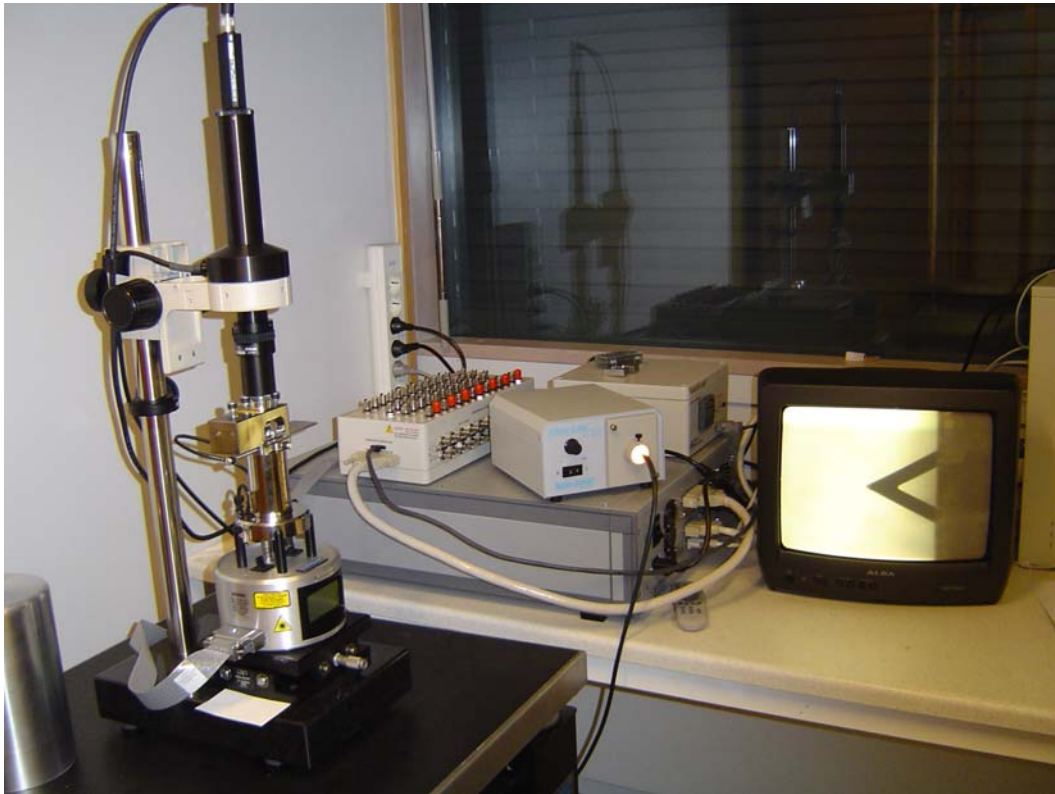


Figure 1: Atomic Force Microscope

The phenomenon of electrorheology is discussed in relation to possible mechanisms involving polarization of dispersions in flow and comparisons between electrorheological activity and dielectric properties are made. The importance of the rate of polarization as well as its magnitude is stressed. How such considerations led to electrorheological fluids based on dispersed semiconducting polymers as an alternative to traditional water containing polyelectrolytes is discussed, and some of the dielectric and electrorheological properties of these new electrorheological fluids are described.

Rheology is defined as the science of the deformation and flow of matter and describes mainly the material properties of fluid and semi-solid materials. Rheology is interdisciplinary and is used to describe the properties of a wide variety of materials such as clay (Figure 2).



Figure 2: Rheometer

Differential scanning calorimetry (DSC) is a well established measuring method which is used on a large scale in different areas. Measurement values obtained by DSC allow heat capacity, heat of transition, kinetic data, purity and glass transition to be determined. DSC curves serve to identify substances, to set up phase diagrams and to determine degrees of crystallinity (Figure 3).



Figure 3: Differential Scanning Calorimeter

Thermogravimetric analysis (TGA), in which the mass of a sample is monitored as a function of temperature, is one of the oldest analytical techniques used in clay mineralogy. TGA has been used to obtain a variety of information on minerals, particularly hydrous phases, such as clay and zeolite (Figure 4).



Figure 4: Thermogravimetric analyser

II – PRESENTATION OF FLUOROHECTORITE CLAY

1) General characteristics of clay

Smectites are composed of flat particles with a diameter going from a few microns to several hundred microns. These particles represent a sheet stacking, their structure form a “house of cards”, showed in figure 5 [1].

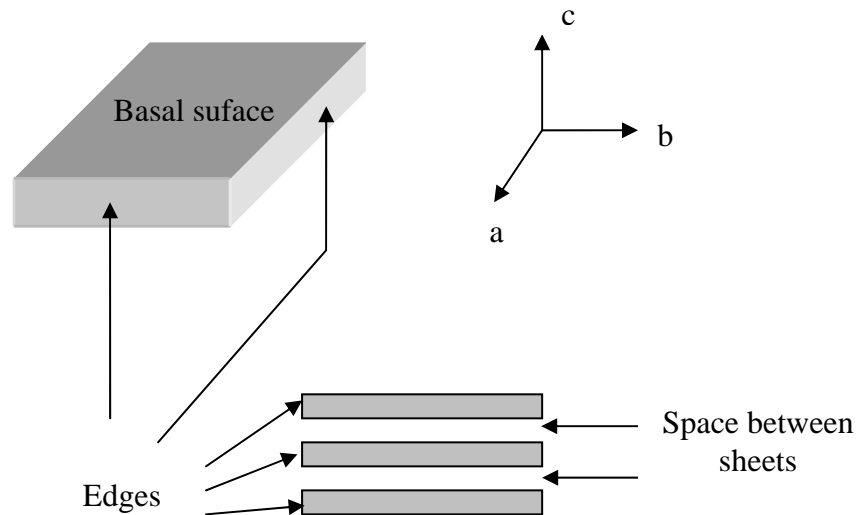
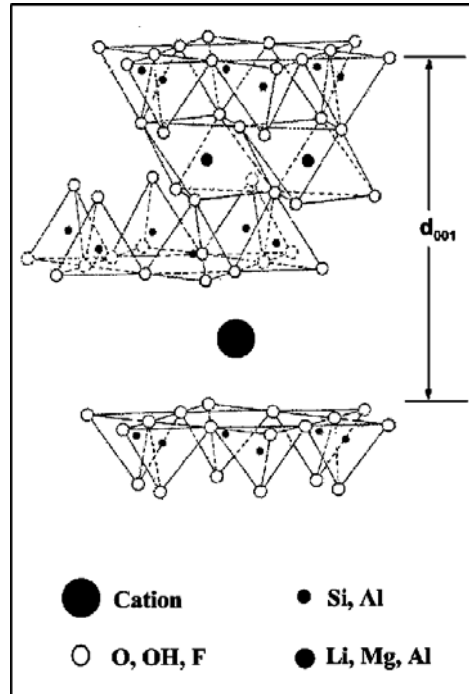


Figure 5: Sheet stacking, showing the basal surface, the particles edges, and the space between each sheet

Smectites sheets consist of octahedral layer confined between two silicate layers in tetrahedral structure. The total thickness of sheet and space between two sheets is about 1 nm. Clay can consist of 10 to 100 platelets. They have the capacity to swell with water, as explained after, and then their thickness could grow. Figure 6 shows this tetrahedral and octahedral structure.

Clays have the unique ability to be pillared by intercalated guest ions, making their study of fundamental importance within the general context of “nanosandwiches” as a basis for nanotechnologies [2].



*Figure 6: The structure of a typical 2:1 layered silicate clay,
The distance d_{001} is about 1 nm*

Here, we study the synthetic smectite clay Na-Fluorohectorite. This clay has the chemical formula per half unit cell $\text{Na}_{0.6}(\text{Mg}_{2.4}\text{Li}_{0.6})\text{Si}_4\text{O}_{10}\text{F}_2$. Hectorite is a 2:1 phyllosilicate, meaning that the platelets are formed by two inverted silicate tetrahedral sheets, sharing their apical oxygens with one octahedral sheet sandwiched in between. It is classified as a trioctahedral smectite since Li^+ substitutes for Mg^{2+} in the octahedral sheet sites, which are fully occupied. Fluorohectorites differ from natural hectorites in that the OH groups have been replaced by Fluor (F).

X-ray scattering showed that clay contain pores in the meso-scale. The way the stacks organize with respect to one another during sedimentation and drying with external pressure, may induce the creation of mesopores between the grains of clay.

2) Water absorption

The small particle size and microporous structure of clay give them their extremely important capability to absorb water.

As clay takes in the water, the layer spacing may expand, and the expansion or swelling mechanism can be described according to two ranges of interactions, dependent on the distance between the silicate sheets [3]. In the first range of distances, lower than a few nanometers, the water is absorbed in successive monolayers on the surface of the silicate sheets, thus pushing them apart. The attractive energy results from the electrostatic and Van der Waals attractions. The second range of platelet distances is reached when more than about four monomolecular layers of water are intercalated. The electrical double-layer repulsion becomes the major repulsive force between platelets and it dominates the swelling process.

For Na-Fluorohectorite, this intercalation process, which can be controlled by temperature and relative humidity, yields three stable hydration states [4]. These are characterized by small interplatelet distances and thus the first range of interaction forces. The structures, referred to as having either 0, 1 or 2 intercalated water layers, are quite well ordered along the stacking direction (z axis). The unit cell along the stacking direction is given by the distance between the stacked platelets: around 1 nm for 0 water layers and 1.2 and 1.5 nm for 2 and 3 water layers respectively.

3) Preparation of sample Na-Fluorohectorite

The samples are based on synthetic sodium fluorohectorite (Corning Inc., New York) [2]. First the fluorohectorite powder is dissolved in deionized water and stirred for several days. Thereafter an ion exchange method is used, adding Na^+ in the form of NaCl , and in an amount of about 10 times the interlayer charge. After stirring for 2 days we obtained a two-phase system from which the supernatant was removed. The resulting part is then placed in dialysis membranes, and excess ions are removed by dialysis, exchanging the deionized water every 2 days. A check of this procedure is made by adding AgNO_3 to the system to detect possible Cl^- ions, which would precipitate as insoluble AgCl . The suspensions of sodium fluorohectorite are thereafter heat pressed at 120°C by exerting mechanical force onto a disc shaped sample volume. The load used was 10^4 kg, giving a pressure of 26 MPa. The final result is a smectite dehydrated clay where the clay platelets (1 nm thick) are stacked with the preferential orientation such that the main platelet direction is normal to the axis of compression (Figure 7).

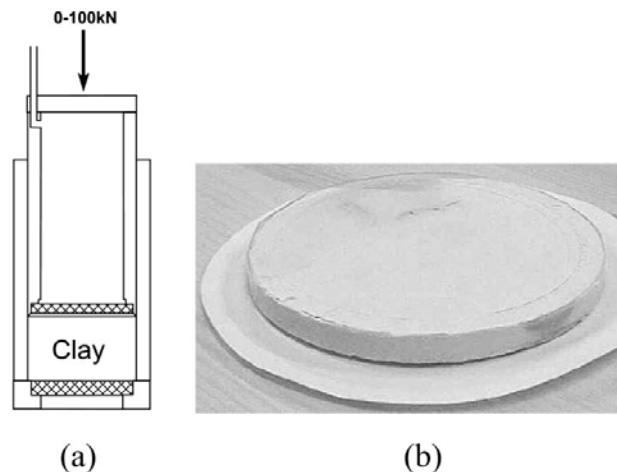


Figure 7 (a) The press used to make the dehydrated clay samples

Figure 7 (b) A fluorohectorite sample after leaving the clay press

III – EXPERIMENTS

1) Thermogravimetry

a) Principle

Thermogravimetry analysis (TGA) is one of the oldest analytical techniques used in clay mineralogy. TGA is essentially a mean of observing the weight of a sample as a function of temperature (dynamic heating or cooling) or time (isothermal heating). The equipment consists of a sensitive balance, a furnace arranged such that the sample holder sits inside the furnace, and a thermocouple to monitor the sample temperature and heating controller to keep temperature constant or to change it [5].

The experiments were performed with the TGA/SDTA851e, from Mettler-Toledo.

b) Devices

The TGA/SDTA851e/LF1100 module of the STARe system permits to measure the weight changes of a substance which occur during a controlled temperature program and in a defined gas atmosphere.

The module has a large furnace for maximal sample size 900 μ l, and the maximal furnace temperature of the measuring cell (balance and furnace) is 1600°C. Wide measurement range of the Mettler-Toledo balance is 1g and its resolution is 1 μ g. Its temperature accuracy is $\pm 0.25^\circ\text{C}$. The sample sensor is placed directly under the sample holder to guarantee an accurate measurement of the sample temperature.

The balance must be purged constantly with protective gas. Here, one uses Nitrogen with a flow rate of 20ml/min. One uses air as a reactive gas with a flow rate of 50ml/min. The use of thermostat is obligatory because the balance housing must be thermostated to ensure the reproductibility of the signal. The bath temperature of the thermostat must be 22°C. One uses a circulator from ThermoHaake, fills up the bath with 50% of distilled water and 50% of

ordinary antifreeze. One has to add distilled water regularly in the bath if else the temperature can decrease down to -15°C .

For the operation of the TGA module one needs the STARe software version 8.10. Installation and utilisation details are explained in appendix. This software drives the TGA module, permits the calibration and the treatment of the data. During the operation the entire database can be automatically saved.

The module should have been placed somewhere where the effect of random vibrations can be avoided, and it should have been moved with greater caution.

2) Operative mode

a) Samples

The experiments are run on four kinds of sample. Na flhc powder, thin sediment sample, thick sediment sample, and thin sample sealed with silicon rubber so that water only can enter or exit through open ends of sample (Figure 8). Samples are placed in a crucible, alumina $70\mu\text{l}$.



Figure 8: Na-Flhc Powder, Thin sediment sample, and thick sediment sample

b) Methods

On one hand, we perform fast dehydration and rehydration on different samples. On the other hand, we will perform slow dehydration and rehydration on different samples. The experiments are run under wet and dry atmosphere. We will perform experiments in temperature range from 25°C to 130°C, because all the water inside the clays is evaporated at 110°C.

Fast dehydration and rehydration : The temperature increases from 25°C to 130°C in one shot with heating rate of 30°C/min under dry conditions, followed by an isothermal segment at 130°C during 90 minutes. After that the temperature decreases from 130°C to 25°C in one shot with cooling rate of -3,5°C/min under wet conditions, and finally an isothermal segment at 25°C during 180 minutes.

Slow dehydration and rehydration : The temperature increases from 25°C to 130°C with a heating rate of 5°C/min with an isothermal segment during 20 minutes at each 5°C step under dry conditions. Thereafter the temperature decreases from 130°C to 25°C with a cooling rate of -5°C/min and with an isothermal segment during 20 minutes at each 5°C step under wet conditions.

c) Control of the Humidity

As noted before, one performs experiments under wet and dry conditions. Depending on the desired atmosphere, one can use salt to obtain different relative humidity (Figure 9).

T/°C	LiCl	MgCl ₂	K ₂ CO ₃	Mg(NO ₃) ₂	NaCl	KCl	K ₂ SO ₄
20	11.31 %	33.07 %	43.2 %	54.38 %	75.47 %	85.11 %	97.6 %
25	11.30 %	32.78 %	43.2 %	52.89 %	75.29 %	84.34 %	97.3 %
30	11.28 %	32.44 %	43.2 %	51.40 %	75.09 %	83.62 %	97 %
35	11.25 %	32.05 %		49.91 %	74.87 %	82.95 %	96.7 %

Figure 9: Standard salt solutions function of temperature, relative humidity in %

Here one wants to perform experiments with a dry atmosphere about 20% RH, and a wet atmosphere about 97% RH.

Then, we use a pump which pumps air at flow rate at 50ml/min, and the air passes through a desiccator. One of the desiccators is filled with silica gel dissicant in order to have dry atmosphere, and another is filled with saturated salt solution of potassium sulphate to obtain wet atmosphere (Figure 10).

The proportion of potassium sulphate in distilled water is 11mg/100ml.



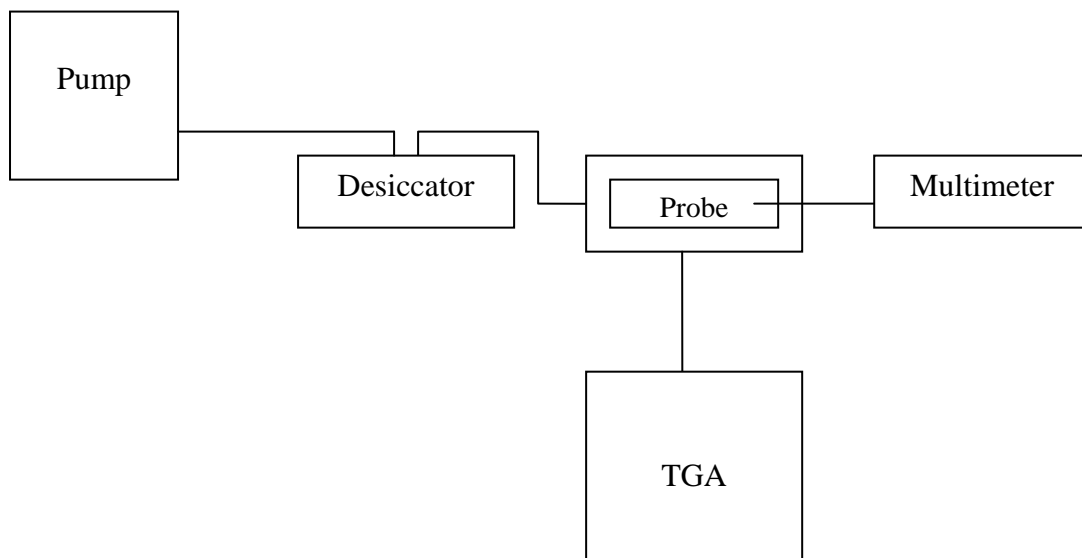
Figure10 : Desiccator with salt saturated solution (right) and silicat gel dissicant (left)

Relative humidity indicates how moist the air is. It may be defined as the ratio of the water vapor density (mass per unit volume) to the saturation water vapor density, relative to the temperature of the air and is usually expressed in percent.

$$RH = \frac{D_{H_2O}}{D_{sat}(T)}$$

To measure the relative humidity, we place a humidity sensor just after the desiccator and just before the module, because one wants to measure the relative humidity entering in the TGA. For this purpose, a special tight box has been conceived to place the probe inside. One can read RH on the multimeter associated. The probe used has an accuracy of $\pm 2\%$ RH from 0 to 90% RH, and $\pm 3\%$ RH from 90 to 100% RH. During the experiment, we measure the RH at a temperature about 25°C.

The control humidity system is composed as follows :



IV – RESULTS AND DISCUSSION

1) Fast dehydration and rehydration

As explained earlier, one performs fast dehydration by quickly heating the sample from 25°C up to 130°C, this heating is followed by an isothermal segment at 130°C during 90 minutes in order to observe the time required for the sample weight to stabilize. In the same way, one performs a fast rehydration by quickly cooling the sample from 130°C down to 25°C, and it is followed by an isothermal segment at 25°C during 120 minutes. The heating and cooling rate, as the isothermal segment duration, are different because the rehydration is slower than the dehydration. For thick sediment and thin silicon samples, the method had been modified because they absorb water slower than the other samples.

Na Flhc Powder sample

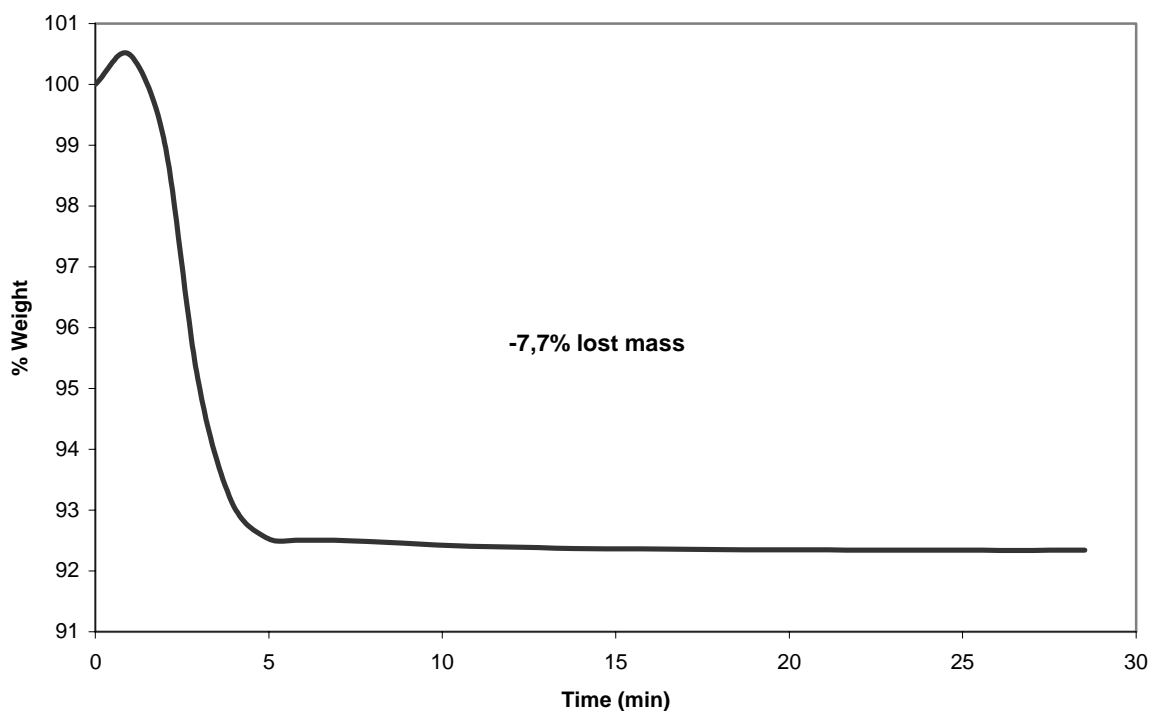


Figure 11: Fast dehydration Na Flhc Powder

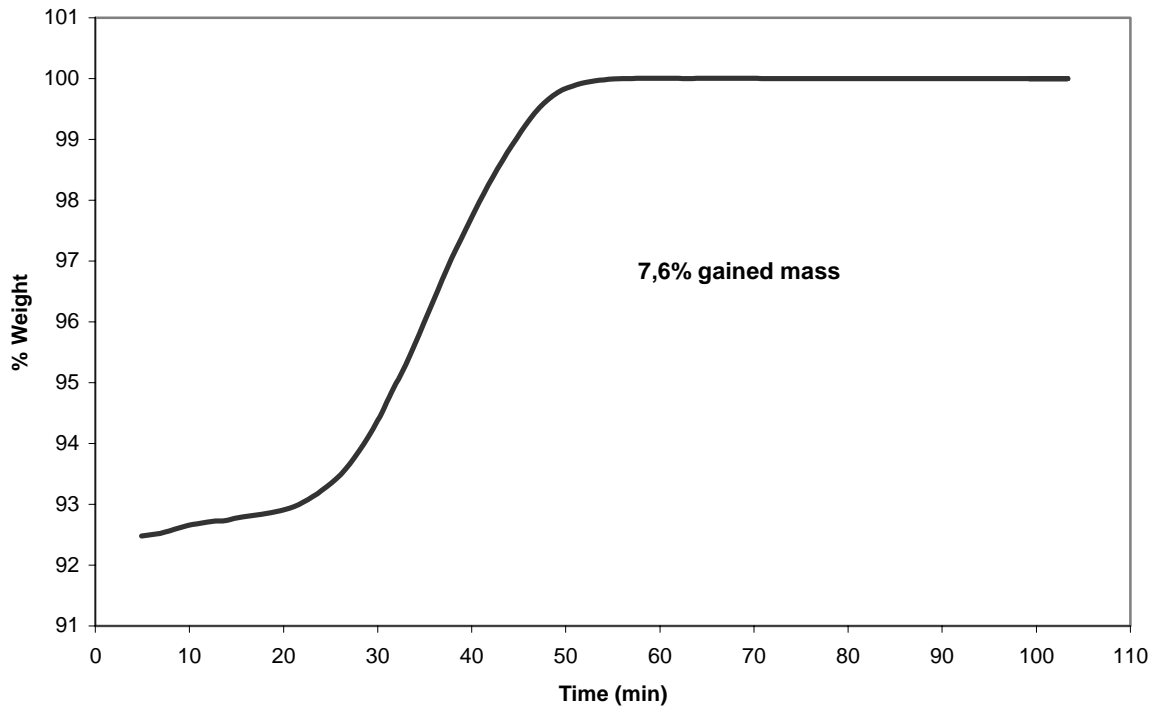


Figure 12 : Fast rehydration Na Flhc Powder

The maximum loss of mass for the dehydration is -7,7%, all the water disappeared from the clay in about 5 minutes, that the dehydration occurs essentially between 60°C and 110°C.

It can also be observed that the clay experiences a weight gain during the first minute. This phenomena is also observed for the other samples. The sensor is responsible of such variations, because temperature increases by 105°C in less than 3 minutes. This may considerably disturb the sensor.

The maximum of gained mass for the rehydration is +7,6%, the stabilization time is about 55 minutes, and we can see that the rehydration occurs essentially between 65°C and 30°C.

The sample re-absorbs completely the water during the experiment.

Thin sediment Na Flhc Sample

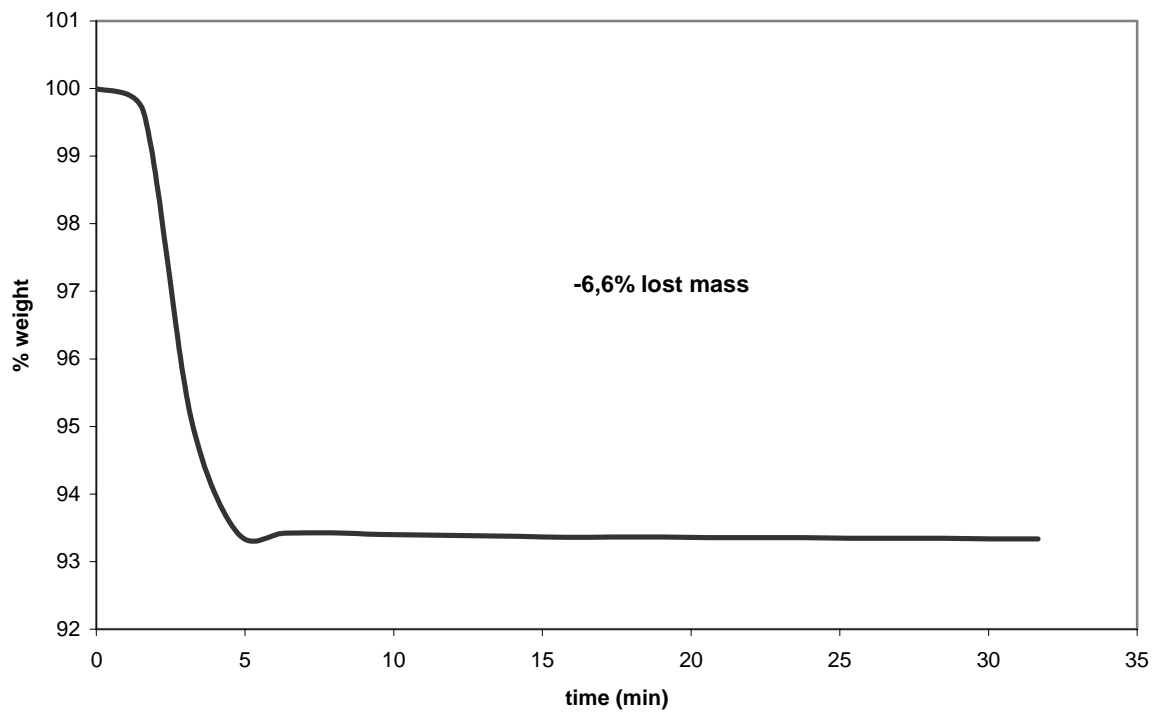


Figure 13: Fast dehydration thin sediment

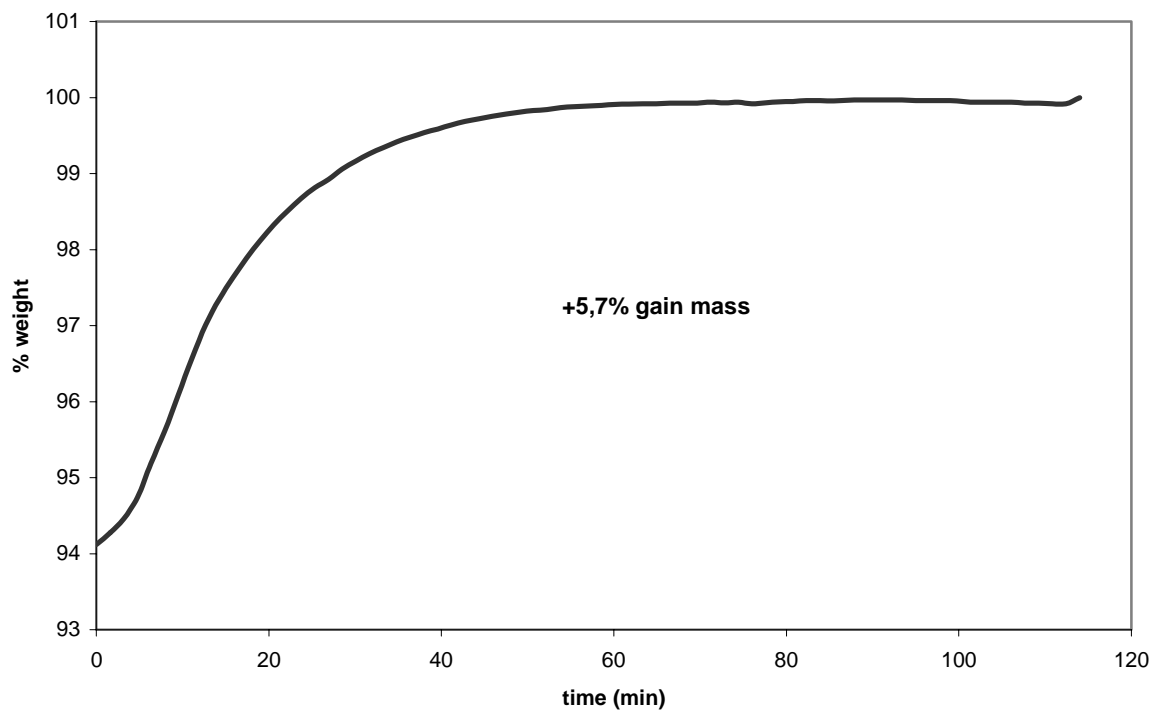


Figure 14: Fast rehydration thin sediment

The dehydration occurs between 60°C and 120°C for the thin sediment sample with maximum lost mass around -6,6%.

The stabilization time is about 5 minutes while the sample gains +5,7% during rehydration with stabilization time around 60 minutes.

Thick Sediment Na Flhc Sample

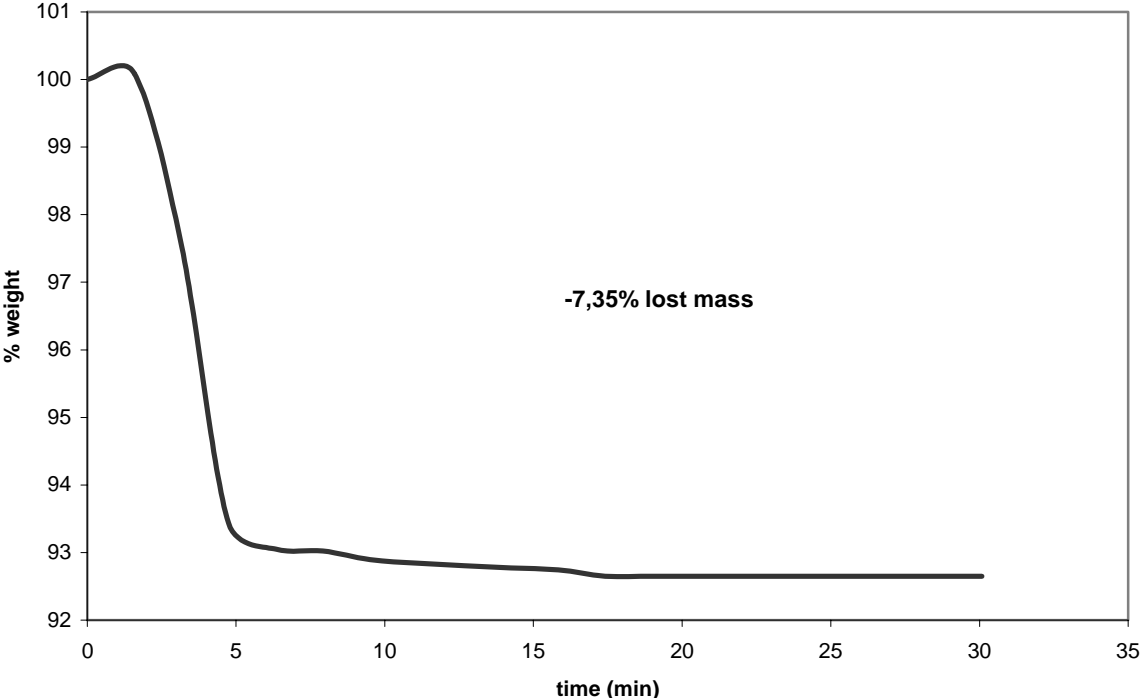


Figure 15 : Fast dehydration thick sediment

For the dehydration of thick sediment sample, the maximum of lost mass is -7,35%, the stabilization is observed in about 5 minutes and essentially occurs between 70°C and 120°C.

During the rehydration (Figure 16), the maximum of gained mass is +7,07%, the time stabilization is about 120 minutes, and the rehydration occurs between 50°C and 30°C.

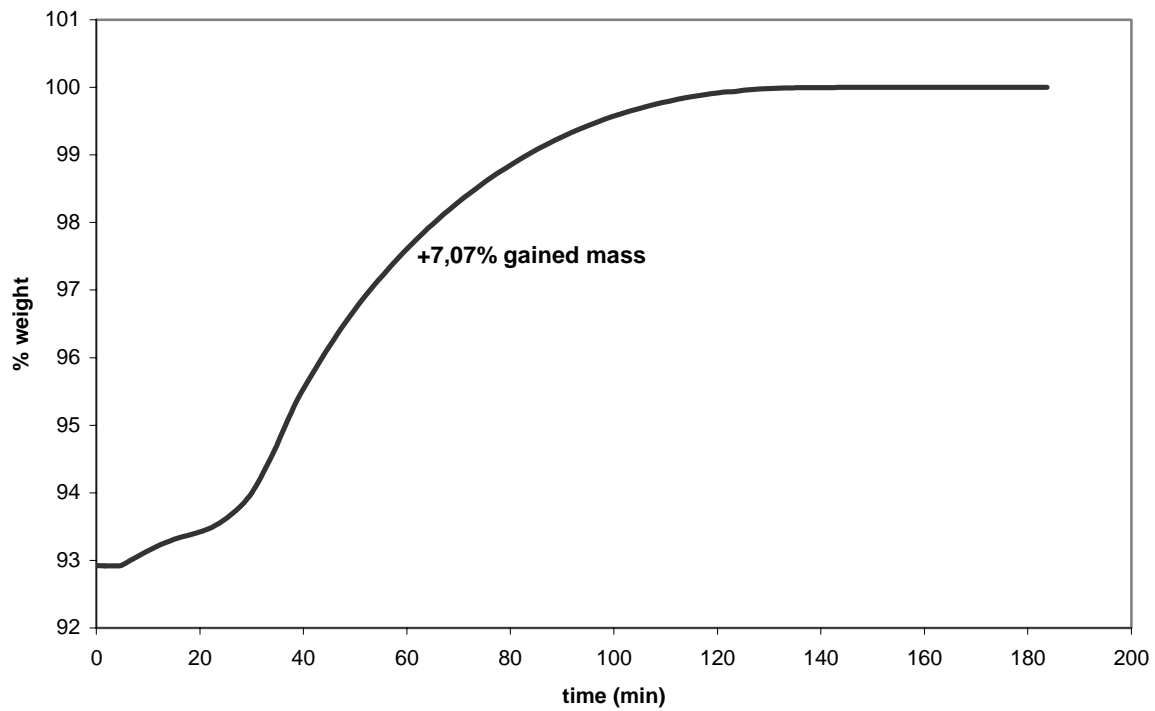


Figure 16 : Fast rehydration thick sediment

Thin silicon sample

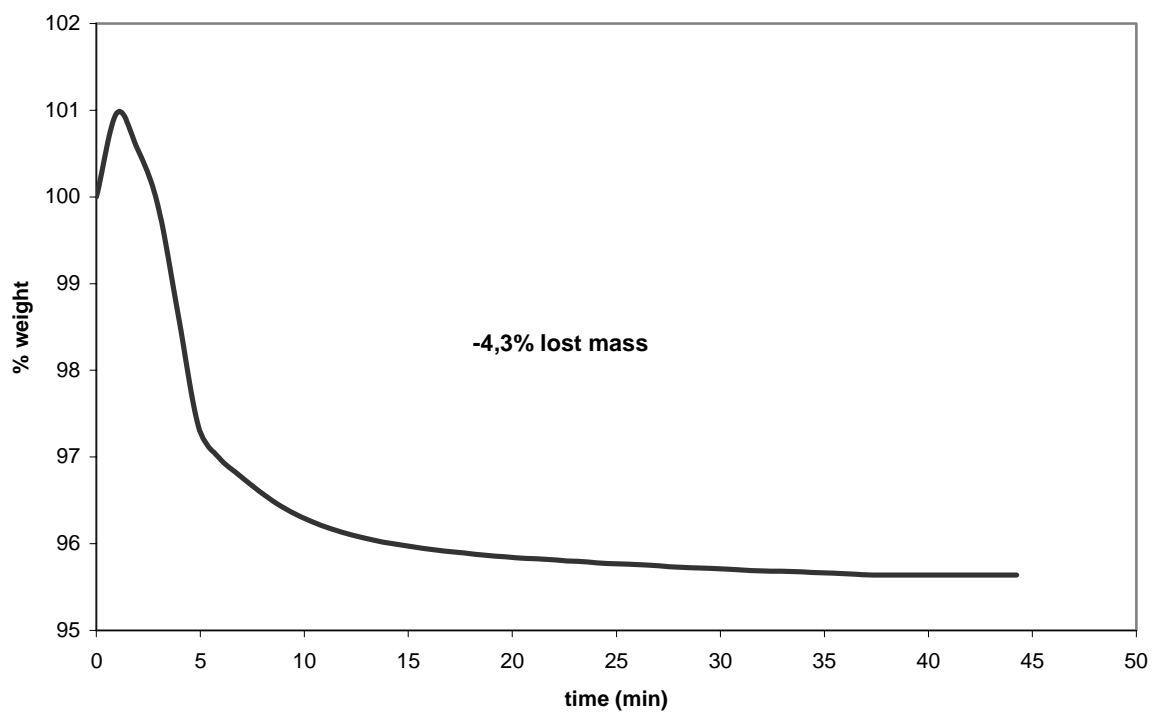


Figure 17: Fast dehydration thin silicon

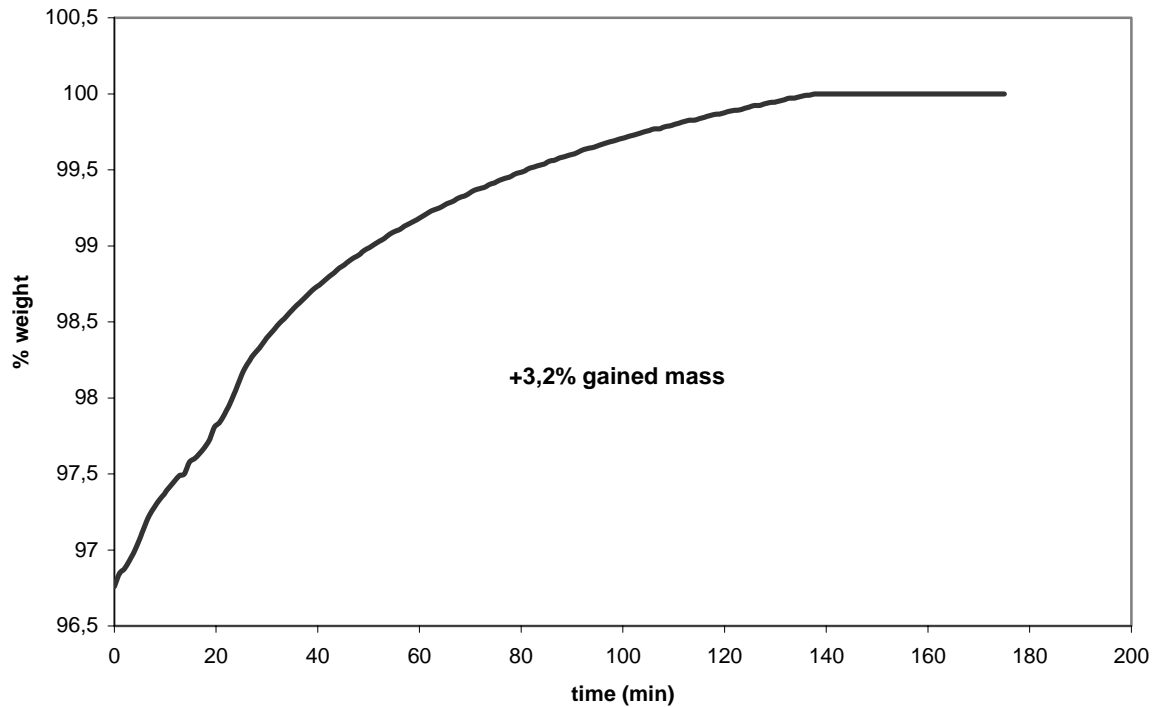


Figure 18: Fast rehydration thin silicon

In the case of the thin sediment silicon rubber, the maximum of lost mass is -4,3%, the stabilization of the weight sample is about 30 minutes, and the dehydration occurs between 130°C and 30°C; this sample needs almost all the period of isothermal segment to be dehydrated completely.

For the rehydration, the maximum of gained mass is +3,2%, the clay reabsorbs water during the 140 minutes and then the weight is stabilized, the rehydration occurs between 130°C and 30°C.

We observe approximatively the same results than the previous experiments [6].

2) Slow dehydration and rehydration

The slow dehydration is performed by heating from 25°C up to 130°C with isothermal segment during 20 minutes at each temperature step. The sample is thereafter cooled from 130°C down to 25°C with isothermal segment during 20 minutes at each temperature step. The hysteresis resulting of experiments are as follows:

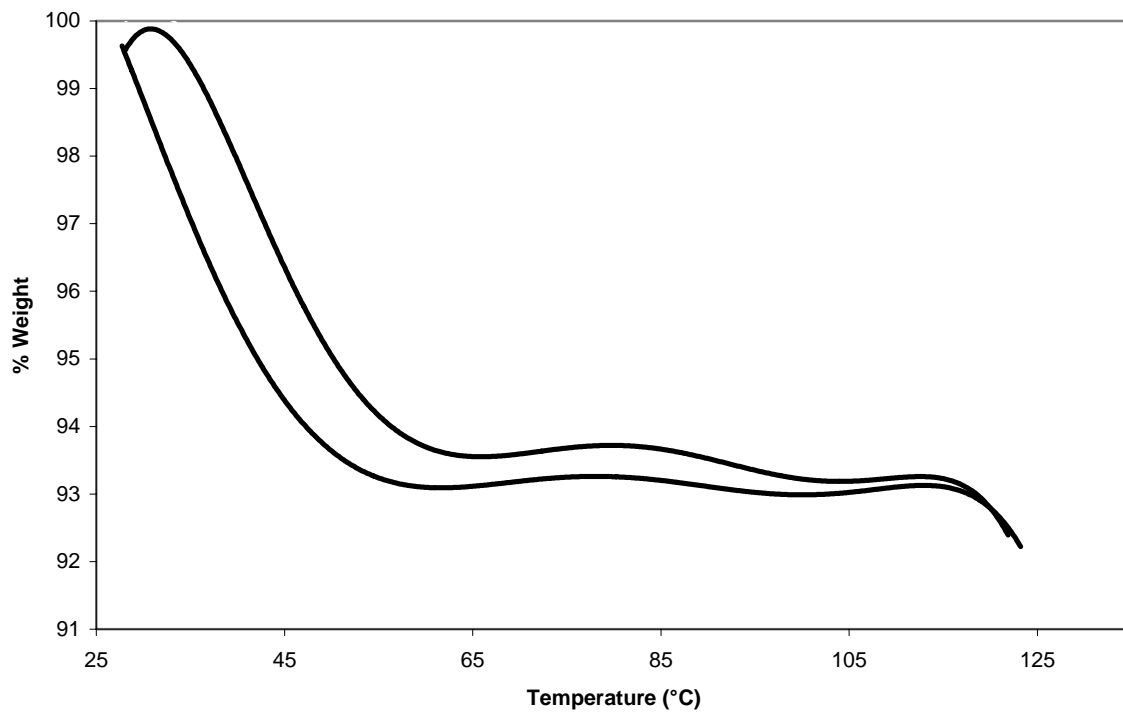


Figure 19: Slow dehydration and rehydration Na Flhc powder

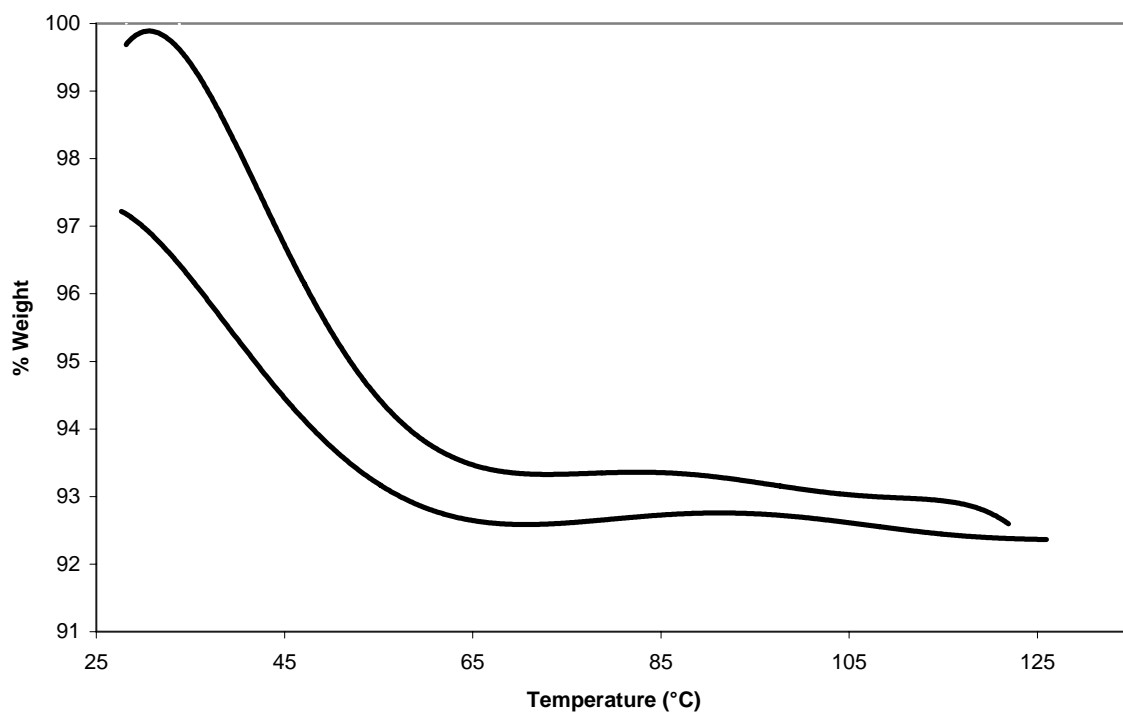


Figure 20: Slow dehydration and rehydration thin sediment

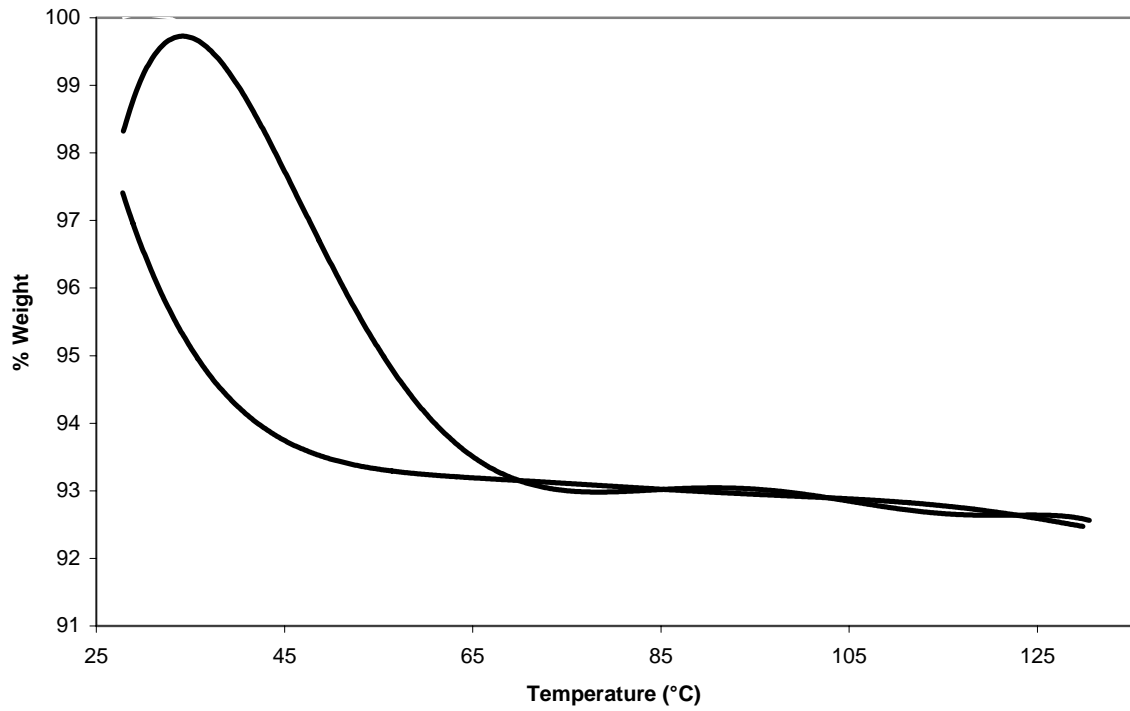


Figure 21: Slow dehydration and rehydration thick sediment

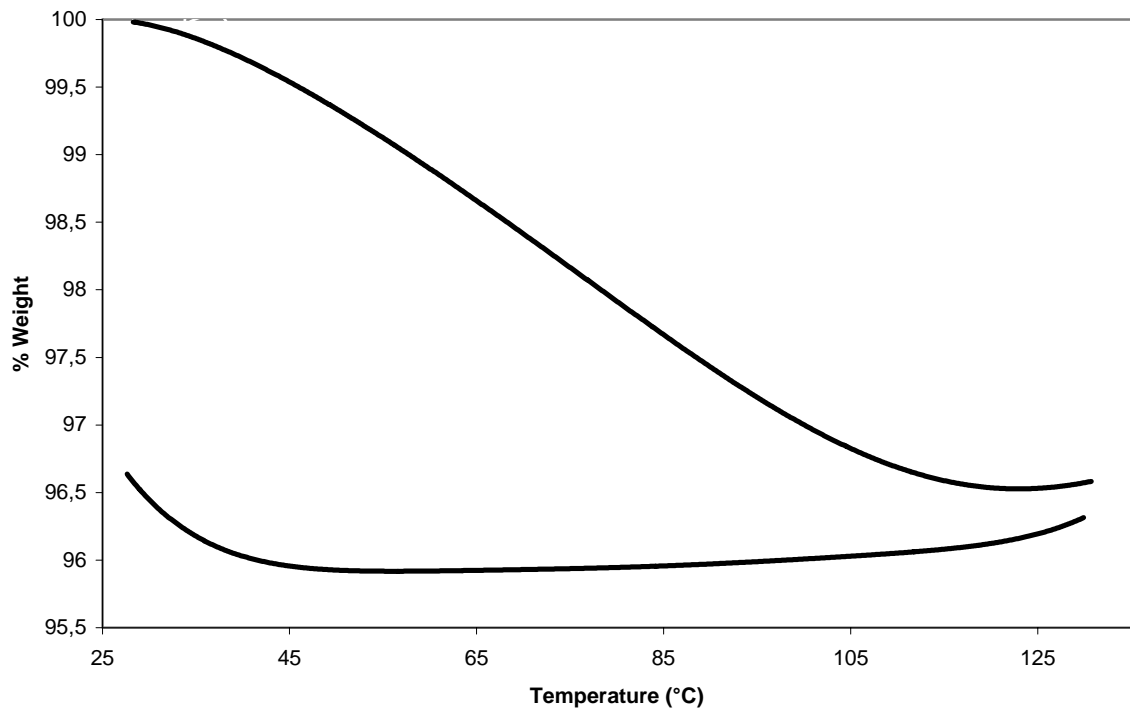


Figure 22: Slow dehydration and rehydration thin silicon

3) Discussion

During a fast process (dehydration and rehydration) the three samples (powder, thin and thick sediment) have relatively the same behaviour. No significant changes were observed.

Na-Fluotohectorite exhibits a maximum weight loss around 7% during the dehydration, which occurs essentially in the [60-120°C] range. These results are in good agreements with previous observations [6].

The rehydration occurs with maximum mass gained between 5 and 7%, most of the absorption of water is observed in the [60-30°C] range.

Concerning the time stabilization (time needed to remain sample mass constant during the experiment), the three samples have the same behaviour: mass stabilization after 5 minutes during the dehydration. The main difference is observed during the inverse process: the thick sediment takes about 120 minutes to stabilize the weight while the other samples have stabilization time around 60 minutes. This difference can be explained by the sample nature: thick sediment sample takes more time to reabsorb water molecules.

Slow dehydration and rehydration are used to obtain thermodynamical equilibrium for day systems.

The Na-Flhc powder sample presents a hysteresis between dehydration and rehydration. The main rehydration occurs under 65°C and the rehydration is complete (Figure 19).

Thin and thick sediments samples present a partial rehydration. The weight sample after rehydration is around 3% below the initial value (Figures 20 and 21).

Concerning thin silicon sample (Figure 22), it was made in order to permit water rehydration by only two sides. This sample takes only 0.5%, this is probably due to the small water quantities which can enter the sample. Thin silicon sample needs a couple of days to rehydrate completely.

In this case, we should increase the time of the isothermal segment. Another explanation is that the bad rehydration is due to the silicon interaction with the temperature and the relative humidity, and therefore it does not permit the sample to reabsorb water correctly.

CONCLUSION

Experiments performed on synthetic clay Na-Fluorohectorite gave us information about the equilibrium of weight sample during rehydration and dehydration. All these experiments were based on the use of a very accurate thermobalance. The module had been moved several times since its last utilisation and was completely decalibrated. And therefore, during this project, the main work I had to do was to make the module function correctly, and make its use easy for the next users, hence a manual for the STARe software was written.

Concerning the experiments, it would be interesting to study the behaviour of clay (powder, thin or thick sediments) as function of relative humidity. For exemple, fast dehydration could be run on Na Flhc powder with different relative humidity (10%, 20%, 30%, 40% and 50%).

This training period taught me to work independtly as well as I learnt to work in a steam.

I experienced how to make decisions on my own, find solutions to physical and instrumentation-oriented problems. It was also a rewarding challenge to integrate in a different country with a different language.

In conclusion, I learnt a lot on both professional and personal levels.

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APPENDIX A - DIFFICULTIES

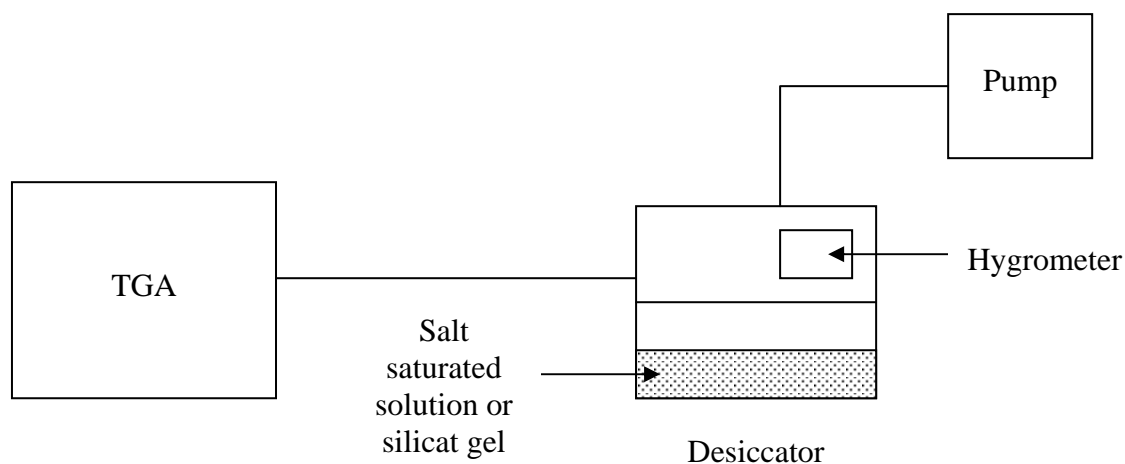
The module does not allow us to perform experiment with more than 10 segments and not more than 60 000 measures per experiment (1 measure per second). So, one has to split up one experiment into several to obtain around 100 segments. In the end, we export all the data from the experiments to a file. The final curves have been obtained in Excel.

The default temperature is 25°C and we can not perform experiment under 25°C. I contacted Frederick Einarsson, Mettler Toledo Sweden, about these problems. He will write another method in the firmware to decrease the temperature under 5°C.

APPENDIX B – CONTROL OF HUMIDITY SYSTEM

The box containing the probe is not sealed perfectly. Therefore, it is difficult to obtain 97% RH. The maximum RH obtained is about 93%.

I proposed the following system as a solution:



The components list will be ordered to VWR International.

(Website: <http://no.vwr.com/app/Home>)

Components	Nr. Article	Price
Termohygrometer Digital Testo 608-H2 Humidity range +2 to +98% RH Temperature range -10 to +70°C	139581-1	1120,- Kr
Eksikator, med sidekran, Mobilex, SCHOTT Flens diam 215 mm	116134-150	1172,50 Kr
Eksikator Kran, Mobilex	116138-1	287,- Kr
Propp, teflon, PTFE, NS 14/20	130820-14	350,- Kr

APPENDIX C - STARE SOFTWARE

Installation of Ingres 2.6 software

Before installing the Ingres software, don't forget to create an administrator account named Ingres if it does not exist. (user account : ingres, password : 815flhc). Follow the instructions given in the manual.

To check the Ingres II 2.6 license:

Call up the windows command prompt.

C:\Documents and settings\Ingres>cd\ ENTER (change directory)

C:\> d: ENTER (cd rom directory)

D:\>Ingres II 2.6 SP2 ENTER

D:\>Ingres II 2.6 SP2> LicCheck ENTER

Follow the instructions to complete the installation of the Ingres software license.

Installation of STARe software version 8.10

Follow the instructions given in the manual to install it and to start the software for the first time.

Database administrator : METTLER, password : flhc815.

The database name can be changed. In default it is STARe Default DB V8.10.

You need some numbers to start the software for the first time:

System Identification on Hardlock : (0) 11391.

Authorization for the software : F9170F92EFBC5FD4.

To install the options proceed as follows :

STARe windows → *function* → *Install windows*, click on the topic *options*. You have to enter several numbers for these options:

Authorization for the specific heat : 800900BCCC92BBF6.

Authorization for the routine windows : ABF5CB87C677E716.

Authorization for Mathematics : 93042FA0519495D7.

When you start the software, sometimes, an error message appears. If so, you have to verify that the Ingres database is started. You can do that by going to *Administrative Tools* in the *control panel*, and *service* then check if the Ingres Intelligent Database [II] is started.

Connections and Install windows

In the install window, click connections. For the first utilisation, you have to import the TGA data from the floppy. After, click on “connect/disconnect” and choose the TGA (same method for the DSC). The TGA is connected, and the routine windows appears. Click on the topic “module” → file → open, choose the TGA/SDTA851e/LF1100. All the parameters appear in the window.

ID number : 492

Standby temperature : 25°C

Time delay : 5 s

Sensor : MT1

No gas controller

Option : cryostat

Don't change the topic or close the windows, if else all these data will be erased (!!!). The TGA module must be connected to COM1 on the computer.

Check calibration

Once per month, you must perform a check in order to verify if the module is within the specifications.

Before running an experiment, verify if the bubble is in the circle to be sure that the module is horizontal. Use the screws feet and a level to adjust the TGA horizontally.

In the routine editor, select the method called *check calib In/Al (SDTA/TGA)*. Follow the instructions for the sample preparation. Tare the balance with the crucible, for that, insert the crucible in the furnace, wait for the stabilization (ST on the display crystal), and press *tare* on the module. Weigh your sample and click on *send experiment*. Follow the instructions on the display crystal (or on the computer screen).

After performing the check, open the curve in the evaluation window. Select the curve and in the topic *TA*, choose *SDTA*. It analyses the data, and if the commentaries are :”the module is within the specifications”, you can perform experiments. If the commentaries are :”Please calibrate the TGA851”, you have to perform a total calibration or manual calibration.

Total calibration

This experiment permits to calibrate the following parameters: tau lag adjustment, furnace temperature adjustment and sample temperature adjustment in one experiment.

In the installation window, module, select *Adjustment overview*, and then choose the right parameters. Keep this window open, if else, all the datas will not be saved.

In the routine editor, select the method called *Total Calib In/Al*. Follow the instructions for the sample preparation. After performing the calibration, a table appears with the new parameters, select save and run a check again to verify if the module is calibrated. If, after performing the calibration, an error message appears: “Total calibration failed”, the module is too far from the specifications, and then you must do a manual calibration.

Manual calibration

Manual calibration is very tricky to perform, because the results you obtain and the parameters you enter are very uncertain. Normally, only a qualified person could do that.

Manual calibration permits the adjustments of all the parameters quoted before, one at a time. Before starting, you need to perform a check to have the sample temperature and the furnace temperature for indium and aluminium. In the routine editor, select *calib/adjust*, and then *Single sample temperature*. Choose the indium in first position, enter the onset value for the sample temperature (as shown on the check curve on page 33). Do it again for the aluminium in second position, and save the values.

Still on the topic *calib/adjust*, select *Single temp adjust*. Choose indium in first position and enter the onset value for the furnace temperature (as shown on the check curve on page 33), the gas used (air), and the crucible used for the TGA Alumina Pan 70µl. Do it for the aluminium on the second position and save the values.

A table with values called A, B, C appears. Tau lag values are false so enter the values between the brackets, and then save the parameters. But, if the new values are too far from the specified ones, the manual calibration can fail and then an error message will appear. So, you need to enter other onset values than those are on the check curve.

After doing that, you need to perform a check, and then you will see the new values after evaluation. You need to do manual calibration and perform checks until you obtain the right values and then: “the module is within the specifications”.

Create a method

In the routine editor, select *new* method. You can create a method with only 10 segments. There are two kinds of segment: dynamic segment, with which the temperature varies with heating rate, and the isothermal segment, with which the temperature stays constant during a fixed period.

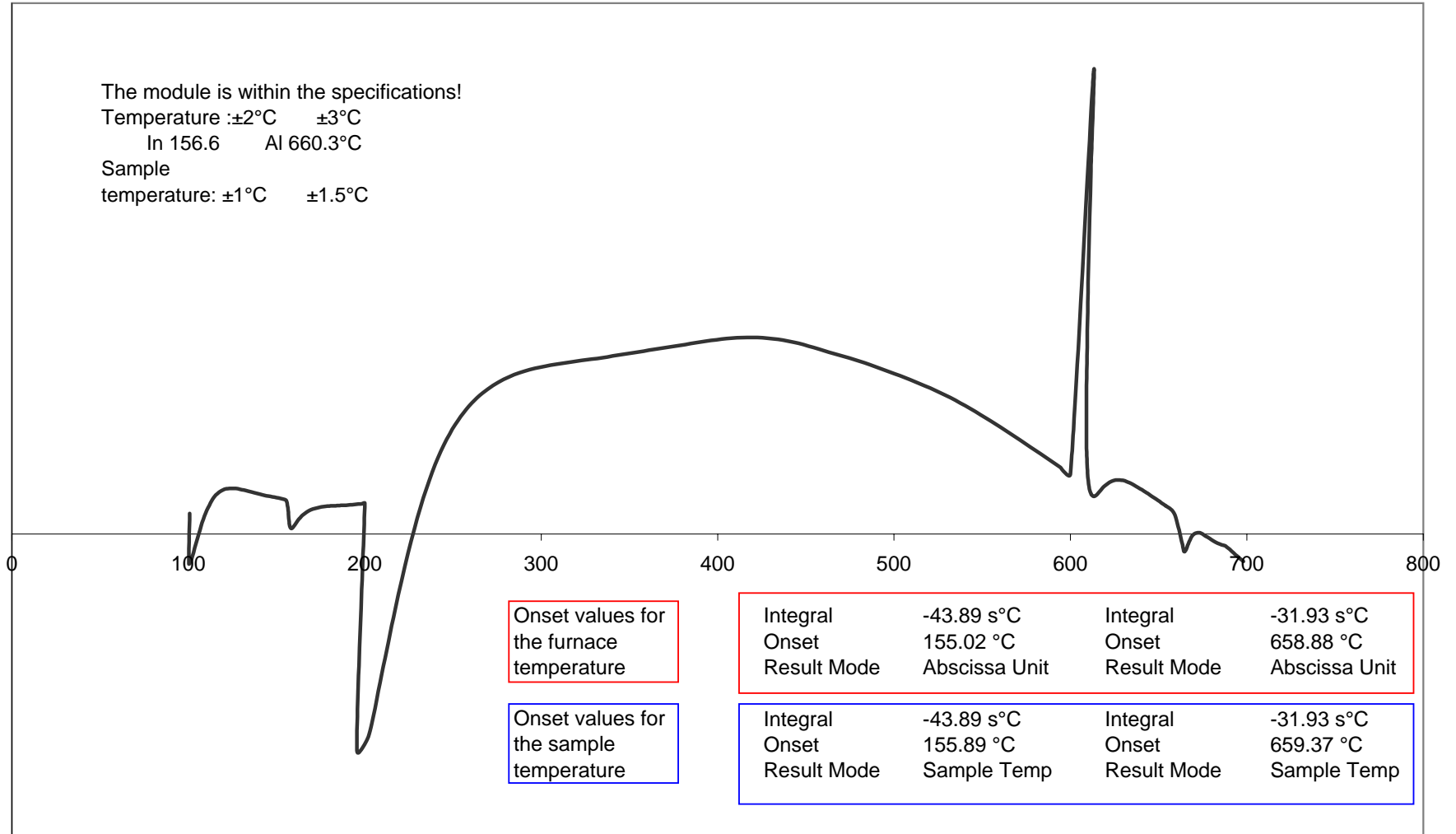
For that, select *add dyn*, enter the departure temperature and the arrival temperature, with heating rate. If the temperature decreases, the cooling rate needs to be negative. Or select *add iso*, enter the duration of the segment. You can specify the gas flow rate you want to use with the gas segment.

Export files

Open the curve to be exported in the evaluation window. Select the topic *settings*, then *Print/Export*, select the data to export and write the maximum number of points you want (the machine measures one point every 1 second). Then choose *File, Import/Export* and *Export other format* (it will be exported in .txt format). It is possible to superpose several curves and to save data of all these curves in the same file. The data related to each curve will be written one after the other.

Check In/Al (Manual Calibration)

The module is within the specifications!
 Temperature : $\pm 2^{\circ}\text{C}$ $\pm 3^{\circ}\text{C}$
 In 156.6 Al 660.3 $^{\circ}\text{C}$
 Sample
 temperature: $\pm 1^{\circ}\text{C}$ $\pm 1.5^{\circ}\text{C}$



APPENDIX D – PERSONS TO CONTACT

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