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"Water diffusion in synthetic smectite clays"
"Diffusion de l'eau dans une argile smectite synthétique"

This work has been carried out at the Department of physics at the Faculty of Natural Science and Technology, under supervision of Jon Otto Fossum and Yves Méheust.

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Abstract

This study addresses hydration of the synthetic smectite clays Sodium and Nickel Fluorohectorites, using thermogravimetry analysis (TGA). The absorption of water in these materials is a complex phenomenon due to the existence of a porosity both at the nano and meso scale. TGA consists in measuring the weight of clay sample as a function of time or temperature, thus recording the variations of weight in clays, caused by absorption or evaporation of water. We carried out experiments where clays were either heated from 25°C up to 130°C under a dry atmosphere or cooled from 130°C down to 25°C under a humid atmosphere. The humidity was measured at the same time. In a first series of experiments, clays were slowly heated and reached 130°C with steps of 5°C and then clays returned to 25°C in the same way. In a second series, clays were heated up to 130°C in one shot. When the weight was steady at this temperature, clays were cooled down to 25°C also in one shot. From the experimental curves it appears that the response of the sensor to temperature changes must be taken into account before analyzing curves. Taking this correction into account, we analyzed the curves of slow dehydration and hydration and could draw the curves of weight at equilibrium as a function of temperature. Then with the curves of fast dehydration and hydration we found time constants characterizing evaporation from nanopores and absorption in nano and mesopores.

Introduction

Clay minerals were originally defined in the nineteenth century as the crystallised particles with diameters lower than 2 μm, because of the microscopic limit. Nowadays it is well known that many particles belong to this size range and the term clay mineral is normally reserved for fine-grained layered silicates. Natural clays are the smallest structures in geology as it is shown in the Wentworth's scale (figure 1), widely used in geology. Most of the natural mineral clays form very heterogeneous mixtures, and this can cause both theoretical and experimental difficulties. Therefore it is very interesting to produce synthetically pure clay minerals, with well-controlled structure and chemistry. The synthetic clays studied here are sodium and nickel fluorohectorites. These smectite clays are also studied by the other members of the Complex Materials laboratory, who are carrying out X-ray diffraction experiments. Nowadays the use of X-ray diffraction is undoubtedly the most valuable method for clay minerals investigations. Nevertheless thermal methods can give a considerable amount of information and can be used to supplement the results by X-ray examination. Those thermal methods have been used is this present work, in order to study hydration of synthetic clays. This has been done thanks to thermogravimetric analysis (TGA). Thermogravimetric analysis consists in measuring the weight of a clay sample as a function of time or temperature. In our experiments we firstly heated the sample under a dry atmosphere and cooled it under a humid atmosphere very slowly and then we heated and cooled the sample in one shot.

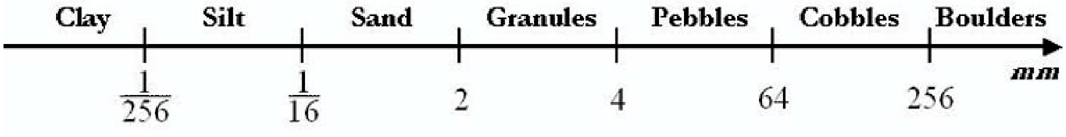

Figure 1: *The Wentworth's scale presents the different sizes of structures met in geology*

After a short presentation of clays, this report will deal with the experimental part of the work, which is based on a thermal balance called TGA/SDTA851e from the firm Mettler Toledo and on the STARe software. All the experiments were performed on both thin and thick samples of Fluorohectorites under a control of humidity, which has not been done before. In a third part the results are finally reported and discussed.

Chapter 1

Presentation of Fluorohectorite Clays

1.1 Clay Structure

1.1.1 Clay platelets

Every crystal flake of clay minerals is composed of a stacked arrangement of silicates layers. Each layer consists of an association of two different sheets, named the tetrahedral sheet and the octahedral sheet. As it is shown on figure 1.1, the four tips of the tetrahedra are occupied by Oxygen ions and their center by Silicon ion which shares its four positive charges with the four Oxygen ions of the tips. The six tips of the octahedra are occupied by Oxygen ions or hydroxyl groups, and their center by a cation such as Al^{3+}, Mg^{2+}, Fe^{2+} and Fe^{3+}. We are working on the synthetic clay called Fluorohectorite. This clay 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. Moreover all hydroxyl groups have been replaced by fluorine, which gives the name Fluorohectorite instead of hectorite.

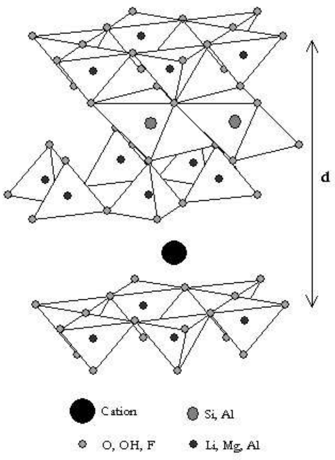

Figure 1.1: *The structure in platelets of a layered silicate clay. The interlayer distance d is about 1nm.*

1.1.2 Platelets stacking

Clays also have the ability to be pillared by intercalated guest ions, playing a significant role in clay structure. Actually the substitution of Mg^{2+} by Li^{+} in the octahedral layer creates a negative surface charge on the sheets. And this charge deficit is balanced by the charge of the interlayer cation. In the present work, the interlayer cations are Ni^{2+}or Na^{+}. The chemical formula of the used clays are per half unit cell[1]: $Na_{0,6}(Mg_{2,4}Li_{0,6})Si_4O_{10}F_2$ called Na-Fluorohectorite and $Ni_{0,3}(Mg_{2,4}Li_{0,6})Si_4O_{10}F_2$ called Ni-Fluorohectorite. The clay platelets tend to stack on top of each other, on the average about one hundred platelets, which gives a typical total height of about 0,1 μm.

1.1.3 Dehydrated clay

X-ray scattering showed that clays contain pores in the mesorange[2]. 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.

1.2 Water absorption

The absorption of water consists both in the filling of mesopores, between the platelets stacks and in the interaction of water molecules inside the clay particles, between platelets.

The absorption of water between the layers, changes the average interlayer distance. This swelling mechanism can be described by two kinds of interactions, dependant on the distance between the silicate sheets.

- If the interlayer distance d is 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. This intercalation process yields three stable hydration states[3] in the case of Na-Fluorohectorite: 0, 1 or 2 intercalated water layers and four states[4] for Ni- Fluorohectorite: 0, 1, 2 or 3 intercalated water layers which are quite well ordered along the stacking direction. The distance between the stacked platelets depends on the amount of water layers:

For Na-Fluorohectorite	For Ni-Fluorohectorite
– for 0 water layer, d=1,0 nm	– for 0 water layer, d=1,1 nm
– for 1 water layer, d=1,2 nm	– for 1 water layer, d=1,4 nm
– for 2 water layers, d=1,5 nm.	– for 2 water layer, d=1,6 nm
	– for 3 water layers, d=1,8 nm.

- When more than four monomolecular layers of water are intercalated, the electrical double-layer repulsion dominates the swelling process. This situation had not been studied here.

When water intercalates between the sheets during this swelling process, the surface charge can no longer keep the cation in place and by adding salt to this water, the original interlayer cation can be exchanged with the one from the salt. Two different Fluorohectorites could be made in this manner.

The amount of water which can be intercalated between the clay platelets per half a unit cell has been estimated for Na-Fluorohectorite[1] to:

0	if 0 water layer
1,2	if 1 water layer
2,8	if 2 water layers

Chapter 2

Thermogravimetry

My experimental work has been devoted to studying the absorption of water in the synthetic clays presented in part 1.1: Na-Fluorohectorite and Ni-Fluorohectorite, while controlling the temperature and humidity of the surrounding air.

2.1 Technical facilities

2.1.1 Principle of thermogravimetry

Thermogravimetry is a tool widely used for the characterisation of clay minerals and which can give a considerable amount of information. In this method, the weight of a substance, in an environment heated or cooled at a controlled rate, is recorded as a function of time or temperature. Automatic equipment has been developed for this study. It mostly consists of a very accurate balance and a furnace. The sample cup is attached to a balance arm and the furnace is placed around the sample and can heat it.

2.1.2 Devices

The main machine that I made use of was a thermobalance from Mettler Toledo called TGA/SDTA851e/LF1100 . Its furnace is able to heat samples up to 1100°C, providing that the right crucible[1] is used for such temperatures. Except for the calibration of this apparatus[2], it has not been necessary to reach temperatures higher than 130°C.

The TGA monitored by a computer should continuously register weight changes of the sample with an accuracy of 5 μg in the range of 0 to 5 mg. This balance is thus of high sensitivity and therefore the least air current may affect the weighting system. That is the reason why the sample is enclosed by the furnace while weighting. The furnace should be completely tight to avoid such perturbations. The atmosphere surrounding the sample is totally controlled. Indeed, all the gases entering the machine come from the gas inlets on the right of the figure B.1 and all the gases escape through the same outlet. The flow rate should not exceed 70 mL/min. There are three gas inlets:

- the reactive gas, which can be introduced into the sample chamber so as to investigate chemical reactions with the sample.
- the protective gas, which should purge the balance in order to protect its mechanism from any harmful reaction with air, such as oxidation reactions.

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[1] in Alumine Oxyde

[2] see appendix B

- the purge gas, surrounding the sample, which should allow all vapor products formed during the experiment to evacuate from the sample chamber. Thereby it minimizes the evolved gas concentration in the sample and it reduces the interactions between sample and evolved gases.

The use of a thermostat with the TGA is well-recommended to obtain reproducible experiments. Maintained at a temperature of 22°C [3], the thermostat allows to cool the sample and to avoid fluctuations of temperature while the furnace heats the sample. Of course it is not possible to cool the sample below the temperature of the thermostat. This cooling system includes a circulator and a bath filled with distilled water and antifreeze. During cooling the gas current prevents any condensation in the furnace and balance system. Moreover, a box had been designed by the laboratory to protect the very fragile electronics from dust and condensation. Desiccant is put in this box to absorb humidity.

2.2 Experiments

2.2.1 Experimental plan

Figure 2.1: *thin and thick samples of Fluorohectorites with a 1 Krone coin which provides the scale*

We should bear in mind that the purpose of these experiments is to study the absorption of water in clay minerals, with a control of temperature and humidity in the surrounding air. The experimental plan which was decided in this aim was the following:

Samples of Na and Ni-fluorohectorite of two sizes, pointed out by thin or thick (see figure 2.1) have been hold in closed tubes at room temperature, about 22°C, since their preparation. A portion of each of them was put by turns inside the furnace and underwent the following sequence of temperature and atmosphere changes. For each sample:

- Firstly, the temperature increased from 25°C [4] to 130°C by steps of 5°C, staying two hours at each temperature. The heating rate used was 5°C/min. This heating was made with a dry atmosphere surrounding the sample.
- Secondly, the same method was employed to decrease temperature from 130°C to 25°C, using this time a humid atmosphere instead of a dry one.
- Then the sample was heated from 25°C to 130°C in one shot, under dry conditions.
- Finally the sample was cooled until 25°C in one shot, under humid conditions.

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[3] since the balance was calibrated at this temperature

[4] the temperature of the sample chamber

2.2.2 Control of humidity

In order to supply dry or humid atmosphere to the sample inside the furnace, two systems were available. In both of them, air was pumped with a peristaltic pump at a flow rate of 50 mL/min, and it passed either through a silica gel desiccant as shown in figure 2.2 to reduce its humidity, either on the top of a saturated solution of potassium sulphate as shown in figure 2.3 so as to increase moisture in air. The humidity of air was measured with the humidity sensor located just after. Then the humid or dry air entered into the TGA, precisely into the furnace just above the sample. The change in weight was continuously measured and recorded.

Figure 2.2: *The silica gel dissicant, located before the TGA, supplies a dry atmosphere.*

Figure 2.3: *The saturated salt solution, located before the TGA, supplies a humid atmosphere.*

2.2.3 Difficulties

I was faced with several difficulties:

- The major was that the firmware of the TGA should have been modified to allow to cool the sample down to 5°C. Indeed the standard TGA has a security that prevents from cooling the sample below 18°C. That is the reason why experiments start at 25°C instead of 5°C as planned initially.

- Another limit related to the software was that it was impossible to program a function of temperature versus time containing more than 10 segments. But for each experiment I needed about one hundred segments! So I had to chop each experiment into several experiments, which may have induced some unwanted temperature variations between two experiments.

- The thermostat caused also a problem, which was easily solved: after few days of experiments, the water in the bath of the thermostat evaporated so much that its level became too low. The alarm set off and the temperature of the thermostat decreased until -14°C , which caused important perturbation on the balance. This happened during the night, so it could not have been stopped immediately. The water level in the bath has to be looked after!

- The best thing would have been to measure the relative humidity of the atmosphere surrounding the sample. But it was impossible to put the RH sensor inside the furnace. Therefore it was installed just after the drying or wetting system and before the purge gas inlet. I designed and made a little plastic box fitting the sensor. This box was optimized for this sensor and perfectly tight. It did not let much space for the air, so that the measured humidity in this box is the closest to the humidity of the air entering into the TGA.

- It would also have been of great interest to measure the relative humidity of the air going out of the furnace. This had not been possible because there was nearly no gas flow rate at the gas outlet, even if Nitrogen, the protective gas, was put into the balance at 30 mL/min and air, the purge gas, at 50 mL/min. Only the furnace is supposed to be perfectly tight. Obviously the TGA was leaking, preventing us from detecting gas outlet.

2.3 Relative humidity

In order to measure the humidity of the air, we have two things at our disposal: absolute and relative humidity. Absolute humidity (AH) is a measure of the actual amount of water vapor in the air, regardless of the air's temperature. The higher the amount of water vapor, the higher the absolute humidity. Absolute humidity can be expressed in different ways but it will be estimated here as the partial water pressure.

$$AH = P_{H_2O} \tag{2.1}$$

Relative humidity (RH) (expressed as a percentage) also measures water vapor, but relative to the temperature of the air. In other words, it is a measure of the actual amount of water vapor in the air compared to the total amount of vapor that can exist in the air at its current temperature. Relative humidity is more significant than absolute humidity because minerals, animals and plants are only sensitive to the value of relative humidity.

$$RH = \frac{P_{H_2O}}{P_{sat}(T)} \tag{2.2}$$

In my experiments I could only measure relative humidity of the air entering the TGA, at air temperatures between 22°C and 25°C. I made use of a humidity sensor put in a box that I personally realized (see on figure 2.4) and which was located just after the drying or wetting system. For dry air, RH reached 5% at minimum and for humid air, RH reached 97% at maximum. Even if I could not measure directly the relative humidity inside the sample chamber, it was possible to derive it from the registered relative humidity[5]. Indeed RH was considered as constant during each experiment and the temperature inside the sample chamber was known every time.

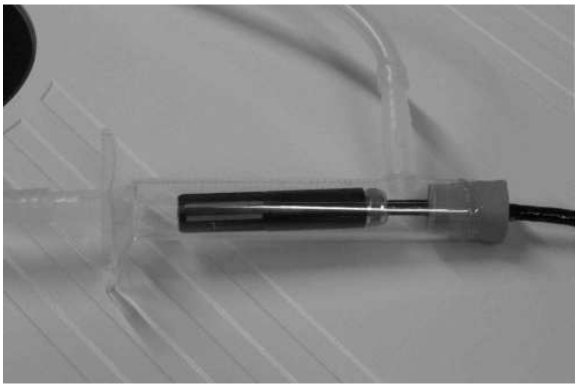

Figure 2.4: *Humidity sensor inside its tight box*

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[5] see appendix D.1

Chapter 3

Results and discussion

3.1 Slow dehydrations and hydrations of clays

A major restriction, coming from the STARe software and that I mentioned before is that I was obliged to split each experiment called slow dehydration or hydration into five experiments. The memory of the system is indeed limited. I used Labview to put all the experiments end to end and to export data in a file. Then I could easily plot all my curves with the software Origin.

The figures 3.1, 3.2, 3.3 and 3.4 have been finally obtained with Origin. They are examples of dehydration and then hydration of thick Na-Fluorohectorite and thick Ni-Fluorohectorite. All the curves weight versus time are presented in appendix E and F.

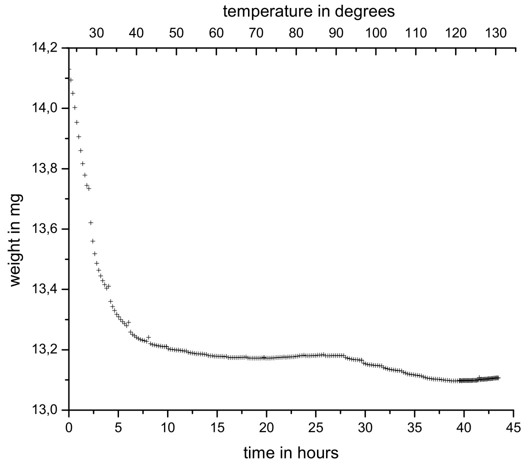

Figure 3.1: *slow dehydration of thick Na-Fluorohectorite under dry conditions*

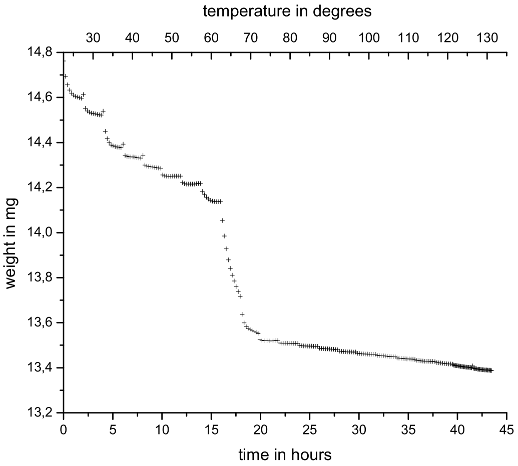

Figure 3.2: *slow dehydration of thick Ni-Fluorohectorite under dry conditions*

From these curves, it is fairly clear that the variations of weight perform in different way for two clays. Na-Fluorohectorite undergoes a significant loss of weight from the beginning of dehydration, it means at low temperatures from 25°C to 40°C. Then the steepness of the curve drops off significantly and the curve follows a pretty straight line until 130°C. Ni-Fluorohectorite has a different behaviour with three steps made out: between 25°C and 65°C the clay loses 3,7 % of its initial weight with the mean rate of 0,06 mg for 5°C, but its major loss of weight occurs at temperature between 65°C and 70°C. Here the clays loses 4,1 % of its initial weight. Then

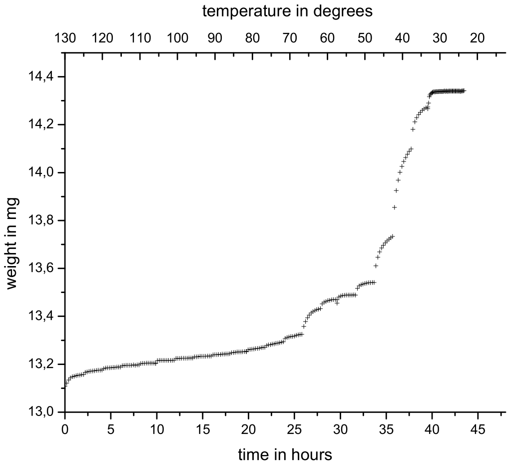

Figure 3.3: *slow hydration of thick Na-Fluorohectorite under wet conditions*

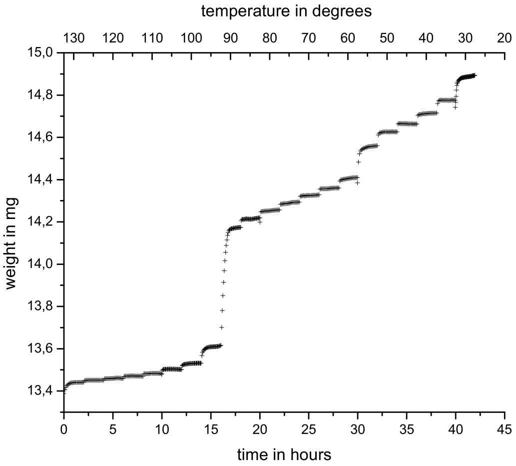

Figure 3.4: *slow hydration of thick Ni-Fluorohectorite under wet conditions*

the curve follows a regular and slow loss of weight until the end of the experiment, it is to say 0,01 mg for 5°C. The weight of both samples becomes quite steady at the end of the experiment. Therefore the dehydration of clays seems to be finished and dry clays are obtained at 130°C. All the water contained in clays must have disappeared. Thus hydration of clays performs in a similar way on dry samples. The main gain of weight happens between 45°C and 30°C for Na-Fluorohectorite. This clay has a constant weight as soon as 30°C. Three steps are still visible for Ni-Fluorohectorite, with a huge increase of weight around 90°C. Graphes of dehydration and hydration of thin clays show the same pattern as graphes of thick clays.

3.2 Fast dehydrations and hydrations of clays

The figures 3.5 and 3.6 show the experiments consisting in rapidly increasing and then decreasing temperature[1] respectively under dry and wet conditions . We can see on the curve 3.5 that the loss of weight takes less than 5 minutes. The gain of weight showed in figure 3.6 takes however more time. This clay absorbs water mainly during the first 30 minutes.

Nevertheless both of these curves present changes of weight which can not be explained at first sight. In figure 3.5 we see that the clay begins by gaining in weight during the first thirty seconds. The weight of clay raises of 1% of its dry mass. Moreover after five minutes the clay seems to absorb water once more: its weight increases of 0,2%. In figure 3.6 we note that the weight of clay decreases of 0,1% during the first 80 seconds.

But this phenomena is also observed for other clays, as it is showed in appendix H.1 and H.2, where values are reported. This leads me to suspect that the sensor is responsible of such variations. The fact that temperature varied of 105°C in 2,5 minutes may disturb considerably the sensor. In order to know more about it, I decided to perform the same experiments with a crucible filled with aluminium[2]. This may allow us to discover the response of the sensor.

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[1] heating took about 5 minutes whereas cooling took 20 minutes. For more details see in appendix G.1

[2] the same material than the crucible which is considered to be inert

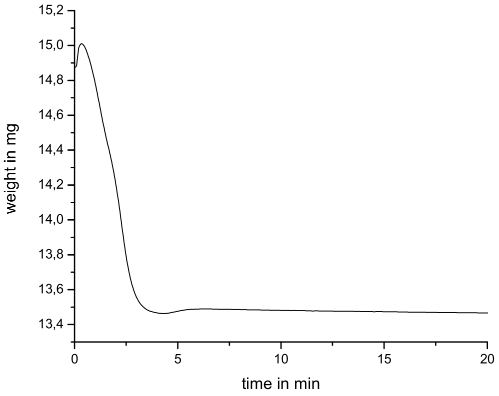

Figure 3.5: *fast dehydration of thick Ni-Fluorohectorite under wet conditions*

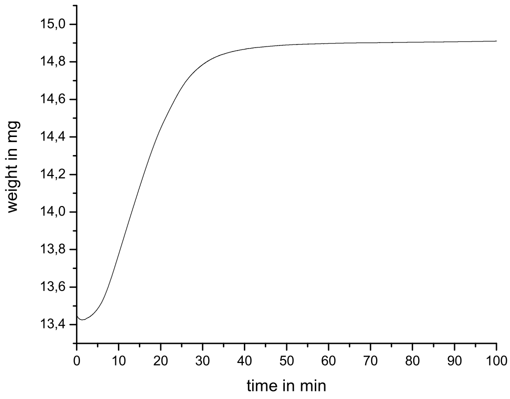

Figure 3.6: *fast hydration of thick Ni-Fluorohectorite under wet conditions*

3.3 Influence of the sensor

3.3.1 Slow heating and cooling of the sensor

The response of the sensor when it undergoes slow heating and then cooling is reported in Appendix J. This experiment has been done with the same conditions as for the clays excepted that plateaus lasted less than two hours. To find out the behavior of the sensor when temperature changed, I wrote down for each temperature the steady weight of the crucible filled with aluminum at the end of each step. Then I fitted the curves which were different for heating and for cooling[3]. I obtained the weight detected by the sensor as a function of temperature. As I knew the sample temperature for all clay samples, I could easily correct the values of weight for experiments of slow dehydration and hydration.

The corrected graphs presented in figures 3.7 and 3.8 and also in appendix E and F show that this response should be taken into account when one wants to derive quantitative results from experimental curves. This correction brought by the sensor changes the values of the whole mass of water contained in clays by about 3%. Thus this is far more significant than the error of the very accurate balance of the TGA[4].

3.3.2 Fast heating and cooling of the sensor

One should remember that the study of the sensor response had been suggested when seeing the curves of fast dehydration and hydration of clays which contained unexplained area. After subtracting to these curves the curve giving the variations due to the sensor around 13,5mg, I obtained the corrected curves showed in Appendix H.1, H.2 and in figures 3.9 and 3.10. At first sight one could be very satisfied by the resulting curves, because one doesn't see abnormal area anymore: the registered weight is always decreasing when heating and increasing when cooling.

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[3] see appendix J

[4] the accuracy of the balance is estimated for 5 μg

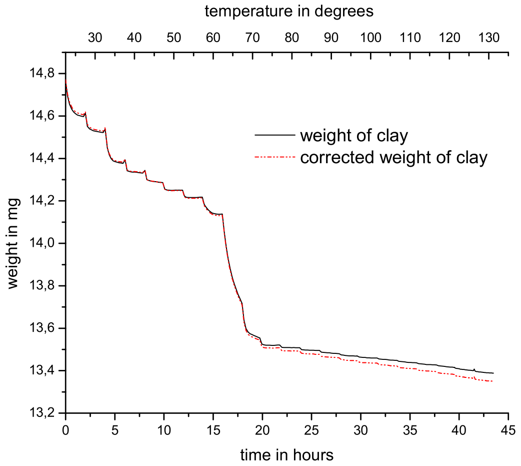

Figure 3.7: *slow dehydration of thick Ni-Fl after correction*

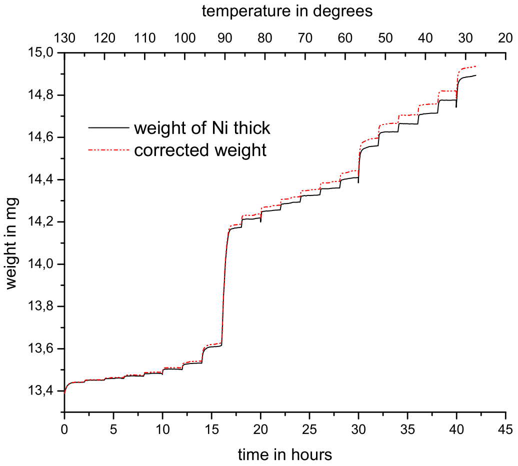

Figure 3.8: *slow hydration of thick Ni-Fl after correction*

3.4 Discussion on corrected curves

3.4.1 Curves of slow dehydration and hydration

Interpretation

We are now able to calculate the amount of water that evaporated or entered the clays thanks to the corrected curves. Basically the clays are supposed to be completely dry at 130°C. Therefore it would be relevant to evaluate the amount of water gained or lost by the clays. This has been done on figures 3.11, 3.12, 3.13 and 3.14 where the ratio of the clay mass at temperature T to its dry mass (i.e mass at T=130°C) has been drawn for slow dehydrations and hydrations.

To draw these curves which are representative of the amount of water as a function of temperature when clays are on equilibrium, I wrote down the corrected weight of clay at the end of each step of two hours at a constant temperature. In some cases two hours were enough to allow clays to reach their weight at equilibrium, but in other cases, this last was not enough. However I could guess the weight at equilibrium by fitting each step of the experimental curves with an exponential function. Then I could easily plot the curves of weight at equilibrium versus temperature.

The curves 3.11 and 3.13 of Ni-Fluorohectorite show very similar patterns for both thin and thick sample (I did not try with a powder). From the curves of dehydration, it seems that water stored in mesopores firstly evaporates between 25°C and 45°C for thin Ni-Fl and between 25°C and 55°C for thick Ni-Fl. The very steep lines seen around 55°C for thin Ni-Fl and 60°C for thick Ni-Fl reveal the evaporation of water from the nanopores. Then the evaporation from mesopores is going on, until clays reach their dry mass. The curves of hydration can be analysed in the same way: the huge gain of water at a very small range of temperatures is the result of absorption of water in nanopores. In both cases of dehydration and hydration, Ni-Fluorohectorites lose or gain about 4,3% of their dry mass after evaporation or absorption in nanopores.

The curves 3.12 and 3.14 of Na-Fluorohectorite also show very steep lines, characteristic of evaporation or absorption by nanopores. The curve of Na powder lost about 7,5% of its dry mass between 25°C and 50°C and then it remains constant. This may be due to the fact that there are

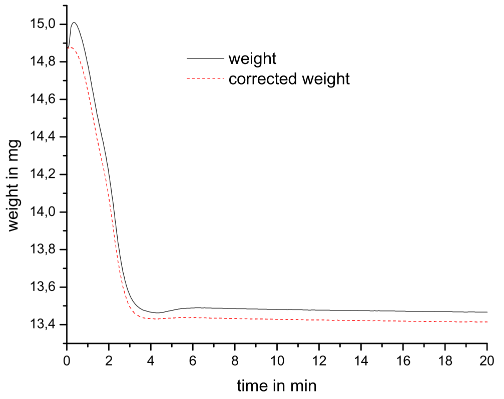

Figure 3.9: *fast dehydration of thick Ni-Fluorohectorite under dry conditions after correction*

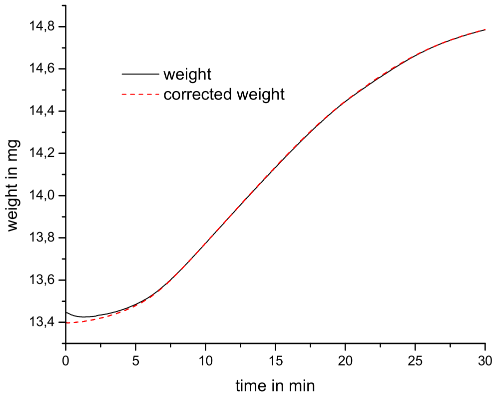

Figure 3.10: *fast hydration of thick Ni-Fluorohectorite under wet conditions after correction*

less mesopores in powder than in other samples. Concerning thin and thick samples, we don't see any flagrant difference, meaning that the mesopores have the same range of sizes for these two samples.

On the curves 3.12 and 3.14 we also observe that water evaporates more easily from Na-powder than thick Na-Fluorohectorite and that water is absorbed more easily in thick Na-Fluorohectorite than in Na-powder. We think that this tendency is linked to the different geometry of pores in powdered and thick samples. During dehydration strengths of superficial tension help water to go out of clays (this is called drainage) whereas during hydration the same strengths are opposed to the invasion of water (this is called imbibition).

Comparison with theory

The Na-Fluorohectorite and Ni-Fluorohectorite used in these experiments have the chemical formula $Na_{0,6}(Mg_{2,4}Li_{0,6})Si_4O_{10}F_2$ and $Ni_{0,3}(Mg_{2,4}Li_{0,6})Si_4O_{10}F_2$ per half unit cell. In addition comes x.H_2O where x depends on the number of water layers between the stacked platelets (see paragraph 1.2):
We know that for Na-Fluorohectorite, x= 1,2 if there is 1 water layer and 2,8 if there are 2 water layers. We assume that those figures are quite the same for Ni-Fluorohectorite.
The mass percentage X_m of water for one and two water layers has been calculated in table 3.1 thanks to the formula 3.1 and 3.2.

- with 1 water layer:

$$X_m = \frac{1,2 \times M_{H_2O}}{0,6 \times M_{Na} + 2,4 \times M_{Mg} + 0,6 \times M_{Li} + 4 \times M_{Si} + 10 \times M_O + 2 \times M_F} \tag{3.1}$$

- with 2 water layers:

$$X_m = \frac{2,8 \times M_{H_2O}}{0,6 \times M_{Na} + 2,4 \times M_{Mg} + 0,6 \times M_{Li} + 4 \times M_{Si} + 10 \times M_O + 2 \times M_F} \tag{3.2}$$

where M_X are the atomic weights.

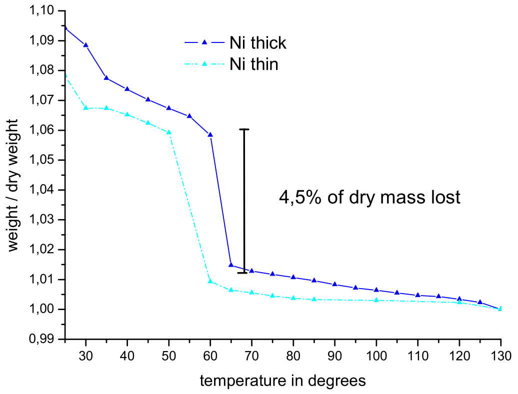

Figure 3.11: *dehydration of thick and thin Ni-Fluorohectorite*

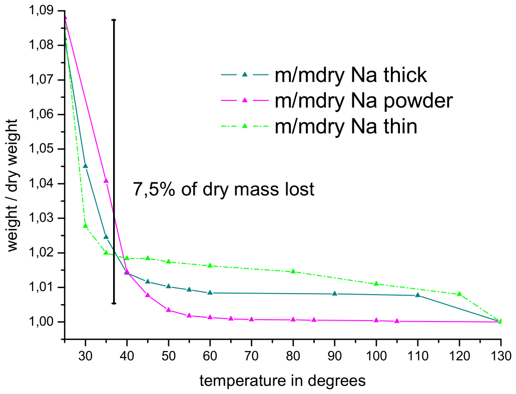

Figure 3.12: *dehydration of thick, thin and powdered Na-Fluorohectorite*

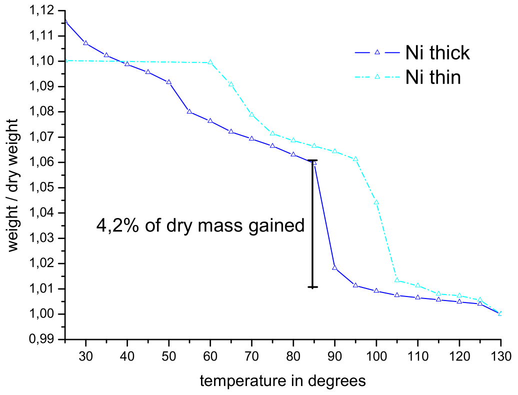

Figure 3.13: *hydration of thick and thin Ni-Fluorohectorite*

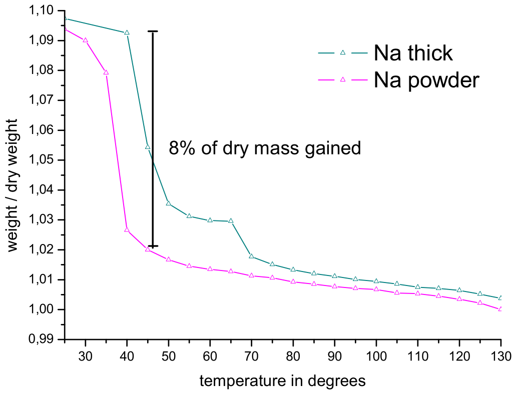

Figure 3.14: *hydration of thick and powdered Na-Fluorohectorite*

The figures showed in table 3.1 correspond to the theoretical mass percentage in Na-Fluorohectorite and Ni-Fluorohectorite when we disregard water stored in mesopores. Therefore they are lower than those obtained in experiments.

The X-ray studies have shown that the two hydration states 1 water layer and 2 water layers can coexist in clays. Therefore we can only compare the order of magnitude of water lost or gained in nanopores. We saw in the case of Na-Fluorohectorite (see figures 3.12 and 3.14)that nanopores lead clay to lost or gain between 7 and 8% of its dry mass, which proves that clay contains the two hydration states. In the case of Ni-Fluorohectorite (see figures 3.11 and 3.13) only 4,5% of dry mass is lost or gained. So we assume that there is only 1 water layer in nanopores.

3.4.2 Hysteresis in the hydration and dehydration curves

As all the samples have been cooled down after being heated, one can inquire whether the loss and gain of water use the same path or if there is some kind of hysteresis loop for the process. It appears on these curves that the main changing in weight begins at a lower temperature when

	Na-Fl
1 water layer	5,5%
2 water layers	12,9%

Table 3.1: *mass percentages of water for one and two water layers in Na-Fluorohectorite*

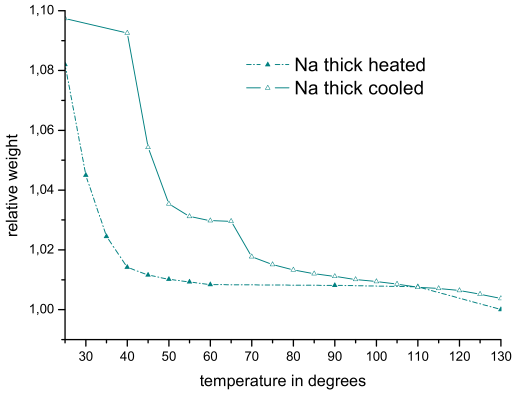

Figure 3.15: *Hysteresis of thick Na-Fluorohectorite*

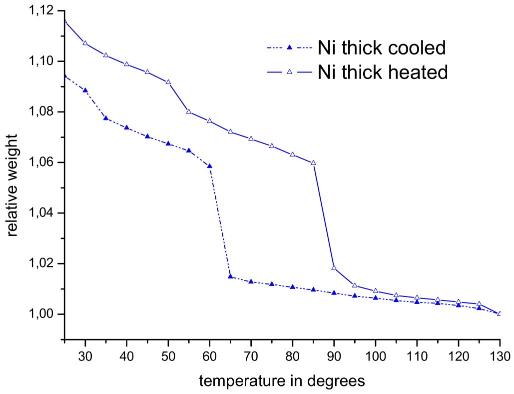

Figure 3.16: *Hysteresis of thick Ni-Fluorohectorite*

heating clays than when cooling them. Typically those variations take place between 60°C and 70°C when heating a thick Ni-Fluorohectorite and between 85°C and 90°C when cooling it. Absorption of water thus occurs earlier than evaporation. Consequently more water is present in clay when it has been cooled under humid atmosphere than when it has been heated under dry atmosphere for the same temperature. This phenomena is clear if one looks at the weight of clay at 25°C: 14,6 mg when thick Ni-Fluorohectorite is heated and 14,9 mg when it is cooled.

3.4.3 Curves of fast dehydration and hydration

First order of determination

Thanks to the corrected values found previously, I tried to fit the fast dehydrations and hydrations of clays with an exponential. I obtained the curves showed in figures 3.17 and 3.18 and the equations are reported in table K.1.

The graph of fast dehydration unveils a more or less deep hole located around 4 minutes for all clays (see appendix K), at the same time as the hole previously seen on the curves H.1. After a correction due to the sensor, one couldn't see a hole anymore on these curves. But the logarithm function brings to the fore that a hole still exists even after a correction. Indeed the TGA was supposed not to exceed 130°C, but the sample temperature curve (see in appendix G) shows that the clay exceeds the limit of 130°C and then returns to this temperature. Therefore the hole is completely explained: it is due to absorption of water while the temperature of clay decreases to reach 130°C. This last point leads us to think that the clay reacts very fast to a change of temperature. The characteristic time of response of the clays may be smaller than the time for the TGA to increase temperature from 25°C to 130°C. Consequently the clay may follow the temperature variations, which doesn't reveal anything about the clay. That is the reason why we were only interested by the second part of the curves. I fitted this part which gave me

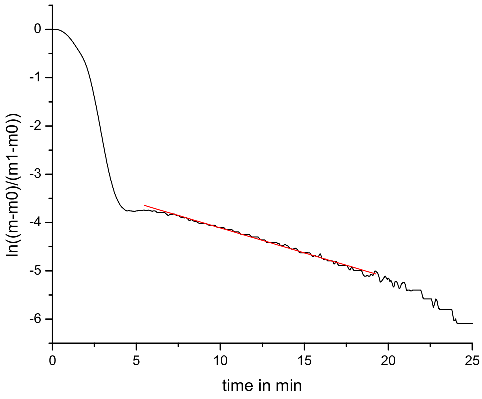

Figure 3.17: *fit of the fast dehydration of thin Ni-Fluorohectorite*

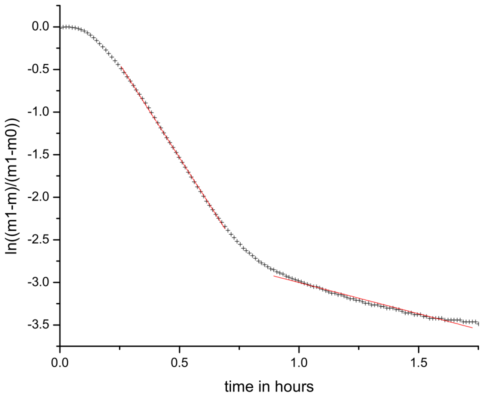

Figure 3.18: *fit of the fast hydration of thin Ni-Fluorohectorite*

	2 exponentials	sum of 2 exponentials	numerical fit
τ_1	14 min	11 min	10 min
τ_2	178 min	174 min	100 min

Table 3.2: *the different time constants found with 3 fits*

a characteristic time of evaporation of water from clays (see table K.1). I found approximately $\tau = 10$min for all clays. I thought that this time constant was characteristic of evaporation from nanopores because this phenomenon is assumed to be the slowest.

Concerning the graphs of fast hydration 3.18, I have to precise that the thermostat takes about 20 minutes to decrease temperature from 130°C to 25°C[5] (see in appendix G). Since clays follow the variations of temperature as it was said previously, the only relevant part of the curve is located after 20 minutes. The curve 3.18 shows two parts very distinct: before and after 45 minutes. I fitted each part by an exponential and I therefore found two speeds of water absorption (see table K.1). We assume that the fastest is related to absorption by mesopores and that the two kinds of absorption don't occur at the same time. To check this last assumption I decided to fit the entire curve by a sum of two exponentials (see figure 3.19). I finally found two time constants very closed to the previous ones (see table 3.2). So we can conclude that when one kind of absorption is taking place, the other one can be neglected. From this fit, I can also appreciate the proportion of water absorbed in mesopores and in nanopores: about 92% of water is absorbed in mesopores and 8% in nanopores (see appendix L, part L.2).

Second order determination

In order to improve the last fit, I tried a numerical approach which allowed me to take into account the fact that temperature decreased progressively and not like an echelon (see in appendix L). I finally obtained the same time constant than before for the first part but a smaller time constant for the second part. Moreover I did not need to introduce a time discrepancy. The curve is showed in figure 3.19.

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[5] the thermostat is at a temperature of 22°C

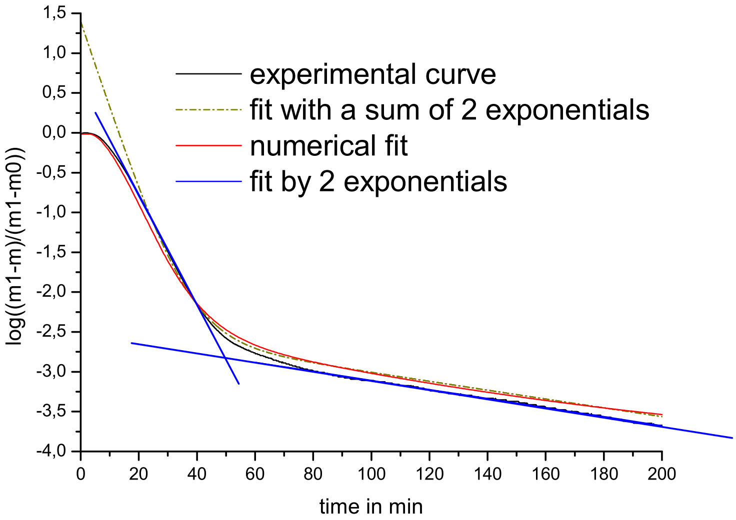

Figure 3.19: *different fits of the fast hydration of thin Ni-Fluorohectorite after 20 minutes*

If I compare now the time constants relative to nanopores concerning dehydration and hydration, I see that τ is 10 times smaller for dehydration than hydration, which seems strange. However I can not really compare these two time constants because in the case of dehydration, the clay, "filled with water" is heated under a dry atmosphere. In the case of hydration, the dry clay is cooled but under an atmosphere very poor in water (see appendix G). So we understand that it is easier for water molecules to go out of the clays than entering it. This may explain the difference between the two time constants.

Conclusion

Experiments performed on synthetic clays Na-Fluorohectorite and Ni-Fluorohectorite gave us information about the intercalation of water in these synthetic smectite clays. All these experiments were based on the use of a very accurate thermobalance. But this balance proved to be disturbed by sudden temperature changes. Therefore a large part of the work has been devoted to correct the experimental curves, taking into account the response of the sensor to such temperature changes. This sensor response was calculated with an empty crucible filled with aluminium and which underwent the same temperature changes than the clays.

Several information have been drawn from these curves. The curves of thin and thick samples (and even powdered sample) were very similar for each clay. No flagrant difference was noticed between the two sizes of clay. When comparing the curves of slow dehydration of sodium and nickel clays, we can see that these clays don't evolve with the same way: we can distinguish three parts for Ni-Fluorohectorite and only two for Na-Fluorohectorite. But such a difference could be attributed to the range of temperature we used: the balance forced us to work at higher temperatures than 25°C. However after modifying the firmware of the balance, the same experiments could be performed at lower temperatures. This may tell us if the pattern of Na-Fluorohectorite dehydration is finally the same as for Ni-Fluorohectorite.

Thanks to the curves of slow dehydration and hydration, I obtained the curves giving the weight at equilibrium as a function of temperature and showing that water invasion in nanopores occurs at a nearly constant temperature. Thanks to these curves I could also draw hysteresis curves. These last curves show that evaporation and absorption of water have a similar pattern but they don't occur at the same temperatures in clays. Consequently a clay contains more water when it is cooled under wet conditions than when it is heated under dry conditions for the same temperature. Another interesting experiment would be to study hydration and dehydration of clays but with the same condition on humidity.

Knowing that absorption of water in clays is the result of absorption by what are called mesopores and nanopores, I tried to separate and characterise each of these phenomena. In this aim I looked at the behaviour of clays when they were fast heated and cooled. The furnace is able to increase temperature very fast whereas the thermostat takes quite a long time to decrease temperature. However we can observe that clays follow the variations of temperature. Thus it appears that the time constant of clay is much lower than the one of the system. We could not therefore conclude anything from the first part of the curves of dehydration. We can nevertheless conclude that water evaporates from clay following an exponential law and that absorption of water in clays can be fitted in a satisfactory manner by the sum of two exponentials by a numerical method. The time constants can be evaluated: water evaporates from clay with a characteristic time of 10 minutes, and water is absorbed in about 10 minutes in mesopores in a proportion of 90% and in about 100 minutes in nanopores.

Appendix A

Preparation of samples

The samples were based on synthetic fluorohectorite purchased from Corning Inc. US. The sample preparation was divided in three steps:

- first the fluorohectorite powder was dissolved in deionized water and stirred for several days.
- thereafter Na^+ was added in the form of NaCl, and in an amount of about 10 times the interlayer charge. After the solution divided into two phases, the clear water phase was sucked out. The resulting part was then placed in dialysis membranes and excess ions were removed by dialysis, exchanging deionized water every 2 days. A check of this procedure was made by adding $AgNO_3$ to the system to detect possible Cl^- ions.
- finally this suspension of Sodium fluorohectorite was heat pressed at 120°C exerting mechanical force with a load of ten tons, thanks to an hydraulic press. The final result is a dehydrated "thick" sample clay, where the platelets are stacked with preferential orientation: the main platelet direction is normal to the axis compression.

The "thin" samples were obtained after sedimentation.

Appendix B

TGA

B.1 Apparatus

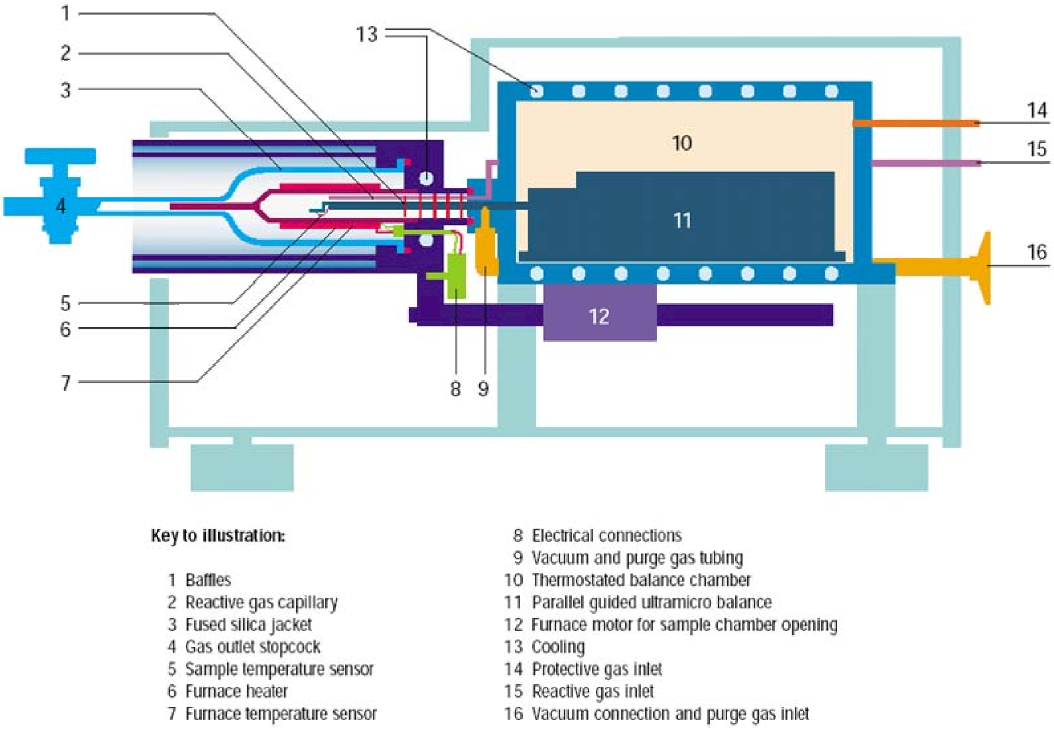

Figure B.1: *TGA*

B.2 Calibration of the TGA

Before performing calibration of the TGA, you have to check that the TGA needs one. This had been done easily by following the instructions in the manual. It proved that there was no need of calibration. The text given with the curve was the following:

The Module is within specifications!
Temperature: +- 2°C +- 3°C
In 156.6°C Al 660.3°C

Sample temperature: +- 1°C +- 1.5°C

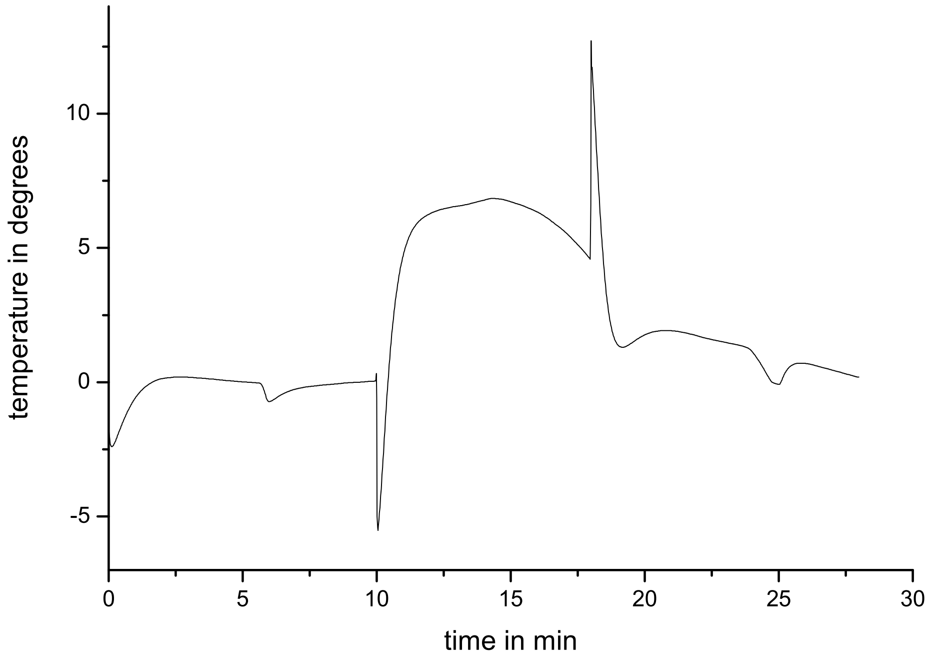

Figure B.2: *check of calibration*

Appendix C

Calibration of the peristaltic pump

In order to evaluate the air flow rate entering the furnace, the peristaltic pump had to be calibrated. This was done thanks to a very simple device, as shown on figure C.1:

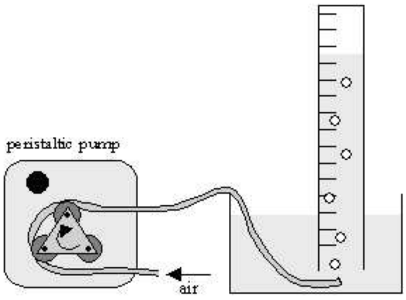

Figure C.1: *device for calibration*

A graduated tube was turned over in a bowl filled with water. A flexible tube of a certain diameter brought the pumped air inside the graduated tube. By measuring for different speeds of the pump, the time taken by it to fill a certain volume of air, the chart air flow rate versus speed of the pump could have been established. Of course this calibration is only suitable for one diameter of flexible tube.

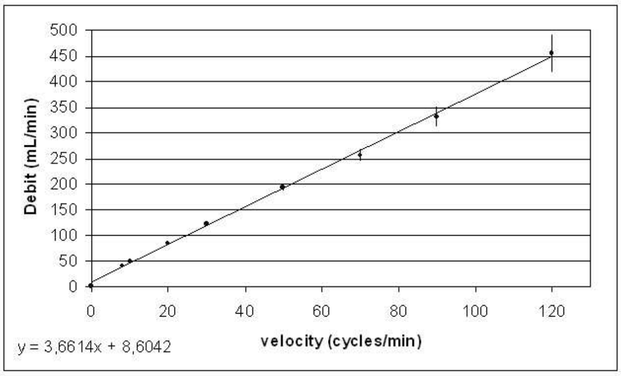

Figure C.2: *air flow rate versus velocity of the pump*

Appendix D

Relative humidity inside the TGA

The relative humidity reached two constant values at the room temperature of 23°: around 95% with humid conditions and around 5% with dry conditions. To calculate this relative humidity, I used the formula:

$$RH_{\text{inside}} = \frac{P_{H_2O}}{P_{sat}(T)} = \frac{RH_{\text{outside}} \times P_{sat}(23^o)}{P_{sat}(T)} \tag{D.1}$$

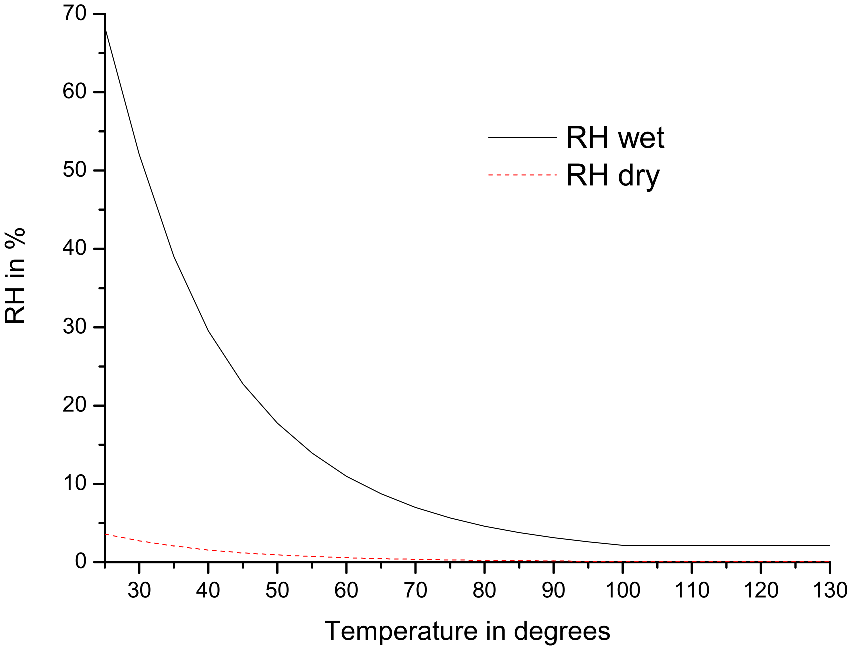

Figure D.1: *Relative Humidity inside the TGA under dry and wet conditions*

Appendix E

Slow dehydrations of clays under dry conditions

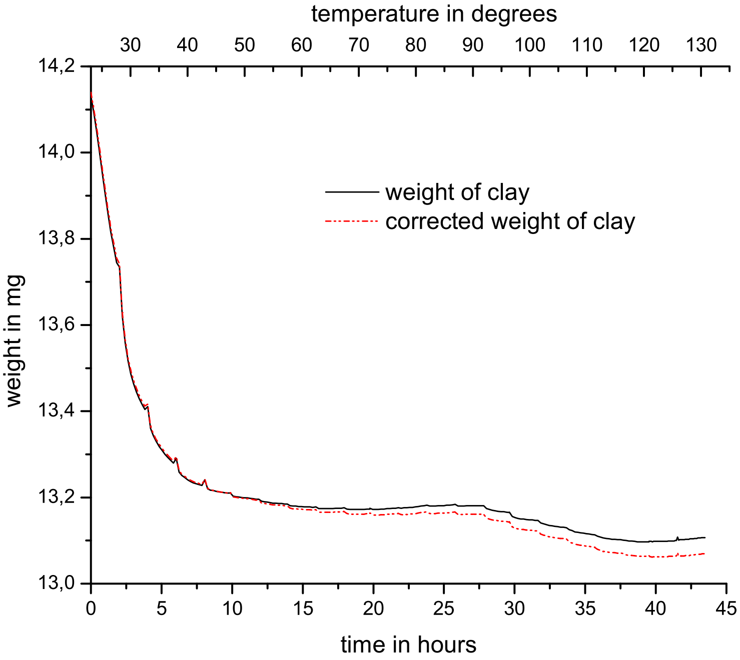

Figure E.1: *dehydration of Na-Fluorohectorite thick*

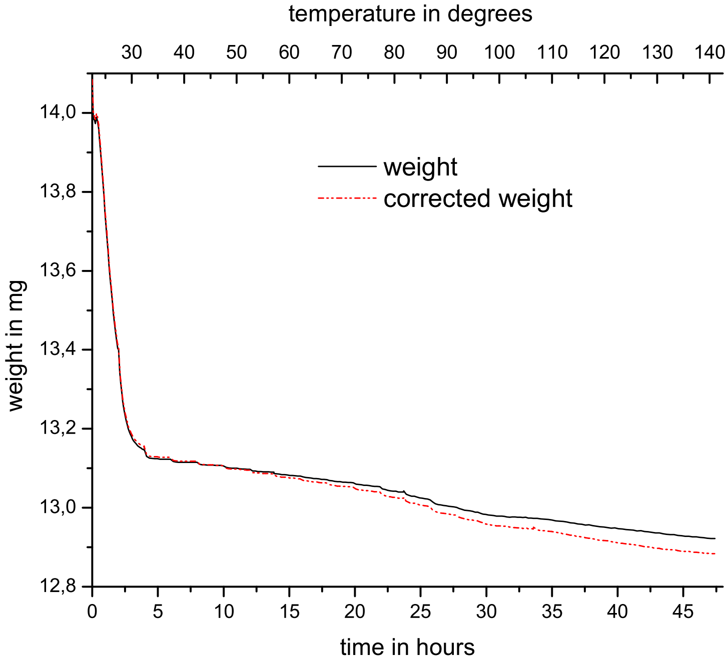

Figure E.2: *dehydration of Na-Fluorohectorite thin*

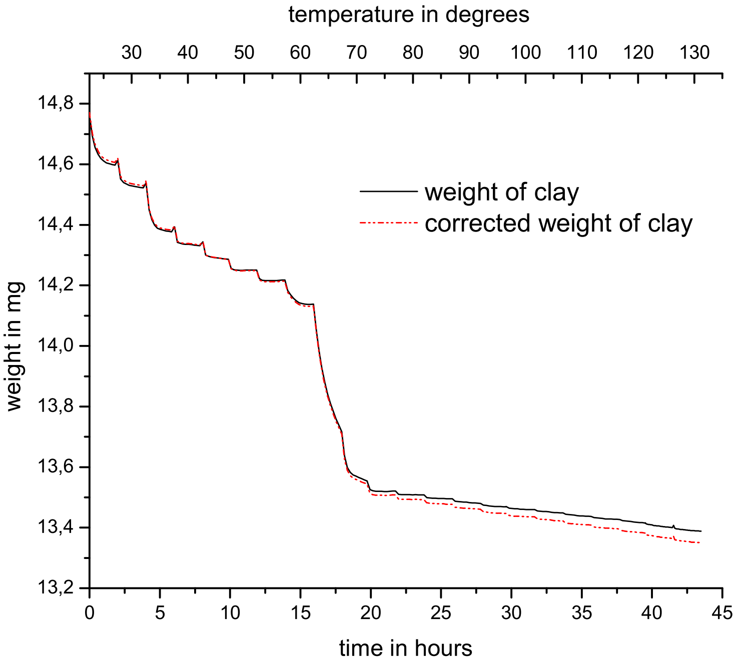

Figure E.3: *dehydration of Ni-Fluorohectorite thick*

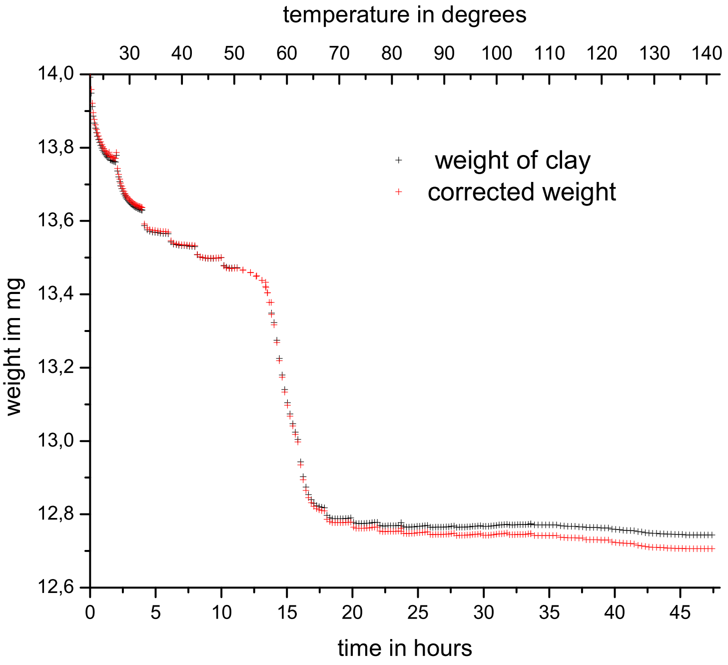

Figure E.4: *dehydration of Ni-Fluorohectorite thin*

Appendix F

Slow hydrations of clays under wet conditions

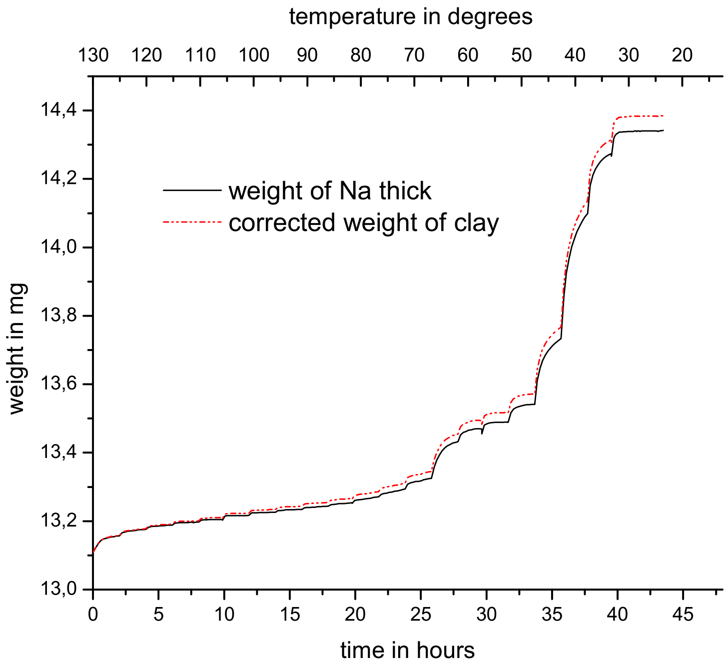

Figure F.1: *hydration of Na-Fluorohectorite thick*

The curve F.2 shows a strange pattern caused by the too low water level in the thermostat (see paragraph 2.2.3).

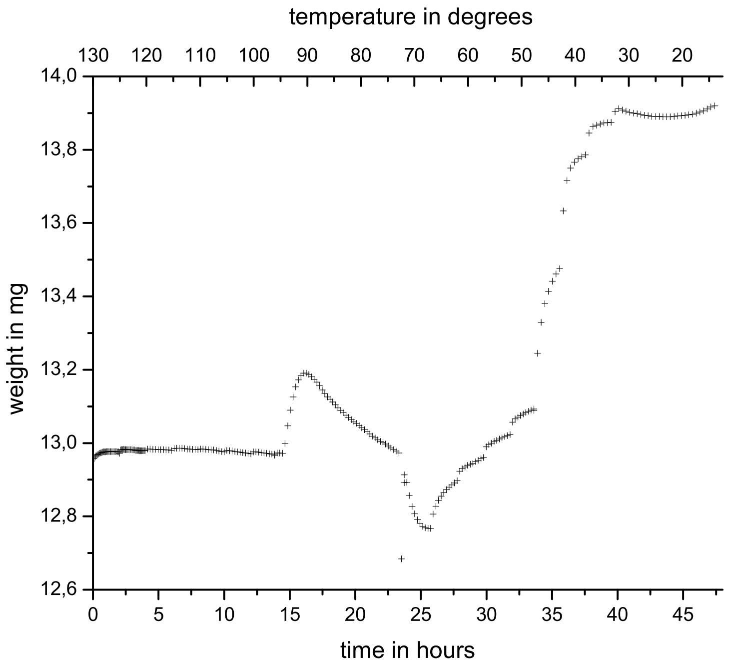

Figure F.2: *hydration of Na-Fluorohectorite thin*

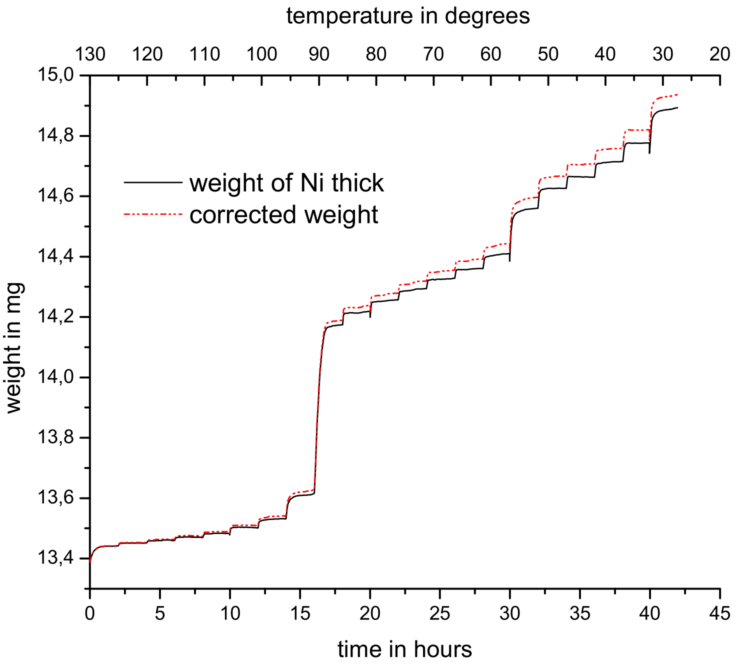

Figure F.3: *hydration of Ni-Fluorohectorite thick*

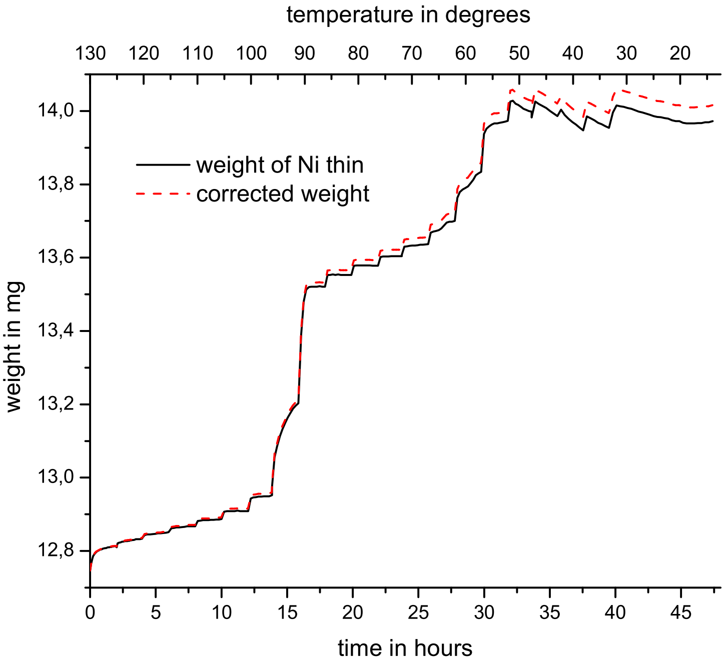

Figure F.4: *hydration of Ni-Fluorohectorite thin*

Appendix G

The way the temperature evolves under fast changes

It is of course easier to increase temperature with the furnace than to decrease it until 25°C with a thermostat at 22°C. We wanted to change rapidly the temperature, but thermostat limited us, whatever the temperature rate we programmed. The temperature proved to increase from 25°C to 130°C in 5 minutes but it decreased from 130°C to 25°C in 25 minutes, as it is showed on figure G.1. From this figure it appears that the system reached 160°C before coming back to 130°C. This last point implied significant consequences.

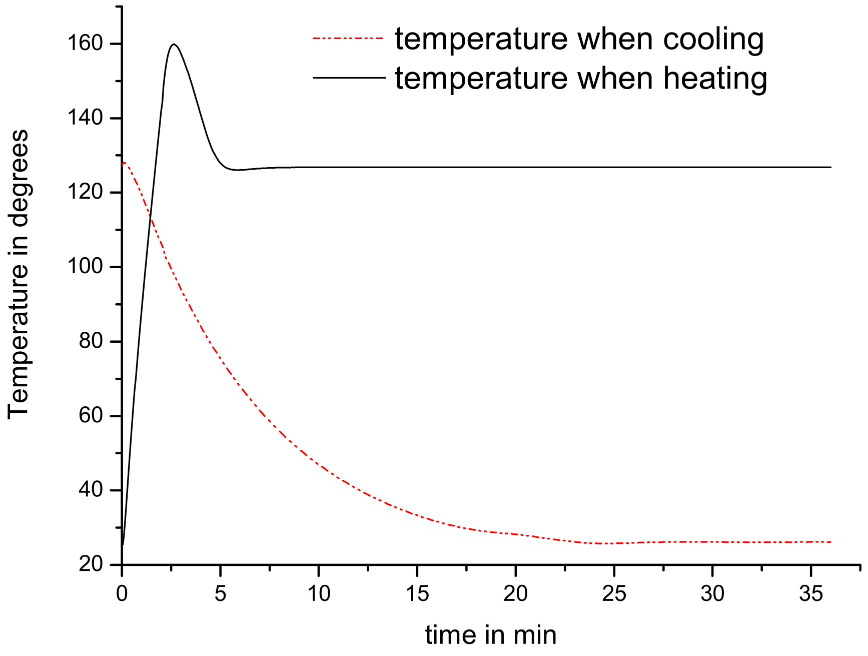

Figure G.1: *last of temperature changes when heating and when cooling*

Appendix H

Fast dehydrations and hydrations of clays

H.1 Fast dehydrations of clays under dry conditions

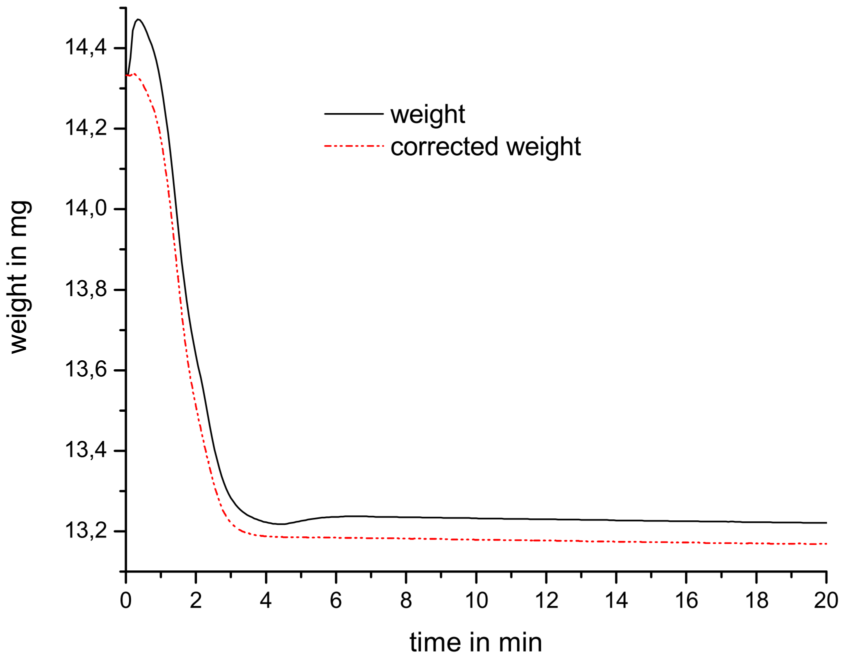

Figure H.1: *fast dehydration of Na-Fluorohectorite thick*

H.2 Fast hydrations of clays under wet conditions

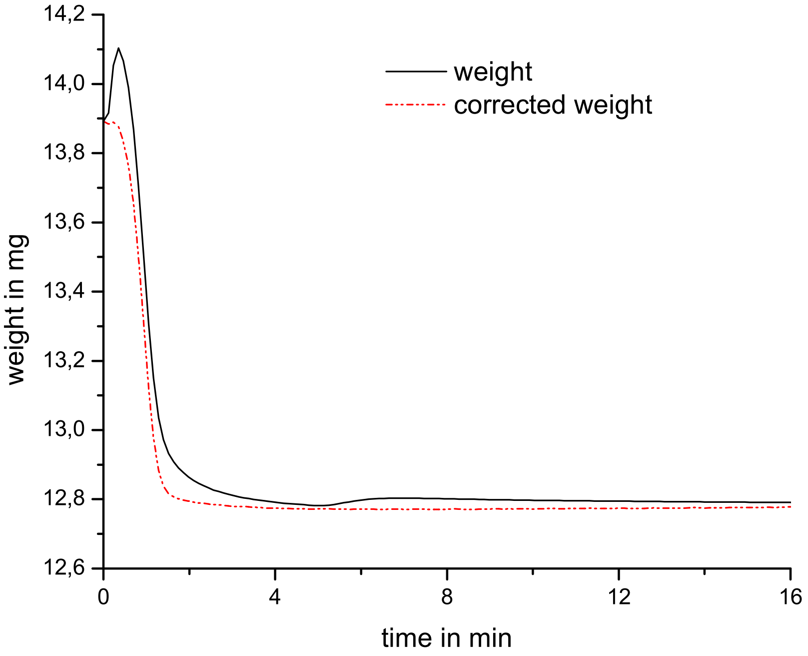

Figure H.2: *fast dehydration of Na-Fluorohectorite thin*

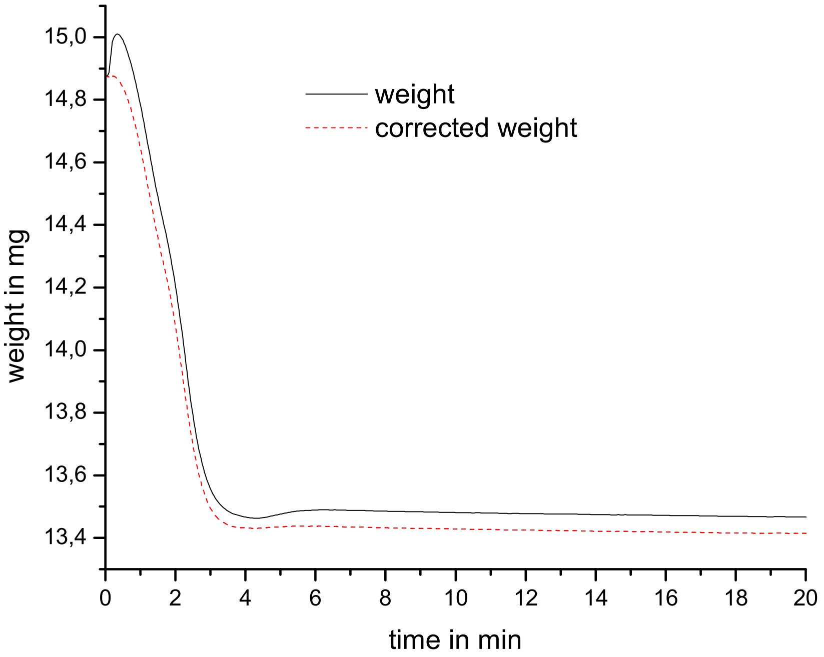

Figure H.3: *fast dehydration of Ni-Fluorohectorite thick*

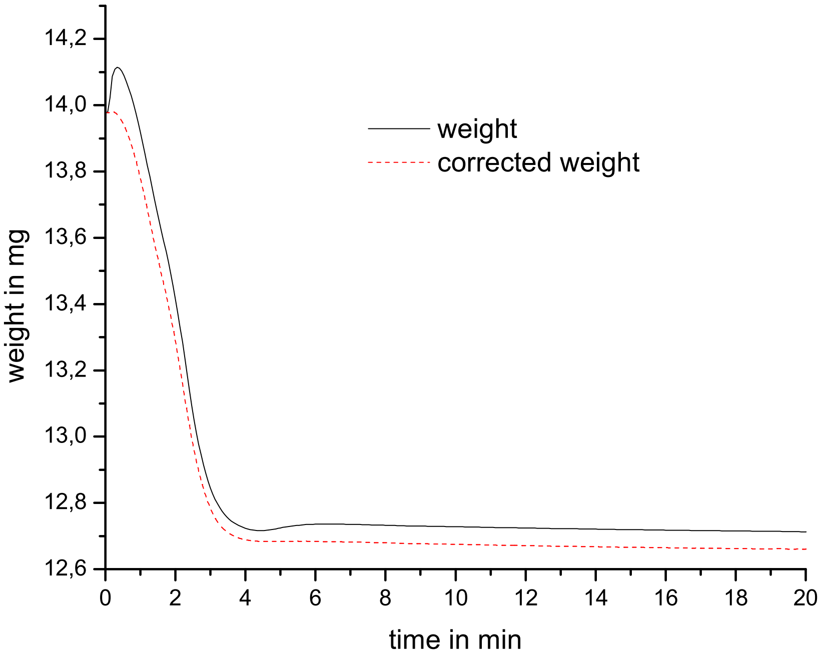

Figure H.4: *fast dehydration of Ni-Fluorohectorite thin*

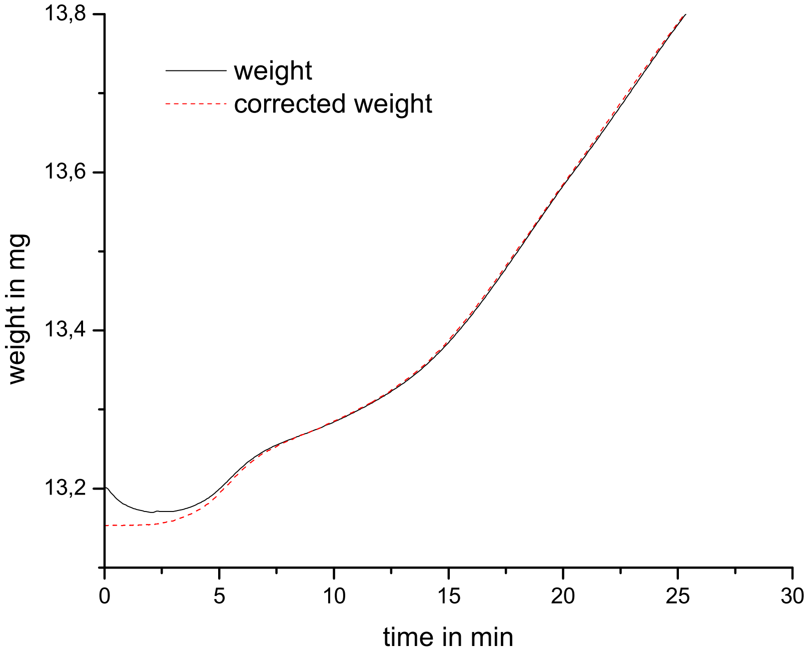

Figure H.5: *fast hydration of Na-Fluorohectorite thick*

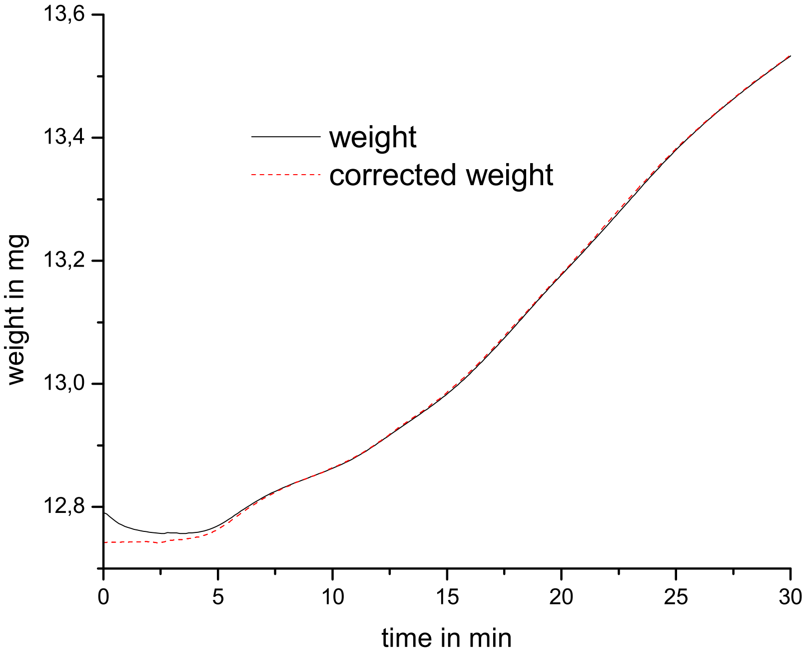

Figure H.6: *fast hydration of Na-Fluorohectorite thin*

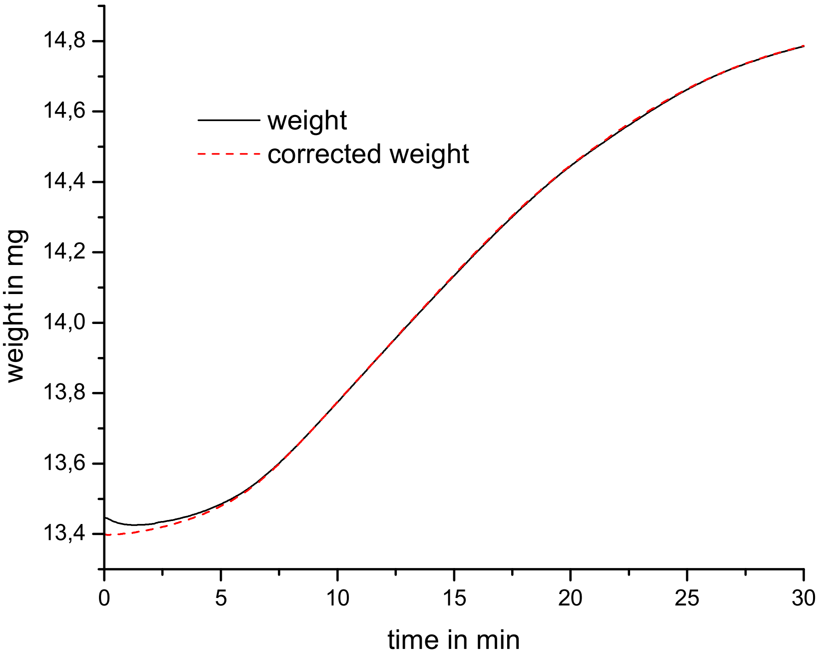

Figure H.7: *fast hydration of Ni-Fluorohectorite thick*

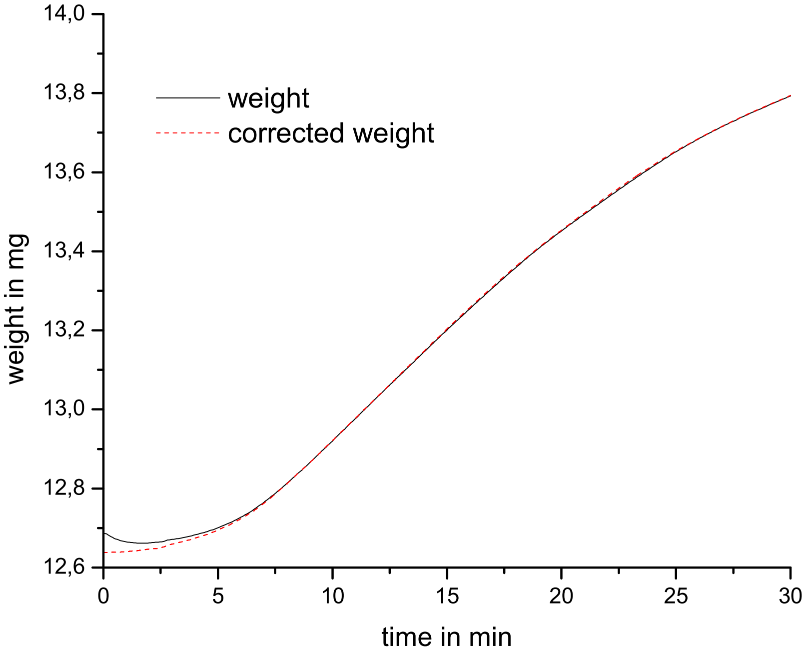

Figure H.8: *fast hydration of Ni-Fluorohectorite thin*

Figure H.9: *magnitude of curves variations for a rapid change of temperature in mass percentage of the dry clays*

		Na-Fl thin	Na-Fl thick	Ni-Fl thin	Ni-Fl thick
fast heating	first jump	1,6%	1,0%	1,1%	1,0%
	second jump	0,2%	0,1%	0,1%	0,2%
fast cooling		0,3%	0,2%	0,2%	0,1%
dry mass		12,883 mg	13,061 mg	12,706 mg	13,350 mg

Appendix I

Hysteresis of clays

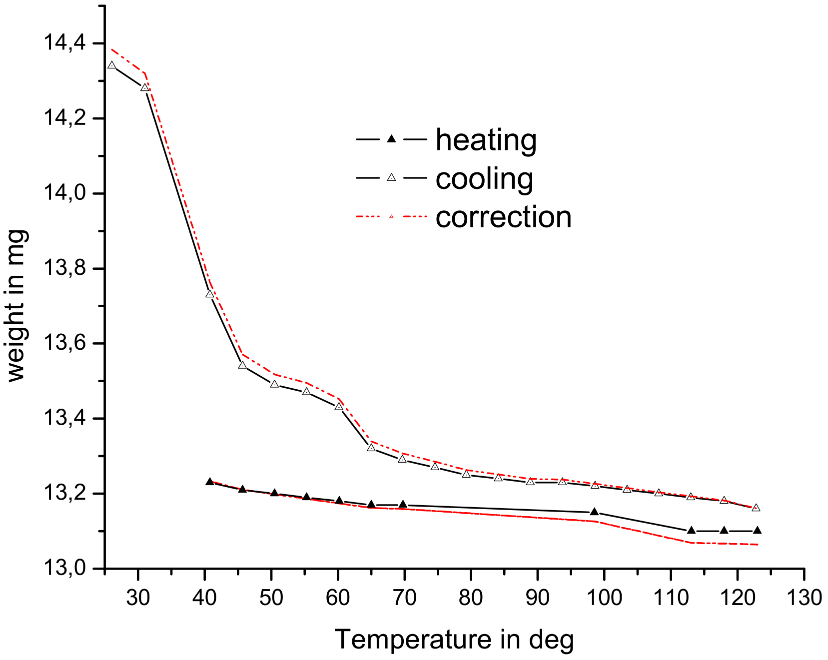

Figure I.1: *hysteresis of Na-Fluorohectorite thick*

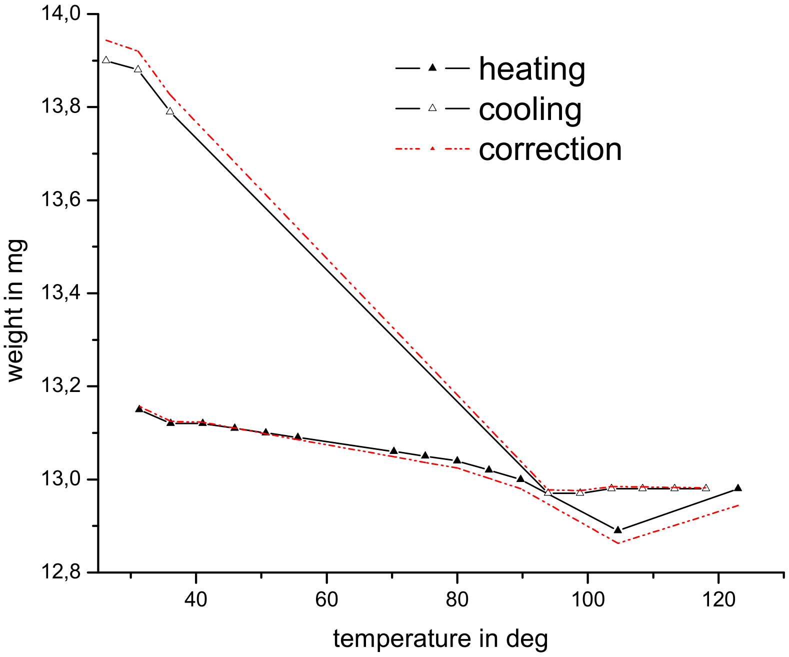

Figure I.2: *hysteresis of Na-Fluorohectorite thin*

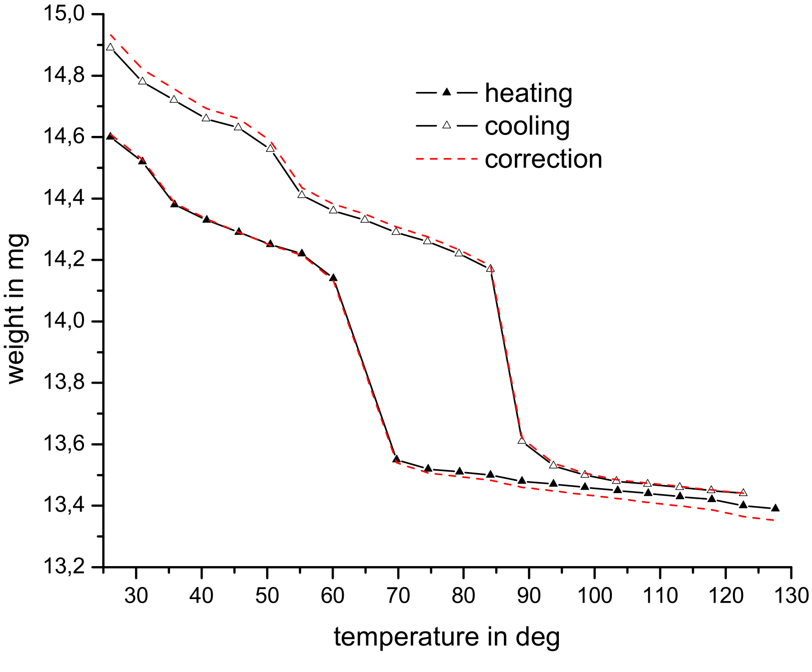

Figure I.3: *hysteresis of Ni-Fluorohectorite thick*

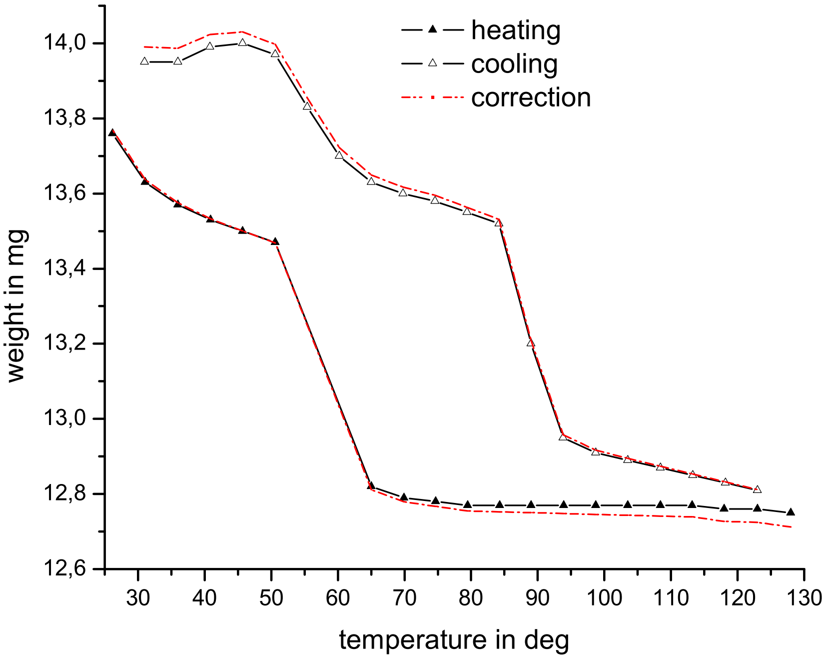

Figure I.4: *hysteresis of Ni-Fluorohectorite thin*

Appendix J

Response of the sensor

The graphes J.1 and J.2 show the behaviour of the sensor when crucible is filled with aluminium, an inert material for such temperatures. Every peak corresponds to a variation of 5°C of the temperature, which disturbs a lot the sensor.

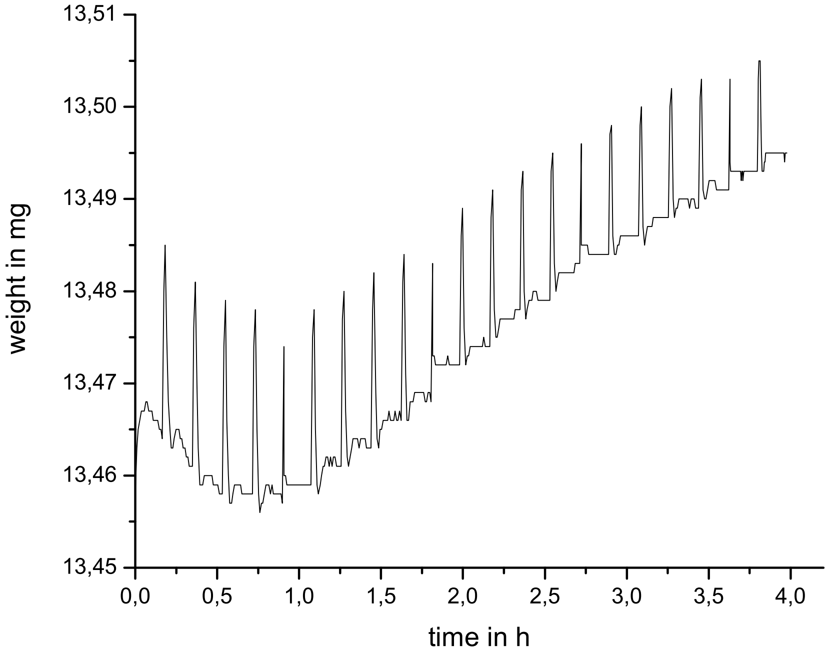

Figure J.1: *Crucible filled with aluminium is heated*

In order to foresee the response of the sensor to temperature changes, the weight measured by the balance between two peaks and the sample temperature have been recorded. Then I fitted these curves (J.3 and J.4)so as to obtain a continuous curve for the weight changes caused by the sensor versus temperature.

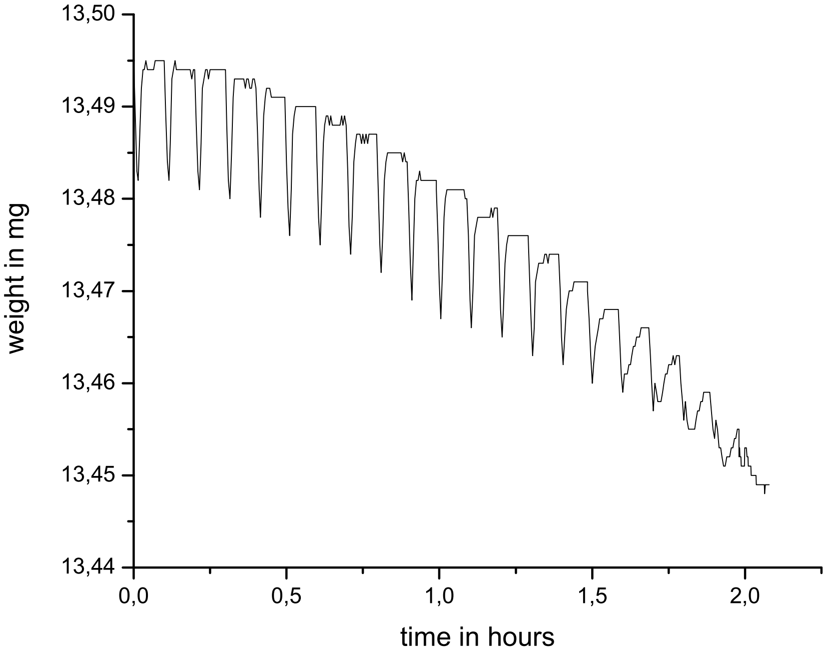

Figure J.2: *Crucible filled with aluminium is cooled*

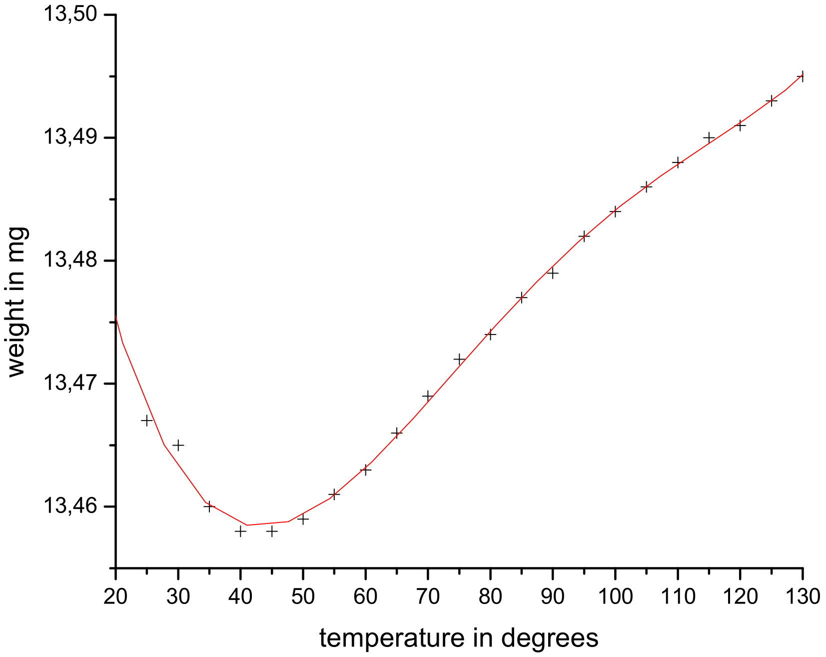

Figure J.3: *fit of the response of the sensor when heating it*

$$m(T) = 13,5 - 4.10^{-3} \times T + 8.10^{-5} \times T^2 - 6.10^{-7} \times T^3 + 2.10^{-9} \times T^4 \qquad \text{(J.1)}$$

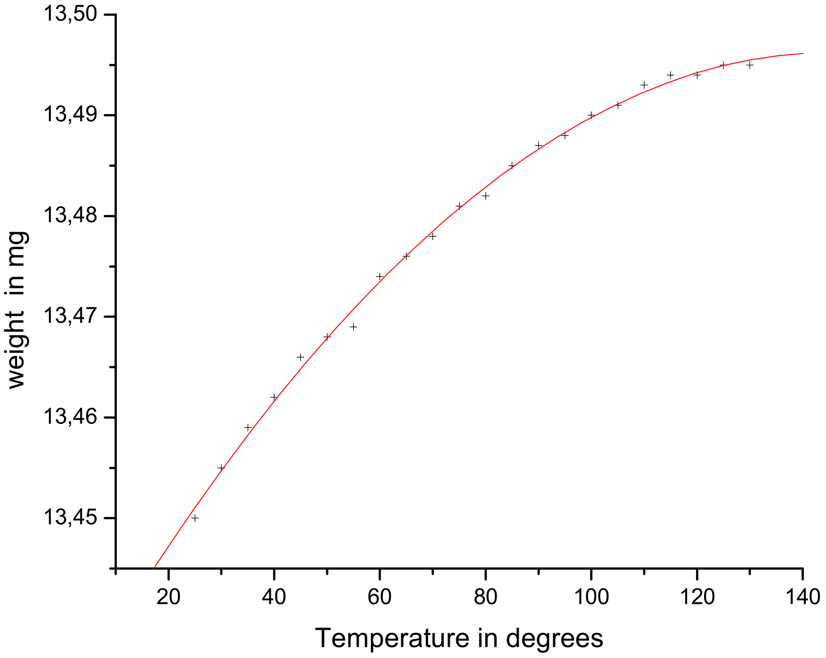

Figure J.4: *fit of the response of the sensor when cooling it*

$$m(T) = 13,4 + 9.10^{-4} \times T - 3.10^{-6} \times T^2 \qquad \text{(J.2)}$$

Appendix K

Fitting fast dehydrations and hydrations

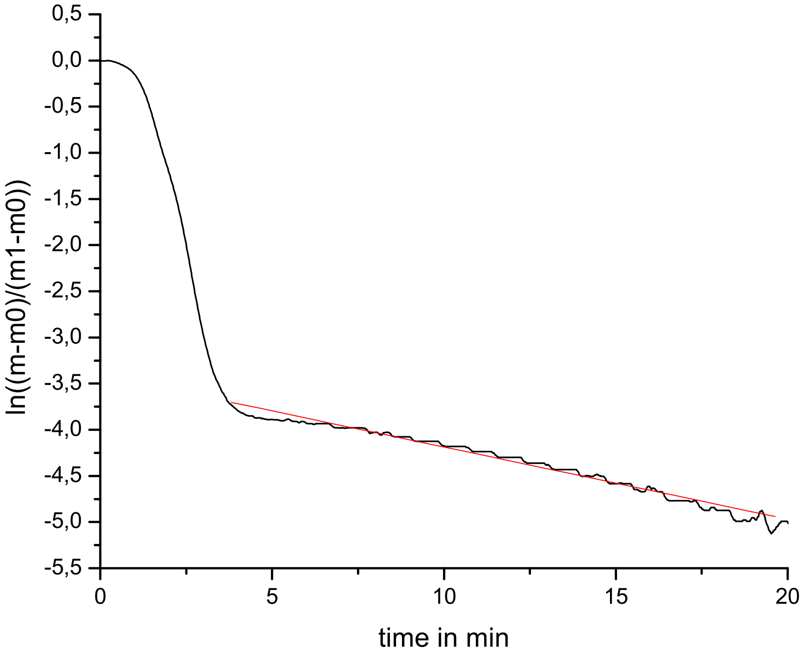

Figure K.1: *fit of the fast dehydration of thick Na-Fluorohectorite*

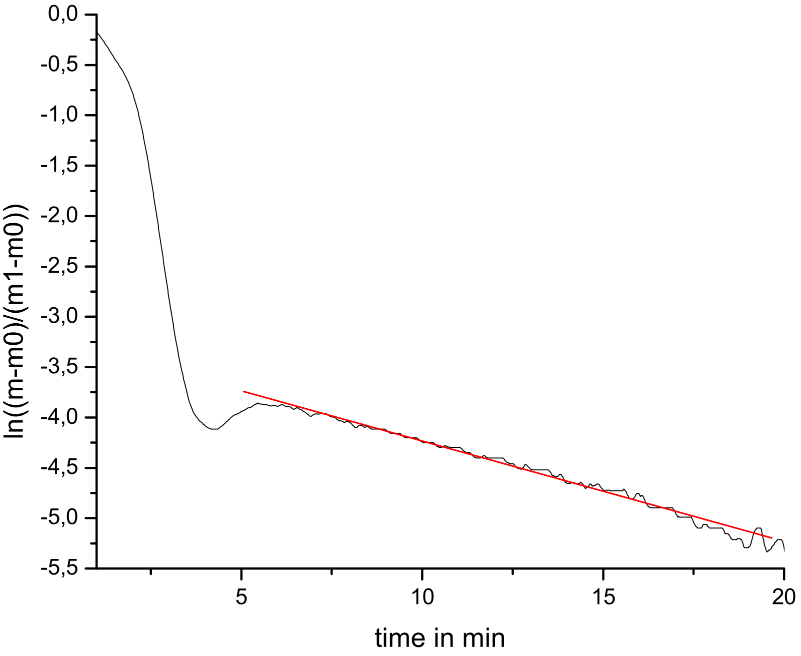

Figure K.2: *fit of the fast dehydration of thick Ni-Fluorohectorite*

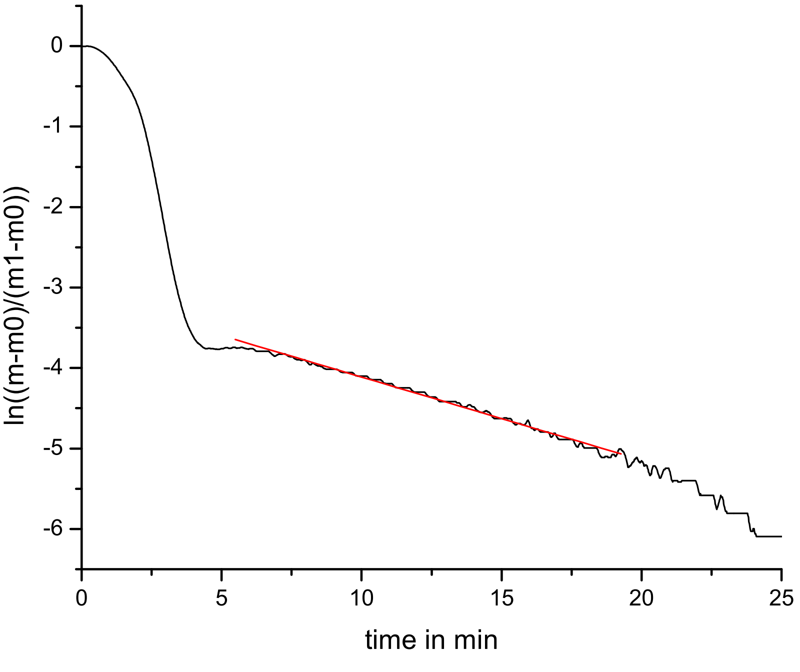

Figure K.3: *fit of the fast dehydration of thin Ni-Fluorohectorite*

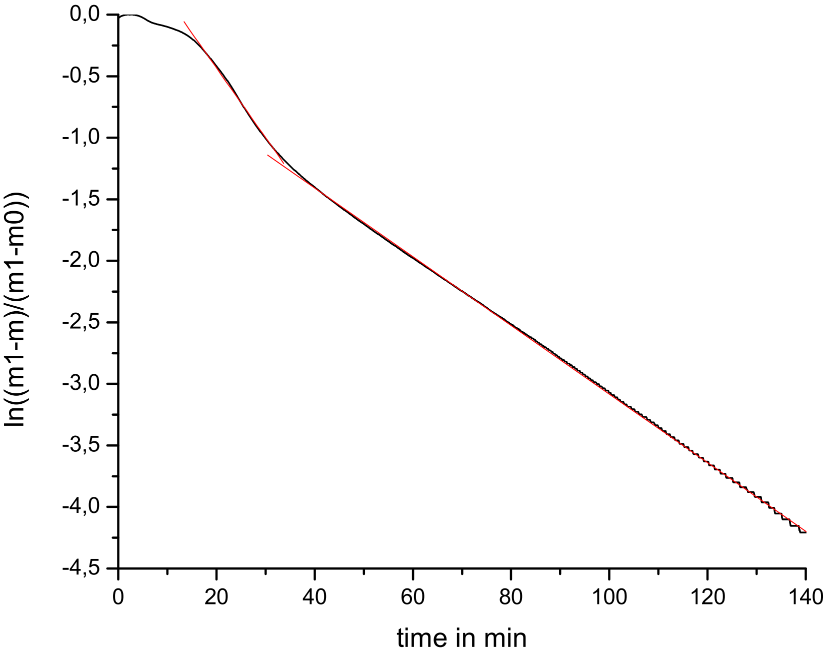

Figure K.4: *fit of the fast hydration of thick Na-Fluorohectorite*

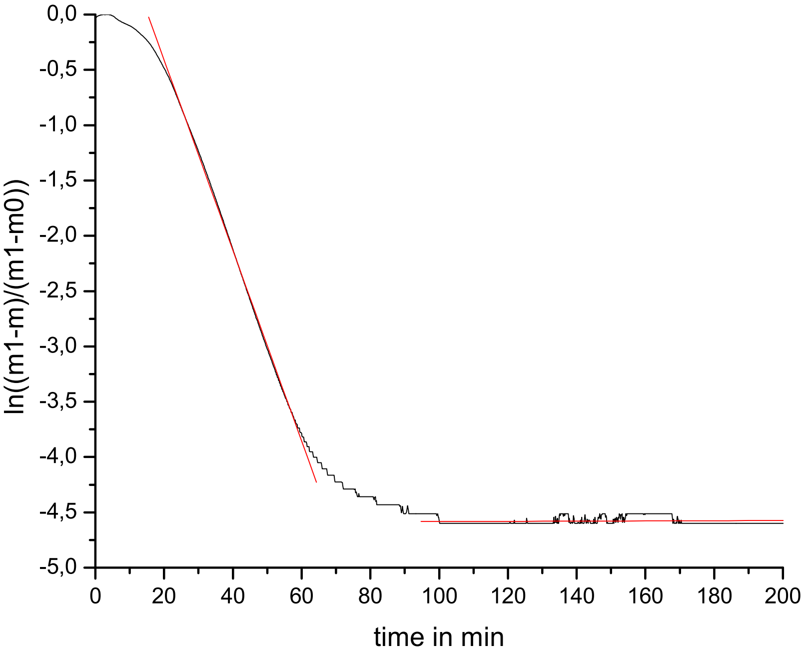

Figure K.5: *fit of the fast hydration of thin Na-Fluorohectorite*

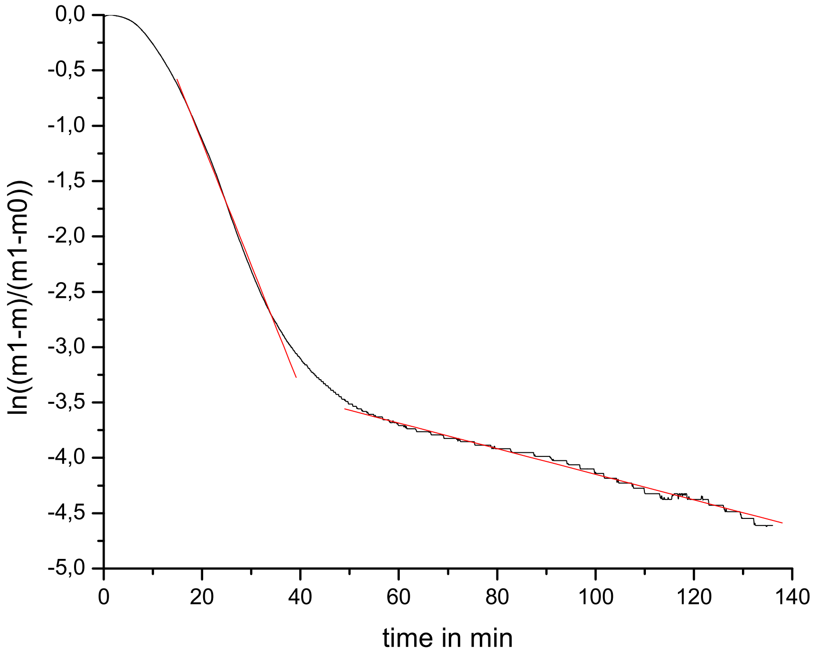

Figure K.6: *fit of the fast hydration of thick Ni-Fluorohectorite*

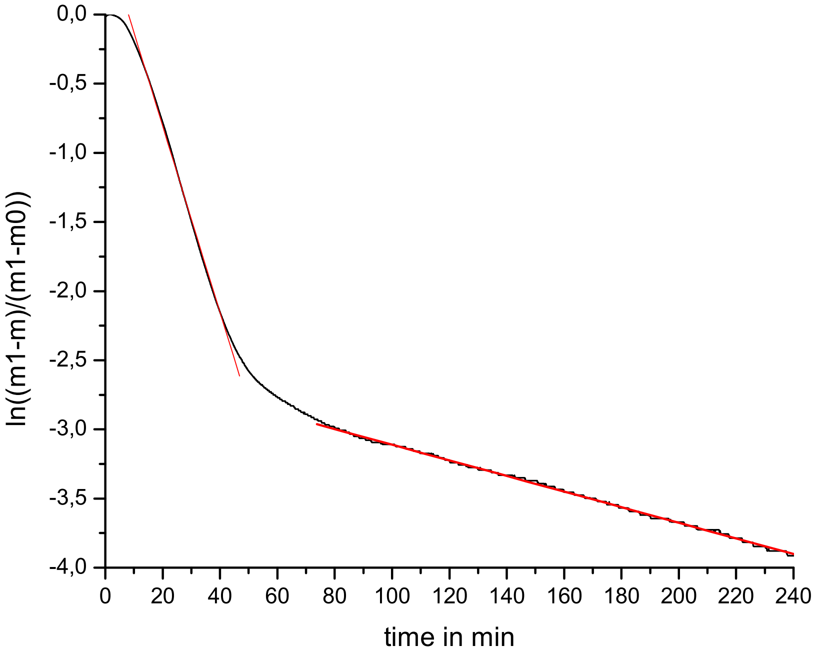

Figure K.7: *fit of the fast hydration of thin Ni-Fluorohectorite*

Fast Dehydration

	Na-Fl thick	Ni-Fl thick	Ni-Fl thin
A	$-3,41 \pm 0,07$	$-3,228 \pm 0,008$	$-3,08 \pm 0,07$
B (min^{-1})	$-0,078 \pm 0,025$	$-0,10 \pm 0,02$	$-0,10 \pm 0,03$
τ (min)	13 ± 3	10 ± 2	10 ± 3
correlation	0,9921	0,9956	0,9974

Fast Hydration

	Na-Fl thick	Ni-Fl thick	Ni-Fl thin
first straight line			
A	$0,76 \pm 0,02$	$1,07 \pm 0,09$	$0,54 \pm 0,05$
B (min^{-1})	$-0,06 \pm 0,03$	$-0,11 \pm 0,02$	$-0,07 \pm 0,01$
τ_1 (min)	16 ± 5	9 ± 3	14 ± 2
correlation	0,99912	0,99943	0,99983
second straight line			
A	$-0,3 \pm 0,1$	$-2,98 \pm 0,01$	$-2,54 \pm 0,05$
B (min^{-1})	$-0,0277 \pm 0,0033$	$-0,011 \pm 0,0019$	$-0,006 \pm 0,002$
τ_2 (min)	36 ± 4	90 ± 13	167 ± 40
correlation	0,9999	0,9944	0,9973

Table K.1: *coefficients of the linear regression:* $Y = A + B \times X$

Appendix L

Fits of fast hydration of thin Ni-Fluorohectorite

I suspected fast hydration for being the result of two kinds of water absorption: absorption in mesopores and in nanopores. The first absorption was supposed to be far quicker than the second one. I wanted to find two time constants characterising each of these absorptions.

L.1 Fit by a sum of two exponentials

I believed that water entered the clays following an exponential law, more precisely the sum of two exponentials, as it is written in equation L.1.

$$m(t) = m_0 + m_{\text{meso}} \times (1 - e^{-\frac{t}{\tau_{\text{meso}}}}) + m_{\text{nano}} \times (1 - e^{-\frac{t}{\tau_{\text{nano}}}}) \tag{L.1}$$

with m_0 the initial weight of clay at 130°C
τ_{meso} is the characteristic time of absorption of water in mesopores
τ_{nano} is the characteristic time of absorption of water in nanopores
$m_0 + m_{\text{meso}} + m_{\text{nano}}$ is the final weight of clay at 25°C

I supposed that τ_{meso} « τ_{nano} and then I looked at a time t » τ_{meso}. The equation L.1 became $m(t) \sim m_0 + m_{\text{meso}} + m_{\text{nano}} \times (1 - exp(-t/\tau_{\text{nano}}))$. I plotted with the software Origin $\ln(m_0 + m_{\text{meso}} + m_{\text{nano}} - m(t))$ as a function of time and it gave me the values of m_{nano} and τ_{nano}.

I found for Ni-Fluorohectorite thin $m_{\text{nano}} = 0,12 \pm 0,01$ mg
$\tau_{\text{nano}} = 174 \pm 10$ min

Then I evaluated m_{meso} thanks to the weight at t=τ_{nano}, which gave me $m_{\text{meso}} = 1,36 \pm 0,01$mg. Finally I found the last unknown value τ_{meso} by looking at weight at t= 30 min. I found $\tau_{\text{meso}} = 15 \pm 5$min. When I superpose both curves: the experimental curve and the fit, I was obliged to introduce a time delay of about 10 min, so that the curves become quite similar after 20 minutes, the time needed by the TGA to decrease its temperature until 25°C. I obtained the curve showed in figure L.1.

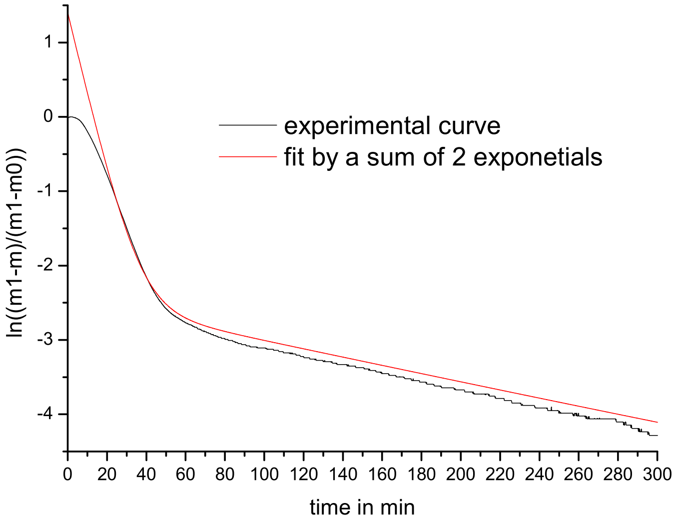

Figure L.1: *fit of the fast hydration of thin Ni-Fluorohectorite by a sum of 2 exponentials* $m(t) = 12,641 + 1,36 \times (1 - exp(-(t-13)/11)) + 0,116 \times (1 - exp(-(t-13)/174))$

L.2 Numerical fit

However I thought that I could improve my fit using a numerical method. In fact one matter with the previous fit was that I did as if temperature was changing like an echelon, but we saw that temperature decreased from 130°C to 25°C in 20 minutes (see appendix G). I thought that the behaviour of the clay was well modeled by the equation:

$$\frac{d(\Delta m(t))}{dt} + \frac{\Delta m(t)}{\tau} = \frac{\Delta m_f(T)}{\tau} \tag{L.2}$$

$\Delta m_f(T)$ is the gain of weight of the clay at a certain temperature and it is given by the curves m=f(T), where m is the weight at equilibrium (see part 3.4.1. In first approximation, it is possible to write that $\Delta m_f(T) = \Delta m_f \times (T-130)/(25-130)$ with m_f the final gain of weight at 25°C. The curve L.2 shows this approximation.

I discretised equation(L.2) which gave me:

$$\Delta m_{n+1} = \frac{\delta t}{\tau} \times (\Delta m_f - \Delta m_n) + \Delta m_n \tag{L.3}$$

I chose a time step δt of 22 seconds to solve this equation. I calculated the solution for the area located before 45 minutes (the frontier between absorption by nanopores and mesopores showed in figure 3.18 and after 45 minutes. I also found before that $m_{\text{meso}} = 1,36$ mg and $m_{\text{nano}} = 0,12$ mg. These figures allow us to evaluate the proportion of water absorbed in mesopores: 1,36/(1,36+0,12), it is to say 92% and in nanopores 0,12/(1,36+0,12), it is to say 8%.

I have the final solution by adding the two solutions in the following manner:

$$\Delta m_{final}(t) = 0,92 \times \Delta m_{\text{meso}}(t) + (1-0,92) \times \Delta m_{\text{nano}}(t) \tag{L.4}$$

I finally obtained the curve L.3.

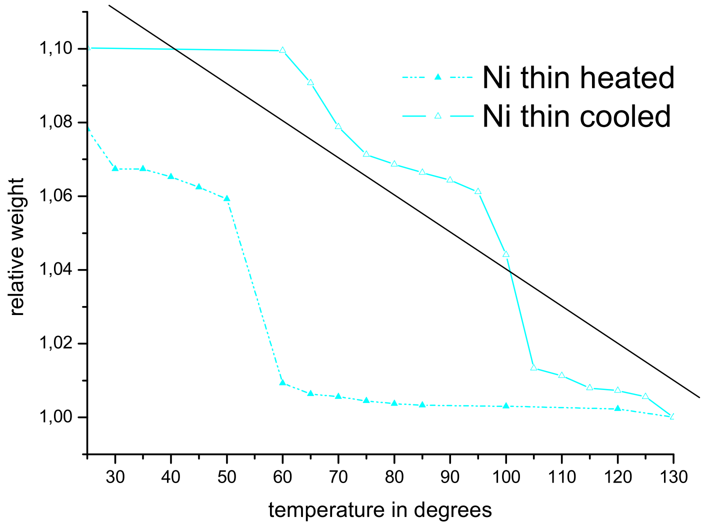

Figure L.2: *approximation of* $\Delta m_f(T)$ *during the hydration of thin Ni-Fluorohectorite*

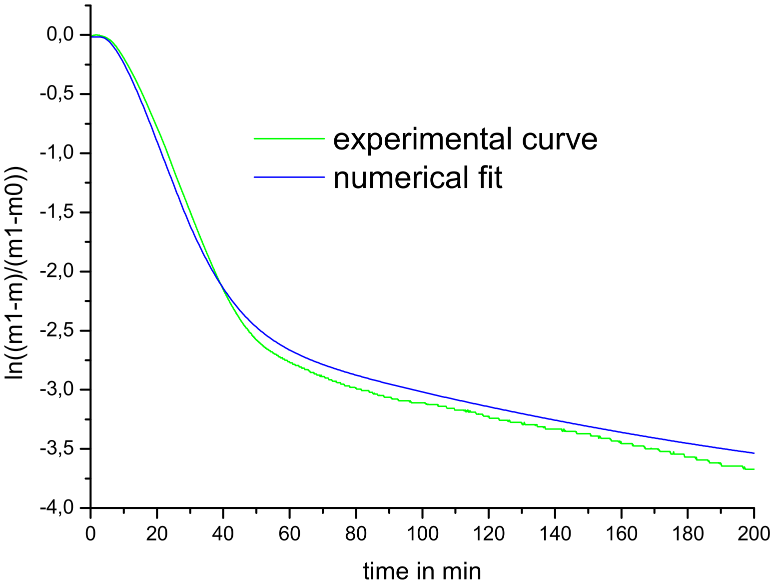

Figure L.3: *numerical fit of the fast hydration of thin Ni-Fluorohectorite*
τ_1= 10 min and τ_2= 100 min.

Appendix M

for the next users of STARe software

The STARe software works with Windows NT 4.0 and with a Service Pack 3 or higher. Service Pack 6 has been installed on the computer. This software accepts only one user called "star" with the password: flhc815. This user doesn't have administrator rights. In case of installation of STARe software, remember that the user called "ingres" must have administrator rights. The password for this user is: 815flhc.

For the installation of the TGA/SDTA851e/LF/1100, you have to enter these information:

identification number: 492
standby temperature: 25°C
time dela: 5 seconds
sensor: MT1
There are no gas controller.
option: cryostat

For the installation of the DSC822e/500, you have to enter these information:

identification number: 388
standby temperature: 25°C
time dela: 5 seconds
option: cryostat

Only one module can be linked to the computer on COM1 (for the TGA) or COM2 (for the DSC).

For the installation of the software, you have to enter several numbers:

System Identification on Hardlock: 11391
Authorization for the software: F9170F92EFBC5FD4
Authorization for the Specific Heat: 800900BCCC92BBF6
Authorization for the Routine Window: ABF5CB87C677E716
Authorization for the Mathematics: 93042FA0519495D7

A method has been specially written for us by Mr. Larbanois, a person from Mettler Toledo in Belgium. This method allows us to use more than 10 segments in one experiment. So it is now possible to increase (decrease) temperature from 5°C to 130°C every 5°C (from 130° to 5°) with a flat of 120 minutes at each temperature.

To draw curves with Origin for instance, you have to export your data from the evaluation window: choose Settings then Print/Export, select the data you want to export and write the maximum number of points you want (the machine measures one point every 5 seconds). Then choose File, Import/Export and Export other 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.

You must save your data regularly on diskettes or on another hard disk thanks to database maintenance. Choose System/Database Maintenance and then choose Backup. Enter the path and the name of the folder for the backup in the location box (for example: C:\STAReSW\Backup). Then click Run to perform the backup of the database.

To restore a database from a hard disk, click the device Disk in the window Database maintenance. Enter the path and the name of the folder of the database to be restored in the Location box. Then click Run.

When you are doing experiments with the TGA, make sure that the thermostat is at 22°. You should fill it with antifrozen and distilled water. But be careful of the level of water inside the thermostat. Indeed when the level is too low, the thermostat rings and its temperature decreases until -14°. You have to add regularly water inside.

Remember also that you shouldn't program more than 30 experiments in the buffer. You don't need to be there for all your experiments: in the Routine Window, click on system/configuration and choose "autostart" and don't click on "wait for remove sample" if you are doing experiments with the same sample.

A man from Mettler Toledo has been contacted to solve the matter with the thermostat. He knows the problem.
Here are his whereabouts:

Joerimann Urs <Urs.Joerimann@mt.com> (suisse)
Address Sonnenbergstrasse 74
CH-8603 Schwerzenbach
Direct dial ++41 1 806 73 87
Direct fax ++41 1 806 72 40

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