



GLOBAL JOURNAL OF ADVANCED RESEARCH
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ISOTHERM 28°C OF TERNARY SYSTEM

H₂O-NH₄Cl-CaCl₂

ELABORATION AND CHARACTERIZATION OF DOUBLE SALTS OF AMMONIUM AND CALCIUM CHLORIDES

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ABSTRACT

The study of the ternary system H₂O-CaCl₂-NH₄Cl by developing the polythermic diagram powered by Thermal Isoplethic Analysis highlighted crystallization areas of new compounds. By this technique and with reference to the data on the isothermal 28°C, the hydrous double salt and more stable 2NH₄Cl.CaCl₂.2H₂O has been synthesized surrounding ambient temperature. Thermal decomposition of this hydrated double salt helped to highlight the existence of five double salts hydrated and anhydrous: 2NH₄Cl.CaCl₂.1/2H₂O; 2NH₄Cl.CaCl₂.1H₂O; 2NH₄Cl.CaCl₂.3/2H₂O; 2NH₄Cl.CaCl₂; NH₄Cl.CaCl₂. The isolation and characterization of these double salts showed that anhydrous one 2NH₄Cl.CaCl₂ and NH₄Cl.CaCl₂ are much more stable than double salts intermediate hydrated.

Keywords: ternary system, Isoplethic Analysis, polythermic diagram, double salt

1. INTRODUCTION

The study of the phase change materials (PCMs) is developed due to their storage capacity of the cooling or heating power. These materials have many applications in diverse sectors such as housing, transport, protection of electronic circuits exposed to high temperature variations or in the cooling of chain for frozen foods. Their development requires specific selection criteria (Cardenas and Leon, 2013; Rognon and Guidant, 2011; Lane, 1991).

In the housing area, many studies showed the possibility to use calcium chloride tetrahydrate CaCl₂.4H₂O associated with ammonium chloride to store heat and ensure thermal regulation (Oyang *et al.*, 2011). The same authors showed that calcium chloride hexahydrate CaCl₂.6H₂O could be used as a PCM in the temperature range of 298K and 299,63K (Oyang *et al.*, 2011). A study of the ternary system H₂O- CaCl₂-NH₄Cl through the development of a series of isothermal between -20 and 70°C Thermal Isoplethic Analysis (TIA) has highlighted areas crystallization of a series of compounds, these studies have



shown that the addition of ammonium chloride does not stabilize the tetra hydrate sodium chloride and subsequently avoid major segregation of decomposition of the hydrate (Berthet and Counioux, 2004; Tenu *et al.*, 2011).

To deepen the results obtained by TIA, hydrated double salt $2\text{NH}_4\text{Cl}\cdot\text{CaCl}_2\cdot 2\text{H}_2\text{O}$ (2.1.2) the more stable was synthesized by TIA from the data of the isothermal 28°C adjacent to the room temperature and thereafter the heat decomposition of the latter, to isolate and characterize the novel compounds. For this more additional analytical techniques coupled SEA were used, in particular the combined thermogravimetry chemical assays and the X-ray diffraction.

2. EXPERIMENTAL TECHNIQUES

2.1. Thermal analysis Isoplethic

The Thermal Analysis Isoplethic is a synthetic method for isothermal isobaric analysis best suited to the study of phase diagrams (Berthet and Counioux, 2004). It is used to follow the evolution of one or more physical properties of the system when changing the composition. In particular, it takes into account the thermal effects that occur in the system when the temperature is changed. The experimental device consists of a digital thermometer which detects the temperature with a relative error of 1/100 degree, an Heto 03DBT6 thermostat having a temperature range between -45 and 150°C coupled with a temperature set CryoBath® Heto 8-30e at -20°C , a reactor placed inside a thermostatic jacket surrounded by rock wool to minimize the influence of the external temperature, the reactor consists of a lab tube in which are immersed a platinum sensor and an injection tube solution, an automatic burette Metrohm, a magnetic stirrer and a microcomputer.

2.2. Thermogravimetry

Thermogravimetric analyses are well suited to properly follow the phenomena of hydration and dehydration of hydrated double salts. The complete installation of the device consists of a thermobalance Linseis L81 (A), equipped with two ovens, one horizontal up to 1100°C and the other vertical maximum power 1550°C . The steering (balance, oven), the collection and analysis of data was performed using a compatible IBM PC AT and a plotter. The maximum mass of the sample was 10g in horizontal and 25g in vertical. The optimal sensitivity of the scale was 1mg, the measuring range resolution 1%.

2.3. X-ray diffraction

The powder X-ray diffraction were carried out on an apparatus equipped with a PHILIPSTM goniometer two circles and a copper anticathode tube $\lambda\text{CuK}\alpha=1,5418\text{\AA}$. This set is composed of a Philips PW 1720 generator; a goniometer θ - 2θ wide angle PW 1050/25, a proportional detector gas flow (xenon) PW 1965/60, a counting Bay PW 1370-1301. Analyses were performed between 10 and 60°C with a counting time of 1 second.

2.4. Chemical analysis

Chemical analysis were performed by titration of chlorine ions and calcium ions. Chlorine ions Cl^- were determined by potentiometer using a silver indicator electrode and a reference electrode extended by a protective sleeve calomel containing a conductive electrolyte (KNO_3 1mol/l) free of chlorides not skew the results. The potential difference between the two electrodes was measured using a type of electronic TACUSSEL mV ISIS 2000. A standard solution of silver nitrate concentration of 0.1mol/l for the analyses of the chloride ions has been used. Measurement accuracy was 0.2%.

Calcium ions were determined by complexometric using a standard solution of EDTA concentration 0.1mol/l. Measurement accuracy was 0.3%.

3. RESULTS AND DISCUSSION

3.1. Summary of the double salt hydrate 2.1.2

Figure 1 shows the experimental curve of the isotherm 28°C at the precipitation. The crystals were synthesized based on the data of the isotherm of 28°C of the diagram of $\text{CH}_2\text{O}\cdot\text{NH}_4\text{Cl}\cdot\text{CaCl}_2$ by TIA. The initial mixture was prepared in the field in three phases (4α , 2.1.2 solution).

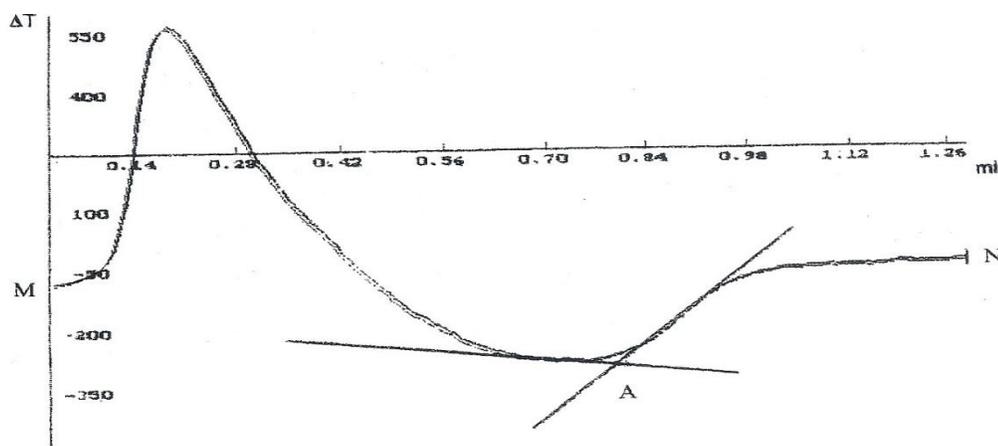


Fig 1: Experimental curve of the isotherm 28°C at the precipitation

The maximum volume of injected pure water was calculated to obtain a mixture of final composition located in the area of the precipitation of compound 2.1.2 (point N). This mixture was then filtered under vacuum using a Buchner funnel and the crystals obtained were then subjected to the analysis. The titration of calcium and chloride ions gives the following average composition reduced to one mole of $\text{CaCl}_2 \cdot 1.7\text{NH}_4\text{Cl} \cdot 1\text{CaCl}_2 \cdot 2,8\text{H}_2\text{O}$.

We do not find exactly the stoichiometric formula because the crystals are always impregnated solution, however, this compound is well within the crystallization field of 2.1.2 and NS combination (Figure 2) of the right converges to the double salt 2.1.2.

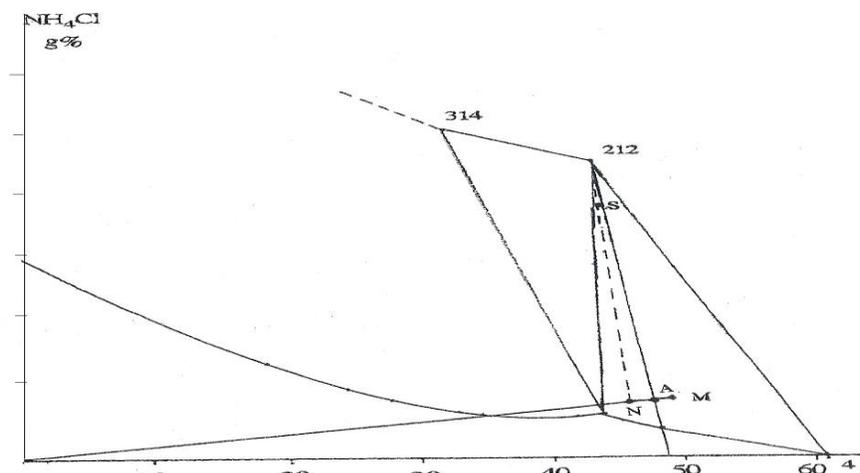


Fig 2: Isoplethic section of the isotherm 28°C from the point M

3.2. X-ray diffraction

2.1.2 hydrated double salt is very hygroscopic therefore for the X-ray diffraction analysis, the crystals were placed in a sample holder and covered by a thick Kapton film of 25 microns which has many advantages: permeability to X-rays, high thermal, chemical and physical stability at room temperature and humidity protection.

XRD patterns of the double salt 2.1.2 (Figure 3.a) was recorded under the same conditions as the Kapton but with a counting time of 10s to avoid a very important background noise.

The observation of these XRD patterns shows the presence of the characteristic diffraction lines of ammonium chloride (see the XRD patterns of pure ammonium chloride on figure 3.b). Another series of different lines of both those NH_4Cl and CaCl_2 are also observed, they can only correspond to a new crystalline phase $2\text{NH}_4\text{Cl} \cdot \text{CaCl}_2 \cdot 2\text{H}_2\text{O}$. The angular positions and the relative heights of the most important of this new phase peaks are reported in Table 1.

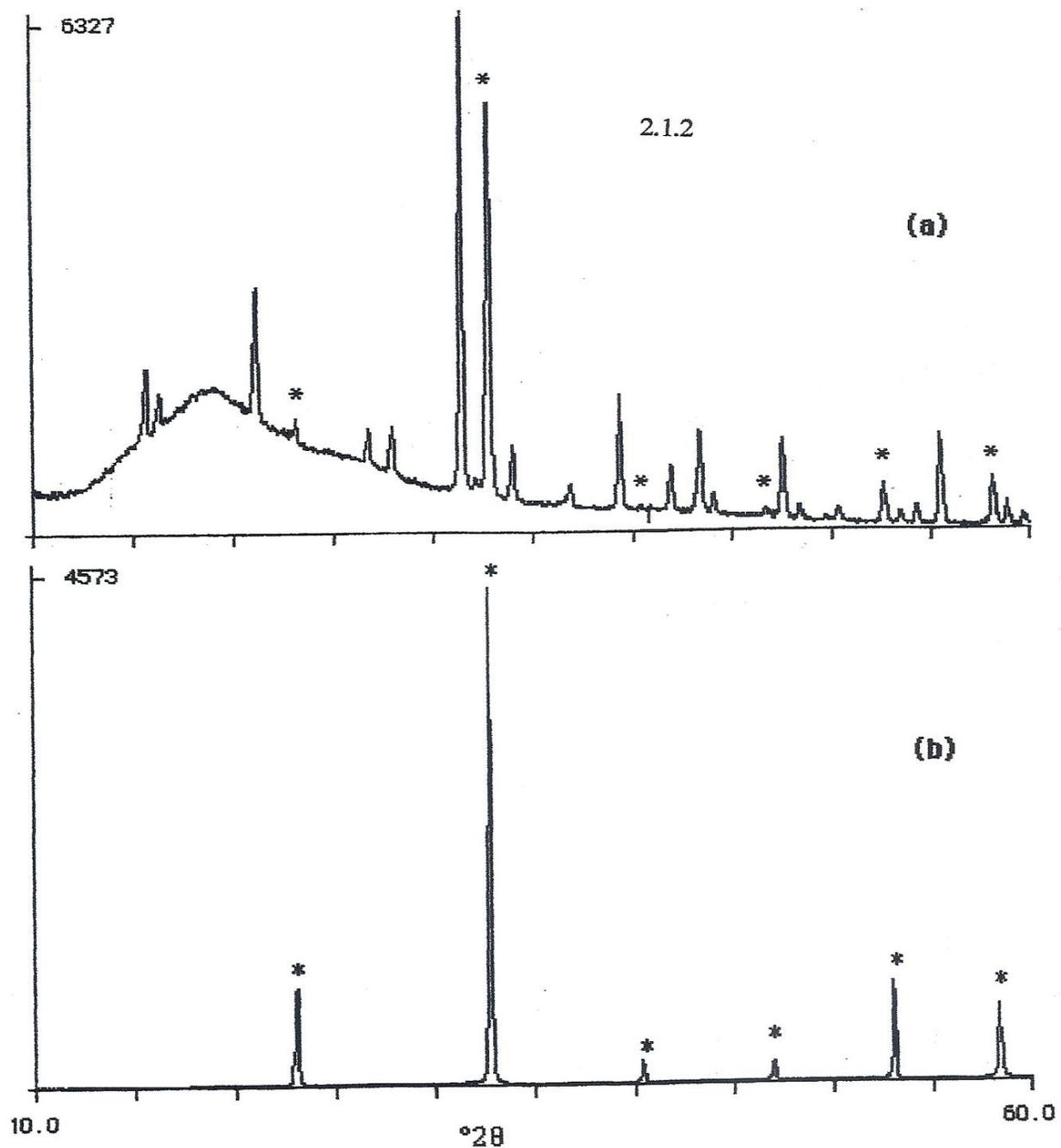


Figure 3: (a) XRD pattern of the double salt 2.1.2
(b) XRD pattern of pure NH_4Cl



Table 1. Values of the most important lines obtained by X-ray diffraction for phase 2.1.2 (* some reflections may be obscured by NH_4Cl lines)

2θ	I/I _{obs}
15.80	15.1
21.27	26.5
31.58	100
34.08	11.8
39.41	23
42.98	16.8
47.18	16.0
55.03	18.3

Although the sample is isolated from the outside by the Kapton film, the preparation of the sample holder and the analysis time (about 8 hours) leads probably to a slight decomposition of the double salt as indicated by the presence of rays of NH_4Cl (Figure 3.b).

3.3. Thermogravimetric analysis of the hydrated double salt 2.1.2

To confirm the formula of the double salt hydrate, thermal decomposition of the salt in the same conditions (1 $\text{K}\cdot\text{min}^{-1}$ heating rates) and under anhydrous atmosphere (argon or nitrogen) were performed.

Preliminary tests of heating to temperatures above 350°C show that TGA bearing is obtained from 335°C . Analysis of the solid residue remaining in the nacelle shows that only anhydrous CaCl_2 lines are present on the XRD patterns (Figure 4), this result was confirmed by chemical analysis of both Cl^- and Ca^{2+} .

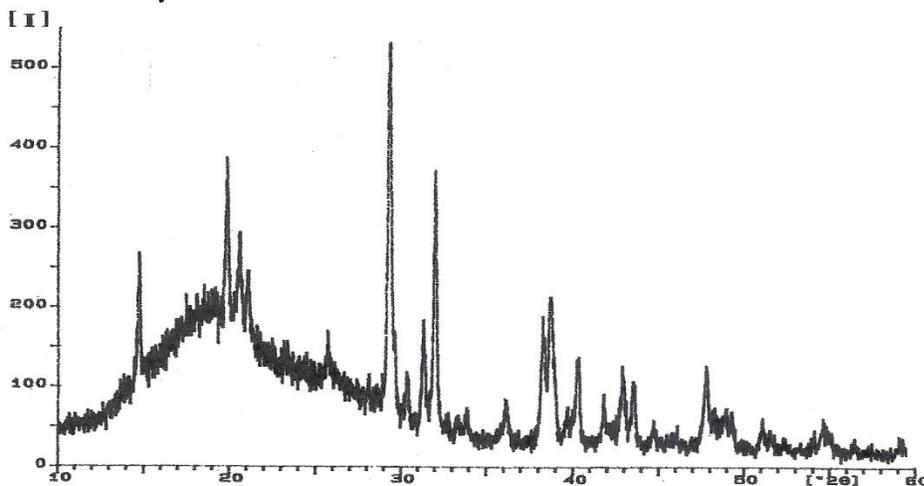


Fig 4: XRD patterns of the solid residue

Two types of thermal images are observed; they are shown in Figures 5 and 6. Figure 6 highlights four sharp weight loss, while Figure 5 shows 6.

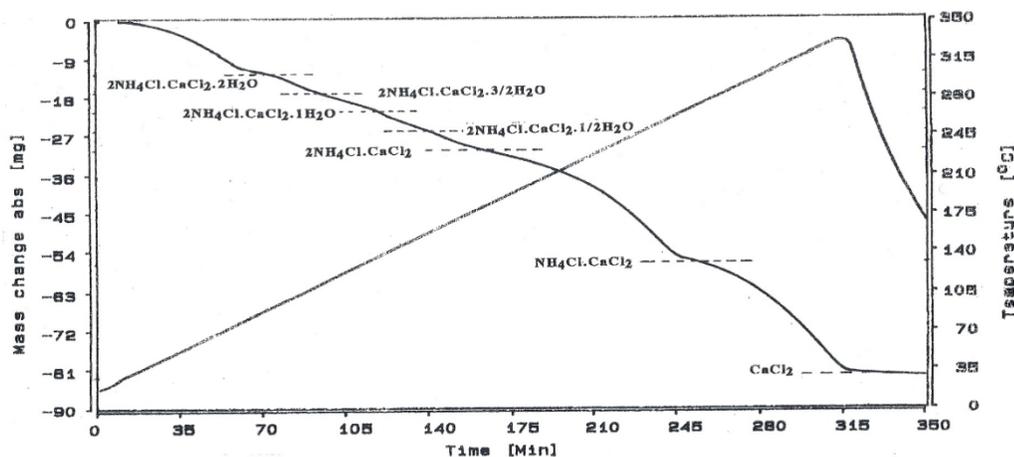


Fig 5: Thermogravimetric analysis curve 1

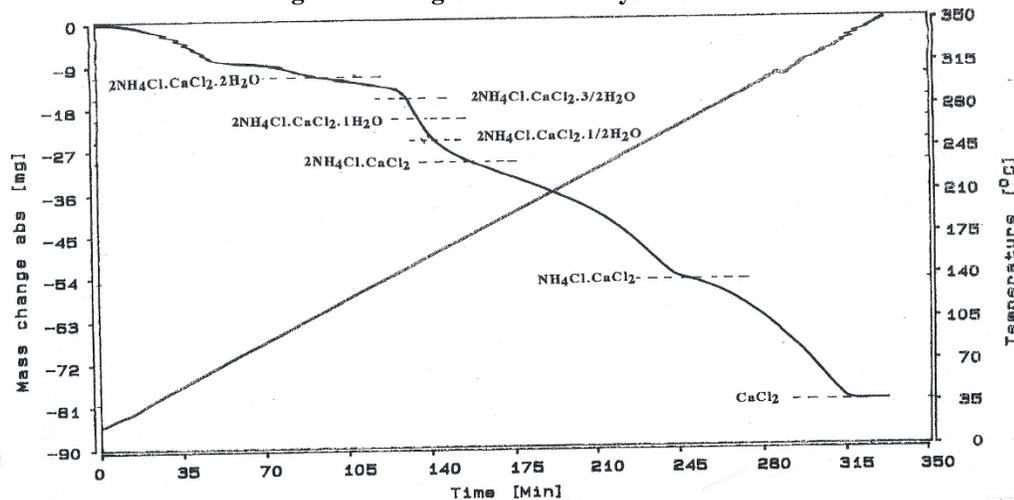


Fig 6: Thermogravimetric analysis curve 2

A theoretical calculation from the total mass loss corresponding to anhydrous compound CaCl_2 was undertaken to determine a consistent pattern of thermal decomposition. Table 2 summarizes the decomposition temperatures observed on the thermograms.

Table 2: Decomposition temperatures observed on the thermograms 1 and 2

Compounds	1 Figure 4 *139.1 mg (under N_2)	2 Figure 5 *137.0 mg (under Ar)
1.1.0	263	259
2.1.0	172	169
2.1.1/2	153	153
2.1.1	131	-
2.1.3/2	115	144
2.1.2	91	100



*Mass in mg corresponds to that of the initial sample

1.1.0: $\text{NH}_4\text{Cl} \cdot \text{CaCl}_2$

2.1.0 : $2\text{NH}_4\text{Cl} \cdot \text{CaCl}_2$

2.1.1/2 : $2\text{NH}_4\text{Cl} \cdot \text{CaCl}_2 \cdot 1/2\text{H}_2\text{O}$

2.1.1 : $2\text{NH}_4\text{Cl} \cdot \text{CaCl}_2 \cdot \text{H}_2\text{O}$

2.1.3/2 : $2\text{NH}_4\text{Cl} \cdot \text{CaCl}_2 \cdot 3/2\text{H}_2\text{O}$

2.1. 2 : $2\text{NH}_4\text{Cl} \cdot \text{CaCl}_2 \cdot 2\text{H}_2\text{O}$

Note that the two major accidents on the TGA curves correspond to successive loss of two molecules of ammonium chloride (between 165 and 175°C for the first and between 255 and 266°C for the second). The main differences appear in the temperature range 80-250°C. Accidents obtained suggest that the loss of two water molecules of the double salt comes in stages of half-molecules. The differences between 1 and 2 provide on the fact that the compound 2.1.2 remains stable at a higher temperature on the thermogram 2. Therefore, the loss of the first half-molecule of water occurs at 144°C on the same thermogram, whereas it is only about 110°C for the second. It is conceivable that the transition to 2.1.1 compound that occurs around 130°C on the thermogram 1 be hidden on the thermogram 2.

In conclusion, the thermogravimetric analysis shows that two intermediates anhydrous (2.1.0) and (1.1.0), very stable while hydrated compounds seem very sensitive to temperature fluctuations. Figure 7 shows a sketch of decomposition of hydrated double salt 2.1.2.

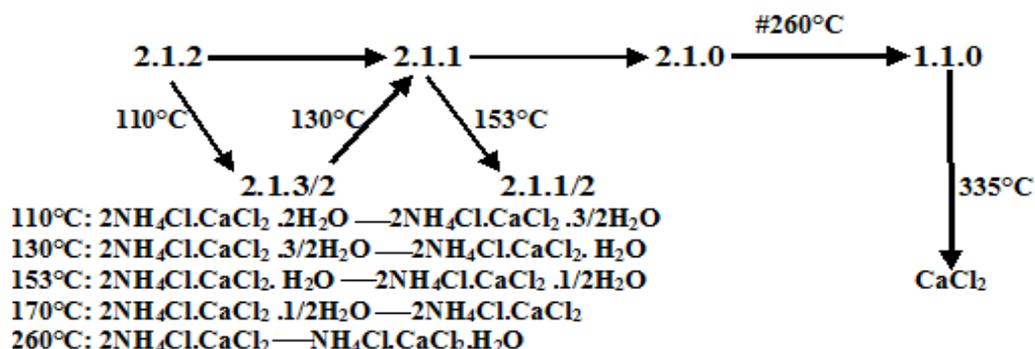


Fig 7: Sketch of decomposition step of hydrated double salt $2\text{NH}_4\text{Cl} \cdot \text{CaCl}_2 \cdot 2\text{H}_2\text{O}$

3.4. Chemical analysis and characterization of anhydrous compounds

The previous Thermogravimetric analysis showed that the anhydrous compounds transformation temperatures 2.1.0 and 1.1.0 are respectively 170°C and 260°C.

3.4.1. Analysis of double salt $2\text{NH}_4\text{Cl} \cdot \text{CaCl}_2$

This compound is prepared by deshydration of the hydrated double salt at room temperature in a desiccator filled with silica gel. The mass loss curve as a function of time (Figure 8) shows that after about 20 hours, the weight of the sample remains constant. Chemical analysis of Cl^- ions and Ca^{2+} gives the following results: $1,87\text{NH}_4\text{Cl} \cdot \text{CaCl}_2 \cdot 0,25\text{H}_2\text{O}$. This composition is very close to that of compound 2.1.0.



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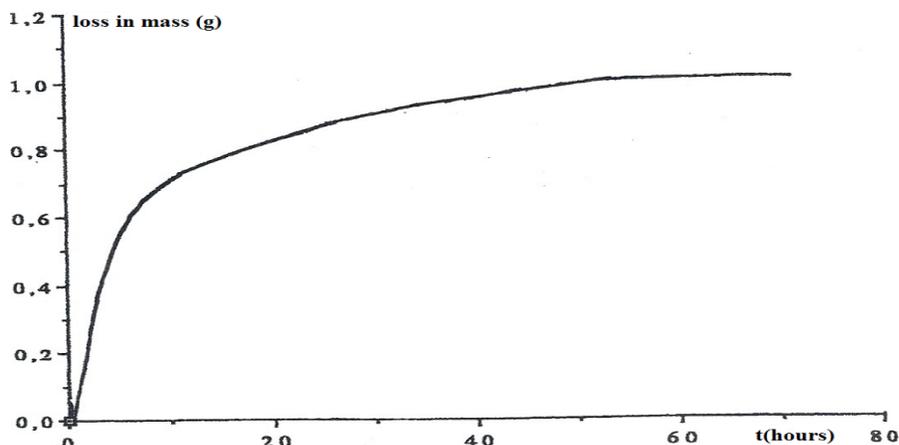


Fig 8: Loss of mass of the double hydrated salt $2\text{NH}_4\text{Cl} \cdot \text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ at 110°C

The diffractogram of this compound is shown in Figure 9 and the angular positions and relative intensities of the most important diffraction peaks are shown in Table 3.

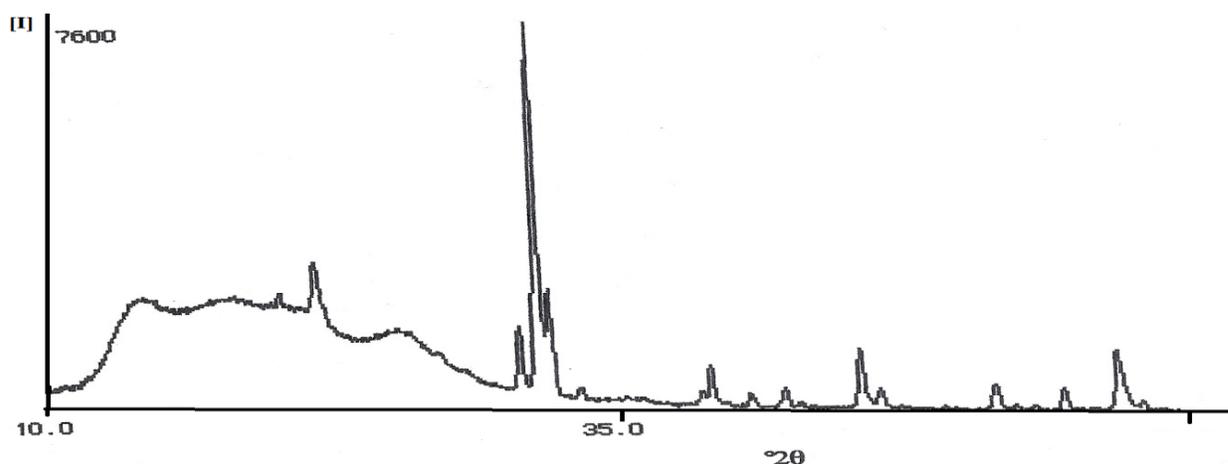


Fig 9: XRD pattern of the anhydrous double salt 2.1.0

The diffractogram of this treated sample 70 hours at room temperature shows no characteristic reflection of NH_4Cl and CaCl_2 or hydrates of calcium chloride. The observed lines can correspond to a new compound, anhydrous double salt 2.1.0.

Table 3: Values of the most important lines obtained by X-ray diffraction for phase 2.1.0

2θ	I/I _{obs}
22.53	16.7
31.24	15.6
32.02	100
32.58	28.9
39.46	10.2
45.95	16.6
57.10	15.6



3.4.2. Analysis of double salt $\text{NH}_4\text{Cl} \cdot \text{CaCl}_2$

This compound was prepared by deshydration of hydrated double salt in an oven heated to 110°C .

Figure 10 shows the mass loss as a function of time. A constant mass is obtained after 60 hours heating. Chemical analysis of the dried product leads to a formula $0,92\text{NH}_4\text{Cl} \cdot \text{CaCl}_2$ very close to the double salt $\text{NH}_4\text{Cl} \cdot \text{CaCl}_2$.

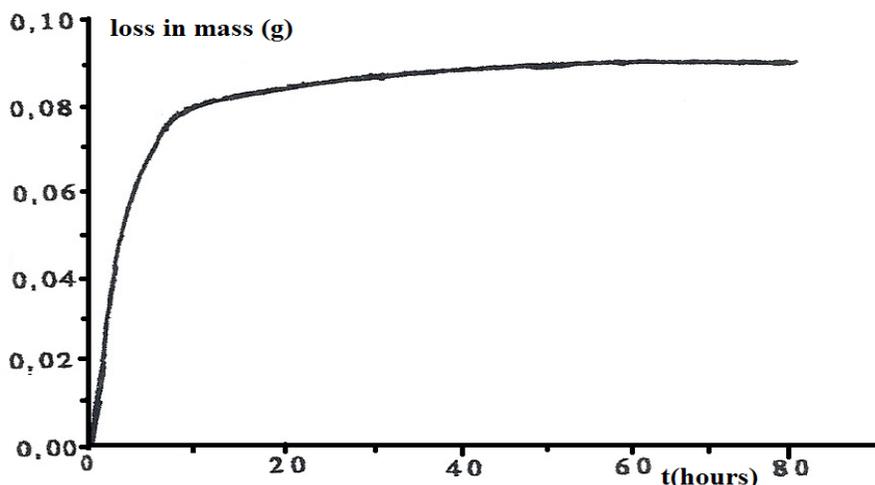


Fig 10: Loss of mass of double anhydrous salt 1.1.0 at 110°C

The X-ray diffractogram recorded between 10 and $60^\circ 2\theta$ in steps of 0.02°C with a counting time of 10 seconds is shown in Figure 11.

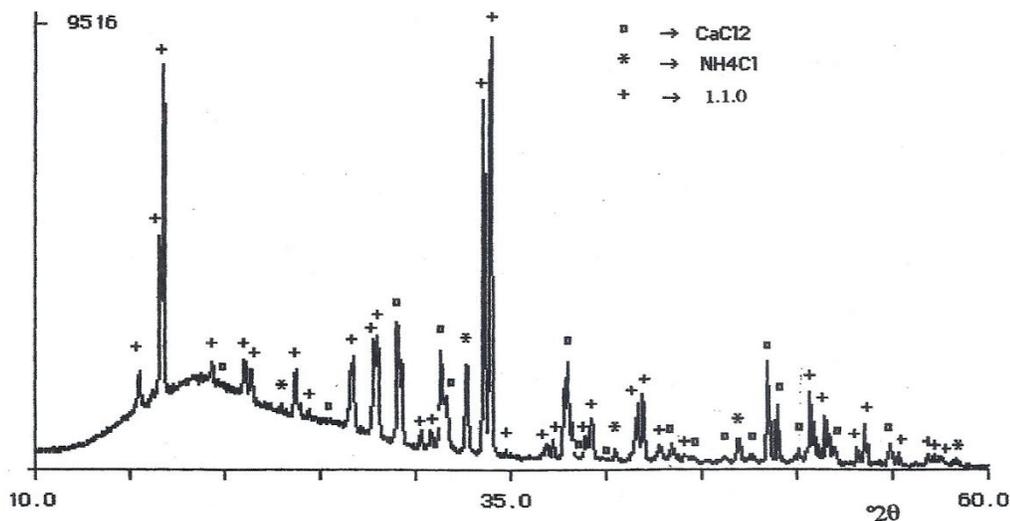


Fig 11: XRD pattern of double anhydrous salt 1.1.0

If some characteristic lines anhydrous CaCl_2 and NH_4Cl are observed, it appears a series of additional lines which can only correspond to a new crystalline phase, hydrated double salt $\text{NH}_4\text{Cl} \cdot \text{CaCl}_2$. Table 4 shows positions and relative intensities of the most important diffraction peaks, taking into account the fact that some reflections may be masked by other lines of NH_4Cl and CaCl_2 .



Table 4: Positions and intensities of the most important diffraction peaks 1.1.0 phase

2θ	I/I₀
15.58	13.7
16.68	39.0
16.88	86.4
19.45	17.3
21.11	18.2
21.46	16.3
23.79	17.1
26.81	21.0
27.88	23.6
28.11	26.4
33.66	81.0
33.76	29.4
34.01	100
41.71	13.3
41.97	16.0
50.76	16.6
51.56	11.1

4. CONCLUSION

The study of the synthesis of hydrated double salt $2\text{H}_2\text{O}\cdot\text{NH}_4\text{Cl}\cdot 2\text{CaCl}_2$ from the data of the isotherm of 28°C ternary system $\text{H}_2\text{O}\cdot\text{NH}_4\text{Cl}\cdot\text{CaCl}_2$ and thermal decomposition of the latter, helped to highlight and therefore confirm the existence of very unstable intermediate double hydrated salts $2\text{NH}_4\text{Cl}\cdot\text{CaCl}_2\cdot 1/2\text{H}_2\text{O}$; $2\text{NH}_4\text{Cl}\cdot\text{CaCl}_2\cdot 1\text{H}_2\text{O}$; $2\text{NH}_4\text{Cl}\cdot\text{CaCl}_2\cdot 3/2\text{H}_2\text{O}$ and two stable double anhydrous salt hydrates $2\text{NH}_4\text{Cl}\cdot\text{CaCl}_2$, $\text{NH}_4\text{Cl}\cdot\text{CaCl}_2$.

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