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Pierre Braconi, Andrès Cyrille, Jean-Claude Mutin. Interaction of CaSO<sub>4</sub> with water vapour at high relative humidity. 2010. hal-00454539

**HAL Id: hal-00454539**

**<https://hal.science/hal-00454539>**

Preprint submitted on 8 Feb 2010

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## Interaction of CaSO<sub>4</sub> with water vapour at high relative humidity

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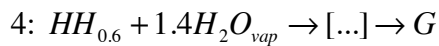
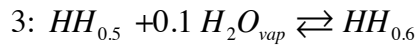
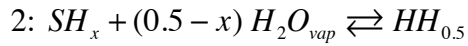
## **Abstract**

Soluble anhydrite  $\beta$ -CaSO<sub>4</sub> reacts with water vapour at room temperature to form CaSO<sub>4</sub>-0.5H<sub>2</sub>O at 20-30% RH and CaSO<sub>4</sub>-0.6H<sub>2</sub>O at 70-80% RH. At higher RH, additional water uptake can only add-up to an adsorbed water layer. The present work provides evidence that a small amount of the adsorbent dissolves in the adsorbed layer and gypsum starts precipitating at 97-98 %RH even though condensation of the vapour phase does *not* take place. After several days the adsorbent is almost entirely and irreversibly converted. The kinetics of weight gain clearly discriminates between adsorption and dissolution-precipitation. If a minute amount of a deliquescent salt (NaCl) is added to the initial sample, the same phenomenon is observed when relative humidity reaches the deliquescent point of the salt. After return to ambient conditions, X-ray diffraction shows that in all cases the sample is essentially made of gypsum with only traces of not dissolved hemihydrate.

Keywords: calcium sulfate, deliquescence, gypsum, precipitation.

## Introduction

At room temperature, soluble anhydrite A3 reacts with water vapour according to the following successive steps :



SH is meant for subhydrate, HH for hemihydrate and G for gypsum.

The final object of the present work is to clarify the equilibrium states of the system  $CaSO_4-H_2O$  at high relative humidity, typically above 80%, following step 4 above. In 1960 Razouk et al. [1] reported that fully dehydrated gypsum recovers its initial di-hydrate stoichiometry and structure when re-exposed to *saturated* water vapour at 30°C for several days. That and previous works reportedly confirm the statement that the direct formation of the dihydrate from the hemihydrate “without the solid passing into solution is improbable”.

The crystal structure of the hydrate  $HH_{0.6}$  cannot incorporate extra water molecules [2] on any lattice sites. In other words, any water uptake beyond 0.6 mol  $H_2O$ /mol  $CaSO_4$  may formally be regarded as the fraction of water pertaining to a separate phase: either an adsorbed water film (the adsorbate in the following) or liquid water (the liquid phase) if homogeneous vapour condensation takes place at 100% RH. Actually, such condensation is carefully avoided throughout the present work, and the adsorbate actually is the only “liquid like” phase ever present in the system. The morphology of the final product provides unequivocal evidence of that. Notice also that if the adsorbed layer starts building-up from the lowest RH values on, the saturation of the lattice sites corresponding to composition  $HH_{0.6}$  will actually be reached at a (slightly) higher water content. This point is addressed in the result section.

As a clue to the potential role of a limited amount of “liquid like” water in the system we investigate the modifications of the equilibrium states of the later induced by the addition of a (very) small amount of NaCl. NaCl being a deliquescent salt, a saturated aqueous solution forms when the deliquescent point, 75 %RH at 25°C, is reached.

Beside equilibrium data, the kinetics of weight change following an increase or decrease of relative humidity is systematically investigated.

## Experimental

The dynamic vapour sorption set-up (DVS) from VTI corp. is used to investigate the isothermal reaction-adsorption isotherm at relative humidity values ranging from 2% to 99% using nitrogen (3vpm  $\text{H}_2\text{O}_{\text{vap}}$  nominal content) as carrier gas. All experiments are carried out at the constant nominal temperature of 25°C. The actual sample temperature is continuously recorded over an entire adsorption-desorption cycle: the actual mean value is always found close to 24.7°C and the difference between the *extreme* values always lower than 0.25°C. At constant RH, the standard deviation is between 0.03 and 0.05°C.

The dew point of the incoming gas phase is measured using the EdgeTech model 2002 system and the relative humidity in the gas flow is thus determined with an accuracy of  $\pm 0.5\%$ .

The DVS is built around a Cahn RH microbalance whose equals either  $1.5\mu\text{g}$  or  $1 \times 10^{-5}$  of the total beam load, if larger. However, in the present experimental conditions the relative uncertainty on the initial gypsum sample weight (measured under nitrogen flow) is about 0.01%. The accuracy of the isotherm is mainly dependent on the long-term stability of the balance. Because of the small weight changes involved, the recordings have to be carefully corrected of any incidental weight jumps and next by subtraction of an average blank file recorded without sample in the same conditions..

A3 anhydrite ( $\beta\text{-CaSO}_4$ ) is prepared *in situ* by dehydration of natural gypsum. A small lump cleft from a large transparent (pure) piece is heated to 120°C under dry nitrogen flow for 2-5 hours. After return to RT, the relative humidity range is scanned automatically stepwise from 2% to 5% and then typically by 10% increments. The recorded RH and sample weight data are carefully checked and average values over selected time ranges are substituted to the automatically acquired data when they appear a better choice. The corrected sample weight changes are converted into numbers of mole of water per mole of anhydrous calcium sulfate and noted  $n$ . Relative humidity are converted in relative pressures,  $p/p_{\text{sat}}$ .

The kinetics of weight change from one equilibrium state to another is systematically investigated. The last equilibrium data point recorded at a given  $p/p_{\text{sat}}$  value is taken to be the origin of the kinetic curve at the next  $p/p_{\text{sat}}$  value and the fractional up-take (or loss) parameter is defined by the ratio of instantaneous weight change over the difference between the initial and final values. By necessity, the very first points of such curves are obtained in transient conditions and are not kinetically relevant, but the most part of the curve is representative of a process taking place at constant relative humidity and temperature.

Complementary analyses are carried out by XRD using a position sensitive linear detector with Cu  $K\alpha_1$  radiation, and by SEM (carbon deposition).

## Results

### *System $CaSO_4-H_2O_{vap}$ at $25^\circ C$*

The description and analysis of the isotherm is made by referring to the singular points labelled A to J in Fig.1 that shows a loop over the largest technically achievable range of relative humidity values, with a final return to simulated ambient conditions. Additional points from another experiment have been added to help appreciate the reproducibility of the upward branch of the isotherm.

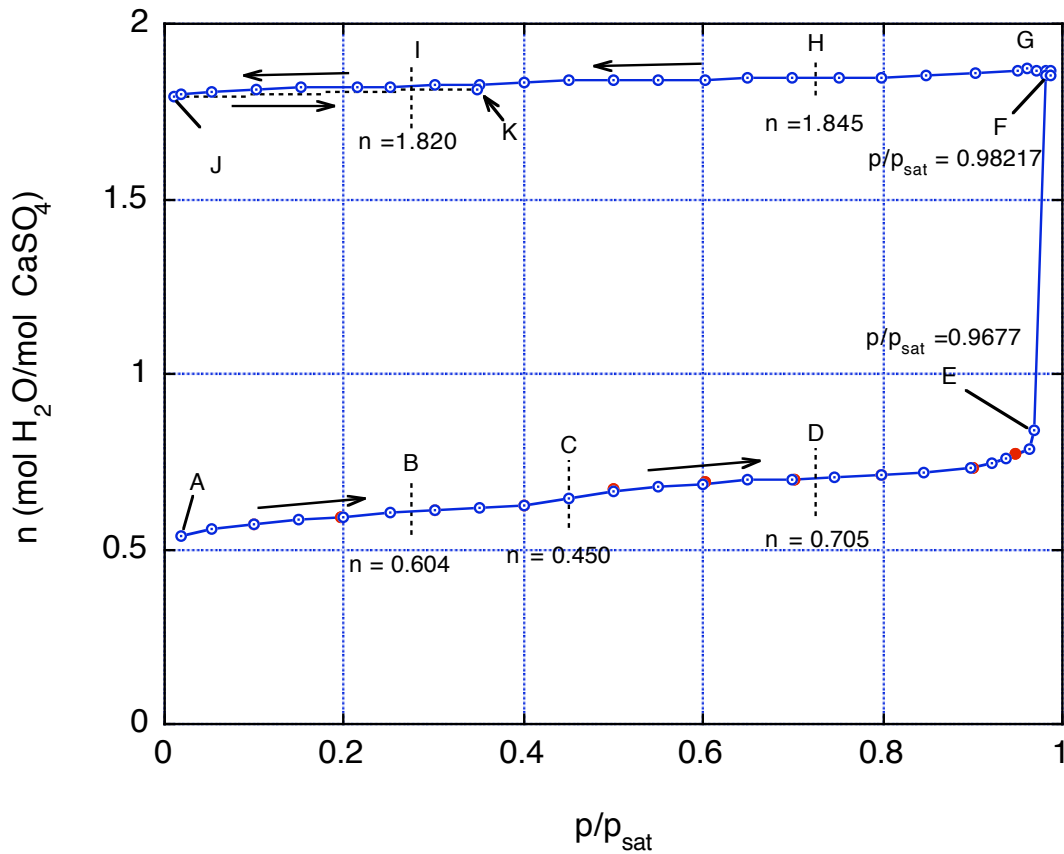


Fig.1 adsorption-reaction isotherm of pure  $CaSO_4$

An apparent intermediate equilibrium state at low  $p/p_{sat}$  has been noted in early investigations: at room temperature by Jury and Light [3] for  $p/p_{sat} \approx 0.0003$  and  $n = 0.033$  and at  $100^\circ C$  by Southard et al. [4] for  $p/p_{sat} \approx 0.0071$  and  $n = 0.069$ . The DVS is not adapted to

measurements at RH values lower than 2% and that initial part of the isotherm is not dealt with here. The first equilibrium point A at about 2%RH is always found above the  $n=0.5$  limit

Points B and D are the points with the lowest slope on the upward branch. Fig.2a and 2b show that the amount taken up increases by 0.1 mol H<sub>2</sub>O/mol CaSO<sub>4</sub> in that range. As this is the exact amount required by the phase change  $HH_{0.5} \rightarrow HH_{0.6}$  it is tempting to assume that the *bulk* composition of the adsorbent is precisely equal to 0.5 and 0.6 mol H<sub>2</sub>O/mol CaSO<sub>4</sub> at point C and D respectively. In support of that view, it must be underlined that the inflection point (marked in Fig.2a) lies on the equilibrium curve  $HH_{0.5} \rightleftharpoons HH_{0.6}$  that has been independently determined based on X-ray diffraction experiments under controlled water vapour pressure (see **appendix 1**).

In accordance with the foregoing, the amounts of water *adsorbed* on the surface of HH<sub>0.5</sub> at point B and on the surface of HH<sub>0.6</sub> at point D could be readily estimated as  $n_{\text{ads}} = n-0.5$  mol H<sub>2</sub>O/mol CaSO<sub>4</sub> and  $n_{\text{ads}} = n-0.6$  mol H<sub>2</sub>O/mol CaSO<sub>4</sub> respectively. But then one should also have to accept that  $n_{\text{ads}}$  remains constant over the B-D interval, at variance with accepted models of physical adsorption of vapours (BET, GAB, BDDT).

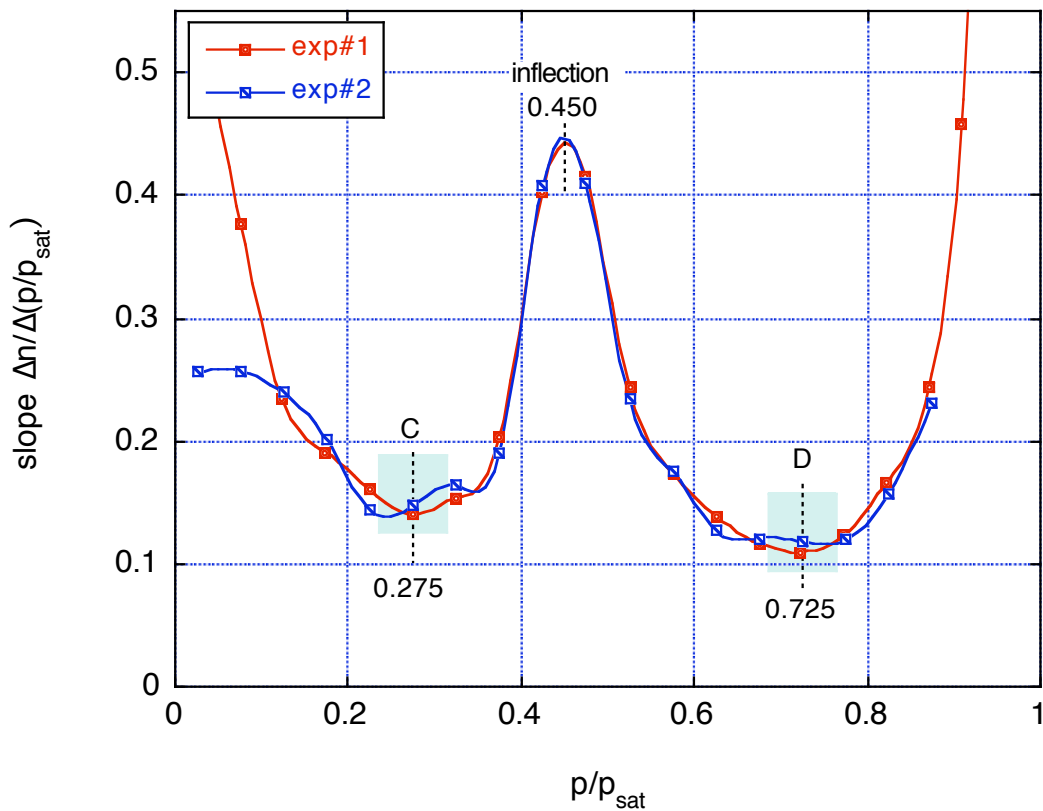


Fig.2a Differential isotherm  $\Delta n/\Delta(p/p_{\text{sat}})$ . Inflection point at  $p/p_{\text{sat}} = 0.450$

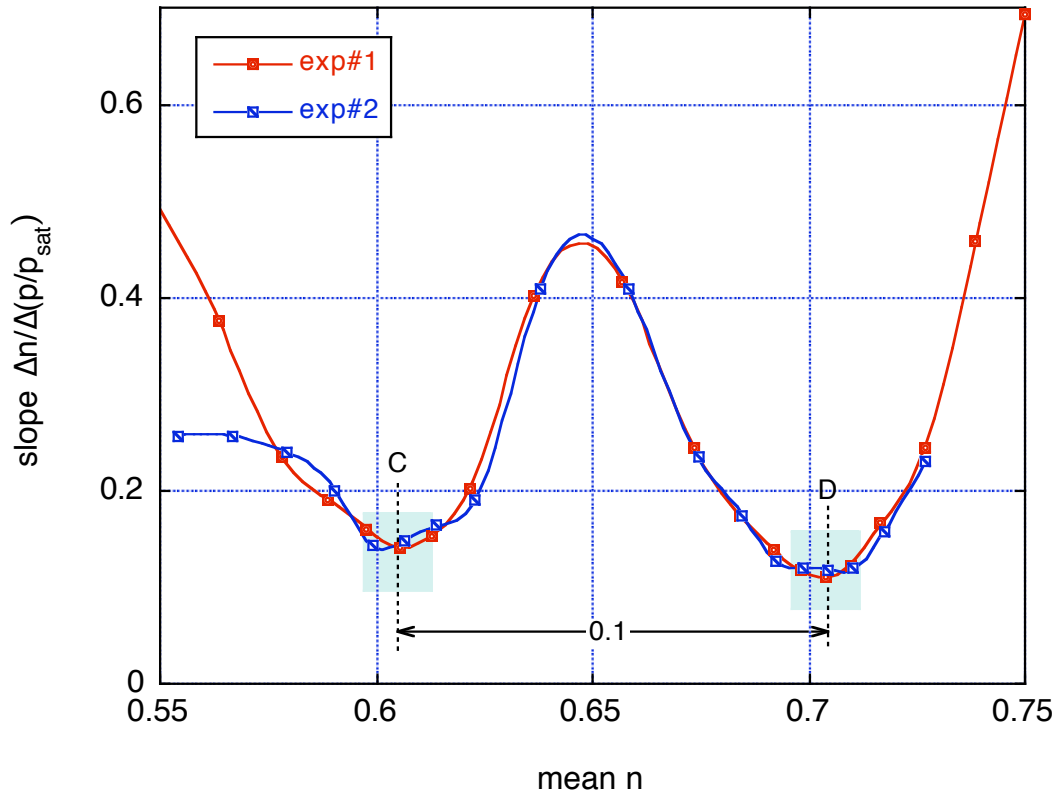


Fig.2b Differential isotherm  $\Delta n / \Delta(p/p_{sat})$  vs n

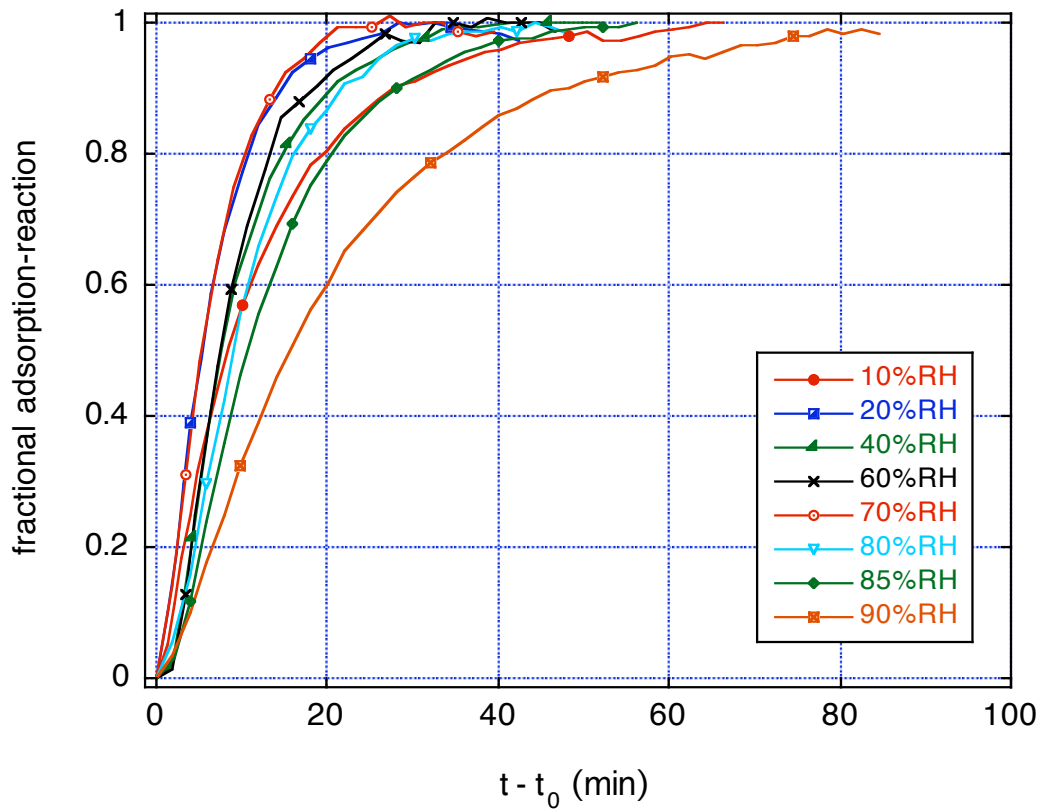


Fig.3: kinetics of adsorption: fractional adsorption vs reduced time



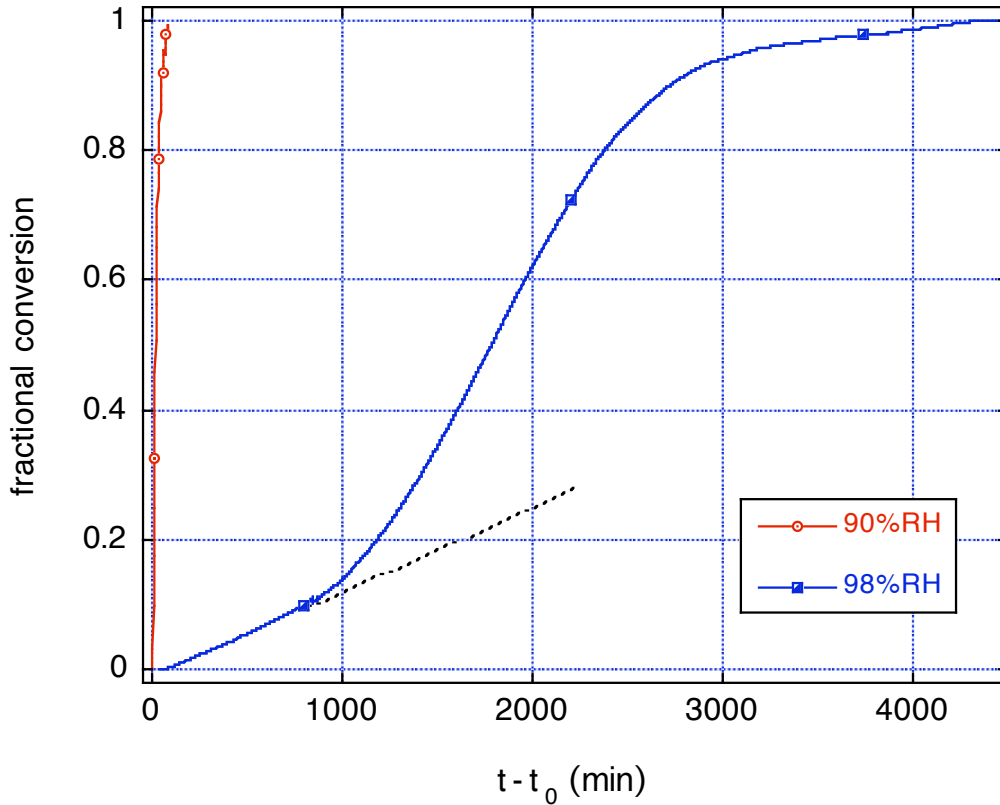


Fig.4: kinetics of conversion of hemihydrate to gypsum (fractional conversion vs reduced time) at 98.5%RH.

In step E-F, the weight gain is very high compared to the other RH steps. In the considered experiment, the overall water content in F is not much lower than in the initial gypsum sample. The kinetics of weight gain also is significantly modified as shown by Fig.3 and Fig.4. Compared to adsorption kinetics at 90%RH the time for completion is larger by 2 orders of magnitude (Fig.4). The shape of the curve also is modified: an initial induction period of about 20 min is followed by a linear increase over the first 10% of the water up-take and then by an accelerated period up to about 50%. When the humidity level is further increased up to 99% RH, the water content remains unchanged but it must be underlined that at such high a level - and already at 98% - the weight-vs-time curve and RH-vs-time curve are very noisy, making the selection of the representative equilibrium point somewhat inaccurate. When  $p/p_{\text{sat}}$  is decreased by one percent steps a very small increase is still observed up to point G (96.1 %RH) and this may be related to the RH fluctuations just mentioned. The maximum water content at point G amounts to 1.868 mol H<sub>2</sub>O/mol CaSO<sub>4</sub> but full conversion (2.01) has been achieved in a partial experiment.

Point K marks the return to simulated ambient conditions within the VTI. Here it is observed that the product has maintained the initial gypsum lump shape as well as sufficient cohesion to allow its safe handling. XRD analysis was carried out in the same ambient conditions on one face of the final sample, i.e. on the “relic” of one of the 001 cleft surface of the initial gypsum lump. The diffraction spectrum of the dihydrate is observed (see Fig.6) with only traces of hemihydrate (Bassanite) in accordance with the fact that 100% conversion to dihydrate could not be achieved in the time imparted to the experiment.

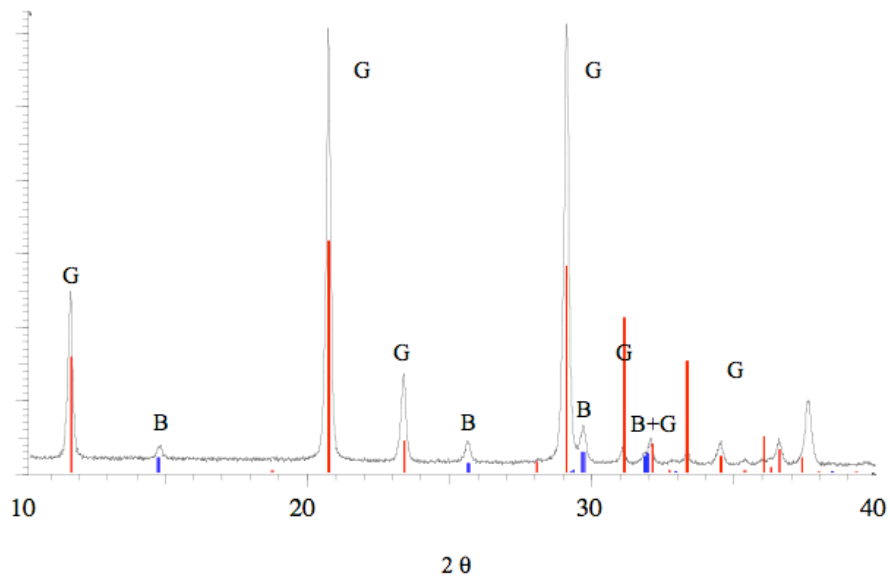


Fig.5 XRD spectrum of final product. G = Gypsum (ASTM file 01-070-0983), B = Bassanite (ASTM file 01-074-2787)

SEM micrographs of the same surface are shown in Fig.6a-b. Firstly, it must be emphasized that the X shaped pattern in the middle of Fig.6a is a perfect example of the so-called “Uhr Glass” patterns that developed on the 001 surface during the initial dehydration of gypsum. The fact that such patterns are still present after the final reversion to gypsum while the microstructure at a finer scale is modified is a direct evidence that *complete* deliquescence of the hemihydrate pseudomorph did *not* take place between equilibrium states E and F.

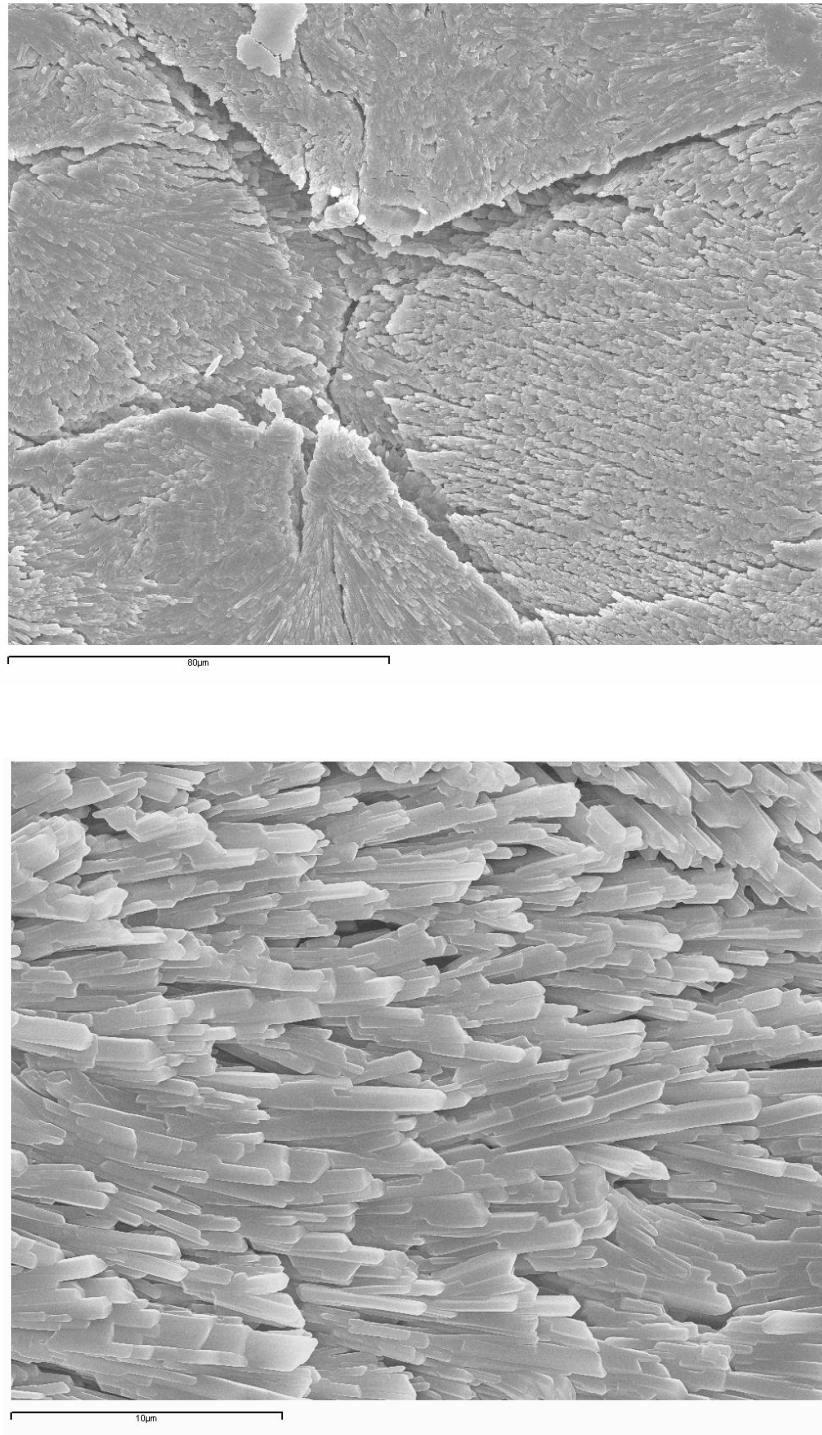


Fig 6. SEM micrographs of the  $(001)_G$  surface of the reversed sample. a: scar of a “Uhr Glass” pattern formed during dehydration of the initial sample. b: bunch of dihydrate needles with diameter in the range  $0.5-1 \mu\text{m}$  and length to diameter ratio larger than 10.

*System  $\text{CaSO}_4\text{-NaCl-H}_2\text{O}_{\text{vap}}$  at  $25^\circ\text{C}$*

A micro crystal of high purity sodium chloride whose weight was estimated at 0.5 mg was placed in a central position on the 001 flat surface of a gypsum cleft sample. It does *not* contribute significantly to the weight gain curve until the deliquescent point of NaCl - expected at  $75(\pm 0.5) \%RH$  - is exceeded: the initial section of the upward branch of the isotherm in Fig.7 is essentially unchanged up to point E compared to the isotherm of the pure system in Fig.1. The 3 major differences between both are the following.

When the deliquescent point of NaCl is first exceeded (point F), a droplet of NaCl solution forms in place of the initial NaCl crystal. This is evidenced by the change of weight gain kinetics from Fig.8 to Fig.9. The first linear section of the curve in Fig.9 corresponds to an adsorption of  $7.149 \times 10^{-5}$  mol  $H_2O$ . If the molality of the solution formed is assumed equal to the *saturation* molality at  $25^\circ C$  ( $6.144 \text{ mol.Kg}^{-1}$ ), one computes that the initial amount of dry NaCl should equal 0.46 mg, a figure that compares well with the 0.5 mg direct weighing.

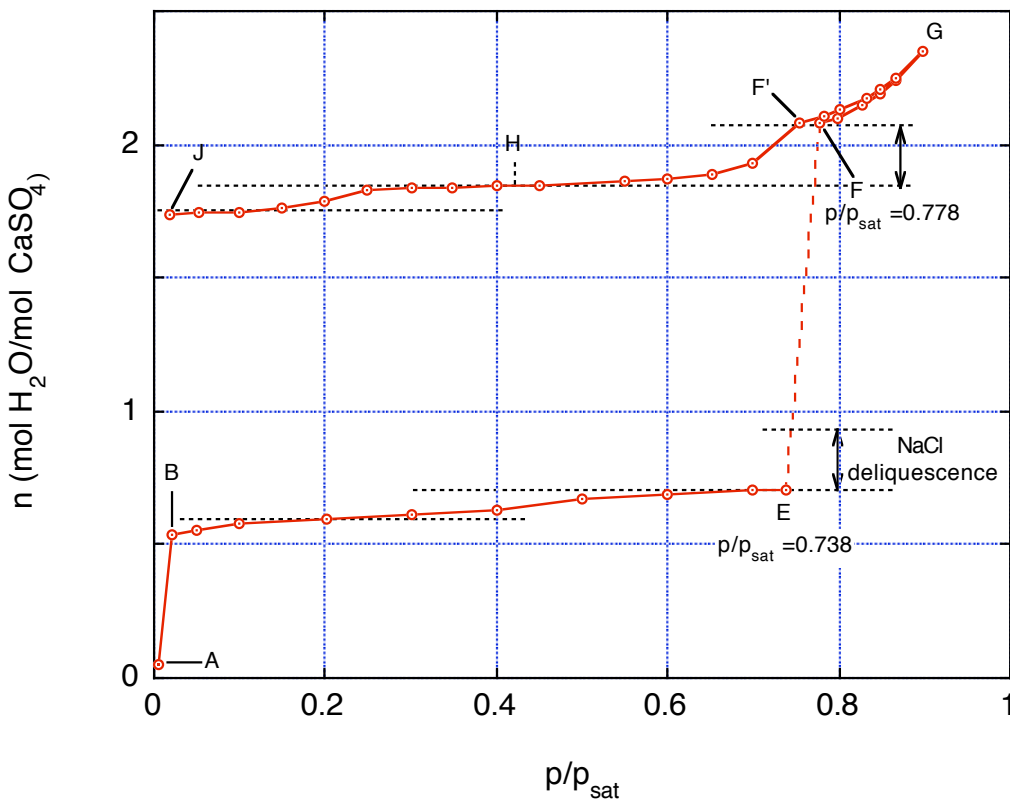


Fig.7 adsorption-reaction isotherm of  $CaSO_4$  in presence of NaCl

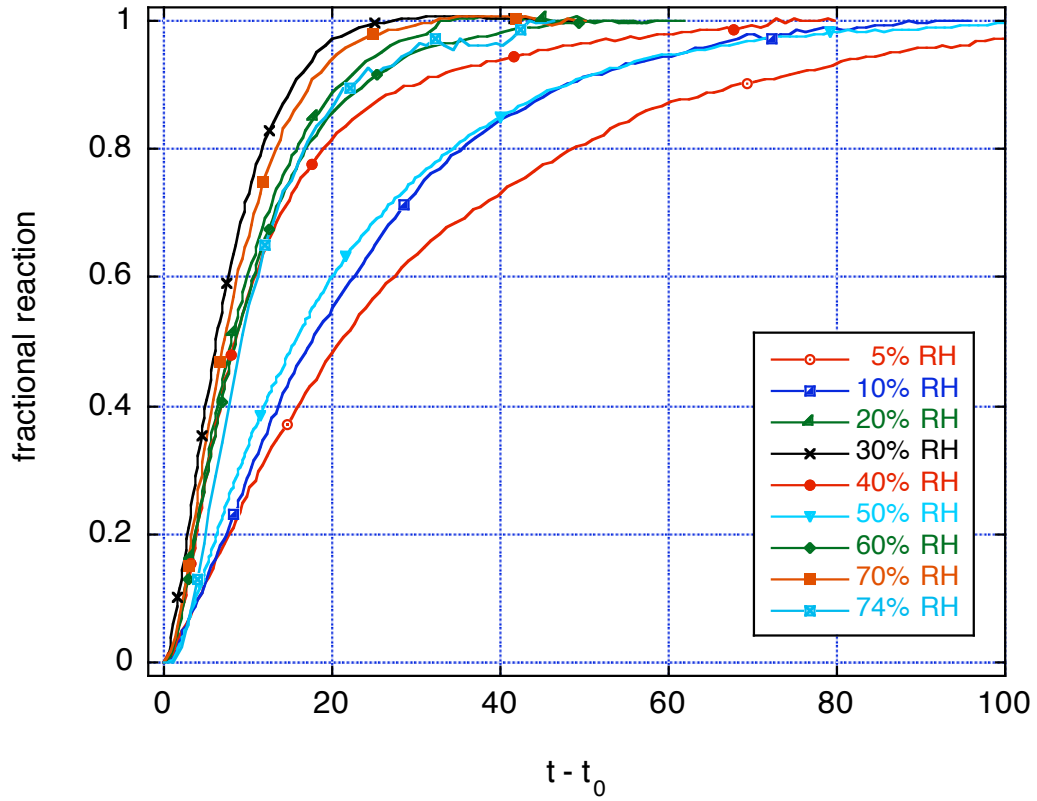


Fig.8 kinetics of adsorption: fractional adsorption vs reduced time in presence of NaCl

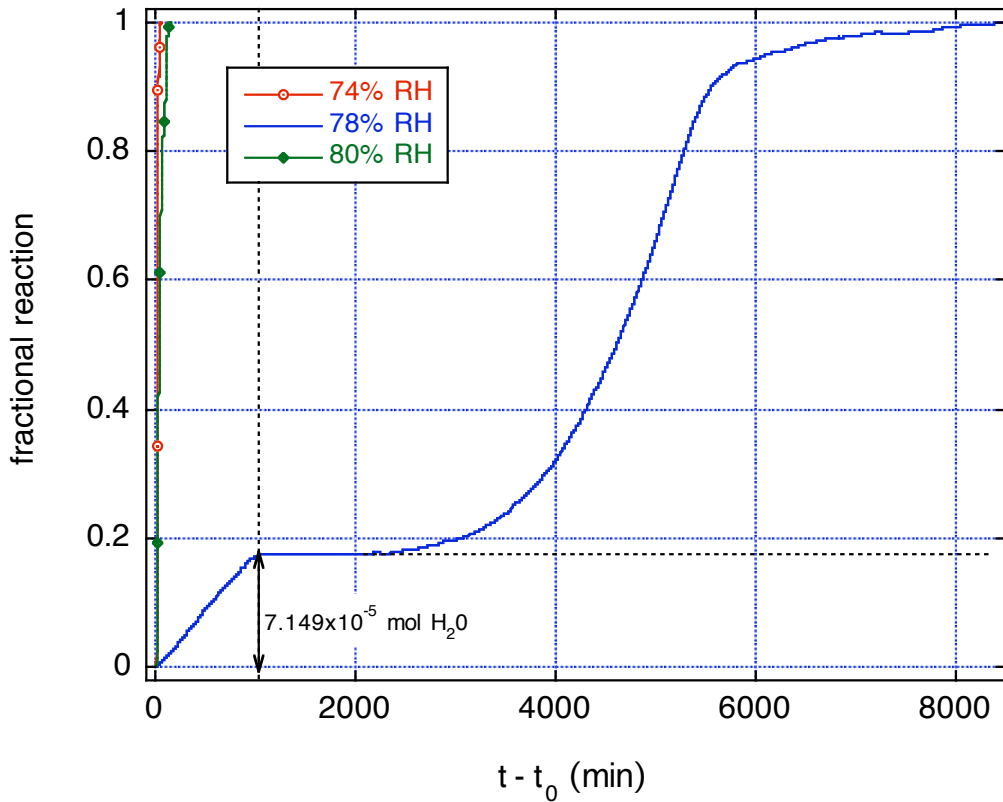


Fig.9: kinetics of conversion of hemihydrate to gypsum at 77.5%RH (fractional conversion vs reduced time) .

The section FGF' is at variance with the FG section in Fig.1 because it is determined by the equilibrium between the liquid NaCl solution with water vapour. This could readily be demonstrated by the coincidence of the FG section with the same section of the weighted adsorption isotherm (not shown) of *pure* NaCl above its deliquescent point. The drop from F' to H exactly corresponds to the amount of water taken up in the deliquescence step in Fig.9. It is clear that the 1. mol H<sub>2</sub>O/mol CaSO<sub>4</sub> present in the sample are not bound to NaCl

After return of the sample to ambient conditions, SEM and observations of the upper surface shows re-crystallized NaCl over a small central area only. All other aspects including the final shape and cohesion of the sample are similar to those observed with the pure CaSO<sub>4</sub>-H<sub>2</sub>O system.

## Discussion

In order to understand the experimental observations and model the reactions involved it proves necessary either to formally regard the hemihydrate H<sub>0.6</sub> as a deliquescent salt, with a room temperature deliquescent point at about 97-98 %RH, or to revive the assumption that it might react directly with water vapour to form gypsum via a nucleation and growth process. In both cases, the complete sequence of observed water gains and losses may logically follow, but we limit the present discussion to the former assumption.

a) The upward branch of the isotherm up to point E must be regarded as a *reaction-adsorption isotherm* combining steps 1, 2 and 3 detailed in §-1 with pure adsorption on the free surface of the solid phase(s). Since one is dealing with equilibrium states, the contribution of reactions and adsorption simply add-up to form the experimental reaction-adsorption isotherm .

If the solid-vapour equilibrium is assumed to be univariant, the isotherm will exhibit a stepwise increase of 0.5 mol H<sub>2</sub>O at the equilibrium pressure ( $p/p_{\text{sat}} = 0.3-0.6\%$  at 25°C). Hence, subtracting 0.5 mol to the initial *concave* section of the isotherm, below point C, should formally yield the pure adsorption contribution. Using the basic BET model for physical adsorption to analyse the experimental data corrected in that way, one should be able to estimate the surface area of the adsorbent . If, based on a literature review, the surface coverage is set equal to 12.5 ( $\pm 2.5$ ) Å<sup>2</sup> per H<sub>2</sub>O molecule, it comes  $S_{\text{BET}} = 36.5 (\pm 7.5) \text{ m}^2 \cdot \text{g}^{-1}$ . However, our experience with adsorption of water vapour on insoluble *not reactive* βA2 anhydrite tells us that a coverage of 42 ( $\pm 2$ ) Å<sup>2</sup> per H<sub>2</sub>O molecule is required to make water adsorption at 25°C yield the same surface area value nitrogen adsorption at 77 K. In that case

the surface area value of the hemihydrate would amount to  $S_{\text{BET}} = 10.9 (\pm 0.6) \text{ m}^2 \cdot \text{g}^{-1}$ . This is in excellent accordance with the BET surface area value measured by nitrogen adsorption of secondary A3 anhydrite obtained by dehydration of gypsum under water vapour pressure.

b) The water up-take between points C and D equals  $0.1 \text{ mol H}_2\text{O} / \text{mol CaSO}_4$ , which is the exact amount of structural water required by the reaction  $\text{HH}_{0.5} \rightarrow \text{HH}_{0.6}$ . There exist direct evidence that the reaction  $\text{H}_{0.5} \rightarrow \text{H}_{0.6}$  actually takes place in the AB interval : the inflection point of the isotherm (i.e. the point of maximum slope in Fig.2a) at different temperature lies on the equilibrium curve determined by XRD under controlled temperature and pressure conditions.

Accordingly, any water uptake beyond point B can only contribute to the increase of an adsorbed film by an amount equal to  $n_{x=0.6} - 0.6$ . Evaluating the thickness of the adsorbed film is important for the following of the discussion. This was achieved by assuming the adsorbate density equal to that of liquid water and using the BET surface area value estimated in a). At point E the adsorbed film would be made of only ? molecular layer.

c) Section E-F. When relative humidity is increased from 97.7 to 98.2%, both the kinetics and amplitude of weight gain change dramatically compared to the previous equilibrium points. The kinetics of adsorption (in the case of multilayer adsorption) is excessively difficult to model [10] but is expected to be characterized by a continuously decreasing adsorption rate. This is what is actually observed below point E, as shown in **Fig.3**. In contrast, the kinetics of weight gain from points E to F may be considered typical of either a nucleation and growth process in solid-gas reaction, or of a dissolution-precipitation process.

d) Section H-I: If the loss of  $0.025 \text{ mol H}_2\text{O}/\text{mol}$  of initial  $\text{CaSO}_4$  when going from H to I actually marks the loss of water from a fraction of unconverted  $\text{H}_{0.6}$  to  $\text{H}_{0.5}$ , one may infer that  $0.75 \text{ mole}$  of gypsum actually have been precipitated and  $0.25 \text{ mole}$  of hemihydrate have not been converted. Thus the total amount of structural water in both solid phases equals  $1.75 \text{ mole}$  per mole of initial  $\text{CaSO}_4$ . This would leave about  $0.07 \text{ mol H}_2\text{O}/\text{mol}$  of initial  $\text{CaSO}_4$  of excess water at the maximum content in G. Assuming that this amount makes up a monolayer of physically adsorbed water spread over one mole of gypsum would require the specific surface area be equal to  $39 (\pm 8) \text{ m}^2 \cdot \text{g}^{-1}$ . Assuming a coverage of  $12.5 (\pm 2.5) \text{ \AA}^2$  per physically adsorbed water molecule, the specific surface area of gypsum with the microstructure shown in Fig.6b may be grossly estimated at  $2 \text{ m}^2 \cdot \text{g}^{-1}$ . Clearly, some liquid phase ( $\text{CaSO}_4$  solution

containing 0.07 mol H<sub>2</sub>O) should still be present at point G. The saturation concentration of CaSO<sub>4</sub> at 25°C is

e) at the final point K relative humidity and temperature correspond closely to local ambient conditions. The equilibrium molar composition is the same as at point I which corresponds to 89 w% gypsum, in qualitative accordance with the low relative intensity of bassanite in the XRD spectrum of Fig.5. A crucial additional observation at this stage was that the bulk shape of the initial gypsum lump remains unchanged in the overall process. Even the “scars” left by the initial dehydration of gypsum are visible on the vestiges of the 001 cleft faces. This allows us to state that the transformation occurring in section E-G of the isotherm is *not just* the deliquescence of the hemihydrate for this would lead to the formation of a bulk saturated liquid solution CaSO<sub>4</sub>-H<sub>2</sub>O in the microbalance stirrup and consequently to the loss of the initial shape memory. In fact, we speculate that once the deliquescence of the sample has started (possibly in the time laps during which a linear kinetic curve prevails in Fig.4), the precipitation of gypsum would continuously “consume” liquid water from the solution, water that would be replaced at the same rate by adsorption to maintain the equality of chemical potential between the vapour and liquid phase. The gypsum so formed crystallizes in bunches of fine needles consistent with crystal growth from a solution *oversaturated* with respect to gypsum. Here the reader is referred to the equilibrium phase diagram CaSO<sub>4</sub>-H<sub>2</sub>O<sub>liq</sub> for instance in [10].

f) All these conclusions are in accordance with the results of the experiment on the CaSO<sub>4</sub>-NaCl-H<sub>2</sub>O system. First, the “true” deliquescence of the NaCl micro-crystal is demonstrated by the value of relative humidity at which it takes place, by the typical linear kinetics associated with this phenomenon (mere interfacial mass transfer) and by the weight gain reached at the end of the process that corresponds quantitatively to the formation of a saturated NaCl-H<sub>2</sub>O solution (molality 6.144). Next, the same relative humidity being maintained, a long induction period (time lag) is observed, followed by a sigmoidal kinetic curve already observed with the pure CaSO<sub>4</sub>-H<sub>2</sub>O system. SEM observation of the final sample shows that NaCl re-crystallizes in the small area where it was initially placed on the upper face of the initial gypsum lump. An indirect evidence that gypsum has already precipitated at point F is that the upper reversible branch FGF’ coincides with the expected behaviour of the pure NaCl aqueous solution in equilibrium with water vapour.



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