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GHGT-11

Dehydration of gypsum under dry CO₂ injection

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Abstract

Experiments in microcapillary tubes have been developed to mimic the effect of dry CO₂ onto hydrated minerals such as gypsum. It is concluded that gypsum-bassanite-anhydrite transformations are controlled by the state of the fluid phase. For samples of gypsum heated in vacuum, gypsum-bassanite transition occurs by pseudomorph substitution at 120°C. For samples of gypsum in aqueous medium, the gypsum-bassanite transition starts at 135°C and then the bassanite-anhydrite transition occurs by dissolution / recrystallization at 220°C. There is a strong CO₂ effect that facilitates the dehydration of gypsum. In the presence of dry CO₂, gypsum-bassanite transition is instantaneous at 31°C. In aqueous media saturated with CO₂, gypsum - anhydrite transition appears at 125°C. These experimental results are in full agreement with the conclusions of thermodynamic simulations.

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Keywords: CO₂, gypsum, dehydration, microcapillary, experiment

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1. Introduction

One option for performing CO₂ geological storage is to inject anhydrous CO₂ in the reservoir rock. Amongst other disturbances, this may impact the stability of hydrated minerals present in the rock and favor their dehydration, even at low temperature. As a consequence, water can be released in the rock formation but, mostly, recrystallizations and therefore changes in molar volumes may occur. These phase

transitions can lead to major petrophysical changes with an increase or a decrease of porosity and permeability and the possible occurrence of fracture networks. Through both experimental and numerical methods, this study aims to explore the dehydration mechanisms of hydrous minerals during injection of anhydrous CO₂.

It was chosen to study the behavior of gypsum (CaSO₄·2H₂O), a mineral present in the rock formations of low temperature (e.g. the Triassic reeds sandstone of Lorraine, France).

There are 3 main types of minerals for the Ca-SO₄-H₂O system: gypsum CaSO₄·2H₂O, hemihydrate or bassanite CaSO₄·1/2 H₂O and anhydrite CaSO₄. Transition temperatures between minerals of Ca-SO₄-H₂O system at saturation vapor pressure in water have been the subject of several studies. Because of uncertainties about solubility diagrams of minerals and the kinetics of the dehydration reactions, the phase transition temperatures are estimated to be between:

- 42 and 60°C for gypsum → anhydrite transition
- 80 and 110°C for the gypsum → bassanite transition [1]

According to the literature, the rate of dissolution of gypsum is in most cases rapid and mainly controlled by transport rather than by the reaction surfaces (low activation energy of 41.8 kJ / mol, [2]) while the kinetics of crystallization, in particular for anhydrite, is slow [1]. This kinetics of dissolution and crystallization thus encourage, at least in water, the dehydration of gypsum in the metastable form of alpha-hemihydrate before the formation of anhydrite.

Blount and Dickson (1973) [3] and Monnin et al. (2003) [4] showed that the equilibrium diagrams was affected by pressure. Hardie (1967) [5] and Vanko and Bach (2005) [6] also shows the effect of dissolved salts in water on the stability of the sulfate species.

The objective of this work is to show if an atmosphere of CO₂ can act as an accelerator of the dehydration process, lowering the transition temperatures. For that, an experimental work has been developed and couple to numerical simulations.

2. Experiment setups

The behavior of this mineral has been checked at different pressures and temperatures, in pure supercritical CO₂ or gaseous nitrogen atmospheres. Three different experimental setups have been used, allowing acquiring different types of information: two kinds of batch reactors (gas pressure controlled autoclaves, gold capsules) and the microcapillary technique.

Gas pressure controlled autoclaves

Experiment was carried out in a gas pressure autoclave Parr Instrument[®] with a capacity of 250 cm³. This device achieves a maximum pressure of 345 bar and a temperature of 360°C. Sealing is ensured by a flat joint “Graphoil” supporting a maximum temperature of 350°C and a pressure of 420 bar. The rock and aqueous solution are placed in the autoclave and carbon dioxide is then injected from a CO₂ cylinder positioned upside down to ensure a pumping of liquid CO₂. The pressure is adjusted up to 130 bar with a CO₂ pump connected to a compressed air circuit with 6 to 7 bar pressure. One low temperature has been applied (40°C).

Gold capsules:

Experiments were conducted in batch type micro-reactors consisting in flexible gold capsules of which were introduced in hydraulic pressure vessels and maintained at 200 and 280 bar. An original gas-loading device [7] was designed in order to fill accurately the gold capsules with known quantities of gas (Fig. 1). CO₂ was condensed in a cryogenic bath to ensure a low pressure gas handling. Two temperatures have been applied: 75 and 100°C.

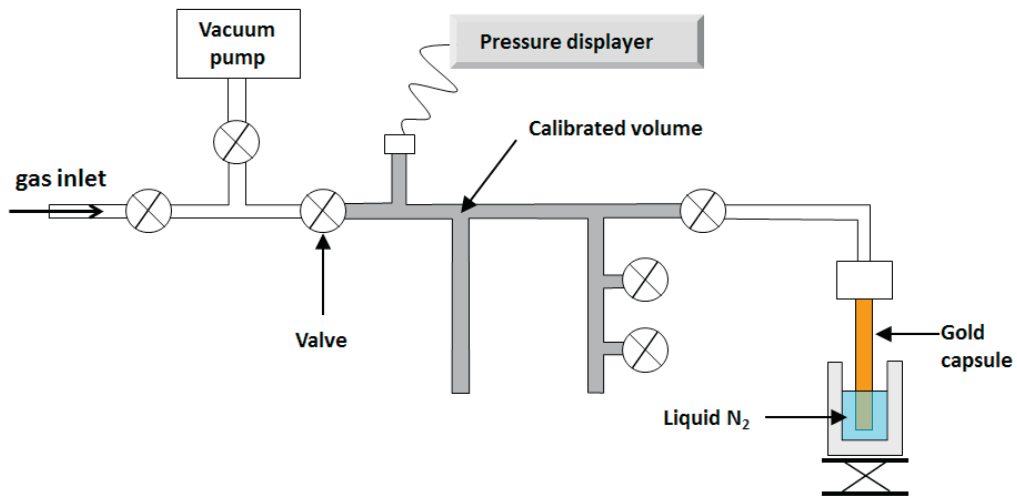


Fig. 1: Experiment setup for the study of gypsum dehydration in gold capsules.

However batch reactors have severe limitations. They do not allow a kinetic control, mass balances are not accurately quantified, the control of water activity is difficult, the effects of mass and surface are not taken into account and the analyses are post-mortem. In order to counterbalance these limitations, specifications for a suitable experimental approach were established:

- To monitor the kinetics we must acquire data during the experiments
- To be more specific on the mass balance we must analyze the different phases (solid / fluid) individually and simultaneously
- To better control the water activity we need to quantify the amount of H₂O in gas phase and we must work at $P_{\text{H}_2\text{O}}$ lower than saturation vapor pressure
- To manage the effects of mass and surface we need to develop ad hoc analysis on the micrometer scale on small single crystals
- To avoid post-mortem analyzes and risk of sample degradation we must work in a sealed system to prevent contact of the atmosphere

The best solution to fit with these specifications is the *microcapillary technique* [8]. A silica capillary tube of 100 micrometer in diameter is filled with gypsum, liquids and gases and sealed (fig. 2). Phase transitions and chemistry are controlled under Raman microspectrometry (Labram by Horiba-Jobin Yvon) coupled with a heating Linkam stage.

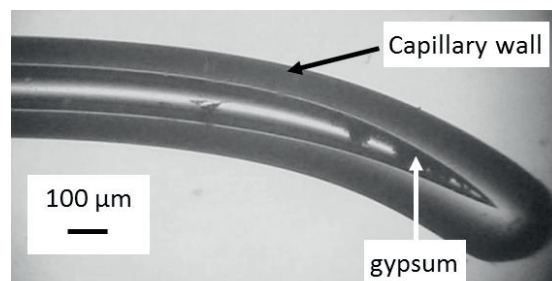


Fig. 2: Example of microcapillary tube filled with tiny crystals of gypsum.

3. Results

As a result, it has been possible to demonstrate the influence of supercritical CO₂ on the kinetics of dehydration of gypsum and to detect the gypsum-anhydrite-bassanite transitions.

From batch experiments with gas pressure control, gypsum-anhydrite transformation shows a higher reaction rate in presence of supercritical CO₂ than in presence of N₂:

- for reeds sandstone

Powder samples of reeds sandstone (500 mg) were placed in the presence of CO₂ (85 bar) and brine (1.5 M of NaCl) for 2 months. The experimental conditions are the reservoir conditions at about 2000 m considering a thermal gradient of 3°C/100 m (ie 75°C and 200 bar). The salinity of the brine used is an average salinity encountered in the Triassic sandstones. In parallel, experiments were led by replacing the CO₂ by N₂. The samples were analyzed at the end of the experiment by X-ray diffraction. The composition of reeds sandstone has been changed. The final state shows a signature of anhydrite (CaSO₄) not present at initial state and a decrease of the intensity of the gypsum peaks. Other minerals are not affected.

- for monocrystal of gypsum

Each sample consists of a single crystal of gypsum placed in the presence of different fluids: CO₂, nitrogen, air and brine. They are brought to 100°C and 280 bars, in order to preserve the thermal gradients and hydrostatic conditions of the previous experiment. The pressure and temperature selected is higher in order to accelerate the reaction kinetics. The experiments lasted 28 days.

Whatever the experimental conditions, gypsum was partially or totally transformed into anhydrite. However, the transformation is not the same in all environments. In presence of brine, samples showed dissolution of gypsum and complete recrystallization of the mineral, in the form of tabular to acicular crystals of anhydrite. Samples of gypsum in the presence of CO₂ and air show partial transformations. The transformation took place only at the surface of the mineral; the heart remained made up of gypsum. However, the transformation is more developed in an atmosphere of CO₂ than in an air atmosphere: the gypsum surface is coated by an anhydrite film, while in an atmosphere of air; only a few patches of anhydrite are visible (fig. 3).

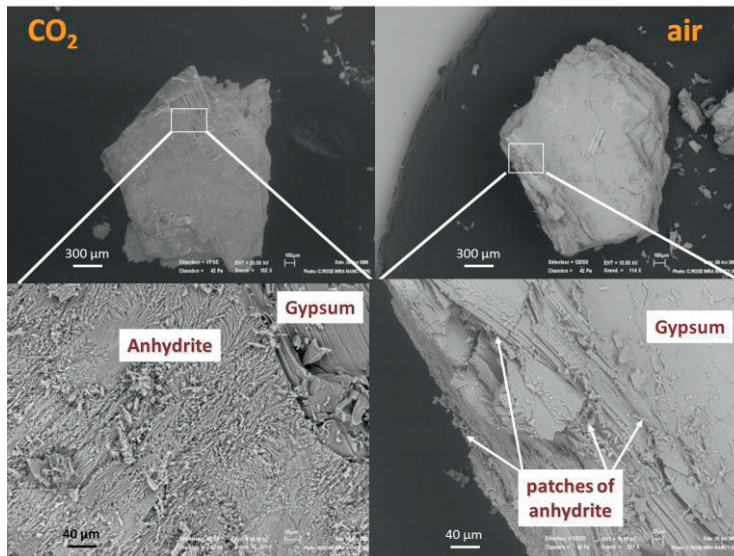


Fig. 3: Dehydration of gypsum in gold capsules in CO₂ (left) and air (right) atmospheres

To move away from the stability field of anhydrite, experiments were carried out at low temperatures, in the range of stability of gypsum, but close to the stability field of anhydrite. The equipment used is a type PARR autoclave where CO₂ pressure is imposed between 120 and 135 bar. The temperature varies from 35 to 48°C. The reagents (gypsum and water) are placed at the bottom of the autoclave in separate containers. The experiment lasted two weeks. At the end of the experiment gypsum samples were collected. No trace of dehydration was observed on X-ray diffractograms where anhydrite was not identified.

Experiments using microcapillaries needed to develop a specific loading device for dry CO₂ and the establishment of a protocol for inserting crystals in microcapillary tubes. The in situ analysis was performed by Raman spectroscopy coupled to an optical microscope equipped with a microthermometric stage. This stage has been designed by the Linkam company especially for application to microcapillaries. Various experiments have been conducted and repeated in welded capillaries for different fluid-rock systems i) gypsum under vacuum ii) gypsum and water, iii) gypsum and anhydrous CO₂ iv) gypsum with CO₂ and water.

For samples of gypsum in vacuum, the gypsum-bassanite transition occurs by pseudomorphism at 120°C. For samples of gypsum in liquid water (Fig. 4), it can be detected two mineralogical transitions determined by their Raman signatures. Gypsum transformed to bassanite from 135°C and bassanite into anhydrite from 220°C. This last transition occurs by dissolution / recrystallization. In the presence of anhydrous CO₂ the transformation of gypsum into bassanite cannot be temperature controlled because it appears before putting sample into the microthermometric stage. Transformation is instantaneous. Experiments led in CO₂-saturated liquid water have shown that gypsum-anhydrite transition appears at 125°C.

Gypsum-anhydrite-bassanite transitions are controlled by the state of the fluid phase. There is a strong effect of the CO₂ that facilitates anhydrous gypsum dehydration which then occurs at room temperature, lower than the transition temperature of gypsum-anhydrite in air. Observed reactions are not reversible under the conditions of our experiments.



Fig. 4: Gypsum dehydration observed in a microcapillary with increasing temperature in presence of liquid water.

4. modeling

Thermodynamic calculations are used to compare the effect of gas (N₂ or CO₂) on gypsum-anhydrite phase transition. For each binaries (N₂-H₂O and CO₂-H₂O), fig. 5 presents the dew point curves (appearance of the first drop of liquid) and the gypsum-anhydrite equilibrium curves as a function of pressure, temperature and water content. All calculations assumed the binary N₂-H₂O as an ideal mixture. Water properties come from Wagner and Pruss (2002) [9]. Calculation of binary CO₂-H₂O used equations from Spycher et al. (2003) [10]. Thermodynamic properties of minerals come from Thermoddem

(www.thermoddem.brgm.fr) and the combined effect of temperature and pressure is calculated using Thermo-ZNS [11].

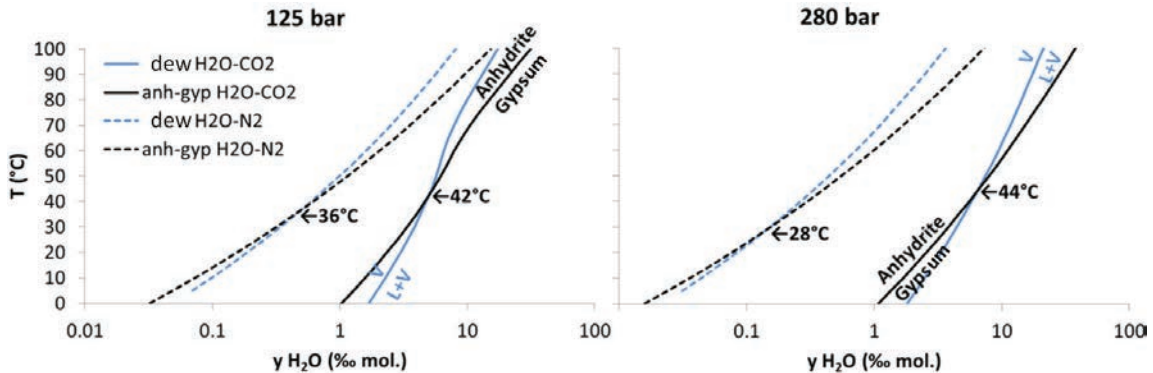


Fig. 5: Dew curves (blue) and gypsum-anhydrite equilibrium curves (black) in temperature vs. water content diagram at 125 bar (left) and at 280 bar (right). Solid lines are for binary CO₂-H₂O and dotted lines are for binary N₂-H₂O.

Assuming the binary N₂-H₂O as a perfect gas mixture, thermodynamics provides the same type of behavior as the binary H₂O-CO₂. However, two important differences can be noted:

- For the binary N₂-H₂O, the transition temperatures are lower: 36°C to 125 bar and 28°C at 280 bar. The gas has an influence on the temperature of transition. But in both cases (CO₂ or N₂), changes in the transition temperature with the pressure is in agreement with the known transition temperature of 42°C at 1 bar. It will be noted that in addition to the transition temperature, the nature of gas also influences the behavior in relation with pressure: in presence of CO₂, a pressure increase results in an increase of the transition temperature, while under N₂ atmosphere, the increase in pressure causes a decrease in the transition temperature. The focal point is the pure H₂O system, along the dew point curve of the water.
- For the binary N₂-H₂O, the liquid-vapor and gypsum-anhydrite equilibriums are achieved for lower mole fractions of water in the gas phase.

This second difference shows that using dry N₂ rather than anhydrous CO₂ during experiment of dehydration of gypsum, equilibrium is reached with a smaller amount of water in the gas phase. Thus the thermodynamic force (ie, the engine) of dehydration is less important with N₂ than CO₂. And we can expect a lower rate of dehydration with N₂. It is even conceivable that the anhydrite-gypsum equilibrium is reached with a very low rate of dehydration of gypsum, justifying the appearance of a small amount of anhydrite on the surface of primary gypsum.

These results are consistent with experimental observations.

5. Discussion and conclusion

Experiments of dehydration of gypsum were conducted in gold capsules, gas pressure controlled autoclave and microcapillary tubes on samples of rock (reeds sandstone) and gypsum. For sandstone samples, we show that the major mineralogical transformation corresponds to the dehydration of gypsum and its replacement by anhydrite. The "accelerator" effect of CO₂ on gypsum-anhydrite transformation was suspected in experiments on single crystals in gold capsules at high temperatures. Indeed, the transformation is intense in CO₂ atmosphere whereas it remains moderate in the presence of air.

To better control the partial pressures of gases and perform in situ analyses during heating of gypsum, we developed a new experimental approach, based on the microcapillary technique coupled to temperature controlled Raman microspectrometry.

We summarize the results of experiments as follows:

- initiation of the conversion of gypsum into anhydrite with a greater rate in presence of CO₂ than N₂ was observed for samples of rock (reeds sandstone) at 75°C in the presence of water. This dehydration of gypsum is also observed for single crystals of gypsum at 100°C with a CO₂ pressure of 280 bar for the same duration. The dehydration is complete (integral transformation of gypsum into anhydrite) in the case of experiments carried out in liquid water. No dehydration of gypsum was observed at 40°C (temperature at which gypsum is stable), in the presence of water vapor, for P_{CO₂} from 120 to 135 bar, and a duration of 2 weeks.

- For samples of gypsum under vacuum, the gypsum ⇒ bassanite transition occurs as pseudomorphosis at 120°C. For samples of gypsum in aqueous medium, the transition gypsum ⇒ bassanite occurs from 135°C and the transition bassanite ⇒ anhydrite occurs by dissolution/recrystallization from 220°C. In the presence of anhydrous CO₂, the gypsum ⇒ bassanite transformation is instantaneous, whereas in liquid water saturated with CO₂, this transition appears at 125°C.

The overall results of the experiments are summarized in Table 1.

Table 1 : Synthesis of the experiment results obtained in gold capsules (cap), autoclaves (auto) and microcapillaries (mc).

<i>N° exp.</i>	<i>Solid RS : reeds sandstones G : gypsum</i>	<i>CO₂</i>	<i>Air/N₂</i>	<i>H₂O</i>	<i>T (°C)</i>	<i>P (bar)</i>	<i>Duration</i>	<i>Reaction products A : anhydrite B : bassanite G : gypsum</i>
Autoclaves with gas pressure control (auto) and gold capsules (cap)								
1 cap	RS	+	-	+	75	200	4 weeks	AAG
2 cap	RS	-	+	+	75	200	4 weeks	AGG
3 cap	G	+	-	-	100	280	4 weeks	AAG
4 cap	G	-	+	-	100	280	4 weeks	AGG
5 cap	G	+	-	+	100	280	4 weeks	AAA
6 auto	G	+	-	+	40	130	2 weeks	GGG
7 auto	G	+	-	-	40	130	2 weeks	GGG
Micro-capillaries (mc)								
8 mc	G	-	-	-	120	-	25'	G⇒B
9 mc	G	-	-	+	135	-	instantaneous	G⇒B
					220		instantaneous	B⇒A
10 mc	G	+	-	-	31	73	20'	G⇒B
11 mc	G	+	-	+	125	-	9'	G⇒A

These experimental results are in full agreement with the conclusions of thermodynamic simulations. Indeed, they show that, because of an enhanced solubility of water in CO₂ when supercritical, the thermodynamic force of dehydration is more important with CO₂ than with N₂. Thus a higher kinetic of dehydration is expected with CO₂ than with N₂. On the other hand, calculations suggest that the anhydrite-gypsum equilibrium can be reached after a very low amount of gypsum is dehydrated, allowing the appearance of a small amount of anhydrite at the surface of primary gypsum.

However, in order to be in good accordance with experimental or in situ physico-chemical conditions, these thermodynamic calculations should benefit from the following improvements:

- Take into account the salinity in the calculation of dew curves and of gypsum – anhydrite equilibrium,

- Repeat the same type of calculations with bassanite which was observed in some microcapillary experiments.
- The same experimental approach could be refined with a control of pressure in the microcapillaries and taking into account the effect of pressure on reaction rate.

The results of this experimental study show that injection of anhydrous CO₂ into an injection well can cause non reversible mineralogical transformations with consequences on porosity and permeability (change of molar volume) and release of water.

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