

# ON THE BEHAVIOUR OF THE $\text{Ca-SO}_4\text{-H}_2\text{O}$ SYSTEM

By

Iván Berdugo<sup>1</sup>, Enrique Romero<sup>1</sup>, Maarten Saaltink<sup>1</sup> & María Albis<sup>2</sup>

## Abstract

**Berdugo, I., E. Romero, M. Saaltink & M. Albis:** On the behaviour of the  $\text{Ca-SO}_4\text{-H}_2\text{O}$  system. *Rev. Acad. Colomb. Cienc.* **32**(125): 545-557, 2008. ISSN 0370-3908.

Thermotropia, barotropia and hygotropia of the  $\text{Ca-SO}_4\text{-H}_2\text{O}$  system is reviewed and discussed and a three-dimensional representation of the phase diagram for system at atmospheric pressure is derived. It is concluded that the behaviour of the system is a coupled thermo-hydro-chemical phenomenon in which water activity is the key factor for existence of high concentration of  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  and confinement pressure plays a secondary role.

**Key words:** anhydrite, gypsum, water, solubility, temperature, pressure, vapour, relative humidity.

## Resumen

Se revisan y discuten la termotropía, barotropía e higriscopía del sistema  $\text{Ca-SO}_4\text{-H}_2\text{O}$  y se deriva una representación tridimensional del diagrama de fases del sistema a presión atmosférica. Se concluye que el comportamiento del sistema es un fenómeno termo-hidro-químico acoplado en el cual la actividad del agua es el factor determinante para la existencia de altas concentraciones de  $\text{Ca}^{2+}$  y  $\text{SO}_4^{2-}$  y la presión de confinamiento juega un papel secundario.

**Palabras clave:** anhidrita, yeso, agua, solubilidad, temperatura, presión, vapor, humedad relativa.

## Introduction

Interacting with water calcium sulphate can exist in six different solid phases, presented hierarchically here in the

order of increasing solubility: one dihydrate (gypsum,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ); two hemihydrates (bassanite:  $\alpha\text{-CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$  and  $\beta\text{-CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ ); and three anhydrous (anhydrite: AI-unstable- or  $\alpha\text{-CaSO}_4$ , AII –moderately soluble– or  $\beta\text{-CaSO}_4$ ,

<sup>1</sup> Departament d'Enginyeria del Terreny, Cartogràfica i Geofísica – Universitat Politècnica de Catalunya, Barcelona, Spain. Correos electrònics: ivan.berdugo@upc.edu, enrique.romero-morales@upc.edu, maarten.saaltink@upc.edu

<sup>2</sup> Programa de Ingeniería Civil – Universidad de La Salle, Bogotá, D.C. Colombia. Correo electrónico: malbis@unisalle.edu.co

and AIII-totally soluble- or  $\gamma$ -CaSO<sub>4</sub>). However, it is pointed out by **Sattler & Brückner** (2001) that in addition to the hemihydrate other “sub-hydrates” with crystal water contents between 1/2 and 4/5 have recently been produced and investigated crystallographically.

The behavior of calcium sulphate-rich water is an important aspect in several environmental, geotechnical and industrial processes involving either dissolution or crystallization of calcium sulphate-based minerals (Table 1). The doline collapse in anhydritic-gypsiferous soils and rocks is a typical case of sulphate-based mineral dissolution conducing to ground loss and instabilities of existing structures. On the other hand, solvent-way gypsum growth is typical case of crystallization that often causes –among other–, scale induced duct obstructions as well as swelling in soils, rocks and stabilized materials. In general, excluding production of building materials, calcium sulphate minerals –gypsum in particular–, often appear as undesirable crystallizations.

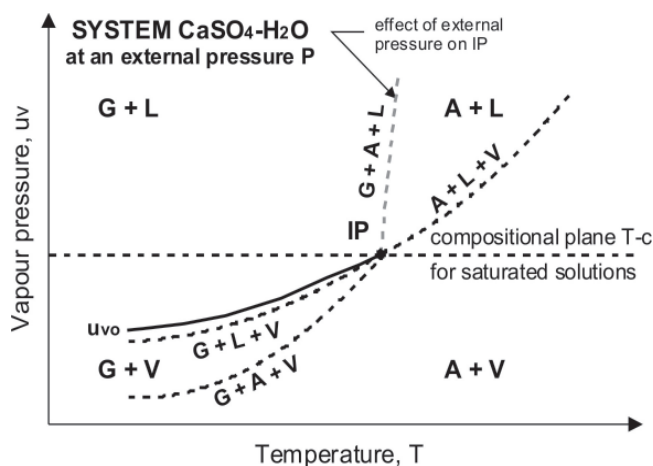
An accurate analysis of mechanisms underlying dissolution and crystallization of calcium sulphate-based minerals requires a previous knowledge on factors controlling the behaviour of calcium sulphate-rich water. This paper deals with the effects of temperature, confinement (external) pressure and water activity on the solubility and the characteristic vapour pressure of the Ca-SO<sub>4</sub>-H<sub>2</sub>O system. A comprehensive review of contributions on the theme is presented and a three-dimensional representation of the phase diagram for the Ca-SO<sub>4</sub>-H<sub>2</sub>O system at atmospheric pressure is derived.

### Univariants of the Ca-SO<sub>4</sub>-H<sub>2</sub>O system

Due to the hemihydrate is an intermediate phase between the dihydrate and the anhydrous, which is metastable at all temperatures, in standard analyses of the Ca-SO<sub>4</sub>-H<sub>2</sub>O system only the dihydrate and the anhydrous phases are considered. Solubility of gypsum (G) and anhydrite (A) depends on three basic variables: (i)

temperature, T, (ii), confinement (external or reference) pressure P, and (iii) water activity, *a<sub>w</sub>*. Then, the occurrence of stable phases of both minerals in the presence of saturated solutions (L) and vapour (V) (namely, binary states G + V, G + L, A + L and A + V) is a multi-dependent phenomenon associated with specific values of vapour pressure, *u<sub>v</sub>*.

Boundaries for these binary states constitutes the so-called univariant three-phase equilibria (G + L + V, A + L + V, G + A + L and G + A + V), which intersect at IP point representing the invariant four-phase equilibrium (G + A + L + V); where gypsum, anhydrite, saturated solution and vapour are all stable and phases exist at a unique condition temperature-solubility-vapour pressure (figure 1).



**Figure 1.** Schematic representation of the CaSO<sub>4</sub>-H<sub>2</sub>O system phase diagram on the barometric plane.

Solubility of calcium sulphate has been extensively studied during decades since the pioneer contributions by van't Hoff and co-workers at the early twenty century (**van't Hoff et al.**, 1903). Criteria on their values as a function of temperature, pressure and water activity have a long

**Table 1.** Some enviromental, geotechnical and industrial processes involving calcium sulphate-rich water.

Environmental processes	Geotechnical processes	Industrial processes
<ul style="list-style-type: none"> <li>• Marine intrusion</li> <li>• Water desalination</li> <li>• Nanofiltration of saline drainage</li> <li>• Geothermal energy generation</li> <li>• Hydrothermal energy generation</li> <li>• Flue gas desulfurization</li> <li>• Waste storage in evaporite rocks</li> </ul>	<ul style="list-style-type: none"> <li>• Doline collapse</li> <li>• Gypsum growth induced swelling</li> <li>• Ground improvement using calcium-based stabilizers</li> <li>• Sulphate attack to mortars and concrete</li> </ul>	<ul style="list-style-type: none"> <li>• Production plaster of Paris</li> <li>• Production of phosphoric acid</li> <li>• Production of hydrogen fluoride</li> <li>• Production of cooper</li> <li>• Refining of zinc</li> <li>• Secondary oil recovery</li> </ul>

history with successive changing opinions. However, a review of some recent contributions reveals that within the ranges of temperature and pressure relevant to environmental and geotechnical processes (0°C to 50°C and 0 to 10 MPa) there is a consensus regarding the characteristic values (Freyer, 2000; Kontrec *et al.*, 2002; Freyer & Voigt, 2003, 2004; Vanko & Bach, 2005). Most important experimental and theoretical contributions to the study of effects of temperature, pressure and water activity on solubility of gypsum and anhydrite are summarized and discussed below.

### Thermotropia

Univariants G + L + V and A + L + V, representing the equilibrium of gypsum and anhydrite with saturated solutions and vapour, constitute the solubility diagram -or the compositional plane temperature-concentration (T-c)-, for the dihydrate and the anhydrous phases of the CaSO<sub>4</sub>-H<sub>2</sub>O system. Figure 2 is the solubility diagram for gypsum and anhydrite (AII) in pure water within the

temperature range 10°-80°C in an ideal thermodynamically closed system at atmospheric pressure. Curves from empirical correlations between temperature and calcium sulphate molality or concentration proposed by Blount & Dickson (1973) (Eq. 1 and Eq. 2), and Innorta *et al.* (1980) (Eq. 3 and Eq. 4) are also presented. Finally, results obtained by thermodynamic calculations by Møller (1988) are also included as theoretical references.

Figure 2 indicates that under atmospheric conditions gypsum has direct solubility behaviour until 49,5°C; it is that solubility increases with increasing temperature. In excess of this temperature threshold inverse solubility behaviour holds. On the contrary, anhydrite has always inverse solubility behaviour. At a given temperature the phase with the lowest solubility represents the stable phase. Below the temperature threshold gypsum is the stable phase and at high temperatures it is anhydrite. Thus, the transition temperature (IP) in the compositional plane temperature-concentration (T-c) is required to define the right occurrence of hydrated or anhydrous phases.

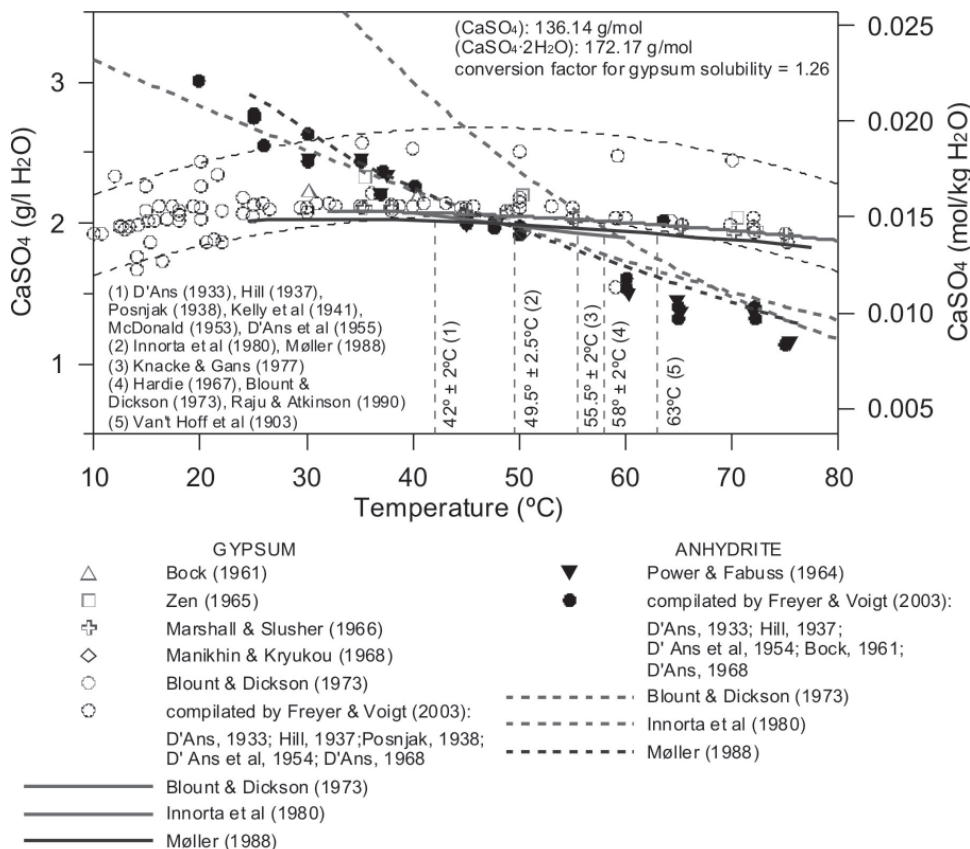


Figure 2. Solubility diagram for the CaSO<sub>4</sub>-H<sub>2</sub>O system at 0,10 MPa (1 bar).

Blount & Dickson (1973)

Gypsum:

$$\ln m(G)_{(CaSO_4)} = -4.355 + 8.4 \times 10^{-4} P + 1.05 \times 10^{-2} T - 1.7 \times 10^{-4} T^2 + 5.8417 \times 10^{-7} T^3 \quad (\text{Eq. 1})$$

Anhydrite:

$$\ln m(A)_{(CaSO_4)} = -2.87 + 1.22 \times 10^{-3} P - 2.37 \times 10^{-2} T - 2.8 \times 10^{-6} PT + 1.0 \times 10^{-6} T^2 + 1.4 \times 10^{-8} PT^2 \quad (\text{Eq. 2})$$

$$m: \left[ \frac{\text{mol}}{\text{kg } H_2O} \right]; P: [\text{bar}]; T: [^{\circ}\text{C}]$$

Innorta et al (1980)

Gypsum:

$$c(G)_{(CaSO_4)} = 8.69 \times 10^{-5} T^2 - 1.73 \times 10^{-2} T + 2.624 \quad (\text{Eq. 3})$$

Anhydrite:

$$c(A)_{(CaSO_4)} = 1.14 \times 10^{-4} T^2 - 3.667 \times 10^{-2} T + 3.517 \quad (\text{Eq. 4})$$

$$c(G, A)_{(CaSO_4)}: \left[ \frac{\text{g}}{\text{l } H_2O} \right]; T: [^{\circ}\text{C}]$$

The invariant IP (four-phase equilibrium point G + A + L + V or transition temperature gypsum-anhydrite) is defined as the intersection of solubility curves for gypsum and anhydrite on the compositional plane (T-c). However, two shortcomings are associated with this criterion:

(i) Anhydrite does not crystallize in water with measurable rate at temperatures below 70°C -even in the presence of anhydrite seed crystals (**Hardie**, 1967). Then, the solubility equilibrium of this phase cannot be proved experimentally from both sides, that is, from under and supersaturation. In fact, most solubility measurements approached equilibrium only from the undersaturated side (**Freyer & Voigt**, 2003, 2004). Only experimental values reported by **Innorta et al.** (1980) have been obtained from the supersaturated side.

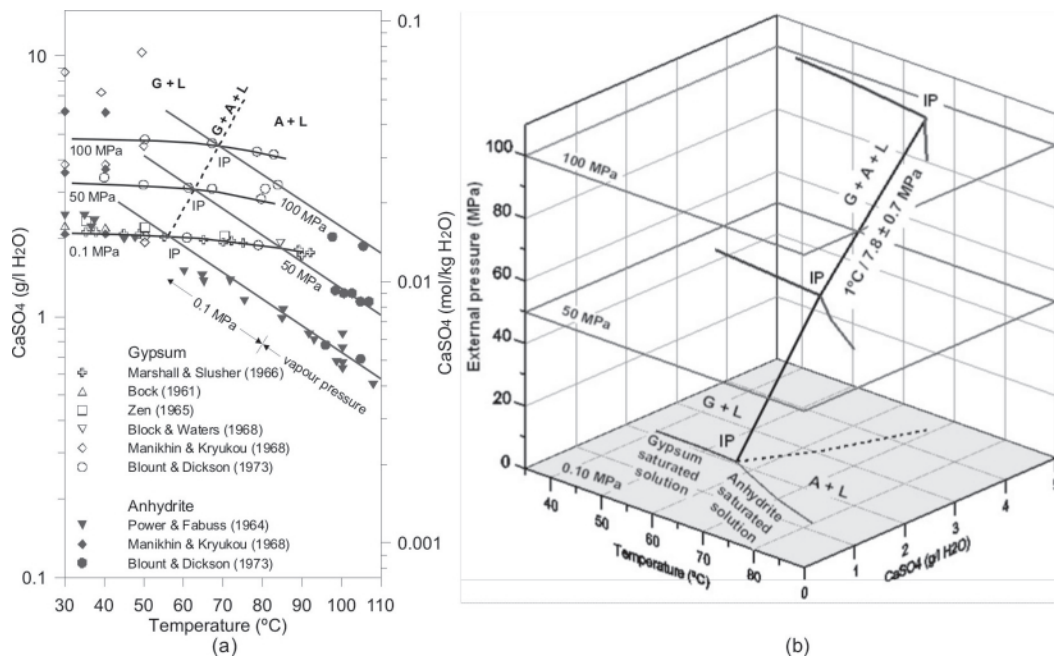
(ii) Experimental data are often considerably scattered; then, IP vary depending on selected parameters.

Due to these shortcomings, some authors have postulated that temperature transition predicted using this criterion would be considered only as a minimum value (**Hardie**, 1967; **Blount & Dickson**, 1973; **Knacke & Gans**, 1977; **Raju & Atkinson**, 1990). It can be seen in figure 2 that borderlines for experimental data on solubility of gypsum and anhydrite yield transition temperatures from about 25°C to 58°C; although the usual proposed values varies between 42°C and 63°C.

## Barotropia

The univariant G + A + L -the equilibrium of gypsum, anhydrite and saturated solutions in pure water-, represents the effect of the confinement pressure on the behaviour of the CaSO<sub>4</sub>-H<sub>2</sub>O system. It is really the envelope of invariants IP respect to P and T, in which invariants IP are deduced from solubility curves for gypsum and anhydrite (G + L + V and A + L + V) obtained at different confinement pressures, in excess of the atmospheric pressure. Unfortunately measurements of the vapour pressure imposed by the CaSO<sub>4</sub>-H<sub>2</sub>O system at high external pressures are not available. Then, even nowadays only projections of this univariant on the compositional plane T-c are really known, and projections on the barometric plane T-uv remain unknown.

In general, the solubility of gypsum and anhydrite increases with pressure; a fact that has been verified repeatedly in laboratory tests (figure 3a); however, the increase of solubility with pressure is higher for anhydrite than for gypsum. Consequently, an increase in transition temperature gypsum-anhydrite is generated when the CaSO<sub>4</sub>-H<sub>2</sub>O system is exposed to pressures in excess of the atmospheric pressure. A series of values representing such a dependence has been postulated, for example: 1°C/8,3 MPa (**Marsal**, 1952), 1°C/8,54 MPa (**McDonald**, 1953), 1°C/7,1 ± 0,19 MPa (**Zen**, 1965) and 1°C/7,8 ± 0,7 MPa



**Figure 3.** Effect of the confinement pressure on the solubility of the CaSO<sub>4</sub>-H<sub>2</sub>O system. (a) Experimental data. (b) Three-dimensional representation of the univariant G + A + L –equilibrium of gypsum, anhydrite and saturated solutions–, following Blount & Dickson (1973).

(Blount & Dickson, 1973). Subsequent researches seem to be in agreement with the latest of these values (Monnin, 1990; Freyer, 2000). A three-dimensional representation of the univariant G + A + L following Blount & Dickson (1973) is presented in figure 3b.

### Hygrotopia

Information on the vapour pressure ( $u_v$ ) or the relative humidity ( $u_v/u_{vo}$ ) imposed by the CaSO<sub>4</sub>-H<sub>2</sub>O system at atmospheric pressure in data-bases on properties of saturated solutions is poor, and only isolate data are reported by some authors (Schneider, 1960; Lide & Frederikse, 1997; Delage *et al.*, 1998; Romero, 2001; Tang & Cui, 2005). The reason is, of course, that gypsum and anhydrite are not effective dehydrators and it lacks interest for industrial applications. Analyses presented here concern to gypsum-saturated solutions (univariant G + L + V) due to information on the relative humidity imposed by anhydrite-saturated solutions (univariant A + L + V) is inconclusive.

Blount & Dickson (1973) postulate a value of vapour pressure of 124 torr (16.53 kPa) at the transition temperature gypsum-anhydrite of 56°C (239,15°K). Using Eq. 5 to calculate the vapour pressure imposed by pure water at 56°C and atmospheric pressure, a value of relative humidity ( $u_v/u_{vo}$ ) =

99,5% is obtained following these authors. On other hand, in measurements using a saturated solution of pure gypsum Panreac® (purity > 98%) in distilled water the dependence of the relative humidity on the temperature was obtained for the range 5°C £ T £ 56°C, and a value of relative humidity ( $u_v/u_{vo}$ ) = 97.8% was obtained at 56°C (Berdugo, 2007).

$$u_{vo} = 136075 e^{\left(\frac{-5239.7}{T+273.15}\right)} \text{ [MPa]} \quad (\text{Eq. 5})$$

$$T: (\text{°C})$$

$$1 \text{ MPa} = 7500.617 \text{ torr}$$

An alternative to evaluate the relative humidity imposed by gypsum-saturated solutions is the use of thermodynamical considerations in the analysis of the stoichiometric equation for the formation of this mineral (Eq. 6). It is possible to write the Gibbs free energy of the reaction in terms of the water activity ( $a_w$ ) as a simplified expression for the solubility constant (K) (Eq. 7). The validity of this approach –used since the early contribution by Kelly *et al.* (1941) until recent works by Freyer & Voigt (2003) and Vanko & Bach (2005), among others–, was confirmed in a recent publication by Coussy (2006) on crystallization of salts in porous media.



At equilibrium,  $\Delta G_{(T)}$  is zero. Therefore, at equilibrium the relative humidity will be related to the standard Gibbs free energy,  $\Delta G^{\phi}_{(T)}$ , (Eq. 8).  $\Delta G^{\phi}_{(T)}$  corresponds strictly to the difference between the total standard Gibbs free energy of formation of the products and the reactants.

This exercise was performed in this research using expressions for  $\Delta G^{\phi}_{(T)}$  (gypsum) proposed by **McDonald** (1953) (Eq. 9), and **Hardie** (1967) (Eq. 10) in order to calculate the dependence of the relative humidity imposed by gypsum-saturated solutions at atmospheric pressure on the temperature. Results of this exercise are presented in figure 4, with relative humidity data from other sulphate-saturated solutions.

It is clear from this figure that relative humidity obtained by means of thermodynamical calculations depends on the transition temperature gypsum-anhydrite selected as thermodynamical reference: 40°C (**McDonald**, 1953) and 58°C (**Hardie**, 1967). In spite of the direct or inverse dependence of relative humidity on temperature, sulphate-saturated solutions in general and gypsum-saturated solutions in particular impose high relative humidities; usually above 80%.



$$\Delta G_{(T)} = \Delta G^{\phi}_{(T)} + RT \ln a_w \quad (\text{Eq. 7})$$

$\Delta G_{(T)}$ : Gibbs free energy of the reaction ( $\text{J mol}^{-1}$ )

$\Delta G^{\phi}_{(T)}$ : standard Gibbs free energy ( $\text{J mol}^{-1}$ )

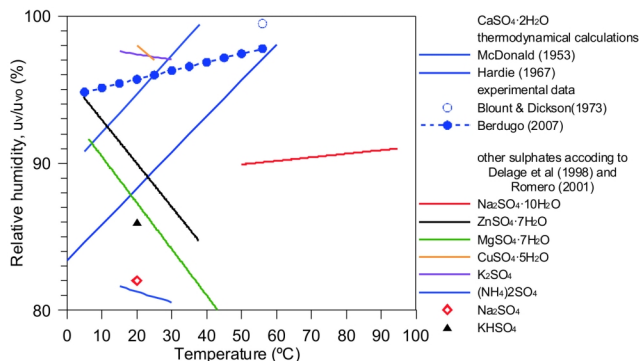
$R$ : universal gas constant ( $8.314 \text{ J mol}^{-1} \text{ T}^{-1}$ )

$T$ : absolute temperature in °K

$a_w$ : water activity or relative humidity,  $\frac{u_v}{u_{vo}}$

$u_v$ : vapour pressure imposed by the solution at atmospheric pressure

$u_{vo}$ : vapour pressure imposed by pure water at atmospheric pressure



**Figure 4.** Dependence of the relative humidity on the temperature for different saturated sulphate solutions at atmospheric pressure.

$$0 = \Delta G^{\phi}_{(T)} (\text{gypsum}) + 2RT \ln \frac{u_v}{u_{vo}} \quad (\text{Eq. 8})$$

$$-(-2495 + 163.89T + 0.0215T^2 - 65.17T \log T) =$$

$$2RT \ln \frac{u_v}{u_{vo}} (\text{McDonald, 1953}) \quad (\text{Eq. 9})$$

$$-(-2870 + 180.43T + 0.0262T^2 - 71.44T \log T) =$$

$$2RT \ln \frac{u_v}{u_{vo}} (\text{Hardie, 1967}) \quad (\text{Eq. 10})$$

The univariant  $G + A + V$ —representing the equilibrium of gypsum, anhydrite and vapour—, only can be estimated by means of second-order empirical correlations between calcium sulphate concentration–vapour pressure, once the latter has been obtained from data on temperature–vapour pressure–salt concentration measured in electrolytic solutions in simultaneous equilibrium with anhydrite and gypsum. The reason is that, even nowadays, temperatures and vapour pressures at which gypsum and anhydrite coexist in the presence of vapour cannot be determined directly due to kinetic hindrances to attain the equilibrium (**Freyer & Voigt**, 2004, **Vanko & Bach**, 2005).

Due to interactions between electrolytic solutions and calcium sulphate do not generate new solid phases, the univariant  $G + A + V$  has been usually studied using the  $\text{CaSO}_4\text{-NaCl-H}_2\text{O}$  system as geochemical reference. Then, the influence of electrolytes on gypsum and anhydrite solubilities—in terms of either NaCl concentration or solution activity—, can be studied and transition temperature values for the  $\text{CaSO}_4\text{-H}_2\text{O}$  system can be determined by means of two different approaches:

(i) The experimental approach: a procedure based on the equilibrium of gypsum and anhydrite in calibrated solutions of  $\text{CaSO}_4\text{-NaCl-H}_2\text{O}$  (**Toriumi & Hara**, 1938; **Posnjak**, 1940; **D’Ans et al.**, 1955; **Bock**, 1961; **Power & Satterfield**, 1966; **Hardie**, 1967; **Bount & Dickson**, 1973; **Freyer**, 2000; **Freyer & Voigt**, 2003).

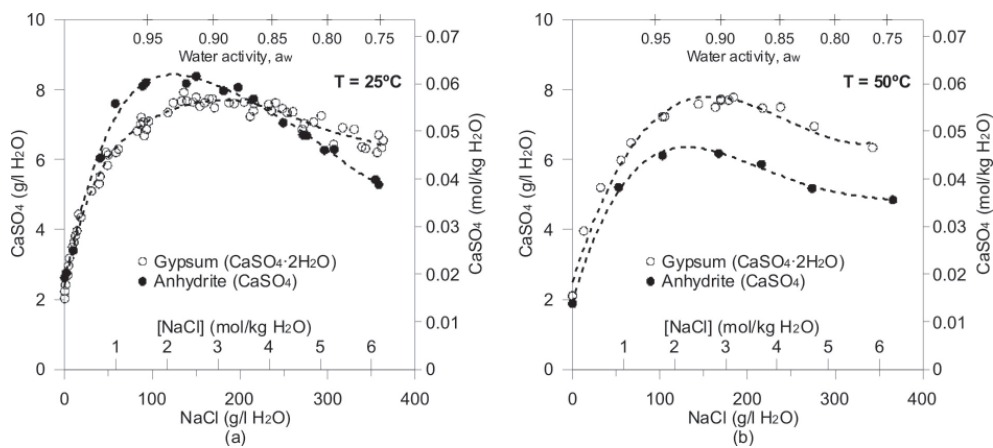
(ii) The transformation energy approach: a theoretical procedure based on the Gibbs free energy dependence on solution activity (**D’Ans**, 1933; **Hill**, 1937; **Posnjak**, 1938; **D’Ans et al.**, 1955; **McDonald**, 1953; **Harvie & Weare**, 1980; **Møller**, 1988; **Raju & Atkinson**, 1990; **Freyer & Voigt**, 2003; **Vanko & Bach**, 2005).

Results of experimental approaches indicate that the addition of non-common ion electrolytes under isothermal conditions increases the solubility of both gypsum and

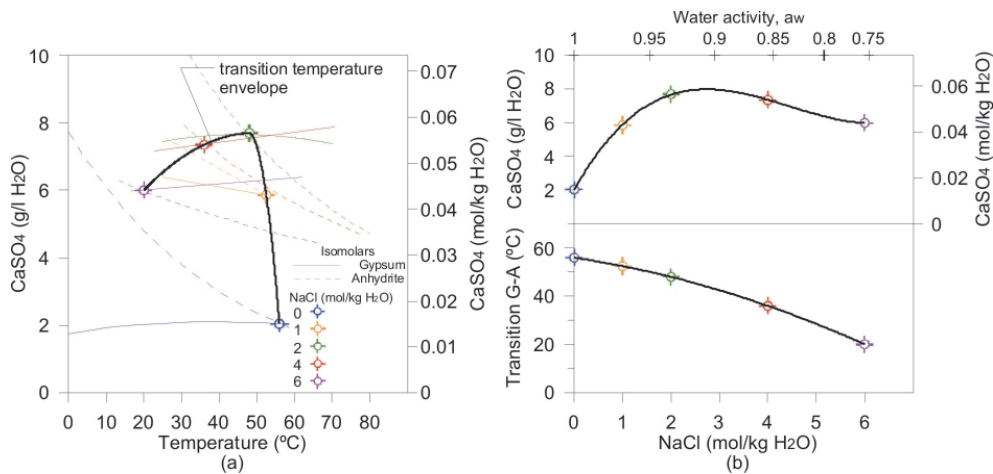
anhydrite until a certain optimum solution activity. Then, a decrease in solubility is related to the hydration ability of the electrolyte; and at very low values of solution activity –a very high salinity–, solution could be undersaturated (or subsaturated) respect to both gypsum and anhydrite. These features are illustrated in figure 5. At 25°C, a classic reference temperature in geochemistry, solubility curves intersect at a NaCl concentration of approximately 4 mol/kg H<sub>2</sub>O (233.8 g/l). Below this value gypsum represents the stable phase, and above it is anhydrite (figure 5a). On other hand, at 50°C, just above the transition temperature gypsum-anhydrite proposed by **Innorta et al.** (1980) and **Møller** (1988), anhydrite is always the stable phase (figure 5b).

When solubility diagrams for gypsum and anhydrite are obtained for several systems CaSO<sub>4</sub>-NaCl-H<sub>2</sub>O following the experimental approach –that is, isomolal solutions with respect to NaCl–, the variation of the transition temperature gypsum-anhydrite with the NaCl molality (or the water activity) can be obtained. This exercise was performed in this research applying the geometrical criterion for IP determination (intersection between solubility curves for anhydrite and gypsum) to isolated experimental data reported by **Blount & Dickson** (1973), and their results are presented in figure 6.

From this figure it seems that the apparent super-saturation associated whit the presence of non-common



**Figure 5.** Solubility of gypsum and anhydrite and its dependence on sodium chloride concentration at atmospheric pressure: (a) at 25°C (Freyer & Voigt, 2003), (b) at 50°C (Møller, 1988).



**Figure 6.** CaSO<sub>4</sub>-NaCl-H<sub>2</sub>O system: gypsum-anhydrite-sodium chloride equilibrium at 0.10 MPa (1 bar). (a) isomolal curves (solubility diagrams) for gypsum and anhydrite, (b) transition conditions in terms of temperature and solubility.

ion electrolytes has an upper limit at a water activity value near 0.92 (figure 6b). However, an inverse relationship between the temperature transition gypsum-anhydrite and the electrolyte concentration remains in spite of the limit value for IP imposed by the water activity.

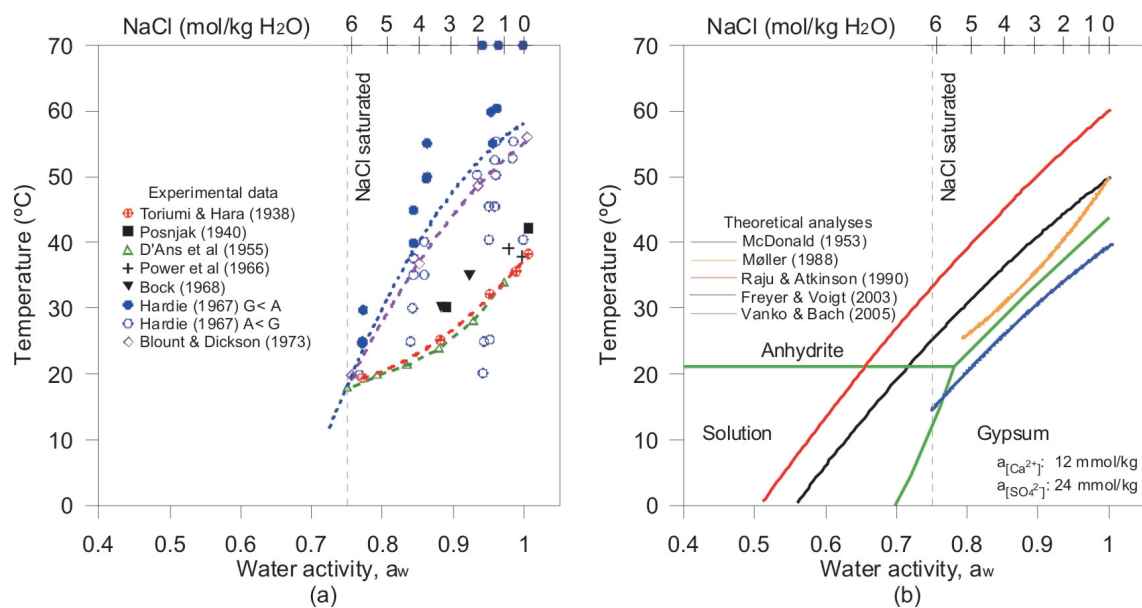
A comparison between experimental data and thermodynamical calculations on the dependence of the transition temperature gypsum-anhydrite on the water activity, using the  $\text{CaSO}_4\text{-NaCl-H}_2\text{O}$  system at 0,10 MPa as barometric reference, is presented in figure 7. Transition temperatures in pure water according to these results are also indicated in figure 2. From figures 6 and 7 the fact that the transition temperature decreases with decreasing water activity is unquestionable, but two characteristic values seem exist for pure water: 40°C and 56°C.

Discrepancies between these values are often attributed to partial anhydrite-gypsum or gypsum-anhydrite transition in experimental procedures (Hardie, 1967 and Blount & Dickson, 1973); as well as to differences in standard Gibbs free energies selected in order to fit the transition temperature in theoretical procedures (Berdugo, 2007). The latter shortcoming has been avoided correcting the standard entropy of anhydrite in by  $1.6 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ .

Univariant  $G + A + V$  can be obtained from information obtained in the  $\text{CaSO}_4\text{-NaCl-H}_2\text{O}$  system, but it requires some preliminary considerations.

(i) According to a basic principle of physical chemistry, if one of the phases conforming a multi-phase system in equilibrium at given temperature and pressure is removed the system remains at equilibrium, whenever other circumstances are being held constant. Then, gypsum and anhydrite equilibrated with vapour and NaCl (aqueous) remain in equilibrium with the vapour phase even if the  $\text{NaCl}\cdot\text{H}_2\text{O}$  solution is removed. Consequently, the vapour pressure along univariant  $G + A + V$  can be estimated from relationships between NaCl concentrations and transition temperatures gypsum-anhydrite obtained in  $\text{CaSO}_4\text{-NaCl-H}_2\text{O}$  systems. It requires empirical correlations between the NaCl concentration (or the water activity) and the vapour pressure of  $\text{NaCl}\cdot\text{H}_2\text{O}$  at different temperatures.

(ii) A series of equations for thermodynamic properties of the  $\text{NaCl-H}_2\text{O}$  system has been proposed by Sparrow (2003). They are polynomials that depend only on composition and temperature, which were adjusted using relationships for the thermodynamical properties of aqueous sodium chloride proposed by other authors (Pitzer *et al.*, 1984 and Archer, 1992). For the case of vapour pressure ( $p_v$ ) between 0°C and 150°C, a expression given by Eq. 11 is proposed for molalities  $> 0$ . Concentration of NaCl is expressed in terms of the salt mass fraction,  $M_f$ , a parameter related to the solution molality,  $m$  (mol/kg  $\text{H}_2\text{O}$ ), and the molar mass of the salt (58.443 g/mol). The vapour pressure associated with pure water ( $p_{v0}$ ) can be calculated using Eq. 5.



**Figure 7.**  $\text{CaSO}_4\text{-NaCl-H}_2\text{O}$  system: gypsum-anhydrite-saturated solution equilibria at 0.10 MPa (1 bar). Summary of approaches to define the transition temperature gypsum-anhydrite following the activity criterion. (a) experimental approach, (b) transformation energy approach.



$$u_v = A + BT + CT^2 + DT^3 + ET^4 \quad [\text{MPa}] \quad (\text{Eq. 11})$$

$$A = (0.9083 - 0.569M_f + 0.1945M_f^2 - 3.736M_f^3 + 2.82M_f^4) \times 10^{-3}$$

$$B = (-0.0669 + 0.0582M_f - 0.1668M_f^2 + 0.6761M_f^3 - 2.09M_f^4) \times 10^{-3}$$

$$C = (7.541 - 5.143M_f + 6.482M_f^2 - 52.62M_f^3 + 115.7M_f^4) \times 10^{-6}$$

$$D = (-0.0922 + 0.0649M_f - 0.1313M_f^2 + 0.8024M_f^3 - 1.986M_f^4) \times 10^{-6}$$

$$E = (1.237 - 0.753M_f + 0.1448M_f^2 - 6.964M_f^3 + 14.61M_f^4) \times 10^{-9}$$

$$M_f = \frac{mM_{(\text{NaCl})}}{1000 + mM_{(\text{NaCl})}}$$

$m$ : Molality, mol NaCl / kg H<sub>2</sub>O

$M_{(\text{NaCl})}$ : molar mass of NaCl = 58.443 g / mol

A comparison between Sparrow's formulation and experimental data by **Romero** (2001) for the relative humidity ( $u_v/u_{v0}$ ) in the NaCl-H<sub>2</sub>O system at 20°C (Eq. 12) is illustrated in figure 8a. The percent error (figure 8b) is expressed using experimental values as reference.

$$\frac{u_v}{u_{v0}} = 1 - 0.035m - \chi m(m - 3) \quad (\text{Eq. 12})$$

$$\chi = 1.142 \times 10^{-3} \text{ for } m < 3 \text{ mol / kg}$$

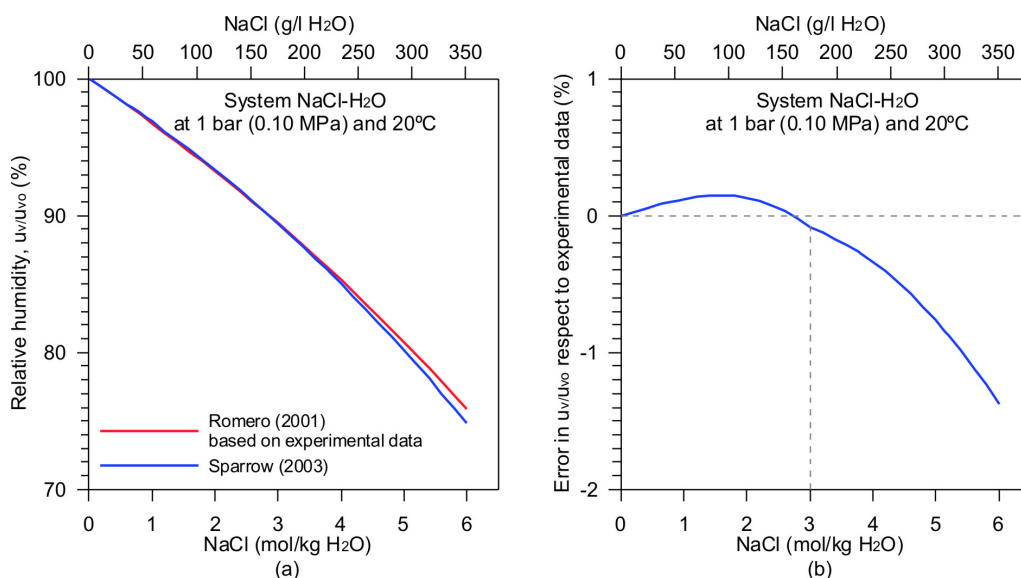
$$\chi = 1.739 \times 10^{-3} \text{ for } m \geq 3 \text{ mol / kg}$$

From this exercise it can be postulated that Eq. 11 predicts the vapour pressure of a sodium chloride solution with reasonable accuracy up to  $m = 3$  mol/kg H<sub>2</sub>O, just the critical value recognized by **Romero** (2001). Beyond 3 mol/kg H<sub>2</sub>O

reliability diverge significantly and may be used with reduced confidence to estimate  $u_v$  at high concentrations.

The formulation by **Sparrow** (2003) was applied to experimental data reported by **Hardie** (1967) and **Blount & Dickson** (1973) for the CaSO<sub>4</sub>-NaCl-H<sub>2</sub>O system at atmospheric pressure –which converge at a transition temperature 56°C in pure water–. The result was the univariant G + A + V shown in figure 9a. At 56°C this univariant give a saturation vapour pressure  $u_v = 121,8$  torr (16,24 kPa); associated with  $u_{v0} = 124,6$  torr (16,61 kPa). Then, a relative humidity ( $u_v/u_{v0}$ ) = 97,8% is obtained at the invariant four-phase equilibrium G + A + L + V. This value for  $u_v$  at IP is within the experimental error recognized by **Hardie** (1967) and **Blount & Dickson** (1973):  $124 \pm 9$  torr. However, in those works the invariant IP was fixed to  $a_w = 1$  in order to extrapolate the vapour pressure from low activity to the saturation condition in pure water. This implies that the invariant point was estimated neglecting the effect that dissolved Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> exert on the vapour pressure. This simplification is founded on the idea that the tiny lowering of the vapour pressure resulting from dissolved Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> is compensated by the positive effect of the confining pressure (0,10 MPa), as was pointed out by **Blount & Dickson** (1969, 1973). In reality, when saturated in calcium sulphate at atmospheric pressure water is characterized by a truly high relative humidity (near 98%, as was calculated here), but not by an ideal value of 100%.

This consideration invalidates the theoretical relative humidity value reported by **Blount & Dickson** (1973)



**Figure 8.** NaCl-H<sub>2</sub>O system at 20°C: (a) relative humidity according to Romero (2001) and Sparrow (2003), (b) error of the formulation proposed by Sparrow (2003) respect to experimental data reported by Romero (2001).

(figure 4), based on the saturation vapour pressure at 56°C: 99,5% for  $u_v = 124$  torr. It is proposed that a value of  $u_v/u_{vo} = 97,8\%$  for  $u_v = 121.8$  torr at 56°C under atmospheric pressure –considering the solubility at equilibrium–, is more consistent with experimental data. From figure 9b it is clear that at high water activity hydration ability of electrolyte governs the imposed relative humidity and, as it was mentioned above, calcium sulphate solutions could be subsaturated respect to both gypsum and anhydrite.

### Three-dimensional representation of the phase diagram for the $\text{Ca-SO}_4\text{-H}_2\text{O}$ system

Considerations presented above suggest that for a proper analysis of phase relationships in the  $\text{CaSO}_4\text{-H}_2\text{O}$  system the incorporation of the compositional plane T-c is necessary and the three-dimensional representation of univariants in terms of temperature-concentration-vapour pressure is unavoidable.

In this research the  $\text{CaSO}_4\text{-H}_2\text{O}$  system at atmospheric pressure as barometric reference is associated with a temperature transition gypsum-anhydrite of 56°C (**Blount and Dickson, 1973**), and the solubility curves for gypsum and anhydrite proposed by these authors are used as reference (Eq. 1 and Eq. 2, respectively). In these conditions, at IP the equivalent ( $\text{CaSO}_4$ ) concentration is 2.05 g/l, which in terms of gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) solubility corresponds to 2.58 g/l.

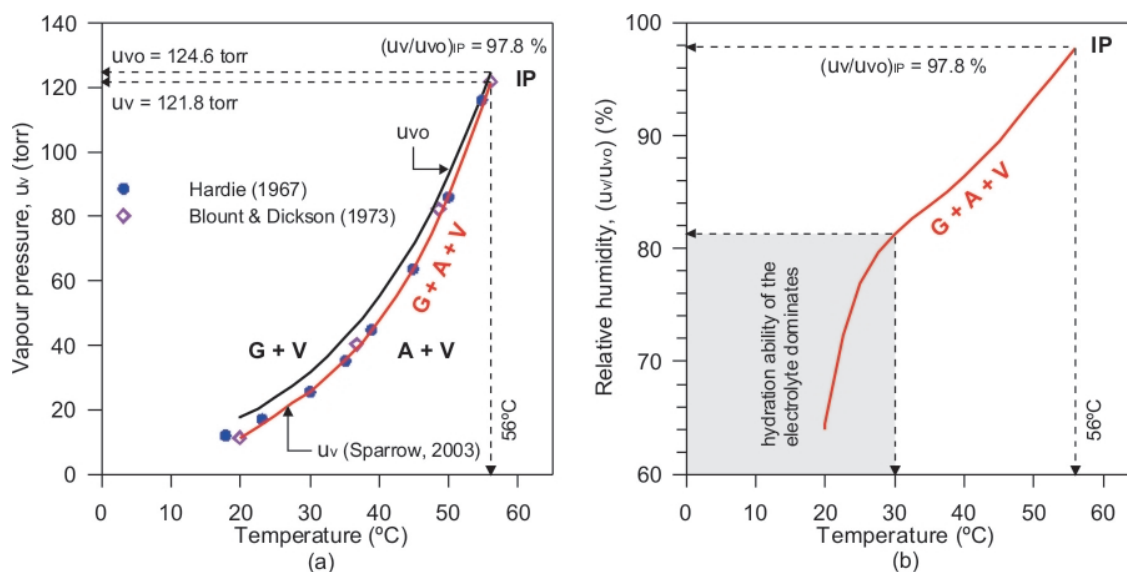
In the absence of additional information on the relative humidity imposed by gypsum-saturated solutions at atmospheric pressure, the single linear relationship T-( $u_v/u_{vo}$ ) based on experimental data by **Berdugo (2007)** is adopted (Eq. 13). Then, the combination of Eq. 1, Eq. 5 and Eq. 13 give the three-dimensional form of univariant G + L + V. Univariant A + L + V is only represented as a projection on the compositional plane due to information on relative humidity imposed by anhydrite-saturated solutions is only available for very high temperatures ( $T > 90^\circ\text{C}$ ) –the case of desalinization processes or industrial applications (**Freyer & Voigt, 2004**)–.

For univariant G + A + L, the criterion proposed by **Blount & Dickson (1973)** ( $1^\circ\text{C}/7,8 \pm 0,7 \text{ MPa}$ ) is adopted. Finally, univariant G + A + V is formulated using parameters presented in table 2, which were obtained from figures 6 and 9a. The result of this exercise is presented in figure 10.

A important feature presented in figures 3 and 6 can be now properly visualized in figure 10: water activity (salinity or the associated relative humidity) is the key factor for existence of high concentration of  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  in the aqueous system, and confinement pressure plays a secondary role, even at very high values (for example  $> 50 \text{ MPa}$ ). On the other hand, the increases in water activity generates true metastable conditions for both gypsum and anhydrite occurring at vapour pressures below the vapour pressure imposed in pure water.

$$\left( \frac{u_v}{u_{vo}} \right)_{\text{gypsum}(\%)} = 5.81 \times 10^{-2} T + 94.548 \quad (25^\circ\text{C} \leq T \leq 56^\circ\text{C}) \quad (\text{Eq. 13})$$

$P = 1 \text{ atm}, T$



**Figure 9.**  $\text{CaSO}_4\text{-H}_2\text{O}$  system at 0.10 MPa (1 bar) deduced from the  $\text{CaSO}_4\text{-NaCl-H}_2\text{O}$  system: (a) univariant G + A + V in terms of vapour pressure, (b) univariant G + A + V in terms of relative humidity.

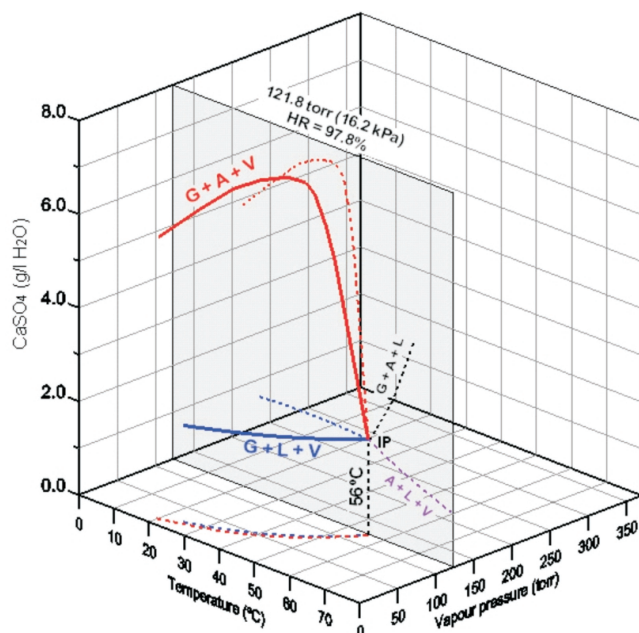
**Table 2.** Representative parameters for univariant  
G + A + V, P = 0,10 MPa (1 bar).

NaCl (mol/kg H <sub>2</sub> O)	T (°C)	CaSO <sub>4</sub> (g/l H <sub>2</sub> O)	uv (torr)
0	56	2.05	121.8
1	52	5.86	97.0
2	48	7.70	76.8
4	36	7.34	37.5
6	20	6.00	11.4

### Conclusive remarks

From the review presented above it is clear that only univariants G + L + V, A + L + V and G + A + L have been directly obtained by means of experimental methods using pure water as solvent, and the univariant G + A + V is often indirectly obtained using the CaSO<sub>4</sub>-NaCl-H<sub>2</sub>O system as referent.

The precise value for the transition temperature gypsum-anhydrite is an open discussion –even in the simplest case of calcium sulphate saturated solutions in pure water at atmospheric pressure–, and an accurate knowledge on the vapour pressure associated with univariants at different confinement pressures is not available. Therefore, the three-dimensional representation of the CaSO<sub>4</sub>-H<sub>2</sub>O system presented in figure 10 illustrates only partially the behaviour of the system.

**Figure 10.** Three-dimensional representation of the CaSO<sub>4</sub>-H<sub>2</sub>O system at atmospheric pressure as barometric reference

Experimental and thermodynamical analyses indicate that the transition temperature gypsum-anhydrite in pure water at atmospheric pressure varies between 42°C and 63°C. In this case a direct dependence of the relative humidity on the temperature can be adopted for gypsum-saturated solutions within the range 5°C=T=56°C, and the characteristic relative humidity is about 96%. On the other hand, the solubility, the transition temperature and the vapour pressure are strongly affected by presence of other ions. The addition of non-common ion electrolytes increases the solubility of gypsum and anhydrite and decreases both the transition temperature and the vapour pressure; so, a reduction in relative humidity occurs. However, thermotopia of both phases solubility is not affected.

Metastable states for gypsum and anhydrite without dissolution or precipitation can exist below the transition temperature as a result of water salinity. Alterations of this metastable equilibrium are undoubtedly related with temperature changes, but mainly with variations in the relative humidity imposed by the surrounding environment. The cause is that in spite of the direct or inverse nature of both solubility and vapour pressure, sulphate-rich solutions impose high values of relative humidity, often above 80%. Then, exposed to moderate dry environments these solutions are capable to transfer vapour towards the environment increasing the concentration in Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> and generating true supersaturated conditions; the basic requirement for solvent-way precipitation and gypsum crystal growth. Nevertheless, above the transition temperature anhydrite is the stable phase at any relative humidity.

The behaviour of the CaSO<sub>4</sub>-NaCl-H<sub>2</sub>O system is a coupled thermo-hydro-chemical (THC) phenomenon in which water activity is the key factor for existence of high concentration of Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup>, and confinement pressure plays a secondary role. Consequently, the selection of the most representative values for solubility, transition temperature gypsum-anhydrite and relative humidity deepens on the boundary conditions imposed by environmental, geotechnical or industrial concerning processes.

### Acknowledgements

The Spanish Ministry for Infrastructures was the financial supporter for this research. The authors wish to thank the advising provided by their colleagues Prof. Dr. Ing. Lucila Candela-Lledó, Prof. Dr. Ing. Marcos Arroyo-Álvarez de Toledo and Dr. Ing. Juliana Knobeldorff.

## References

- Archer, D.G.** 1992. Thermodynamic properties of the NaCl-H<sub>2</sub>O system II. J. Physical and Chemical Reference Data 21, Issue 4: 793-829.
- Berdugo, I.R.** 2007. Tunnelling in sulphate-bearing rocks – expansive phenomena. Dr. Thesis, Universitat Politècnica de Catalunya.
- Block, J & Waters, O.B.** 1968. The CaSO<sub>4</sub>-Na<sub>2</sub>SO<sub>4</sub>-NaCl-H<sub>2</sub>O system at 25° to 100°C. J. Chem. Eng. Data 13: 336-344.
- Blount C.W. & Dickson F.W.** 1969. The solubility of anhydrite CaSO<sub>4</sub> in NaCl-H<sub>2</sub>O from 100 to 450°C and 1 to 1000 bars. Geochim. Cosmochim. Acta 33: 227-245.
- Blount C.W. & Dickson F.W.** 1973. Gypsum anhydrite equilibria in systems CaSO<sub>4</sub> and CaCO<sub>3</sub>-NaCl-H<sub>2</sub>O. The American Mineralogist, 58: 323-331.
- Bock, E.** 1961. On the solubility of anhydrous calcium sulfate and of gypsum in concentrated solutions of sodium chloride at 25°C, 30°C, 40°C and 50°C. Can. J. Chem. 39: 1746-1751.
- Coussy, O.** 2006. Deformation and stress from in-pore drying-induced crystallization of salt. Journal of the Mechanics and Physics of Solids, v 54, n 8: 1517-1547.
- D'Ans, J.** 1933. Die Lösungsgleichgewichte der System der Salz ozeanischer Salzablagerungen. Berlin: 118-123.
- D'Ans, J., Bredtscheider, D., Eick, H. & Freund, H.E.** 1955. Untersuchungen über die Calciumsulfate. Kali Steinsalz, 9: 17-38.
- D'Ans, J.** 1968. Der Übergangspunkt Gips – Anhydrite. Kali U. Steinsalz, 5: 109-111.
- Delage, P., Howat, M.D. & Cui, Y.J.** 1998. The relationship between suction and swelling properties in a heavily compacted unsaturated clay. Engineering Geology 50: 31-48.
- Freyer, D.** 2000. Zur Phasenbildung und -stabilität im System Na<sub>2</sub>SO<sub>4</sub>-CaSO<sub>4</sub>-H<sub>2</sub>O. Dissertation, TU Bergakademie Freiberg.
- Freyer, D. & Voigt, W.** 2003. Crystallization and Phase Stability of CaSO<sub>4</sub> and CaSO<sub>4</sub> – Based Salts. Monatshefte für Chemie 134: 693-719.
- Freyer, D. & Voigt, W.** 2004. The measurement of sulfate mineral solubilities in the Na-K-Ca-Cl-SO<sub>4</sub>-H<sub>2</sub>O system at temperatures of 100, 150 and 200°C. Geochimica et Cosmochimica Acta, Vol. 68, No. 2: 307-318.
- Hardie, L.A.** 1967. The gypsum-anhydrite equilibrium at one atmosphere. Amer. Mineral. 52: 171-200.
- Harvie, C.E. & Weare, J.H.** 1980. The prediction of mineral solubilities in natural waters: Na-K-Mg-Ca-Cl-SO<sub>4</sub>-H<sub>2</sub>O system from zero to high concentration at 25°C. Geochim. Cosmochim. Acta 44: 981-997.
- Hill, A.** 1937. The transition temperature of gypsum to anhydrite. J. Am. Chem. Soc. 59 (11): 2242-2244.
- Innorta, G., Rabbi, E. & Tomadin, L.** 1980. The gypsum-anhydrite equilibrium by solubility measurements. Geochim. Cosmochim. Acta 44: 1931-1936.
- Kelly, K.K., Southard, J.C. & Anderson, C.T.** 1941. Thermodynamic properties of gypsum and its dehydration products. U.S. Bur. Mines, Tech. Papers. 625.
- Knacke O, Gans W.** 1977. The thermodynamics of the system CaSO<sub>4</sub>-H<sub>2</sub>O. Z. Phys. Chem. 104: 41-48.
- Kontrec, J., Kralj, D. & Brecevic, L.** 2002. Transformation of anhydrous calcium sulphate into calcium sulphate dihydrate in aqueous solutions. Journal of Crystal Growth, 240, n 1-2: 203-211.
- Lide, D.R. & Frederikse, H.P.R.** 1997. CRC Handbook of chemistry and physics. A ready reference book of chemical and physical data. CRC Press, New York.
- Manikhin, V.I. & Kryukou, P.A.** 1968. Effect of pressure on the solubility of sodium and calcium sulfates. Porovye Rastvory Metody Ikh. Izuch., 133-44.
- Marsal, D.** 1952. Der Einfluss des Druckes auf das System CaSO<sub>4</sub>-H<sub>2</sub>O. Heidelberger Beit. Mineral Petrol 3: 289-296.
- Marshall, W.L. & Slusher R.** 1966. Thermodynamics of calcium sulphate dihydrate in aqueous sodium chloride solutions, 0-110°C. J. Phys. Chem. 70: 4015-4027.
- McDonald, G.J.F.** 1953. Anhydrite-gypsum equilibrium relations. American Journal of Science, vol. 251: 884-898.
- Monnin, C.** 1990. The influence of pressure on the activity coefficients of the solutes and on the solubility of minerals in the system Na-Ca-Cl-SO<sub>4</sub>-H<sub>2</sub>O to 200°C and 1 kbar and to high NaCl concentration. Geochimica et Cosmochimica Acta, Volume 54, Issue 12: 3265-3282.
- Møller N.** 1988. The prediction of mineral solubilities in natural waters: A chemical equilibrium model for the Na-K-Ca-Cl-SO<sub>4</sub>-H<sub>2</sub>O system, to high temperature and concentration. Geochim. Cosmochim. Acta 52: 821-837.
- Pitzer, K.S., Peiper, J. C., & Busey, R.H.** 1984. Thermodynamic properties of aqueous sodium chloride solutions. J. Phys. Chem. Ref. Data 13: 1-102.
- Posnjak E.** 1938. The system CaSO<sub>4</sub>-H<sub>2</sub>O. Am. Jour. Sci., 5th ser., 35A: 247-272.
- Posnjak E.** 1940. Deposition of calcium sulfate from sea water. Am. J. Sci. 238: 559-568.
- Power, W.H. & Fabuss, B.M.** 1964. Thermodynamic properties of saline water. Office of Saline Water Research and Development Progress Rept. 104.
- Power, W.H. & Satterfield, C.N.** 1966. Transient solute concentrations and phase changes of calcium sulfate in aqueous sodium chloride. J. Chem. Eng. Data 11: 149-154.
- Raju, K. & Atkinson, G.** 1990. Thermodynamics of 'scale' mineral solubilities. 3. Calcium sulfate in aqueous NaCl. Journal of Chemical and Engineering Data, v 35, n 3: 361-367.
- Romero, E.** 2001. Controlled-suction techniques. 4° Simpósio Brasileiro de Solos Não Saturados. W.Y.Y. Gehling & F. Schnaid (eds.): 535-542.
- Sattler, H. & Brückner, H.** 2001. Volumen- und Dichteänderungen bei der Hydratation von Gipsbindemitteln in Abhängigkeit vom

- Wasserangebot. Zement, Kalk, Gips international, Vol. 54 No. 9: 522-529.
- Schneider, A.** 1960. Neue diagramme zur bestimmung der relativen luftfeuchtigkeit uber gesattigten wasserigen salzlosungen und wasserigen schwefelsaurelosungen bei verschiedenen temperaturen. Holz als Rohund Werkstoff 18: 269-272.
- Sparrow, B.** 2003. Empirical equations for the thermodynamic properties of aqueous sodium chloride. Desalination 159: 161-170.
- Tang, A.M. & Cui, Y.J.** 2005. Controlling suction by the vapour equilibrium technique at different temperatures and its application in determining the water retention properties of MX80 clay. Can. Geotech. J. 42: 287-296.
- Toriumi, T. & Hara, R.** 1938. On the calcium sulfate in sea water II. Solubilities of calcium sulphate hemihydrate in sea water of various concentrations at 65°-1 50°. Technol. Rep. Tohoku Imp. Univ. 12: 560-571.
- Vanko, D.A. & Bach, W.** 2005. Heating and freezing experiments on aqueous fluid inclusions in anhydrite: recognition and effects of stretching and the low-temperature formation of gypsum. Chemical Geology 223: 35-45.
- van't Hoff, J.H., Armstrong, E.F., Hinrichsen, W., Weigert, F. & Just, G.** 1903. Gips und Anhydrit. Z. phys. Chem. 45: 257-306.
- Zen, E.-AN.** 1965. Solubility measurements in the system  $\text{CaSO}_4\text{-NaCl-H}_2\text{O}$  at 35°C, 50°C and 70°C and one atmosphere pressure. J. Petrol. 6: 124-164.

Recibido: noviembre 5 de 2008

Aceptado para su publicación: noviembre 18 de 2008