ON THE BEHAVIOUR
OF THE CA-SO$_4$-H$_2$O SYSTEM

By
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Abstract


Thermotropia, barotropia and hygroscopía of the Ca-SO$_4$-H$_2$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 Ca$^{2+}$ and SO$_4^{2-}$ and confinement pressure plays a secondary role.

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

Introduction

Interacting with water calcium sulphate can exists in six different solid phases, presented hierarchically here in the order of increasing solubility: one dihydrate (gypsum, CaSO$_4$·2H$_2$O); two hemihydrates (bassanite: $\alpha$-CaSO$_4$·½H$_2$O and $\beta$-CaSO$_4$·½H$_2$O); and three anhydrous (anhydrite: AI-unstable- or $\alpha$-CaSO$_4$, AII–moderately soluble– or $\beta$-CaSO$_4$, AIII–soluble– or $\gamma$-CaSO$_4$).
and AH·totally soluble- or γ-CaSO₄. 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 or reference) pressure and water activity on the solubility and the characteristic vapour pressure of the Ca-SO₄-H₂O system. A comprehensive review of contributions on the theme is presented and a three-dimensional representation of the phase diagram for the Ca-SO₄-H₂O system at atmospheric pressure is derived.

### Univariants of the Ca-SO₄-H₂O 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-SO₄-H₂O 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. 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.

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).

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

<table>
<thead>
<tr>
<th>Environmental processes</th>
<th>Geotechnical processes</th>
<th>Industrial processes</th>
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<tbody>
<tr>
<td>• Marine intrusion</td>
<td>• Doline collapse</td>
<td>• Production plaster of Paris</td>
</tr>
<tr>
<td>• Water desalination</td>
<td>• Gypsum growth induced swelling</td>
<td>• Production of phosphoric acid</td>
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<tr>
<td>• Nanofiltration of saline drainage</td>
<td>• Ground improvement using calcium-based stabilizers</td>
<td>• Production of hydrogen fluoride</td>
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<tr>
<td>• Geothermal energy generation</td>
<td>• Sulphate attack to mortars and concrete</td>
<td>• Production of cooper</td>
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<tr>
<td>• Hydrothermal energy generation</td>
<td></td>
<td>• Refining of zinc</td>
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<tr>
<td>• Flue gas desulfurization</td>
<td></td>
<td>• Secondary oil recovery</td>
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<td>• Waste storage in evaporite rocks</td>
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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 (0ºC to 50ºC 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 Ca-\(\text{SO}_4\)-H\(_2\)O system. Figure 2 is the solubility diagram for gypsum and anhydrite (AII) in pure water within the temperature range 10º-80ºC 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 49,5ºC; 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\(_4\)-H\(_2\)O system at 0,10 MPa (1 bar).](image-url)
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 70ºC - 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 25ºC to 58ºC; although the usual proposed values vary between 42ºC and 63ºC.

**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 \( \text{CaSO}_4\cdot\text{H}_2\text{O} \) 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 on the compositional plane (T-c). However, two shortcomings are associated with this criterion:

Blount & Dickson (1973)

\[
\ln m(G)_{\text{CaSO}_4} = -4.355 + 8.4 \times 10^{-4} P + 1.05 \times 10^{-2} T - 1.7 \times 10^{-2} T^2 + 5.841.7 \times 10^{-7} T^3
\]  
(Eq. 1)

Anhydrite:

\[
\ln m(A)_{\text{CaSO}_4} = -2.87 + 1.22 \times 10^{-3} P - 2.37 \times 10^{-2} T - 2.8 \times 10^{-6} PT
\]  
+ 1.0 \times 10^{-6} T^2 + 1.4 \times 10^{-8} PT^2

\( m : \frac{\text{mol}}{\text{kg} \ H_2O}; \ P: [\text{bar}]; \ T: [^\circ\text{C}] \)

Innorta et al. (1980)

Gypsum:

\[ c(G)_{\text{CaSO}_4} = 8.69 \times 10^{-5} T^2 - 1.73 \times 10^{-2} T + 2.624 \]  
(Eq. 3)

Anhydrite:

\[ c(A)_{\text{CaSO}_4} = 1.14 \times 10^{-4} T^2 - 3.667 \times 10^{-2} T + 3.517 \]  
(Eq. 4)

\[ c(G,A)_{\text{CaSO}_4} : \frac{g}{l \ H_2O}; \ T: [^\circ\text{C}] \]

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 \( \text{CaSO}_4\cdot\text{H}_2\text{O} \) 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 \( \text{CaSO}_4\cdot\text{H}_2\text{O} \) 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-u 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 \( \text{CaSO}_4\cdot\text{H}_2\text{O} \) system is exposed to pressures in excess of the atmospheric pressure. A series of values representing such a dependence has been postulated, for example: 1ºC/8.3 MPa (Marsal, 1952), 1ºC/8.54 MPa (McDonald, 1953), 1ºC/7.1 ± 0.19 MPa (Zen, 1965) and 1ºC/7.8 ± 0.7 MPa
(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.

Hygrotropia

Information on the vapour pressure (uv) or the relative humidity (uv/uvo) imposed by the CaSO₄-H₂O 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 56ºC (239.15ºK). Using Eq. 5 to calculate the vapour pressure imposed by pure water at 56ºC and atmospheric pressure, a value of relative humidity (uv/uvo) = 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 5ºC ≤ T ≤ 56ºC, and a value of relative humidity (uv/uvo) = 97.8% was obtained at 56ºC (Berdugo, 2007).

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\text{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 (aw) 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.}
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At equilibrium, $\Delta G^0(T)$ is zero. Therefore, at equilibrium the relative humidity will be related to the standard Gibbs free energy, $\Delta G^0(T)$ (Eq. 8), $\Delta G^0(T)$ 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 $\Delta G^0$ (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: 40ºC (McDonald, 1953) and 58ºC (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%.

\[ \text{CaSO}_4 \cdot 2\text{H}_2\text{O(s)} = \text{Ca}^{2+} + \text{SO}_4^{2-} + 2\text{H}_2\text{O} \]  
(Eq. 6)

\[ \Delta G^0(T) = \Delta G^0 + RT \ln a_w \]  
(Eq. 7)

$\Delta G^0$: Gibbs free energy of the reaction (J mol$^{-1}$)

$\Delta G^0$: standard Gibbs free energy (J mol$^{-1}$)

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

T: absolute temperature in K

aw: water activity or relative humidity, $u_w$

uw: vapour pressure imposed by the solution at atmospheric pressure

$u_{w_0}$: vapour pressure imposed by pure water at atmospheric pressure

\[ 0 = \Delta G^0_{\eta} \text{(gypsum)} + 2RT \ln \frac{u_w}{u_{w_0}} \]  
(Eq. 8)

\[ -(-2495 + 163.89T + 0.0215T^2 - 65.17 T \log T) = 2RT \ln \frac{u_w}{u_{w_0}} \]  
(McDonald, 1953)  
(Eq. 9)

\[ -(-2870 + 180.43T + 0.0262T^2 - 71.44T \log T) = 2RT \ln \frac{u_w}{u_{w_0}} \]  
(Hardie, 1967)  
(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 CaSO$_4$-NaCl-H$_2$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 CaSO$_4$-H$_2$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 CaSO$_4$-NaCl-H$_2$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; Moller, 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 25ºC, a classic reference temperature in geochemistry, solubility curves intersect at a NaCl concentration of approximately 4 mol/kg H₂O (233.8 g/l). Below this value gypsum represents the stable phase, and above it is anhydrite (figure 5a). On other hand, at 50ºC, 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 CaSO₄-NaCl-H₂O 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 supersaturation associated with the presence of non-common

![Figure 5. Solubility of gypsum and anhydrite and its dependence on sodium chloride concentration at atmospheric pressure: (a) at 25ºC (Freyer & Voigt, 2003), (b) at 50ºC (Møller, 1988).](image)

![Figure 6. CaSO₄-NaCl-H₂O system: gypsum-anhydrite-sodium chloride equilibrium at 0.10 MPa (1 bar). (a) Isonomol curves (solubility diagrams) for gypsum and anhydrite, (b) transition conditions in terms of temperature and solubility.](image)
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 CaSO₄-NaCl-H₂O 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: 40⁰C and 56⁰C.

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 J·mol⁻¹·K⁻¹.

Univariant G + A + V can be obtained from information obtained in the CaSO₄-NaCl-H₂O 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 NaCl·H₂O 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 CaSO₄-NaCl-H₂O systems. It requires empirical correlations between the NaCl concentration (or the water activity) and the vapour pressure of NaCl·H₂O at different temperatures.

(ii) A series of equations for thermodynamic properties of the NaCl-H₂O 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 (uᵥ) between 0⁰C and 150⁰C, a expression given by Eq. 11 is proposed for molalities > 0. Concentration of NaCl is expressed in terms of the salt mass fraction, Mₑ, a parameter related to the solution molality, m (mol/kg H₂O), and the molar mass of the salt (58.443 g/mol).

The vapour pressure associated with pure water (uᵥ₀) can be calculated using Eq. 5.

![Figure 7. CaSO₄-NaCl-H₂O 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.](image-url)
\[ u_v = A + BT + CT^2 + DT^3 + ET^4 \quad [\text{MPa}] \]  

(Eq. 11)

\[ A = (0.9083 - 0.569M_s + 1.945M_s^2 - 3.736M_s^3 + 2.82M_s^4) \times 10^{-3} \]

\[ B = (-0.0669 + 0.0582M_s - 0.1668M_s^2 + 0.676M_s^3 - 2.09M_s^4) \times 10^{-3} \]

\[ C = (7.541 - 5.143M_s + 6.482M_s^2 - 52.62M_s^3 + 115.7M_s^4) \times 10^8 \]

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

\[ E = (1.237 - 0.753M_s + 0.1448M_s^2 - 6.964M_s^3 + 14.6M_s^4) \times 10^{-9} \]

\[ M_s = \frac{mM_{NaCl}}{1000 + mM_{NaCl}} \]

\( m \): Molality, mol NaCl / kg H2O

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

A comparison between Sparrow’s formulation and experimental data by Romero (2001) for the relative humidity \( u_v/u_{vo} \) in the NaCl-H2O system at 20ºC (Eq. 12) is illustrated in figure 8a. The percent error (figure 8b) is expressed using experimental values as reference.

\[ \frac{u_v}{u_{vo}} = 1 - 0.035m - \chi m (m - 3) \]  

(Eq. 12)

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

\( \chi = 1.739 \times 10^{-3} \) 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 \( m = 3 \text{ mol/kg} \) H2O, just the critical value recognized by Romero (2001). Beyond 3 mol/kg H2O 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 CaSO4-NaCl-H2O system at atmospheric pressure—which converge at a transition temperature 56ºC in pure water—. The result was the univariant G + A + V shown in figure 9a. At 56ºC this univariant give a saturation vapour pressure \( u_v = 121.8 \text{ torr} \) (16.24 kPa); associated with \( u_{vo} = 124.6 \text{ torr} \) (16.61 kPa). Then, a relative humidity \( u_v/u_{vo} = 97.8\% \) 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 ± 9 torr. However, in those works the invariant IP was fixed to \( aw = 1 \) 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 Ca2+ and SO42− exert on the vapour pressure. This simplification is founded on the idea that the tiny lowering of the vapour pressure resulting from dissolved Ca2+ and SO42− 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 4), based on the saturation vapour pressure at 56°C: 99.5% for \( u_v = 124 \) torr. It is proposed that a value of \( \frac{u_v}{u_{vo}} = 97.8\% \) 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 CaSO\(_4\)-H\(_2\)O system

Considerations presented above suggest that for a proper analysis of phase relationships in the CaSO\(_4\)-H\(_2\)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 CaSO\(_4\)-H\(_2\)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 (CaSO\(_4\)) concentration is 2.05 g/l, which in terms of gypsum (CaSO\(_4\cdot2\)H\(_2\)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 (\( T > 90^\circ C \)) –the case of desalinization processes or industrial applications (Freyer & Voigt, 2004)–.

For univariant \( G + A + L \), the criterion proposed by Blount & Dickson (1973) (1ºC/7.8 ± 0.7 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 Ca\(^{2+}\) and SO\(_4^{2-}\) in the aqueous system, and confinement pressure plays a secondary role, even at very high values (for example > 50 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.

\[
\frac{u_v}{u_{vo}} = 5.81 \times 10^{-2}T + 94.548 \quad (25^\circ C \leq T \leq 56^\circ C) \quad (Eq. 13)
\]

**Figure 9.** CaSO\(_4\)-H\(_2\)O system at 0.10 MPa (1 bar) deduced from the CaSO\(_4\)-NaCl-H\(_2\)O system: (a) univariant \( G + A + V \) in terms of vapour pressure, (b) univariant \( G + A + V \) in terms of relative humidity.
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, thermotropia of both phases solubility is not affected.

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 CaSO₄-NaCl-H₂O 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 CaSO₄-H₂O system presented in figure 10 illustrates only partially the behaviour of the system.

The behaviour of the CaSO₄-NaCl-H₂O system is a coupled thermo-hydro-chemical (THC) phenomenon in which water activity is the key factor for existence of high concentration of Ca²⁺ and SO₄²⁻, 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.

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