Chapter I.2

THE DISSOLUTION AND CONVERSION OF GYPSUM AND ANHYDRITE

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The development of karst is a complex system driven by the dissolution of a host rock and the subsequent removal of dissolved matter by moving water. It is the process that, at various stages, initiates or triggers associated processes including erosion, collapse and subsidence. The dissolution of sulphate rocks proceeds by different mechanisms and at different rates to those associated with the dissolution of carbonate rocks. For each rock type different factors influence the process. This chapter is an attempt to summarise the present knowledge of the dissolution chemistry and kinetics of gypsum and anhydrite. These are important for the genetic interpretation of karst features in these rocks. The gypsum-anhydrite-gypsum transitions and recrystallization processes are also addressed, because of their importance to karst development.

Many studies have been undertaken on the solubility and dissolution of sulphate minerals, in the context of construction engineering and karst processes. Important works include these of Laptev (1939), Kuznetzov (1947), Shternina (1949), Zdanovsky (1956), Sokolov (1962), Zverev (1967), Lui & Nancollas (1971), Blount & Dickson (1973), Mel'nikova & Moshkina (1973), Wigley (1973), Gorbunova (1977), James & Lupton (1978), Kushnir (1988). The most comprehensive recent account is that of James (1992).

1. Chemical equilibria

Gypsum dissolves by a simple two phase dissociation (solid and solvent):

$$CaSO_4 \cdot 2H_2O == Ca^{2+} + SO_4^{2-} + 2H_2 \qquad [1]$$

Gypsum, like $CaCO_3$ and salt, dissolves reversibly, but anhydrite does not. When anhydrite is dissolved it forms a solution of calcium sulphate which, at common temperatures and pressures, is in equilibrium with the solid phase of gypsum, but not with anhydrite. If disequilibrium of the solid-solvent system occurs, gypsum precipitates. This is due to the instability of anhydrite under normal surface and shallow sub-surface thermobaric conditions (Fig.1).

The solubility of gypsum in pure water at 20°C is 2.531 g/L, or 14.7 mM/L. It is roughly 140 times lower than the solubility of common salt (360 g/L) but four orders of magnitude greater than the solubility of $CaCO_3$ (1.5 mg/L); however, in the presence of CO_2 the dissolution of calcite is enhanced and the difference in solubility between calcite and gypsum decreases to 10-30 times.

The dependence of the solubility of gypsum on temperature is reported by many authors (Blount & Dickson, 1973; James, 1992; Liley et al, 1963; see Fig.2). Between 0 and 30°C, the range encompassing most natural waters, the solubility of gypsum increases by 20%, reaching a maxi-

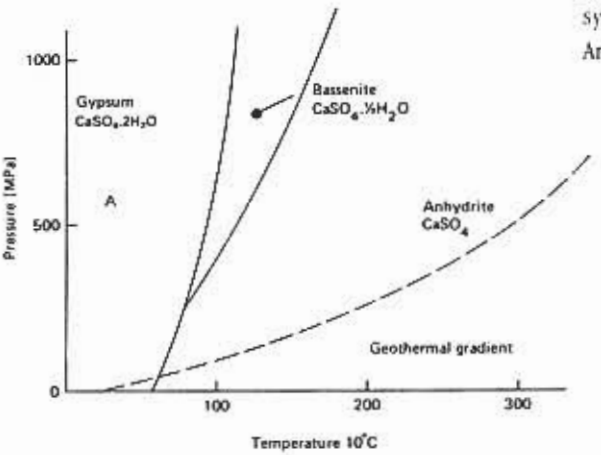


Fig.1. - Equilibrium diagram for the system $CaSO_4$ - H_2O (after Zanbak & Arthur, 1986).

mum (about 2.66 g/L) at 43°C. Cigna (1985) examined the possible effects on gypsum solubility caused by mixing waters at different temperatures. He found that when mixing equal amounts of two saturated waters (one at 10°C, and another at temperatures ranging from 40 to 100°C) the solubility in the mixture increased by between 2 and 13%. This effect may play some role in the karstification of areas with geothermal waters.

Anhydrite may be considered to have no characteristic solubility. This is because of its chemical instability in commonly encountered shallow sub-surface conditions (James, 1992). Some values given in the literature are misleading: the true solubility of anhydrite under normal temperatures is equivalent to that of gypsum. When dissolved in water, anhydrite produces a solution of $CaSO_4$ that ultimately attains the same equilibrium concentrations as the gypsum-H_2O system in pure water, this is 2.00 g/L at 20°C. James (1992) pointed out that anhydrite in contact with water

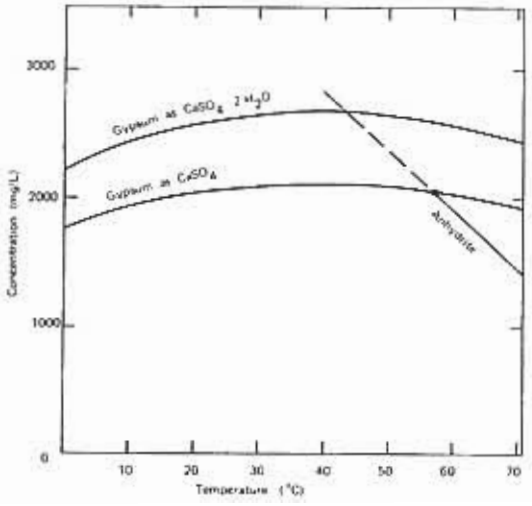


Fig. 2. Solubility curves for gypsum and anhydrite based on the experimental data of Blount & Dickson (1973). The upper curve pertains to the mass loss of gypsum rock in solution. The lower curve is calculated as $CaSO_4$ and displays the invariant point at 58°C, where gypsum, anhydrite and liquid coexist (After White, 1988).

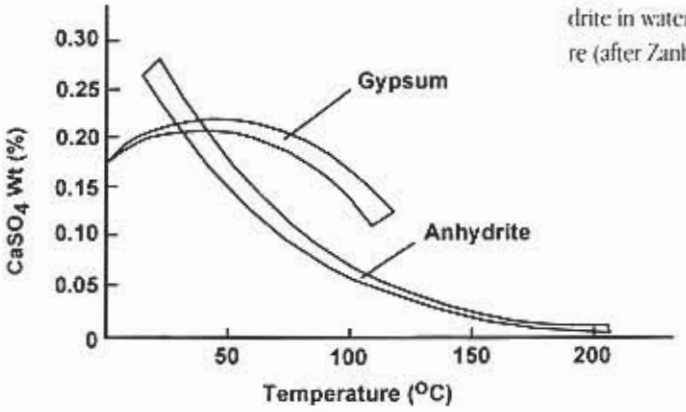


Fig. 3. - Solubility of gypsum and anhydrite in water at one atmosphere pressure (after Zanbak & Arthur, 1986).

tends towards a metastable state characterised by supersaturated solutions. These probably account for some of the high solubilities quoted for anhydrite, which range up to 3.5 g/L. The subject of gypsum/anhydrite conversion is described in detail in section 5 below.

Figure 3 shows the solubility data for anhydrite and gypsum in their stability regions; this information was summarised by Zanbrak & Arthur (1986). The solubility of anhydrite is lower than that of gypsum under these pressure conditions, and decreases with increasing temperature.

Pressure does not substantially affect the solubility of gypsum within common geological environments. In contrast the $CaCO_3$-CO_2-H_2O system is influenced by the presence of a gas phase that makes it sensitive to pressure. The solubility of gypsum increases slightly at pressures exceeding 100 bars (Manikhin, 1966), but at depths of less than a thousand metres or so, the influence is negligible. The effect of pressure applied to the mineral is discussed below.

Equilibrium constants. Different equilibrium constant values for gypsum Kg are reported by various authors, reflecting varying experimental conditions and the use of different thermodynamic data in the calculations. The constants are most usually given for 25°C and higher temperatures. However, in many karst environments the water temperature range is more normally between 5 and 15°C. Aksem & Klimchouk (1991) provided thermodynamic calculations of Gubbs free energy values and equilibrium constants for the gypsum dissolution reaction in water at temperatures of 0-50°C (Table 1). The results agree closely with the values previously provided by Wigley (1973). The data in Table 1 give the following Kg function of temperature:

$$pKg = 4.667 - 5.197 \times 10^{-9} \times t + 1.133 \times 10^{-3} \times t \qquad [2]$$

Saturation index. Karst waters in equilibrium with a solid phase are rare. When a solution is undersaturated with respect to the soluble mineral, dissolution proceeds; no dissolution occurs, or there may be precipitation, when the solution is supersaturated. Precipitation does not always occur in supersaturated solutions, its triggeringand progress depend on many causative factors.

The deviation of a solution from equilibrium is measured by the saturation index SI, introdu-

ced by Langmuir (1971) and used widely by karst researchers (see White, 1988; Ford and Williams, 1989, for a description of the general concept). The saturation index is defined as the relation of the ion activity product for the dissociation of the mineral to the thermodynamic equilibrium constant K of the reaction. For gypsum the saturation index is:

$$SIgyp = \log a(Ca^{2+}) \; a(SO_4^{2-}) \; \gamma Ca \; \gamma SO_4 / Kg \qquad [3]$$

where: γCa and γSO_4 are coefficients accounting for the ion pairing effect.

SI is zero if water is in equilibrium with the mineral, it has negative values for undersaturated (aggressive) solutions, and positive values for supersaturated solutions.

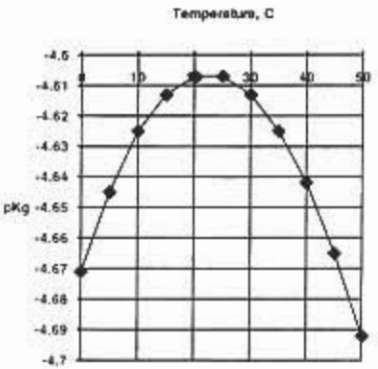


Fig. 4. Equilibrium constant Kg as a function of temperature.

In natural conditions equilibrium is rarely attained, or it is disrupted by changes in factors and conditions that affect solubility. The dependence of the solubility on various properties of a solvent and solid are not clearly and unambiguously described either theoretically or by quantifiable means. The main factors affecting the *solubility of gypsum* are oulined below.

2. Main factors affecting the solubility of gypsum

Pressure applied to the rock. Korzhinsky (1953) showed that the solubility of minerals increases when the rock fabric experiences pressures higher than that of the groundwater. Experimental data by Manikhin (1966) suggest that the solubility of anhydrite increases sharply with the increase in pressure: each 0.01 Pa increase in pressure results in a 3 to 5 times increase in the solubility. The solubility of gypsum is reported to increase 4 times with each additional 0.1 Pa. Consequently, the solubility of anhydrite becomes higher than that of gypsum under applied stress. Pecherkin (1986) discussed the stress field in the Polazna gypsum/anhydrite massif of the Urals and, referring to Manikhin's data, evaluated that the solubility of anhydrite in the zones of high stress should be 2 to 5 times higher than in the low stress areas. This factor is believed to have a significant role in the differentiation of dissolution-recrystallization and hydration processes on a massif scale. For gypsum, the increase in solubility with depth caused by the above effect will be about 6% at a depth of 50m (average pressure 1.5 x 10^{-3} Pa) and about 14% at a depth of 100 m (2.3 x 10-4 PA). The effect is likely to be important to karst development in all

T °C	GT, kal	pKg	Kg x 10^5
0	5839	4.671	2.131
5	5912	4.645	2.266
10	5993	4.625	2.370
15	6082	4.613	2.439
20	6183	4.607	2.472
25	6286	4.607	2.471
30	6400	4.613	2.436
35	6522	4.625	2.370
40	6653	4.642	2.278
45	6791	4.665	2.165
50	6938	4.692	2.034

environments, not just in deep-seated ones.

Grain size. G.Hewlett reported that saturation with respect to gypsum for grains of 2m in size is reached at a concentration of 15.3 mM/L. However, for 0.3m-sized grains the solution becomes saturated at 18.2 mM/L and the solubility effectively increases by 20% (cited after Sokolov, 1962). Sonnenfeld (1984) indicated that the solubility of gypsum reaches a maximum for crystals in the size range of 0.2 - 0.5μ, whereas the solubility of anhydrite is highest for crystals around 2.8μ in size.=

Differential solubility with respect to grains of different sizes results in interstitial (pore) waters that can be undersaturated with respect to small-sized grains, but supersaturated with respect to large grains. This plays an important role in recrystallization and hydration processes (see sections 5 and 6 below), and perhaps in the development of irregular small-scale porosity. Selective dissolution within heteroblastic rock may facilitate surface retreat by water because of the preferential removal of small-sized grains that initially provide a cement between the larger ones. The differential solubility of crystals of various sizes is illustrated well by observations made in the gypsum caves of the Western Ukraine, where single giant crystals of selenite within the heteroblastic rock mass commonly protrude from the walls and ceilings as pendants. They are apparently less soluble than the surrounding, finer-grained, matrix.

Solubility in various salt solutions. All natural waters contain some dissolved salts, and it is well known that these can affect the solubility of other minerals.

Ion pairing effects reduce the activity of ions and result in increased solubility. Ford & Williams (1989) noted that an increase of up to 10% in gypsum solubility was possible in typical karst waters. However, they stressed the far greater importance of the effect on the values of calculated saturation indexes. If pairing is not taken into account, the SI values are overestimated. It is likely that many reported cases of supersaturated waters in gypsum karst are actually related to this effect.

The presence of ions foreign to the solid phase considerably increases the solubility of gypsum due to the enhanced ionic strength of the solution; figure 5 shows the effect of NaCl (after Shternina, 1949). With increasing concentrations of sodium chloride the solubility of gypsum increases. After quickly reaching a maximum of 7,326 mg/L at 138.75 g/L of NaCl, it then decreases slowly, but remains much higher than the solubility in pure water. The solubility of gypsum in solutions containing other salts is higher still; the presence of $Mg(NO_3)^2$ can boost the solubility of gypsum by almost 6 times when compared with the value for pure water. Figure 6 is taken from the work of Shternina (1949) and shows similar curve shapes, although characteristic points are different. The study of complex systems, common in nature (Mel'nikova & Moshkina, 1973) indicates gypsum solubilities of 5.9 to 6.3 g/L in solutions containing high concentrations of $MgSO_4$ (5.6 to 18.2%) and NaCl (0.2 to 14.1%). James (1992), referring to Paine et al, (1982), quoted a good example from the Poechos dam in Peru. Here direct determinations of the solubility of gypsum in groundwater samples from wells, gave $CaSO_4$ values as high as 6.2 g/L , three times the solubility in pure water and 35% more than the maximum solubility in sea water; these water samples also contained Na, K, Mg, HCO_3, Cl, SO_4 and NO_3 ions.

The effect of foreign ions is very important for gypsum karst development. Other salts are

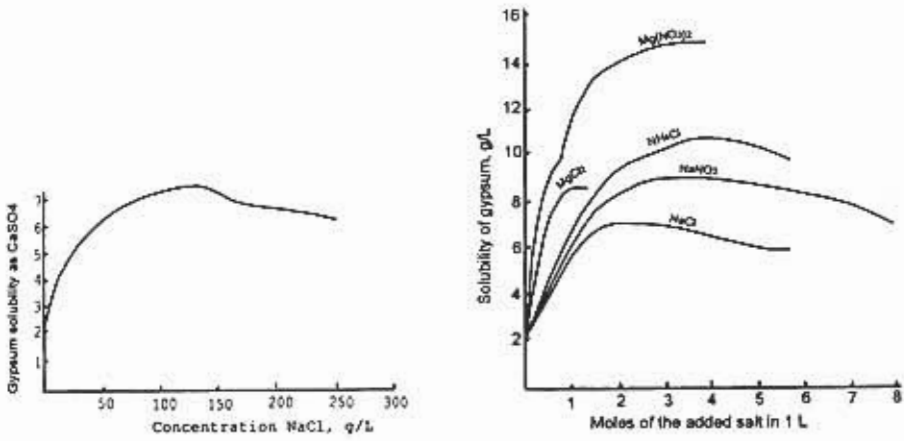


Fig.5. The dependence of solubility of $CaSO_4$ on concentrations of NaCl in solution at 25°C (After Shternina, 1949).

Fig.6. The solubility of gypsum in water solutions of salts at 25oC (After Shternina, 1949).

commonly associated with gypsum in evaporate formations and the groundwater of many aquifers, particularly the deep-seated ones, may contain high levels of dissolved salts.

The presence of common ions in solution (ones which are the same as the dissolving mineral, but introduced from some other source), decreases the solubility of the common mineral. Ca^{2+} is the common ion for gypsum and calcite and the effect occurs in many karst areas where intercalated or adjacent sulphate and carbonate layers occur. The effect is more pronounced with respect to the solubility of calcite and is of lower significance for gypsum dissolution. The study of the system Ca^{2+} -HCO_3^- - SO_4^{2-} - H_2O by Wigley (1973) allows the assessment of the relative contributions to the total concentration of calcium of calcium derived respectively from gypsum and calcite. It also allows the evaluation of the equilibrium (disequilibrium) for each mineral (Fig.7). The partial pressure of CO_2 is an independent variable influencing the solubility of calcite, but it has a negligible effect on gypsum solubility (Sokolov, 1962). Zdanovsky (1956) suggested that the solubility of some salts, including gypsum, decreases slightly with increasing CO_2. Where only gypsum dissolves, but CO_2 is supplied to the water from soil cover or from other sources, net deposition of calcite may occur as saturation with respect to $CaCO_3$ is quickly reached. The relationship between gypsum dissolution and calcite deposition in the presence of CO_2, in the shallow subsurface, was studied by Forti & Rabbi (1981). They calculated the equilibrium pattern for the CO_2 - H_2O - calcite - gypsum system with respect to CO_2 and pH (Fig.8). The effect is responsible for calcite deposition in many gypsum caves that are close to the surface, but it is also responsible for the replacement of gypsum with calcite in the reducing environment of some confined aquifers. However, since the effect has a low influence on gypsum solubility, and since much gypsum disso-

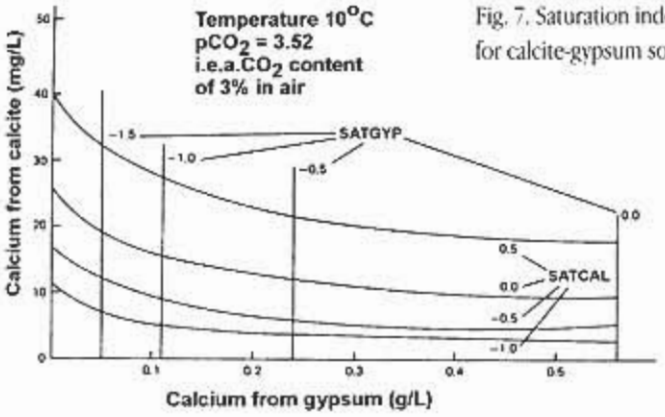


Fig. 7. Saturation index curves for calcite-gypsum solutions (After Wigley, 1973).

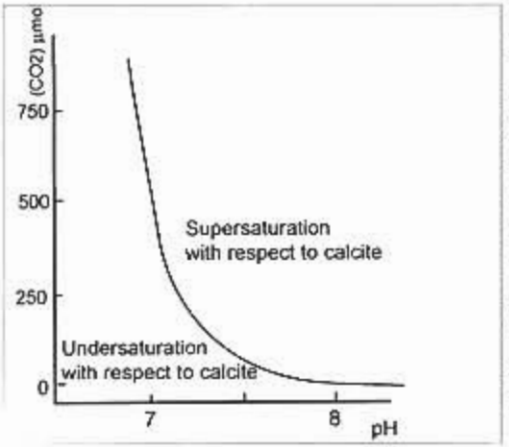
lution occurs without any CO_2 involvement, it appears unreasonable to claim gypsum karst as a three-component system (Forti & Rabbi, 1981).

3. Factors maintaining the dissolution potential with respect to sulphates

Sulphate reduction. The reduction of dissolved sulphates by microbes (including heterogeneous assemblages of Desulfo-x) is a common process in confined aquifer systems where sulphate rocks and dispersed organic matter are present. The process is described by the following simplified reaction:

$$SO_4^{2-} + 2CH_2O \xrightarrow[\text{anaerobic bacteria}]{} H_2S + 2HCO_3^- \quad [4]$$

Fig. 8. The equilibrium pattern for the system CO_2 - H_2O - calcite - gypsum with respect to CO_2 and pH at 10°C (After Forti & Rabbi, 1981).



During sulphate reduction, sulphate ions are consumed and removed from the solution, making it able to dissolve more sulphates. Calcium and bicarbonate commonly react to precipitate $CaCO_3$, utilising the HCO_3^- generated by the above reaction. Epigenetic calcite masses can also form as a result. Calcium cations can also be exchanged with sodium derived from intercalated or surrounding rocks. Sulphate reduction appears to be a very important mechanism in maintaining the dissolution potential of groundwater with respect to gypsum in confined aquifers, especially if vertical cross-formational hydraulic communication is present (see Klimchouk, 1997, Chapter I.5 in this volume). In hydrochemistry the effect has

been known for a long time and its possible general relevance to karst development had been outlined by Kaveev (1963), Turyshev (1965) and some other workers. Recently its actual importance for speleogenesis in gypsum has been emphasised by Klimchouk (1994; 1996).

De-dolomitization. Dolomite is commonly associated with or intercalated with gypsum. Stankevich (1970) pointed out that the process of de-dolomitisation generates further dissolutional capacity with respect to gypsum, because Ca^{2+} is removed from solution and the sulphate ions react with the Mg. The process favours the development of gypsum karst in deep-seated environments.

Suspended crystals. Pechorkin (1986) reported experimental results suggesting that when a solution approaches gypsum saturation, small crystals originate in the presence of the solid phase. These can then be carried in suspension by flowing water. Such crystals begin to form at $CaSO_4$ concentrations of 1.1 to 1.5 g/L and reach a maximum of 10-15% of the total dissolved $CaSO_4$ at concentrations of 2.2 g/L. Thus, an additional 0.28 - 0.42 grams of gypsum can be dissolved in each litre of water. The cited author did not discuss what causes precipitation in undersaturated solvents.

4. The dissolution kinetics of gypsum and anhydrite

Dissolution is a heterogeneous reaction occurring at the boundary between two phases. Molecular dissociation of gypsum occurs almost instantaneously, so that dissolution is controlled solely by diffusion across the boundary layer. Dissolution rates depend on boundary layer conditions and the concentration gradients across it; they are described by the following equation:

$$dC/dt = (KA/V)\ (C_s - C)^n$$

Where dC/dt is a rate of change of concentration in a volume V of solution with a bulk concentration C, Cs is the solubility of the dissolved substance, A is a surface area and K is a rate constant varying with boundary layer conditions, mineral properties and surface roughness.

Theoretical and experimental studies of the dissolution kinetics of gypsum and anhydrite are numerous, although many of the results are conflicting. The most comprehensive treatment of the topic is given in James & Lupton (1978) and James (1992). The brief summary below is based largely on these works.

The main difference in the dissolution kinetics between gypsum and anhydrite lies in the power of the term n. It was shown by Zdanovsky (1956), Liu & Nancollas (1971) and James & Lupton (1978) that the gypsum dissolution follows the first order equation, while the dissolution rate of anhydrite obeys the second order equation. The latter reflects partial control of the surface reaction rate, which is assumed to be hydration. Figure 9 shows this difference by plotting concentration against time, with an overlay of theoretical curves. For gypsum, the flow time (distance) at which solution approaches 90% of saturation is very short; the rate of dissolution decreases by several orders of magnitude above this limit. Similar dependence of gypsum dissolution rates on the saturation were reported by Laptev (1939), Kuznetzov (1947) and Pechorkin (1986). This fact

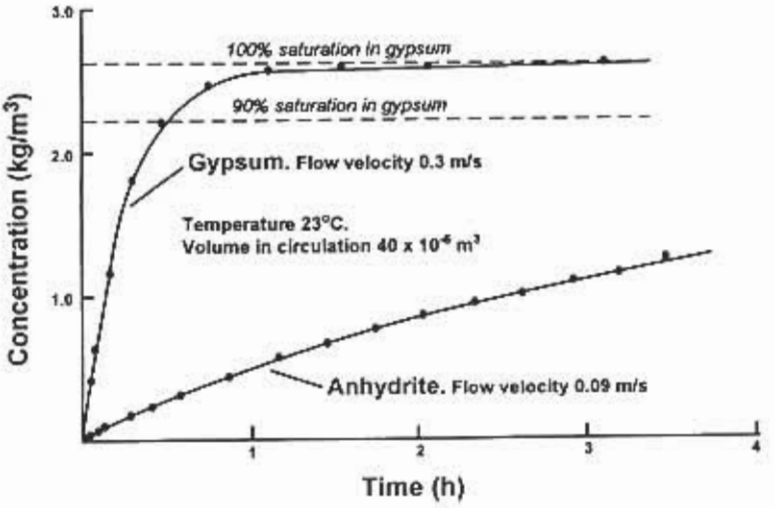


Fig. 9. Dissolution rates of gypsum (a) and anhydrite (After James & Lupton, 1978).

has important speleogenetic consequences (see Klimchouk, 1997, Chapter 6 in this volume).

The second order equation for the dissolution of anhydrite causes much lower dissolution rates. The travel distance for water flowing through fissures in anhydrite could be rather long before sufficient $CaSO_4$ is dissolved to precipitate gypsum. The conditions required for gypsum to be precipitated from solutions that have dissolved anhydrite are reached gradually due to the second order dissolution kinetics, but when they are achieved the precipitated gypsum may seal the seepage paths.

The main concern of dissolution kinetics studies are variations in K, which is not a true constant but one that varies with changing boundary layer conditions. These conditions affect the thickness of the layer, which varies with the flow velocity over the dissolving surface, the ionic strength of the solution and its temperature. The appropriate values of K that encompass these variables are considered briefly below, along with some other parameters, including the diffusion coefficient that reflects ion mobility (values for the common inorganic ions are rather similar). Theoretical calculations of rate constants for transport-controlled dissolution are rarely adequate and experimental data are used in most cases (Frank-Kamenetsky, 1987).

Gypsum and anhydrite, (which are polar molecules with strong electrical dipoles) tend to form thick boundary layers, which are thus easily subjected to thinning (stripping) by flowing water. This explains why K values and dissolution rates are strongly dependent upon flow velocities. Figure 10 shows linear dependencies for dissolution within a laminar flow regime; for each doubling of flow velocity over gypsum, K doubles, but for anhydrite it only increases by one and half times. Note that K has small positive values even in stationary water. Anhydrite shows a rapid increase in K with only a very small flow velocity. As a turbulent regime sets in, K is expected to

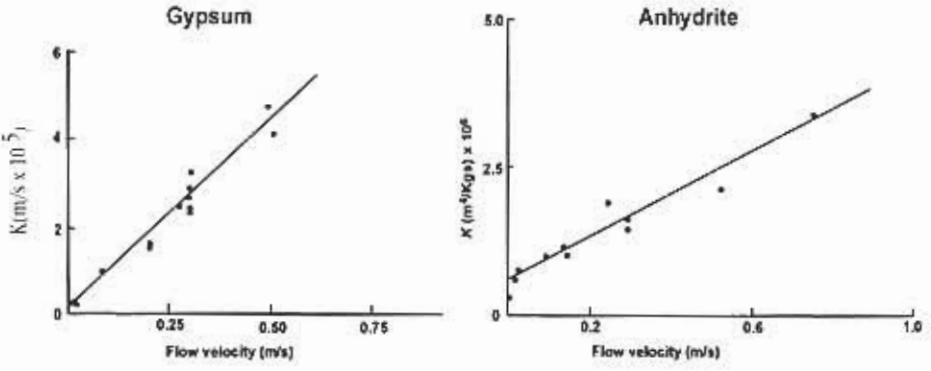


Fig. 10. The dependence of the rate constant for gypsum and anhydrite upon flow velocity (After James & Lupton, 1978).

increase abruptly, but there are no experimental data for gypsum. In the case of calcite an increase by a factor of ten is reported to occur. James (1992) postulates that gypsum and anhydrite should exhibit similar increases. The strong dependence of gypsum dissolution rates upon flow velocity has speleogenetic implications (see Klimchouk, 1997; Chapter 1.6 in this volume). It also has a morphological expression manifested in a variety of dissolutional sculpting features that form readily on gypsum surfaces (see Sauro & Macaluso, 1997; Chapter 1.8 in this volume).

The presence of other dissolved salts increases the ionic strength of a solution causing compression of the diffusion layer and hence raising K values. This is illustrated Table 2, which summarises data presented by James & Lupton (1978). The rate constant almost doubles for gypsum, but it increases by a factor of 9 for anhydrite, as the salt concentration rises from 0 to 10 g/L. Apparently, the effect needs to be allowed for when considering karst development in deep-seated settings, where a high content of sodium chloride ions commonly occurs. This is especially true if anhydrite rocks are considered.

Data on the temperature dependence of K for gypsum are given in Table 3. James (1992) suggests that a proportional relationship of log K to 1/T should be used to adjust K values from one temperature to another.

5. Gypsum-anhydrite-gypsum conversions

The thermodynamic stability and the solubility of gypsum and anhydrite are greatly affected by changes in the physical and chemical parameters that occur within common geological environments. The conversions of gypsum to anhydrite and back to gypsum are common processes.

Geological data suggest that in evaporitic environments at shallow depths sulphates occur mainly in the form of gypsum, but at depths exceeding 450m anhydrite predominates. However, there are numerous exceptions to this usual situation, with gypsum occurring at greater depths, and localised or dispersed anhydrite being found in the shallow sub-surface (for a brief review see

Table 2. The effect of sodium chloride on the dissolution rates of gypsum and anhydrite (After James & Lupton, 1978)

Concentration of NaCl, g/L	Gypsum: $K \times 10^5$ (m/s)	Anhydrite: K ($m^3\ kg^{-1}s^{-1}$)
0	1.5	0.45
10	2.9	0.77
30	3.2	1.7
100	5.8	5.8

Table 3. Variation of the rate constant of gypsum dissolution with temperature: flow velocity 0.25 m/s (After James & Lupton, 1978)

Temperature, C°	$K \times 10^5$
5	0.8
15	1.7
23	2.6

Klimchouk & Andrejchouk, 1997; Chapter 1.1 in this volume). Theoretical and experimental data on the stability of sulphate minerals and the mechanisms of conversions are also controversial, with some misleading views. This section discusses the modern understanding of the problem, which is important for the interpretation of karst processes and associated phenomena in gypsum and anhydrite.

The stability fields for gypsum and anhydrite are depicted in Figure 1. The presence of other salts, such as sodium chloride, also affects their stability and solubility. In evaporitic basins calcium sulphates primarily precipitate in the form of gypsum (Strakhov, 1962; Sonnenfeld, 1984). Anhydrite is believed to originate mainly by the dehydration of gypsum due to the effects of high pressure and temperature during burial. However, Sonnenfeld (1984) suggested that the factors of high pressure and temperature alone are insufficient to explain the transition of gypsum to anhydrite. He showed that gypsum dehydration occurs widely during early diagenesis, where it takes place at shallow burial depths, by interaction with hygroscopic brines of Na, Mg or Ca chlorides. James (1992) noted that in very hot climates gypsum can dehydrate to anhydrite when it is exposed at the surface, with to in excess of 42°C, or where highly saline water is present. These changes are slow and mainly unaffected by diurnal cycles, but over longer periods they can be affected by seasonal changes. It can be concluded that in such conditions the conversion will occur through the dissolution of gypsum and subsequent precipitation of anhydrite, not by alteration of the solid phase.

Regardless of how the anhydrite formed, most mature gypsum rocks appear to be secondary and to have formed by hydration of anhydrite to gypsum after uplift to shallow sub-surface levels. Consequently, the conversion of anhydrite to gypsum is a major significant process for karst development. It also has important implications for engineering and construction practices.

The common view is that the conversion of anhydrite to gypsum is accompanied by an overall increase in rock volume. Kushnir (1988) quoted an increase in rock volume of 18.25%, Pettijohn (1975), 30-50%; Gorbunova (1977), 64.9% and Ford (1989), 30-67%. Sonnenfeld (1984) quoted an increase of 61%, but stressed that a pressure of 60-150 kPa, corresponding to a 60-75m thickness of overlying rocks, would effectively balance the pressure generated by hydration and thus prohibit expansion. This effect is referred to widely in texts about karst (e.g. Jakucs, 1977). These argue that such expansion would seal most of the fissures in the gypsum/anhydrite rock, preventing water circulation and karst development. When expressed in this generalised form such views are misleading. Close examination of the problem reveals that expansion need not necessarily occur,

and that a variety of mechanisms may be involved in the conversion processes. The problem is not clear theoretically, especially when rate processes are concerned, and the field data are controversial. Reported observations of heave and swelling, claimed to have resulted from the hydration of anhydrite, may relate to specific local conditions. Geological observations of folded structures in gypsum and the deformation of adjacent layers (assumed to prove expansion by anhydrite-gypsum conversion) may well be explained by other mechanisms (see Klimchouk et al, 1995 for an example). Furthermore, other field data show that in some underground and opencast anhydrite mines no heave has occurred (e.g. Kaiser, 1976; James, 1992). Experimental data and interpretation also conflict, suggesting that expansion during the conversion from anhydrite to gypsum is not always the rule.

Nekrasov (1945) derived an expression describing the limit of compression in a system Δ_{lim} caused by full hydration:

$$\Delta lim = (A/d_a + B) - c/d_c \qquad [5]$$

Where A is the quantity of the original substance of specific weight d_a, B is the quantity of added water (d=1) and C is the quantity of hydration product of specific weight d_c. A system will compress proportionally to the volume of water involved in the reaction; this means that changes depend on whether the process proceeds in an open or a closed system.

Theoretical calculations (Zanbak & Arthur, 1986; Pechorkin, 1986; Kushnir, 1988; James, 1992) suggest that when anhydrite converts completely to gypsum the molar volume of the solid phase increases by factor of 1.626, but the overall volume of the system reduces by 8.7%. Pechorkin (1986) reported experimental data for a closed system. He used 18-22 gram samples of anhydrite placed respectively in distilled water and in a saturated solution of $CaSO_4$. These were hermetically sealed for 1.5 years under normal pressure conditions. Complete conversion to gypsum occurred, resulting in a reduction in the overall system volume of 3% in the case of the distilled water and 2.8% for the saturated solution. Simultaneously, the solid volumes increased respectively by 3.1% and 4.1%. However, the short time reported for the complete conversion to gypsum apparently conflicts with another experiment performed by James (1992). He used a small disk of anhydrite immersed in water for 12 years. This displayed the growth of gypsum crystals on it, but it was not fully converted to gypsum.

In nature the mechanisms and rate of hydration of anhydrite to gypsum depend on many factors including: 1) the texture and structure of the rock, 2) the form and chemical composition of water coming into reaction and 3) the temperature and pressure conditions.

Most authors believe that hydration proceeds through the dissolution phase, so that anhydrite dissolves to provide a solution of $CaSO_4$ which then precipitates from solution as gypsum (e.g. Kuznetsov, 1947; Mossop & Shearman, 1973; Quinlan, 1978; Kushnir, 1988; James, 1992). However, Pechorkin (1986) argued that hydration through dissolution-precipitation accounts for only a minor proportion of re-hydrated rocks. He considered that the main process proceeded through the diffusion of water molecules (or hydroxyl ions) into the anhydrite crystal lattice; crystal lattice defects are said to favour this process. This is also supported by data suggesting that

the crystal lattice defects in gypsum are inherited from anhydrite (Pechorkin, 1986). In reality, it is likely that the mechanisms of dissolution-precipitation and diffusion are closely interrelated.

There are two main types of water that are in contact with anhydrite rocks: 1) interstitial water, which is retained in pores within a rock and, 2) water that circulates freely, through joints and other partings. The former is disseminated throughout the rock mass, while the latter contacts only the surfaces of large rock blocks. The author believes that interstitial water plays the most important role in the hydration of anhydrite rocks, even though its volume is relatively small, due to the low porosity of anhydrite (note that not only the effective porosity, which is negligible in anhydrite, but total porosity should be considered). If fissuring within a deep-seated anhydrite is low, then such a system can be viewed as closed, with no additional water entering or leaving the system. When anhydrite is under thermobaric conditions in its stability region, the associated water saturated with $CaSO_4$ is in dynamic equilibrium with the mineral. When the rock becomes less buried and moves out of the stability field of anhydrite the equilibrium is disturbed and the interstitial solutions precipitate gypsum. In closed or semi-closed conditions only partial conversion may be achieved resulting in mixed anhydrite-gypsum rock, apparently with no expansion of the solid phase. Conversely, some shrinkage of the overall solvent-solid system may cause some water to be sucked from adjacent beds into the hydration zone. With continuing emergence of the rock to progressively shallower depths, imposed fissuring and free water circulation can result in open system conditions, allowing water to partially recharge the remaining pore spaces. In this situation, localised hydration along flow paths becomes increasingly important. Water circulation through open fissures in anhydrite and gypsum at shallow depths may be fast enough to ensure that dissolution will remove any excess gypsum. In this situation, no overall expansion of the rock may be expected to occur. The importance of the dissolutional removal of material is supported by the fact that the porosity of secondary gypsum is evidently higher when compared with that of anhydrite.

This explanation combines several possible hydration mechanisms and encompasses most of the known geological peculiarities of gypsum-anhydrite formations. It suggests that, in natural conditions, the mechanisms and rates of anhydrite to gypsum conversion depend on the tectonic regime, the water-bearing properties of surrounding sediments and both the regional and local flow regimes. It also suggests that, in most cases, no expansion in volume occurs during hydration. Expansion resulting in heave can be expected where thin layers of anhydrite are suddenly (in a geological sense) released from their confining pressure and exposed to water; perhaps a specific mode and rate of water ingress is required for expansion to occur. This view is in agreement with the occurrences of heaves definitely identified as being due to hydration of anhydrite to gypsum, which have been reported from tunnels or mines (James, 1992).

6. Recrystallization

Sulphate rocks undergo recrystallization throughout their diagenetic and catagenetic history. Evaporites precipitated from aqueous solutions contain connate pore water preserved from their original deposition. Some of these connate brines are expelled from the pores by compaction during burial, but some remain. When meteoric water begins to circulate through open partings,

it can replace part of these interstitial connate brines and induce recrystallization. The gypsum-anhydrite-gypsum conversions discussed above further complicate the water-rock interaction. All these processes continuously disturb the water-rock equilibrium and are accompanied by recrystallization of the deposits.

Recrystallization considerably affects the various properties of gypsum and anhydrite by altering, among other things, a rock's texture and structure, porosity and strength. Consequently, it may influence karst development in many ways. Aggradation recrystallization is an important factor because generally the solubility of gypsum is higher for the smaller crystals. The different solubilities and dissolution rates for crystals of mixed size are the main cause of recrystallization and directly influence the karst process (see sub-chapter 2 above and Chapter 1.3 below for details). However, the most important effect of recrystallization on karst is the alteration of the rock permeability. Two extreme examples are cited below to illustrate the possible effects.

In the Western Ukraine recrystallization has caused severe textural and structural differentiation of the buried gypsum sequence, with the formation of three distinct horizons (Klimchouk et al, 1995). This differentiation has also caused the formation of largely independent superimposed networks of lithogenetic fissures confined to each horizon. These fissure networks have served as primary paths for meteoric waters, which have entered the sequence from the underlying aquifer and circulated upwards under artesian conditions (Klimchouk, 1992). The structure of the lithogenetic fissuring was exploited by dissolution to generate the structure of huge maze cave systems. Thus, textural-structural differentiation of the gypsum by recrystallization was a primary guiding factor of this speleogenetic effect.

In Sicily, where gypsum massifs are exposed at the surface, a distinct crust, up to one metre thick, is formed and within this all the open fissures tend to seal (for details see Macaluso & Sauro, this volume; 1997). This is probably the result of gypsum recrystallization caused by the loss of interstitial water from the exposed rock, and by a specific set of dissolution-precipitation processes related to local climatic conditions. The exact mechanisms are not yet clear and need to be studied, but the effect upon karst development is obvious. The crust prevents the dispersed recharge of the gypsum massifs from the surface, and water is thus allowed to penetrate deeper into the gypsum only along selected major fissures and faults.

Another morphogenetic effect of recrystallization of the uppermost exposed layer is the formation of small ridges, blisters or tumuli, which occur where the crust coincides with the sedimentary bedding. These forms clearly result from the deformation of the geomechanically independent (detached from the substrate) outer layer by compressive stress, possibly caused by recrystallization. However, for expansional recrystallization to occur some specific conditions are required: 1) gaping bedding planes sub-concordant with the surface, 2) pathways for meteoric water to access the bottom of the outer layer and, 3) appropriate climatic conditions. Contraction and fracturing of the outer layer precede the expansional recrystallization, having first provided conditions 1 and 2 above. Meteoric waters, which escaped surface evaporation and run-off to the shallow sub-surface, are drawn continuously upwards back to the surface by capillary action through the pores in the outer layer, and this leads to aggradational recrystallization. The stresses generated by the volume expansion are released through swelling of the outer layer and manifested as ridges and blisters.

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