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ORIGINAL ARTICLE

Gypsum: a review of its role in the deterioration of building materials

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Abstract The deterioration of buildings and monuments by gypsum is the result of crystallization cycles of this salt. Although gypsum can dehydrate to a hemihydrate, the mineral bassanite, and to an anhydrate, the mineral anhydrite, this reaction occurs in nature on a geological time scale and therefore it is unlikely to occur when gypsum is found on and in building materials. The $CaSO_4$–H_2O system appears deceptively simple, however there are still discrepancies between the experimental and thermodynamically calculated data. The reason for the latter can be attributed to the slow crystallization kinetics of anhydrite. Apart from this, the large numbers of studies carried out on this system have focused on industrially important metastable phases, such as the hemihydrate and soluble anhydrite. The paper presents a review of the studies dealing with the phase equilibria of the $CaSO_4$–H_2O system as well as the influence of other salts on the solubility of gypsum. It tries to glean out the relevant information that will serve to explain the deterioration observed on building materials by the crystallization of gypsum and thus allows developing improved conservation methods.

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Introduction

Gypsum is one of the most ubiquitous compounds found both in nature as well as on buildings and monuments. On the latter, its presence as black crusts can be attributed mostly to sulphur bearing air pollutants. Thus, it is one of the most generalized deterioration factors in urban environment. However, given its low solubility, it is not as aggressive as other more soluble salts such as sodium sulphate. Nonetheless, with a better understanding of the various deterioration mechanisms, the importance of gypsum as a deterioration factor over time has been increasingly recognized. For example, the decay rate of mural paintings resulting from salt contamination was carefully measured and it was established that gypsum veils cause a significant deterioration but that this is 10–100 times slower than that caused by a more soluble salt such as nitratine ($NaNO_3$) (Zehnder 1996).

Gypsum, as sodium sulphate, can dehydrate to a lower hydrate, the hemihydrate, and to an anhydrous phase, anhydrite. Therefore the possibility of the dehydration–hydration reaction playing a critical part in the deterioration mechanism, as it does for sodium sulphate, was seriously considered.

The industrial importance of the hemihydrate, commonly known as plaster of paris, prompted many of the studies that were carried out on the $CaSO_4$–H_2O system. Nonetheless, nearly 70 years ago, Posnjak pointed out *"It seemed very surprising that, considering the relative simplicity of the system $CaSO_4$–H_2O, and its* *accessibility for study, it could remain over a period of so many years the subject of so much controversy"* (Posnjak 1938, p 248). That this is, in part, still the case can be attributed to the crystallization kinetics of the different phases in the system. Thus, a comprehensive approach to understand the true nature and behaviour of this ubiquitous compound with regards to its function in the deterioration of monuments is still missing. This paper attempts to correct this situation by synthesizing the various studies undertaken by different disciplines with the aim of elucidating the deterioration function of this salt. However, it does not attempt to address the issue of gypsum or anhydrite mortars or that of plasters and stuccos since this topic deserves a review of its own.

The vast literature published on gypsum and related compounds, the apparently contradictory information presented, have resulted in much confusion regarding the behaviour of this compound. This is clearly evident when considering questionable conservation interventions such as described by Grassegger (2002) where an alabaster sarcophagus was vacuum impregnated with methyl methacrylate monomer, after several days of drying at 100°C, and then re-heated to 80°C to ensure complete polymerization. Within a year, severe damage such as warping and cracking had developed.

Background information

Geological background

Gypsum is the most abundant sulphate mineral occurring in extensive bedded sedimentary deposits, sometimes of considerable thickness, and in association with limestone, shale and marls, particularly in Permian and Triassic formations (Deer et al. 1975). It also occurs in evaporite minerals giving rise to considerable deposits in saline lakes and salt pans. When deposited from concentration of sea water, gypsum ($CaSO_4{\cdot}2H_2O$) precipitates out first, followed by the deposition of anhydrite ($CaSO_4$) as the salt concentration increases.

Both gypsum and anhydrite are rock-forming minerals, the former sometimes referred to as gyprock. Some of these deposits can be hundreds of metres thick. In dry climates, anhydrite deposits have remained as such for over a millennia. However, in the presence of groundwater they can turn into gypsum to some 15 to 40 m depth, this depth increasing two-fold in humid climates (Ottemann 1952). To be noted is that gyprock, as well as anhydrite deposits can give rise to karst formations, similar to those of limestone but with some unique forms developing, such as creep bubbles. The hydration of anhydrite (generally called gypsification) and the volume expansion associated with this reaction has been considered the cause for the observed powdering of the surface of anhydrite rock into gypsum (Lazzarini and Laurenzi Tabasso 1986) or the formation of the creep-bubbles in gypsum rock. However, for the latter case it has been clearly established that the deterioration occurs due to dissolution of gypsum and the consequent expansion upon its reprecipitation (Calaforra Chordi 1998, pp. 90–95). The hydration reaction has been shown to be significantly accelerated when other salts, such as NaCl, are present as discussed in a subsequent section.

Mineralogy

Calcium sulphate can appear as three distinct minerals: gypsum (dihydrate), bassanite (hemihydrate) and anhydrite (anhydrous). These are the three phases which can crystallize in contact with water, although it is to be remembered that the hemihydrate is a metastable phase. Gypsum occurs in several varieties: crystallized as selenite, massive as alabaster, or fibrous as satin spar. Gypsum crystals are monoclinic, taking elongated tabular shape of various thicknesses or prismatic to acicular shape and, many times, forming rosette-like aggregates for both shapes. This description corresponds mainly to those observed in the growth of gypsum efflorescence. Bassanite occurs as microscopic needles, and anhydrite crystals are orthorhombic, dipyramidal, and usually massive. They also occur in aggregates and often as groups of parallel or radiating fibres. The natural anhydrite is referred to as $CaSO_4$(II) or β-CaSO4.

Industrial phases

Industry has studied extensively the procedures for manufacturing the hemihydrate, generally called plaster of paris, by dehydrating gypsum. Depending on the dehydration procedure, two varieties have been obtained, α- or β-$CaSO_4{\cdot}0.5H_2O$. Heating gypsum in a humid atmosphere produces the first variety, while heating it in a dry atmosphere results in the second variety (Kelley et al. 1941; Freyer and Voigt 2003). The hemihydrate has been found to have a monoclinic structure which allows channels to accommodate the water molecules. Hence, dehydration of this compound can proceed without disruption of the structure.

The dehydration of the hemihydrate produces what has been called "soluble anhydrite", $CaSO_4$(III) or γ-$CaSO_4$. Its properties vary depending on the condition under which is was obtained and whether the original compound was an α- or β-hemihydrate (Kelley et al. 1941; D'Ans 1968). It has been reported to have hexagonal symmetry (Freyer and Voigt 2003). There also exists a high temperature variety of anhydrite, $CaSO_4$(I) or α-CaSO4, which is stable above 1,180°C.

Phase equilibria: a chronological review

Since the late nineteenth century, the equilibria between gypsum, anhydrite and hemihydrate have been studied by researchers such as Le Chatelier, Erlenmeyer, Kohlrausch and van't Hoff. Le Chatelier (1887) was the first to show that the heating curve of gypsum showed two breaking points, corresponding to the partial dehydration into the hemihydrate and the subsequent dehydration into the anhydrous phase, at 128 and 163°C, respectively. He alerts to the fact that the establishment of the equilibrium point for the dehydration reaction of gypsum to hemihydrate is very slow. Finally, he explains the setting of plaster (the hemihydrate having a much higher solubility than gypsum) as corresponding to a precipitation of gypsum from a solution of the hemihydrate as the solution would be supersaturated with regards to gypsum.

Hulett and Allen (1902) studied the solubility of gypsum and found that this reaches a maximum at 40°C, decreasing afterwards. Further work by Hulett (1905) points to the unusual behaviour of gypsum requiring over half-a-day to produce a saturated solution—approaching from an undersaturated solution—and even weeks, if approached from a supersaturated solution.

van't Hoff et al. (1903) suggest the existence of a second anhydrous form—"soluble anhydrite"—capable of undergoing a fast re-hydration. However, in their experiments, they sometimes mistake this compound for the hemihydrate, and thus consider that there can be a direct dehydration of gypsum into anhydrite without passing through the intermediate hydration step. This assumption plus some experimental errors have been responsible for much of the resulting confusion in this area (see Posnjak 1938; D́Ans et al. 1955 for a thorough discussion). However, they do point out some interesting facts such as:

1. The hemihydrate does not dehydrate to soluble anhydrite below 36°C and that below this temperature the soluble anhydrite is capable of absorbing moisture to form the hemihydrate;
2. The dissolution of gypsum in water occurs with a volume contraction of the system while its precipitation results in an expansion (as is the case for most soluble salts);
3. The dehydration of gypsum to hemihydrate in solution results in an expansion; and,
4. The hydration of the hemihydrate (setting of plaster) results first in a contraction (as the water binds chemically—opposite reaction to point (3) above—and is followed by an expansion originating by the subsequent crystallization of gypsum from the remaining solution between the original fibrous growth formed as indicated in point (2).

Heusinger von Waldegg (1906) published a state-of-the-art review on gypsum and its related compounds. He highlights the fact that the kinetics of the dehydration of gypsum to hemihydrate is slow. To initiate a relatively fast reaction a temperature of 120°C is required, though dehydration will continue even at lower temperatures as long as it does not fall below 107°C. A faster dehydration can be achieved by increasing the temperature to 128°C. The dehydration will occur by loss of liquid water, even when occurring in solution, as long as the temperature is above 107°C. A significant difference in dehydration rate can be observed depending on the physical condition (crystallinity, particle size, etc.) of the gypsum. Poorly crystallized gypsum will lose its hydration water faster than a well crystallized variety. In addition, as discussed below, solutions of other salts, such as NaCl, $MgCl_2$ and $CaCl_2$, can dehydrate gypsum as a result of the lower water vapour pressure of these solutions.

Posnjak (1938) confirms the existence of the soluble anhydrite postulated by van't Hoff and already confirmed by Weiser et al. (1936). He gives a transition temperature for the gypsum–hemihydrate reaction of 97.5°C (in reasonable agreement with the 100°C determined by Davis 1907). Since above 42°C the stable phase is anhydrite, gypsum in contact with its solution can remain in a metastable condition up to 97.5°C (the vapour pressure of the saturated solution of gypsum) at which point it will turn into the metastable hemihydrate (Hill 1937).

Posnjak (1940) points out that gypsum and anhydrite can only coexist at a four-phase equilibrium point: the two solids, the solution and the vapour above it. This has geological significance for the interpretation of the deposition conditions for gypsum and/or anhydrite from sea water. When calcium sulphate precipitates out of a sea water solution (and this could be

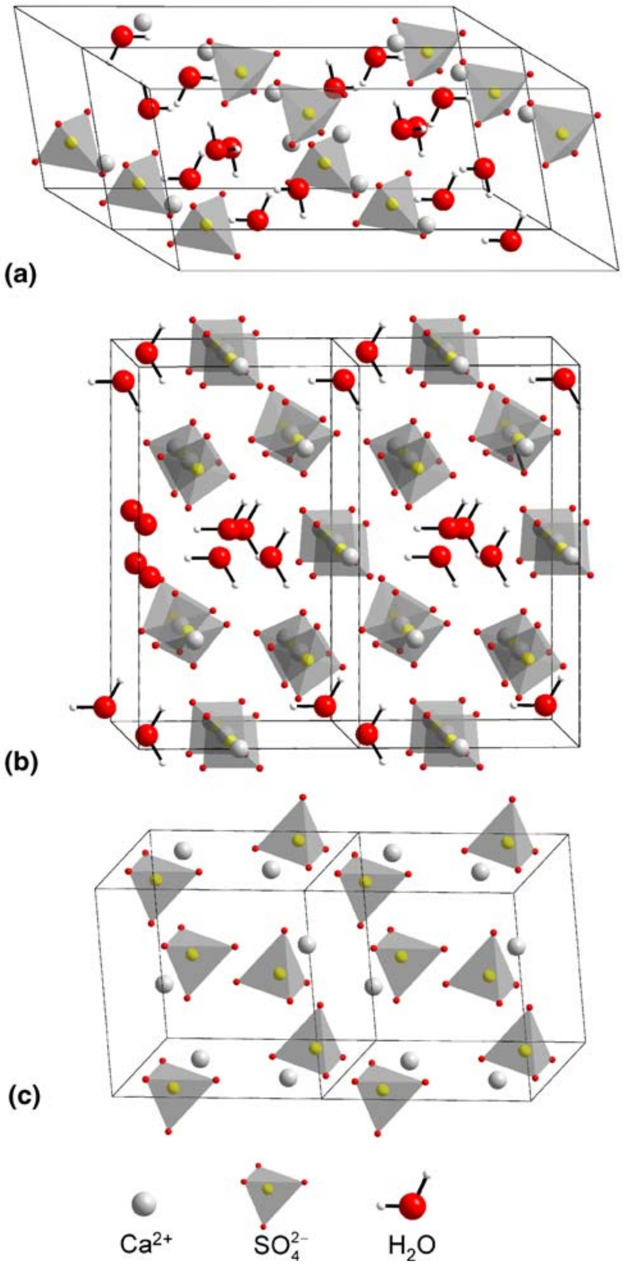

Fig. 1 Crystal lattices of **a** gypsum, **b** hemihydrate and **c** anhydrite

applicable to a concentrated solution of NaCl) at 30°C, it will do so as gypsum until the concentration of sea salts increases to about five times the normal concentration of sea water, at which point, it will precipitate out as anhydrite.

The 1941 publication from the US Bureau of Mines (Kelley et al. 1941) presents an updated review on gypsum and its related compounds with the aim to complete the stability diagram for these compounds by means of calorimetric measurements. The publication highlights the importance of the position occupied by the water within the gypsum lattice and in that of the hemihydrate. Gypsum shows a layered structure with the water molecules alternating with calcium sulphate layers explaining the easy cleavage of this mineral. The hemihydrate has the water molecules arranged in channels between chains of calcium sulphate and explains the ease with which this compound can lose most of its coordinated water without disrupting the structure. Figure 1 shows the crystal lattices of gypsum, hemihydrate and anhydrite.

The induction period required for the dehydration of gypsum can be explained by the fact that the water cannot be removed without reorganization of its lattice. On the other hand, the hemihydrate can lose at least part of its water without recrystallizing, the structure changing only by the time it is totally dehydrated (see D'Ans et al. 1955 for a thorough discussion).

A good state-of-the-art situation is presented by D'Ans et al. (1955) who confirm the temperature of 42°C for the transition of gypsum to anhydrite as originally determined by Posnjak (1938). They discuss the dehydration mechanism of gypsum crystals, indicating that when the top surface loses water molecules it results in a metastable state whose water vapour pressure is lower than either that required for dehydration to anhydrite or to the hemihydrate. While the initial loss of water molecules is slow, once several layers of water molecules have been lost from the crystal, the reaction can proceed at a faster rate. This reaction leads to the formation of hemihydrate and is used in industry to produce plaster of paris by heating gypsum in the presence of moisture to around 140°C. However, heating gypsum in a dry environment can also produce the hemihydrate because the formation rate of the hemihydrate is faster than that of anhydrite. Since the hemihydrate is metastable with regards to anhydrite and, below 97°C, also with regards to gypsum—as already indicated by Kelley et al. (1941)—it tends to turn into a mixture of the stable minerals over time.

Nonetheless, a direct dehydration of gypsum to anhydrite can occur if the water vapour pressure is kept below that of the gypsum → anhydrite reaction but above that for the gypsum → hemihydrate reaction as discussed in the following section. However, this direct dehydration is not easily achieved in practice but rather results in the production of various different metastable phases thus explaining the confusing amount of data obtained in previous studies. Dehydration under humid conditions is far more easily achieved which explains why this method is used in industry.

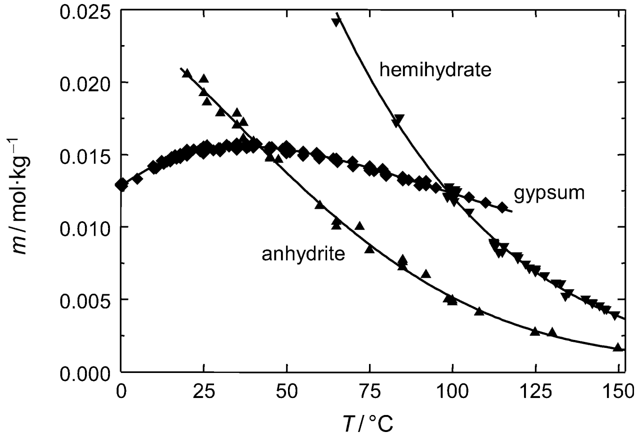

Fig. 2 Solubility curves for gypsum, anhydrite and hemihydrate in the temperature range from 0 to 150°C

Dehydration of the hemihydrate produces an anhydrous pseudo structure after the hemihydrate—this is the only variety that has been properly characterized by XRD (see Ottemann 1952)—which is metastable with respect to the latter when in solution. This metastable phase, γ-$CaSO_4$ or soluble anhydrite, has the characteristic of rapidly taking up water and turning back into the hemihydrate.

Finally, the review paper by Freyer and Voigt (2003) points out that the uncertainties in the transition temperatures of the solubility diagram can be attributed to slow crystallization kinetics in particular that of anhydrite, as discussed in more detail in the following section.

The $CaSO_4$–H_2O phase diagram and the gypsum-anhydrite equilibrium

Ever since the early work of van't Hoff et al., the phase diagram of the $CaSO_4$–H_2O system was subject to a never ending controversial debate. Recently, Freyer and Voigt (2003) reviewed the various attempts to fix the gypsum–anhydrite transition temperature. The original value suggested by van't Hoff was 63.5°C (van't Hoff et al. 1903) and later 65°C (van't Hoff 1909). However, careful solubility measurements by different authors suggested a considerably lower transition temperature close to 40°C (Partridge and White 1929; Hill 1937; Posnjak 1938; D'Ans et al. 1955), which was also confirmed by calculations based on thermochemical data of the two solid phases (Kelley et al. 1941). But some years later, it was claimed that these model calculations were subject to large errors due to inconsistent input data (Zen 1965). Hardie (1967) reported measurements of the equilibrium relative humidities for the gypsum–anhydrite equilibrium yielding 58°C as the transition temperature. Finally, Knacke and Gans (1977) reported a transition temperature of 55°C. Nevertheless, Freyer and Voigt (2003) pointed out possible experimental problems affecting the accuracy of the measurements of both Hardie (1967) as well as Knacke and Gans (1977).

Figure 2 depicts the most reliable solubility data in the $CaSO_4$–H_2O system from 0 to 150°C. The best fit line for the gypsum solubility is a representation of a consistent set of 176 individual data points. The curve for anhydrite is largely based on the very careful measurements of Partridge and White (1929), Hill (1934), Hill (1937), Hill and Yanick (1935), Hill and Wills (1938), Posnjak (1938), D'Ans et al. (1955) and Power et al. (1964). The intersection of the two solubility curves yields a transition temperature of 42 ± 2°C, far below the transition temperature reported by Hardie (1967). The transition temperature derived from the most reliable solubility data is also in excellent agreement with the value of 41.5°± 3.5°C reported by Robie et al. (1989) based on accurate thermochemical data. These authors measured heat capacities of gypsum and anhydrite which were then used together with the heat of solution measurements by Kelley et al. (1941) to calculate the transition temperature. It is concluded that the most reliable experimental data consistently suggest a transition temperature close to 42°C.

The curve of the hemihydrate solubilities is largely based on the data of Partridge and White (1929), Posnjak (1938), D'Ans et al. (1955) and Power et al. (1964) yielding a gypsum to hemihydrate transition temperature of 99 ± 4°C, which is in reasonable agreement with the values of 97.5°C (Posnjak 1938) and 97°C (D'Ans et al. 1955). According to Fig. 2 the hemihydrate can be prepared from solutions saturated with gypsum above the gypsum—hemihydrate transition temperature. The hemihydrate formed under such conditions, i.e. by crystallization from solution, is the α-hemihydrate. It should be noted however, that this is only possible due to the fact that the crystallization of anhydrite, the thermodynamically stable phase at that temperature, is kinetically hindered and proceeds at very low rates. At lower temperatures, it is even more difficult to obtain anhydrite (Freyer and Voigt 2003). Highly supersaturated solutions of anhydrite can persist without precipitating for weeks or months. This is also the main reason why there are so few reliable measurements of anhydrite solubilities.

The equilibrium constant K of the dehydration reaction of gypsum to anhydrite

$$CaSO_4 \cdot 2H_2O \rightleftharpoons CaSO_4 + 2H_2O \tag{1}$$

is given by

$$\ln K = -\frac{\Delta\mu^\circ}{RT} = \ln\frac{p}{p^\circ} \tag{2}$$

where the μ° are the standard state chemical potentials of gypsum, anhydrite and water, p and p° are the vapour pressure and the saturation vapour pressure of water, so that p/p° is an appropriate expression for the activity of water vapour assuming ideal behaviour. Similarly, the equilibrium constant for the gypsum–hemihydrate equilibrium

$$CaSO_4 \cdot 2H_2O \rightleftharpoons CaSO_4 \cdot 0.5H_2O + 1.5H_2O \tag{3}$$

can be represented by Eq. (2) as well. Based on the solubilities of gypsum, anhydrite and hemihydrate, and using additional thermodynamic data, D'Ans et al. (1955) calculated the equilibrium water vapour pressures of both the gypsum–anhydrite and the gypsum–hemihydrate transition. Their results, which are consistent with the solubility data discussed before, are shown as solid lines in the RH/T diagram depicted in Fig. 3. Gypsum is the stable phase below 42°C and at relative humidities above the gypsum–anhydrite equilibrium curve (a). Above 42°C anhydrite is the stable phase at any humidity. Curve (b) represents the equilibrium humidities for the gypsum–hemihydrate equilibrium. Below 97°C, the hemihydrate is metastable with regards to gypsum, and both these phases are metastable with regards to anhydrite at temperatures above 42°C. This explains why the hemihydrate may decompose into a mixture of gypsum and anhydrate upon storage as previously mentioned.

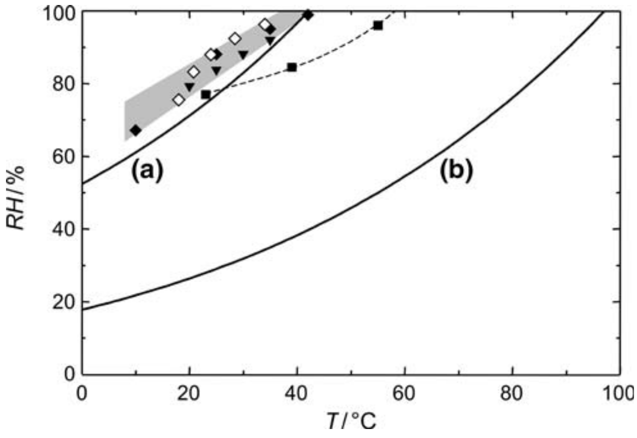

Fig. 3 Phase diagram for the system $CaSO_4$–H_2O in a plot of relative humidity versus temperature, where: **a** gypsum-anhydrite equilibrium curve; **b** gypsum–hemihydrate equilibrium curve. Symbols represent experimental data and have the following meanings: *open diamond*: solubilities in NaCl solutions of D'Ans et al. (1955); *filled nabla*: solubilities in NaCl solutions of Bock (1961); *filled diamond*: solubilities in H_2SO_4 solutions of Zdanovskii and Vlasov (1968); *filled square*: solubilities in H_2SO_4 solutions of Hardie (1967). *Solid lines* are equilibrium humidities calculated by D'Ans et al. (1955) from solubility and thermochemical data; the *dashed curve* represents equilibrium humidities based on the measurements of Hardie (1967)

As pointed out before, it follows from the equilibrium curves (a) and (b) in Fig. 3 that the dehydration of gypsum to hemihydrate requires a lower relative humidity than the dehydration of gypsum to anhydrite. Therefore, the direct dehydration of gypsum and formation of anhydrite is possible in the humidity range between the equilibrium curves (a) and (b). Again however, for kinetic reasons, the rate of formation of anhydrite is very slow. A two-step dehydration with intermediate formation of hemihydrate is only possible at relative humidities below curve (b) which is discussed in more detail by D'Ans et al. (1955). This offers another possibility for the formation of hemihydrate. At temperatures above the gypsum–hemihydrate transition, gypsum can be dehydrated to hemihydrate at any relative humidity (see Fig. 3) in a topotactic solid state reaction (Freyer and Voigt 2003). The hemihydrate formed under such conditions, i.e. in the absence of a solution, is the β-hemihydrate.

Solubilities of gypsum and anhydrite in the presence of other salts

Due to their very low solubilities all three calcium sulphates are essentially non-hygroscopic, thus, their deliquescence humidities are close to 100% RH. For instance, the deliquescence humidity of gypsum at 25°C is > 99.9% RH. Hence, liquid water is usually not present and the equilibrium curves (a) and (b) in Fig. 3 refer to the equilibrium of the two solids and water vapour. However, we are not aware of any successful direct measurements of the equilibrium vapour pressures. As mentioned before, the lack of reliable data is largely the result of the extremely slow transformation rates. However, in the presence of other, more hygroscopic salts, the situation is different. For instance, NaCl is deliquescent above 75% RH. Therefore, in the case of a mixture of $CaSO_4$ and NaCl, the conversion of gypsum to anhydrite proceeds in the presence of a liquid solution, if the deliquescence humidity of the second salt is exceeded. In this case, p/p° in Eq. 2 may be replaced by the water activity a_w of the solution. It should be noted however, that the water activity of an electrolyte solution at equilibrium equals the relative humidity above the solution. It follows that the conversion of gypsum to anhydrite is a function of temperature and water activity (or RH). Since the water activity decreases with increasing concentration of a solution, there is a shift of the gypsum–anhydrite transition to lower temperatures with increasing salinity of a solution. The lowest transition temperature is obtained in the saturated solution of a given electrolyte. This offers the opportunity to determine the equilibrium humidities for the gypsum–anhydrite equilibrium from their solubilities in mixed solutions.

The solubilities of gypsum and anhydrite are strongly influenced by the presence of other salts. In general, the behaviour follows the rule that the addition of unlike ions increases the solubility, while the addition of like ions causes a solubility decrease. Therefore, the solubilities of gypsum and anhydrite are considerably increased in solutions containing the chlorides and nitrates of sodium, potassium and magnesium. In contrast, there is a solubility decrease in calcium chloride and calcium nitrate solutions.

Figure 4 shows the solubility of gypsum and anhydrite at 25°C as a function of sodium chloride concentration. Initially, the solubilities of both solids increase with increasing NaCl concentration until they run through a maximum and, finally decrease in the more concentrated NaCl solutions. Since this solubility decrease is more pronounced in the case of anhydrite, the solubility curves intersect at a NaCl molality of about 4 mol kg^{-1}.

Figure 4 also shows the water activities of NaCl at different molalities. Due to the very low concentration of $CaSO_4$ it is a reasonable assumption that the water activities of the saturated gypsum and anhydrite solutions are determined by the NaCl molality. Then, the intersection of the two solubility curves corresponds to a water activity, or equilibrium humidity, of 85 ± 2.5%. The large uncertainty is due to the small angle at which the two curves intersect together with the considerable scatter in the experimental data. This means that above 85% RH, i.e. at lower molalities, the stable phase is gypsum, while below 85% RH, corresponding to higher molalities, anhydrite is the stable phase.

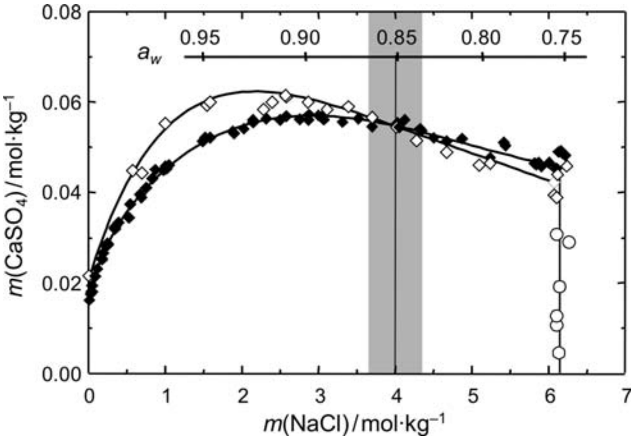

Fig. 4 Solubilities of gypsum and anhydrite in NaCl solutions at 25°C. Symbols represent experimental data (Shternina 1949; D'Ans et al. 1955; Madgin and Swayles 1956; Shternina 1957; Bock 1961; Dudnikova and Samoilov 1963; Marshall and Slusher 1966; Power et al. 1966; Block and Waters 1968; Yeatts and Marshall 1972) and have the following meanings: *open diamond*: anhydrite solubilities; *filled diamond*: gypsum solubilities; *open circle*: NaCl solubilities

Bock (1961) carried out solubility measurements at different temperatures to determine the NaCl molalities at which gypsum and anhydrite exhibit the same solubility. Using an equation provided by Archer (1992), we have calculated the water activities of these NaCl solutions which correspond to the equilibrium humidities of the gypsum–anhydrite transition. The results are shown in Fig. 3 together with data derived in the same way from solubility measurements by D'Ans et al. (1955) of gypsum and anhydrite in NaCl solutions. Finally, Zdanovski and Vlasov (1968) measured gypsum and anhydrite solubilities in sulphuric acid solutions and determined the equilibrium temperatures for the dehydration of gypsum. The water activities of the respective H_2SO_4 solutions were taken from Clegg et al. (1994) and are also shown in Fig. 3. Though there is considerable scatter in the available experimental data, most results fall in the shaded area in Fig. 3 and are, therefore, consistent with a gypsum–anhydrite transition temperature close to 40°C. Nonetheless, the agreement between the different types of experimental data and the curve calculated by D'Ans et al. (1955) is still not satisfying, highlighting the need for additional investigations into the gypsum–anhydrite equilibrium. There is no doubt however, that the values of Hardie (1967) who determined the equilibrium temperatures for the dehydration of gypsum in H_2SO_4 solutions lack consistency with the data of the other authors. His transition temperature, obtained by extrapolation to RH = 100% (cf. Fig. 3) appears to be far too high.

Figure 5 depicts the solubilities of gypsum in solutions of different nitrates. As in the case of NaCl, the addition of unlike ions, i.e. $NaNO_3$, KNO_3, and $Mg(NO_3)_2$, increases the gypsum solubility. However, due to the paucity of available experimental data, particularly for anhydrite, the solubilities in nitrate solutions could not be used for the determination of the equilibrium humidities for the gypsum–anhydrite equilibrium. As expected, there is a decrease in the gypsum solubility in $Ca(NO_3)_2$ solutions.

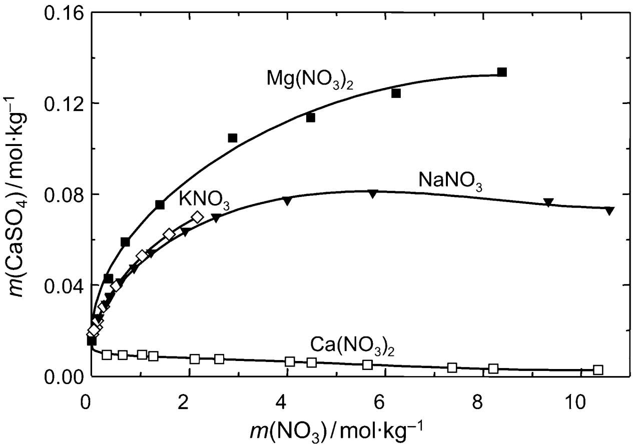

Fig. 5 Solubilities of gypsum in nitrate solutions at 25°C. Symbols represent experimental data (Seidell and Smith 1904; Yeatts and Marshall 1969; Zhang and Muhammed 1989)

The situation is more complicated in mixed solutions containing other sulphates due to the formation of double salts. Table 1 lists a number of common double salts containing $CaSO_4$ that can exist at near ambient temperatures. Most of the salts are naturally occurring minerals and many of them have also been detected as deterioration products in building materials. In particular, sodium, potassium and ammonium form a number of double salts with $CaSO_4$ which add to the complexity of the phase transformations involving this latter compound. In more complex mixtures of sulphates and chlorides in the Na^+–K^+–Mg^{2+}–Ca^{2+}–SO_4^{2-}–Cl–H_2O system additional compounds can exist depending on the mixture composition. The most relevant of these compounds are also included in Table 1.

Gypsum in the deterioration of monuments

Gypsum is one of the most ubiquitous salts found on historic monuments and there is no question as to its deteriorating action. However, its contribution to the overall deterioration of materials is yet to be clearly established. A first attempt at measuring the importance of deterioration was made by Zehnder (1996) who determined that the decay rate of mural paintings from gypsum veils was 10- to 100-fold slower than that caused by nitratine ($NaNO_3$).

Table 1 Double salts in the system Na^+–K^+–Mg^{2+}–Ca^{2+}–SO_4^{2-}–Cl^-–H_2O

Glauberite	$Na_2SO_4 \cdot CaSO_4$
Labile salt	$2Na_2SO_4 \cdot CaSO_4 \cdot 2H_2O$
Pentasulphate	$Na_2SO_4 \cdot 5CaSO_4 \cdot 3H_2O$
Syngenite	$K_2SO_4 \cdot CaSO_4 \cdot H_2O$
Goergeyite	$K_2SO_4 \cdot 5CaSO_4 \cdot H_2O$
Polyhalite	$K_2SO_4 \cdot MgSO_4 \cdot 2CaSO_4 \cdot 2H_2O$
Glaserite	$Na_2SO_4 \cdot 3K_2SO_4$
Bloedite	$Na_2SO_4 \cdot MgSO_4 \cdot 4H_2O$
Langbeinite	$K_2SO_4 \cdot MgSO_4$
Leonite	$K_2SO_4 \cdot MgSO_4 \cdot 4H_2O$
Schoenite	$K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$
Kainite	$KCl \cdot MgSO_4 \cdot 6H_2O$

Although gypsum can start dehydrating to form the hemihydrate (bassanite) at 42°C, only in few instances has this salt been found in nature, such as in semiarid gypsum deposits in south Tunisia, where a white, some centimetres thick layer of fibre-like or thin prismatic bassanite crystals formed on top of the gypsum layer showing a relic structure of the primary gypsum crystals (Smykatz-Kloss et al. 1985). The extreme conditions in this area where temperatures can range up to 70 or 80°C with very low humidity can explain this formation. Another instance is provided by the oxidation of pyrite in some rocks, such as the Swiss molasse sandstone (Zehnder 1982). The slow kinetics of anhydrite crystallization and the unstable condition of the hemihydrate at temperatures below 42°C preclude that these minerals or phases be found in efflorescences except under very dry conditions as shown in Fig. 3. Therefore, the deterioration caused by gypsum in stone and related building materials cannot be attributed to hydration pressures as has been claimed (Winkler 1975; Goudie and Viles 1997) but is the result of its crystallization within the porous material matrix as for any other non-hydrating salt.

For the particular case of materials containing calcareous components (and this includes lime mortars), this damage is compounded by the actual formation of this salt as a result of the dissolution reaction with sulphur containing air pollutants. This topic has been studied in far more detail elsewhere with various publications providing good reviews (Baboian 1986; Rosval and Aleby 1986; Building Effects Review Group 1989; Charola 2001; Charola and Ware 2002) and will therefore not be addressed here. Rather, the review will try to bring together the most relevant information regarding the deterioration induced by the crystallization of gypsum.

One of the main reasons for the prevalence of gypsum is that this salt is the least soluble of the so-called soluble salts that are usually found crystallizing in building materials. Other atmospheric pollutants, such as nitrogen oxides, generate nitrates, but these salts are far more soluble, deliquescent at normal temperature and relative humidity, and in outdoor conditions may be washed away. However, because of their deliquescent nature, they tend to keep moisture in the material, and this allows for an increased solubility and migration of the less soluble gypsum. The damage that results from these combinations has been clearly demonstrated in practice, such as the case of the Romanesque wall paintings of St. Georgen in Styria, Austria (Weber 1993; Weber et al. 1996; Leitner 2005).

Because of its low solubility, calcium sulphate is far less mobile in building materials than any of the other commonly found soluble salts. The mobility of a salt may be conveniently defined as the total amount of salt present in the pore space that can just be dissolved, if the pore space is completely filled with water. For example, in a natural stone with a water accessible porosity of 10%, the mobility of gypsum is only about 0.1 g kg^{-1} while, in the same material, the mobility of NaCl is 14 g kg^{-1} (Steiger 2003). Typically, the concentration of calcium sulphate in historic masonry exceeds its mobility by several orders of magnitude. Hence, only a very small fraction of calcium sulphate present in the pores can be dissolved, even if the pore space is saturated with water. In other words, gypsum once deposited in the pore space of a building material tends to continue accumulating over time. Its extremely low mobility also explains why the desalination of materials contaminated with calcium sulphate is so difficult.

Crystallization of gypsum

A review of the habits under which gypsum has been found and reported in publications dealing with the deterioration of buildings and monuments is relevant. From a saturated solution, the standard microtest for its identification, gypsum crystallizes out as small needles (acicular habit) sometimes forming flower-like structures, typical of the gypsum formed by the setting of plaster of paris. Similar needles (~5 μm long) have been collected on air filters (<0.8 μm) in Venice (Fassina et al. 1979). In artificial weathering studies (gaseous SO_2 at 70–80% RH), prismatic crystals (~70 μm long) were formed on the surface of Istrian stone, while broader swallow-tail twins were formed on marble (Rossi Manaresi et al. 1979). The habit of these crystals changed when protective coatings were applied as confirmed by other studies, either in the laboratory (Tucci et al. 1985) or in the field, as for the case of terracotta ornaments in Pavia (Abrate-Zohar et al. 1985).

Laboratory studies also showed that, when Carrara marble was attacked with sulphuric acid, the gypsum crystallized as thin tabular crystals in an open structure that covered the surface of the marble. Whereas, if the Carrara marble was a naturally weathered sample, gypsum crystallized in the acicular habit forming flower-like structures that tended to grow out of the surface cavities and cracks (Badan et al. 1976). Similar acicular crystals were obtained with artificial ‘‘acid’’ rain on sandstone (Snethlage 1984). Further studies have shown that artificial weathering can also result in the growth of the typical platelets that are normally found in the field (Ausset et al. 2000).

In typical ‘‘black’’ gypsum crusts, gypsum tends to crystallize in lenticular tabular habit (generally between 10 and 50 μm diameter), usually adopting the ‘‘desert rose’’ shape (Arnold and Kueng 1985) as found on marble (Franchi and Manganelli del Fà 1979; Lazzarini and Fassina 1979; Charola and Lewin 1979), limestone (Bortolaso et al. 1988), mortars and renders, brick, sandstones (Bläuer 1985; Neumann et al. 1993, 1997) and granite (Grimm and Schwarz 1985; Young et al. 1996). For the latter stone, it has been shown that the powdery disintegration, occurring from rising damp of water containing soluble salts (mainly sodium chloride and sodium sulphate given the vicinity of the Douro river) results from the formation of massive gypsum crystals rather than the usual tabular habit that occurs under flaking surfaces and in black crusts (Begonha and Teles 2000).

On higher areas of mural paintings (and sometimes on archaeological objects) white veils of gypsum are formed. In these cases, gypsum crystallizes in small particles (around 3 μm diameter) and the mechanism of their formation at this higher location is correlated to the presence of hygroscopic salts that would allow the slow migration of gypsum to this location (Zehnder 1993). A review of the deterioration patterns observed can be found elsewhere (Charola 2000).

It is to be remembered that different conditions during crystallization will change the habit of the crystallizing salt (Zehnder and Arnold 1989; Zehnder 1996). In solution, the crystals tend to be isometric, but as less water is available on the surface of the substrate, the habit turns to columnar and eventually to acicular growth.

Deterioration mechanism for gypsum crystallization

The low solubility of gypsum tends to reduce the drying rate of the porous substrate as shown in laboratory studies (Franke and Grabau 1998) or observed in the field (Bayer 2006). This can be attributed to the accumulation of gypsum at the evaporation front and the resulting pore clogging at the surface and subsurface of the porous material. Consequently, the material will remain damp for longer periods of time thus allowing for enhanced migration of soluble salts, biological colonization, soiling and dry deposition of air pollutants with the consequent corrosive reactions. Increased moisture retention and the presence of hygroscopic salts tend to facilitate creep of the most soluble salts (Pühringer 1983a, b) and although gypsum per se does not creep, it does migrate in the presence of other salts (Zehnder 1993). In general, migrating salts tend to crystallize out as cryptocrystalline formations which may adhere to the pore walls and induce shear stresses upon expansion–contraction cycles with moisture absorption or release (Charola and Pühringer 2005). Moisture absorption will be enhanced by the large specific surface that these formations show, apart from the fact that salt solubility may be increased at this particle size range.

The low mobility of gypsum favours its accumulation in porous building materials. The most important source of gypsum in these materials is atmospheric pollution. In the case of calcareous materials, the formation of gypsum is a chemical deterioration process, i.e. calcite is replaced by gypsum. In the case of non-calcareous stones, such as some sandstones and granites, both sulphate and calcium originate from external sources, for example, chemical attack of mortars. The accumulation of gypsum in these materials fills most of the available pore space just beneath the stone surface. A characteristic feature at a later stage of the damage process is the complete destruction of the original internal fabric which is replaced by a secondary gypsum supported fabric (Neumann et al. 1993, 1997; Steiger 2003). Figure 6 shows an example of these gypsum crusts on a quartzitic sandstone (Wealdensandstein).

The crystallization of gypsum plates on grain boundaries, especially in the case of large crystal-sized rocks, such as marbles, appears to induce a wedge action that displaces crystals initiating a powdering (or grus) deterioration type. As has been pointed out, this deterioration is closely linked to flaking and contour scaling, as observed on sandstones (Snethlage and Wendler 1997). The wedge action induced by gypsum crystallization has been postulated on the basis of laboratory studies (Snethlage et al. 1996) where the hydric expansion induced by a saturated solution of gypsum suddenly increases three- to four-fold from the value that pure water would achieve. This increase can only be attributed to the crystallization of gypsum. Scanning microscopy of deteriorated calcarenite (Leithakalk) sampled from different monumental buildings in Vienna (Charola and Koestler 1985/86) shows gypsum crystallizing in fissures or between larger calcite crystals, as illustrated in Figs. 7 and 8. A similar action has been found to occur in the Debnik limestone used for some monuments in Cracow. Deterioration results from the accumulation of gypsum along cracks and discontinuities of this nodular stone giving rise to loss of lens shaped chips which Haber et al. (1988) call "chipping".

The damage mechanism in all discussed cases is the stress generated during the growth of gypsum crystals, generally called crystallization pressure. Because of its low mobility, gypsum tends to accumulate in large pores. As discussed above, this results in an enhanced moisture retention thus facilitating gypsum recrystal-

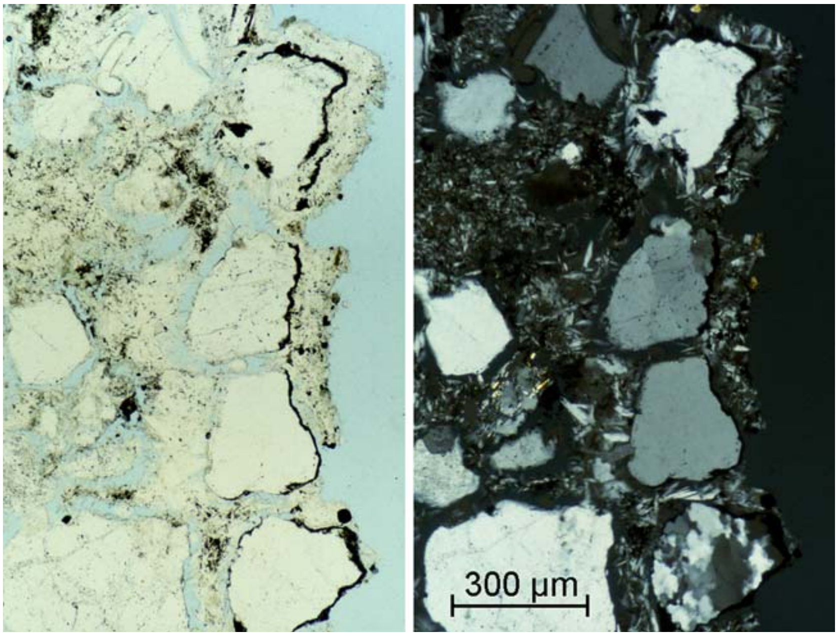

Fig. 6 Thin section of gypsum crust on a quartz bound sandstone at Leineschloss (Hanover) with Nicols (*left*) and X Nicols (*right*). Note the loss of cohesion of the surface quartz grains due to secondary gypsum growth. The gypsum crystals growing on the original thin black surface layer resulted from the subsequent development of a leak above this area. (from Neumann et al. 1993, reproduced with permission)

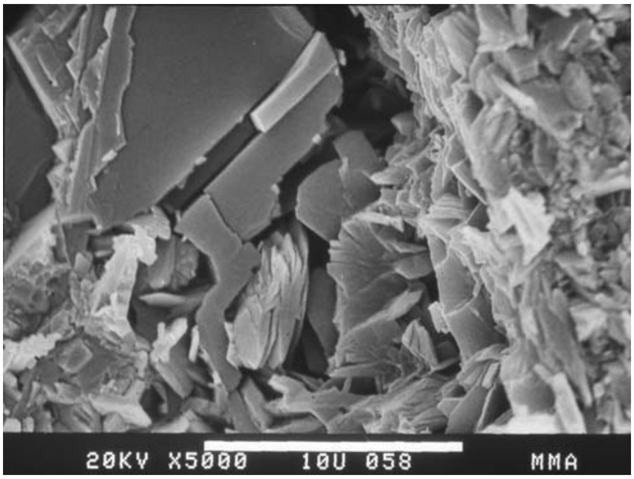

Fig. 7 SEM photomicrograph showing a calcite crystal etched at the lower left-side and fractures by the growth of gypsum crystals. The calcarenite sample was taken from St. Stephen's cathedral in Vienna (from Charola and Koestler 1985/86, reproduced with permission)

lization and development of larger crystals (as seen in Fig. 6). These, as described above, induce stresses when confined in fissures or interstitial spaces at grain or crystal contacts. The pronounced tendency of calcium sulphate solutions to supersaturate provides another condition for the generation of high crystallization pressures as determined from theoretical model calculations (Steiger 2005).

Although dehydration of gypsum to hemihydrate has not been found to occur on monuments, this does not preclude that gypsum, particularly in cryptocrystalline formations, may partially dehydrate and eventually rehydrate giving rise to further contraction–expansion cycles. Although minimal, this cycling could possibly contribute to the overall deterioration over time. However, the dehydration of gypsum is extremely slow below 42°C and is affected by the nature of other materials present in the system, as would be the case in monuments (Charola and Centeno 2002). Thus the nature and porosity of the substrate plays a critical role in determining the amount of damage suffered (Charola 2003). It also determines the amount of moisture absorbed by hygroscopic salts (Charola and Weber 1992; Charola and Pühringer 2005). Also important is the fact that even minimal changes in relative humidity, if repeated long enough, i.e, cycling between 43 and 55% RH over 6 months, will induce damage (Nunberg and Charola 2001). Finally, the rate at which thermohygric conditions change will influence the degree of deterioration suffered. Fast changes in humidity (2–4 days) induce more damage than slow changes (3 weeks) (von Konow 2001).

Conclusions

The $CaSO_4$–H_2O system appears misleadingly simple and over a century of studies have failed to elucidate its behaviour completely. These can be summarized as follows: there are two stable phases, gypsum and anhydrite, and two metastable ones, hemihydrate and the so-called soluble anhydrite. Because of the commercial importance of the hemihydrate, many of the studies have focused on its industrial production, taking advantage of the fact that the crystallization rate of anhydrite is slower than that of the hemihydrate. To complicate matters, the dehydration products of gypsum, either hemihydrate or anhydrite, may show significant differences in stability, and consequently in solubility, depending on the method by which they were obtained. The differences in behaviour of the hemihydrate obtained by wet or dry dehydration methods are still to be explained. These problems are not directly relevant to the deterioration of buildings and monuments but they may be relevant to plasters and stuccos as well as gypsum and anhydrite mortars, since these have been used historically.

The phase diagram of this system shows a dispersion of data which has been attributed, in part, to the slow crystallization kinetics of anhydrite. And calculations based on thermodynamic data still require further studies to clarify the experimental data obtained.

It has been shown that gypsum is the main phase found on buildings and monuments since bassanite forms only under very specific conditions. Thus, the

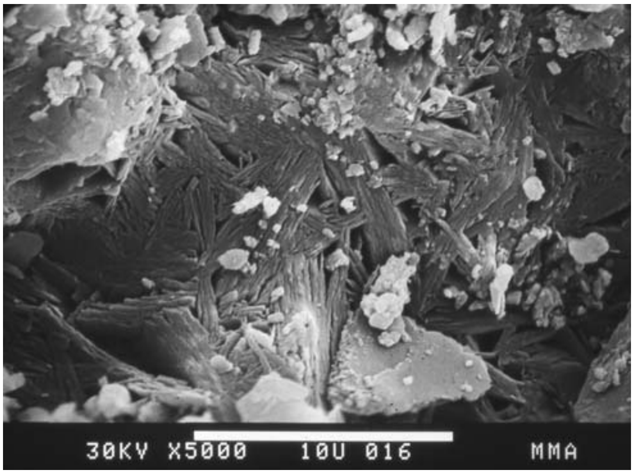

Fig. 8 SEM photomicrograph of platy gypsum crystals that developed against the surface of a calcite crystal which detached, within a calcarenite sample from the post office building at Ungargasse in Vienna (from Charola and Koestler 1985/86, reproduced with permission)

main cause of the induced damage is related to crystallization cycles of gypsum within the porous material, the latter playing a critical role in determining the amount and type of deterioration. The deterioration induced by gypsum is enhanced by the presence of other salts, in particular, deliquescent salts, that allow for an increased solubility and migration of the less soluble gypsum. Since much of the gypsum originates from dry or wet deposition of acid air pollutants, calcareous materials also suffer a dissolution reaction which compounds the deteriorating effect of resulting gypsum and its subsequent crystallization cycles.

Several hypotheses have been formulated to explain the deterioration mechanism of gypsum crystallization within porous materials but further research is required to elucidate the complex interaction between salt and substrate.

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References

Abrate-Zohar MA, Zezza U, Veniale F, Setti M (1985) Decay stage and causes of the terra-cotta ornaments (Cloister of the Carthusian Monastery, Pavia. Italy. In: 5th International congress on deterioration and conservation of stone. Presses Polytechniques Romandes, Lausanne, pp 443–451

Archer DG (1992) Thermodynamic properties of NaCl + H2O system. II. Thermodynamic properties of NaCl (aq), NaCl 2H2O (cr), and phase equilibria. J Phys Chem Ref Data 21:793–821

Arnold A, Kueng A (1985) Crystallization and habits of salt efflorescences on walls. I. Methods of investigation and habits. In: 5th International congress on deterioration and conservation of stone. Presses Polytechniques Romandes, Lausanne, pp 255–277

Ausset P, Lefèvre RA, Del Monte M (2000) Early mechanisms of development of sulphated black crusts on carbonate stone. In: Fassina V (ed) 9th Intl. Congress on Deterioration and Conservation of Stone (Venice), vol 1. Elsevier, Amsterdam, pp 329–337

Baboian R (1986) Materials degradation caused by acid rain. ACS Symposium Series 318, American Chemical Society, Washington, DC 1986

Badan B, Bacelle G, Marchesini L (1976) Surface reactivity of marble and stone: Quarry and Altered Samples. In: Rossi-Manaresi R (ed) The conservation of stone I. Centro per la Conservazione delle Sculture all'aperto, Bologna, pp 89–101

Bayer K (2006) Gypsum—An overlooked corrosive factor for some types of silicate sandstones in Bohemia. In: Proceedings of the SALTeXPERT Workshop ARIADNE 13, Prague, ARCCHIP and GCI, 2002 (in press)

Begohna A, Teles M (2000) Study of stone deterioration in the Palácio do Freixo in Oporto. In: Fassina V (ed.) 9th Intl. Congress on Deterioration and Conservation of Stone (Venice), Vol.2. Elsevier, Amsterdam, pp 593–601

Bläuer C (1985) Weathering of Bernese sandstone. In: 5th Intl. Congress on Deterioration and Conservation of Stone. Presses Polytechniques Romandes, Lausanne, pp 381–409

Block J, Waters OB (1968) The CaSO4-Na2SO4-NaCl-H2O system at 25° to 100°. J Chem Eng Data 13:336–344

Bock E (1961) On the solubility of anhydrous calcium sulphate 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

Bortolaso G, Lazzarini L, Mengazzo Vitturi L, Rampazzo G (1988) The deterioration of "Rosso Ammonitico Veronese" nodular limestone: Comparison between a quarry and a Venetian monument. In: 6th Intl. Congress on Deterioration and Conservation of Stone. Nicholas Copernicus University Press Department, Torun, pp 97–109

Building Effects review group report (1989) The effects of acid deposition on buildings and building materials. Her Majesty's Stationary Office, London

Calaforra Chordi JM (1998) Caracterización geomorfológica del karst en yeso (Geomorphological characterization of gypsum karsts). In: Karstología de yesos (Karst formation in gypsum deposits). Universidad de Almería, Servicio de Publicaciones. Instituto de Estudios Almerienses, Almería, 69–195

Charola AE (2000) Salts in the deterioration of porous materials: an overview. J Am Inst Conserv 39:332–343

Charola AE (2001) Acidic deposition on stone: a literature survey. US/ICOMOS Sci J 3:19–58

Charola AE (2003) Salt deterioration: open questions. In: Mauersalze und Architekturoberflächen (Salts in walls and architectural surfaces). Leitner H, Laue S and Siedel H (eds). Hochschule für Bildende Künste, Dresden: 10–24

Charola AE, Lewin SZ (1979) Efflorescences on building stones—SEM in the characterization and elucidation of the mechanisms of formation. Scanning Electron Microscopy/1979/I:378–386

Charola AE, Koestler RJ (1985/86) SEM Study of the deterioration of monumental stones in Vienna. In: Vendl A, Pichler B, Weber J, Banik G (eds) Wiener Berichte über Naturwissenschaft in der Kunst. Vol.2/3. Orac,Vienna, pp 176–186

Charola AE, Weber J (1992) The hydration-dehydration mechanism of sodium sulphate. In: Delgado Rodrigues J, Enriques F, Telmo Jeremias F (eds) 7th International congress on deterioration and conservation of stone. Laboratório Nacional de Engenharia Civil, Lisbon, pp 581–590

Charola AE, Centeno SA (2002) Analysis of gypsum-containing lime mortars: Possible errors due to the use of different drying conditions. J Am Inst Conserv 41:269–278

Charola AE, Ware R (2002) Acid deposition and the deterioration of stone: a brief review of a broad topic. In: Siegesmund S, Weiss R and Vollbrecht A (eds) Natural stone, weathering phenomena, conservation strategies and case studies. Geol Soc Lond Spec Publ 205:393–406

Charola AE, Pühringer J (2005) Salts in the deterioration of porous materials: a call for the right questions. Restor Build Monum 11:433–42

Clegg SL, Rard JA, Pitzer KS (1994) Thermodynamic properties of 0–6 mol kg^{-1} aqueous sulfuric acid from 273.15 to 328.15 K. J Chem Eng Data 90:1875–1894

D'Ans (1968) Der Übergangspunkt Gips → Anhydrit (The transition point gypsum → anhydrite). Kali Steinsalz 5:109–111

D'Ans J, Bredtschneider D, Eick H, Freund H-E (1955) Untersuchungen über die Calciumsulphate (Investigations on the sulfates of calcium). Kali Steinsalz 1:17–38

Davis WA (1907) The nature of the changes involved in the production and setting of plaster of paris. J Soc Chem Ind 26:727–738

Deer WA, Howie RA, Zussman J (1975) Rock-Forming Minerals Vol. 5 Non-Silicates. Longman, London (1962) 7th impression: 202–218

Dudnikova KT, Samoilov OYa (1963) Solubility of gypsum in aqueous solutions of salting-out agents. Sov Radiochem 5:644–646

Fassina V, Lazzarini, Biscontin G, Calogero S (1979) Influenza del materiale particellare atmosférico sui processi di degradazione della pietra a Venezia (Influence of atmospheric particulates on the deterioration process of the stones in Venice). In: 3rd International congress on deterioration and conservation of stone (Venice). Università degli Studi di Padova, Padua, pp 43–53

Franchi R, Manganelli Del Fà C (1979) Ricerche sulla degradazione delle ''Pietre'': IX. Il Cristo del Sansovino. In: 3rd Intl. Congress on Deterioration and Conservation of Stone (Venice). Università delgi Studi di Padova, Padua, pp 481–490

Franke L, Grabau J (1998) Influence of salt content on the drying behavior of brick. In: Baer NS, Fitz S, Livingston RA (eds) Conservation of historic brick structures. Donhead, Shaftesbury, pp 59–68

Freyer D, Voigt W (2003) Crystallization and phase stability of $CaSO_4$ and $CaSO_4$-based salts. Monatsh Chem 134:693–719

Goudie A, Viles H (1997) Salt weathering hazards. Wiley, Chichester

Grassegger G (2002) Restoration of the sarcophagus of Duke Melchior von Hatzfeld—the accompanying scientific and technical investigations. Otto Graf J 13:141–154

Grimm WD, Schwarz U (1985) Naturwerksteine und ihre Verwitterung an Münchner Bauten und Dankmälern (Natural stone and their deterioration in buildings and monuments in Munich). In: Natursteinkonservierung. Arbeitsheft 31. Bayerisches Landesamt für Denkmalpflege, Munich, pp 28–118

Haber J, Haber H, Kozlowski R, Magiera J, Pluska I (1988) Air pollution and decay of architectural monuments in the city of Cracow. In: Rosvall J, Aleby S (eds) Air pollution and conservation. Safeguarding our cultural heritage. Elsevier, Amsterdam, pp 499–547

Hardie LA (1967) The gypsum–anhydrite equilibrium at one atmosphere pressure. Am Mineral 52:171–200

Heusinger von Waldegg E (1906) Der Gips (Gypsum). In: Moye A (ed) 2nd edn. Theod. Thomas Verlag, Leipzig

Hill AE (1934) Ternary systems. XIX. Calcium sulfate, potassium sulfate and water. J Am Chem Soc 56:1071–1078

Hill AE (1937) The transition temperature of gypsum to anhydrite. J Am Chem Soc 59:2242–2244

Hill AE, Yanick NS (1935) Ternary system. XX. Calcium sulfate, ammonium sulfate and water. J Am Chem Soc 57:645–651

Hill AE, Wills JH (1938) Ternary systems. XXIV. Calcium sulfate, sodium sulfate and water. J Am Chem Soc 60:1647–1655

Hulett GA (1905) The solubility of gypsum as affected by size of particles and by different crystallographic surfaces. J Am Chem Soc 27:49–56

Hulett GA, Allen LE (1902) The solubility of gypsum. J Am Chem Soc 24:667–679

Kelley KK, Southard JC, Anderson CT (1941) Thermodynamic properties of gypsum and its dehydration products. US Bur Mines Tech Pap 625

Knacke O, Gans W (1977) The thermodynamics of the system $CaSO_4$–H_2O. Z Phys Chem NF 104:41–48

Lazzarini L, Fassina V (1979) Studio scientifico sullo stato di conservazione delle pietre e dei marmi della Porta della Carta di Venezia (Scientific study on state of conservation of the stones and marbles of the Porta della Carta in Venice). In: 3rd Intl. Congress on Deterioration and Conservation of Stone (Venice). Università delgi Studi di Padova, Padua, pp 647–660

Lazzarini L, Laurenzi Tabasso M (1986) Il restauro della pietra (The restoration of stone) Cedam, Padua: 22

Le Chatelier H (1887) Recherches expérimentales sur la constitution des mortier hydrauliques (Experimental research on the composition of hydraulic mortars). Dunod, Paris

Leitner H (2005) The treatment of wall paintings affected by salts: an interdisciplinary task as seen from a conservator's perspective. Restor Build Mon 11:365–380

Madgin WM, Swayles DA (1956) Solubilities in the system $CaSO_4$-NaCl-H_2O at 25° and 35°. J Appl Chem 6:482–487

Marshall WL, Slusher R (1966) Thermodynamics of calcium sulfate dihydrate in aqueous sodium chloride solutions, 0–110°. J Phys Chem 70:4015–4027

Neumann HH, Steiger M, Wassmann A, Dannecker W (1993) Aufbau und Ausbildung schwarzer Gipskrusten und damit zusammenhängender Gefügeschäden von Naturwerksteinen am Beispiel des Leineschlosses, Hannover (Formation and development of black gypsum crusts and related deterioration of the structure of natural stones as exemplified by the Leineschloss in Hanover). In: Snethlage R (ed) Steinzerfall-Steinkonservierung, Vol. 3–1991, Verlag Ernst & Sohn, Berlin, pp 51–167

Neumann HH, Lork A, Steiger M, Juling H (1997) Decay patterns of weathered quartz sandstones: evidence of gypsum induced structural changes. In: Sveinsdottir EL (ed) Proceedings of the 6th Euroseminar on microscopy applied to building materials, Icelandic Building Research Institute, Reykjavic, pp 238–249

Nunberg S, Charola AE (2001) Salts in Ceramic Bodies II: deterioration due to minimal changes in relative humidity. Int J Restor Build Mon 7:131–146

Ottemann J (1952) Baustoff Anhydrit. (Construction material anhydrite) Verlag Technik, Berlin

Partridge EP, White AH (1929) The solubility of calcium sulfate from 0 to 200°. J Am Chem Soc 51:360–370

Posnjak E (1938) The system $CaSO_4$–H_2O. Am J Sci 35A:247–272

Posnjak E (1940) Deposition of calcium sulfate from sea water. Am J Sci 238:559–568

Power WH, Fabuss BM, Satterfield CN (1964) Transient solubilities in the calcium sulfate-water system. J Chem Eng Data 9:437–442

Power WH, Fabuss BM, Satterfield CN (1966) Transient solute concentrations and phase changes of calcium sulfate in aqueous sodium chloride. J Chem Eng Data 11:149–154

Pühringer J (1983a) Salt disintegration: salt migration and degration by salt—a hypothesis. D15:1983 Swedish Council for Building Research, Stockholm

Pühringer J (1983b) Salzwanderungen und Verwitterung durch Salze (Salt migration and weathering through salts). In: Wittmann FH (ed) Materials Science and Restoration. Edition Lack + Chemie, Filderstadt, pp 361–366

Robie RA, Russel-Robinson S, Hemingway BS (1989) Heat capacities and entropies from 8 to 1000 K of langbeinite ($K_2Mg_2(SO_4)_3$), anhydrite ($CaSO_4$) and of gypsum ($CaSO_4{\cdot}2H_2O$) to 325 K. Thermochim Acta 139:67–81

Rossi-Manaresi R, Alessandrini G, Fuzzi S, Peruzzi R (1979) Assessment of the Effectiveness of Some Preservatives for Marble and Limestones. In: 3rd Intl. Congress on Deterioration and Conservation of Stone (Venice). Università degli Studi di Padova, Padua, pp 357–376

Rosval J, Aleby S (1986) Air pollution and conservation. Safeguarding our architectural heritage. Elsevier, Amsterdam

Shternina EB (1949) Solubility of gypsum in salt solutions. Izvest Sektora Fiz-Khim Anal, Inst Obshchei Neorg Khim, Akad Nauk S.S.S.R. 17:351–369 (in Russian)

Shternina EB (1957) Maximums on the solubility isotherms for calcium sulfate and calcium carbonate. Zh Neorg Khim 2:933–937 (in Russian)

Seidell A, Smith JG (1904) The solubility of calcium sulphate in solutions of nitrates. J Phys Chem 8:493–499

Smykatz-Kloss W, Istrate G, Hötzl H, Wohnlich S (1985) Vorkommen und Entstehung von Bassanit, $CaSO_4{\cdot}0.5H_2O$), im Gipskarstgebiet von Foum Tatahouine, Südtunesien. (Occurrence and formation of bassanite in the gypsum karst region of Foum Tatahouine, South Tunesia). Chem Erde 44:67–77

Snethlage R (1984) Steinkonservierung 1979–1983 (Stone conservation 1979–1983) Arbeitsheft 22, Bayerisches Landesamt für Denkmalpflege. Munich: 13–83

Snethlage R, Wendler E (1997) Moisture cycles and sandstone degradation. In: Baer NS, Snethlage R (eds) Saving our architectural heritage: the conservation of historic stone structures. Wiley, Chichester, pp 7–24

Snethlage R, Wendler E, Klemm DD (1996) Tenside im Gesteinschutz—Bisherige Resultate mit einem neuen Konzept zur Erhaltung von Denkmälern aus Naturstein (Tensides in the protection of stone—Results from a new concept for the conservation of monuments in natural stone). In: Snethlage R (ed) Denkmalpflege und Naturwissenschaft. Natursteinkonservierung I. Ernst & Sohn, Berlin, pp 127–146

Steiger M (2003) Crusts and salts. In: Brimblecombe P (ed) The effects of air pollution on the built environment. Air pollution reviews, vol 2. Imperial College Press, London, pp 133–181

Steiger M (2005) Crystal growth in porous materials: I. The crystallization pressure of large crystals. J Cryst Growth 282:455–469

Tucci A, Koestler RJ, Charola AE, Rossi-Manaresi R (1985) The influence of acid rain and UV radiation on the ageing of acrylic and silicone resins. In: 5th International congress on deterioration and conservation of stone. Presses Polytechniques Romandes, Lausanne, pp 891–898

van't Hoff JH (1909), Zur Bildung der ozeanischen Salzablagerungen (On the formation of the oceanic salt deposits). Zweites Heft. Vieweg und Sohn, Braunschweig

van't Hoff JH, Armstrong EF, Hinrichsen W, Weigert F, Just G (1903) Gips und Anhydrit (Gypsum and anhydrite). Z Phys Chem 45:257–306

von Konow T (2001) Mechanisms of brick deterioration due to salts: new results on salt behaviour from in-situ studies at the Suomenlinna Fortress in Finland. Int J Restor Build Monum 7:675–688

Weber J (1993) Salt-induced deterioration of Romanesque wall paintings in the church of St. Georgen, Styria, Austria. In: Biscontin G, Graziano L (eds) Conservation of architectural surfaces: stones and wall coverings. Il Cardo, Venice, pp 97–103

Weber J, Leitner H, Gaggl W and Szambelan R (1996) Crystallization of sulphate salts induced by selective salt extraction by poultices: results from a case study. In: Preprints of the european research workshop on origin, mechanisms and effects of salts on degradation of monuments in marine and continental environments, Bari, pp 169–170

Weiser HB, Millligan WO, Ekholm WC (1936) The mechanism of the dehydration of calcium sulfate hemihydrate. J Amer Chem Soc 58:1261–1265

Winkler EM (1975) Stone: properties, durability in man's environment, 2nd edn. Springer, Vienna and New York

Yeatts LB, Marshall WL (1969) Apparent invariance of activity coefficients of calcium sulfate at constant ionic strength and temperature in the system $CaSO_4$–Na_2SO_4–$NaNO_3$–H_2O to the critical temperature of water. Association equilibria. J Phys Chem 73:81–90

Yeatts LB, Marshall WL (1972) Solubility of calcium sulfate dihydrate and association equilibria in several aqueous mixed electrolyte salt systems at 25 °C. J Chem Eng Data 17:163–168

Young ME, Jones MS, MacDonald J, Urquhart DCM, Nicholson K, McHardy WJ (1996) Investigations on the soiling and cleaning of some Scottish granites. Degradation and conservation of granitic rocks in monuments. Research report No.5. Environmental Protection and Conservation of the European Cultural Heritage. European Commission, Brussels, pp 429–434

Zdanovskii AB, Vlasov GA (1968) Determination of the boundaries of the reciprocal transformations $CaSO_4{\cdot}2H_2O$ and γ-$CaSO_4$ in H_2SO_4 solutions. Russ J Inorg Chem 13:1318–1319

Zen E-an (1965) Solubility measurements in the system $CaSO_4$–NaCl–H_2O at 35°, 50°, and 70°C and one atmosphere pressure. J Petrol 6:124–164

Zehnder K (1982) Verwitterung von Molassensandsteinen an Bauwerken und in Naturaufschlüssen (Weathering of Molasse sandstones in buildings and in natural occurrences) Beiträge zur Geologie der Schweiz, Geotechnische Serie 61:86

Zehnder, K (1993) New aspects of decay caused by crystallization of gypsum. In: Thiel M-J (ed) Conservation of stone and other materials. Vol 1 E & FN Spon, London, pp 107–114

Zehnder, K (1996) Gyspsum efflorescences in the zone of rising damp. Monitoring of slow decay processes caused by crystallizing salts on wall paintings. In: Riederer J (ed) Proceedings 8th International congress on deterioration and conservation of stone. Möller Druck, Berlin, pp 1669–1678

Zehnder K, Arnold A (1989) Crystal growth in salt efflorescence. J Cryst Growth 97:513–521

Zhang Y, Muhammed M (1989) Solubility of calcium sulfate dihydrate in nitric acid solutions containing calcium nitrate and phosphoric acid. J Chem Eng Data 34:121–124