Crystallization Properties of Salt Mixtures:
Comparison of Experimental Results and Model Calculations

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SUMMARY

A chemical model is used to examine the phase behaviour of salt mixtures. The principal types of phase changes including crystallization/dissolution, hydration/dehydration and the formation and decomposition of double salts are illustrated for simple mixtures of two salts. The model is successfully applied to predict the crystallization properties of a four-component system. It is shown how several possible sequences of salt deposition and phase transformations are induced by changes of the ambient relative humidity. In addition an X-ray diffraction technique is presented which can be used to study the phase behaviour of salts under controlled conditions of temperature and relative humidity.

1 Introduction

Water-soluble salts are a major cause of decay in porous materials such as stone, brick, mortar etc. Numerous studies have established that crystal growth in the pores leads to severe damage of these materials. The basic mechanisms generating the internal pressures are still not well understood, though. It is certain, however, that damage is caused by phase transformations such as crystallization or hydration. Phase changes of water-soluble salts are induced by environmental factors, namely variation of temperature and relative humidity.

The situation is quite simple if a porous material is contaminated with a single salt. At low relative humidities the salt remains a crystalline solid. Slowly increasing the relative humidity at a given temperature a point will be reached, the deliquescence or saturation humidity, where the salt picks up water from the gas phase and forms a saturated solution. As the relative humidity is further increased the salt solution becomes more dilute. If the relative humidity drops below the saturation humidity again the salt crystallizes out and all of the water evaporates. The deliquescence humidities of single salts are well documented. Values for several salts are shown in Fig. 1. Salt damage has to be expected if fluctuations above and below the temperature/relative humidity curves cause cyclic dissolution and crystallization. On the other hand, damage can be effectively prevented, if the climatic conditions are kept at an appropriate level, either continuously above or below the equilibrium curves of the respective salt.
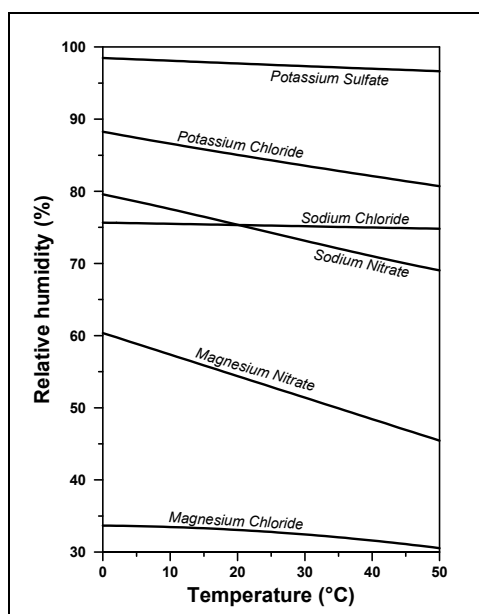

Fig. 1. Deliquescence humidities

The exact knowledge of critical temperature and humidity conditions inducing phase transformations are obviously very important for the conservator. This is particularly true for the indoor environment where the climatic conditions can be controlled at least to a certain extent (e.g. heating, ventilation etc.) and may be effectively used for passive conservation of stonework contaminated with salts. However, salt accumulations usually found in porous materials comprise of many different ions. Typically, the chlorides, nitrates and sulfates of sodium, potassium, magnesium and calcium have to be considered.

Unfortunately the situation becomes a lot more complicated for mixtures compared to pure salts. The systems of interest differ widely in terms of their physical and chemical characteristics and the concept of the saturation humidities of the individual salts does no longer apply to the mixtures. Salt efflorescences on walls containing complex salt mixtures have been observed at considerably lower relative humidities than would have been expected from the saturation humidities of the pure salts[1].

It has been shown recently[2,3,4] that the properties of salts in mixed systems can be analysed on the basis of the thermodynamic properties of aqueous electrolyte solutions.

The chemical model of Pitzer[5] has been used in these studies to investigate the properties of simple salt mixtures. The results obtained are in good qualitative agreement with the observed phenomena[1] in that the model calculations also revealed lower relative humidities for the crystallization of a solid phase than for the respective pure salt. It could be further demonstrated that crystallization of one salt from a mixture does not occur at a specific value but across a range of relative humidities.

In continuation of our previous work on the properties of salt mixtures in porous materials the present paper is concerned with more complex mixtures including hydration/dehydration equilibria and the formation and decomposition of double compounds. In addition to model calculations first results obtained from the application of a new X-ray diffraction technique which has been developed to study phase transformations in salt mixtures under controlled conditions of temperature and relative humidity are presented.

2 Thermodynamics of salt mixtures

To predict the phase behaviour of a mixed salt system in a porous material the solubilities of mineral phases in the mixed system are required. In addition, we need to know the critical relative humidities at which a mixed solution becomes saturated with respect to one or more solid phases. In equilibrium the chemical potential of water in the vapor phase, $\mu_{w,v}$ equals that of the liquid phase, $\mu_{w,l}$. If ideal gas behaviour for water vapor is assumed, we obtain:

$$\mu_{w,l} = \mu_{w,l}^{\circ} + RT \ln(a_w) = \mu_{w,v} = \mu_{w,v}^{\circ} + RT \ln(p_w/p_w^{\circ}) \tag{1}$$

where R is the gas constant, T is the absolute temperature, a_w is the water activity, p_w is the water vapor partial pressure, and p_w° is the saturated water vapor pressure at temperature T. Since the standard potentials (μ_w°) are equal, one obtains from equation (1):

$$a_w = p_w/p_w^{\circ} = RH \tag{2}$$

Thus the relative humidity (RH) equals the activity of water which is related to the osmotic coefficient, ϕ, by the following equation:

$$\ln(a_w) = -\phi (M_w/1000) \Sigma(m_i) \tag{3}$$

Here, M_w is the molecular mass of water and m_i is the molality of an ion i in the solution. If the composition of a saturated solution (given by the m_i) and the osmotic coefficient of that solution are known the saturation humidity can be calculated according to equations (2) and (3).

The basic theory for calculation of solubility equilibria is well known. Given a solid phase with a fixed composition $M_{v_M}X_{v_X} \cdot v_0 H_2O$ consisting of v_M positive ions, M, of charge z_M, v_X negative ions, X, of charge z_X and v_0 molecules of water the equilibrium constant K_{MX} for the dissolution reaction is given by

$$\ln(K_{MX}) = v_M \ln(m_M) + v_X \ln(m_X) + v_M \ln(\gamma_M) + v_X \ln(\gamma_X) + v_0 \ln(a_w) \tag{4}$$

where γ_M and γ_X stand for the activity coefficients of the cation and anion, respectively.

To predict the behaviour of mixed electrolyte solutions it is therefore required to know the values of the osmotic and activity coefficients as a function of composition and temperature. As has been already mentioned, the ion interaction model of Pitzer[5] has proved very helpful in modelling various thermodynamic properties. Details of the model will not be discussed here but may be found in in the paper of Pitzer[5]. Briefly, the equations used are semi-empirical which means that the form of the equations is based on theory but there remain empirical parameters which have to be determined from experimental data (e.g. osmotic and activity coefficients). Data of pure aqueous salts are used for the determination of the binary interaction parameters, whereas simple mixtures (two salts with a common ion) reveal the mixing parameters required for the treatment of salt mixtures. Once the model has been adequately parameterized it allows for the calculation of osmotic and activity coefficients in mixed solutions. It is then possible to calculate solubilities in salt mixtures by using iterative numerical techniques.

3 Crystallization properties of salt mixtures

Once a consistent set of model parameters has been determined the crystallization properties of pure salts and salt mixtures can be calculated as a function of temperature and relative humidity. Different types of phase behaviour can be observed in systems consisting of water and two or more salts: (1) systems without chemical reactions, (2) systems involving hydration/dehydration equilibria, (3) systems with chemical reactions (formation and decomposition of double compounds). The properties of systems without chemical reactions have been already described in some detail[2,3,4]. The only phase changes that have to be considered are crystallization and deliquescence. Examples for the latter two systems will be discussed in the following sections.

3.1 Hydration/dehydration equilibria

Compared to other salts particular attention has been paid to sodium sulfate in the past due to the fact, that salts existing in anhydrous and hydrated forms have been found to cause increased damage in salt crystallization tests (e.g. DeQuervain and Jenny[6], Schmölzer[7] among many others). The actual damage mechanism is still not clear. Recent work[8,9,10], however, indicates that the classical idea of simple volume expansion during the hydration of thenardite (Na_2SO_4) to mirabilite ($Na_2SO_4 \cdot 10H_2O$) is not sufficient to explain the deleterious effects of the salt. Though the basic mechanism is not understood it is important to exactly know the conditions for phase transformations, either due to hydration/dehydration or dissolution/crystallization. The phase diagram of the binary system Na_2SO_4/water is shown in Fig. 2.

The critical conditions for crystallization and dissolution are given by curves A and B in Fig. 2 representing the equilibrium relative humidities of sodium sulfate solutions saturated with respect to mirabilite (<32.4°C) and thenardite (>32.4°C). Below 32.4°C thenardite is not stable in the presence of a sodium sulfate solution, but can be formed due to the dehydration of mirabilite at relative humidities less than given by curve C. At temperatures above 32.4°C thenardite is always stable at any humidity below the deliquescence humidty (line B).

It is interesting now to see whether the critical conditions for crystallization/dissolution or hydration/dehydration are influenced if another salt is present. We have therefore made calculations on the ternary system $NaCl/Na_2SO_4$/water. The solubility diagram obtained at 15°C is shown in Fig. 3a. It belongs to the simple type (1) mentioned above, i.e. only two solid phases and no chemical reactions.
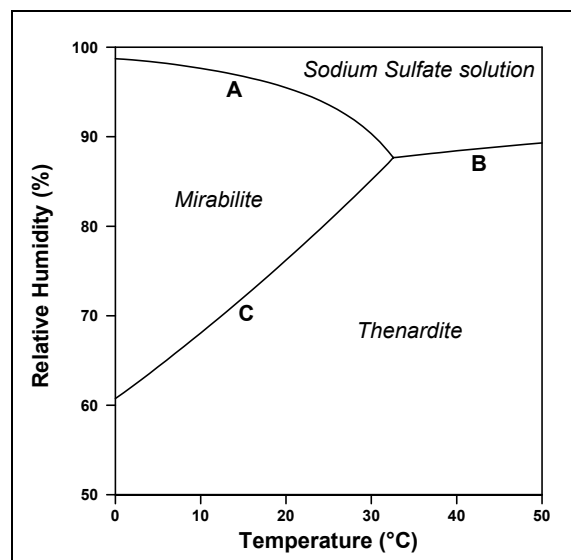

Fig. 2. The Na_2SO_4/H_2O system from 0 to 50°C

Though this type of system has been already discussed[2,3,4] the crystallization properties may be briefly summarized here. Each point on the solubility curves represents the composition of a saturated solution with respect to one solid phase. The intersection of the two solubility curves is the invariant point of the system at 15°C giving the composition of the solution saturated with respect to both solids. This point is also often referred to as the eutonic point. Whenever the mixing ratio of the two salts is different from that of the eutonic there will be one solid precipitating first. The remaining solution is then depleted with respect to the salt already deposited and the mixing ratio of the solution approaches the eutonic. If more water evaporates the eutonic composition is finally reached and further evaporation will lead to the crystallization of both solid phases and complete drying.

The crystallization humidities at 15°C are shown in Fig. 3b as a function of the mixing ratio of the two salts. They show the usual behaviour for mixtures of two salts. Depending on the mixing ratio one of the two salts, mirabilite or halite, starts to crystallize out at a relative humidity lower than that of the respective pure salt. The intersection of the two branches of the saturation humidity curve represents the relative humidity below which the system evaporates completely. It is also referred to as the drying-up point of the system. Thus, in contrast to a single salt, a mixture is not simply characterized by a single critical relative humidity but rather a range of the relative humidity within which fluctuations continuously cause dissolution and reprecipitation of one compound of the mixture. The lower limit of this humidity range is given by the drying-up point. If the relative humidity falls below this value also the second salt crystallizes out. The upper limit depends on the mixing ratio and approaches the saturation humidity of a pure salt, if there is a large excess of that salt in the mixture. If the mixing ratio equals that of the eutonic point, the salt mixture behaves like a pure salt. A dilute solution of that composition will completely crystallize without fractionation if the humidity falls below the drying-up point.

The solubility diagram for the $Na_2SO_4/NaCl/H_2O$ system at 25°C shown in Fig. 4a is an example of a system involving hydration/dehydration equilibria. At the eutonic point E the solution is saturated with respect to halite and thenardite. At 25°C mirabilite is not stable in the presence of halite. The second invariant point is the reaction point R for the hydration/dehydration of thenardite and mirabilite. A solution of composition R is saturated with respect to both solids. The crystallization paths for different mixing ratios of the two salts can be simply derived from the solubility diagram. Depending on the initial mixing ratio either of the three solids may start to crystallize out. For ratios $m(SO_4)/m(Cl)>0.42$ mirabilite is the first solid to be deposited. The crystallization path of a dilute solution of composition A (equimolal mixture) is shown as an example in Fig. 4a. Decreasing the relative humidity would lead to the evaporation of water and the solution would become more concentrated (line AB). At point B the solution is saturated with respect to mirabilite, which would start to

crystallize out if the humidity is further decreased. The composition of the remaining solution then changes along the line BR. At point R any further removal of water would cause the complete dehydration of mirabilite and as the relative humidity continues to fall thenardite will be continuously deposited until the eutonic point E is reached (line RE). Any further decrease of the relative humidity will cause the simultaneous crystallization of thenardite and halite and complete drying.
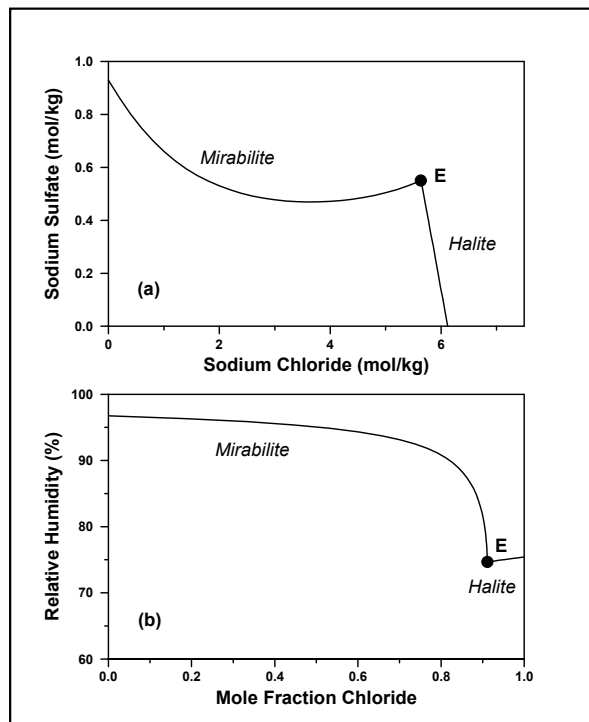

Fig. 3. The NaCl/Na$_2$SO$_4$/H$_2$O system at 15°C
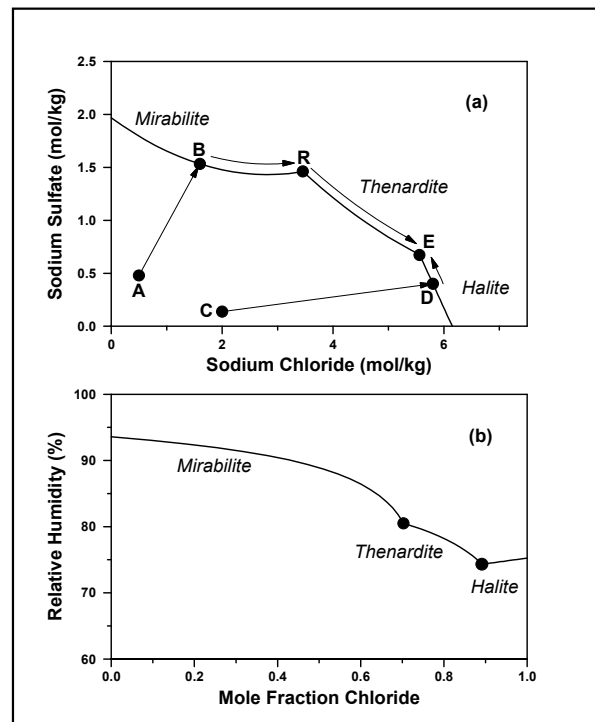(a) solubilities; (b) saturation humidities

Fig. 4. The NaCl/Na$_2$SO$_4$/H$_2$O system at 25°C
(a) solubilities; (b) saturation humidities

Crystallization paths for other mixing ratios can be evolved in much the same way. The behaviour of a mixture with a large excess of sodium chloride also shown in Fig. 4a (lines CD and DE) is straightforward. The saturation humidities of the system are shown in Fig. 4b. Calculated relative humidities for the hydration/dehydration equilibrium and the drying-up point are 80.5% and 74.3%, respectively. They are in excellent agreement with experimental values of 80.5% and 74.5% determined by Platford[11].

We have only discussed the behaviour of the salt mixture on evaporation of water from a dilute solution so far. The same arguments, however, also apply to the reverse process, i.e. the water uptake as humidity increases. As an illustration suppose that the dry mixture of thenardite and halite obtained after complete evaporation of water from solution A (Fig. 4a) is subjected to an increase in relative humidity again. If the relative humidity reaches 74.3% enough water will be absorbed to dissolve all of the halite and part of the thenardite. A saturated solution is formed having the composition of the eutonic. As the relative humidity continues to rise an increasing amount of thenardite is dissolved while the composition of the solution moves along line ER in Fig. 4a. Finally, at a relative humidity of 80.5% all of the remaining thenardite is hydrated. Further increasing the relative humidity then leads to continuous dissolution of mirabilite until reaching point B where all soluble material goes into solution.

Compared to the properties of pure Na$_2$SO$_4$ two points should be noted. First, the hydration of thenardite (or dehydration of mirabilite) at 25°C always occurs in the presence of a salt solution. Therefore kinetic effects observed for the "dry hydration" of thenardite[8,9,10] due to the formation of a mirabilite surface layer may not be observed in the mixture with sodium chloride. Second, at 25°C and mixing ratios m(SO4)/m(Cl)<0.42 mirabilite is never formed at any humidity.

3.2 Formation and decomposition of double compounds

There are many cases of ternary salt mixtures known where the two dissolved salts combine in fixed proportions to form a definite double compound which obviously further adds on the complexity of phase diagrams of salt mixtures. Many double salts have already been observed as efflorecences on the walls of historic monuments[1] and their crystallization from pore solutions certainly has to be considered as another source of salt damage. To illustrate the formation and decomposition of double compounds the solubility diagram of the $K_2SO_4/MgSO_4/H_2O$ system at 25°C is shown in Fig. 5. Due to the formation of the double compound schoenite $(K_2Mg(SO_4)_2 \cdot 6H_2O)$ a stable solution in equilibrium with both single salts, arcanite (K_2SO_4) and epsomite $(MgSO_4 \cdot 7H_2O)$ does not exist at 25°C. There are two invariant points instead.
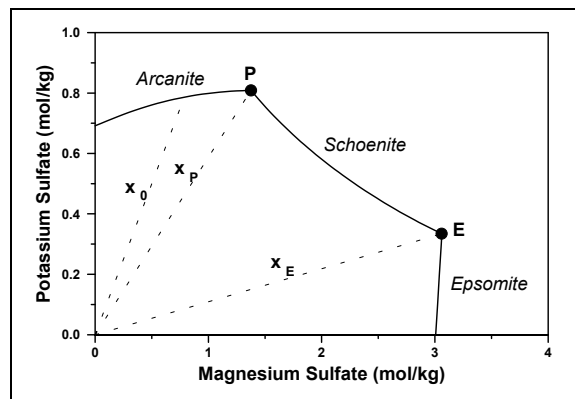

Fig. 5. Solubilities in the $K_2SO_4/MgSO_4/H_2O$ system at 25°C

The crystallization paths may now be discussed briefly. For convenience we define the mixing ratio of the two salts as $x=m(K_2SO_4)/m(MgSO_4)$. Then several limiting mixing rations x_0, x_P and x_E, indicated as dashed lines in Fig. 5 have to be considered. The mixing ratios of the invariant points P and E are given as x_P and x_E, respectively. For an equimolal mixture of the two sulfates we have $x=x_0=1$. Point P is the eutonic or drying-up point for all solutions with $x>1$, point E that for solutions with $x<1$. Therefore, depending on the initial composition, complete drying of a mixed solution of the two salts leads to either a mixture of arcanite and schoenite, or epsomite and schoenite, but never to a mixture of arcanite and epsomite. Several possible crystallization paths on evaporation of water are possible.

They are summarized in Table 1 and may be easily derived from Fig. 5. There is one particular case which should be discussed in more detail. From solutions with mixing ratios $1>x>x_P$ the first solid to be deposited is arcanite. The composition of the remaining solution approaches point P as arcanite is removed. Since $x<1$, however, P is not the drying-up point in this particular case. Further decrease of the relative humidty will rather cause the dissolution of arcanite and the crystallization of schoenite according to:

$$K_2SO_4 + Mg^{2+} + SO_4^{2-} + 6H_2O \rightarrow K_2Mg(SO_4)_2 \cdot 6H_2O \tag{5}$$

Finally, if humidity continues to fall the drying-up point E is reached. In this particular case the crystallization sequence therefore involves an additional phase transformation at point P and we expect different behaviour of such a mixture with respect to damage in porous materials. We are not aware, however, of any systematic experimental studies of salt damage involving double salts.

Table 1. Crystallization sequences in the $K_2SO_4/MgSO_4/H_2O$ system at 25°C

	initial composition	first solid and transformation	dry composition
I.	$x>1$	arcanite	arcanite + schoenite (94.6%)
II.	$x_P<x<1$	1. arcanite 2. schoenite (94.6%)	epsomite + schoenite (88.6%)
III.	$x_E<x<x_P$	schoenite	epsomite + schoenite (88.6%)
IV.	$x<x_E$	epsomite	epsomite + schoenite (88.6%)

The crystallization humidities of the $K_2SO_4/MgSO_4/H_2O$ system at 25°C show the same behaviour as other systems already discussed. The deliquescence humidities of the pure salts are 97.5% and 90.4% for the potassium and the magnesium salt, respectively. The crystallization of arcanite and epsomite from the mixed solutions starts at lower relative humidities than in the single salt solutions. The drying-up points are reached at relative humidities of 88.6% and 94.6% for points E and P, respectively.

3.3 Crystallization properties of a four-component system

The model calculations presented so far have proved very helpful for the discussion of the crystallization properties and the critical relative humidities at which phase transformations occur. However, the ternary

systems treated do not provide a real test for the predictive power of the chemical model because the solubility data of the systems themselves have been used for the parameterisation of the model. A stringent test for the model approach is the calculation of solubilities in a system containing more than three different ions and comparison to experimental data. We therefore applied the model to predict the solubilities in a four-component system. The calculated solubility diagram of the $K^+/Mg^{2+}//NO_3^-/SO_4^{2-}/H_2O$ system at 25°C is shown as the Jaenecke projection in Fig. 6. All possible mixtures of the four ions are represented in terms of ionic percentages of potassium and nitrate. The corners of the square therefore represent the four pure salts (KNO_3, K_2SO_4, $Mg(NO_3)_2$, $MgSO_4$). Each of the four sides of the square represents one of the ternary subsystems from which the mixing parameters for the model have been obtained, e.g. the $K_2SO_4/MgSO_4/H_2O$ system discussed before.
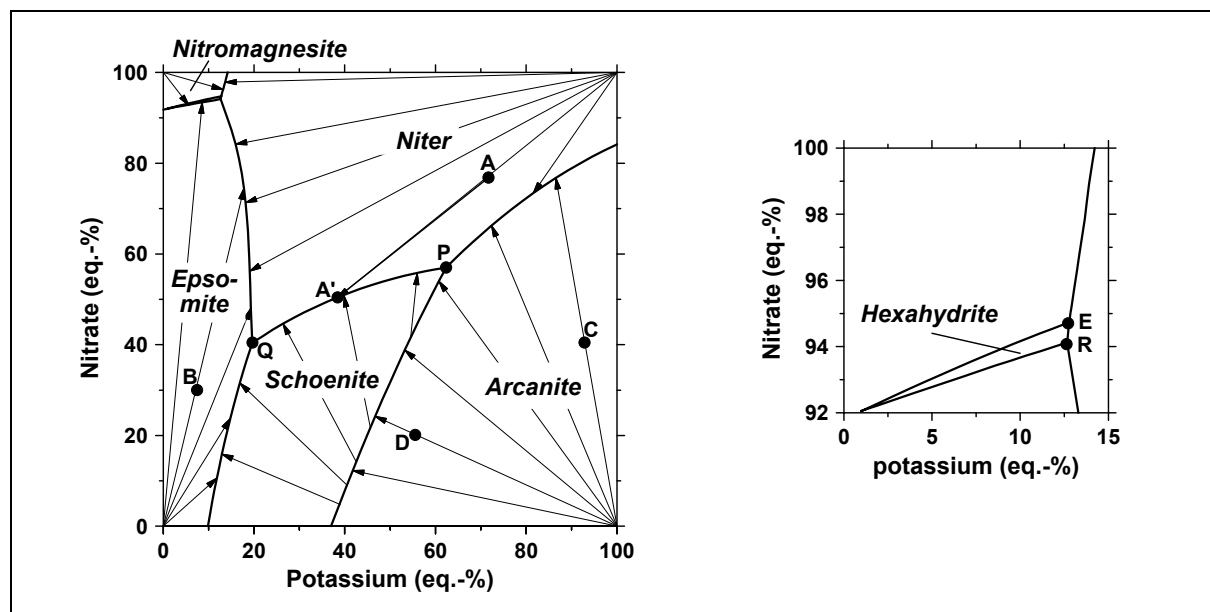

Fig. 6.   Solubility diagram of the $K^+/Mg^{2+}//NO_3^-/SO_4^{2-}/H_2O$ system at 25°C

The lines in the interior of the square are the saturation curves for solutions coexisting with two solid phases. These curves define the crystallization fields of six different minerals which can be observed as stable solids depending on the composition. In addition to KNO_3 (niter), K_2SO_4 (arcanite), $Mg(NO_3)_2 \cdot 6H_2O$ (nitromagnesite), $MgSO_4 \cdot 7H_2O$ (epsomite), and $K_2Mg(SO_4)_2 \cdot 6H_2O$ (schoenite) which are the stable solids at 25°C in the binary and ternary subsystems, there also appears a very small crystallization field of $MgSO_4 \cdot 6H_2O$ (hexahydrite), which can be seen from the enlarged magnesium nitrate rich corner of the diagram also shown in Fig. 6. According to the phase rule a maximum of three different solids can coexist with a solution. The coresponding isothermal invariant points are given as the intersections of the two salt coexistence curves (points P, Q, R and E in Fig. 6). Literature data on the solubilities in the $K^+/Mg^{2+}//NO_3^-/SO_4^{2-}/H_2O$ system at 25°C are available[12] and may be used to validate the model calculations. It can be seen from Table 2 that there is very good agreement between calculated and experimental invariant points.

A lot of information about the crystallization properties of the four-component system can be readily derived from Fig. 6. It can be seen that there are solutions coexisting with niter and espomite, but not with arcanite and nitromagnesite. Therefore niter and epsomite are referred to as the stable salt pair in this system. For a dilute solution of any composition the first solid to be deposited is defined by the crystallization fields of the six salt minerals. For example, niter, epsomite and arcanite would first crystallize out from solutions of compositions A, B, and C in Fig. 6, respectively. The arrows in the crystallization fields indicate how the composition of the remaining solution changes if the respective salt crystallizes out. Solution A would, for example, be depleted in potassium and nitrate if niter is deposited. If the relative humidity continues to fall the composition of the solution will move along line AA' being also saturated with respect to schoenite at A'. Further removal of water then causes the simultaneous crystallization of niter and schoenite until at point Q there is also saturation with respect to epsomite. In this particular case Q is not the drying-up point of the system. Further decreasing the

relative humidity would therefore cause the decomposition of schoenite according to equation (6) and continuous crystallization of niter and epsomite.
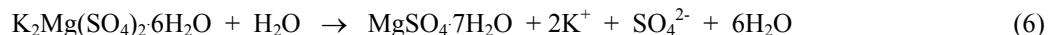
$$K_2Mg(SO_4)_2 \cdot 6H_2O + H_2O \rightarrow MgSO_4 \cdot 7H_2O + 2K^+ + SO_4^{2-} + 6H_2O \quad (6)$$

Table 2. Invariant points of the $K^+/Mg^{2+}//NO_3^-/SO_4^{2-}/H_2O$ system at 25°C (concentraions are molalities, experimental molalities[12] in brackets, relative humidities are calculated values)

point	$m(K^+)$	$m(Mg^{2+})$	$m(NO_3^-)$	$m(SO_4^{2-})$	solid phases	RH
P	3.18	0.96	2.91	1.10	arcanite + schoenite + niter	90.1%
	(3.27)	(1.01)	(2.94)	(1.16)		
Q	1.36	2.78	2.80	2.06	epsomite + schoenite + niter	83.0%
	(1.51)	(2.76)	(3.00)	(2.01)		
R	1.46	5.03	10.84	0.34	epsomite + hexahydrite + niter	52.8%
	(1.55)	(4.50)	(9.71)	(0.42)		
E	1.53	5.23	11.36	0.32	hexahydrite + niter + nitromagnesite	50.5%
	(1.62)	(5.18)	(11.27)	(0.36)		

The dehydration of epsomite to form hexahydrite occurs at point R before the crystallization end point or drying-up point of solution A is reached at point E. For other compositions of the initial solutions, however, the sequences of salt deposition may be different. Examples for the solutions of compositions A, B, C, and D from Fig. 6 are shown in Table 3. The evaporation path of solution D in Fig. 6 involves the formation of schoenite according to equation (5) above.
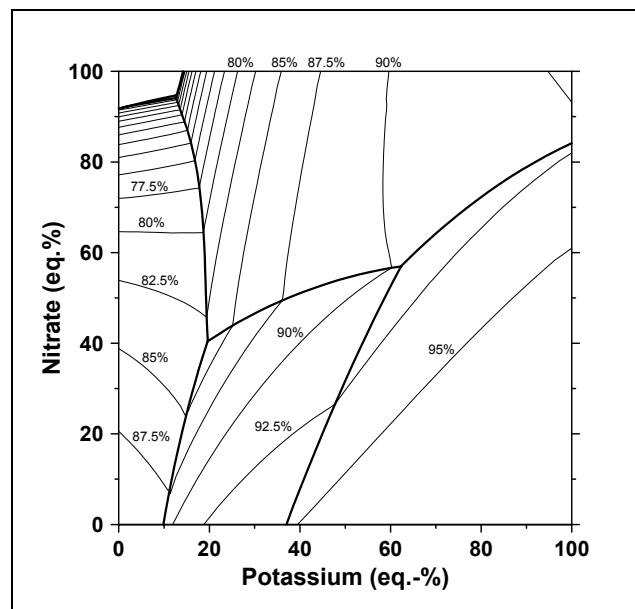

Fig. 7. Lines of equal saturation humidity in the $K^+/Mg^{2+}//NO_3^-/SO_4^{2-}/H_2O$ system at 25°C (2.5% RH intervals)

The relative humidities corresponding to the various drying-up points listed in Table 3 have been already given in Table 2. A complete graphical presentation of the relative humidities in equilibrium with the saturated solutions of the system is shown as lines of equal relative humidity in Fig. 7. It can be seen how increasing amounts of nitrate and magnesium lead to shift of the saturation humidities to lower values. This behaviour had to be expected from the deliquescence humidities of the pure salts (K_2SO_4: 97.5%, KNO_3: 92.6%, $MgSO_4 \cdot 7H_2O$: 90.4%, $Mg(NO_3)_2 \cdot 6H_2O$: 53.7%). Again the crystallization starts at lower relative humidities than would be expected from the respective solutions of the pure salts. As in the ternary systems above there is a range of relative humidities within which fluctuations cause continuous crystallization or dissolution or other phase changes of one or more of the various solid phases. The upper limit of this range depends on the initial solution composition. The lower limit is given by the relative humidity at the drying-up point corresponding to the respective initial compositions.

Critical relative humidities for any particular composition can be either obtained with sufficient accuracy from Fig. 7 by interpolation or can of course be exactly calculated applying the chemical model. For example, the crystallization of niter from solution A (Fig. 6) starts if the relative humidity drops below 90.9%. Schoenite would be deposited in addition at humidities below 87.9% (point A' in Fig. 6). Critical relative humidities for the remaining phase transformations in the course of the evaporation path, which are the decomposition of schoenite and the simultaneous crystallization of epsomite and niter (point Q), the dehydration of epsomite (point R) and the complete drying including the crystallization of nitromagnesite (point E), may be found in Table 2.

Table 3. Sequences of salt deposition for evaporation of water from dilute solutions of initial compositions A, B, C and D (see Fig. 6); crystalline solids after complete evaporation are printed bold

A	B	C	D
niter	epsomite	arcanite	arcanite
niter + schoenite	espomite + niter	arcanite + niter	schoenite
niter + epsomite	hexahydrite + niter	**arcanite + niter**	schoenite + niter
niter + hexahydrite	**hexahydrite + niter**	**+schoenite**	**schoenite + niter**
niter + hexahydrite	**+ nitromagnesite**		**+ epsomite**
+ nitromagnesite			

4 X-ray diffraction studies

It has been shown in the previous sections that phase behaviour of salt mixtures is quite complex. Though the chemical model could be successfully used for the prediction of the crystallization properties of the four-component system it should be noted that more complex systems also inolving other ions are typically found in historic monuments. Therefore the chemical model has to be extended to include all of the relevant ions and to cover the full range of ambient temperature and humidity conditions. The resulting systems which will have to be treated are very complex, however, and the model will have to be validated experimentally. In addition, since the model used is based on equilibrium thermodynamics nothing can be said about other aspects of salt crystallization in porous materials such as kinetics of phase changes and the influence of porous structures on it, or the formation of supersaturated solutions and metastable phases.

Thus, there are several reasons why experimental techniques are required, which can be used to study the behaviour of salt mixtures under controlled conditions of temperature and relative humidity. One such technique, environmental scanning electron microscopy, has been recently used to study the dynamics of the hydration and dehydration of sodium sulfate in stone[10]. The classical technique for the direct detection of mineral phases is X-ray diffraction (XRD), which has also been applied as a time and temperature resolved dynamic technique[13]. In the present study we have used a modified diffractometer permitting measurements to be made under controlled conditions of both, temperature and humidity ("ambient XRD"). A previous version of the instrument has been successfully applied to study the deliquescence properties of ammonium salts in atmospheric aerosols[14]. The experimental set-up consists of a brass measurement chamber fitted to a Siemens D5000 diffractometer with position sensitive detector (PSD). Relative humidity in the chamber is controlled by passing dry air through a thermostatted bubbler. A second thermostat connected to the brass chamber is used for temperature control. Humidity could be controlled to approximately ±1% RH in the early version of the instrument that has been used for the measurements presented here. Temperature can be held constant within ±0.4°C.

Ambient XRD measurements can be done in two different ways. First, it is possible to start with a dilute solution containing the salts of interest. Stepwise decreasing the relative humidity then yields the critical relative humidities of crystallization or phase transformation and, finally, the identity of the crystalline solids that remain after complete evaporation of water. Alternatively, a mixture of the crystalline solids may be exposed to stepwise increases in the relative humidity yielding the deliquescence humidities and the phase transformations of the solids.

In a first application of the technique the deliquescence properties of a mixture of sodium chloride and sodium nitrate have been studied. Samples of different mixing ratios on quartz fibre filters were prepared from a salt solution. A conventional nebulizer was used to generate solution droplets which were subsequently evaporated and collected on the filters as solid particles by filtration[15]. The quartz fibre filters have then been placed into the measurement chamber and were exposed to stepwise increases of the relative humidity at constant temperature. The deliquescence humidities obtained at 25°C for different mixing ratios of the two salts given as the mole fraction of $NaNO_3$ are shown in Fig. 8 together with the calculated deliquescence humidities using the equilibrium model.

As has been already discussed the deliquescence of a salt mixture having a composition different from that of the eutonic mixture cannot be simply characterized by a specific value of relative humidity. This may be

illustrated for a mixture of NaCl and NaNO$_3$ with a mole fraction of nitrate smaller than that of the eutonic. If this mixture is subjected to a relative humidity corresponding to the water activity of the eutonic solution it will absorb water. At this point nitratine (NaNO$_3$) dissolves completely. On the other hand, halite, which is enriched in the mixture with respect to the eutonic, only partly dissolves. As humidity is gradually increased more halite goes into solution and is finally dissolved completely. Therefore the corresponding relative humidity gives the upper limit of the deliquescence of NaCl in that mixture, or, vice versa, if the relative humidity falls below this value again halite would start to crystallize out.

The points in Fig. 8 give the experimental relative humidities of complete dissolution of the two salts for different mixing ratios. Taking into account the experimental uncertainties the results obtained are in reasonably good agreement with the theoretically predicted values. The experimental uncertainties are mainly determined by two influences. First, the measurements are affected by the accuracy and reproducibility of the humidity control in the measurement chamber. Second, measurements are based on stepwise increases of relative humidity and there remains some uncertainty in the exact deliquescence humidities depending on the intervals chosen for humidity increase. The overall uncertainty of the measurements presented is estimated to ±2%RH. Ambient XRD can be also used to observe how deliquescence evolves within a range of the relative humidity. The process is illustrated for the dissolution of NaNO$_3$ in Fig. 9, where the relative intensity of an X-ray peak of nitratine during the stepwise decrease of relative humidity is shown.
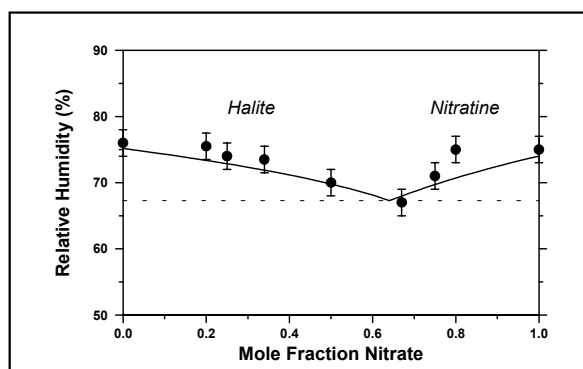

Fig. 8. Deliquescence humidities of NaCl/NaNO$_3$ mixtures (curve: calculated)
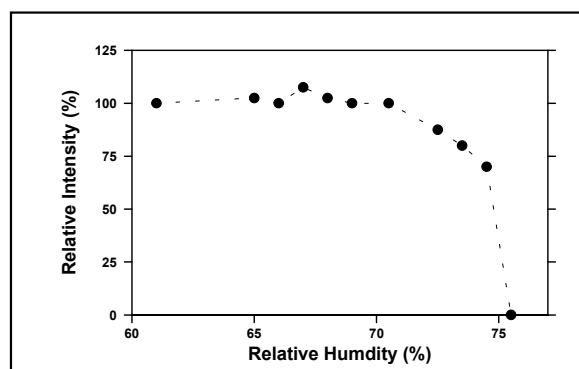
Fig. 9. Relative X-ray intensities of nitratine (mole fraction nitrate: 0.8)

The following example illustrates how this kind of deliquescence measurements can also find very practical applications. Heavy efflorescences of halite have been observed at the wall surfaces inside a 13th century brick monument (Kampischer Hof, Stralsund). The question arised, wether it would be possible to avoid halite crystallization by keeping temperature and relative humidity at an appropriate level. Salt analyses of brick and mortar samples have been carried out and revealed very high concentrations of sodium, calcium, chloride and nitrate. Other ions were found to be of minor importance. The molar concentrations indicated that, treating the salt system as a simple mixture of NaCl and Ca(NO$_3$)$_2$ would be a reasonable approximation.

Ambient XRD measurements of the deliquescence of NaCl in mixtures with Ca(NO$_3$)$_2$ have therefore been carried out. The deliquescence of halite in two different mixtures covering the range of mixing ratios found in the wall has been studied at 25°C. The relative humidities above which halite is completely dissolved were found to be 71-72% and 65% for mole fractions of NaCl x_{NaCl}=0.75 and x_{NaCl}=0.66, respectively. Again the experimental values compare well to the calculated values of 64.0% and 69.1%. Final recommendations with respect to an optimum room climate require measurements to be made also at temperatures other than 25°C, which are not finished yet. The results obtained so far clearly indicate, however, that ambient XRD is a very promising new experimental technique to study the properties of salt mixtures.

5 Conclusions

The phase behaviour of multicomponent salt mixtures is extremely complex. Even in the case of the comparably simple four-component system described in detail in this study several possible sequences of salt deposition and phase transformations have to be considered. It is by no means possible to predict the behaviour of a salt mixture

from the properties of the pure components. Also attempts to conduct the huge number of experiments required to cover the whole range of possible mixture compositions seem to be hopeless. Nevertheless, the understanding of the properties of salt systems in porous materials is an area of major concern in conservation. Thus, one needs chemical models that allow the prediction of the phase behaviour of salt mixtures over appropriate ranges of temperature and humidity. In the present study the chemical model of Pitzer[5] has been successfully applied to predict the phase behaviour of a four-component system. In the future this model needs to be extended and validated including all ions typically found in porous materials.

In addition, experimental techniques are required which can be used to study the phase behaviour of salt mixtures under controlled conditions of temperature and humidity. It has been shown that ambient XRD is a very promising new technique in this respect. Though it has been only applied to study the deliquescence properties of rather simple salt mixtures, the technique should be an appropriate experimental technique to validate model predictions for complex mixtures, as well. In addition, ambient XRD as a dynamic technique might also be successfully applied to study kinetic influences on phase changes in porous materials.

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