MODELLING THE CRYSTALLISATION BEHAVIOUR OF MIXED SALT SYSTEMS: INPUT DATA REQUIREMENTS

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Abstract

The use of chemical equilibrium models to predict the crystallisation behaviour of complex salt mixtures is demonstrated. Input data requirements of such models are briefly discussed with special emphasis on problems arising from inadequate sampling strategies, incomplete analytical data and measurement uncertainty. The violation of the electroneutrality requirement is discussed in more detail and a procedure for routine control and processing of analytical data is recommended.

Keywords: salts, salt mixture, modelling, salt analysis

1. Introduction

The crystallisation behaviour of mixed salt systems is much more complex than that of pure single salts and it is usually not a trivial task to predict empirically, for a given mixture composition, the crystallisation sequence, i.e. the nature of the solid phases that crystallise out and the critical changes in the climatic conditions that induce phase changes and crystal growth. There is a huge number of possible mixture compositions found in historic buildings and for practical applications it is impossible to conduct in the laboratory all the measurements necessary to predict the respective crystallisation pathways.

However, there has been considerable progress in the use of chemical equilibrium models such as ECOS or ECOS–RUNSALT, which make it possible to predict the crystallisation pathways even for complex salt mixtures, and also the environmental conditions for salt phase transitions. It is then possible to define for an object the safe ranges of climatic conditions, i.e. temperature and relative humidities, under which salt damage can be avoided or at least minimized. Using equilibrium models it is also possible to calculate the hygroscopic moisture uptake of salt contaminated masonry.

Though equilibrium models can be extremely useful, there are limitations that have to be taken into account. First, thermodynamic models are based on the assumption that the salt–water system is at equilibrium, and as such, the models only predict equilibrium pathways. However, in reality this is not necessarily the case. Kinetic influences can result in the formation of metastable phases (which are less stable than the equilibrium ones, but quicker to form), plus the effects of supersaturation (as crystallisation does not occur precisely at saturation but at some unspecified point beyond) are not accounted for by the model.

Second, the models do not reflect the fact that salt transitions are taking place within a porous medium – and that saline solutions are mobile. Phenomena such as capillary transport and fractionation, and the potential anomalous behaviour of salt–water systems in micropores are not considered. Thirdly, model predictions can be only accurate if the salt mixture contains only those ions that are included in the model parameterization.

Finally, the successful application of an equilibrium model depends largely on the quality of the input data, which in turn are grossly affected by how the samples are collected, and how they are analysed. A correctly devised sampling strategy is needed to ensure that the "right" samples are taken in an appropriate manner. Furthermore, a thermodynamic model requires quantitative analytical measurements, and assumes that from these the composition of the salt mixture is known exactly. The latter assumption is usually not fulfilled as the mixture composition data is based on measurements – and is therefore limited by what can be measured, and the accuracy of those measurements. Therefore, the first step in a careful study always has to be a quality check of the input data. The present contribution focuses on input data restrictions imposed by equilibrium models and we will present guidelines and tools to handle these restrictions in practical applications.

2. Chemical equilibrium models

Chemical equilibrium models involve the thermodynamic treatment of the equilibria that control phase changes of salt mixtures and their interaction with the surrounding climate. Such models usually consist of two parts: an electrolyte solution model to calculate activity coefficients in mixed salt solutions; and an equilibrium model to calculate the phase changes (dissolution, crystallisation, hydration) in response to changes of the environmental conditions. Such a model can then be used to predict the response of a salt mixture in an object to environmental fluctuations, namely temperature and relative humidity (RH). There are various useful applications of thermodynamic models in conservation (Steiger 2005). First of all and most useful, they can be used to interpret the results of salt measurements in building materials, in order to predict the conditions under which salt damage can occur.

A typical example of an application of an equilibrium model is shown in Figure 1. On the left (Figure 1a) is shown the measured composition of a salt mixture found in a surface sample taken from a sandstone masonry wall. The right hand diagram (Figure 1b) shows the crystallisation pathway of the salt mixture as a function of relative humidity, as calculated by the equilibrium model. The model predicts that there is quite a substantial amount of gypsum, $CaSO_4 \cdot 2H_2O$ (127 mmol kg^{-1}) in the sample, most of which (more than 99%) remains in crystalline form over the whole range of ambient RH fluctuations (and so is not plotted on the graph). However, the remaining fraction of the salt mixture is subject to crystallisation–dissolution processes triggered by fluctuations in RH as shown in Figure 1b. From the graph it can be seen that at above 77% RH this hygroscopic salt fraction is completely dissolved. Decreasing the humidity below 77% RH (i.e. moving from right to left along the x-axis), first niter (KNO_3), then nitromagnesite ($Mg(NO_3)_2 \cdot 6H_2O$), nitratine ($NaNO_3$) and, finally, halite ($NaCl$) crystallise out. From this calculation it can be understood that this salt mixture is responsible for the very high hygroscopic moisture content that was observed in this wall. The high amount

of nitrates found in the wall is related to the former use of this part of the building as a stable, while the high gypsum concentration is probably of atmospheric origin.
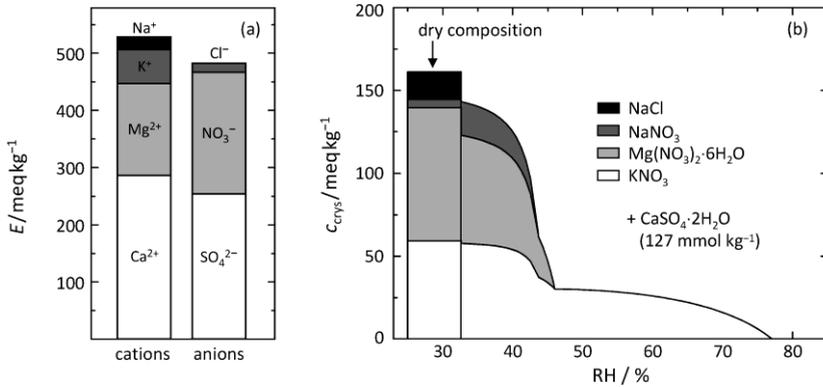

Figure 1 Behaviour of salt mixture present in a sandstone sample, (a) measured salt composition, E, given as equivalent ion concentrations (see Section 3.2.1), (b) crystallisation pathway of the salt mixture as calculated with an equilibrium model, with respect to RH (at 25 °C); c_{cryst} is the amount of crystalline solids present in the sample at the respective RH.

It is obvious that such a modelling approach is particularly useful as a predictive tool. In instances where other measures to prevent salt damage, e.g. desalination, are not applicable, preventive conservation through environmental control might be the only option to reduce the incidence of salt damage. Following appropriate measurements of the salt contamination of an object, it is possible through careful application of a thermodynamic model to predict the temperature and relative humidity conditions that would minimize the frequency of undesired phase changes inducing crystal growth, and hence damage. In the example shown in Figure 1, typical fluctuations in ambient RH in an outdoor environment cause cyclic dissolution and crystallisation of KNO_3 and damage has to be expected. Additional crystallisation of the other salts only occurs at very low RH. However, although such events are less frequent they may cause severe damage as a large amount of salt crystallises in a pore space that is already partially filled with niter and gypsum.

In a collaboration between the University College London (C. Price), the University of East Anglia Norwich (P. Brimblecombe, S. Clegg) and the University of Hamburg (M. Steiger) funded by the European Commission the computer program ECOS (Environmental Control of Salts) was developed. A detailed description of the project and the ECOS program is provided by Price (2000). Up to now the ECOS thermodynamic model is the only computer program generally available to conservation scientists and conservators that is suitable for the calculation of the crystallisation behaviour of salt mixtures in cultural objects. An improved user interface for ECOS known as RUNSALT was developed by Bionda (2006). Retaining the fundamental algorithms of ECOS, RUNSALT facilitates the operation of the program. In the meantime several authors have reported successful applications of ECOS or ECOS–RUNSALT (e.g. Sawdy and Price 2005a, Bionda 2006, Price 2007, Klenz-Larson 2007, Prokos 2008).

3. Input data requirements

When trying to run ECOS, ECOS–RUNSALT or any other equilibrium model, the user is faced with different problems many of which are related to the quality of the input data for the model calculations. Some of these problems arise from inappropriate sampling strategies or are related to the imperfection of the experimental data. Other problems are due to shortcomings of the model itself.

3.1 Sampling problems

When investigating salt deterioration problems within monumental porous structures—such as wall paintings and historic masonry—one of the primary challenges that has to be addressed is that of devising a suitable sampling strategy, as this is fundamental to the ultimate utility of any subsequent investigations. However, this is not straightforward. Not only is it abundantly clear that the salt content of these types of objects is not uniform—since neither is the spread of deterioration phenomena—but also the distribution of the salts is apt to change, as evidenced by the seasonal appearance and disappearance of salt efflorescences. Indeed, temporal variability is rarely taken into account as site investigations tend to be conducted at times that fit with the work-schedule of the investigator, rather than those which might yield the most useful information with respect to the salt damage. In cases where environmental control is a consideration, the degree to which any one part of the object is representative of the whole is an important question to be answered—since only one environmental regime can be selected for a single airspace.

Therefore a sampling strategy has to take into account the likely spatial and temporal variability of the object's salt distribution, the construction and condition of the object, and the prevailing environmental conditions. This is greatly facilitated by the use of a few simple techniques: a consistent sampling methodology and a balanced experimental design which will allow for the subsequent application of statistical techniques to assess and interpret the salt measurement data (for a more detailed case study example see Sawdy and Price 2005a and 2005b). Indeed, the interpretation of results has to be backed up by statistical analysis to validate the inferences drawn. Here standard statistical techniques such as basic descriptives, principal components analysis, analysis of variance (ANOVA), and general linear models (GLM), and can be extremely useful to assess the quality of the data, and the significance of any perceived trends and relationships between factors. Finally, the fundamental importance of historical information about the object, and in situ observations must be stressed. Investigations must be centred primarily on the object, and the story that it tells. The collection of phenomenological information (e.g. the condition of the object, and the type and pattern of deterioration phenomena) provides the vital key for assembling and interpreting other types of data. By adopting a combined approach to in situ investigations that includes sampling and analysis with condition recording, and environmental monitoring, with careful scheduling of site visits to collect this information over time at different seasonal intervals, the overall usefulness of the information obtained is greatly enhanced.

3.2 Imperfections of the experimental data

No lab can measure with absolute accuracy all ions that are present in a real sample. Therefore, problems are related to the selection of ions that have to be measured and to the measurement uncertainties. The main constituents of salt mixtures typically found in building materials are the four cations Na^+, K^+, Mg^{2+} and Ca^{2+}, and, the anions Cl^-, NO_3^-, SO_4^{2-}. This set of ions is also expected as input data for the use of ECOS. There are situations where other ions may have significant contributions and these must not be neglected, However, these other ions are rarely measured on a routine basis and even if they were, there is no model that can treat all relevant solution and solubility equilibria including all ions that could possibly be found in samples from building materials. The main problems that arise from this are outlined below.

3.2.1 Problems with charge imbalances

In any saline solution, the sum of the cation and anion charges must be equal: i.e. the solution is charge neutral. Therefore the charge balance of the analytical data is a good indication of the how accurately the true composition of the solution is reflected in the measurements collected. Both experimental errors in the determination of the ion concentrations and missing ions, i.e. ions that are present in a sample but were not analysed, affect the ionic charge balance and need to be considered. Analytical data of salt analysis are usually reported on a weight fraction basis (mass of an ion per total mass of the sample), i.e. in units of mass percent or $mg\,kg^{-1}$. However, for quality control or for the use of a thermodynamic model the use of molar quantities is more appropriate. For example, the molar concentration c_i of an ion is related to the weight fractions w_i by

$$c_i = 10^6 \; w_i / M_i \tag{1}$$

where c_i and w_i are given in $mmol\,kg^{-1}$ and $mg\,kg^{-1}$, respectively, and M_i is the molar mass of the ion (in $g\,mol^{-1}$). In any electrolyte solution it follows from the neutrality requirement that the sum of positive and negative charges is exactly balanced. Since different ions have different charges (e.g. Na^+, Mg^{2+}, Cl^- SO_4^{2-}), the charge balance is calculated from the charge equivalent concentrations of each ion. For an ion of charge z_i the charge equivalent concentration e_i (in units of $meq\,kg^{-1}$) is given by

$$e_i = |z_i| \, c_i \tag{2}$$

and the total equivalent concentration of positive and negative charges is

$$E_c = \sum_c e_c \quad \text{and} \quad E_a = \sum_a e_a \tag{3}$$

where subscripts c and a refer to cations and anions, respectively. The charge balance B_z is defined as

$$B_z = \frac{2(E_c - E_a)}{E_c + E_a} \tag{4}$$

Considering typical analytical errors, values of $|B_z| > 0.05–0.1$ may be an indication of a problem with the analysis. This could be either a gross error in the determination of

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one or more ions, or it can be an indication for a missing ion. Though the above mentioned seven ions are the most important constituents of the salt mixtures that are typically found in building materials, there are sometimes other ions with significant contributions. The most important source of additional anions is alkalinity which can be a major constituent in building materials, particularly, for buildings where concrete or other alkaline materials were extensively used. Alkalinity is defined as the sum of the charge equivalent concentrations of hydroxide, bicarbonate and carbonate, thus: $c_{alk} = c(OH^-) + c(HCO_3^-) + 2c(CO_3^{2-})$. Arnold and Zehnder (1991) reported several examples of alkaline salts that are formed after use of alkaline materials. Other anions that might have a significant contribution to the total charge balance are fluoride, phosphate, oxalate, acetate and formate.

Apart from the four cations mentioned before, ammonium (NH_4^+) may also be an important cation in building materials. It is a major ion in rain water and atmospheric aerosols. Missing ammonium measurements in samples strongly affected by atmospheric deposition can be the cause of a significant anion excess. It should be noted that ammonium is not stable in carbonaceous material and should volatilize as ammonia.

As long as their contribution to the total charge imbalance is small compared to the analytical uncertainty, the influence of missing is negligible. However, if the charge imbalance exceeds the estimated analytical uncertainty, the results should be carefully interpreted and the application of a sophisticated computer program for further data analysis is hardly justified.

3.2.2 Missing carbonate measurements

Even if the charge imbalance of the analytical results for a single sample is considered insignificant compared to the expected analytical precision, there might still be a systematic imbalance that is only detected if a large number of samples is analysed. This is illustrated in Figure 2. The samples shown were taken from several limestone monuments and the analysis included the standard set of seven ions, i.e. Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^- and SO_4^{2-}. The data clearly show that there is a systematic imbalance with a cation excess that is particularly pronounced at low salt concentrations. For most single samples, the cation excess is moderate to small and one would not necessarily expect it to be significant compared to the analytical uncertainty. However, from the large number of samples shown in Figure 2 it is obvious that the cation excess is systematic. In this case (i.e. analysis of limestone samples), the cation excess is simply the result of missing carbonate and bicarbonate measurements.
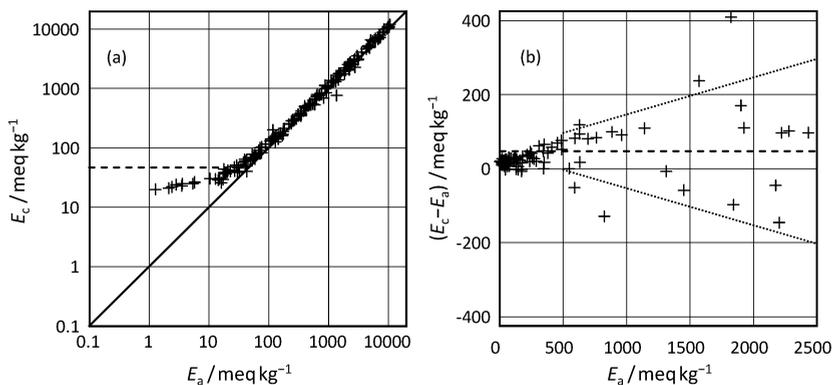
Figure 2. Charge balances of limestone samples. (a) Plot of cation vs. anion charge equivalent concentrations E_c and E_a, (b) Absolute charge balance deviations ($E_c–E_a$) as a function of the total anion equivalent concentration (only samples with $v/m_s = 50$ mL g^{-1}, see explanation in text). In both graphs, the dashed line represents Ca concentrations or excess Ca, respectively, calculated from the solubility of calcite (CaCO$_3$) for $v/m_s = 50$ mL g^{-1}. In graph b, the dotted curves represent limits of ±5% experimental errors.

For the determination of the water soluble salts in the samples shown in Figure 2, the limestone samples were first crushed and ball-milled and then extracted with twice distilled water. Due to the low but finite solubility of calcite a small fraction of the calcite (CaCO$_3$) matrix of the limestone is mobilised by the extraction procedure as dissolved Ca^{2+} and HCO$_3^-$ ions. The total amount of dissolved calcite depends on the ratio v/m_s of the volume of water (v) and the weight of the sample (m_s). The majority of the samples shown in Figure 2 were extracted with 50 mL g^{-1}. Higher values of v/m_s (typically 250 mL g^{-1}) were used for the analysis samples with high calcium sulfate content (e.g. samples with gypsum crusts) to ensure that sparingly soluble gypsum is completely dissolved as discussed below (see Section 3.4). The equilibrium solubility of calcite in water at room temperature yields an apparently soluble calcium concentration that is shown as the dashed line in Figure 2 for $v/m_s = 50$ mL g^{-1}. It is important to note that this amount of soluble calcium is only an analytical artefact. Moreover, calcite is not an environmentally active salt, and therefore is not of concern with respect to the evaluation of soluble salt problems. In the original porous stone, v/m_s and, thus, the mobility of calcite, is limited by the water accessible porosity, i.e. the pore space that can be filled with water. For example, in a limestone with a porosity of 20% and a corresponding density of 2.15 g cm^{-3} a ratio of v/m_s of 0.023 mL g^{-1} is obtained if the pore space is completely filled with water. Therefore, more than three orders of magnitude less calcium is mobilised in the pore solution of a limestone than during the extraction procedure for the determination of soluble salts. It is obvious that the calcium fraction mobilised by partial dissolution of calcite during the extraction of the samples leads to an overestimation of the soluble calcium content in samples containing calcite and an apparent cation excess.

The influence of partial calcite dissolution is particularly strong at very low salt concentration (Figure 2a). The plot of the absolute charge balance deviations for

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samples with $v/m_s = 50$ mL g^{-1} (Figure 2b) confirms the systematic deviation at low salt content (<250 meq kg^{-1}). However, in no instance the cation excess exceeds the value calculated from the solubility of pure calcite (see dashed lines in the diagrams). At higher salt content (>250 meq kg^{-1}), the charge imbalances are more scattered and seem to be largely controlled by measurement uncertainty. In order to evaluate charge balances in a set of analytical data, it is important to consider both realistic measurement errors and the solubility of calcite at the v/m_s ratio used. The dotted lines in Figure 2b represent the upper and lower limits of a combined overall error of 5% measurement uncertainty (precision) and the systematic error of partial calcite dissolution and missing carbonate measurements (horizontal dashed curve). It is obvious that only few samples fall above or below these realistic limiting values of the imbalance. In many cases the observed cation excess may then be attributed to either the partial dissolution of the stone matrix or to measurement imprecision. Such charge imbalances do not cause any problems in the further data evaluation. However, if the cation excess exceeds the combined analytical uncertainty and the error expected from the partial dissolution of calcite, there is evidence for the presence of an anion that was not analysed. Then, further data treatment with an equilibrium model is not useful and may even be misleading. The missing ion may in most cases still be carbonate or bicarbonate. However, if it cannot be attributed to partial calcite dissolution, it must be present in the form of the very soluble sodium and potassium salts (i.e. alkali carbonates). ECOS and many other equilibrium models cannot treat mixed solutions containing alkali carbonates and further data treatment with such a model is not possible. The same is true if there is an anion excess exceeding the combined analytical uncertainties, thus, indicating the presence of an additional cation that cannot be handled by the equilibrium model.

The samples shown in Figure 2 are limestone samples, however, due to the ubiquitous occurrence of calcite in construction materials, similar effects are also expected for other types of materials such as sandstone or brick and of course mortar and plaster. Finally, other alkaline compounds that are sometimes present in building materials like portlandite, $Ca(OH)_2$, are much better soluble than calcite and may cause even more problems with charge imbalances if the corresponding anion is not analysed. In this case, the missing ion is hydroxide which can be easily detected by taking pH measurements in the aqueous extracts.

3.3 The gypsum problem

Electrolyte solution models for complex mixed solutions require quite a number of interaction parameters and their temperature dependence (see Reeves et al. 2000, Steiger et al. 2000 in Price 2000). These parameters have to be determined from experimental data. With every additional ion the number of parameters increases significantly. In an attempt to minimize this large number of parameters, the developers of ECOS tried to reduce the number of ions that have to be treated with the model. Considering the Na^+–K^+–Mg^{2+}–Ca^{2+}–Cl^-–NO_3^-–SO_4^{2-}–H_2O system, the calcium sulfate salts have an exceptionally low solubility compared to all other salts, and are therefore much less active in response to changes in RH and temperature. Therefore it was decided to focus on the more soluble salts, and where possible to exclude calcium sulphate salts from the calculation. Consequently, the total system of these seven ions was split into two six ion subsystems, the Na^+–K^+–Mg^{2+}–Ca^{2+}–Cl^-–NO_3^-–H_2O and the Na^+–K^+–Mg^{2+}–Cl^-–NO_3^-–

SO_4^{2-}–H_2O system. Neither of these two systems contains Ca^{2+} and SO_4^{2-} at the same time, hence, while the ECOS model can treat very simple mixtures containing both calcium and sulphate, nevertheless it cannot be used to predict solubilities in complex mixed solutions that contain calcium and sulfate at the same time. As a result, for complex mixtures including all seven ions, one often obtains an error message recommending the removal of calcium sulphate from the data.

At first glance, it appears to be surprising to exclude calcium sulfate as gypsum is a major salt in many buildings. However, though the solubility of gypsum is much higher than that of calcite, it is still two orders of magnitude lower than for all other salts in the Na^+–K^+–Mg^{2+}–Ca^{2+}–Cl^-–NO_3^-–SO_4^{2-}–H_2O system. This has important consequences. Gypsum is by comparison inactive with respect to environmental fluctuations (i.e. it does not undergo substantial phase transitions in response to changes in RH and temperature), and as a result, the mechanisms by which gypsum can cause damage are somewhat different to those by which more soluble salts cause damage. However, the solubility of gypsum is large enough that gypsum is completely dissolved in the aqueous extracts of samples at common values of v/m_s. This is illustrated in Figure 3a. The diagram depicts the maximum amount of gypsum in a sample that can be completely dissolved in a single extraction as a function of the ratio v/m_s. It can be seen that for common ratios v/m_s of 50–100 mL g^{-1} gypsum is completely dissolved in the aqueous extracts as long as its content in the samples does not exceed 10–20% by weight. In contrast, the gypsum solubility is so small that the salt is essentially immobilized once it is deposited in the pore space of the material. This is illustrated in Figure 3b.
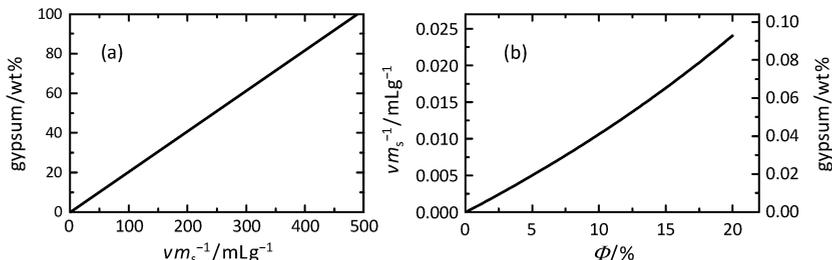

Figure 3. Mobility of gypsum. (a) Amount of gypsum (as percentage weight fraction) that can be extracted from a sample as a function of the ratio v/m_s. (b) Ratio v/m_s (left axis) and extractable amount of gypsum in porous stone as a function of porosity Φ.

The curve shows, as a function of the total porosity Φ, the maximum amount of gypsum present in a porous material that can be completely dissolved if the available pore space is filled with water (right hand y-axis). For example, if a porous stone with a porosity of 20% is completely filled with water, the pore solution can only dissolve a small amount of gypsum corresponding to a content of about 0.1% by weight. The gypsum content in building materials is typically much higher. It follows that gypsum once formed in building materials is essentially immobilised. Due to its very low solubility only a very small fraction of the total gypsum deposit actually present in the pore space can be dissolved and the concentration of calcium sulfate in a pore solution is so small that it does not affect the remaining ions and their solubility equilibria, thus

neglecting calcium sulfate in the equilibrium calculations does not pose any problems. Therefore, it is reasonable to remove calcium sulfate from the mixed salt system data that has to be treated with an equilibrium model. This can be simply done by assuming that the molar calcium sulfate content of a sample is equal to the molar concentration of either calcium or sulfate, whichever is smaller. The concentration of the other ion is then corrected accordingly, i.e. the molar concentrations of calcium and sulphate are compared, the one with the lower molar concentration is removed from the system, while the other is reduced by the same amount. This correction yields one of the two subsystems mentioned before that can be more easily treated with an equilibrium model such as ECOS. However, this correction should only be applied after an appropriate treatment of charge imbalances as described in the following section.

4. Recommended treatment of input data

Figure 4 depicts a recommended procedure for the evaluation of input data for use with ECOS–RUNSALT or other equilibrium models. Measurements of the salt content in samples from historic monuments should include the seven ions mentioned. The calculation of a charge balance should be always carried out in order to evaluate the quality of the data. The next step is a crucial as one has to decide at this stage whether the data are appropriate for further evaluation using an equilibrium model. For this purpose, the user has to define values for the maximum acceptable analytical error. Relative errors of about 5–10% might be realistic assumptions. However, this needs to be carefully evaluated.

Then, if there is an anion excess exceeding the acceptable imprecision, any further data evaluation should be terminated as there is indication that unacceptable large errors or missing ions may substantially bias the model calculations. At this stage, an experimental error limit should be defined by the user, based on realistic assumptions of analytical uncertainties, i.e. a maximum acceptable anion excess, $(E_a/E_c)_{max}$. If the anion excess is acceptable in comparison to the analytical uncertainty, all anion and cation concentrations are corrected such that the electro-neutrality is guaranteed (see Figure 4).

In the case of a cation excess, the evaluation of the imbalance should consider both influences, partial dissolution of calcium (and missing carbonate data) and additional analytical uncertainty. The first step should always be the correction of missing carbonate data. This is simply done by initially assuming that the whole cation excess is caused by partial calcite dissolution. Then, a corrected calcium concentration ($c_{Ca,corr}$) can be calculated from the measured calcium concentration (c_{Ca}) according to

$$c_{Ca,corr} = c_{Ca} - 1/2\Delta E \tag{5}$$

where $\Delta E = (E_c - E_a)$ is the absolute charge balance deviation. It should be noted that the factor ½ accounts for the fact that E_c and E_a are charge equivalent concentrations while c_{Ca} is a molar concentration of a divalent cation. The next step is the evaluation of the correction (½ΔE) which has to be compared to the maximum amount of calcium that can be mobilised by calcite dissolution ($c_{calcite}$). A maximum value of $c_{calcite}$ can be calculated from the solubility of calcite at room temperature and atmospheric CO_2 pressure (0.0005 mol calcite per kg water) and the ratio v/m_s used in the aqueous extractions. If the calculated correction (1/2ΔE) does not exceed, to within acceptable experimental uncertainty, the value of $c_{calcite}$, the correction according to

Equation (5) is reasonable. This yields the following expression as a criterion for an unacceptable large correction:

$$\tfrac{1}{2}\Delta E > (1+f)c_{\text{calcite}} \qquad\qquad (6)$$

where f is the experimental error limit in the calcium determination (e.g. $f = 0.05$ for 5% maximum error). However, if the correction exceeds the experimental error limit, any further data evaluation should be terminated as there is a clear indication for a missing anion leading to erroneous model calculations. If the correction ΔE is acceptable, the concentrations of the remaining six ions can be used together with the corrected calcium concentration as a set of appropriate input data for an equilibrium model. If necessary, as is usually the case for use with ECOS–RUNSALT, a further correction to remove calcium sulfate as discussed before may then be applied.

It should be noted that there is also an auto charge balance option in the ECOS–RUNSALT program. The procedure is simply an algebraic correction of the charge imbalance by proportionally increasing the concentrations either of all cation or all anion concentrations, respectively, depending on whichever are smaller. Hence, there is no critical evaluation of the charge imbalance by comparison with an experimental error limit, nor, is there a correction for dissolved calcite. Therefore, the autobalance option in the ECOS–RUNSALT program can only be recommended to experienced users who know exactly what they are doing. Sometimes it might be a useful option to handle charge balance problems in simulation with artificial samples. However, it is not recommended for the treatment of measured concentrations in real samples that are usually affected by calcite dissolution.
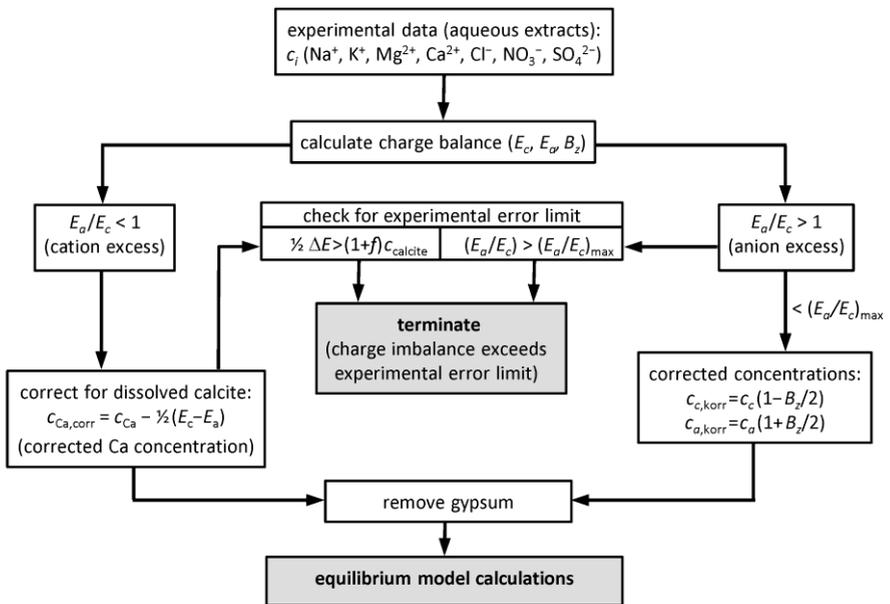

Figure 4. Recommended treatment of input data for use with chemical equilibrium models such as ECOS–RUNSALT (removal of charge imbalance).

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5. Conclusions

Equilibrium models provide an extremely useful tool for the prediction of the crystallisation behaviour of complex salt mixtures and for the definition of safe ranges of climatic conditions surrounding an object. However, equilibrium models have their limitations, and problems arising from input data requirements are frequently encountered. It is important to realize that a model can never compensate for inadequate sampling strategies or incomplete and erroneous analytical data of salt concentration and composition. In the present work, we have focused on problems arising from incomplete analytical data (missing ions such as carbonate) and measurement errors and the resulting violation of the electroneutrality requirement. An analysis of a salt sample from an object should include at least the seven ions Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^- and SO_4^2 and the measurement uncertainty should ideally not be larger than about 5–15% relative standard deviation. Our recommended procedure can then be used for routine quality control of analytical data based on charge balance considerations. On the basis of plausibility checks, the procedure can be used for the correction of charge imbalances caused by partial calcite dissolution and missing carbonate measurements. Such corrections are only applicable if the charge imbalance does not exceed the acceptable limit defined by the extraction procedure and the measurement uncertainty. Finally it should be stressed that output predictions from such models should always be cross referenced with site based observations and collected phenomenological data, to check if other significant factors have been overlooked, and that the conclusions drawn fit with what is observed in reality.

6. References

Arnold, A. and Zehnder, K. 1991. Monitoring wall paintings affected by soluble salts. In *The conservation of wall paintings* (Cather S., ed.), The Courtauld Institute of Art and The Getty Conservation Institute, 103–135.

Bionda, D. (2006) *Modelling indoor climate and salt behaviour in historic buildings: A case study*. Dissertation, ETH Zürich.

Klenz Larsen, P. 2007. The salt decay of medieval bricks at a vault in Brarup Church, Denmark. *Environ Geol* **52**: 375–383.

Price, C.A. 2000. *An expert chemical model for determining the environmental conditions needed to prevent salt damage in porous materials*. London: Archetype Publications.

Prokos, P. 2008. Equilibrium conditions of marine originated salt mixtures: An ECOS application at the archaeological site of Delos, Greece. In *Salt weathering on buildings and stone sculptures*, Technical University of Denmark, Lyngby, 139–148.

Sawdy, A. and Price, C. 2005a. Salt damage at Cleeve Abbey, England. Part I: a comparison of theoretical predictions and practical observations. *J Cult Heritage*, **6**: 125–135.

Sawdy, A. and Price, C. 2005b, Salt damage at Cleeve Abbey, England. Part II: seasonal variability of salt distribution and implications for sampling strategies, *J Cult Heritage*, **6**: 361-367.

Steiger, M. 2005. Salts in porous materials: thermodynamics of phase transitions, modelling and preventive conservation. *Restor Build Monum*, **11**: 419–431.