

# 9

## **Modelling the Behaviour of Salts Mixtures in Walls: A Case Study from Tenaille von Fersen**

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### **Abstract**

The response to changing environmental conditions (relative humidity and temperature) of the salts in the test room of the Tenaille von Fersen building, Suomenlinna, Finland, was simulated using the thermodynamic model of ECOS (Price 2000) and the computer program RUNSALT (Bionda 2002). The results show that for any ionic combination tested, the range of relative humidity where the largest variations in the amount of solid salt minerals occur lies between about 60 and 75%. Above 72-75% relative humidity, all salts except mirabilite and gypsum, if enough calcium, respectively calcium and sulphate are available, are in solution. Temperature variations, on the other

hand, have little influence on this range. In the presence of sulphate, low temperatures can favour the formation of mirabilite at higher relative humidity.

## 9.1 Introduction

When planning a conservation scheme for a salt-contaminated object, it is usually crucial to be able to estimate the environmental parameters that are most appropriate for the good preservation and the limitation of damage to the object in question. Salt damage is directly attributable to crystal volume changes, which principally occur when a salt crystallises or dissolves and, if the salt can exist in more than one hydration state, when it hydrates or dehydrates. Every soluble salt at any given temperature has a critical relative humidity, the equilibrium relative humidity (RHeq), above which it absorbs moisture from the air and below which it crystallises. In materials contaminated with a single salt, damage can be avoided by permanently keeping the relative humidity (RH) above or below this value. Unfortunately, porous historic materials are more commonly contaminated with a mixture of salts, whose behaviour is much more difficult to predict because the cations and anions present can combine in several ways to form different salts and because the RHeq of every single salt is affected by the presence of the others. An experimental determination of the RHeq of every salt in a given system is theoretically possible, but in practice it is fully inconceivable to carry out measurements for every possible ion combination. In such cases, computer modelling can be a valuable tool, permitting the determination of the solid minerals present at any given RH and, thus, the prediction of "safe" ranges of RH that do not enforce any substantial change in the state of the salts present.

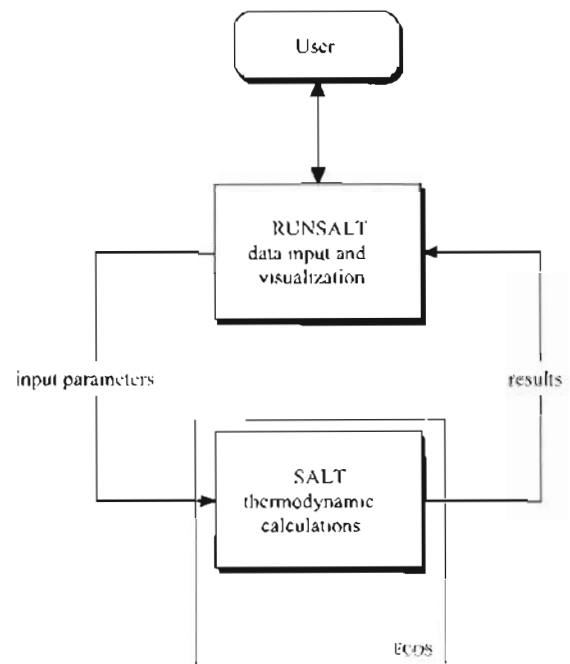


Figure 9.1 Schematic representation of the structure of the modelling software.

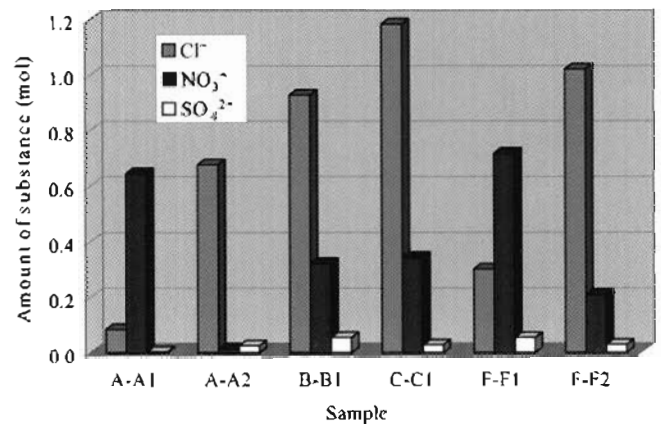


Figure 9.2 Relative amount of the anions in the selected salt samples.

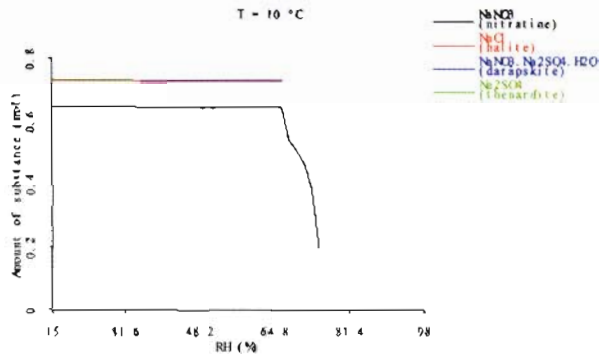


Figure 9.3 Sample A-A1. Input ion amounts (wt.%):  $\text{Na}^+ = 16.919903$ ,  $\text{Cl}^- = 3$ ,  $\text{NO}_3^- = 40$ ,

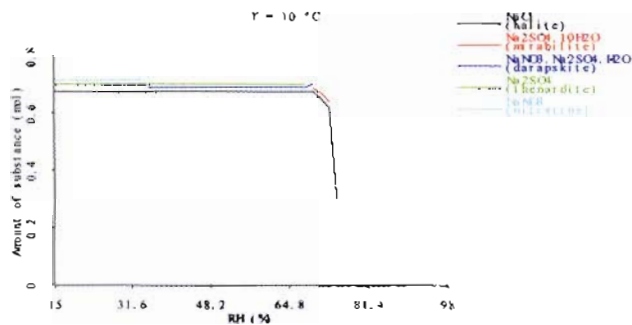


Figure 9.4 Sample A-A2. Input ion amounts (wt. %):  $\text{Na}^+ = 17.04542$ ,  $\text{Cl}^- = 24$ ,  $\text{NO}_3^- = 0.9$ ,  $\text{SO}_4^{2-} = 2.4$ .

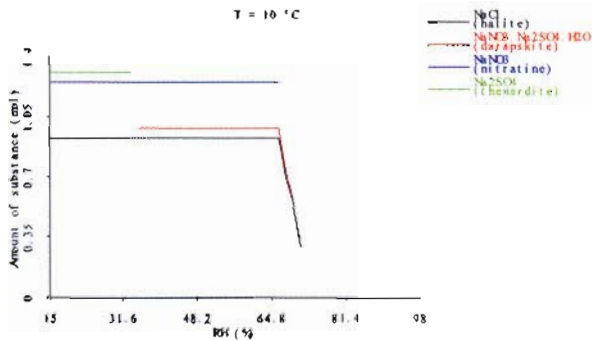


Figure 9.5 Sample B-B1. Input ion amounts (wt. %):  $\text{Na}^+ = 31.2865259$ ,  $\text{Cl}^- = 32.9$ ,  $\text{NO}_3^- = 20$ ,  $\text{SO}_4^{2-} = 5.3$

## 9.2 Methods

The computer modelling was performed using the thermodynamic model of ECOS (Price 2000). ECOS is an expert system capable of predicting the behaviour of aqueous solutions in porous materials. Given the ionic analysis of salts ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  ions), it calculates the combination and the amount of solid minerals present under equilibrium conditions at any given temperature and RH. The thermodynamic calculations are based on the Pitzer theory of electrolyte solutions (Pitzer 1973, Clegg and Whitfield 1991). In order to access the thermodynamic model of ECOS, a MS-WINDOWS computer program (RUNSALT) was developed (Bionda 2002) to act as a user-friendly front end to the MS-DOS application (SALT) responsible for the thermodynamic calculations. RUNSALT has a graphical user interface that allows data entry and manipulation as well as visualisation of the results. A schematic representation of the software setup used is shown in Fig. 9.1.

## 9.3 Results and discussion

The computer model was applied to the test room of the Tenaille von Fersen (TvF) building. In a typical situation, one would expect to have a complete ionic analysis of the anions and cations present in the salt mixture and would feed them to the model, which would then compute the possible salt combinations that can theoretically form from that mixture. In the case of the TvF test room, only the analytical data of the anions ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ ) was available, but the salt species actually observed on the walls were identified as sodium chloride and -nitrate, proving the presence in the system of the  $\text{Na}^+$  cation. Consequently,  $\text{Na}^+$  was input to every simulation in such an amount as to obtain charge balance. However, it is

very likely that other cations were present in solution in the system. For this reason, further runs of the model were performed with the addition of  $K^+$ ,  $Mg^{+2}$  and  $Ca^{+2}$  to the input parameters. The respective amount of these ions was estimated according to the average amounts reported from other rooms of the TvF building. Since no salts other than sodium ones were ever observed in the test room, it was assumed that  $K^+$ ,  $Mg^{2+}$  and  $Ca^{2+}$  did not play a major role in the salt system. However, a more detailed and systematic investigation of the salt efflorescence on the walls, as well as a complete analysis of the ions required by the model, would be needed to carry out a more accurate and realistic simulation of the whole system. The presence of high amounts of  $K^+$ ,  $Mg^{2+}$  or  $Ca^{2+}$  could dramatically change the properties of the whole salt system (see below). Since the ECOS model cannot handle  $CO_3^{2-}$  ions, only the samples containing very low amounts of it (up to 1 wt. % of the whole salt sample) were considered (Table 9.1). The most abundant anion in the selected samples was either  $Cl^-$  or  $NO_3^-$ . In addition, every sample contained a low amount of  $SO_4^{2-}$  (Fig 9.2).

Figs. 9.3 to 9.12 show the results of the computer simulation in the form of cumulative plots. The lines indicate the amount of a particular solid mineral against the RH at a given temperature. Every plot exhibits a common feature: above 72-75% RH, all salts except mirabilite and gypsum, if enough sulphate, respectively calcium and sulphate are available, go into solution. The main salt formed is either sodium nitrate, if nitrate is in excess of chloride, or halite, if chloride is in excess of nitrate. When sodium is the only cation in the mixture, the dissolution of the main salt occurs suddenly at around 66% RH. In the presence of low amounts of potassium and magnesium (2 wt. % each, Fig. 9.9), the shape of its equilibrium curve is smoothed: the dissolution starts at a lower RH (around 38%), but the process is gradual. Moreover, a number

Sample	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	CO <sub>3</sub> <sup>2-</sup>	Observed salts
A-A1	3.0	40.0	0.3	0.6	NaCl NaNO <sub>3</sub>
A-A2	24.0	0.9	2.4	1.0	NaCl NaNO <sub>3</sub>
B-B1	32.9	20.0	5.3	<0.2	NaCl NaNO <sub>3</sub> Na <sub>2</sub> (CO <sub>3</sub> )(SO <sub>4</sub> ) <sub>2</sub>
C-C1	42.0	21.3	2.7	<0.2	Not available
F-F1	10.7	44.5	5.2	<0.2	NaCl Na <sub>2</sub> CO <sub>3</sub> ·xH <sub>2</sub> O
F-F2	36.2	13.0	2.8	<0.2	NaCl Na <sub>2</sub> CO <sub>3</sub> ·xH <sub>2</sub> O

Table 9.1 Anionic composition and observed mineralogy of the salt samples. All values are expressed as wt. % of the whole sample.

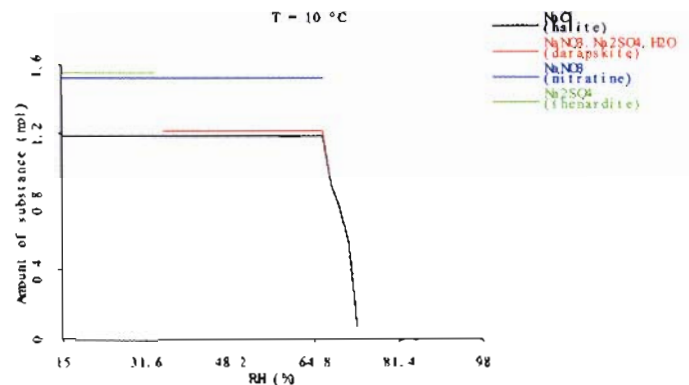


Figure 9.6 Sample C-C1. Input ion amounts (wt. %):  $Na^+ = 36.4250285$ ,  $Cl^- = 42$ ,  $NO_3^- = 21.3$ ,  $SO_4^{2-} = 2.7$ .

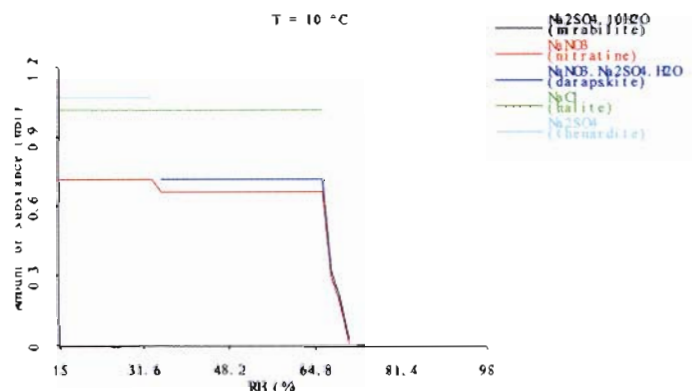


Figure 9.7 Sample F-F1. Input ion amounts (wt. %):  $Na^+ = 25.9268505$ ,  $Cl^- = 10.7$ ,  $NO_3^- = 44.5$ ,  $SO_4^{2-} = 5.2$ .



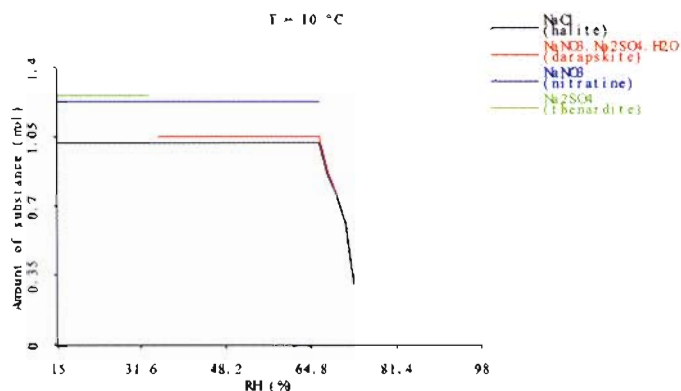


Figure 9.8 Sample F-F2. Input ion amounts (wt. %):  $\text{Na}^+ = 29.6344185$ ,  $\text{Cl}^- = 36.2$ ,  $\text{NO}_3^- = 13$ ,  $\text{SO}_4^{2-} = 2.8$ .

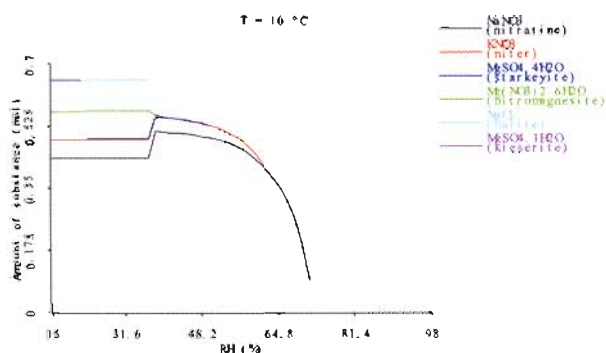


Figure 9.9 Sample A-A1 with addition of equal low amount of potassium and magnesium. Input ion amounts (wt. %):  $\text{Na}^+ = 11.9603587$ ,  $\text{K}^+ = 2$ ,  $\text{Mg}^{2+} = 2$ ,  $\text{Cl}^- = 3$ ,  $\text{NO}_3^- = 40$ ,  $\text{SO}_4^{2-} = 0.3$ .

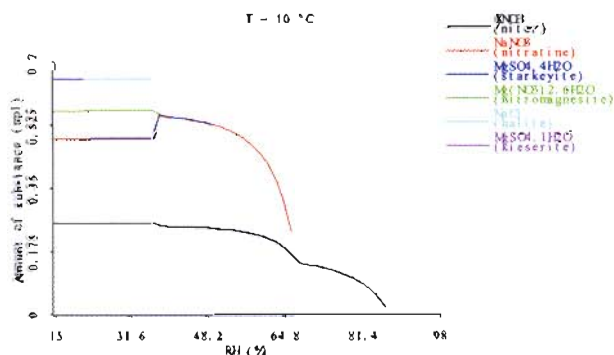


Figure 9.10 Sample A-A1 with addition of a large amount of potassium and less magnesium. Input ion amounts (wt. %):  $\text{Na}^+ = 7.256365$ ,  $\text{K}^+ = 10$ ,  $\text{Mg}^{2+} = 2$ ,  $\text{Cl}^- = 3$ ,  $\text{NO}_3^- = 40$ ,  $\text{SO}_4^{2-} = 0.3$ .

of hygroscopic salts forms at lower RH. If the amount of potassium is increased, a potassium salt, in this case potassium nitrate, can still be present as solid mineral at high RH (Fig. 9.10). Similar situations are observed if, for example, magnesium is replaced by an equal amount of calcium.

## 9.4 Conclusions

The main conclusions that can be drawn from the computer modelling of the salts in the TvF test room are summarised as follows:

- The results show that for any ionic combination run through the computer model, the range of relative humidity where the largest variations in the amount of solid salt minerals occur lies between about 60 and 75% (Figs. 9.3 to 9.12). Above 72-75% RH, all salts except mirabilite and gypsum (see below) are in solution.
- Additional small amounts (2 wt. %) of  $\text{Ca}^{2+}$ ,  $\text{K}^+$  or  $\text{Mg}^{2+}$  have little influence on this RH range. They generally lead to the formation of a number of hygroscopic salts at lower RH (Figs. 9.9 and 9.10).
- In the presence of  $\text{SO}_4^{2-}$ , mirabilite (Fig. 9.11) and, if  $\text{Ca}^{2+}$  is also present, gypsum (Fig. 9.12), may form at even higher RH. The formation of mirabilite is favoured by low temperatures because its solubility is considerably lowered. Otherwise, temperature variations within the value ranges commonly found in buildings have little influence on the overall salt pattern.

The interpretation and application of these conclusions must consider the limitations of the model used, extensively discussed by Price (2000), and the incompleteness of the available data. Particularly critical was the inability of the ECOS model to handle  $\text{CO}_3^{2-}$  ions. This did not allow inclusion of carbonate salts in the model, which are abundant in the TvF building. The relative amounts of  $\text{Na}^+$ ,  $\text{K}^+$ ,

$\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  input to the model had to be estimated semi-arbitrarily, because of the lack of a quantitative analysis. Since it was wholly impracticable to test all possible combinations of cations and amounts, the simulation was restricted to a few of them. However, making concession for the aforementioned limitations, the results presented here nonetheless give some significant indication of the behaviour of the salt system in the test room of the Tenaille von Fersen.

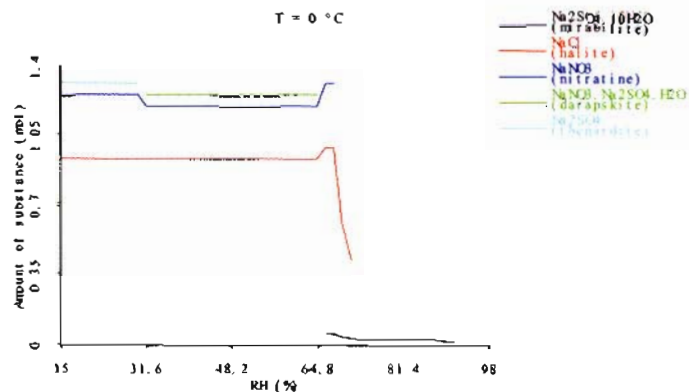


Figure 9.11 Sample B-B1. Formation of mirabilite at low temperature and high RH. Input ion amounts as in figure 9.5.

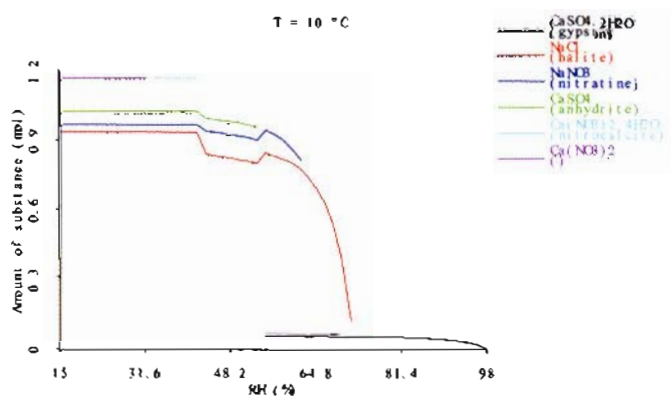


Figure 9.12 Sample B-B1 with addition of calcium. Formation of gypsum at high RH. Input ion amounts (wt. %):  $\text{Na}^+ = 22.108515$ ,  $\text{Ca}^{2+} = 8$ ,  $\text{Cl}^- = 32.9$ ,  $\text{NO}_3^- = 20$ ,  $\text{SO}_4^{2-} = 5.3$ .

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