

# **Determination of moisture and salt content distributions by combining NMR and gamma ray measurements**

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## **1. Introduction**

In case of salt-charged masonry exposed to natural weather conditions there are occurring two interdependent mechanisms of transport: moisture- and salt-transport. For the purpose of investigating these coupled processes, the Fraunhofer Institute for Building Physics developed a new measurement technique which allows a non-destructive determination of both water content and salt content distribution in capillary porous building materials. By the use of a combination of two different physical measurement procedures, Nuclear Magnetic Resonance (NMR) and gamma-ray attenuation, a non-destructive determination of salt- and water content distributions is enabled. The water content distribution is determined independent from the existing salt content by using the NMR technique. The absorptive capacity of the  $\gamma$ -rays depends on the water- and salt content. Because of this the  $\gamma$ -ray attenuation measurement method always delivers the sum of water and salt content. By combining the measured water content distribution of the NMR-measurement with the results of the  $\gamma$ -measurement, it is possible to detect the salt content distribution. At the Institute for Building Physics, Holzkirchen, several investigations were performed. From the transient evolution of the determined profiles, it is possible to draw conclusions in respect of the occurring transport processes and their interdependency. Furthermore the experimental results are the basis for the development of novel coupled moisture and salt transfer models.

## **2. Description of the measuring methods and units**

### **2.1 Nuclear magnetic resonance**

Nuclear magnetic resonance is based on the angular momentum of the positively charged protons (spin) and the resultant magnetic moment. In an external constant magnetic field the hydrogen nuclei act like precessing magnetic dipoles; there are two allowed proton energy levels corresponding to the orientation of their magnetic moment parallel or opposed to the direction of the applied magnetic field. An alternating magnetic field of a specified frequency, at right angles to the constant field, induces transitions between the two energy levels. The amount of high frequency energy hereby absorbed by the specimen is dependent on the number of protons in the specimen and can serve as a measure of moisture content since hydrogen nuclei in building materials in general occur only in the form of water. Therefore in contrast to most other methods (including gamma-ray) the NMR can be regarded as a direct method of measuring moisture in materials. It is further distinguished by its high accuracy at high measuring speed.

The heart of the equipment setup is an NMR unit consisting of an electronic control unit and a magnet with measuring coil. In the measuring field of the magnet, the magnetic field strength is 0.47 Tesla, meaning that the resonance frequency for hydrogen nuclei is about 20 MHz. The

measuring head is located between the poles of the magnet. Because good spatial resolution is necessary for determining water content distributions, a special measuring head was developed. Its coil length is only 3 mm in contrast to the 25 mm standard for this type of unit. Moreover use of a fully open measuring head allows stepwise scanning of the specimen. The measuring head allows the use of prismatic specimens having sectional dimensions up to 50 x 50 mm<sup>2</sup>. The magnet is mounted on a sliding carriage in such a way that the opening with the measuring head lies horizontally in the direction of travel of the carriage. The carriage is positioned by a step motor. Thus the measuring coil can be gradually passed over the specimen to record moisture profiles.

## 2.2 Gamma ray absorption

Gamma-ray absorption is another method for the non-destructive measurement of moisture distributions in solids [1, 2, 3, 4]. It employs the fact that photons from a radioactive source are interacting with matter. The interaction mechanisms for the sources usually used in gamma-ray absorption measurements (Am-241, Cs-137 or Co-60) are photon absorption and Compton scattering. Since these interaction processes are strongly energy-dependent, monoenergetic sources are used for measurements. An Am-241 source provides photons with an energy of about 60 keV. The attenuation of a beam of gamma-rays penetrating a sample depends both on the material and the water content. The number of photons is reduced according to the Beer's attenuation law. Measurement of the attenuation allows to determine the water content.

The gamma-ray absorption unit of the Fraunhofer Institute for Building Physics contains 9 line sources stacked on top of each other. These sources consist of Am-241 with a total activity of 15 GBq. A NaI(Tl) [5] thin-crystal detector counts the number of photons with an energy of 60 keV. Exchangeable slit apertures are inserted between the source and the specimen as well as between the specimen and the detector. Depending on the desired spatial resolution and beam intensity, 1, 2 or 3 mm wide slits can be used. A computer controls the positioning carriage and acquires and stores the measurement data.

## 2.3 Determination of the coupled liquid and salt transport

NMR measurements and gamma absorption both allow to determine the water content with good precision. While the NMR only detects the water content, even in a material containing salt, the gamma attenuation measurement registers absorption of the photons by the water content as well as by the salt load. Application of the attenuation law and the mixing rule on a material with both water and salt content yields the amount of salt as follows:

$$s = \frac{\ln \frac{N_{\text{dry}}}{N_{\text{water+salt}}} - \beta_{\text{water}} \cdot u}{d \cdot \rho_{\text{dry,stone}} \beta_{\text{salt}}} \quad \text{equation 1}$$

s	[kg/kg]	mass based salt content
u	[kg/kg]	mass based water content
N	[cps]	number of photons per second
μ	[1/m]	linear attenuation coefficient
d	[m]	thickness of the penetrated matter

$\rho$	[kg/m <sup>3</sup> ]	density of the penetrated matter
$\beta$	[m <sup>2</sup> /kg]	mass attenuation coefficient

If the water content has been determined by an NMR measurement and the salt has been identified chemically so that its mass absorption coefficient is known, the salt content can be calculated according to equation 1.

### 3. Examples of applications

#### 3.1 Determination of salt profiles and validation by chemical analysis

In order to validate the measurement of salt content with this new measurement technique as described above, a sandstone with coarse pores is submerged in a saturated MgSO<sub>4</sub> solution until it has reached capillary saturation. After determination of the salt distribution by NMR and gamma ray absorption, the specimen is sawed up into ten equal pieces, and a wet chemical analysis is performed on them. Figure 1 compares the salt distributions obtained with these two different methods. As can be seen, they are in good agreement. Only at the edges of the sample a perceptible difference between the two determination methods can be observed. The reason for this is the lower spatial sensitivity of the used NMR.

#### 3.2 Absorption of a salt solution

The following experiment is a practical example for this novel non-destructive determination of salt content. A coarse-grained sandstone is laterally sealed water- and vapour-tight in order to obtain a one-dimensional situation. One of the faces is submerged in saturated NaNO<sub>3</sub> solution. After 1, 2, 4 and 8 hours the specimen is weighed and run through the two measurement units. Figure 2 shows the water, solution and salt content distributions determined at these times. The penetration depths for the water, the solution and the salt content turn out to be the same.

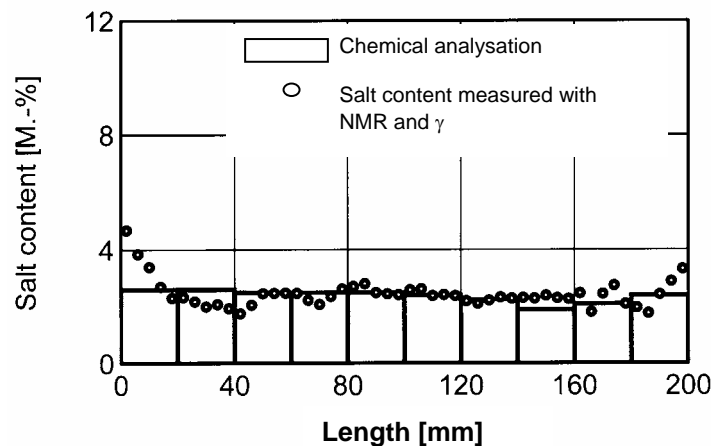


Figure 1: The salt content profile of a sample as determined non-destructively by combining NMR and gamma attenuation is successfully validated by wet chemical analysis of the salt content of individual slices of that sample

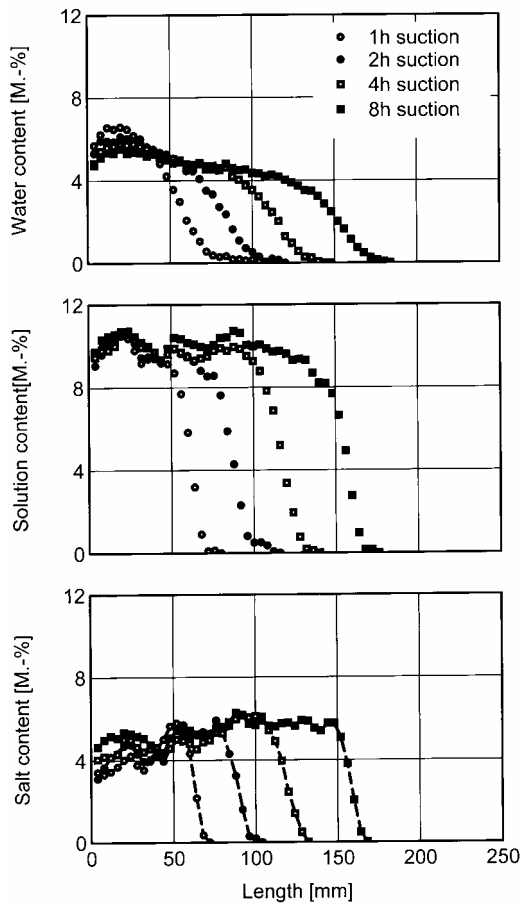


Figure 2: Combining the results of NMR and gamma attenuation measurements during a salt solution absorption experiment allows to sort out the pure water and pure salt components. In this case the migration flux is the same for water and salt (no chromatography effect).

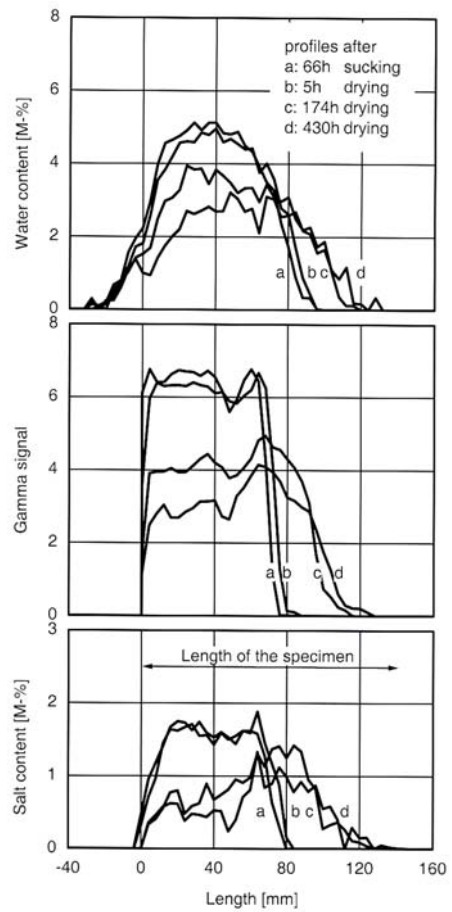


Figure 3: Water and salt content distribution of a Sander Sandstone loaded with saturated sodium chloride solution during the drying process.

Top: Water content distribution (NMR measuring)  
 Center: gamma signal  
 Bottom: salt content distribution (by the combination)

### 3.3 Drying process

As a further example of salt content determination by the combination of NMR- and  $\gamma$ -spectroscopy, the drying-behaviour of a Sander Sandstone subjected to 100 per cent sodium chloride solution is determined.

For this purpose, after an absorption time of 66 hours, the specimens are dried in a drying furnace at 40°C. The drying procedure takes place at the two unsealed surfaces at the beginning and the end of the sample. After drying times of 5, 174 and 430 hours the decrease in weight of the specimen is determined. Subsequently, the measurements with NMR- and  $\gamma$ -system are executed.

Figure 3 (bottom) shows the salt content distribution of the Sander Sandstone sample charged with saturated sodium chloride solution during the drying process. It can be observed that the salt

profiles move toward the evaporation surface according to the water profiles. With the beginning of the drying process, the sample contains 0.8 M-% sodium chloride. After a drying time of 430 hours a sodium chloride content of 0.5 M-% results. Since it is impossible that the salt evaporates with the water, the determined salt content would have to remain constant. The reduction of the salt content at the front part of the specimen may be due to efflorescences at the samples surface. Efflorescences are not recorded by the gamma measurement.

A determination of the salt solution profiles during the drying process exclusively with the gamma measurement is not possible. The reason for this lies in the increase of the concentration of the salt solution, caused by the evaporating water. A prerequisite for the determination of solution profiles with the gamma measurement is the knowledge of the salt concentration. In contrast to the suction experiment (assuming that no chromatography effects take place), this concentration is not known from the outset. Therefore, the diagram in figure 3 (center) represents a measuring signal, but not the solution content distribution.

#### **4. Interpretation of the results in respect to transport process**

Numerous absorption tests as well as drying tests on natural stone samples were carried out with saline solutions of different salts and concentrations. Periodically the profiles of water and salt content were measured. From the transient evolution of these profiles it is possible to draw conclusions in respect of occurring transport processes and their interdependency.

##### **4.1 Chromatography**

As figure 2 and other results of investigations with the salts NaCl, MgSO<sub>4</sub> and NaNO<sub>3</sub> with different concentrations of the solution show, the water front determined with the NMR unit moves through the specimen with the same speed as the salt profiles, found by the combination. This suggests that the salts are transported through the material with the water. No substantial chromatography effects occur.

##### **4.2. Transport coefficients for the salt solutions**

For the evaluation of the salt transport models in masonry the knowledge of the transport coefficients is also of decisive importance. Those depend strongly on water and solution content respectively. For not salt-loaded material there exist approximation methods for the simple determination of transport coefficients. The attempt here is to transfer these procedures also to salt-loaded materials, in order to estimate in particular the transport coefficients for the drying process.

##### Determination of the capillary transport coefficients for the suction process from the A-value

With means of simple suction tests the absorption coefficients for water and salt solutions of different concentrations are determined. From the absorption coefficient  $A_{Sol}$ , appropriate A-values for the absorption of the water contained in the solutions are determined. Table 1 indicates the respective values. Subsequently, the capillary transport coefficients  $D_{WS}$  are calculated with an approximation method developed by [6]. This method is based on an exponential approximation for the moisture dependent capillary transport coefficient. Thereby for the sorption moisture content corresponding to 80% R.H. the capillary transport coefficient is fixed on  $2 \cdot 10^{-10} \text{ m}^2/\text{s}$  independent of the material. Additional input parameters for the determination of these coefficients are the capillary saturation and the solution absorption coefficient L as well.

Table 1: Moisture-related material coefficients of the Sander Sandstone for solutions of different salts and concentrations

salt	concentration of the solution [%]	absorption coefficient of the solution $A_{Sol.}$ $\left[\frac{kg}{m^2\sqrt{s}}\right]$	volume-related absorption coefficient of the solution $L = A_{Sol.}/\rho_{Sol.}$ $\left[\frac{l}{m^2\sqrt{s}}\right]$	salt content-dependent water absorption coefficient $A_{H_2O,S}$ $\left[\frac{kg}{m^2\sqrt{s}}\right]$	water content at free solution saturation $w_f$ $\left[\frac{kg}{m^3}\right]$	$D_{ws}(w)$ $\left[\frac{m^2}{s}\right]$		$D_{ww}(w)$ $\left[\frac{m^2}{s}\right]$	
						$w_{80}$	$w_f$	$w_{80}$	$w_f$
H <sub>2</sub> O	0	0.0255	0.0255	0.0255	130		$1.39 \cdot 10^{-7}$		$4.63 \cdot 10^{-8}$
NaCl	25	0.0243	0.0232	0.0227	128.8	$2 \cdot 10^{-10}$	$1.07 \cdot 10^{-7}$	$2 \cdot 10^{-10}$	$3.57 \cdot 10^{-8}$
	50	0.0213	0.0195	0.0185	122.2		$7.63 \cdot 10^{-8}$		$2.54 \cdot 10^{-8}$
	75	0.0202	0.0175	0.0162	119.4		$7.06 \cdot 10^{-8}$		$2.35 \cdot 10^{-8}$
	100	0.1950	0.0163	0.0143	111.9		$5.28 \cdot 10^{-8}$		$1.76 \cdot 10^{-8}$
NaNO <sub>3</sub>	25	0.0243	0.0225	0.0215	126.5		$9.85 \cdot 10^{-8}$		$3.28 \cdot 10^{-8}$
	50	0.0225	0.0195	0.0173	115.5		$7.44 \cdot 10^{-8}$		$2.48 \cdot 10^{-8}$
	75	0.0215	0.0173	0.0140	105.3		$5.78 \cdot 10^{-8}$		$1.93 \cdot 10^{-8}$
	100	0.0188	0.0143	0.0100	91		$3.74 \cdot 10^{-8}$		$1.25 \cdot 10^{-8}$
MgSO <sub>4</sub>	25	0.0217	0.0202	0.0203	129.6		$8.12 \cdot 10^{-8}$		$2.71 \cdot 10^{-8}$
	50	0.0183	0.0160	0.0160	129.2		$4.65 \cdot 10^{-8}$		$1.55 \cdot 10^{-8}$
	75	0.0155	0.0127	0.0126	122.1		$3.03 \cdot 10^{-8}$		$1.01 \cdot 10^{-8}$
	100	0.0113	0.0087	0.0085	120.2		$1.16 \cdot 10^{-8}$		$3.87 \cdot 10^{-9}$

### Determination of the capillary transport coefficients for the drying process

The capillary transport coefficients for the absorption process differ substantially from those for the drying process in most building materials. In [7] a method was developed which allows a good approximation for the transport coefficients of the drying process by means of simple drying tests. In this context a relation between the transport coefficients for absorption and those for the drying process was found for different materials. For the examined Sander Sandstone this relation of  $D_{ws}/D_{ww}$  is 3.

## **5. Influence of salt content on moisture transport- calculational investigations with WUFI and comparison with experiments**

With the help of the computer program WUFI and the found transport coefficients, water content profiles are calculated and compared to the measurement results of the NMR unit. This enables to draw conclusions to what extent such a procedure is transferable at all and where deviations occur.

### Calculational investigations with the help of WUFI

WUFI is a program which permits realistic calculations of the transient hygrothermal behaviour of composed building components under natural climate conditions. It is based on latest findings regarding the vapour diffusion and liquid transport in building materials. The program is well

validated on numerous applications [8]. But it has to be taken into consideration that within WUFI there is no salt transport model integrated.

The hygrothermal material characteristics of the Sander Sandstone are taken from the WUFI data base. In this case for the capillary saturation the water content of the salt solution is to be used. The measured profiles after an absorption time of 66h serve as starting conditions for the WUFI-calculations. The calculated profiles for the drying after 5h, 174h and 430h are compared with the measured ones.

## 5.1 First results

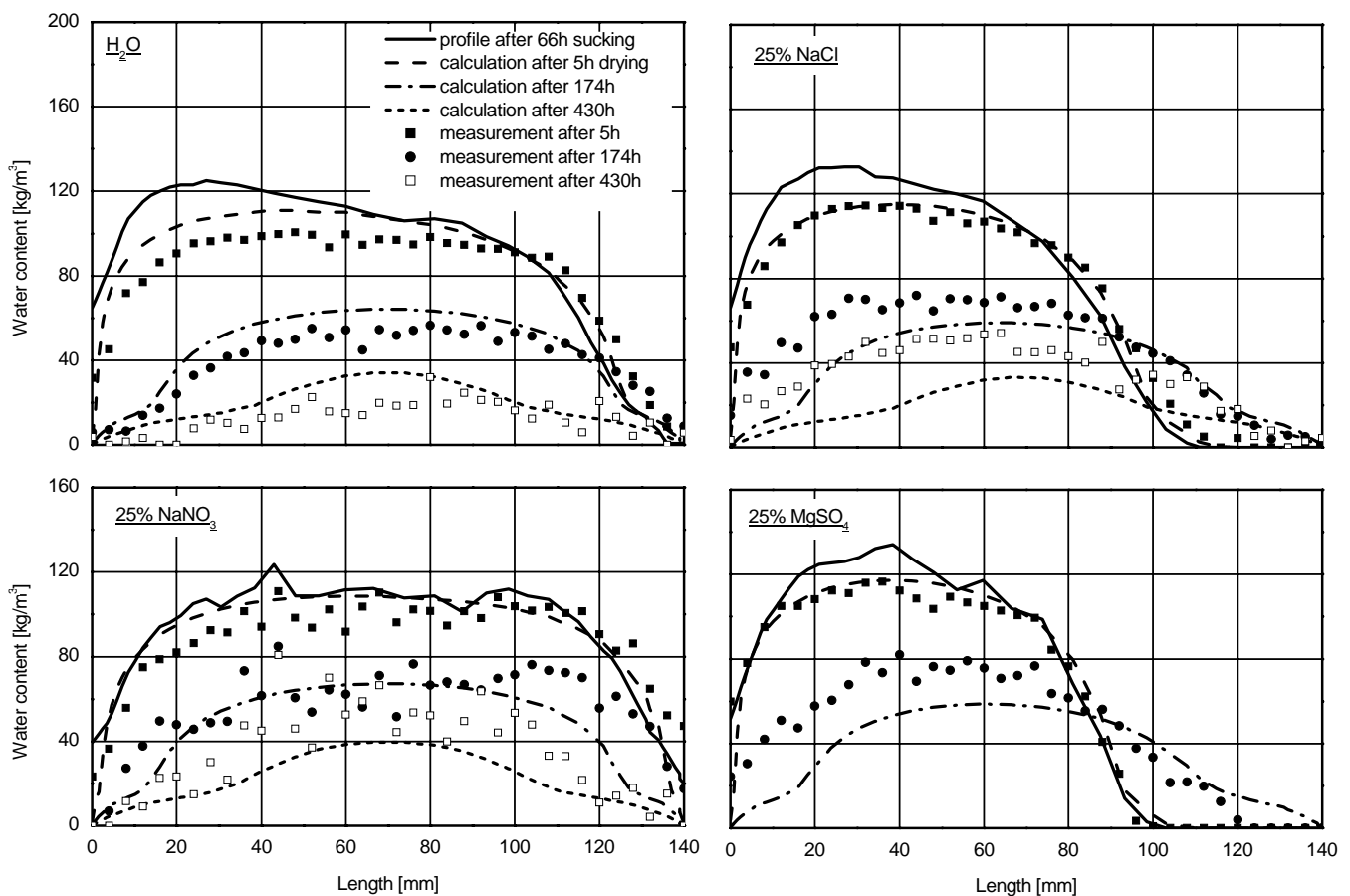


Figure 4: Comparison of the calculated with the measured water content profiles.  
left top: water  
right top: 25% sodium chloride solution  
left bottom: 25% sodium nitrate solution  
right bottom: 25% magnesium sulphate solution

In figure 4 the calculated profiles and the measurement results are compared with each other. For the drying process of pure water the fit of the curves is as good as expected. For the salt solutions with a saturation degree of 25 % after a drying period of 5 h a good correspondence was found in all cases. In contrast to the specimen charged with pure water and those loaded with 25 % nitrate

solutions the samples described below are not completely saturated after an absorption time of 66 h. The specimen exposed to 25 % sodium chloride solution shows that the moisture front only penetrated the sample up to a depth of approximately 100 mm (figure 4 right top). At the end of the moisture front almost no drying process takes place because of the high diffusion resistance of the rear part of the sample. The salts move deeper into the specimen due to redistribution effects. Here a good fit between measurement and calculation can be detected. In contrast to this at the front of the sample the loss of water is obviously less than calculated. The reason for this is that with the evaporation of water the solution becomes more and more concentrated yielding in lower transport coefficients (see front sides in figure 4). With sodium nitrate the specimen was completely saturated at the start of the drying process (Figure 4 left bottom). For this the effect described above can be observed on both ends of the specimen.

## 5.2 Adaptation of the moisture retention curve

If the pore structure of a building material is loaded with salts, the salts affect the form of the sorption isotherms at the point of the insertion of the hygroscopic effect. The contained salt yields to a precipitous modification of the material humidity content at a relative humidity  $\varphi_h$  (insertion of the hygroscopic effect of the salt) [9, 10, 11, 12, 13]. Below  $\varphi_h$  the isotherms of salt-loaded samples are identical to those of salt-free building materials. Therefore the water content of the samples is influenced only by the sorptive accumulation at the pore walls and the capillary condensation adjusting in fine pore spaces. Around  $\varphi_h$  the water content increases rapidly up to capillary saturation and stays constant above. The absence of a water content gradient in this area results in an interruption of the capillary transport process.

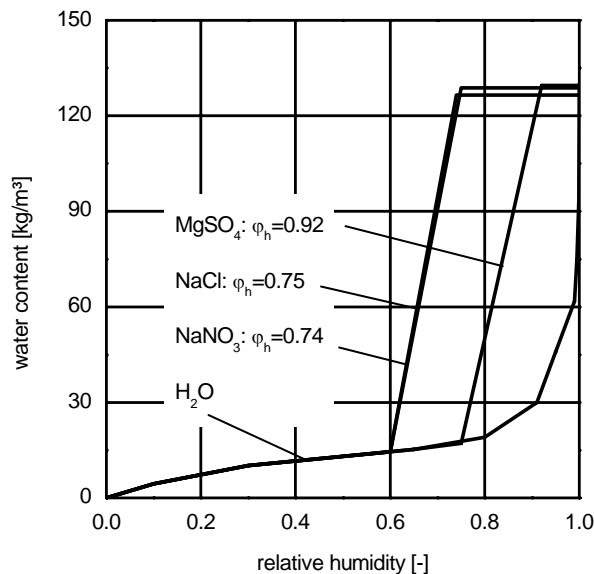


Figure 5: Simplified moisture retention curves used for the WUFI calculations.

Investigations of Larsen [14] show that in reality the modification of the material moisture content takes place steadily. For the following calculations a simplified moisture retention curve of the salt solution according to figure 5 is used.

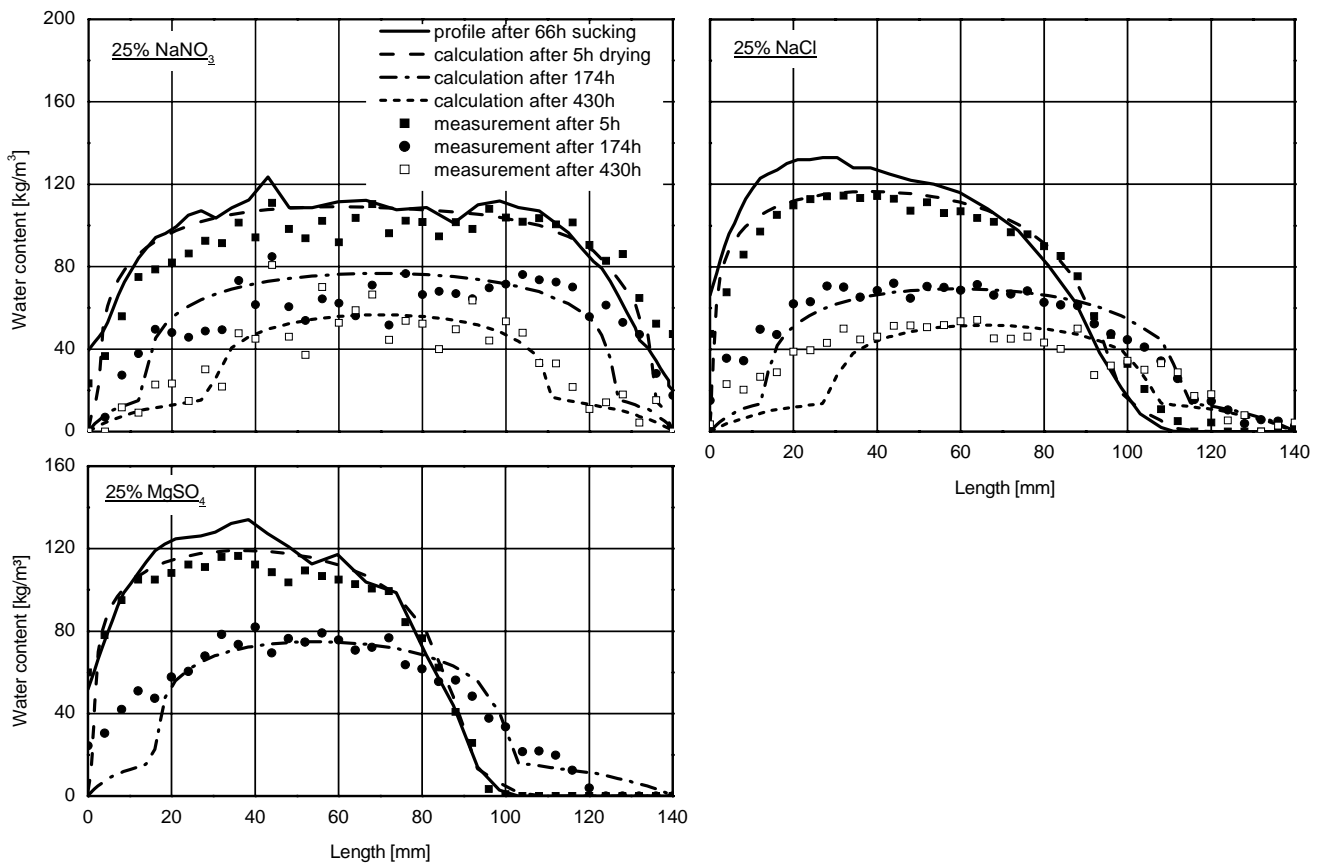


Figure 6: Comparison of the calculated with the measured water content profiles.  
left top: 25% sodium nitrate solution  
right top: 25% sodium chloride solution  
left bottom: 25% magnesium sulphate solution

Figure 6 shows the comparison of the calculated and measured water content distributions. For all three salts a markable better fit can be found. Above  $\varphi_h$  no more liquid moisture transport takes place due to the modified moisture retention curve. This becomes quite particularly clear with the comparison of the calculated profiles after a drying time of 430h. With the changed moisture retention curve a substantially better agreement can be observed. Only near the front of the sample the calculated moisture contents are too low. This can be attributed on the one hand to the increase of the concentration of the solution due to the evaporated water at the front side of the sample. A further reason could be the effloresces at the surface of the samples and the associated increased diffusion resistance.

## 6. Summary

For the purpose of investigating the two interdependent mechanisms of moisture- and salt transport the Fraunhofer-Institut for Building Physics developed a new measurement technique which allows a non-destructive determination of both water content and salt content distribution in capillary porous building materials. Numerous absorption as well drying tests on natural sandstone samples with saline solutions of different salts and concentrations were carried out in order to check the new method. With the PC-Programm WUFI first calculations were carried out. The comparison of measured and calculated results shows that with an adapted moisture storage function the drying out process of „low-concentrated“ saline solutions can be calculated.

## 7. Literature

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