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ASSESSING THE RISK OF SALT WEATHERING IN SANDSTONE BY INSTRUMENTED MONITORING OF THE ELECTRICAL IMPEDANCE

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ABSTRACT

Salt weathering of natural stone is one of the most severe and most costly deterioration at historic buildings. The existence of salts and salt mixtures within the material requires adequate measures to avoid further deterioration. An inevitable prerequisite before conservation activities can be conducted is the preliminary assessment by laboratory investigations, but also by increasing the knowledge of the environmental influences that affect the salt weathering rate and the actual processes in the stone. The instrumented monitoring of a material's electrical impedance in combination with the ambient conditions allows the acquisition of information on its moisture content, both with and without salts. A joint analysis including the supplemental measured parameters may be used to draw conclusions on the dynamic interaction between moisture and salt transport, as well as salt phase changes, and hence provides the possibility to evaluate the risk of salt weathering to the structure.

KEYWORDS : *Electrical impedance, instrumented monitoring, moisture and salt transport, salt damage, preservation of historic monuments.*

INTRODUCTION

The use of the electrical impedance spectroscopy method is based on the dependence of a material's electrical properties on its moisture and salt content. It was first used on solids in the 1920s for sub-surface exploration and has since made its way into many fields of materials science and engineering, such as the investigation of fuel cells, corrosion inspection, and laboratory characterisation of solid materials.

In civil engineering, some experimental use of the method is reported, most prominently the observation of the setting and hardening behaviour of concrete [1], and the monitoring of sea-water influence on concrete [2]. The reasons for this lack of use are the still limited informative value in real-world applications due to the manifold influencing parameters, and the rather large and costly measurement equipment, which is designed to work under laboratory conditions. We have therefore designed a small and portable measurement system, which can be permanently installed directly on site to continuously monitor the electrical impedance of a structure in combination with the surrounding environmental conditions [3]. The aim of the measurements is the observation and qualitative analysis of moisture and salt transport within the medium, which is the main cause for material deterioration at historic structures.

1 SALT DAMAGE AND THE TRANSPORT OF WATER

When salts are brought into the material through capillary uptake of brine, they start to accumulate in the regions where the evaporation rate matches the brine supply, i.e. at the capillary head. There are several factors which then influence whether damage occurs or not.

- **A sufficient amount of salt** has to be present in the accumulation areas. This depends on the brine concentration and the frequency of supply and evaporation, which describes the basic accumulation cycle. Yet, a certain complexity arises within this context when considering the dynamics of this process. Depending on the source of moisture, (i) capillary rise, (ii) rain and

condensation or (iii) hygroscopicity, the salts may move in different directions in the material and hence either foster or face the accumulation of salt.

(i) As moisture rises from the ground through capillary rise, it can drag salt ions along through advection. This form of transport is believed to be the most effective one for the migration of salt ions [5]. During its way through the porous network, the concentration of the solution constantly rises as result of the surface evaporation. Consequently, the different salts contained in the brine deposition at certain heights according to their solubility and the characteristics of the pore system in a process similar to chromatographic separation. This spreading reduces the absolute increase in the amount of salt in relation to the height.

(ii) When water enters the material not from the ground, but from driving rain, the direction of capillary transport is rather inward than upward and therefore distributes the available salts within the material. As a result of the concentration gradient in the solution, the ions diffuse over a wider area. Upon re-evaporation of the rain or the condensation water, the local salt concentration has changed.

(iii) Salts have the property to crystallise or go into solution at certain characteristic humidity levels, dependent on the ambient temperature. For example, sodium chloride dissolves at any relative humidity above 76 % at 20 °C and crystallises below. Even more, some polymorphic salts can exist in different phases, each chemically binding a different amount of water. If the characteristic humidity of any of these phases is exceeded, the salt recrystallizes under the integration or disposal of water. This has the effect that even without obvious supply of water, liquid brine may exist in the affected material, which favours the accumulation of the salts due to the different curvatures of the crystallisation nuclei [6].

- The **rapidness of crystallisation** has to exceed some critical value. When salt crystals grow against a pore wall, they exert a force both into the surrounding material and to themselves. This pressure reduces the local supersaturation of the brine, making further growth in these directions energetically unfavourable. The built-up of crystallisation forces hence prevents damage to the material by itself. Yet, if certain conditions are met, the rapidness of crystallisation can exceed the self-balancing effects. This can for example be crystallisation triggered by a sudden change in temperature, the separation of the continuous brine network, leading to the retention of a transient high supersaturation, or the change of the crystal phase [7].
- Depending on the **salt type or salt mixture**, the supply and evaporation of pore water can have largely different effects. Sodium sulphate as the example par excellence is known to be a very destructive salt, which can be traced back to the high supersaturations generated when changing its phase from thenardite to mirabilite [7]. For the case of salt mixtures, an important factor is the significant mutual influence on the salt's solubilities. Generally, the presence of more than one salt increases the solubility of both in the brine, meaning an increase of salt transport into the material and with that a much larger chance for damage.

If the ions within the material are known from chemical analyses, it is possible to estimate the ambient temperature and humidity under which the crystallisation and dissolution of the salts takes place (e.g. using "Runsalt" [8]). Using monitoring techniques, the microclimate can be observed and evaluated with respect to these critical conditions. Yet, this approach suffers from some limitations. Even with the chemical composition of the salts being determined, definitive conclusions about salt phase changes are afflicted with some uncertainty. For one thing, sampling for chemical analyses is a destructive process and may, especially at historic structures, be limited to only a few points in selected areas, which can have an influence on the detected salts with respect to the described solubility-induced separation. Apart from that, the ionic interactions and the salt crystallisation behaviour are complex and still not fully understood, despite of the vast progress in this field of science. Especially do the sub-surface conditions differ from the ambient ones, resulting for instance from the material's porosity and the humidity-moisture transfer as function of the material characteristics, or from the influence of present salts themselves. Also hardly quantifiable is the

moisture supply from the ground. But even if the critical environmental conditions were known, the ceasing of crystallisation in the material, through the stabilisation of temperature and humidity in a regime defined as non-critical, would have to be assumed.

2 IMPEDANCE SPECTROSCOPY IN THE CONTEXT OF HISTORIC STRUCTURES MONITORING

Impedance spectroscopy can basically be visualised as measurement of a material's electrical resistance. In fact, most mineral building materials are by themselves non-conductive, i.e. insulators, or, at least, poorly conductive. This includes the majority of natural stones, which are commonly used for the exterior walls of historic structures. Yet, if water, and with it, if available, salt, enters the material for different reasons (see section 1), the ions within this liquid permit the conduction of electricity and hence alter, that is reduce, the electrical impedance. Upon re-evaporation of the water, the impedance rises again, allowing conclusions about active moisture transport processes and the presence of salt in the material.

The measurement of some specimen's resistance would in its basic form only require imposing a constant current on the material and measuring the appearing voltage. However, for ionic conductors like water-charged natural stone, this would result in a diffusion of the ions and an electric decomposition of the brine due to electrolyses. To prevent this effect, an alternating current is used in the measurements instead. The introduction of the AC frequency as new parameter allows a more sophisticated evaluation of the impedance and discriminates purely AC resistive measurements from impedance spectroscopy.

In contrast to laboratory measurements on solids, there are some major differences in the application of monitoring techniques to historic structures. First and foremost, the special requirements of cultural heritage preservation have to be taken into consideration. This mainly means the limitation of interaction with the object to a minimum, both regarding the removal of original material, and the minimization of changes to its appearance resulting from the installation of measuring devices. However, to be able to base any act of preservation on a solid scientific and technical basis, a thorough prior examination of the object's current state is generally inevitable, unless sufficient background data already exists. Even if the cause for the deterioration seems evident, it can be meaningful to at least basically investigate the settings, including the ambient microclimatic conditions, for documentation of the present situation, for reassurance of the assessment, and to be able to estimate the influences of the proposed changes. A practical way to this evidence-based preservation approach is the installation of a monitoring system in the vicinity of the object, which continuously records the microclimatic conditions. This fundamental information has been found to be necessary for almost every piece of cultural heritage, ranging from small objects in encased spaces up to entire buildings and even historic sites. The collected measurement parameters usually include temperature and humidity, but may be supplemented with parameters like wind speed, pollutants or light radiation. If any kind of material deterioration caused by salts is evident [4], additional parameters have to be considered, namely the brine transport in the material, the material temperature and the salt type as described in the previous section.

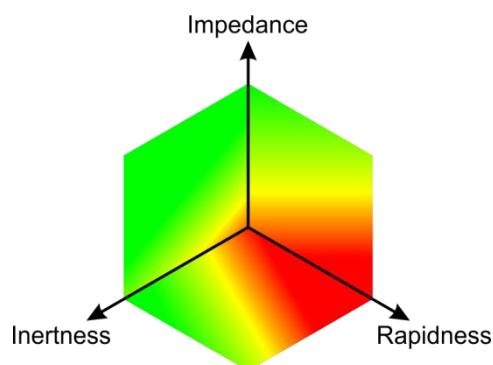


Figure 1: Indicative graph for the risk of salt weathering.

Figure 1 indicatively combines the three factors pointed out in the previous section in a graph for the risk of salt weathering. The amount of salt is hereby estimated based on the impedance. High impedances, in the order of 0.1 to 10 MΩ have shown to be due to moisture without salt ions and therefore imply a low risk. Values below 100 kΩ suggest the presence of salts, which become critical if the environmental influences are unfavourable (rapid crystallisation processes) and of the contained salts are susceptible to change under the given ambient conditions.

The term “monitoring” may generally refer to measurements repeated at any time interval, even in the range of month or years. Some parameters, however, need to be recorded at very closely spaced points in time to be able to deduce meaningful statements about the structural health, which can then be called “instrumented monitoring”. One parameter of this kind is the electrical impedance, owing to two major fast-paced influences on the value. There is, of course, the water or brine that can change the impedance in a matter of seconds. But interfering with this desired effect is a strong dependence on the temperature in the range of up to half an order of magnitude [9]. Successive measurements on a specimen at different temperatures, but with the same moisture content, returns different impedances and can thus lead to a huge misinterpretation of the data.

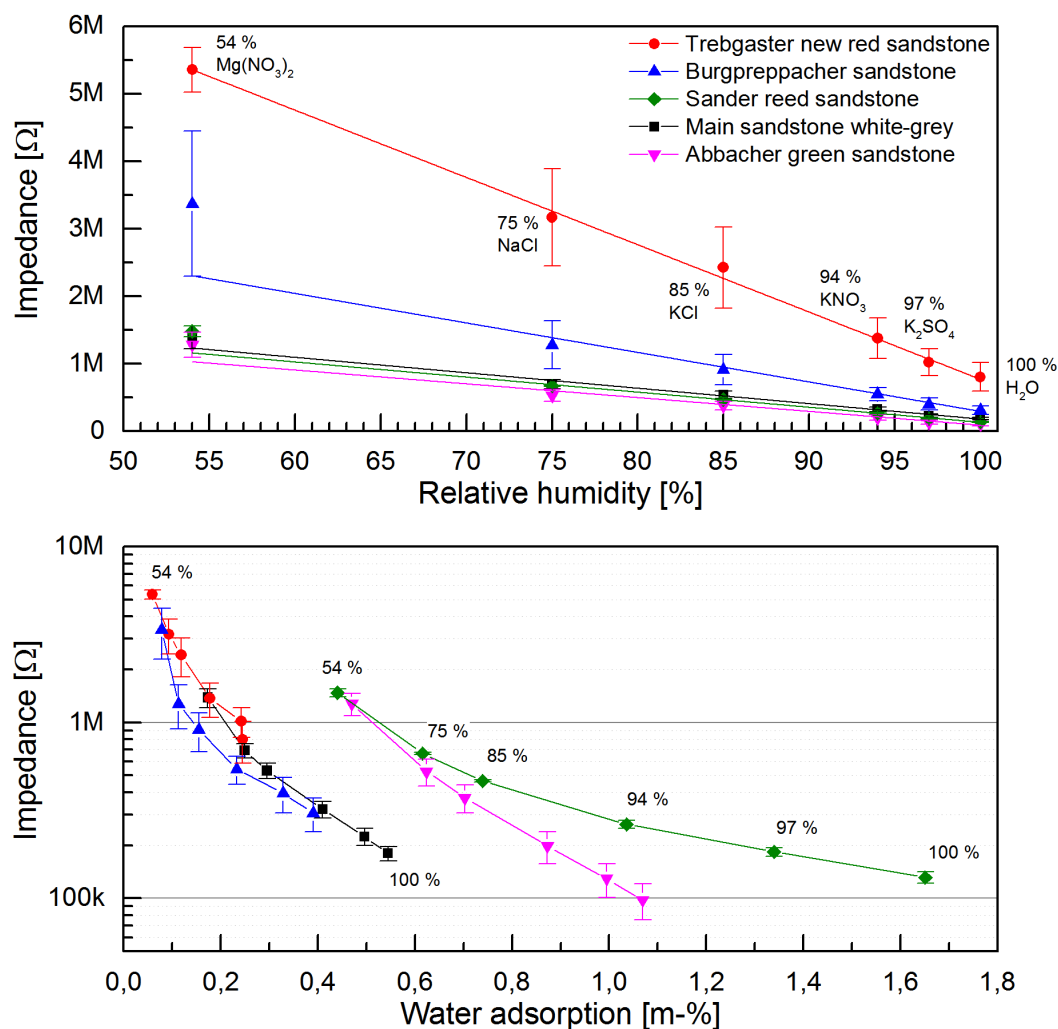


Figure 2: Development of the impedance at 10 kHz in dependence on the humidity and the moisture level.

3 AN APPROACH TO THE INTERPRETATION OF IMPEDANCE DATA

The electrical impedance of ion conductive porous materials is heavily sensitive to changes in the material moisture, up to a point where only slight variations in the relative humidity of the ambient

air are noticeable. In a long-term experiment conducted at the MPA Stuttgart, five sandstone types with different characteristics (Table 1 and Figure 5) were subjected to six humidity levels, starting from 54 % r.h. up to 100 % r.h.. Each level was maintained for one to three months, until a steady impedance had settled. The temperature was kept constant at 22 ± 0.5 °C over the entire time period of about one year. The sandstone samples had an edge length of 40 x 40 x 100 mm. Three separate specimens of each sandstone type were equipped with impedance sensors. At the end of each humidity level, the specimens were weighted. Figure 2 shows the development of the electrical impedance in dependence on the ambient humidity and the material moisture, respectively. A note to the chemical compound that was used to induce and retain the respective humidity level within the desiccator is indicated in the graph. With rising water availability in the surrounding air the impedance decreases. A linear interrelationship between the values seems obvious, which is indicated with the best fit lines in the figure above. This may seem somewhat surprising, since the electrical impedance is dependent on the conductor's cross-sectional area, which is here governed by the sandstone's non-linear sorption isotherms. It may therefore be beneficial to have a look at the water adsorption process which takes place on the pore surface and how this affects the impedance.

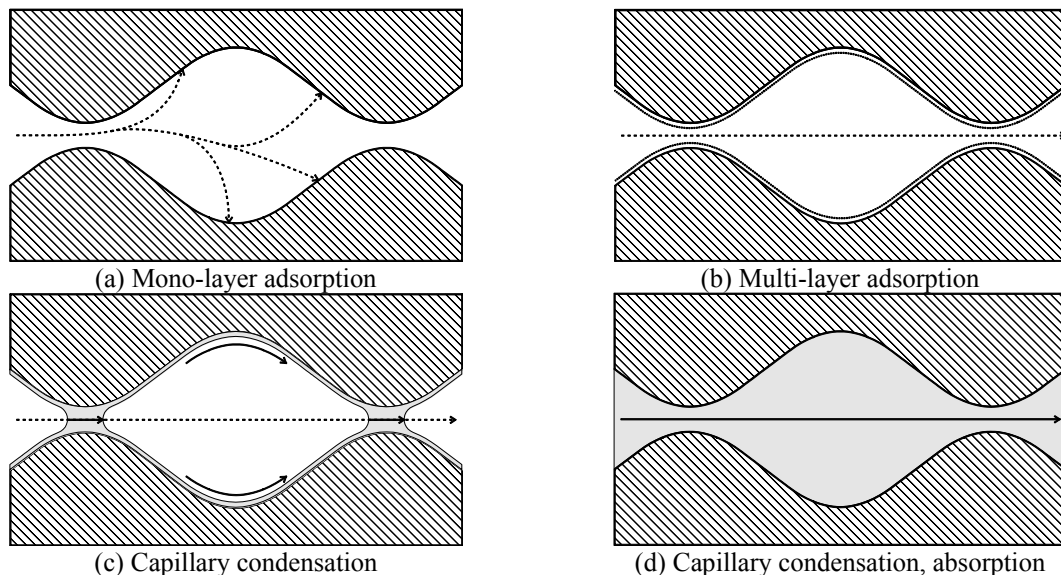


Figure 3: Water adsorption with rising humidity in an idealised pore system. Figures based on [10].

When a dry, porous material is offered moisture through humidity contained in the ambient air, the water molecules first attach to the pore walls in a monomolecular layer (Figure 3a). The reason for this adsorption is the favourable energetic state of the overall system when the polar water molecules are bound to the surface. This shall, however, not be treated in more detail here. Though linked to the surface, the water molecules are free to move laterally. Once a sufficient connection between the electrodes of the impedance measurement electrodes is formed, the “material” becomes conductive. The conductivity is certainly quite low, as the circuit is rather tortuous along the pore surface and the conductive cross-section is very small. As the humidity rises, the water starts to accumulate on the surface in multiple layers (Figure 3b). The length of the circuit path does not substantially shorten in this step, yet, the cross-section available for ionic conduction increases with every new layer. Furthermore, the bonding forces decline exponentially with the distance from the surface, which allows any present ions to move more freely. Once a number of molecular layers have been adsorbed, the water molecules on opposite pore sides start to interact with each other and capillary condensation sets in (Figure 3c), until the pores are entirely filled (Figure 3d). Large amounts of salt are only transported in the last two stages (see section 1). The point at which capillary condensation starts can be estimated with the Kelvin equation, here given in its more common exponential form by Anderson [11]:

$$\varphi = \exp \left[-\frac{2\sigma}{r_{\kappa,m}} \cdot \frac{V_m}{RT} \right] \quad (1)$$

where φ - relative humidity, σ - surface tension (≈ 0.0727 N/m for a water/ air interface), $r_{\kappa,m}$ - capillary radius, V_m - molar volume, R - universal gas constant (≈ 8.314 J/mol · K), and T - absolute temperature. Calculating the capillary radius for 54 % r.h., which is the lowest regarded ambient humidity in the given experiment, returns a value of about 1 nm. In fact, it is arguable whether the Kelvin equation is valid for such small radii, since ions on opposite pore walls can already interact with each other in this case. Yet, this implies that capillary condensation takes place in a constantly increasing number of pores throughout the experiment. The main share of pore volume, with pore radii above 100 nm (Figure 5), is only filled, if at all, very close to 100 % r.h., which is technologically challenging to reach. The impedance measured in the above experiment therefore results mostly from mono- and multi-layer adsorption, with increasing capillary condensation as the available water supply rises.

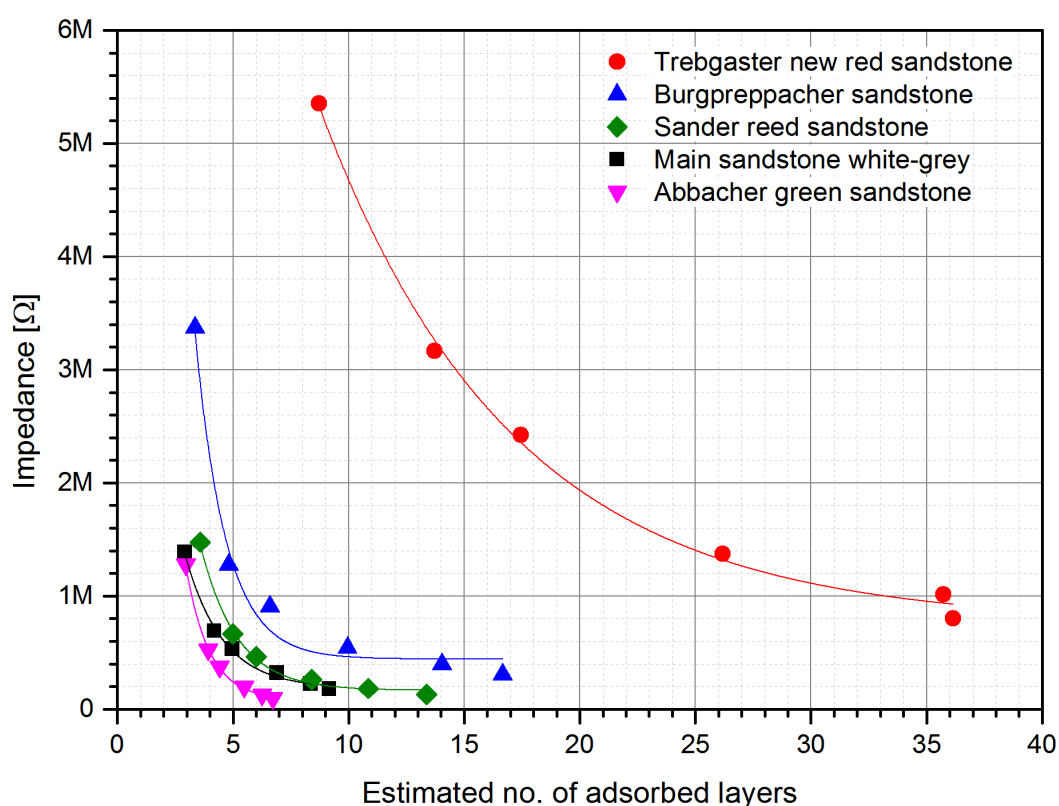


Figure 4: Estimated no. of adsorbed layers in relation to the measured impedance at 10 kHz.

To visualize the influence of water adsorption on the impedance, the increase in weight of the specimens was determined after being exposed to each of the humidity levels. Additionally, the specimen's specific surface areas were measured with the BET method (Table 1). These two parameters allow a theoretic estimation of the number of adsorbed layers for each of the ambient humidities, which is shown in Figure 4. For the calculation of the number of adsorbed molecular layers, the specimen's specific surface areas identified with the BET method were divided by the molecular space requirement for water vapour (0.125 nm²) according to [12], and the Avogadro constant, and multiplied by the molecular weight of water. This yields the weight increase in mass-% for a monolayer of water vapour. The number of layers was then estimated as the quotient of the water uptake and the weight of a single adsorbed water layer based on one gram of dry material.

The results will certainly have to be interpreted with caution due to an experimental and a methodical drawback. On the part of the BET measurements it has to be noted that the procedure includes heating, evacuating and cooling the specimens to 77 K, which may alter their pore surface. Especially if clayey components are present, e.g. in the form of glauconite agglomerations for the case of the regarded Abbacher green sandstone, are the actual specific surface areas most likely smaller than measured. Additionally, the sensitivity of BET measurements using nitrogen may not be sufficient for surface areas below 1 nm², being the case for the Trebgaster new red sandstone. Referring to the methodology, it has to be pointed out that the previously mentioned capillary condensation distorts the calculation, such that the weight increase due to adsorption only is actually less than indicated. That is, the number of specified layers should be somewhat less. In fact, the influence of this effect is presumably relative small, since the main peak in the pore size distribution for all sandstones is around or greater than 10 μm, corresponding to a relative humidity of 95 % for capillary condensation using equation (1).

The estimated number of adsorbed water layers is plotted in Figure 4 against the impedance at 10 kHz that was measured at the end of each moisturisation phase. A set of exponential decay functions can be well fitted to the data, which could be explained with the exponential decrease of the zeta-potential from the surface given in [13]. Most importantly regarding the risk of salt weathering is the fact that a minimum of approximately three adsorbed molecular layers are required before the impedance falls below a measurable level. This corresponds to the adsorption state in Figure 3c and hence to the start of possible ionic transport processes possibly leading to material decay. For the case of the Trebgaster sandstone, the measurement system's upper limit was exceeded with three layers only. The adsorbed water at 54 % r.h. covers only a very small specific surface area, which results in an accordingly small area available for conduction and hence a very high impedance.

Table 1: Key pore parameters of the used sandstones.

Sandstone type	Mean pore volume	Mean bulk density	Specific surface	Water absorption coefficient
Abbacher green sandstone	16.4 %	2.26 g/cm ³	6.63 m ² /g	1.0 kg/m ² √h
Burgpreppacher sandstone	21.2 %	2.12 g/cm ³	0.98 m ² /g	5.4 kg/m ² √h
Main sandstone white-grey	18.9 %	2.17 g/cm ³	2.48 m ² /g	8.3 kg/m ² √h
Sander reed sandstone	19.9 %	2.10 g/cm ³	5.16 m ² /g	10.0 kg/m ² √h
Trebgaster new red sandstone	15.6 %	2.23 g/cm ³	0.28 m ² /g	72.7 kg/m ² √h

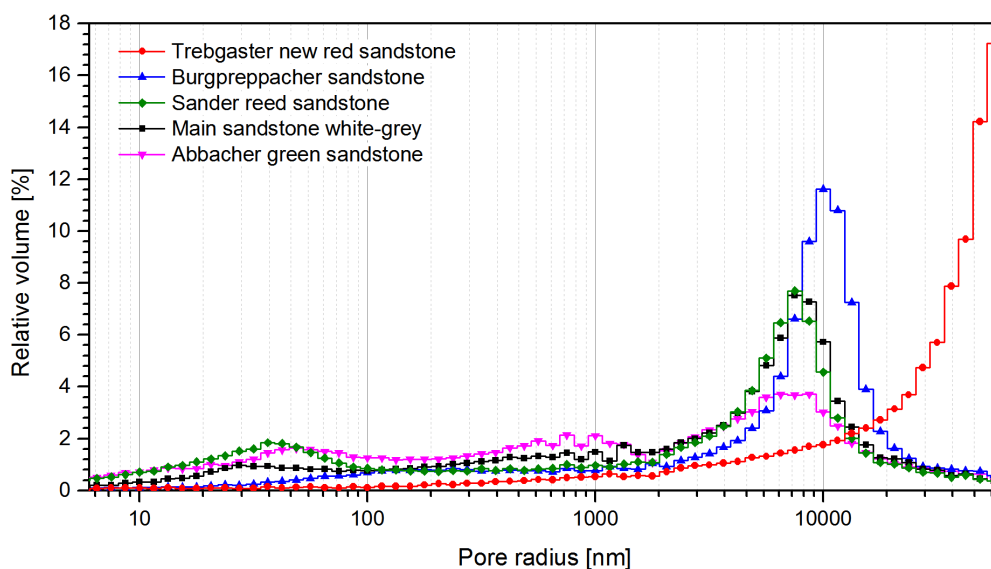


Figure 5: Pore size distributions of the used sandstones.

CONCLUSION

Monitoring the electrical impedance of sandstone or any other porous material subjected to a changing ambient humidity or moisture uptake through capillary action allows a significant knowledge increase for preservation and safeguarding measures of the structure. The method features several advantages compared to conventional moisture measurements:

- A continuous, i.e. installed monitoring of the moisture allows much more balanced information on the actual material state, since temperature effects and especially moisture variations are recorded. This is crucial for determining whether water or brine transport processes take place and hence whether damage may occur to the material.
- The effective moisture measurement range for impedance measurements starts with humidity levels which allow moisture migration and extents well into capillary transport. This supplements humidity readings from widely used capacitive sensors which are only reliable over long periods of time if the relative humidity stays below 85 %.
- The presented impedance monitoring directly regards the moisture in the material and hence avoids parameter conversion related to sorption curves, etc. for water adsorption from the environmental humidity. Additionally, capillary transport processes independent from aerial humidity or precipitation can be detected and, if several sensors are installed, even be traced.

An interpretation of impedance data with regard to water adsorption in layers shows that a certain layer quantity has to be reached before the electrolytic surface impedance falls below the measurement system's upper threshold. This point effectively corresponds to a multi-layer thickness where ionic transport becomes feasible. The presented impedance measurements therefore become sensitive at exactly a moisture level which is critical to potential salt transport and damage.

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