Interaction of Building Stones with Inorganic Water-Soluble Salts

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Abstract—Interaction of inorganic water-soluble salts and building stones is studied in the paper. Two types of sandstone and one type of spongillite as representatives of materials used in historical masonry are subjected to experimental testing. Within the performed experiments, measurement of moisture and chloride concentration profiles is done in order to get input data for computational inverse analysis. Using the inverse analysis, moisture diffusivity and chloride diffusion coefficient of investigated materials are accessed. Additionally, the effect of salt presence on water vapor storage is investigated using dynamic vapor sorption device. The obtained data represents valuable information for restoration of historical masonry and give evidence on the performance of studied stones in contact with water soluble salts.

Keywords—Moisture and chloride transport, sandstone, spongillite, moisture diffusivity, chloride diffusion coefficient.

I. INTRODUCTION

SOME buildings' damage would not arise, if only pure water were presented in inbuilt materials. Usually, the water represents transport medium for water-soluble salts having harmful effect on materials durability and buildings service life. Salt weathering is considered as one of major causes of deterioration of stone and other building materials, whereas the biggest problems can be found especially in historical masonry, where the horizontal water-proof insulation is missing. Here, salts are one of the primary agents in the loss of the built culture heritage, through surface degradation, structural destabilization or complete disintegration [1], [2]. It is therefore a common hazard with significant cultural and economic implications in the field of cultural heritage. For example, many ancient structures such as the Valley of the Kings in Egypt [3] and the Petra monument in Jordan [4] have been partially destroyed by salts.

In historical buildings, their plasters and masonry, several

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degradation mechanisms of water-soluble inorganic salts can be recognized, specifically chemical reaction of salts with components of materials, salt crystallization, enhanced hygroscopic water absorption, salt hydration, efflorescence, and salt leaching. Probably the most harmful mechanism of salt action from the point of view of durability of historical materials represents salts crystallization. It is physicochemical degradation process characterized by salt crystals growth and exerted stresses on the pore system of materials that can lead to serious damage [5]. The degradation can be caused also by salt recrystallization, whereas the substances with higher number of water molecules originate.

There are several salt sources in older buildings. Salts are primarily present in building materials, they can be formed by chemical reaction or decomposition of original material (e.g. dolomitic lime or pure lime, that were in the past very often used in building masonry, in presence of gypsum and moisture creates magnesium sulfate), and can also form in materials used during reconstruction or renovation of buildings. Typical examples of salt sources within the reconstruction process of older building structures represent low quality cements, water glass-based impregnations and infusions, de-icing agents added to mortars to enable work in wintertime etc. In urban areas, huge amount of sodium and calcium chlorides are still used as de-icing agents for roads and pavements during the winter period. From the point of view of salts present in historical masonry and buildings, the main salts are water-soluble salts transported from ground water. The other significant salts are nitrates that are in most cases of biological origin and are usually found in objects where the animal excrements were present [5].

The most frequent salts that cause damages of building materials and structures are sulfates, chlorides and nitrates and in some particular cases also water-soluble carbonates.

Since the harmful effect of salts on materials performance and durability is quite evident, there is a need to improve current state of knowledge in characterization of salt solution transport in porous building materials, and to evaluate the effect of salt content on their behavior at real climatic conditions. On that account, the presented paper is focused on the explanation of chloride solution transport, identification of parameters that can be used for its exact characterization and description, as well as on chloride effect on water vapor storage. Since the biggest problems with salt weathering are observed for historical buildings and monuments, the paper is closely focused on three typical building stones of historical masonry.

II. STUDIED MATERIALS

Building stone can be from the historical point of view considered as one of the oldest construction materials. The first stone structures can be traced to 4000 B.C. Since that time, the building stone documents the architecture evolution and progress. At the historical territory of present Czech Republic, the most often used building stones were spongillite, sandstone, granite, and travertine. In this paper, spongillite and two types of sandstone coming from operating quarries in Czech Republic are studied.

A. Spongillite

Spongillite (SD) is from locality Džbán (Czech Republic). It is highly porous sedimentary material formed in Late Cretaceous epoch. Its compressive strength varies from 8MPa for water saturated state to 11MPa in dry state. Spongillite was historically used at the Czech territory as construction material especially in Romanic and Gothic epoch. Presently, it finds use as facing stone, architectural stone of gardens and is also often used for renovation and reconstruction of historical buildings. From the mineralogical point of view is spongillite formed from calcite, silicon oxide (silica, cristobalite, opal, chalcedony), and clay minerals (illite, kaolinite, glaukonite, and montmorillonite). The spongillite color is usually yellow-brownish or beige.

B. SH Sandstone

First type of sandstone (SH) is coming from quarry Kámen Ostroměř, Ltd., placed in the village Podhorní Újezd. It is presently the biggest operating sandstone quarry in Czech Republic and quarried sandstone is part of Hořice spine formed in Late Cretaceous epoch of Mesozoic Era. This sandstone is light beige with rust mottling and is formed from clastic grains of silica (60 – 80 vol. %), whereas 5 – 20% is formed by clay minerals, especially by kaolinite from the group of clay mica. This material is used mainly for architectural purposes and for structural elements without mechanical loading. Its compressive strength is typically 11 – 30MPa. Historically, SH was used for prominent buildings especially in Prague (Czech Republic). Typical examples are Rudolfinum, National Museum, National Theatre, and finishing of St. Vitus' Cathedral. It is also popular material for sculptures and monuments.

C. SB Sandstone

Second type of sandstone (SB) was quarried close to Božanov, Czech Republic. It is one of the best quality sandstones at the Czech territory. Its compressive strength is for the dry state 65 – 72MPa. SB consists of silica grains having typical size in the range of 0.5 – 1.6mm (71 – 80 vol. %), potassium feldspars and soda-lime feldspars (plagioclases) in volume of 5 – 8%, scales of black mica and muscovite (3 – 4%), and of other minority minerals. The color of SB varies from beige to white-grayish or rust-brownish. Instead its applicability for restoration of historical buildings and monuments, it found broad applicability as paving stone, for example in Prague (Czech Republic), Leipzig and Cologne

(Germany). However, it is often used also as architectonic material, for example as facing stone.

Basic physical properties of researched materials are given in Table I. Since all the researched materials exhibit high inhomogeneity, the presented values must be considered as indicative only.

TABLE I
PROPERTIES OF STUDIED SPONGILLITE AND SANDSTONES

Material	Bulk density (kg/m³)	Matrix density (kg/m³)	Total open porosity (%)
SD	1 353	2 235	39
SH	2 004	2 556	22
SB	2 154	2 563	16

III. EXPERIMENTAL

Within the experimental work, measurements of moisture profiles, chloride concentration profiles, sorption, and desorption isotherms in dependence on chloride content were done.

A. Measurement of Moisture and Chloride Concentration Profiles

For determination of moisture diffusivity as function of moisture content and chloride diffusion coefficient in dependence on chloride concentration, measurement of moisture and chloride concentration profiles was done. Within these transport experiments, coupled water and chloride transport was investigated in the conditions of one-sided water or sodium-chloride-in-water solution uptake. For this purpose, rod-shaped samples with the dimensions of 20x40x300mm were used for the determination of moisture and chloride concentration profiles. Epoxy resin was employed for water and vapor proof insulation on the lateral sides to assure 1-D water and salt solution transport. In the determination of moisture and chloride concentration profiles, the specimens were put in contact with water or 1M NaCl solution, whereas the measurement was realized in the vertical setup (see Fig. 1).
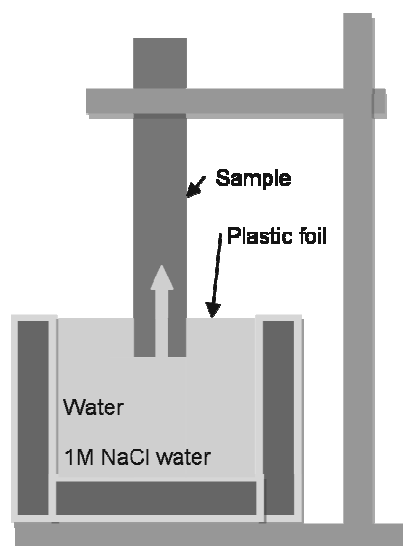

Fig. 1 Experimental arrangement of vertical suction experiment

After chosen time intervals (depending on the rate of moisture propagation) the samples were cut into several pieces 15 mm thick, and the moisture content was determined in each piece by gravimetric method. For the chloride concentration measurement, the particular samples fragments were leached at 200 ml of distilled water and the leaches were analyzed by pH/ION 340i device [6] with utilization of ion selective electrode (ISE).

B. Measurement of Sorption and Desorption Isotherms

Sorption isotherm describes the thermodynamic relationship between relative humidity of materials environment and its equilibrium moisture content at constant temperature and pressure [7]. However, it is generally anticipated that the inorganic salt presence in porous space of materials increased the total water vapor storage capacity due to the hygroscopicity of salts. On this account, the sorption and desorption isotherms were measured for reference samples without chloride content, as well as for samples exposed to penetration of NaCl water solution.

For the measurement, DVS-Advantage device (Surface Measurement Systems Ltd.) was used. The Dynamic Vapor Sorption (DVS) method is designed to measure the equilibrium moisture content of a material at any desired relative humidity and selected temperatures in a short period of time. The humidity range of the applied DVS instrument is 0–98% with the accuracy ±0.5%, whereas the experiments can be realized at temperature range 5-60°C. Particular samples were firstly dried at 110°C and during the cooling were kept in desiccators. The experiments were performed at 25°C, whereas the samples were exposed to the following relative humidity profile: 0; 20; 40; 60; 80; 98%.

IV. COMPUTATIONAL

The experimentally measured moisture and chloride concentration profiles were used for identification of moisture diffusivity as function of moisture content and chloride diffusion coefficient as function of chloride concentration.

In the computational inverse analysis of the coupled water and chloride transport in cement mortar we assumed for simplicity just the diffusion model of both water and salt transport without the cross effects. Therefore, the result of our analysis was the identification of apparent water and salt transport parameters instead of the basic parameters of the coupled water and salt transport defined exactly in the sense of irreversible thermodynamics [8]. Under these simplifying assumptions, we have formally the same parabolic differential equations and the same boundary and initial conditions for both water transport and chloride transport, namely

$$\frac{\partial C}{\partial t} = div(D(C)\,grad\,C) \qquad (1)$$

$$C(0,t) = C_1 \qquad (2)$$

$$C(\infty,t) = C_2 \qquad (3)$$

$$C(x,0) = C_2 \qquad (4)$$

where C (kg/kg) is either water concentration in kg of water per kg of the dry porous body or chloride concentration in kg of Cl⁻ per kg of the dry porous body, $D(m^2/s)$ is either the apparent moisture diffusivity or the apparent chloride diffusion coefficient [8].

Therefore, the calculation of concentration-dependent diffusion coefficients from the measured chloride concentration profiles could be done using basically the same inverse methods as those for the determination of moisture-dependent moisture diffusivity or temperature-dependent thermal conductivity.

On the basis of the previous experience with the solution of inverse problems of moisture diffusion and heat conduction (for a detailed analysis see [9]) we employed for determination of the $D(C)$ function in this paper the Matano method (originally for diffusion in metals [10], for moisture diffusion then e.g. [11]), which is the most frequently used method in the inverse analysis of moisture profiles.

V. RESULTS AND DISCUSSION

Figs. 2-4 show experimentally measured moisture profiles determined for particular materials by gravimetric method at specific times.
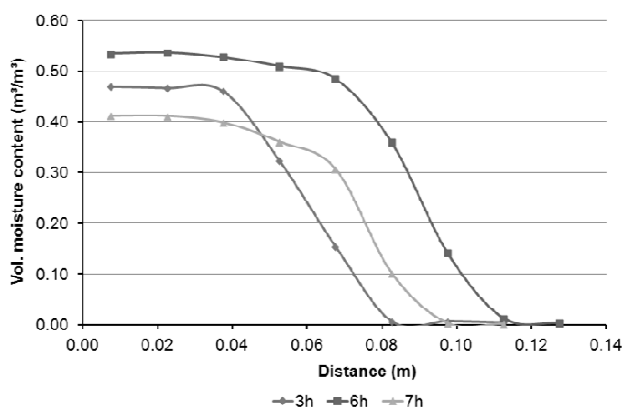

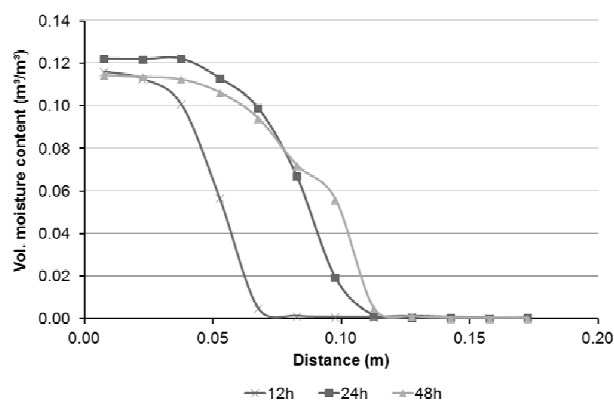Fig. 2 Moisture profiles measured for spongillite

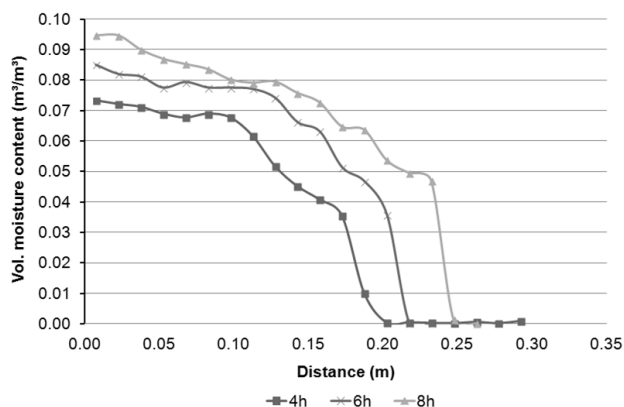Fig. 3 Moisture profiles measured for SH

Fig. 4 Moisture profiles measured for SB

Looking at Figs. 2-4, one can observe high inhomogeneity of researched stones. Above we presented basic physical properties of studied materials and we can see high difference between the total open porosity data presented in Table I and values measured within the moisture profiles analysis. The biggest differences were observed for spongillite. For SH and SB we measured lower porosity compared to data presented in Table I. In this case, the differences can be simply explained. In water suction experiment, the samples are not fully saturated by water as in measurement of total open porosity using vacuum saturation. From the quantitative point of view, the slowest moisture transport exhibited SH, whereas the fastest moisture ingress exhibited spongillite. However, this situation was typical for samples parts close to the surface only. For the distances from the penetrating surface > 0.15m, the fastest moisture transport was observed for material SB. Although the total open porosity of SB is lower compared to SH, the difference in moisture transport can be assigned to variation in pore size distribution, properties of mineral binder and experimental arrangement of the suction experiment. In the vertical orientation of suction experiment, the dimension of capillary pores represents crucial factor. In the case of bigger pores, the water uptake is limited by gravity.

Moisture profiles measured for penetration of 1M NaCl water solution are given in Figs. 5-7.
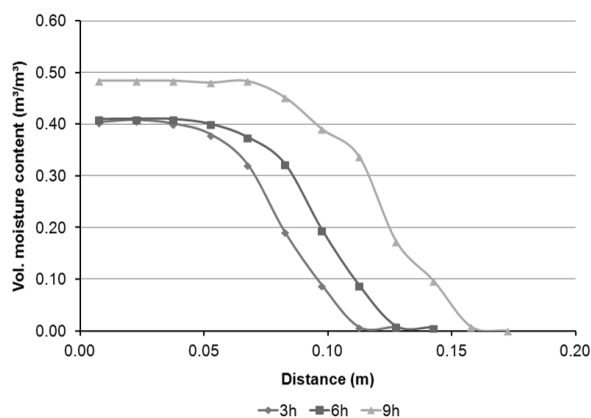

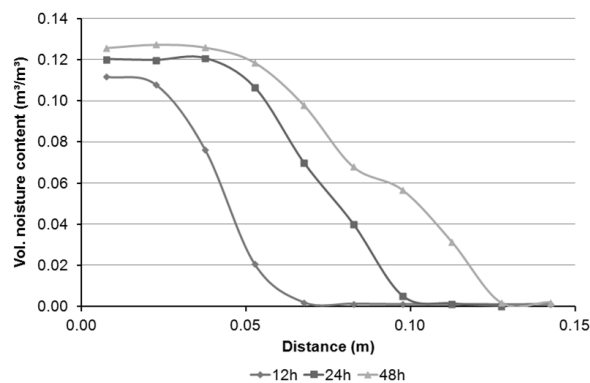Fig. 5 Moisture profiles for penetration of 1M NaCl solution -SD

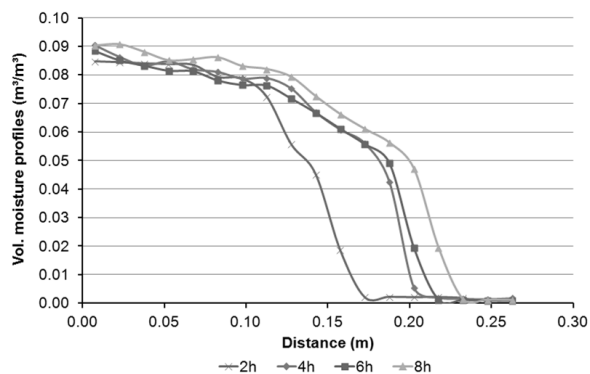Fig. 6 Moisture profiles for penetration of 1M NaCl solution -SH

Fig. 7 Moisture profiles for penetration of 1M NaCl solution -SB

Measured suction curves for penetration of 1M NaCl water solution show similar behavior of studied stones as in the contact with pure distilled water. Although we expected deceleration of moisture transport due to the higher viscosity of NaCl water solution, the high inhomogeneity of materials disabled identification of this effect.

Chloride concentration profiles measured within penetration of 1M NaCl water solution are presented in Figs. 8-10. Here, the measured data correspond with measured moisture profiles accessed for NaCl solution. The highest surface chloride concentration exhibited spongillite, whereas the values measured for SH and SB were even two times lower.
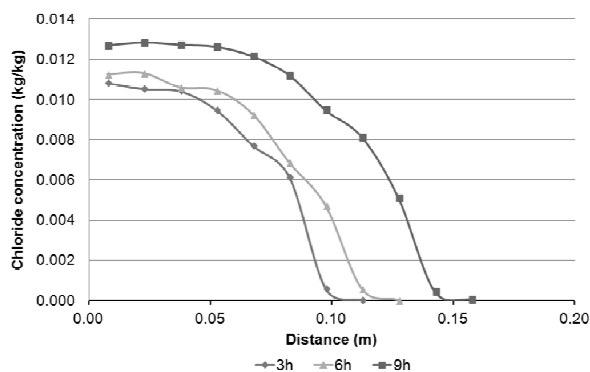

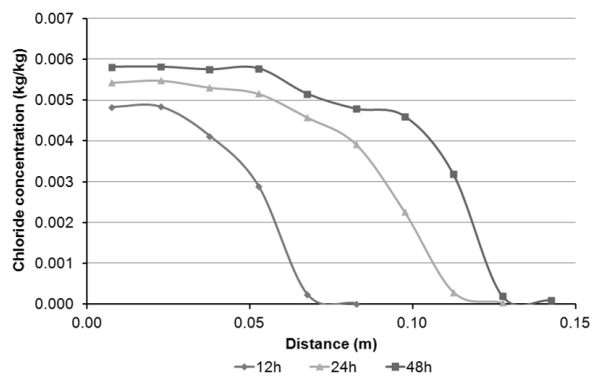Fig. 8 Chloride concentration profiles for spongillite

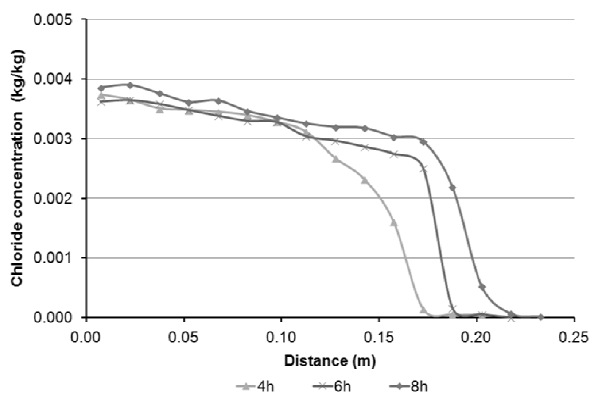Fig. 9 Chloride concentration profiles for SH

Fig. 10 Chloride concentration profiles for SB

Moisture diffusivity as function of moisture content calculated for specific time of water penetration is given in Figs. 11-13. Moisture diffusivities of all tested materials show high dependence on moisture content. High moisture diffusivity has spongillite due to its higher porosity compared to both types of sandstones. The material SB is also characterized by rapid moisture transport, probably due to the properties of clay binder.
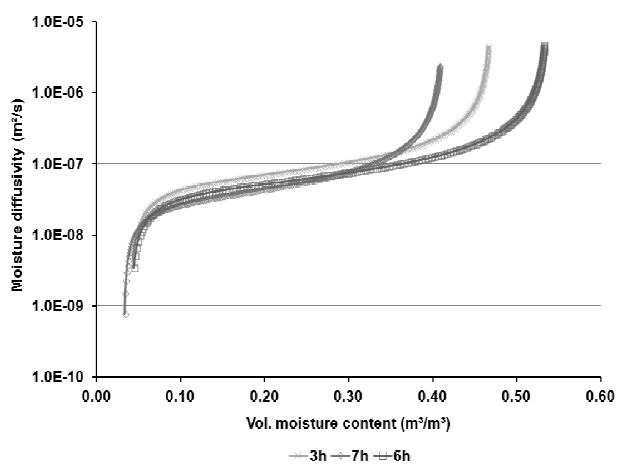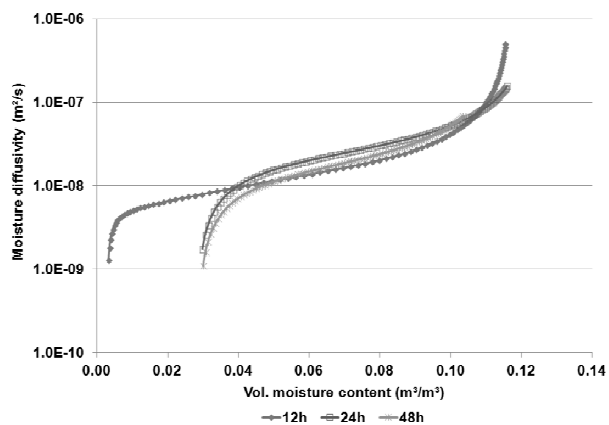

Fig. 11 Moisture diffusivity of spongillite

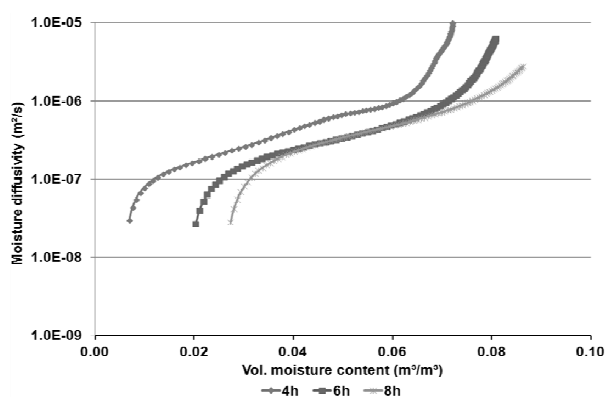Fig. 12 Moisture diffusivity of SH

Fig. 13 Moisture diffusivity of SB

Chloride diffusion coefficients calculated on the basis of inverse analysis of chloride concentration profiles are summarized in Fig. 14. From the comparison of obtained results there is evident that the highest chloride diffusion coefficient has material PB. Despite its relatively low porosity compared to other studied materials, the surface properties of inner space of this material allow rapid salt solution transport by capillary forces.
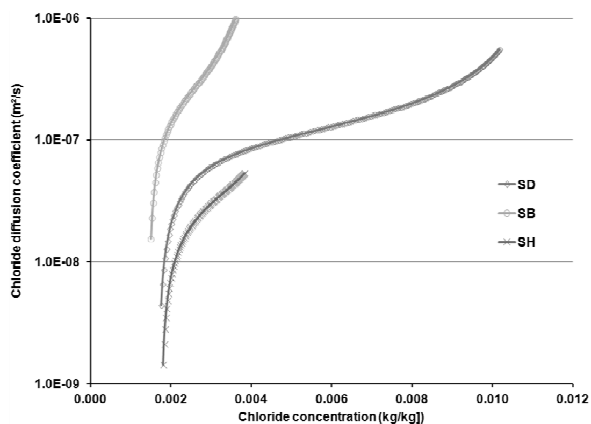

Fig. 14 Comparison of chloride diffusion coefficients of stones

The effect of salt hygroscopicity on water vapor storage is evident from Figs. 15-17.
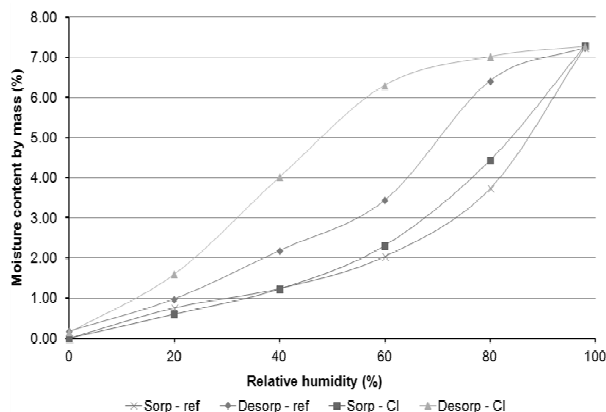

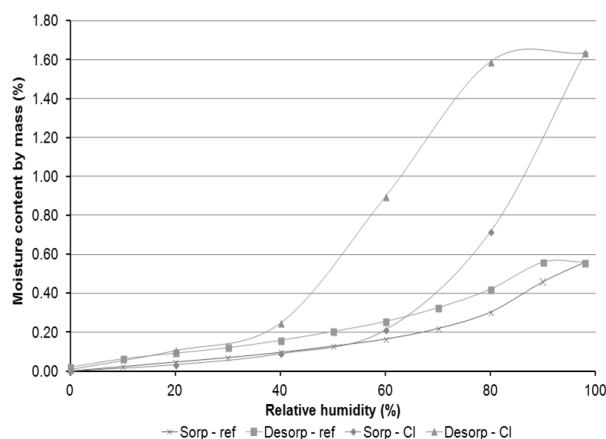Fig. 15 Sorption and desorption isotherms of spongillite

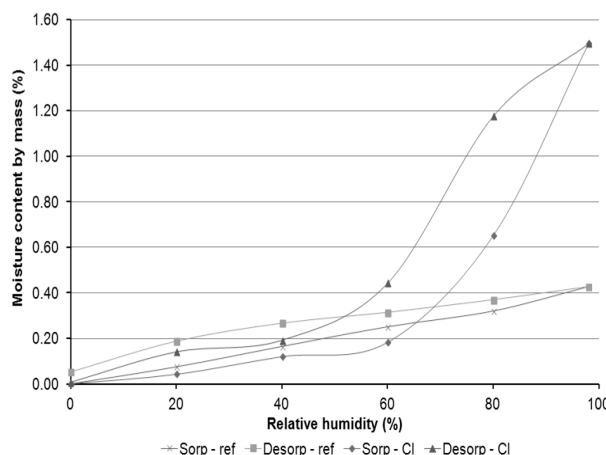Fig. 16 Sorption and desorption isotherms of SH

Fig. 17 Sorption and desorption isotherms of SB

One can observe measurable effect of chloride presence on the enhancement of water vapor storage capacity and hysteresis of sorption/desorption cycle. Chloride concentration was for SD 0.0059kg/kg, for SH 0.0054kg/kg, and for SB 0.0039kg/kg. From the quantitative point of view, the highest water vapor storage capacity has spongillite, the lowest sandstone SB. Accumulated moisture for SH is slightly higher compared to SB.

VI. CONCLUSIONS

Material parameters characterizing water and chloride transport in three typical building stones are determined in the paper. The measured and calculated data pointed out to the high dependence of moisture diffusivity on moisture content as well as on the influence of chloride concentration on chloride diffusion coefficient. This fact must always be considered in application of these materials for renovation of historical buildings, monuments and memorials, as well as in their use as facing stones, stone block paving, stones for garden architecture, etc.

Measured sorption and desorption isotherms confirmed the expected high hygroscopicity of NaCl that highly increased the total water vapor storage capacity of tested stones. These results represent valuable information for building practice especially for reconstruction of damp buildings and structures. Here, although the structure would be dried, it can simply become damp due to the salt hygroscopicity.

REFERENCES

[1] C. Price, *Stone Conservation, an Overview of Current Research.* Los Angeles, The Getty Conservation Institute, 1996.
[2] Z. Pavlík, *Identification of parameters describing the coupled moisture and salt transport in porous building materials.* Prague, CTU, 2009.
[3] A. Nicolaescu, "Conference Review: Salt Weathering on Buildings and Stone Sculptures", *Conserv. Magazine*, no. 8, 2009, pp. 6-13, 2009.
[4] R. A. Wust, R. McLane, "Rock deterioration in the royal tomb of Seti I in the Vallay of the Kings, Luxor, Egypt", *Eng. Geology*, vol. 58, pp. 163-190, 2000.
[5] S. Z. Lewin, "The mechanism of masonry decay through crystallization", *Conservation of Historic Stone Buildings and Monuments*, National Acad. Press: Washington, DC, 120-144, 1982.
[6] M. Jiřičková, R. Černý, "Chloride Binding in Building Materials", *Journal of Building Physics*, Vol. 29, pp. 189-200, 2009.
[7] Z. Pavlík, J. Žumár, I. Medved'. R. Černý, "Water vapor adsorption in porous building materials: experimental measurement and theoretical analysis", Transport Porous Med., vol. 91, pp. 939-954, 2012.
[8] R. Černý, Z. Pavlík, P. Rovnaníková, "Experimental Analysis of Coupled Water and Chloride Transport in Cement Mortar", *Cement and Concrete Composites*, vol. 26, pp. 705-715, 2004.
[9] R. Černý, P. Rovnaníková, *Transport Processes in Concrete*. Spon Press, London, 2002.
[10] C. Matano, "*On the relation between the diffusion coefficient and concentration of solid metals*", Jap. J. Phys., vol. 8, pp. 109-115, 1933.
[11] J. Drchalová, R. Černý, "Non steady-state methods for determining the moisture diffusivity of porous materials", *Int. Comm. Heat Mass Transf.*, Vol. 25, 1998, pp. 109-116.