Water and Chloride Transport Properties of Renovation Plasters Developed for Historical Masonry

Zbyšek Pavlík [1]
Lukáš Fiala [2]
Milena Pavlíková [3]
Robert Černý[4]

ABSTRACT

Water and water-soluble salts represent harmful substances that critically affect materials' durability and service life. Therefore, for the durability improvement of buildings, it is necessary to study water and salt transport properties of materials used in the building structures. Especially in historical buildings, several degradation mechanisms of water and water soluble salts can be usually recognized. On that account, investigation of properties of two types of newly developed mortars that should find application in restoration of masonry of historical buildings is presented in the paper. Within the performed experiments, measurements of chloride binding isotherms, moisture and salt concentration profiles are done. Determination of moisture and chloride concentration profiles is done in the conditions of one-sided water or sodium-chloride-in-water solution uptake. Experimentally determined concentration profiles are then used for identification of chloride diffusion coefficient and moisture diffusivity on the basis of inverse analysis using the diffusion-advection model. These material parameters represent necessary information for assessment of materials' durability from the point of view of possible water and salt induced damage. The obtained results can find use also in the computational modelling of material performance even in the long time period and exposure to harmful climatic conditions.

KEYWORDS

Renovation mortars, moisture and chloride trasnport, salt accumulation, historical buildings

[1] Czech Technical University, Prague, CZECH REPUBLIC, pavlikz@fsv.cvut.cz
[2] Czech Technical University, Prague, CZECH REPUBLIC, fialal@fsv.cvut.cz
[3] Czech Technical University, Prague, CZECH REPUBLIC, milena.pavlikova@fsv.cvut.cz
[4] Czech Technical University, Prague, CZECH REPUBLIC, cernyr@fsv.cvut.cz

Zbyšek Pavlík, Lukáš Fiala, Milena Pavlíková and Robert Černý

1 INTRODUCTION

In the investigation of effect of harmful environmental factors on materials and buildings, one must take into account that the deterioration process is a complex interplay of the effects of climate and local meteorological characteristics, of biological processes and of compex chemical reactions and processes resulting from the impact of environmental pollutants and natural constituents from the surrounding environment. The most of decay processes are usually result of temperature, moisture, solar radiation, wind, air pollutants, water soluble salts and biological organisms' action. According to Mocmanová [2007], the main deterioration mechanisms include erosion, volume change of material and the volume changes in material porous structure, dissolution of a material and the associated chemical changes, and biological processes.

Since the salt weathering is considered by many authors as a major decay mechanism in a wide range of materials and environments [Thorborg von Konow 2006], [Antonova *et al.* 2006], we have focused on this problem in the presented work. There are many ways in which the building materials and structures become contaminated with salts. Probably air pollution is a major source of sulphates and nitrates. Other salt source includes subsoil, from which salts may be carried into the masonry by rising damp. The salts can be also blown by the wind from the sea or the deserts. Another significant source of salt is represented by deicing salts and incompatible building materials [Price, 1996].

The salt related durability problems are observed above all in historical and older buildings, however, for example in highway construction, the harmful salt action is important also in newly built structures, as bridges and highways. On that account, the salt action, mechanism of their transport, crystallization, and accumulation, represent highly actual topic for researches coming from culture heritage and monuments restoration area as well as from areas dealing with design of new building structures. One must take into account also the fact that the salt action is coupled with the liquid water transport and possible water vapour evaporation. Therefore, the process of salt and water transport must be studied together [Pavlík 2009].

Within the salt damage and weathering research, many conservation and redevelopment treatments have been developed for the consolidation and protection of porous building materials affected by salt weathering. However, these methods commonly do not stop the further development of salt damage [Price, 1996]. Protection efforts may even enhance salt damage by preventing the migration of saline solutions towards the material/air interface, thereby inducing subflorescence growth when salts are already present in the pores or when they are supplied by capillary rise. On the other hand, current desalination methods are mainly inefficient in some ways (e.g. poulticing, reverse osmosis). Hence, there is a need for the development of new conservation treatments, which can preferably be applied both for preventing salt damage development, and for obtaining effective desalination. The better understanding to the coupled moisture and salt transport mechanism is needed as well, especially for the optimisation of the conservation and reconstruction treatments, and for the damage assessment of buildings and their inbuilt materials.

The main objective of the presented work is to contribute to the explanation of the process of water salt solution transport in the inner structure of porous building materials. It should be beneficial for practical application of materials, their restoration, protective treatments, as well as for computational analysis of durability problems of existing buildings and estimation of their service life. Also the formulation of experimental and computational approach for the assessment of water and salt properties of building materials that is presented in the paper represents significant contribution to the investigation of salt related problems of buildings and inbuilt materials.

2 EXPERIMENTAL

In the experimental part of the paper, measurement of moisture and chloride concentration profiles was done in the conditions of one-sided 1-D suction experiment. Also the measurement of chloride

binding isotherms was realised. These measurement were done in order to get necessary input data for computational assessment of material parameters characterising the coupled water and chloride ions transport in the inner structure of investigated materials.

2.1 Studied materials

As the chemical analyses of many plasters from historical buildings show, the past centuries external plasters that are preserved until today contain products formed by lime reaction with pozzolanic or hydraulic admixtures. Pozzolanic admixtures appeared to have positive effect on properties of lime binder and the pozzolanic compounds are the cause of the plasters resistance against environmental conditions and in this way of the durability of these plasters [Cabrera & Rojas 2001], [Pernicová *et al.* 2008], [Fiala *et al.* 2010]. On that account, our research focused on the development of lime-based mortars with addition of pozzolanic admixtures. Within the intensive research, applicability of several pozzolanas was tested, among them, metakaolin, milled ceramic brick, and different types of mudstone were the most in detail studied admixtures.

In this paper we studied two lime plasters (denoted S53P and S54P) modified with pozzolana based on calcined kaoline mixed with milled mudstone. This pozzolana material is formed within the calcination of raw kaoline in rotation kiln at temperature close to 750°C and consequent milling in rotation silo. To this "metakaolin" is then added milled mudstone and the mixture is homogenized. The final material is highly fine having specific surface area 14.56 m^2/g and D_{50} 4.09 μm. The chemical composition of used pozzolana measured by X-ray fluorescence analysis is presented in Table 1.

Table 1. Chemical composition of the used pozzolana (in mass %).

SiO_2	52.4
Al_2O_3	41.3
Fe_2O_3	1.19
TiO_2	1.77
CaO	0.14
MgO	0.15
K_2O	0.79
Na_2O	< 0.01
P_2O_5	0.07
ZrO_2	0.03
V_2O_5	0.05
F	< 0.01
Cr_2O_3	0.03
SO_3	0.10

Compostion of the studied plasters is given in Table 2. Lime hydrate is product of the lime kiln Čertovy schody, Inc., Czech Republic, whereas the silicious sand is coming from sand-pit Hlavačov, Czech Republic. Looking at Table 2, one can see that the studied plasters differ in amount of pozzolana only. The water/dry substances (w/d) ratio was then slightly modified in order to keep the workability of fresh mixtures on the same level.

Table 2. Composition of studied plasters.

Plaster	Lime hydrate [kg]	Pozzolana [kg]	Sand 0 – 4 mm [kg]	w/d ratio [-]
S53P	200	50	750	0.23
S54P	150	100	750	0.21

The basic properties of studied plasters are given in Table 3. We can see that both developed plasters exhibit high total open porosity what is promising feature, as for their application in historical buildings.

Table 3. Basic properties of renovation plasters.

Plaster	Bulk density [kg/m^3]	Matrix density [kg/m^3]	Total open porosity [-]
S53P	1688	2560	0.341
S54P	1694	2582	0.344

2.2 Experimental Determination of Moisture and Chloride Concentration Profiles

For determination of moisture diffusivity and chloride diffusion coefficient of studied plasters, the measurement of moisture and chloride concentration profiles was necessary. In the 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 20 x 40 x 290 mm were used for the determination of moisture and chloride concentration profiles. Epoxy resin was employed for water and vapour 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 distilled water and 1M NaCl solution, whereas the measurements were realised in the vertical setup. After chosen time intervals (1h, 2h, 24h) the samples were cut into several pieces 20 mm thick, and the moisture content was determined in each piece by gravimetric method. The chloride concentration was measured in each piece by means of ion chromatography.

2.3 Measurement of Chloride Binding Isotherms

Within the salt transport, part of salt ions is accumulated in the porous structure of materials and bonded on the pore walls. This process is realised both on physical as well as on chemical principle. For the description of material capacity do bound salt ions, the salt binding isotherms are measured as complex parameter taking into account physically as well as chemically bonded ions. The binding isotherm represents dependence of the amount of bound ions C_b [kg/m$^3_{(sample)}$] in the material on the free ions concentration C_f [kg/m$^3_{(solution)}$] in the pore solution in equilibrium conditions. In this work, the chloride binding isotherms of studied plasters were measured using modified adsorption method [Jiřičková & Černý 2006]. For the measurement, samples having dimensions of 40 x 40 x 10 mm were used. Experimental procedure is quite simple. Within the measurement, the samples are put into water salt solution of specific known concentration until the equilibrium is reached. Then, the salt concentration in particular sample is measured and point wise function $C_b = C_b(C_f)$ is determined. In this paper, the salt concentration in the analysed solutions was measured using pH/ION 340i device with utilization of ion selective electrode. On the basis of measured concentrations, the content of bound chlorides was obtained by calculating the difference between the concentration of the initial solution and the concentration after certain period of exposure, when the equilibrium is reached.

3 Computational Assessment of Moisture Diffusivity and Chloride Diffusion Coefficient

Moisture diffusivity and chloride diffusion coefficient as main parameters characterising the materials' capability to transport water and salt were calculated using inverse analysis of measured moisture and salt concentration profiles. For the inverse analysis, there is crucial to formulate optimised and reliable mathematical model that describes coupled moisture and salt transport. Here we assumed diffusion-advection mechanisms of chloride ions transport [Bear & Bachmat 1990], whereas the partial chloride binding was taking into account as well. In model formulated by Bear and Bachmat [1990] the chloride mass balance is expressed by the following equation

$$\frac{\partial(wC_{fCl})}{\partial t} = div(wDgradC_{fCl}) - div(C_{fCl}\vec{v}) - \frac{\partial(C_{bCl})}{\partial t}, \tag{1}$$

where C_{fCl} [kg/m^3] is the concentration of free chlorides in water, C_{bCl} [kg/m^3] the concentration of bound chlorides in the whole porous body, D [m^2/s] the chloride diffusion coefficient, $\vec{v}$ [m/s] the Darcy's velocity, and w [m^3/m^3] the volumetric moisture content measured for salt solution penetration.

The water mass balance is expressed by equation

$$\frac{\partial w}{\partial t} = div(\kappa(w)\,gradw), \tag{2}$$

where κ [m^2/s] is the moisture diffusivity dependent on moisture content determined for transport of salt solution (in our case for penetration of 1M NaCl water solution).

For calculation of $D(C_{Cl})$ and $\kappa(w)$ functions, inverse analysis of concentration profiles using an extension of the Boltzmann-Matano treatment was performed. We have assumed constant initial conditions and Dirichlet boundary conditions on both ends of the specimen for both moisture content and salt concentration, where one of the Dirichlet boundary conditions was equal to the initial condition. For details on inverse analysis procedure and final formulas for determination of chloride diffusion coefficient and moisture diffusivity see Pavlík *et al.* [2006].

4 RESULTS AND DISCUSSION

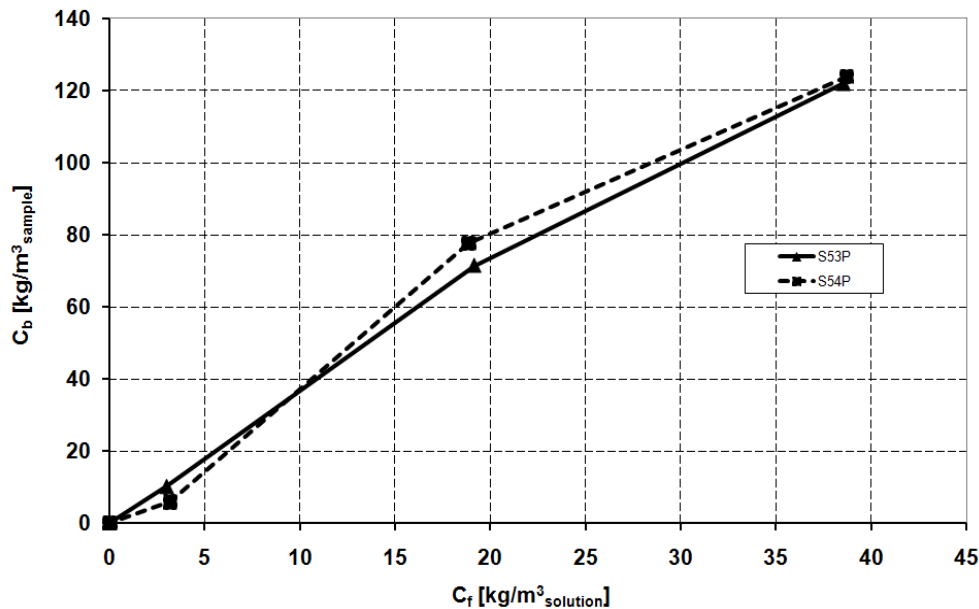The ion binding isotherms measured for NaCl water solution by modified adsorption method are presented in Fig. 1.

Figure 1. Chloride binding isotherms of studied plasters.

This data gives information on binding capacity of studied plasters and represents the highest possible value of steady state bound salt concentration at specific concentrations of NaCl water solution. Looking at this data one can see that the measured binding isotherms are for both studied materials almost similar and exhibit two specific slopes of the measured linear dependence of bound chloride concentration in material on free chloride concentration at solution.

The moisture diffusivity coefficients as functions of moisture content calculated for penetration of 1M NaCl water solution as well as for pure distilled water are presented in Fig. 2.
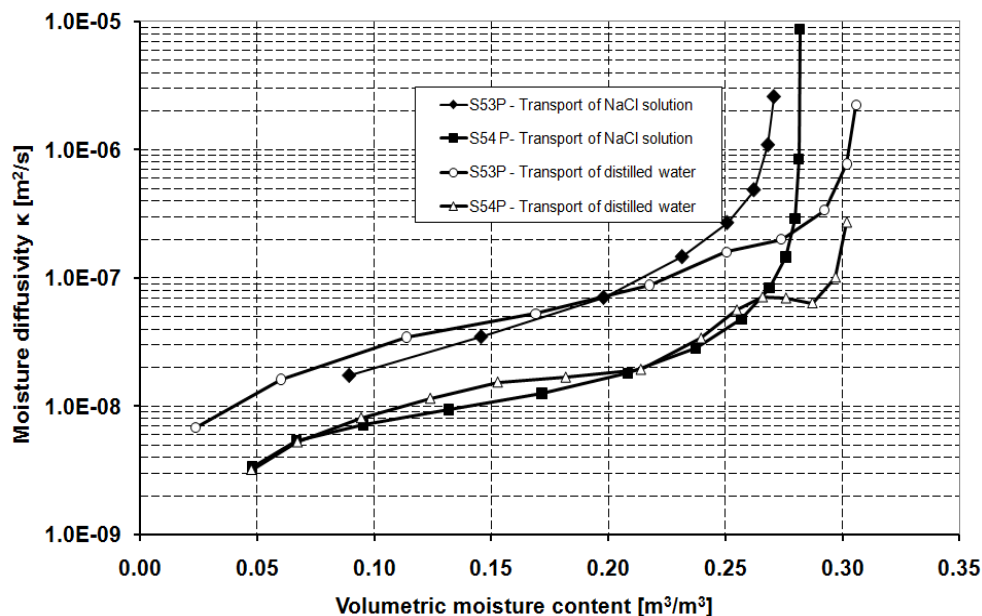

Figure 2. Moisture diffusivity of studied plasters.

This data characterizes the capability of plasters to transport liquid water and salt solutions. The moisture transport was in both studied cases faster for plaster denoted S53P although the total open porosity was found to be more or less the same for both materials. However, this finding is in agreement with pore size distribution measurement that showed for SP53P higher amount of capillary pores having the pore diameter range 0.1 – 1 μm.
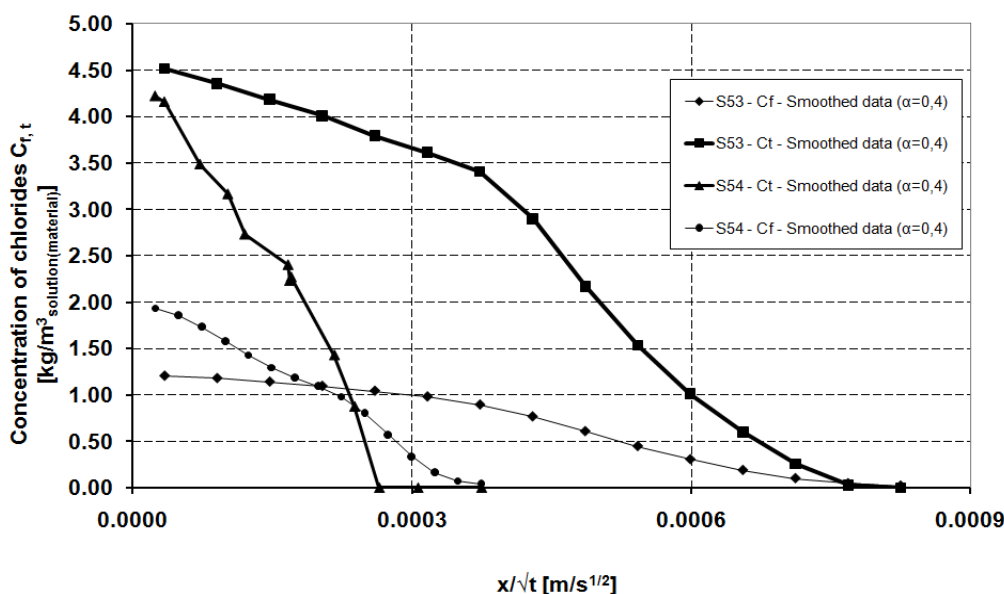

Figure 3. Chloride concentration profiles.

From the comparison of moisture diffusivities measured for distilled water and 1M NaCl water solution penetration, two different features can be distinguished. In lower moisture contents, typically up to 0.2 m^3/m^3, the moisture diffusivities calculated for 1M NaCl penetration were lower and the moisture transport was in this case slower in comparison with transport of pure distilled water. This

finding we assign to the differences in bulk density and viscosity of penetrating media. On the other hand, in higher moisture contents, the moisture transport was for 1M NaCl penetration faster than for pure distilled water and calculated moisture diffusivities were for 1M NaCl water solution transport higher. This can be explained by acceleration of moisture transport by electrochemical forces formed by material interaction with Na^+ and Cl^- ions.

Smoothed concentration profiles of total chloride concentration as well as of free chloride concentration used for calculation of chloride diffusion coefficient are plotted in Fig. 3. We can see slower chloride transport in plaster S54P than in material S53P. These results are also in agreement with pore size distribution measurement as well as with determined moisture diffusivities.
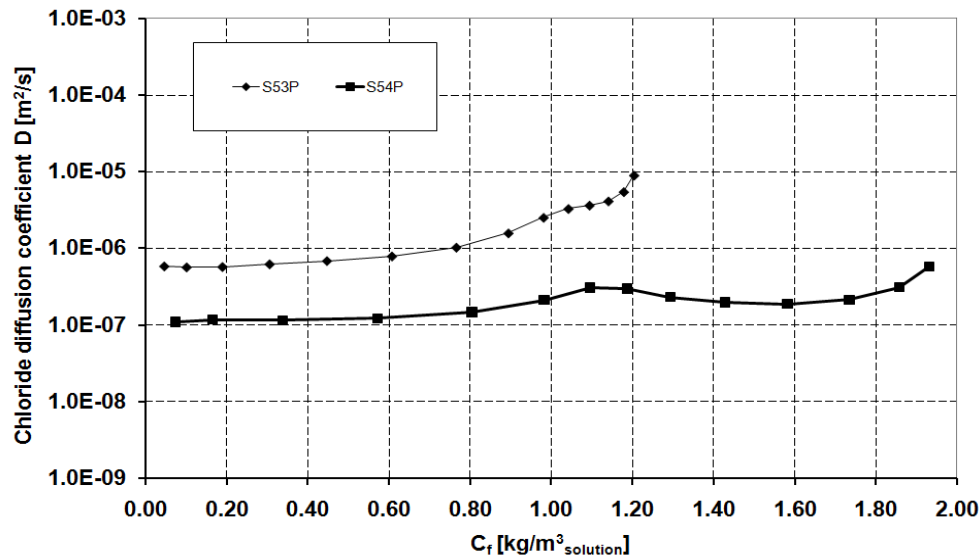

Figure 4. Chloride diffusion coefficients of studied plasters.

Dependences of chloride diffusion coefficient upon its concentration are shown in Fig. 4. We can see systematically lower values of *D(C)* function of renovation plaster S54P in comparison with plaster 353P. On that account we can conclude, the addition of higher amount of pozzolana admixture had positive effect on reduction of moisture and chloride transport in plaster S54P. When we compare the obtained data with chloride diffusion coefficient measured for reference lime plaster [Fiala *et al.* 2010] we can summarize that application of pozzolana was proved to be beneficial for both studied plasters, especially from the point of view enhanced durability of developed materials that is in clear relation with limited moisture and salt transport.

Looking at the results from the quantitative point of view, the calculated chloride diffusion coefficients in plasters were higher at least by two orders of magnitude than in water solution by itself. It indicated that the chloride transport was accelerated by electrochemical interactions of ions with the pore walls and possibly also by osmosis and surface diffusion. Since we have assumed in our calculations only the diffusion-advection-based model of salt solution transport, no other electrochemical analysis is possible on the basis of calculated data.

5 CONCLUSIONS

Moisture diffusivities, chloride diffusion coefficients and chloride binding isotherms of two types of newly developed renovation plasters were studied in the paper. The studied plasters differed in composition, especially in the amount of used pozzolana admixture.

Water and chloride water solution transport properties of both studied materials are in comparison with usually used pure lime plaster much lower, what makes good prerequisites for their application within the restoration of historical buildings' facades even in the case of salt laden materials. On the basis of obtained data, one can assume higher durability of the both studied plasters as compared to the traditional pure lime plaster.

ACKNOWLEDGMENTS

REFERENCES

Antonova, E., Postnikova, O. & Zachorova, A. 2006, *Proceedings of the ARCCHIP Workshops*, European Research of Cultural Heritage, **5**, 295-300.

Bear, J. & Bachmat, Y. 1990, *Introduction to Modelling of Transport Phenomena in Porous Media*, Vol. 4, Kluwer, Dordrecht.

Cabrera, J. & Rojas, M. F. 2001, 'Mechanisms of hydration of the metakaolin-lime water system'. *Cement and Concrete Research*, **31**, 177-182.

Fiala, L., Pavlíková, M., Pavlík, Z., Keppert., M., Pernicová, M. & Černý, R. 2010, 'Chloride accumulation and transport in renovation plasters', Proceedings of 1st Central European Symposium on Building Physics, Lodz: Technical University of Lodz, 127-133.

Mocmanová, A. 2007, *Environmental deterioration of materials*, Chapter No. 1 - Environmental factors that influence the deterioration of materials, WIT Press, Southampton.

Jiřičková, M. & Černý, R. 2006, 'Chloride Binding in Building Materials', *Journal of Building Physics*, **29**, 189-200.

Pavlík, Z. 2009, *Identification of parameters describing the coupled moisture and salt transport in porous building materials*, Habilitation thesis, CTU Press, Prague.

Pavlík, Z., Jiřičková, M., Fiala, L. & Černý, R. 2006, 'Inverse Modeling of Salt Diffusion and Advection in Building Materials', Research in Building Physics and Building Engineering, Taylor and Francis, London, 155-160.

Pernicová, R., Pavlíková, M. & Černý, R. 2008, 'Durability Properties of Innovative Plasters for Renovation of Historical Buildings', Proceedings of Durability of Building Materials and Components 11. Istanbul, Cenkler Matbaacilik Tic. Ltd., 1267-1274.

Price, C., 1996, *Stone conservation, an Overview of Current Research*, The Getty Conservation Institute, Los Angeles.

Thorborg von Konow, 2006, *Proceedings of the ARCCHIP Workshops*, European Research of Cultural Heritage, **5**, 213-223.