Simulation of desalination processes using lime-based mortars

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Lime-based mortars have different applications in the field of restoration of monuments, e.g., bedding, jointing, plastering, mending or filling the gaps and desalination of natural and artificial stone. According to the previous research devoted to restoration mixtures as well as analysis of historical binders, compositions with a different ratio of binder (lime) and filler (sand) were elaborated for desalination of natural dolomite and historical brick. The desalination process of experimental model-samples salinated with NaCl, Na_2SO_4, and $NaNO_3$ solutions was simulated by application of lime-based mixtures for three weeks. The migration process of moisture and aggressive salts from a salinated object into lime mortar was studied. The amount of ions of soluble salts in the different depths of desalinated stone and lime plaster was determined by chemical and XRD analysis.

Introduction

Destructive processes, both in natural and artificial stone materials of industrial and historical buildings, are often caused by a low environmental quality, historical and weather conditions, the influence of solutions contaminated with different soluble salts. In order to provide the continuity of Latvian cultural heritage and functions of buildings, desalination of masonry is often the most frequent maintenance activity necessary to carry out. Depending on a salinated object and circumstances in all particular cases, the materials and methods for desalination purposes are described to be different. Most popular are clay minerals (zeolite, kaolinite or bentonite), cellulose, lime and combinations of different materials in the technique of poultices [1–3]. Thus, there are two important stages in the desalination process: selection and studies of a desalination method and control of the desalination process. In the first step, the material with the highest ability to absorb more popular soluble salts causing stone disintegration – chlorides, sulphates and nitrates – are chosen depending on a particular masonry and on the object subjected to desalination.

In order to control the desalination process, both quantitative and qualitative analysis of ions of soluble salts at a different height and depth of material are recommended. Both desalting material (poultice) as well as the salinated building material are analysed before and after desalination.

The present report reflects studies concerning the properties and desalination ability of lime-based mortars applied to a natural material – dolomite and low temperature burned brick ("Sencis") contaminated with sodium salts (chlorides, sulphates and nitrates) as well as the modelling of the desalination process in laboratory conditions.

Experimental

As stated in the previous studies, the binder-to-filler ratio for Latvian historical mortars is often close to the classical – 1 : 3 [4]. For laboratory investigations of the project, three series of lime-based mixtures with a different lime / sand ratio were prepared (Table 1). Lime mixtures prepared in the shape of rectangular samples (cubes about 40 × 40 × 40 mm) were used for further experiments after two months of hardening at a temperature of 20 °C and humidity 90%. Free and forced absorption of water as well as of 1M NaCl, 1M $NaNO_3$ 0.1M Na_2SO_4 solutions and their mixtures was measured after maturing. From the obtained data, the absorption capacity, pore volume accessible for water and water solutions, density and other physical properties were calculated [5].

Table 1. Composition of experimental lime mixtures and their physical / mechanical properties

Sample code	Lime, parts by weight	Sand, parts by weight	Dimensions, mm	Weight, g	Density, kg/m^3	Compr. strength, MPa
Ca (1 : 3)	1	3	D H	68.3	1689	0.58
2Ca (1 : 2)	1	2	38 39	80	1625	0.35
3Ca (1 : 2.5)	1	2.5	(±3) (±3)	76	1653	0.42

Thus, for calculating the total porosity, the following equation was used:

$$P = (1 - \rho_r / \rho_a).\ 100\%,$$

were ρ_r is the real density and ρ_a is the apparent density.

The amount of Cl^-, NO_3^- and SO_4^{2-} (mg/l) was determined at a different depth of a specimen by chemical analysis.

The mineralogical composition of lime mortars, before and after treatment in salt solutions, was analysed by X-ray powder diffraction at a different depth (diffractometer Rigaku Optima Plus) using $Cu_{K\alpha}$ radiation. The morphology of samples was characterized using an optical microscope (*Optical Stereomicroscope Leica 420*).

The second step of investigations included desalination of artificially salinated dolomite and brick ("Sencis") by applying the tested lime mortars to evaluate and compare their desalination ability. Prior to the experiment, dolomite and brick had been salinated with NaCl, $NaNO_3$, Na_2SO_4 solutions for three months.

In order to allow the diffusion of salt solution only in one direction, e.g., only through one of the rectangular faces of a salinated specimen, the five others were covered with paraffin. An uncovered faces of salinated samples were coated with a layer of lime mortar. Salt extraction over time was monitored both in removed poultice and the treated dolomite or brick. The amount of migrated ions was controlled by chemical and X-ray diffraction analysis.

Results and discussion

PROPERTIES OF LIME MORTAR. Lime mortars, in some cases called also "sacrificial layers" used for desalination purposes, have to meet several requirements: adhesion between the sacrificial plaster and the base should be optimal, migration of water and salt solutions should be promoted, porosity should be in particular limits – the majority of pores should have a diameter over 0.1µm, as pores of this size are responsible for the transportation of ions; the resistance of lime mortar to the influence of a salt solution should be adequate; there should be no interaction between the sacrificial layer and the basement; removal of plaster should be simple and not damaging the historical material, etc.

Data obtained while measuring the absorption of water and salt solutions by capillarity indicated that mixtures with a decreased amount of filler had a better ability to accumulate both water and salts solutions (Fig. 1).

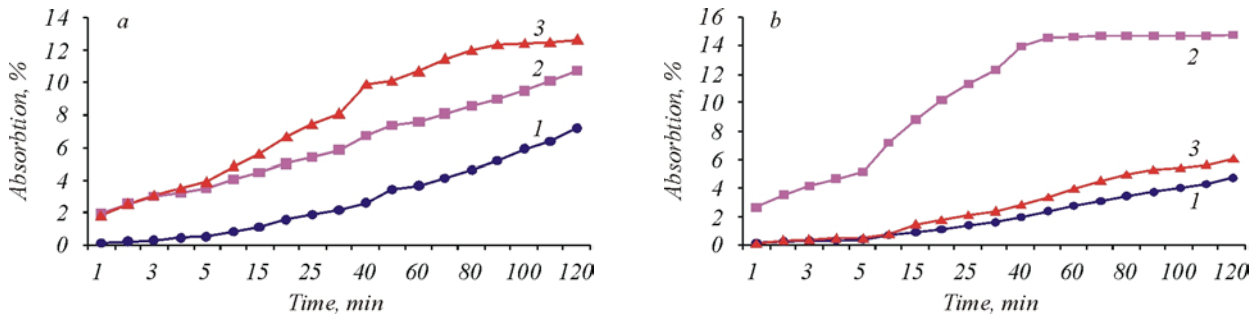

Fig. 1. Absorption of water (*a*) and NaCl salt solution (*b*) by capillarity: *1* – Ca, *2* – 2-Ca, *3* – 3-Ca

The experimental lime mortar 1 : 2.5 (3Ca) is able to absorb up to 14%, of water, solutions of NaCl, $NaNO_3$, Na_2SO_4 or their mixture during their migration.

The mechanics of absorption could be explained as follows:

- lime mortar after maturing for 2 month has mainly large pores with the size of 50–100 µm (porosity up to 25%);
- after treatment with salt solutions and after migration of a salt solution into the pore space, part of salt crystallizes, thus filling the pores and generating micro defects;
- as a result, the number of large pores decreases, but the common porosity increases [6].

Destructive processes in experimental model samples caused by the salt solutions, depending on the type of salt, on average could be observed after 20–25 days (see Fig. 2, b).

According to these data, the optimal application time of sacrificial lime plasters was chosen to be 21 days.

The main crystalline phases in lime mortars detected by XRD before application were the following: calcite $CaCO_3$, portlandite $Ca(OH)_2$, quartz SiO_2 (Fig. 3).

After the treatment in salt solutions to a depth of 5 mm from the surface of samples, extra corresponding phases of salts were present: thenardite (Na_2SO_4) and mirabilite ($Na_2SO_4{\cdot}10H_2O$), halite (NaCl), sodium nitrate ($NaNO_3$) (Fig. 4).

Fig. 2. Lime-based poultice 1 : 2 before exposure (*a*), after exposure to 0.1 M Na_2SO_4 (*b*), 1 M NaCl (*c*) solution for 25 days

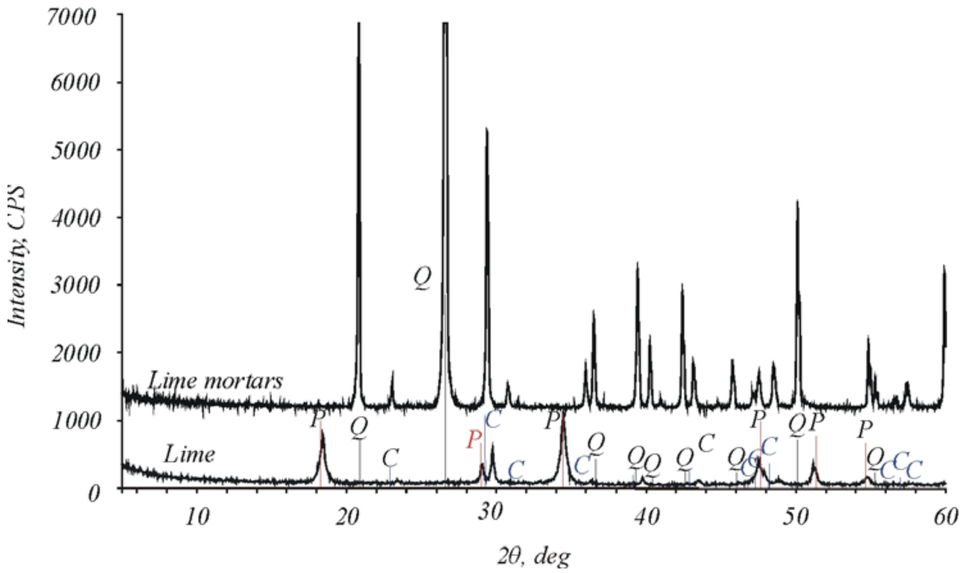

Fig. 3. XRD of lime and lime-based poultice. Q – quartz, C – calcite, P – portlandite

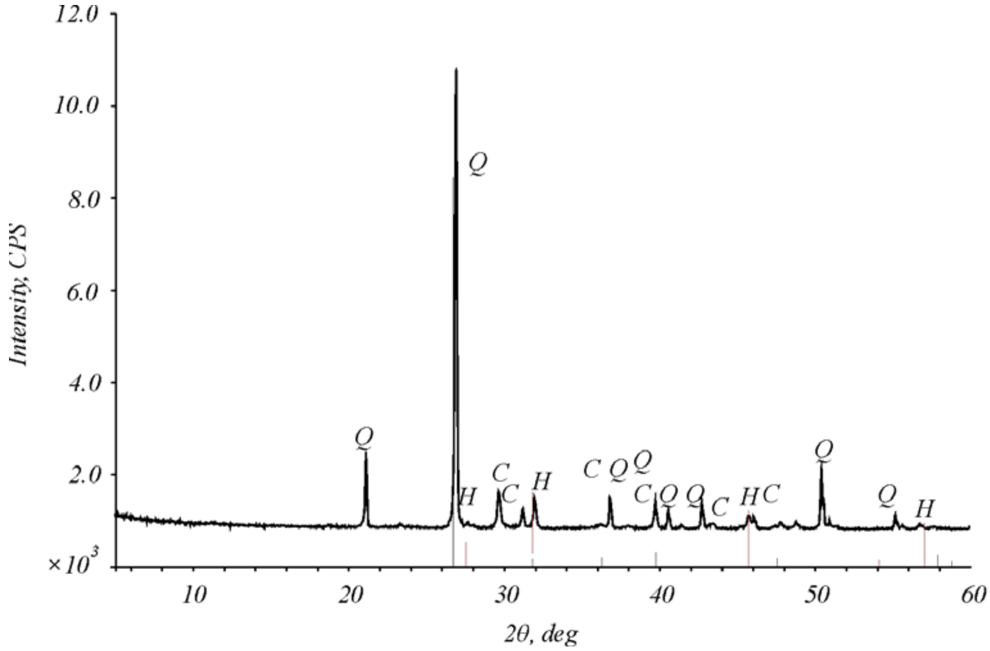

Fig. 4. XRD of lime-based poultice after exposure to NaCl solution at a depth of 5 mm. C – calcite ($CaCO_3$), H – halite (NaCl), Q – quartz (SiO_2)

No products of interaction between lime mortar and salts were detected by XRD, implying that the destructive processes of salts are caused mainly by physical and mechanical processes of crystallization.

After evaluating the chemical composition of lime mortars before and after exposure to salt solutions, compositions with a decreased amount of filler were selected – 1 : 2 (2Ca) and 1 : 2.5 (3Ca).

MODELLING AND STUDIES OF DESALINATION PROCESS. As mentioned before, two building materials typical of the Latvian cultural heritage were selected for artificial salination and desalination in laboratory conditions – low temperature burned brick "Sencis" (produced by the "Lode" factory) with the properties close to historical bricks and dolomite (Saaremaa, Estonia). The average porosity of brick is 23–24 %, the density *d* – 1.80 g/cm^3, the porosity of dolomite being 2.0–2.5% and density *d* 2.80 g/cm^3.

After contamination of samples in solutions of sodium salts for 90 days, the density of both dolomite and brick increased, confirming sodium salt deposition in the pore space of material (Table 2).

Table 2. Changes of brick density (*d*) after exposure to sodium salts

Initial density, g/cm^3	Density after exposure to NaCl solution, g/cm^3	Density after exposure to Na_2SO_4 solution, g/cm^3	Density after exposure to $NaNO_3$, solution, g/cm^3
1.795	2.04	1.93	1.90

According to the methodology of desalination described before, one surface of a salinated brick or stone samples was covered with a 2 cm thick layer of lime mortar (Fig. 5, 6). Lime poultice was kept wet for 20 days. After drying and removal of the application, the amount of Cl^- , NO_3^- and SO_4^{2-} ions was analysed both in lime mortar and in the desalinated material.

Fig. 5. Sacrificial lime layer on brick and dolomite samples

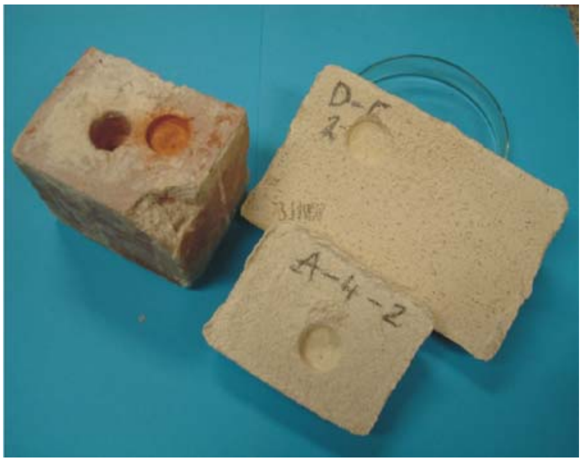

Fig. 6. Brick and poultice after withdrawal of application

Concerning the distribution of Cl^-, NO_3^- and SO_4^{2-} ions inside dolomite and brick, salts accumulated mostly in the upper layer, i.e., 10–20 mm from a sample surface (Tables 3 and 4).

Table 3. Amount of salts before and after brick and dolomite desalination

Mortar from the surface	Depth, mm	Cl^- mg/l Before / after	SO_4^{2-}, mg/l Before / after	NO_3^-, mg/l Before / after
Dolomite	1–2	600 / trace	3120 / 50	10 / 0
	10–15	400 / 0	1680 / 10	< 10 / 0
	15–25	200 / 0	120 / 0	< 10 / 0
Brick	1–2	2500 / trace	3840 / 50	50 / 10
	10–15	1600 / 0	1440 / 10	25 / 0
	15–25	1100 / 0	120 / 0	25 / 0

Table 4. Amount of sodium salts in the removed lime mixture

Mortar from the surface	Contact surface	Cl^-, mg/l	SO_4^{2-}, mg/l	NO_3^-, mg/l
Dolomite	Up to 10 mm	1100	1400	75
	Up to 20 mm	200	100	> 10
Brick	Up to 10 mm	3500	> 1600	50
	Up to 20 mm	<100	100	> 10

Elevated amounts of sulphate were detected at a depth of up to 15 mm, showing a good ability of sulphate salts to migrate in materials with a different density.

XRD analyses of desalinated dolomite and brick at a different depth showed no presence of crystalline salts such as NaCl, Na_2SO_4, $NaNO_3$ (Fig. 7).

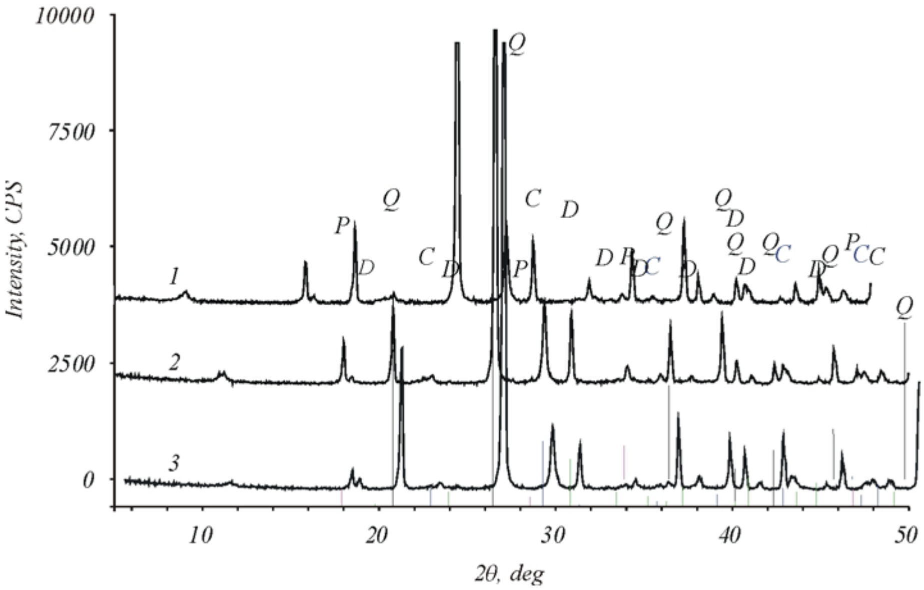

Fig. 7. XRD of desalinated dolomite (exposure to Na_2SO_4 solution) at a different depth: *1* – surface, *2* – 10–15 mm, *3* – 15–25 mm. D – dolomite, C – calcite, P – portlandite, Q – quartz

Conclusions

Concerning the distribution of Cl^- , NO_3^- and SO_4^{2-} ions inside dolomite and brick, we found that in general salts were accumulated in the upper layer, i.e., 10–20 mm from the surface.

Elevated amounts of sulphate were detected at a depth of up to 15 mm, showing a good ability of sulphate salts to migrate in materials with a different density.

Lime–sand mixtures with a decreased content of filler have a better ability to accumulate both water and salt solutions.

The optimal application time of sacrificial lime plasters in wet states is about 21 days.

Destructive processes of salts are caused mainly by physical and mechanical processes of crystallization as no products of interaction between lime mortar and salts were detected by XRD.

The results of simulation of desalination processes using lime-based mortars clearly indicate the ability of lime–sand mixtures to accumulate sodium salts, these, they may be recommended as a desalting material for brick and dolomite.

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DRUSKŲ TIRPALŲ POVEIKIO KALKIŲ SKIEDINIAMS PROCESO MODELIAVIMAS

S a n t r a u k a

Kalkiniai skiediniai plačiai naudojami monumentų restauracijai, pvz., pamatų, tinkų, įtrūkimų taisymui ar užpildymui ir natūralaus ar dirbtinio akmens druskų tirpalų poveikiui mažinti. Remiantis literatūros duomenimis, dolomitinių ar senų plytų restauracijai skirti skiediniai buvo labai skirtingo rišiklio (kalkės) / užpildo (smėlis) santykio. Druskų tirpalų (NaCl, Na_2SO_4 ir $NaNO_3$) poveikis kalkinių mišinių bandiniams tirtas 3 savaites. Analizuota drėgmės ir agresyvių druskų migracija iš tiriamo objekto į kalkių skiedinį. Tirpus druskų jonų kiekis skirtinguose veikiamo akmens ir kalkinio skiedinio sluoksniuose nustatytas cheminiais ir XRD analizių metodais.