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Clay Based Poultices for Desalination of Building Materials

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One of the major threats affecting the lifetime of cultural monuments and residential buildings are the water-soluble salts raising the necessity for desalination activities.

In the following paper three clay-based compositions have been studied by varying ratio of binder (clay) to filler (sand and cellulose) as follows: clay to sand mass ratio 1:2, 1:5 and clay/sand/cellulose mass ratio of 1:4,5:0,5.

The experimental examination of desalination compositions included determination of density, drying shrinkage, pore size distribution using mercury porosimetry before and after exposure to the solutions of water soluble salts.

In order to control desalination process quantitative and qualitative analysis of ions of soluble salts (distribution profiles of nitrate, chloride and sulphate ions as well as crystalline phases of the samples by using chemical and XRD analysis) in both material – poultice, as well as salinated building material have been performed.

The obtained results have shown that the main parameter determining salt transport mechanisms and desalination efficiency is pore size distribution of the substrate and poultice as well as nature and ratio of the binder and filler.

Obtained experimental data can be used for further research as well as planning of practical restoration activities in environments with high concentration of water-soluble salts.

Keywords: *clay-based poultices, building materials, desalination.*

1. Introduction

Deterioration of the natural and artificial stone materials used in industrial and historical constructions is caused by the simultaneous interaction of different factors such as environmental contamination, weather (humidity, freeze and thaw etc.) and presence of different water-soluble salts. Solutions of salts may crystallize in pores of the stone material causing an increased pressure and formation of micro-cracks or interact chemically with material constituents (Carretero et al. 2006). Therefore, a large part of the preventative and restoration activities are devoted to decreasing the salt concentration in building materials. Different methods are available for this purpose depending on particular environmental conditions, physical and chemical properties of the contaminated object as well as its historical background. The most common desalination technique is desalination poultices made of a mixture of clay minerals (zeolite, kaolinite or bentonite), sand and cellulose (Lubelli and Hees 2010). Desalination process can be performed by two main mechanisms: diffusion and advection. The pore size distribution and volume of the pores both in substrate and poultice plays an important role in desalination process. In order to achieve fast and effective desalination it is recommended to perform it by the advection mechanism with simultaneous wetting function. In order to achieve it pore size distribution must be broad, i. e. poultice has to contain both small pores which provide salt extraction and large reservoir pores which provide wetting of the substrate (Lubelli and Hees 2010).

Even though this method is attractive due to its simplicity, effective desalination and use of local raw materials, more explicit examination of desalination mechanisms is necessary.

The desalination process normally consists of two major stages, i. e. selection and studies of desalination composition and control of desalination process. In the first step the material with the highest ability to adsorb common soluble salts causing stone disintegration such as chlorides, sulphates and nitrates is chosen depending on a particular masonry and object subjected for desalination. The control of desalination process is performed by quantitative and qualitative analysis of the salt ion concentration in different height and depth of both desalination poultice as well as contaminated building material (Setina et al. 2009).

The following paper reflects the studies concerning properties and desalination ability of clay based poultices applied to an artificial stone material, low temperature burned brick “Sencis”, contaminated with water soluble sodium salts, i. e. chlorides, sulphates and nitrates as well as modelling of desalination process in laboratory conditions.

2. Methods

The current study has been elaborated in two stages: selection and examination of clay based desalination compositions and control of desalination process.

Three clay based compositions have been studied by varying ratio of binder (clay) and filler (sand and cellulose) as follows: clay to sand ratio 1:2, 1:5 and clay/sand/cellulose ratio of 1:4, 5:0,5. The following compositions have been chosen based on results found in literature (Lombardo and Simon, 2006) in order to study the effect of the addition of cellulose compared to the clay/sand mixture traditionally used for desalination of historical monuments in Latvia (Krage et al. 2006). The quaternary clay from Broceni (Latvia) was used for experiments. The pure clay was used as a reference for the studied desalination compositions.

The specimens with above mentioned compositions were prepared in a rectangular shape (20x25x54 mm). After drying and hardening in a room temperature volume and density of the specimens was calculated based on their weight and size (table 1).

Table 1. *Physical properties of different clay based composition*

	Weight, g	V, cm^3	ρ, g/cm^3
Clay	39,6	25,61	1,54
Clay/Sand 1:2	59,9	29,36	2,04
Clay/Sand 1:5	55,3	32,72	1,69
Clay/Sand/Cellulose 1:4,5:0,5	38,98	30,99	1,26

The dynamics of the drying were studied by monitoring the weight loss of the specimens with different binder to filler ratios. After hardening the drying shrinkage was determined. The functional serving time of the poultice is determined by these properties.

Porosity of the specimens was determined by mercury porosimetry (Autopore IV). The mineralogical composition of Broceni clay and sand was analysed by X-Ray powder Diffraction (difractometer Rigaku Optima Plus) using $Cu_{K\alpha}$ radiation.

The second step of investigations included desalination of artificially salinated brick "Sencis" (produced in factory "Lode") by application of tested clay based poultices in order to evaluate and compare their desalination ability. Prior to the experiment, brick was salinated with the solutions of NaCl, $NaNO_3$, Na_2SO_4 for 90 days.

In order to allow the diffusion of salt solution only in one direction e. g. only through one of the rectangular faces of salinated specimen, the five other sides were covered with paraffin. The uncovered faces of salinated samples were coated with a 2 cm thick layer of a clay based poultice. Salt extraction has been monitored in depth of 10mm both in removed poultice and the treated brick using chemical analysis and X-Ray diffraction (XRD). Chemical analysis has been performed using Merckoquant® test strips (paper chromatography) for determination of SO_4^{2-}, NO_3^- and Cl^- ions in the samples of interest.

3. Results and Discussion

Properties of the clay based poultice

Study of the drying process showed that clay specimens with admixture of sand (1:2 and 1:5) exhibit shorter drying time (2 days) compared to the pure clay and a mixture of clay, sand and cellulose (3 days) (Fig. 1).

However, the lowest drying shrinkage was observed for the compositions with higher proportion of the filler, i. e. clay/sand mixture with the ratio of 1:5 and clay/sand/cellulose mixture with the ratio of 1:4, 5:0,5 (table 2).

Table 2. *Drying shrinkage of different clay based compositions*

Composition	Drying shrinkage (%)
Clay	6,42
Clay/Sand 1:2	5,13
Clay/Sand 1:5	4,63
Clay/Sand/Cellulose 1:4,5:0,5	4,92

Results obtained from mercury porosimetry performed for the clay based samples with different binder to filler

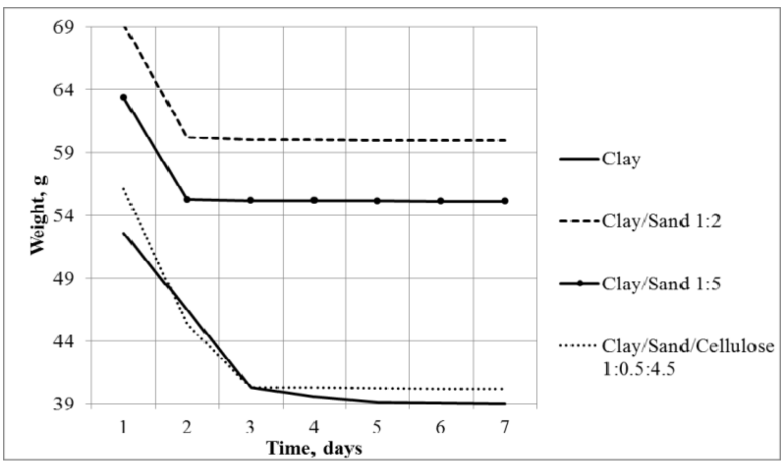

Fig. 1. *Weight loss due to drying in time for the specimens with different binder to filler ratio*

ratios showed that clay samples without additives mainly contain pores in a size range from 0,01 to 0,2 μm (Fig. 2).

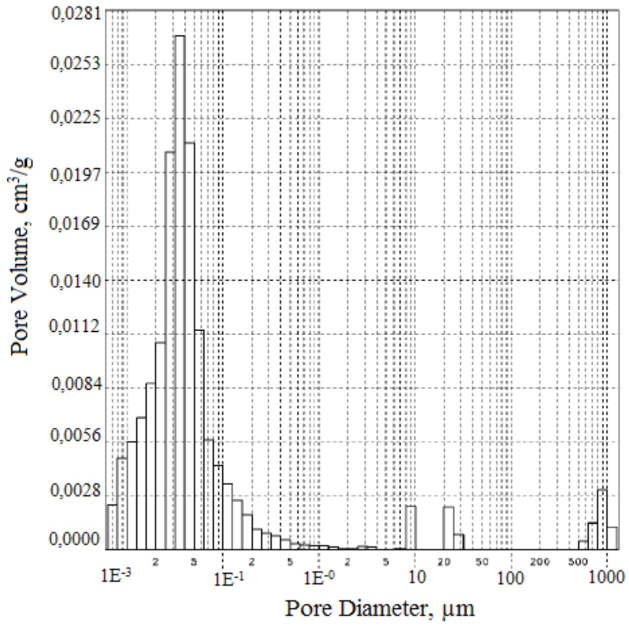

Fig. 2. *Pore size distribution for the clay sample without additives*

Samples with clay/sand ratio of 1:5 exhibit two main pore size ranges – from 0,01 to 0,4 μm and from 2 to 20 μm (Fig.3).

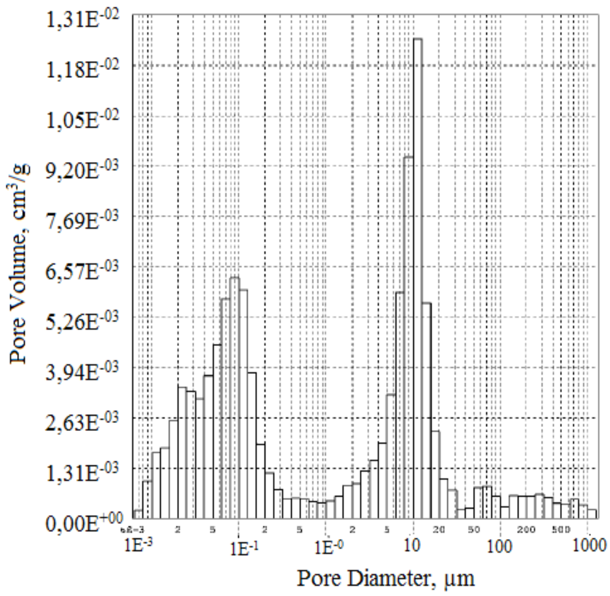

Fig. 3. *Pore size distribution for the samples with clay/sand ratio of 1:5*

Finally, mixture of clay, sand and cellulose exhibits a broad pore size distribution but the main fraction is in the range from 3 to 500 μm (Fig. 4).

Crystalline phases determined by X-Ray diffraction for Broceni clay are kaolinite, illite, calcite, dolomite and quartz. Sand contains mainly quartz.

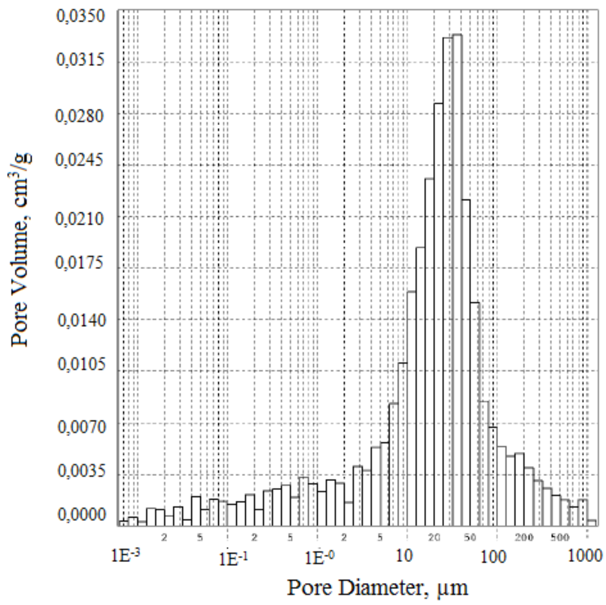

Fig. 4. *Pore size distribution for the samples with clay/sand/cellulose ratio of 1:4, 5:0,5*

Properties of the contaminated substrate

As mentioned, a building material typical for Latvian cultural heritage was selected for artificial salination and desalination in laboratory conditions – low temperature burned brick „Sencis" with the properties close to historical bricks.

The average porosity of brick is 23–24 % and density – 1.80 g/cm³.

The results obtained from the XRD performed for the brick "Sencis" before salination indicated such crystalline phases as spinel ($MgAl_2O_4$), quartz (SiO_2), hematite (Fe_2O_3), and microcline ($KAlSi_3O_8$). After exposure to salt solutions for 90 days same crystalline phases were determined as before salination and additionally thenardite (Na_2SO_4) and mirabilite ($Na_2SO_4 \cdot 10H_2O$) for the samples exposed to 0,1 M Na_2SO_4 solution, halite (NaCl) for the samples exposed to 1 M NaCl solution and sodium nitrate ($NaNO_3$) for the samples exposed to 1 M $NaNO_3$ solution. As it can be seen salts do not interact with the material since no products of chemical interaction were determined by XRD.

Chemical analysis using Merckoquant® test strips was performed for the brick before and after exposure to salt solutions in different depths (Fig. 5).

It can be seen that salts are mainly concentrated next to the surface of the brick (1-15 mm depth). Nitrate ions exhibit very low concentration compared to sulphate and chloride ions.

Modeling of desalination process

According to the methodology of desalination described before, one surface of salinated brick was covered with 2 cm thick layer of lime mortar. Clay based poultice

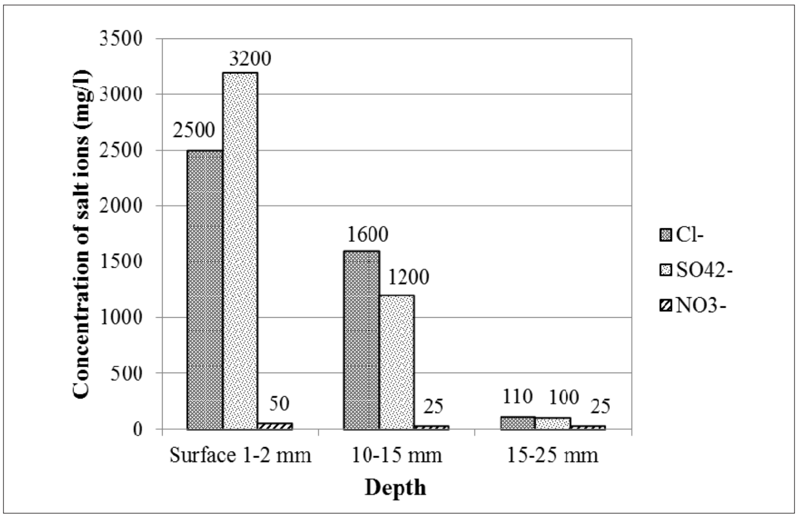

***Fig. 5.** Results of chemical analysis for the brick "Sencis" after exposure to the salt solutions for 90 days in different depths*

was kept wet for 20 days. After drying and removal of application the amount of Cl^- , NO_3^- and SO_4^{2-} ions were analysed both in clay-based poultice as well as desalinated material in 10 mm depth. Results of chemical analysis for the brick and poultice after desalination are given in Table 3 and Table 4 respectively.

It can be seen that the concentration of water soluble salts in substrate decreases drastically after application of the clay based poultices- sulphate ions are completely removed whereas only traces of chloride ions and low concentrations of nitrate ions are present in substrate after desalination.

Chemical analysis of the poultice after removal from the contaminated substrate shows that concentration of the salts is significant in the poultices (table 4).

XRD analysis of the poultices before and after applying them to the substrate have been performed in order to observe migration of the water soluble salts from contaminated substrate into the poultice. The results show that before application main crystalline phases of the clay/sand mixture 1:5 were quartz, plagioclase, calcite, dolomite and illite (Fig. 6).

After removal of the application from the substrate contaminated with water-soluble salts, the crystalline phases determined by X-Ray diffraction were identical to the ones in the mixture of origin and additionally the crystalline phases of water soluble salts have been observed (Fig. 7).

All studied compositions showed acceptable desalination efficiency and thus can be used for desalination of the brick "Sencis" however the most economically feasible options are the compositions with higher ratio of filler, e. g. clay/sand ratio of 1:5 and clay/sand/cellulose ratio of 1:4, 5:0,5. The latter composition exhibited longer drying time and it has a better adhesion with substrate due to cellulose armature and low mass. However, an advantage of the poultice with clay/sand ratio of 1:5 is its relatively low drying shrinkage which is an important parameter for the desalination poultices.

***Table 3.** Concentration of salt ions in brick "Sencis" before and after desalination using clay-based poultices*

Salt ions	Before desalination	After desalination (brick in 10 mm depth)		
		Clay/Sand 1:2	Clay/Sand 1:5	Clay/Sand/Cellulose 1:4,5:0,5
Cl^- (mg/L)	2700	50	Traces	Traces
SO_4^{2-} (mg/L)	1800	0	0	0
NO_3^- (mg/L)	50	10	<10	<10

***Table 4.** Concentration of salt ions in clay based poultices after desalination*

Salt ions	Poultices after desalination (in 10mm depth)	Poultices after desalination (in 10mm depth)	
		Clay/Sand 1:5	Clay/Sand/Cellulose 1:4, 5:0,5
Cl^- (mg/L)	1500	2300	2500
SO_4^{2-} (mg/L)	1200	1500	1500
NO_3^- (mg/L)	10	25	25

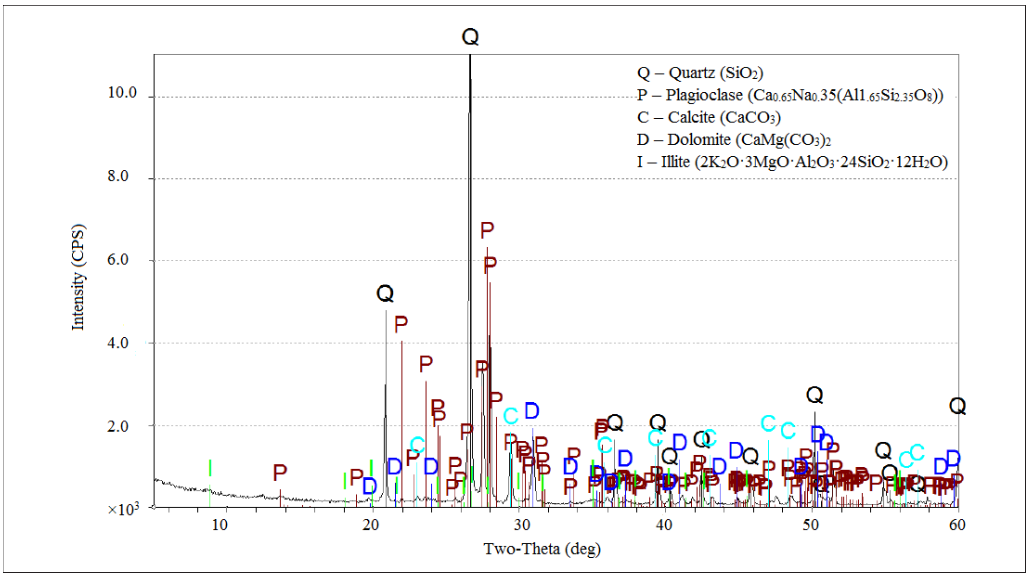

Fig. 6. *Difractogram for the clay/sand 1:5 mixture before application on contaminated substrate*

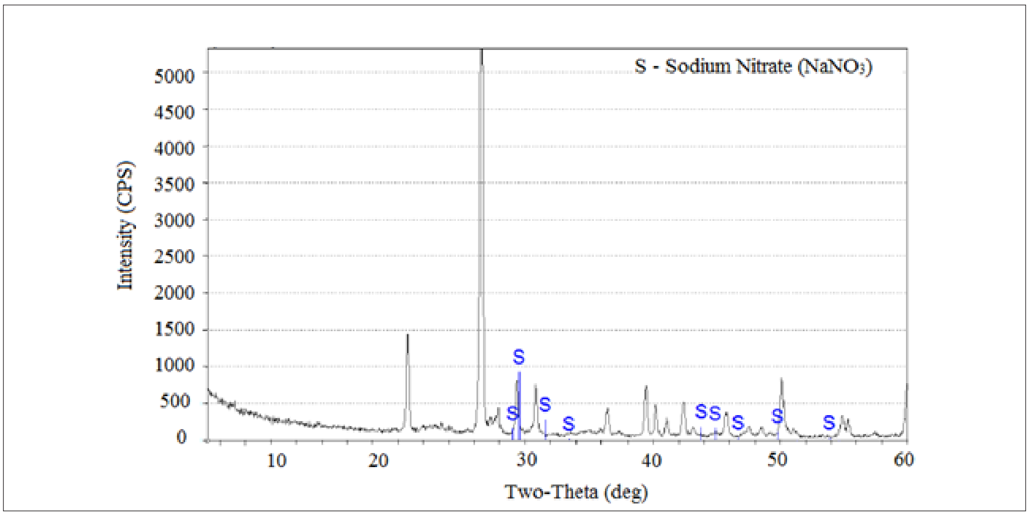

Fig. 7. *Difractogram for the clay/sand 1:5 mixture after removal from the substrate contaminated with 0,1 M* $NaNO_3$

Chemical analysis performed for the poultices after desalination (Table 4) showed rather high concentration of Cl^-, SO_4^{2-} and NO_3^- ions. XRD analysis demonstrated the presence of the crystalline phases of the salts in a clay based poultice removed from the contaminated substrate which confirms the migration of salts from the substrate into the poultice.

Thus, the salt ions are transported from the salinated substrate to the poultice and accumulate in it. XRD analyses of desalinated brick in different depth did not show presence of the crystalline salts as NaCl, Na_2SO_4, $NaNO_3$ which confirms the efficiency of the studied clay based compositions.

4. Conclusions

The compositions with Broceni clay/sand ratio of 1:2 and 1:5 as well as clay/sand/cellulose ratio 1:4, 5:0,5 have been studied.

The results obtained in the following study have shown that the main parameter determining salt transport mechanisms and desalination efficiency is pore size distribution of the substrate and poultice as well as nature and ratio of the binder and filler.

The compositions with higher binder to filler ratio exhibit broader pore size distribution and higher desalination efficiency.

Based on obtained results clay based application with clay/sand/cellulose ratio of 1:4, 5:0,5 and clay/sand ratio of 1:5 can be recommended as effective desalination compositions.

Obtained experimental data can be used for further research for desalination of different construction materials as well as planning of practical restoration activities in environments with high concentration of water-soluble salts.

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