Desalination of Cotta type Elbe sandstone with adapted poultices: Optimization of poultice mixtures

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Abstract

Cotta type Elbe sandstone has been frequently used as construction material and ornamental stone on buildings over centuries. Desalination of this sandstone (often performed with cellulose poultices in restoration practice) is ineffective in many cases due to its high amount of fine pores.

A mixture of cellulose, kaolin and sand (1:2:1 by weight, CKS_121) with a high portion of fine pores was applied for poultice desalination on artificially salt-loaded specimens of Cotta type sandstone. Moreover, another mixture of the same components (CKS_128 with cellulose-kaolin-sand 1:2:8 by weight) and two poultices that are frequently used in restoration practice (ready-made Rajasil (RAJ) poultice and Arbocel® CC1000/BWW40 (ARB) mixture) were applied for comparison. The pore size distributions and the structures of all poultices were characterized by MIP. The results showed highest amounts of extracted salt for the poultices with clay and higher portions of sand (CKS_128, RAJ). The CKS_121 poultice, although fitting best with regard to pore size distribution, shows high shrinkage due to the high amount of kaolin, which leads to loss of adhesion to the substrate during the desalination process. The results clearly demonstrate that in desalination practice of stones with fine pores compromises have to be found between the competitive parameters of "ideal" pore structure and low shrinkage of the poultice, both influenced by clay contents in the mixture.

Keywords: salt reduction, desalination, Cotta type Elbe sandstone, poultice mixtures

1. Introduction

Salt reduction or "desalination" with poultices is a well-known and widely used technique in conservation of natural stone buildings and sculptures.[1] Recent investigations into the transport phenomena of salt and water led to better general understanding of the interaction of poultice and substrate properties during the desalination process.[2-3] As a result, in current discussions of the poultice materials main attention is drawn to the role of an appropriate pore size distribution of the poultice with respect to the substrate material to be desalinated. Analyses of the pore size distribution of the substrate by mercury intrusion porosimetry (MIP) can give useful hints towards the pore size properties needed for the poultice to achieve an efficient desalination. Generally, the wet poultice should provide a portion of pores coarser then those in the substrate to offer enough water to the stone material in the wetting phase on one hand. On the other hand another portion of pores in the poultice finer then those in the stone substrate is needed to extract the water with dissolved salts from the stone by advection in the drying phase.[2] Appropriate structures can be designed in mixtures of cellulose, clay and sand by varying the proportion of the respective components.[3] These principles established in

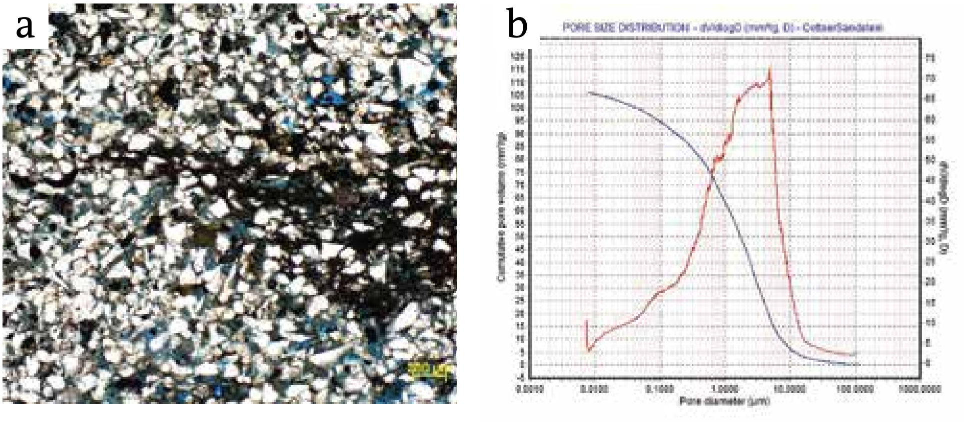

Figure 1: Thin section image of Cotta type sandstone (Nicols II) with pores coloured by blue dye (a) and typical pore size distribution obtained by MIP (b)

the laboratory have already been transferred to conservation practice[4] or tried out in the laboratory for local important building stones. [5]

From a practitioner's point of view properties of the poultice material like adhesion to the substrate, shrinkage while drying, and the removal of the poultice from the stone surface without remnants after drying are of importance beside efficiency. Higher clay contents in the poultice do not only provide the appropriate portion of fine pores needed for efficient desalination of stones with high contents of smaller pores but also change the properties of the poultice towards higher shrinkage and therefore worse adhesion to the substrate. Moreover, very small clay particles tend to adhere to the stone surface and in the pore structure of the substrate after drying and removal of the poultice layer. To match both the problems of salt transport from the stone into the poultice and the practical workability of poultices for desalination, compromises with respect to the clay content are needed in most cases. The study presents investigations carried out to optimize a poultice for desalination of a fine-pored, widely used building and sculptural stone. Moreover the efficiency of poultices often used by restorers in practice is compared to the one designed with respect to pore size distribution of the Cotta type sandstone.

2. Materials and methods

2.1. Cotta type Elbe sandstone and test specimens

Cotta type sandstone is a variety of the Cretaceous Elbe sandstone which has been used for building purposes in East Germany and especially in Saxony over centuries. The sandstone is a fine-grained, clay-bearing quartz arenite with kaolinite and illite contents. The average diameter of grains is 0.12 mm. The sandstone structure in thin section and its pore size distribution (total porosity ca. 20 vol.%) is shown in *Figure 1*. As can be seen from *Figure 1b*, the majority of pores is concentrated between 0.1 and 10 µm. Since the material is vulnerable to salt attack, desalination is a standard procedure in the course of most of the restoration measures planned for historic objects made of Cotta type sandstone.

To investigate the efficiency of desalination, stone specimens of unweathered

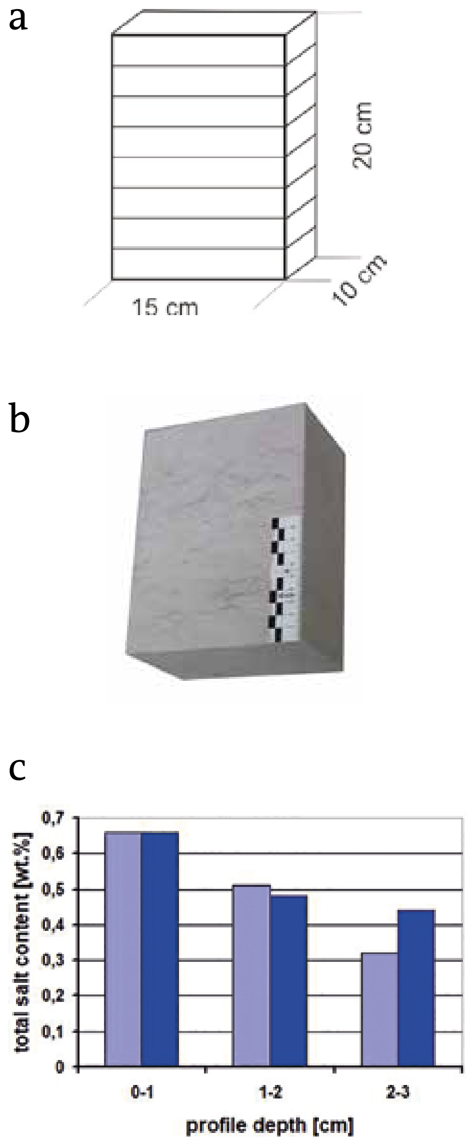

Figure 2: Dimension of the stone specimens used for desalination experiments (a, b) and analytical control of the salt distribution on two random samples (c)

Cotta type sandstone in the dimension of 15x20x10 cm with the largest areas cut perpendicular to the bedding were prepared *(Figure 2a, b)*. After sealing the specimens at the 4 smaller sides with epoxy resin, they were loaded with 3% sodium sulphate solution by capillary suction parallel to bedding over 7 days. After sealing also the bottom side with epoxy resin, the specimens were dried at room conditions over 14 days. Profile analyses of the total salt content on random samples showed a comparable salt distribution within the test specimens, similar to that found in monuments *(Figure 2c)*.

2.2. Poultice materials

According to the pore size distribution of the Cotta type sandstone *(Figure 1b)* and the results presented in[3] a cellulose-kaolin-sand (CKS) 1:2:1 mixture (by weight) with pore sizes in the same range was selected for the starting experiments. Kaolin and sand came from local deposits (Caminau and Ottendorf-Okrilla, respectively) but had grain size distributions very similar to those used in [3] *(cf. Figure 3)*. The chemical composition of the Caminau kaolin *(Table 3)* differs somewhat from the ideal kaolinite (46.5% SiO_2 and 39.5% Al_2O_3) but is similar to that of the Polwhithe™ C material (SiO_2 47%, Al_2O_3 37%) used in.[3] The difference to ideal kaolinite in case of Caminau kaolin might be explained by the presence of small quantities of illite/mica, as indicated by 2.4% K_2O. The mineralogical composition of Caminau washed kaolin is described by contents of 80-90% kaolinite and 10-20% illte/mica, but no swelling minerals like montmorillonite or mixed layers [6]. For comparison, two poultices that are often used in restoration practice were involved in the tests: a pure cellulose poultice (mixture of Arbocel BC 1000 and BWV 40 1:2.1, [5]) and a ready-made poultice currently provided on the market (produced by Rajasil; mixture of Arbocel®, Ca bentonite, Poraver® and quartz sand) were applied. Different poultice mixtures were characterized with respect to their pore size distri bution as well as to their workability and shrinkage behavior. The latter was determined at the beginning of the experiments by

Material	Sand	Kaolin	Cellulose
Origin	Ottendorf-Okrilla (Euroquarz GmbH)	Caminau (Kaminauer Kaolinwerk GmbH)	Arbocel® BWW 40 (Kremer)
Chemical omposition	SiO_2 98% Al_2O_3 1,15%	SiO_2 46.6% Al_2O_3 35.9% K_2O 2.4%	Cellulose 99.5%

Table 1: Material parameters of the poultice components in own mixtures (source of data: data sheets of the producers)

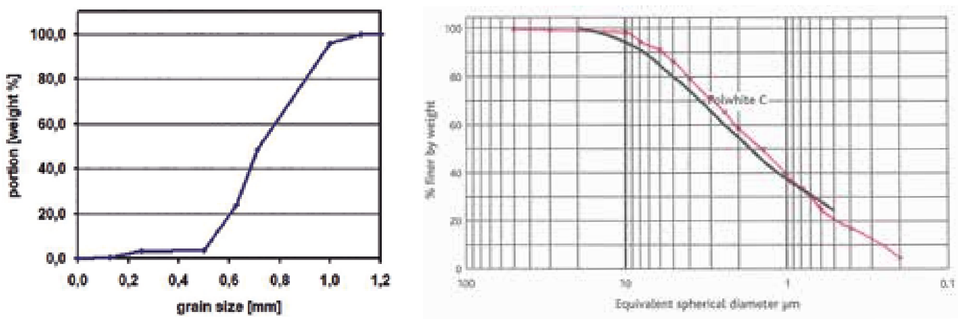

Figure 3: Grain size distribution of the used sand (a) and kaolin (b) components (red line = kaoline Caminau, black line kaoline Polwhite™ C for comparance)

application of 1 cm thick poultices on water saturated specimens (15x20x3 cm) of Cotta type sandstone. Since the shrinkage was remarkable high for the CKS_121 mixture, a mixture CKS_128 of the same components, but with higher amounts of sand was additionally investigated.

The selected different poultice systems *(Table 2)* were applied to the artificially salt-loaded Cotta type sandstone specimens described in 2.1 in the following way: First, all stone surfaces were pre-wetted with 25 ml of demineralised water. Afterwards, the wet poultices were applied with a thickness of 1 cm. Each type of poultice was applied to 3 sandstone specimens. The specimens treated this way were then stored in the workshop (in upright position) for 3 weeks at 18 °C/42% r. H. Observations of visual changes (efflorescence, loss of adherence, cracks) during the drying process were registered. After 3 weeks, the poultices were removed from the sandstone surface for analyses of the extracted salt amounts.

2.3. Analytical methods

MIP measurements for characterization of the pore size distribution of dry poultices were carried out with Porotec Pascal 140 and Pascal 440 systems.

For the assessment of the quantity of salt moved from the stone substrates into the poultice after desalination, parts of the dry poultices (area 13x18 cm, thickness 1 cm each) were put in plastic bottles, and 1 litre of demineralised water was added. The bottles were moved in a shaking apparatus for 12 hours and afterwards placed in the laboratory 30-80 hours for total sedimentation of the solids at the bottom of the bottle. 500 ml of the clear solution were then pipetted from every bottle and filtered. The

Material	Mixture (weight portions)	Water – dry solid ratio (by weight)	Dry weight of poultice (per 100 cm², 1 cm thick) (g)	Shrinkage after drying, length (%)/width (%)
Arbocel® (cellulose) poultice (ARB) [5]	BC 1000 : BWW 40 = 1 : 2.1	4.5*	20.5	1.3/3.0
Rajasil poultice (RAJ)	Ready-made mixture of Ca bentonite, cellulose, sand and Poraver®	0.6**	87.5	0/0
CKS_121 (own mixture)	Cellulose (Arbocel® BWW 40) : kaolin : sand (0.5 - 1 mm) = 1:2:1	0.8***	86.3	4.0/6.0
CKS_128 (own mixture)	Cellulose (Arbocel® BWW 40): kaolin : sand (0.5 - 1 mm) = 1:2:8	0.39***	126.1	0/0

*taken from [6] **as recommended by the producer ***comparable to [3]

Table 2: Material parameters of the applied poultice mixtures

Material	Median pore diameter (µm)	Main range of pore diameters (µm)	Maximum of pore diameter distribution (µm)	Total pore volume (%) (from MIP)
ARB	22.05	5 - 30	22	84.67
RAJ	12.38	1 - 60	50	59.29
CKS_121	1.25	0.1 - 5	1.8	51.75
CKS_128	6.74	0.4 - 30	17	41.91
Cotta stone	1.51	0.1 - 6	5	21.99

Table 3: Data obtained from MIP measurements for different poultice materials

solvent was evaporated in a dry box at 60 °C. The respective evaporate was weighed, and the salt amount extracted per cm2 could be calculated. Moreover, two profiles of drill powder for salt analysis (from the upper and the lower part) were taken from each sandstone specimen before and after desalination, respectively. The samples of drill powder were taken stepwise from the surface to depths of 0-1, 1-2 and 2-3 cm. 2.5 g of each drill powder sample were eluted with 50 ml of demineralised water for 24 hours. Afterwards, the electrical conductivity of the solution was measured with a Hanna Instruments conductivity meter HI 991300.

3. Results

3.1. Characterization of poultice properties

MIP investigations gave insight into the structure and pore size distribution of the applied poultice mixtures. The results are displayed in *Table 3 and Figure 4*. As can be seen from *Table 3*, the distribution of pores in the CKS_121 poultice fits best to the pore size distribution of the Cotta type sandstone with respect to the theoretical optimum transport conditions.[2, 3] The pore size range of the Arbocel® poultice lies above that one of the Cotta type stone; i.e. the wet poultice is expected to provide much water to the substrate but not to actively extract salt solution from the stone by advection in dryer state. The Rajasil ready-made poultice and the CKS_128 mixture have both pores in the range of the Cotta type sandstone and above.

3.2. Observations during the poultice treatment

After the application *(Figure 5a, b)* the poultices were controlled visually every day during the entire desalination cycle of three weeks. Under the specimens with the Arbocel® poultice, which was

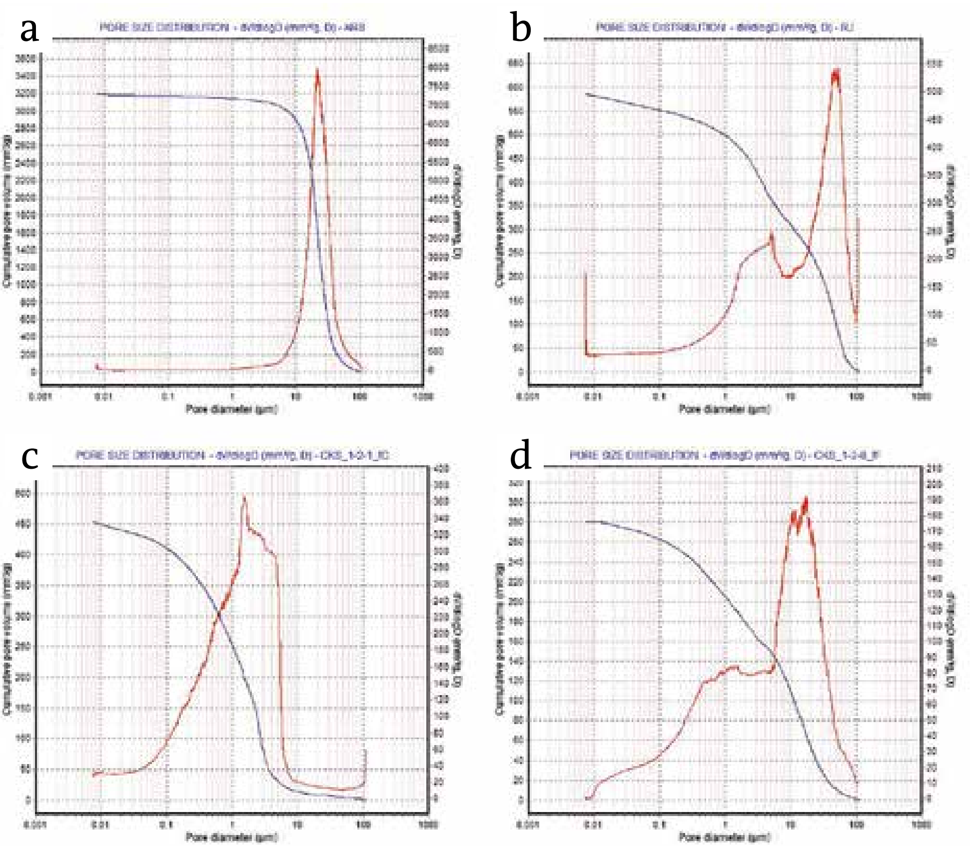

Figure 4: MIP diagrams of the applied poultices: a) pure Arbocel® poultice, b) Rajasil ready-made mixture, c) cellulose-kaolinite-sand 1:2:1 mixture (CKS_121), d) cellulose-kaolinite-sand 1:2:8 mixture (CKS_128)

Figure 5: a) Pre-wetting of the stone surface, b) application of the CKS_121 poultice on the pre-wetted stone specimen, c) loss of adhesion on the CKS_121 mixtures one week after application

still very wet after one day, some droplets of water were found that had come out during the first day after the application. In contrast, the CKS_128 mixture already showed first small cracks on the surface after one day. On the third day, the upper parts of the CKS_121 poultice started to visibly loose adhesion to the substrate. On the fourth day, rims of efflorescing salts appeared around the poultices, apart from the CKS_121 and Arbocel® mixtures (which were the mixtures with the highest water contents, cf. Table 1). After one week, the upper parts of all CKS_121 poultices had lost adhesion; one of them had a distance up to 9 mm to the stone surface *(Figure 5c)*. Moreover, they showed single cracks with a width > 1.8 mm. Cracks were also found on the surface of the CKS_128 poultices, but no loss of adhesion to the substrate was detected here. The Rajasil ready-made mixture showed only few small cracks and still a good adhesion to the substrate. The Arbocel® poultice mixtures started to loose adhesion in the upper parts and showed salt efflorescence behind the poultice in these areas. Two weeks after the application, the Arbocel® poultices had lost contact in the upper parts (distance between poultice and substrate up to 2 mm). The CKS_121 mixture showed now visible shrinking and loss of adhesion also at the bottom of the stone specimens. Nearly no further changes could be observed on the other poultices, apart from RAJ, were in some places efflorescences on the rim lead to minimal loss of poultice material.

3.3. Salt contents in the poultices after desalination

As can be seen in *Figure 6*, different amounts of salts were extracted from the stone specimens by different poultice mixtures under the same drying conditions. The highest average value for all three specimens investigated for each mixture (79.6 g/m²) as well as the highest absolute value for a single specimen (108.1 g/m²) was obtained from the Rajasil ready-made mixture experiment. It is closely followed by the CKS_128 mixture with 74.6 g/m² salt extracted on average, with only small differences between the three specimens (72.6-76.1 g/m²). The CKS_121 mixture extracted only 61.0 g/m² salt on average, whereas the worst result (47.0 g/m² extracted salt on average) was found for the Arbocel® mixture. Although the latter could be expected from theoretical considerations of salt and moisture transport in the poultice and the sandstone substrate (cf. 3.1 and [2, 3]), the low extraction rate for the CKS_121 mixture is astonishing with regard to the appropriate pore size distribution. However, this might be explained by its early loss of adhesion to the stone substrate (see 3.2).

3.4. Efficiency of desalination

The efficiency of desalination was calculated for the different profile depths of

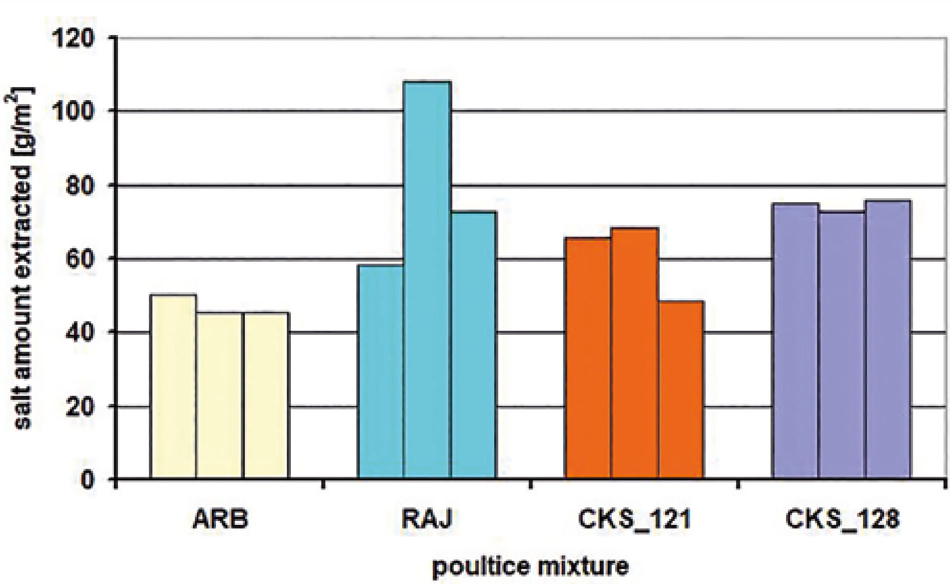

Figure 6: Salt amounts extracted from the salt-loaded Cotta type sandstone specimens with different poultice mixtures during a 3 week's desalination cycle

the sandstone specimens in the stone before and after desalination by using the electric conductivities measured after extraction of salts from the drill powders and the following equation:

$$\text{Efficiency [\%]} = (ec_b - ec_a) \times 100 / ec_b \qquad (1)$$

with ec_b = electric conductivity [µS/cm] before and ec_a = electric conductivity [µS/cm] after the poultice cycle. As can be seen from *Figure 7*, the Rajasil ready-made mixture and the CKS_128 mixture show reductions of salt content in nearly all sections of the investigated profiles. Efficiency is between 10 and 40% (RAJ) and between 5 and 35% (CKS_128) in the majority of the investigated profile sections. In contrast, the Arbocel® mixture and the CKS_121 mixture show a remarkable increase in salt content (negative efficiency) in the outermost profile section (0-1 cm). The efficiency in deeper sections (1-2, 2-3 cm) is comparable to this of RAJ and CKS_128 (between 5 and 35% for ARB and between 5 and 40% for CKS_121).

4. Discussion and conclusions

According to theoretical considerations on transport of salts from the stone substrate to the poultice by advection[2, 3], an appropriate cellulose-kaolin-sand poultice mixture with high kaolin content (cellulose-kaolin-sand = 1:2:1 by weight) was designed for Cotta type Elbe sandstone. However, this poultice showed high shrinkage due to the high clay content

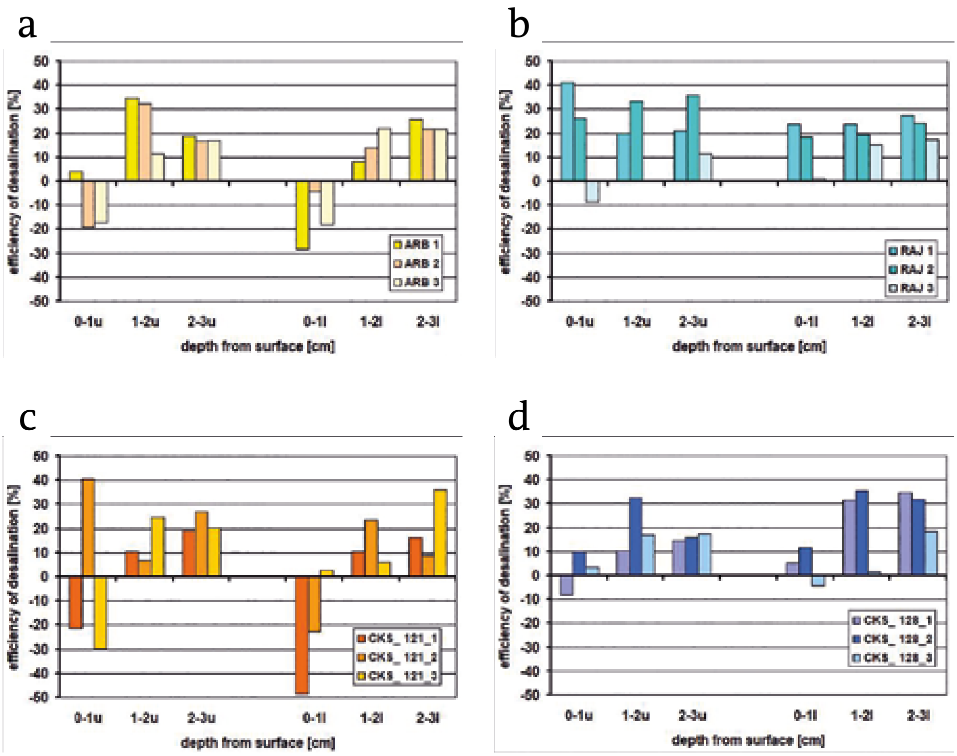

Figure 7: Efficiency of desalination displayed for different profile depths in each of the three sandstone specimens for a) Arbocel® mixture, b) Rajasil ready-made mixture, c) CKS_121 mixture and d) CKS_128 mixture. Positive values indicate salt reduction, negative ones increase of salt content after desalination, related to the original salt content in every specimen (u = upper part, l = lower part of the stone specimen)

(Table 2). Therefore another poultice with cellulose, kaolin and a higher amount of sand (1:2:8 by weight, shrinkage = 0) was additionally tested in the desalination experiment on artificially salt-loaded stone specimens, which also involved a customary Rajasil (RAJ) poultice and an Arbocel® mixture (ARB) often used by restorers. The results showed comparable amounts of extracted salts (75-80 g/m^2) for RAJ and CKS_128 poultices, whereas the CKS_121 (61 g/m^2) and the ARB mixture (47 g/m^2) brought worse results. Visual observations showed an early loss of adhesion of both CKS_121 and ARB, leading to the concentration of salts activated by wetting beneath the stone surface (0-1 cm depth, *Figure 7*). Higher salt contents in the CKS_121 poultice compared to ARB indicate that the mixture with high clay content must be very active in the short period immediately after application until loss of adhesion. This is in accordance with[4], where good results were obtained on materials comparable to Cotta type sandstone with respect to their pore size distribution by repeated treatments with CKS_121 mixtures and very short desalination cycles of only 4-5 days. However, the long-term activity (and the total efficiency) of the mixtures with higher sand contents and no shrinkage is much better, although their pore size distributions do not fit best the theoretical demands for the pore structure of the Cotta type sandstone. The results clearly demonstrate that in desalination practice of stones with fine pores compromises have to be found between the competitive parameters of "ideal" pore structure and low shrinkage of the poultice, both influenced by clay contents in the mixture. Even if the shrinking of kaolin clay is significantly lower than that of bentonite, all poultice mixtures with high clay contents will shrink while drying and therefore raise problems with adhesion. Loss of adhesion before the system substrate-poultice has completely dried to moisture equilibrium with the surrounding air might lead to concentration of the activated salts near the stone surface *(cf. Figure 7 c)*, which could be dangerous to the stone substrate. Alternatively, more frequently repeated short application periods of only a few days (until adhesion gets lost) with the CKS_121 mixture could be tested. This might save time but will increase costs for material and personnel. More practical experiments are needed to work out strategies balanced between appropriate poultice materials, workability and costs.

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